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FOREIGN TECHNOLOGY DIVISION

(PART I)

THERMODYNAMIC PROPERTIES OF INDIVIDUAL SUBSTANCES.
VOLUME I: CALCULATION OF THE THERMODYNAMIC PROPERTIES.
(CHAPTERS 1 THRU 15)

by

A. V. Gurvich, G. A. Khachkuruzov, et al.

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UNEDITED ROUGH DRAFT TRANSLATION

(PART I)

THERMODYNAMIC PROPERTIES OF INDIVIDUAL SUBSTANCES
VOLUME I: CALCULATION OF THE THERMODYNAMIC PROPERTIES
(CHAPTERS 1 THRU 15)

By: A. V. Gurvich, G. A. Khachkuruzov, et al.

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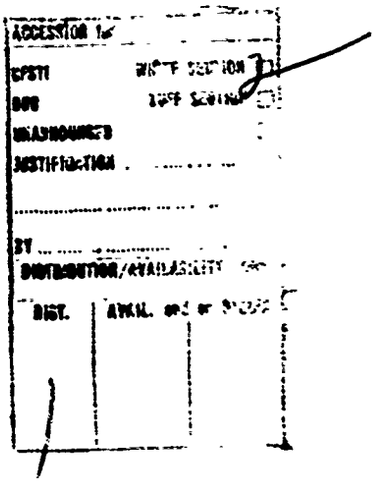
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ABSTRACT: Thermodynamic properties for the ideal gas state in table form for 335 gases, 44 liquids, and 45 solids compounded from 33 chemical elements and their isotopes; viz.: H, D, T. He, Li, Be, B, C, N, O, F, Ne, Na, Mg, Al, Si, P, S, Cl, Ar, K, Ca, Br, Kr, Re, Sr, Zr, I, Xe; Cs, Ba, Hg, and Pb. Thermodynamic properties are given for the following 22 gases in the range from room temperature to 20,000°K: H, H^+, H^-, O, O^+, H_2, O_2^+, O_2, OH, OH^+, H_2O, N, N^+, N_2, N_2^+, NO, NO^+, C, C^+, CO, CO^+, and e^-; for the 14 least stable gases up to 4000°K; and for the remaining 299 gases up to 6000°K. Virial coefficients for 34 gases are also given up to 6000°K.

In Vol. I of the Handbook the methods of calculating the thermodynamic properties of individual substances are described, and critical analysis is given of the literature data until 1960, including the constants necessary for the calculation of the tables of the thermodynamic properties (molecular constants, heats of formation and heats of phase transitions, specific heats, dissociation energies, etc.), the choice of the values of these constants accepted in the Handbook is substantiated and their values are estimated for such cases where experimental data are lacking.

Volume II of the Handbook contains tables of the thermodynamic properties of individual substances. All tables were calculated by the authors of the Handbook on the basis of the data accepted in Vol. I. English Translation: 321 tables, 4392 references; 2409 pages.

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2. Methods of Determining the Virial Coefficients.
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ANNOTATION

The two-volume Handbook contains tables of the thermodynamic properties of 335 gases, 44 fluids, and 45 solids, of altogether 424 components formed by the following 33 elements and isotopes: H, D, T, He, Li, Be, B, C, N, O, F, Ne, Na, Mg, Al, Si, P, S, Cl, Ar, K, Ca, Br, Kr, Rb, Sr, Zr, I, Xe, Cs, Ba, Hg, and Pb.

The thermodynamic characteristics were calculated for the temperature interval of from 293.15 to 4000-20,000°K. The virial coefficients are tabulated for 34 gases.

In Vol. I of the Handbook the methods of calculating the thermodynamic properties of individual substances are described, a critical analysis is given of the literature data until 1960, including the constants necessary for the calculation of the tables of the thermodynamic properties (molecular constants, heats of formation and heats of phase transitions, specific heats, dissociation energies, etc.), the choice of the values of these constants accepted in the Handbook is substantiated and their values are estimated for such cases where experimental data are lacking.

Volume II of the Handbook contains tables of the thermodynamic properties of individual substances. All tables were calculated by the authors of the Handbook on the basis of the data accepted in Vol. I.

The principal aim of this Handbook is to render possible to calculate the thermodynamical processes occurring at high temperatures. The Handbook may also be used in scientific research and experimental de-

sign work of institutes, design offices, universities, and also for the training of specialists in chemical and thermal physics.

PREFACE

The first three-volume edition of the Handbook with the title "Thermodynamic Properties of the Components of Combustion Products" was issued by the Publishing House of the Academy of Sciences USSR in 1956. It was the main purpose of the Handbook to render possible thermodynamic calculations of processes occurring at high temperatures. We began the work of compiling the Handbook, which contains tables of thermodynamic functions and equilibrium constants of the components of combustion products, since the thermodynamic characteristics of combustion products known in literature proved to be insufficient for the calculation of engines and the choice of fuels.

The most complete tables published at the beginning of the fifties, did not contain more than 50 components, constituted by at most 10 elements. The tables of Huff, Gordon, and Morrell [2142], for example contain the functions of 42 components (including such in condensed state) formed by 10 elements (H, Li, B, C, N, O, F, Ar, Al, and Cr). The data of these tables were borrowed from various sources or were calculated, averaged and extrapolated up to 6000°. These tables were used and supplemented by Vanichev, who, on the basis of literature data, summarized the tables of enthalpies, true specific heats, standard entropies, vapor pressures, and equilibrium constants of 50 components, in most cases up to 6000°K [117a].

In 1954 Zeise's book "Thermodynamics" [4384] came on the market, it contains tables of thermodynamic properties which had been published in periodicals until 1953. Since all tables are given without any im-

provements as compared to the original papers, among which we find such that were published at the beginning of the thirties, the book contains numerous obsolete and inaccurate data. The tables of the authors mentioned either cover too narrow a temperature range or are approximated too roughly (often using obsolete initial data), or ignore many components of combustion. The physical and thermal constants of numerous atoms and molecules were then improved or determined, which, owing to the development of the statistical methods of calculating thermodynamic values, made it possible to calculate more complete and exact tables of the thermodynamic properties of a great number of multiphase components of combustion products.

The first edition of the Handbook contained tables of the thermodynamic quantities of 234 components (including such in condensed state) formed by the following 23 elements and isotopes: H, D, T, Li, Be, B, C, N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Br, I, Hg, and Pb. The tables comprised the fundamental components of the combustion products formed by the most probable combination of the listed elements. It had been assumed that all the simplest radicals formed by oxidant and fuel can be found in the combustion products, even if the existence of some of them had not yet been proved experimentally. Unstable compounds, such as LiN, PF_4, SF_3, etc., were not taken into consideration. The possible ionization of lithium, fluorine, chlorine, bromine, and iodine (e^-, Li^+, F^-, Cl^-, Br^-, I^-) was taken into account. This is important with regard to the influence of the ionization of the flame on the transmission of radiowaves under certain conditions. For the same reason atoms and ions of sodium, potassium and calcium were also treated.

Among the compounds of fuel atoms with various oxidants only the carbon oxyfluorides (COF, COF_2) and oxychlorides (COCl, $COCl_2$) were considered; we know also other compounds, such as, e.g., CF_nCl_m, COFCI, as

well as compounds of other fuel atoms with various oxidants. This edition does neither deal with the numerous incompletely substituted fluorine, chlorine, and fluorine-chlorine derivatives of hydrocarbons, nor with the rather complex compounds that may appear as soon as the combustion products have left the nozzle of the engine, and the temperature has further dropped.

Thus, the list of components formed by the 21 elements considered in the first edition of the Handbook did not in the least comprise all components of combustion products produced in the combustion chamber, but permitted calculations which were more reliable than the compendia compiled earlier. Indeed, this Handbook did contain tables of thermodynamic properties of 178 gaseous, 27 liquid, and 29 solid components of combustion products (electrons, ions, atoms, radicals and molecules), of altogether 234 components, including 48 monatomic, 96 diatomic, 49 triatomic, 21 tetratomic, 12 pentatomic, 3 hexatomic, 1 heptatomic, 2 decatomic, 1 dodecatomic molecules and 1 molecule constituted of fourteen atoms.

The thermodynamic properties of the gaseous components were calculated for the state of an ideal gas. The thermodynamic properties of the condensed components were calculated for the case where the sublimation or boiling point of the component does not lie below 1000°K at a pressure of 100 atm. The tables of the thermodynamic functions of all gaseous components were calculated for the temperatures of 293.16°, 298.16°, 400° and then for each other 100° up to 6000°K.

The tables of the thermodynamic properties contained in the first edition of the Handbook were recalculated by means of the most reliable initial data published until 1954, in some cases up to 1955. In this Handbook the tables of the thermodynamic properties of more than 100 substances were published for the first time.

In the years thereafter tables of thermodynamic functions and equilibrium constants were published for the simple substances of the 92 elements (from H to U), calculated by Stull and Sinke [3894] on the basis of initial data published until 1956. These tables were calculated for both elements in crystalline and liquid states (from 298.15° up to the boiling point) as well as for all monatomic and polyatomic gases in the range from 298.15 to 3000°K.

In the past years one has begun to calculate the thermodynamic functions of gases for temperatures exceeding 5000–6000°K, especially for the gases constituting the air. Approximate values of the functions of 9 substances (N_2, O_2, NO, H_2, CO, C_2, H_2O, CO_2, and graphite) at temperatures up to 12,000°K were published by Fickett and Cowan [1555, 1556] in 1955, and the functions of 6 gases (N_2, N_2^+, NO, NO^+, O_2, O_2^+) for temperatures up to 25,000°K by Beckett and Haar [714]. A team of authors under the guidance of Predvoditelev calculated tables of the thermodynamic functions of air for temperatures of from 6000 to 12,000°K and pressures of from 0.001 to 1000 atm [334a]. Unfortunately in this work data on the thermodynamic properties of the individual substances constituting the air are lacking. A paper of the same team, published in 1959, contains tables of the thermodynamic functions of air and its components (N, O, Ar, N^+, O^+, Ar^+) for temperatures of from 12,000 to 20,000°K and pressures of from 0.001 to 1000 atm [335].

It must also be mentioned that various U.S. offices published collections containing tables of the thermodynamic functions of various groups of substances. Let us mention, for example, the third series of tables of the Handbook of the U.S. National Bureau of Standards [3680], the Handbook on the Physicochemical and Thermodynamic Properties of Titanium Compounds and Related Substances [3502a], the Handbook on Thermodynamic Properties of Metal Oxides [2564a], etc. These data are based

mainly on papers published in periodicals.

Compared with the first edition, the present second edition of the Handbook is essentially expanded with regard to the number of components dealt with (424 compared to 234) and the temperature range. This Handbook has been entirely revised, additional literature data have been analyzed and papers were taken into account which were published in 1955 to 1960, partly even such of 1961. 107 of the 207 tables of the first edition were entirely recalculated and 43 tables were partially recalculated. The texts of all chapters were entirely revised.

The compilation of the Handbook was based upon detailed studies of literature concerning investigations of spectra and molecular structures of the substances in question, calorimetric investigations of their specific heats, the heats of phase transitions, the heats of formation, the composition of vapors, and other similar properties. In most cases the experimental data of the original papers were revised, so that it was possible to improve the values of the molecular constants of a number of substances, of their heats of formation, heats of sublimation and energies of dissociation. The recalculation of all chemical constants is of particular importance; owing to this all values given in the Handbook, including the heats of formation, the dissociation energies, and the thermodynamic properties form a system of mutually coordinated values.

For some substances considered in the Handbook several or all data necessary for the calculation of the tables of thermodynamic properties were lacking. Therefore in several laboratories of the Soviet Union a great many of investigations of these properties were carried out, which are necessary for the calculation of the tables of the thermodynamic properties of the substances treated in the present Handbook. The following laboratories participated in these investigations: the Labor-

atory of Molecular Spectroscopy of the Chemical Department of the Moscow State University (head: Professor V.M. Tatevskiy); the Laboratory of Molecular Spectroscopy of the State Institute of Optics (head: Professor B.S. Neporent); the Laboratory of Electronographic Investigations of the Chemical Department of the Moscow State University (head: P.A. Akishin); the Laboratory of Thermodynamics and Chemistry of High-temperature Processes of the Institute of Mineral Fuels of the Academy of Sciences USSR (head: K.A. Nikitin, Candidate of Technical Sciences); the Laboratory of Chemical Thermodynamics of the Chemical Department of the Moscow State University (head: Ya.I. Gerasimov, Corresponding Member of the Academy of Sciences USSR); the Luginin Thermochemical Laboratory of the Chemical Department of the Moscow State University (heads: Professor M.M. Popov [deceased], and Professor S.M. Skuratov); the Laboratory of Radiochemistry of the Chemical Department of the Moscow State University (head: Professor An.N. Nesmeyanov); the Laboratory of Low-temperature Physics of the Institute of Physical Problems of the Academy of Sciences USSR of the All-Union Scientific Research Institute of Physicotechnical and Radio Engineering Measurements of the Committee of Standards (head: P.G. Strelkov, Corresponding Member of the Academy of Sciences USSR); the Division of Heat Measurements of the Khar'kov State Institute of Measures and Measuring Instruments of the Committee of Standards (head: V.V. Kandyba), and the Thermometric Laboratory of the Sverdlovsk Branch of the All-Union Scientific Research Institute of Metrology of the Committee of Standards (head: E.N. Rodigina, Candidate of Chemical Sciences). The results of these investigations are discussed in the present Handbook and also mentioned in papers published in periodicals and reports [1-57].

Moreover, on the basis of various theoretical relationships and empirical regularities the authors of the Handbook have estimated a

great number of molecular constants, thermodynamical and thermochemical values.

The Handbook consists of two volumes. Part 1 of Volume I contains a description of the methods used to calculate the tables of the thermodynamic properties of substances in solid and liquid states and in the state of an ideal gas; fundamental information is given on the energy states of atoms and simple molecules, and methods are described which areused to determine the constants necessary for the calculation of the tables of thermodynamic properties. In the 2nd part the reader may find the results of investigations and approximate estimations of molecular constants, specific heats and heats of phase transitions and also the thermodynamic values of the substances considered in the Handbook. On the basis of a critical analysis, the values of these constants, used for the subsequent calculation of the tables of the thermodynamic properties of individual substances, are compiled in special tables. In the individual sections the calculations of the thermodynamic functions of gases are described, their accuracy is estimated, and they are compared with literature data. In Part 3 various auxiliary means are mentioned, for example, the values of the fundamental physical constants, atomic weights and the percentage of the isotope content, relations linking the force constants with the vibrational frequencies of molecules of various types, and also with the products of their principal moments of inertia and the structural parameters. In the same part the methods of the calculation of corrections for the interaction of the gas molecules to the values of the thermodynamic functions of these gases are described, the data are discussed, which are needed to calculate these corrections for 34 gases, and the critical constants of a series of substances and the methods of their estimation are discussed.

TABLE 1

Components of Combustion Products

Fuel		Oxidant: Fluorine, Valency				Oxidant: Oxygen O, O_2, Valency				Oxidant: Nitrogen N, N_2, Valency		
1	2	2	3	4	≥5	2	3	4	≥5	2	3	≥4
H	H_2	HF				OH OH^+ OH^-	H_2O HO_2	H_2O_2		NH	NH_2	NH_3 N_2H_4
D	D_2 HD	DF				OD	D_2O HDO	D_2O_2 HDO_2				
T	T_2 HT DT	TF				OT	T_2O HTO DTO					
Li zht	Li_2	LiF zht				LiO	Li_2O znt					
Be znt		BeF_2	BeF_2 zht			BeO zht				BeN		
B zht	B_2	BF	BF_2	BF_3		BO	BO_2	B_2O_2	B_2O_3 zht	BN zht		
C znt	C_2	CF C_2F	CF_2 C_2F_2	CF_3 C_2F_3	CF_4 C_2F_4	CO CO^+	CO_2		C_2O_3	CN		C_2N_2
Na zht		NaF zht										
Mg znt		MgF	MgF_2 zht			MgO znt				MgN		
Al znt		AlF	AlF_2	AlF_3 zht		AlO	Al_2O		Al_2O_3 zht	AlN znt		
Si znt	Si_2	SiF	SiF_2	SiF_3	SiF_4	SiO	SiO_2 znt			SiN		
P	P_2	PF	PF_2	PF_3	PF_5	PO			P_4O_6 P_4O_8 P_4O_{10}	PN		
S	S_2	SF	SF_2		SF_4 SF_6	SO	SO_2 S_2O	SO_3		SN		
K znt		KF zht										
Ca zht						CaO zht						
Rb znt												
Sr znt						SrO znt						
Zr zht						ZrO	ZrO_2 znt					
Cs znt												
Ba znt						BaO znt						
Hg		HgF										
Pb zht		PbF	PbF_2 znt			PbO znt						

Oxidant: Chlorine Cl, Cl_2, Valency				Other Components, Valency				
2	3	4	≥5	1	2	3	4	≥5
HCl				e^- H^+, H^- D^+, T^+ He, N^+ O^+ O^-, F^- Ne Cl^- Ar Br, Br^- Kr J, J^- Xe	N_2^+, O_2^+ NO, NO^+ NF, FO ClO, ClF BrF_3, HBr DBr, TBr BrCl BrF, BrCl J_2, HJ DJ, TJ JO, JF JCl, JBr	N_2 O_2 NO_2, N_2O HNO, NF_2 FNO HOCl F_2O, Cl_2O	NF_3	
DCl								
TCl								
LiCl znt				Li^+	LiH znt	LiOH znt		
BeCl	$BeCl_2$ znt				BeH			
BCl	BCl_2	BCl_3			BH	HBO FBO	HBO_2	H_3BO_3
CCl	CCl_2	CCl_3	CCl_4 C_2Cl_4	C^+	CH CP CS	C CH_2, C_2H CS_2, HCN CHO, CHF FCN, COF COCl, OCS	CH_2 C_2H_2, CH_2O CH_2F, CHF_2 C_2HF, COF_2 $COCl_2$, HFCO COFCl	CH_3 C_2H_4 CBr_4
NaCl znt				Na^+				
MgCl	$MgCl_2$ zht			Mg^+	MgH			
AlCl	$AlCl_2$	$AlCl_3$ zht		Al^+	AlH			
SiCl	$SiCl_2$	$SiCl_3$	$SiCl_4$		SiH SiC	SiC_2 Si_2C		
PCl		PCl_3	PCl_5		PH PS		P_4	POF_3 $POCl_3$
					SH	H_2S	SOF_2	SO_2F_2
KCl zht				K^+				
				Ca^+				
				Rb^+				
				Sr^+				
				Cs^+				
				Ba^+				

J = iodine

The second volume of the Handbook contains tables of the thermodynamic properties of 335 gases, 44 liquids, and 45 solids, or altogether 424 components formed by the following 33 elements and isotopes: H, D, T, He, Li, Be, B, C, N, O, F, Ne, Na, Mg, Al, Si, P, S, Cl, Ar, K, Ca, Br, Kr, Rb, Sr, Zr, I, Xe, Cs, Ba, Hg, and Pb.

Table 1 gives a survey of the 370 substances whose thermodynamic characteristics are listed, under the assumption that these individual substances in gaseous or condensed states may be considered components of combustion products. The 42 halogen derivatives of methane and the 12 halogen derivatives of ethylene are not included in this table; for these compounds special tables of thermodynamic characteristics have been compiled.

Except for Al_2O_3, the termodynamic properties for all components considered in the Handbook are calculated for the ideal gaseous state. The letters zh and t at the right side of the component in the tabular summary indicate that the thermodynamic properties of these components are also calculated for the condensed state (fluid or solid). In order to consider the deviation of the gases from the ideal state at high pressures and medium temperatures, the virial coefficients and their derivatives are tabulated for 34 gases.

For 14 of the least stable gases the thermodynamic characteristics are calculated from 293.15 to 4000°K, for 22 gases they are calculated up to 20,000°K (H, H^+, H^-, O, O^+, H_2, O_2, O_2^+, OH, OH^+, H_2O, N, N^+, N_2, N_2^+, NO, NO^+, C, C^+, CO, CO^+, e^-) and for all other gases up to 6000°K.

This extended compilation of substances makes it possible to use the Handbook not only in thermodynamic calculations of heat engines of various types, but also in many cases of thermal processes.

The tables of thermodynamic properties contained in the Handbook are not equally accurate, since the accuracy of the constants used in

the calculations is different for different substances. In order to characterize the accuracy of the tables, a seven-point system is used in the Handbook.

The Handbook was compiled by a team of members of the Institute of Mineral Fuels of the Academy of Sciences USSR and of the State Institute of Applied Chemistry of the State Committee on Chemistry of the Council of Ministers of the USSR under the general scientific guidance of Academician V.P. Glushko. The Chapters 1 – 5, 8, 9, 14, 16 and 20-31, the Supplements 5 and 6, as well as part of the material of the Chapters 6, 7, 10, and 11 were elaborated in the Institute of Mineral Fuels of the Academy of Sciences of the USSR. The Chapters 6, 7, 10 – 12, 15, 17 – 19, the Supplements 1, 2, 3, and 4, and part of the material of Chapter 2 were compiled in the State Institute of Applied Chemistry of the State Committee on Chemistry of the Council of Ministers of the USSR. When writing these chapters the authors of the State Institute of Applied Chemistry used texts dealing with H, H^+, H^-, OH, OH^+, OH^-, Br^-, I^-, and I^-, as well as earlier material concerning deuterium, sulfur and its compounds, C_2H_2, and C_2F_2; these texts had been prepared in the Institute of Mineral Fuels of the Academy of Sciences USSR.

The main work of preparation of the Handbook was done by L.V. Gurvich, G.A. Khachkuruzov, V.A. Medvedev, I.V. Veyts, G.A. Bergman, V.S. Yungman, N.P. Rtishcheva, L.F. Kuratova, and G.N. Yurkov; part of the material of the Handbook was prepared by A.A. Kane, B.F. Yudin, B.I. Brounshteyn, V.F. Baybuz, V.A. Kvlividze, Ye.A. Prozorovskiy, and B.A. Vorob'yev. Moreover, V.V. Kokushkin, I.S. Milevskaya, M.M. Novikov, and F.V. Pospelov participated in the preparation of the material of individual sections.

L.V. Gurvich as the chief author of the Handbook was not only supervising the compilation work of the Handbook, but had also the main

responsibility for the coordination of both the work done in the Institute of Mineral Fuels and in the Institute of Applied Chemistry, and the experimental investigations of the group of cooperating institutions.

The statistical methods of calculation of the thermodynamic functions of gases were improved and their accuracy was estimated by L.V. Gurvich, V.S. Yungman, V.A. Kvlividze (Institute of Mineral Fuels), and B.I. Brounshteyn, G.A. Khachkuruzov and G.N. Yurkov (State Institute of Applied Chemistry). The values of constants, which were necessary for the calculation of tables of thermodynamic properties, but whose values are not given in literature, were estimated in the Institute of Mineral Fuels by L.V. Gurvich, I.V. Veyts, V.A. Medvedev, G.A. Bergman, V.S. Yungman, V.A. Kvlividze and Ye.A. Prozorovskiy, and in the State Institute of Applied Chemistry by G.A. Khachkuruzov, B.F. Yudin, A.A. Kane, and I.S. Milevskaya. The thermodynamic functions of 198 gases were tabulated by N.B. Rtishcheva and V.S. Yungman, assisted by B.A. Vorob'yev (programming for an electronic computer) and supervised by L.V. Gurvich, and those of 137 gases were calculated by L.F. Kuratova and G.N. Yurkov in the Institute of Applied Chemistry under the guidance of G.A. Khachkuruzov. The tables of the thermodynamic properties of 45 substances in condensed state were calculated by G.A. Bergman, the tables of the virial coefficients and their derivatives were computed by V.F. Baybuz for 34 gases. The auxiliary tables of thermodynamic functions of the harmonic and anharmonic oscillator and the interpolation formulas of the tabulated values of thermodynamic properties were computed by B.A. Vorob'yev and N.P. Rtishcheva using the BESM of the Academy of Sciences USSR.

The material of Volume I, Part 1, was compiled and written as follows: Introduction and Chapter 1 by L.V. Gurvich under cooperation of V.A. Kvlividze (Section 2), V.S. Yungman (Section 3), and G.A. Khachkur-

uzov (Section 4); Chapter 2 by L.V. Gurvich and V.S. Yungman, assisted by B.I. Brounshteyn and G.N. Yurkov (Sections 9, 15, 16), Chapter 3 by G.A. Bergman, Chapter 4 by V.A. Medvedev assisted by I.V. Veyts (§21).

The material of Volume I, Part 2, was compiled and written as follows: the divisions concerning the molecular constants by I.V. Veyts (Chapters 16, 20 – 27), and L.V. Gurvich (Chapters 5, 8, 9, the material concerning atoms and part of the molecules in the Chapters 16, 20 – 27, Chapters 28 – 30), G.A. Khachkuruzov (Chapters 6, 7, 8, 15, 17-19), A.A. Kane (Chapters 10 – 12, part of the material of the Chapters 13 and 17), by V.S. Yungman (H_2 in Chapter 6; OH, OH^+, OH^-, in Chapter 7, and Chapter 14) assisted by V.A. Kvlividze (constants of atoms and monatomic ions in the Chapters 5, 6, 14, 16, 22, 24 – 30), Ye.A. Prozorovskiy (O_2, O_2^+ in Chapter 5, OH in Chapter 7, F_2O in Chapter 8, N_2 and NO in Chapter 14, CO and CO^+ in Chapter 16, NaF and KF in Chapter 29), B.I. Brounshteyn (Chapters 10 – 12), M.M. Novikov (ClF, Cl_2 and HOCl in Chapter 9, BeF, BeCl in Chapter 25, PbO in Chapter 30), I.S. Milevskaya (Chapter 19), F.S. Pospelov (Chapter 18) and V.V. Kokushkin (H_2O_2, D_2O_2 and HDO_2 in Chapter 7);

the divisions dealing with the calculation of the thermodynamic functions of gases were compiled by L.V. Gurvich (Chapters 5, 8, 9, 16, 20 – 30), G.A. Khachkuruzov (Chapters 6, 7, 15, 18, 19) V.S. Yungman (H_2 in the Chapter 6, OH, OH^+, OH^- in Chapter 7, Chapter 14), G.N. Yurkov (part of the material on oxygen compounds of D and T in the Chapter 7, Chapter 10 – 12, part of the material of the Chapters 13, 15, 18, 19) under assistance of V.A. Kvlividze (monatomic gases in the Chapters 5, 14, 16, 22, 24 – 30), N.P. Rtishcheva (compilation of the material for the calculation and the comparison with the calculation data in the Chapters 5, 8, 9, 20 – 30), L.F. Kuratova (special material of the Chapters 15, 17 – 19), B.I. Brounshteyn (Chapters 10 – 12), and F.V. Pospe-

lov (compilation of special material of Chapter 18);

the divisions concerning the thermodynamic properties of substances in solid and liquid states were compiled by G.A. Bergman (Chapters 16, 22 – 30);

the divisions dealing with the thermochemical values were compiled by V.A. Medvedev (O_3 in Chapter V, H_2O, H_2O_2, D_2O_2, in Chapter 7, Chapters 8, 9, 14, 16, 20-30); B.F. Yudin (H_2O and D_2O in Chapter 7, Chapters 10 – 12, 15, 17 – 19), G.A. Bergman (heats of sublimation of elements, their fluorides and chlorides in the Chapters 22, 24 – 30, PbO, SiO_2, and ZrO_2), G.A. Khachkuruzov (Chapters 6, 7, 13, 15, part of the divisions of the Chapters 17 – 19); I.V. Veyts (spectroscopic investigations of the dissociation energy in the Chapters 16, 20 – 27), L.V. Gurvich (ionization potential and values of the electron affinity of atoms and molecules with the exception of Chapter 14, spectroscopic investigation of the dissociation energy in the Chapters 5, 8, 9, CO, CO^+ in Chapter 16, Chapters 21, 25, 26, 28 – 30), V.S. Yungman (dissociation energies of H_2 in Chapter 5, of OH and OH^+ in Chapter 6, of diatomic molecules in Chapter 14). Chapter 31 was written by V.S. Yungman.

The material of Part 3 of Volume I was compiled and written as follows: G.A. Khachkuruzov assisted by G.N. Yurkov: Supplements 1 and 2; L.F. Kuratova and G.A. Khachkuruzov: Supplement 3; V.V. Kokushkin: Supplement 4; V.F. Baybuz: Supplements 5 and 6.

The Handbook was edited completely by Academician V.P. Glushko (Editor in Chief), and L.V. Gurvich, Candidate of Chemical Sciences, and G.A. Khachkuruzov, Candidate of Technical Sciences. The divisions dealing with the molecular constants were edited by I.V. Veyts, Candidate of Chemical Sciences, and the divisions dealing with thermochemical Sciences.

The calculations necessary to compile the tables of the thermody-

namic properties and the fundamental work of preparing the material of the Handbook were carried out by I.G. Baybuz, V.S. Shmeleva, E.I. Surkova, N.R. Simagina, L.I. Kopteva, V.M. Kuznetsova, Z.P. Filatova, Laboratory Assistants of the Institute of Mineral Fuels of the Academy of Sciences USSR, and Ye.G. Goland, V.S. Pavlova, V.V. Ivanova, L.P. Serebrennikova, T.A. Mikhaleva, Laboratory Assistants of the Institute of Applied Chemistry.

At the beginning of the work of preparing the material for the first edition of the Handbook (1952-1953) the scientific supervisor was A.B. Chernyshev [deceased], Corresponding Member of the Academy of Sciences USSR, and V.V. Korobov, who assisted in the preliminary analysis of the literature concerning spectra and thermochemistry of individual compounds, and in the calculation of the thermodynamic functions of some gases, (SiO_2, SO_2) was the scientific supervisor of the work done in the Institute of Mineral Fuels of the Academy of Sciences USSR.

V.A. Il'inskiy, Doctor of Technical Sciences, and the Engineers Ye.A. Ivan'kova and L.V. Chernyakova assisted in checking the tables of the first edition of the Handbook.

K.A. Nikitin, Candidate of Technical Sciences and Chief of the Laboratory, organized the work on the Handbook in the Institute of Mineral Fuels of the Academy of Sciences USSR, and I.P. Tverdovskiy, Candidate of Chemical Sciences and Chief of the Laboratory, organized the work in the Institute of Applied Chemistry.

The leading part in the compilation work for the Handbook was played by the members of the Laboratory of the Institute of Mineral Fuels of the Academy of Sciences USSR, who, together with the members of the Laboratory of the State Institute of Applied Chemistry of the State Committee on Chemistry, accomplished a great creative work. The experiences gained by the teams of the Institute of Mineral Fuels and the State

Institute of Applied Chemistry on compiling the Handbook in the course of ten years, shall be used for a future systematic revision of the Handbook and the addenda, which will be issued periodically.

I consider it a pleasant duty to express my highest appreciation to the harmonious team of authors of the Handbook, especially to the chief author of the Handbook L.V. Gurvich, to the Laboratory Chiefs K.A. Nikitin and I.P. Tverdovskiy, and the reviewers of the Handbook, Ya.I. Gerasimov, Corresponding Member of the Academy of Sciences USSR, and Professor S.M. Skuratov, who have given substantial assistance in the editing of the individual divisions dealing with the selection of the thermochemical values, and also to Professor V.M. Tatevskiy, whose valuable counsel has been of great use for the work on the Handbook, and to P.G. Strelkov, Corresponding Member of Sciences USSR.

V.P. Glushko

Manuscript Page No.

[Transliterated Symbols]

10 ж = zh = zhidkiy = liquid

10 т = t = tverdyy = solid

13 ВЭСМ = BESM = bystrodeystvuyushchaya elektronnaya schetnaya mashina = high-speed electronic computer

INTRODUCTION

The still increasing exploration and practical utilization of processes occurring at high temperatures and pressures is one of the characteristic features of the development of science and engineering during the last 20 – 25 years. The experimental examinations of these processes and their application in engineering are usually rather complex and expensive undertakings. Therefore, theoretical investigations have to precede experimental work in this field, in order to find out the principal possibilities of realizing a certain process and to determine the optimum conditions of its execution.

At high temperatures where the kinetic factors are rather insignificant, a sufficiently accurate theoretical investigation of the processes may be carried out on the basis of thermodynamic calculations, provided the data on the thermodynamic properties of the individual substances, which participate in these processes, are known. This explains the interest continually growing in the past years, which is devoted to the study of the thermodynamic properties of substances, especially gases at high temperatures, and also the still increasing application of thermodynamic methods of investigation in the most different fields of science and engineering. It may be noted that the vast successes achieved in the past years in thermotechnics, petrochemistry, metallurgy and some other fields, are immediately connected with the application of thermodynamic calculations.

The widespread application of thermodynamic methods and the perspectives becoming apparent in this field require the compilation of

data on the thermodynamic properties of individual substances; in addition to this the number of the substances to be analyzed is constantly growing, and the temperature range for which the respective data are necessary is continuously extended. Whereas until the end of the thirties mainly data concerning the thermodynamic properties of the common gases and the simplest hydrocarbons were needed for practical calculations in the temperature range from room temperature to 1500-3000°K, at the beginning of the fifties, however, data of the thermodynamic properties of several tens of inorganic compounds at temperatures up to 5000 – 6000°K were required, and in the following years data for temperatures up to 20,000 – 25,000°K became necessary to permit the calculation of high temperature processes.

Experimental investigations of the thermodynamic properties of individual substances (especially of gases) on the basis of calorimetric measurements are only possible in a limited temperature range and present a rather complex and laborious problem. This fact might render much more difficult the spreading of thermodynamic methods of investigation of various processes, but at the beginning of the thirties entirely new methods were developed for the determination of the thermodynamic properties of gases by virtue of the progress of statistical physics and quantum mechanics and thanks to the success achieved in investigating the structure of atoms and molecules. The development of these methods made it possible to calculate the thermodynamic properties of gases on the basis of studying the spectra and the structure of molecules.

Owing to the fact that the statistical methods of calculation are very accurate and rather simple and that these methods can be used in order to calculate the thermodynamic properties of gases at temperatures which cannot be reached in calorimetric measurements, within a short

time tables of the thermodynamic properties of several tens of the most important gases were calculated for a wide temperature range. Though the methods developed permit the calculation of the thermodynamic properties of gases only in the state of an ideal gas, this does not result in a perceptible limitation of the possibilities of applying the calculated values, since in most practical problems especially in the investigation of high-temperature processes, the gases may in fact be considered ideal gases. Furthermore, the deviations of the thermodynam- properties of gases from the properties of an ideal gas can in many cases be taken into account by appropriate corrections.

It was the aim of the present edition to create a Handbook of the thermodynamic properties of individual substances, which must be known for thermodynamic investigations of a wide range of various thermotechnical and chemical processes occurring at high temperatures. The present Handbook surpasses all handbooks and summaries known in literature (references on thermodynamic functions of gases, substances in solid and liquid states, and heats of formation see Chapters 2 – 4) both with regard to the number of elements considered (31) and to the total number of substances (335), as well as to the temperature range for which the tables of thermodynamic properties are calculated.

Unlike the majority of the otner handbooks and summaries, which represent a compilation, the tables of the present Handbook were calculated by the authors themselves. The calculations were made on the basis of values of the initial constants assumed as a result of a critical analysis of the data published in literature up to the end of 1960 (partially, use was made of data published in 1961). In all cases the choice of the calculation method was decided by the completeness of the data necessary for the calculation. In the Handbook the choice of all constants used in the calculations is substantiated, the methods of cal-

culation used in each concrete case are described and the results of calculation are compared with literature data published earlier. For all tables of the thermodynamic functions and equilibrium constants the accuracies are given, allowing for the errors of the constants used in the calculations and the errors of the calculation methods applied. For all substances considered in the Handbook (excluding Al_2O_3) tables of the thermodynamic properties of the corresponding ideal gases were calculated.

Since a large number of hardly volatile substances is dealt with in the Handbook, data on the thermodynamic properties of these substances in solid and liquid states and also data on their vapor pressures are needed for the calculation of the equilibrium of the reactions in which they participate. Therefore the corresponding data have been entered in the Handbook for all substances whose vapor pressures reach up to 100 atm at temperatures higher than 1000°K.

The Handbook consists of two volumes. Volume I gives a short description of the theoretical and methodical problems connected with the calculation of tables of the thermodynamic properties of individual substances (Part 1), reasons are given for the choice of the constants used in the calculation of the tables of the thermodynamic properties of each substance (Part 2), and, moreover, some auxiliary material is given which is necessary to calculate the thermodynamic properties (Part 3). Volume II contains 380 tables of the thermodynamic properties of 335 substances and, moreover, 43 supplementary tables containing the virial coefficients and their derivatives of 34 gases, the virial coefficients and their derivatives of 34 gases, the coefficients of the interpolation formulas for the thermodynamic properties, and various other data.

Contents of Volume I of the Handbook. In Volume I, Part 1, the

methods of calculation of the thermodynamic properties of individual substances are described. This Part contains four chapters in which the modern concepts of the energy states of atoms and molecules are discussed, which are necessary for the calculation of the thermodynamic functions of gases by methods of statistical thermodynamics; moreover, the statistical methods of calculation of thermodynamic functions of gases on the basis of the data of their molecular constants, the methods of calculation of the thermodynamic properties of substances in solid and liquid states on the basis of calorimetric measurements, the thermochemical values needed in the calculation of the thermodynamic properties of substances, and the methods of their calculation and evaluation are described. Besides the statement of the problems mentioned, the fundamental reference literature is discussed in these chapters; it yields data on the molecular constants, thermodynamic properties and thermochemical values.

The second part of Volume I contains 27 chapters (Chapters 5 – 31), in each of which data are listed for the compounds of one or more elements with similar properties. As a rule these chapters consist of an introduction and four divisions which respectively treat: a) the energy states and constants of the atoms and molecules of the gases considered; b) the calculations of the thermodynamic functions of gases; c) the thermodynamic properties of substances in condensed state; d) the heats of formation, energies of dissociation, and heats of sublimation. The introductions to Chapters 5 – 32 deal with problems connected with the definition of the set of compounds of the given element discussed in the Handbook, and indicate which other compounds of this element may play an essential role at high temperatures in the various systems.

The divisions with the title "Molecular Constarts" substantiate the choice of the molecular constants of the compounds of elements con-

sidered in the respective chapter, and also of the energy levels of the atoms of these elements. The accepted values of the constants are listed in special tables. The Tables "Energy Levels of the Atom (Ion)..." contain the excitation energies and the statistical weights of the electron levels, which are taken into account in calculating the thermodynamic functions of the corresponding monatomic gas. The Tables "Accepted Values of Molecular Constants..." give, for diatomic molecules, the values of the oscillation frequencies $\omega_e x_e, \omega_e y_e \ldots$, the anharmonicity constants $\omega_e x_e$, $\omega_e y_e \ldots$, the rotation constants B_e, the interaction constants α_1 and α_2, the constants D_e of centrifugal elongation, the interatomic equilibrium distances r_e, and other constants for all electron states of the molecules of the gas in question, which are taken into account in the subsequent calculations of its thermodynamic functions, and also the excitation energies of these states.

Analogous tables contain the corresponding constants of multiatomic molecules as far as they are known (except for the structural parameters, which are not given in the tables but in the text) and also the degree of symmetry of the molecules and the degree of degeneration of the vibration frequencies. Since for a majority of multiatomic molecules the values of the normal vibration frequencies and of the rotational constants are not known, as a rule the values of the fundamental frequencies ν_n and the products of the principal moments $I_A I_B I_C$ of inertia are tabulated (see pages 106 and 1987).

Of many substances considered in the Handbook there are no experimental data on the values of the constants of their molecules, which were necessary to calculate the thermodynamic functions. In such cases the tables mentioned above contain the values of constants obtained by the authors of the Handbook by way of different approximate estimations; the text of the corresponding divisions substantiates the choice of the

constants chosen according to experimental data, and describes the methods of estimation.

The Sections entitled "Thermodynamic Functions of Gases" specify the method of calculating the functions of the gases treated in the respective chapter, and the accuracy of the calculated values of the thermodynamic functions. The constants of the calculation formulas used, determined on the basis of the accepted values of the molecular constants of these gases, are listed in special tables headed "Values of the Constants Used in the Calculation of the Thermodynamic Functions of..." In the same sections a brief discussion is given of the calculations of the thermodynamic functions of the gases considered, which have been published in literature; for such cases where they differ essentially from the values given in the corresponding tables of Volume II of the present Handbook, the causes of the deviations and the possible sources of the errors are indicated.

The calculations of the thermodynamic properties of substances in solid and liquid states are discussed in the Sections "Thermodynamic Properties of Substances in Solid and Liquid States", which deal with the results of the analysis of the experimental data necessary for the calculation, as well as the estimations carried out by the authors of the Handbook. Special tables, headed "Accepted Values of the Thermodynamic Quantities of ...," give the values of the entropy $S^{\circ}_{298.15}$ and those of the changes of the enthalpy $H^{\circ}_{298.15} - H^{\circ}_{0}$, the equations for the specific heats of the substances in solid and liquid states, and also the melting points and heats of melting and polymorphous transformations, provided the latter were taken into account in calculating the thermodynamic properties. A number of chapters does not contain the Section "Thermodynamic Properties of Substances in Solid and Liquid States," since these chapters only deal with substances in gaseous

state.

The closing Section "Thermochemical Values" of each chapter deals with the choice of the heats of formation and sublimation and that of the energies of dissociation and ionization of the substances treated in the respective chapter. The values accepted for energies of dissociation and ionization and the sublimation heat at 0°K, the heat of formation at 0, 293.15, and 298.15°K, and also the changes of the enthalpies $H^\circ_{293.15} - H^\circ_0$ and $H^\circ_{298.15} - H^\circ_0$ are given in tabular summaries at the end of the chapter for all substances treated in it.

Part 3 of Volume I deals with the accepted values of atomic weights and the data on the occurance and the spins of the nuclei of the stable isotopes of the elements treated in the Handbook (Supplement 1), the accepted values of the fundamental physical constants and of the conversion factors of the energy units (Supplement 2), the formulas needed to calculate the principal moments of inertia of the molecules and their products from the structural parameters (Supplement 3), and the relations linking the vibration frequencies and the force constants of polyatomic molecules for various models of the molecular field of force (Supplement 4). The formulas quoted in the last two supplements were used in the present Handbook in order to estimate the molecular constants, and in other calculations. Supplement 5 deals with the methods of calculating the corrections to the values of the thermodynamic functions of ideal gases, allowing for intermolecular reaction; in the same supplement the data needed to calculate the corresponding corrections for 34 gases are discussed. Supplement 6 contains data on the critical constants of a number of substances considered in the Handbook.

The Contents of Volume II of the Handbook. Volume II contains 380 tables of the thermodynamic properties of 335 substances; 4 tables of

the coefficients in interpolation formulas which approximate the thermodynamic properties of gases at temperatures of 293.15 to 6000°K; 1 table of the nuclear components in the values of Φ_T^* and S_T^* of substances considered in the Handbook; 4 tables of equilibrium constants of the dissociation reactions of some gases and 34 tables of the virial coefficients and their derivatives.

Each table of thermodynamical properties of gases contains the values of the reduced thermodynamic potential Φ_T^*, of the entropy S_T°, of the change of enthalpy $H_T^\circ - H_0^\circ$ and the total enthalpy I_T° and also log K_p and K_p, where K_p is the equilibrium constant of the reactions of dissociation or ionization (the latter are not contained in the tables of thermodynamic properties of monatomic neutral gases). The values of the above thermodynamic properties are given for the temperatures of 293.15° 298.15, 400 and then for every other 100° up to 6000°K. The tables of 22 gases also contain the data for temperatures higher than 6000°K, and this for all other 200° up to 10,000°K, and then for all other 500° up to 20,000°K. The thermodynamic functions of ideal gases for a pressure of 1 atm (760 mm Hg) are all given.

In order to facilitate the interpolation, the first differences of the values of Φ_T^*, S_T°, $H_T^\circ - H_0^\circ$, I_T° and log K_p are also listed in the tables.

The tables of the thermodynamic properties of substances in condensed state give the values of the specific heat C_p°, the reduced thermodynamic potential Φ_T^*, the entropy S_T°, the change of enthalpy $H_T^\circ - H_0^\circ$, the total enthalpy I_T°, the logarithm of the saturated vapor pressure, log p, the vapor pressure p, and also the values of the first differences of Φ_T^*, S_T°, $H_T^\circ - H_0^\circ$, I_T° and log p. The tables of the thermodynamic properties of substances in condensed states contain the data for the temperatures of 293.15; 298.15; 400° and then for every other

100°K up to a temperature at which the vapor pressure reaches a value of the order of 100 atm. These tables also give the values or the thermodynamic properties at the melting point and at the temperatures of polymorphous transformations of the substance.

All values of the thermodynamic functions in the tables of thermodynamic properties have the dimension of cal/mole and cal/mole·degree, the constants of equilibrium and the vapor pressures are given in physical atmospheres (760 mm Hg).

The Layout of the Material of the Handbook. The layout of the material in the Chapters 5 – 31 of Volume I of the Handbook and also the layout of the tables of Volume II was done according to the principles governing the compilation of modern thermochemical handbooks (see Vol. II, Fig. 1). Correspondingly the data for oxygen are listed first, then those for hydrogen, of its isotopes and their oxygen compounds, followed by helium and the other elements of the group of inert gases, fluorine and the other halogens, and then the elements of all the groups of the Periodic System including the elements of the first group. For each element its compounds with all foregoing elements are listed, first the monatomic compounds, then the diatomic followed by the compounds with a growing number of atoms.

It must be mentioned that this order is rigidly observed only in the layout of the tables of Volume II and in the Divisions "Thermodynamic Properties of Substances in Condensed States" and "Thermochemical Values" of the chapters of Volume I. In the Sections "Molecular Constants" and "Thermodynamic Functions" of each chapter the data of the monatomic substances are discussed first, then those of the diatomic ones, and, finally, those of polyatomic compounds; in each group the sequence of treatment depends on the nature of the material; as regards the assignment of the material to the individual chapters, as a rule

each chapter deals with the compounds of a single element (or a number of elements with similar properties). The carbon compounds, which are treated in six chapters, and the hydrogen halides, which constitute an own chapter, are exceptions.

The Chosen Nomenclature of Chemical Compounds. For the inorganic compounds teated in the Handbook in general this nomenclature was observed which corresponds with the Project of the Nomenclature of Inorganic Compounds, developed by the Commission of the Terminology of Chemical Compounds at the Division of Chemical Sciences of the Academy of Sciences USSR, reported on the VIII Mendeleyev Congress (see [338a]). Some deviations from this nomenclature serve the purpose of avoiding cumbersome terms, but only if misunderstandings are impossible. Thus, P_4O_6 was not termed four-six phosphorus oxide, as proposed by the Commission, but was allotted the common term of phosphorus trioxide

For organic compounds such as the halogen derivatives of methane, ethylene, and acetylene, the rational nomenclature is used, and customary names are used for the other compounds. This cannot give rise to misunderstandings, since the Handbook does not contain compounds consisting of more than two carbon atoms (with the exception of C_3 and C_3O_2). All terms and the formulas of the corresponding compounds are listed in the Index of Tables of Volume II.

The Chosen Terminology and the Measuring Units. The Handbook uses the nomenclature and the terminology recommended by the International Union of Theoretical and Applied Chemistry (see [367a]) and the International Union of Theoretical and Applied Physics (see [2230, 2836, 3423]), with the exception of such cases where this recommendation is essentially different from the terminology applied in the Soviet Union. A survey of the symbols and terms chosen in this Handbook is given at the end of Volume I.

The values of the fundamental physical constants are chosen according to the paper of Cohen, Du Mond, Layton, and Rollett, published in 1955 [1143], and, as regards the absolute thermodynamic temperature scale, according to the XI General Conference on Measures and Weights. The accepted values of constants and conversion factors for the energy units are quoted in Supplement 2.

In accordance with the custom of modern literature on chemical thermodynamics and thermochemistry and in agreement with the recommendation of the Commission on Chemical Thermodynamics at the Division of Chemical Sciences of the Academy of Sciences USSR (see [344a]), in the Handbook all thermal units are given in calories per gram-mole,* using the following relation between calory and absolute joule:

$$1 \text{ cal} = 4.1840 \text{ absolute joules},$$

and the atomic weights are given according to the chemical scale (see Supplement 1).

The values of all thermodynamic properties are calculated for the substances in standard state. The standard state of a pure solid or liquid substance is its state at a temperature of 298.15°K and a pressure of 1 physical atmosphere. The standard state of a gas at any temperature is assumed to be its hypothetical state, when its vapor pressure is equal to 1 atm. For ideal gases this state is identical with the gas state at a pressure of 1 atm.

The Numeration of the References, Equations and Figures. The present Handbook contains a coordinated list of references, which is preceded by a list of reports concerning the experimental investigations carried out when preparing the present Handbook. The list of abbreviations chosen for periodicals, and the Russian transcription of the names of foreign authors is based on the recommendations of the Institute for Scientific Information of the Academy of Sciences USSR.

Each equation given in the Handbook has a double numeration specifying the chapter: the first (roman) figure denotes the number of the chapter, the second (arabic) figure the number of the equation within the chapter; with the equations of the Supplement, the letter "P" and the number of the Supplement is given instead of the roman figure. The numeration of the tables and figures is continuing throughout each volume. In order to avoid possible mistakes all references to tables of Volume II contain an indication as to the volume in words, or the number of the volume is given in parentheses following the number of the table. For example: Table 126 of Volume II of the Handbook, or Table 126 (II). If reference is made to tables of Volume I, the number of the volume is not mentioned.

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[Footnotes]

29 For elements and monatomic gases the gram-mole is assumed to be identical with the gram-atom.

Part One

METHODS OF CALCULATION OF THERMODYNAMIC PROPERTIES

OF

INDIVIDUAL SUBSTANCES

§1. GENERAL RELATIONSHIPS BETWEEN THE THERMODYNAMIC QUANTITIES

For heat engineering calculations as well as for the calculation of chemical processes occuring at constant pressure,* two thermodynamic properties, the entropy S_T and the enthalpy H_T, must be known of each substance participating in these processes. In order to calculate the equilibrium of chemical reactions and to determine the equilibrium compositions resulting from any processes in the system investigated, we must also know the equilibrium constants of all independent chemical reactions possible in the system given. In the case of ideal gases the equilibrium constant K_p of the chemical reaction

$$\nu_1 X_1 + \nu_2 X_2 + \nu_3 X_3 + \ldots \rightleftarrows \nu_1' X_1' + \nu_2' X_2' + \nu_3' X_3' + \ldots \quad (1)$$

(ν_i – is the number of moles of the substance X_i), which occurs at constant pressure and at the temperature T, is determined by the formula

$$K_p = \frac{p_{X_1'}^{\nu_1'} p_{X_2'}^{\nu_2'} p_{X_3'}^{\nu_3'}}{p_{X_1}^{\nu_1} p_{X_2}^{\nu_2} p_{X_3}^{\nu_3}}, \quad (2)$$

where p_{X_i} is the equilibrium partial pressure of the substance X_i.** The value of K_p may be calculated from the values of the isobaric-isothermic potential G_T°, if it is known for all substances participating in the reaction considered:

$$RT \ln K_p = -\Delta G_T^\circ = \nu_1' G_T^\circ(X_1') + \nu_2' G_T^\circ(X_2') + \nu_3' G_T^\circ(X_3') + \ldots - \nu_1 G_T^\circ(X_1) - \nu_2 G_T^\circ(X_2) - \nu_3 G_T^\circ(X_3) \ldots, \quad (3)$$

R is the universal gas constant (see Supplement 2); ΔG_T° – is the change of the isobaric-isothermic potential of the system as a result of the reaction (1).*** The isobaric-isothermic potential G_T°, simply called

the thermodynamic potential in what follows, is connected with the entropy and enthalpy by the following simple relation

$$G_T^\circ = H_T^\circ - S_T^\circ \cdot T, \qquad (4)$$

so that in order to calculate the equilibrium constant of reaction (1) we have instead of Eq. (3)

$$R \ln K_p = \Delta S_T^\circ - \frac{\Delta H_T^\circ}{T}, \qquad (5)$$

where ΔS_T° and ΔH_T° – are the change in entropy and enthalpy, respectively, of the system at the temperature T, caused by reaction (1), and ΔH_T° is the thermal effect of the reaction at the same temperature.

We have already noted that the experimental determination of the thermodynamic functions of gases, including the entropy and enthalpy, present a rather complex problem, which at present cannot be solved at temperatures higher than 1000°K. In spite of that the values of the thermodynamic functions of any gas can be calculated theoretically, if the energy states of its molecules are known. The thermodynamic functions are expressed by a statistical sum or the sum of the states of the molecules (or atoms in the case of monatomic gases). The statistical sum is given by the formula

$$Q = \sum_i p_i \exp\left(-\frac{\varepsilon_i - \varepsilon_0}{kT}\right), \qquad (6)$$

where ε_i – is the energy of the ith level of the molecule (or atom), ε_0 – is the level energy corresponding to the minimum values of the quantum numbers, p_i – is the statistical weight of the ith level, k is Boltzmann's constant (see Supplement 2), and T is the temperature of the gas.

In this case the thermodynamic functions of one mole of an ideal gas consisting of identical molecules (or atoms), at constant pressure, are connected with the quantity Q and its derivatives by the following

$$S_T^\circ = R \ln \frac{Q}{N} + RT \left(\frac{\partial \ln Q}{\partial T}\right)_\rho, \qquad (7)$$

$$H_T^\circ = H_0^\circ + RT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_\rho, \qquad (8)$$

$$G_T^\circ = H_0^\circ + RT \ln \frac{Q}{N}, \qquad (9)$$

$$C_\rho^\circ = 2RT \left(\frac{\partial \ln Q}{\partial T}\right)_\rho + RT^2 \left(\frac{\partial^2 \ln Q}{\partial T^2}\right)_\rho. \qquad (10)$$

H_0° is the enthalpy of the gas at 0°K or the zero energy of the gas.

Though Eqs. (7) – (10) only permit the calculation of the values of the thermodynamic functions of a gas at constant pressure, analogous functions at constant volume (internal energy E_T°, isochoric-isothermal potential F_T°, constant-volume specific heat C_V°) can be calculated from the following equations:

$$E_T^\circ = H_T^\circ - RT, \qquad (11)$$

$$F_T^\circ = G_T^\circ - RT, \qquad (12)$$

$$C_v^\circ = C_\rho^\circ - R. \qquad (13)$$

It results from Eqs ( ) – (10) that the theoretical calculations of the values of the enthalpy H_T° and of the thermodynamic potential G_T° through the statistical sum, which, just as the experimental measurements, are based on the third law of thermodynamics, only permit the determination of the difference of these functions at different temperatures, e.g., between a given temperature and 0°K. This fact, however, does not raise any fundamental difficulties in the subsequent calculations, since, in order to investigate arbitrary processes, we need not know the absolute values of the enthalpy and the thermodynamic potential, but only the values of their changes caused by the chemical reactions occuring in the system, or the change in the system's temperature. In particular, another equation can be obtained for the equilibrium constant of the reaction (1) instead of Eq. (3), an equation which is more convenient for the calculation of the termodynamic functions of gases by statistical methods:

$$R \ln K_p = -\frac{\Delta G_T^\circ}{T} = -\frac{\Delta (G_T^\circ - H_0^\circ)}{T} - \frac{\Delta H_0^\circ}{T} = \Delta \Phi_T^\circ - \frac{\Delta H_0^\circ}{T}, \quad (14)$$

where ΔH_0° – is the change in enthalpy caused by the chemical reaction or the thermal effect of the reaction at 0°K; $\Delta \Phi_T^*$ – is the change in reduced thermodynamic potential.

$$\Phi_T^\circ = -\frac{G_T^\circ - H_0^\circ}{T} \quad (15)$$

at the temperature T°K.*

As may be seen from Eqs. (8), (9), and (15), the reduced thermodynamic potential Φ_T^*, is proportional to the natural logarithm of the statistical sum

$$\Phi_T^\circ = R \ln \frac{Q}{N}, \quad (16)$$

and its absolute value may be calculated in the same way as the values of the entropy S_T° and the specific heat C_p°.

When calculating the thermodynamic functions the statistical sum is represented in terms of a product of the components of the statistical sum which are connected with the progressive motion of the gas particles and their intramolecular motions. Correspondingly, the thermodynamic functions of the gas, which are proportional to the logarithm of the statistical sum and its derivatives, are equal to the sum of the logarithms of the components of the statistical sum, connected with the progressive and intramolecular motions. With ideal gases, the components of the progressive motion are simple functions of the temperature and pressure of the gas (see p.124), and the intramolecular components depend essentially on the structure of the molecules or atoms of the gas.**

In cases where the corresponding data are known from experimental investigations (for example as a result of spectroscopic investigations) or where they may be estimated theoretically, the intramolecular com-

ponents may be calculated with a certain degree of accuracy depending on the accuracy of the method of calculation applied. Appropriate methods are described in Chapter II.

At present, in contrast to the thermodynamic functions of gases, the thermodynamic functions of substances in condensed state cannot be calculated theorethically, but are determined on the basis of results of calorimetric measurements of their specific heats or of the change in enthalpy, as well as of the heats of phase transitions and polymorphous transitions from 0°K to the temperature range in question Since at 0°K the specific heats and the entropies of pure substances in crystalline state are equal to zero, we have

$$S_T^\circ = \int_0^T \frac{C_p^\circ}{T} dT + \sum_i \frac{\Delta H^{(i)}}{T^{(i)}}. \qquad (17)$$

where $\Delta H^{(i)}$ and $T^{(i)}$ - are the heats and temperatures of phase transitions and polymporphous transitions. The enthalpy (and intrinsic energy) of solids as well as that of gases is not vanishing at 0°K and cannot be measured or calculated. Thus, measurements of the specific heats and of the heats of phase transitions and polymorphous transitions yield only the difference of the enthalpies of the substance at at the given temperature and at 0°K:

$$H_T^\circ - H_0^\circ = \int_0^T C_p^\circ dT + \sum \Delta H^{(i)}. \qquad (18)$$

If the change in enthalpy and entropy of the substances have been determined, the values of the thermodynamic potential Φ_T^* may be obtained from the relations (15) and (4):

$$\Phi_T^\circ = S_T^\circ - \frac{H_T^\circ - H_0^\circ}{T}. \qquad (19)$$

The problems connected with the calculations of thermodynamic functions of substances in condensed states on the basis of calori-

metric measurements are discussed in Chapter 3.

At the beginning of this section we mentioned that for heat engineering calculations and calculations of the equilibrium of chemical processes two thermodynamic properties must be known for each substance, namely the entropy S_T and the enthalpy H_T. As stressed above, theretical calculations and experimental investigations permit the determination of the absolute value of only one of these quantities, that is the entropy. The determination of the absolute value of the enthalpy of a substance (a solid, liquid or gaseous one) is impossible, since its enthalpy at 0°K or at any other temperature which might be chosen as the reference point, remains unknown. This, however, does not cause any fundamental difficulties with thermodynamic calculations. since it is sufficient to know the change in enthalpy of a substance as a result of the change in temperature of the system, i.e., the value of $H_T^\circ - H_0^\circ$, and the change in enthalpy of the system caused by the chemical processes occurring in it, i.e., the value of ΔH_T°. Thus it is possible to use instead of the absolute values of the enthalpy their relative values, chosing any arbitrary reference system.

In modern literature the choice of a point of reference for the enthalpy of individual substances (as well as for the determination of their heats of formation) is usually based on the assumption that the enthalpy of the elements in standard states is equal to zero at a certain temperature T_0. Standard state of elements is termed their stable state at this temperature and at a pressure of one atmosphere. It is then convenient to replace the absolute enthalpy H_T, which cannot be determined, by a new function, which in heat-engineering literature is called the total enthalpy I_T^c. The value of I_T° is equal to the heat of formation of the given substance at the temperature T from elements in standard states at the temperature T_0:

$$I_T^\circ = \Delta H^\circ f_{T_0} + H_T^\circ - H_{T_0}^\circ, \qquad (20)$$

where H_T° and $H_{T_0}^\circ$ are the enthalpy of the substance at the temperatures T and T_0,

$$H_T^\circ - H_{T_0}^\circ = (H_T^\circ - H_0^\circ) - (H_{T_0}^\circ - H_0^\circ).$$

$\Delta H^\circ f_{T_0}$ – is the heat of formation of the substance from the elements at T_0 and p = 1 atm.

One of the three temperature values 0, 293.15, or 298.15°K is usually chosen as the reference point for the total entropy. As most engineering publications, the present Handbook assumes T_0 = 293.15°K. Consequently, we have

$$I_T^\circ = \Delta H^\circ f_{293.15} + H_T^\circ - H_{293.15}^\circ. \qquad (21)$$

The Eqs. (5), (14), (20), show that, besides the values of the thermodynamic functions S_T°, Φ_T°, and $H_T^\circ - H_0^\circ$, the determination of the total enthalpy I_T° and the equilibrium constants K_p of the reaction, also requires data on the heats of formation of the substances from the elements in their st ndard states $\Delta H^\circ f_T$ and data on the thermal effects of the reactions for which the equilibrium constants are calculated The latter can only be calculated, if the heats of formation of elements in standard state are known for all substances participating in the reaction given, with the help of relation

$$\Delta H_T^\circ = \Delta(\Delta H^\circ f_T) = \nu_1' \Delta H^\circ f_T(X_1') + \nu_2' \Delta H^\circ f_T(X_2') + \nu_3' \Delta H^\circ f_T(X_3') + \ldots - \qquad (22)$$
$$- \nu_1 \Delta H^\circ f_T(X_1) - \nu_2 \Delta H^\circ f_T(X_2) - \nu_3 \Delta H^\circ f_T(X_3) - \ldots$$

Let us recall that the heat of formation at any other temperature may be found by means of the relation

$$\Delta H^\circ f_T = \Delta H^\circ f_{T_0} + \Delta(H_T^\circ - H_{T_0}^\circ), \qquad (23)$$

if the heat of formation of the substance considered is given at the temperature T_0; $\Delta(H_T^\circ - H_{T_0}^\circ)$ – is the difference of the changes in enthalpy the given substance and the elements in their standard states

suffer when the temperature changes from T_0 to T.

In order to calculate the compositions of complex mixtures, which may form in the system as a result of some kind of reaction, we must know the equilibrium constants of all independent reactions possible in the system considered. The number of these reactions is equal to the number of substances which constitute the system minus the number of the elements constituting these substances (and the electron, if ionized gases take part in the reaction). If tables of thermodynamic properties are to be compiled for a great number of substances, it is convenient to calculate the equilibrium constants of all compounds for one of the following two types of reactions: the reaction of formation (or dissociation) of the compounds from the elements in standard states or of the reactions of dissociation into atoms. It is an essential advantage of the first case that the thermal effect corresponding to the reaction is equal to the heat of formation of the substance from the elements in standard state, and does not depend on the data for other substances. But if we want to apply the equilibrium constants of this type in high-temperature calculations, when the elements are in states different from their standard state, we need additional data on the pressure of the saturated vapors of these elements. Furthermore, if the composition of complex mixtures is calculated on electronic computers, it is more convenient to use the equilibrium constants of the atomization reaction. The present Handbook therefore gives the equilibrium constants of their reactions of dissociation into atoms for all diatomic and polyatomic gases (disregarding charged gases); the thermal effects of these reactions are equal to the dissociation (or atomization) of the molecules of the corresponding gases. The ionization constants of the corresponding neutral or negatively charged gases are given for charged monatomic or diatomic gases, and the vapor pressure, which is

an equilibrium constant of the sublimation or evaporation reactions, is given for substances in condensed states. It is evident that in the latter case

$$R \ln K_p = R \ln p = \Delta\Phi_T^* - \frac{\Delta H s_0}{T}, \qquad (24)$$

where $\Delta\Phi_T^*$ – is the change in reduced thermodynamic potential at the evaporation of the substance, and ΔHs_0 – is the thermal effect of the sublimation reaction at 0°K.

Chapter 4 deals with the problems connected with the determination of the heat of formation and heat of sublimation of substances and also with the determination of their dissociation and ionization energies.

The present part of the Handbook (Chapters 1 – 4) does not claim to give a complete representation of the material concerned. As a rule, only those problems have been treated which are immediately connected with the calculation of the tables of thermodynamic properties listed in Volume II. The corresponding sections also contain indications as to the most important literature for each individual question. The reader is assumed to be familiar with the courses on physics, physical chemistry and thermodynamics to an extent which corresponds to the course of instruction of the chemical or heat-engineering higher institutes of learning.*

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[Footnotes]

32* Modern engineering processes are carried out, as a rule, at constant pressure. The corresponding thermodynamic properties at constant volume may be determined by means of the relations given on pages 33 and 34, when the thermodynamic properties of the substance at constant pressure are known.

32** For real gases the partial pressures in Eq. (2) are replaced by their volatilities f_{X_i}.

32*** Here and in the following the change of any thermodynamic property means the difference between its values for the sum of reaction products and the sum of the initial substances. The sign ° means that the corresponding function or its change are related to the standard state of the substance.

35* Instead of the function Φ_T° some papers use a somewhat different reduced potential, which can be designated by the symbol Φ_T', and which is connected with the corresponding functions considered above by the relation

$$\Phi_T' = -\frac{G_T^\circ - H_{298.15}^\circ}{T} = \Phi_T^\circ + \frac{(H_{298.15}^\circ - H_0^\circ)}{T}. \qquad (15a)$$

Thus, instead of Eq. (14) we obtain the following equation for the equilibrium constant:

$$R \ln K_p = \Delta\Phi_T' - \frac{\Delta H_{298.15}^\circ}{T}, \qquad (14a)$$

where $\Delta H^\circ_{298.15}$ – is the thermal effect of the reaction at 298.15°K.

35** Problems of structure and energy states of atoms and molecules are treated in Chapter 1.

40 Cf., for example, Kireyev, Kurs fizicheskoy khimii [Course on Physical Chemistry], [225]; Brodskiy, Fizicheskaya khimiya [Physical Chemistry], [99]; Karapet'yants, Khimicheskaya termodinamika [Chemical Thermodynamics], [214].

Chapter 1

ENERGY STATES OF ATOMS AND MOLECULES

In order to calculate the thermodynamic functions of gases by means of the statistical sum (6), we need data on the energy states which the molecules (or atoms) of the given gas are able to have, as well as data on the energies ε_i of the states and their respective statistical weights p_i. Owing to development of the quantum mechanical conceptions of the structure of matter and to the numerous investigations of spectra during the past 30-40 years, we have accumulated an extensive amount of data dealing with the energy states of many of the atoms and molecules. The corresponding data, needed in order to calculate the thermodynamic functions of gases which will be dealt with in this Handbook, are to be found in the 2nd Part of Volume I in the sections on "Molecular Constants". In this Chapter, general conceptions will be presented treating the energy states of atoms and simple molecules, which are significant for the application of statistical methods of calculation of the thermodynamic functions of gases. A statement of the problems having no direct connection with the fundamental material in the following chapters can be found in the monographs and original papers referred to in the text.

The material of the chapter is divided into three Sections dealing respectively with atoms, diatomic molecules and simple polyatomic molecules, because the energy states of each of these groups possess a number of peculiarities.

§2. ATOMS*

The energy states of atoms** are caused by the motion of their electrons in the electric field of the atomic nucleus, which is a field of central forces. The multiformity of the energy states of the atom and of the transition energies between these states depends on the number of electrons of the atom and on their distribution in the electron shell. It is known that the state of a single electron of an atom is uniquely characterized by the values of the following four quantum numbers of the electron: the principal quantun number n, which may assume any integral value greater than zero for each electron ($n = 1, 2, 3, \ldots$); the quantum number ℓ of the orbital angular momentum of the electron, which, at a given n, assumes integral values within the range of $0 \leq \ell \leq n - 1$; the magnetic quantum number m_ℓ, which assumes $2\ell + 1$ values ($\ell, \ell - 1, \ldots, -\ell$), and the quantum number m_s of the electron spin which is equal to $\pm 1/2$. The energy of the electron depends mainly on the magnitude of the quantum number n, and, to a lesser degree, on the magnitude of the quantum number ℓ. Electrons which differ only in the values of their quantum numbers m_ℓ and m_s, possess the same energy if an external magnetic field is absent, and the states corresponding to them are degenerate. Hence, the distribution of the electrons in the electron shell, or the electron configuration, is uniquely determined by the values of both quantum numbers n and ℓ, of each electron if an external magnetic field is absent. The electron configuration of an atom may be represented symbolically in the form

$$a_1 b_2 n_3 c_4 p_5 d_6 \ldots, \qquad (1.1)$$

where a, b, c, ... are the numbers of electrons with equal values of the quantum numbers n and ℓ.

According to the Pauli principle, two electrons of an atom cannot possess equal values of all four quantum numbers n, ℓ, m_ℓ and m_s. Owing

to this fact, an atom can contain only 2 electrons with the quantum number $n = 1$ ($\ell = 0$, $m_\ell = 0$, $m_s = \pm 1/2$), 8 electrons with $n = 2$ ($\ell = 0$, $m_\ell = 0$, $m_s = \pm 1/2$, and $\ell = 1$, $m_\ell = 1, 0 = -1$; $m_s = \pm 1/2$), 18 electrons with $n = 3$, etc.

Systematics of the electronic states of atoms. One or more energy states correspond to each electron configuration of the atom. The number of states corresponding to a given configuration and the type of each state may be uniquely determined on the basis of the sum rules of addition of the momentum vectors of the individual electrons (or of their quantum numbers) with account of the Pauli principle. In the case of the majority of atoms, especially of the atoms of light elements, the interaction between the orbital momenta of the various electrons of the atom and between their spin momenta exceeds essentially the interaction of the corresponding momenta ($\vec{\ell}$ and $\vec{s}$) of each individual electron (in the case of Russell-Saunders coupling). The electron states of such atoms are characterized by the magnitude of the total orbital angular momentum $\vec{L}$ and the total spin momentum $\vec{S}$, which are equal to the sums of the vectors $\vec{\ell}_i$ and $\vec{s}_i$. The total angular momentum $\vec{J}$ of the atom electrons in the given state is equal to the sum of the vectors $\vec{L}$ and $\vec{S}$. The quantum number of the total orbital momentum L may be found by means of the quantum numbers ℓ_i of the individual electrons assuming that the rules of vector addition hold; the quantum number S may be calculated in a similar manner on the basis of the quantum numbers m_s. The quantum number J, at given values of L and S, assumes $2S + 1$ values*: $|L + S|$, $|L + S - 1|$, ..., $|L - S|$.

Each pair of the values of L and S corresponds to the energy state of the atom, which is termed its electron state or term. The electronic states of an atom are represented symbolically in the form

^{2S+1}L. (1.2)

The quantity 2S + 1 characterizes the multiplicity of the state or the number of its substates which differ by the values of the quantum number J. The states with S = 0 are termed singlet states, those with S>0 are termed multiplet states (doublet, triplet, quartet, quintet, etc., states; with the corresponding values of 2S + 1 = 2, 3, 4, 5, ... or S = 1/2, 1, 3/2, 2, ...). If an external magnetic or electric field is absent, each substate with a given value of the quantum number J is degenerate (2J + 1)-fold, i.e., it has the statistical weight of 2J + 1. Owing to the fact that J assumes the values $|L + S|$ $|L + S - 1|$ ..., $|L - S|$, the statistical weight of the state ^{2S+1}L is equal to (2L + 1) (2S + 1).

Strictly speaking, this is taken for granted when the spin of the atomic nucleus is equal to zero, otherwise the total angular momentum of the atom will be equal to J + I, J + I − 1, ..., J − I, where I is the spin of the atomic nucleus; in this case, the statistical weight of the substate with the given value of J is equal to (2J + 1) (2I + 1), and the statistical weight of the ^{2S+1}L state is equal to (2L + 1) (2S + 1)(2I + 1).

In the case of Russell-Saunders coupling, the energy of the electronic states, related to the same configuration of the electron shell, depends substantially on the value of the quantum numbers L and S and is nearly independent of the quantum number . Due to this fact, the discrete components (substates) of multiplet states possess similar excitation energies.

Another type of coupling between the angular momenta of individual electrons, termed j-j coupling, is possible in atoms of certain heavy elements, Pt and Pd, as an example, and also in atoms of light elements in states corresponding to great values of the quantum number n.

In the case of such a coupling, the interaction is weak between the orbital momenta of the individual electrons and also between their spin momenta, and the interaction between the orbital angular momentum and the spin moment of each electron plays the main part. The resultant of this interaction is the total angular momentum $\vec{j}_i$; it is equal to the sum of the vectors $\vec{l}_i$ and $\vec{s}_i$, and its quantum number is $j_i = l_i \pm 1/2$. The total angular momentum ($\vec{J}$) of the electrons of the atom, in the case of a j-j coupling, is equal to the sum of the total momenta $\vec{j}_i$ of all electrons, and its quantum number J is equal to the sum of the quantum numbers j_i, added according to the rules of vector addition.* It must be noted that definite values of the quantum numbers L and S do not exist with such a type of coupling; the total number of states of the atom, which corresponds to the given configuration of the electron shell, and the quantum J of the total angular momentum in each substate, however, do not depend on the type of coupling. The fundamental difference consists in the relative position of the electronic states which correspond to the given configuration of the atom electrons,** and also in the selection rules for optical transitions, what is not substantial for the problems treated in the Handbook. This fact permits us to use systematics which correspond to the Russell-Saunders coupling in the investigation of the electronic states of almost all atoms,*** including the atoms and ions of all elements which are dealt with in this Handbook.

The electronic state of an atom with a minimum energy is termed its ground state or its normal state; furthermore, the energy of this state will be taken equal to zero****. The other of the electronic states of an atom are termed excited states, and the difference between the excited and the ground state is the excitation energy. If not one but some electronic states of the atom correspond to one elec-

tron configuration, the state with the greatest multiplicity possesses the lowest energy, according to Hund's rule, and, in the case of equal values of S, the state with the highest value of L has the lowest energy. With regard to exclusions from this rule, see [196], p. 391.

In the literature on the theory of structure and of atom and molecule spectra, the electronic states with the quantum numbers $l = 0, 1, 2, 3, 4, 5, \ldots$ are termed s-, p-, d-, f-, g-, ... states,* and the electronic states of atoms with the values $L = 0, 1, 2, 3, 4, 5, 6, 7, 8, \ldots$ are usually termed S-, P-, D-, F-, G-, H-, I-, K-, L-, ... states.

Determination of the electronic states of atoms. The number and the type of the electronic states of an atom, which correspond to a given configuration of its electron shell, are uniquely determinable on the basis of the general rules of angular momentum addition of the individual electrons and the Pauli principle.

According to the statements above, the interaction between the angular momenta may be assumed as corresponding to a Russell-Saunders coupling, if their vectors are to be added. The application of the Pauli principle has two important consequences. Primarily, the quantum numbers of the total angular orbital (L) and the spin (S) momenta of the electrons which form a complete shell are always equal to zero; the resultants of these moments for the two s electrons, the six p electrons, the ten d electrons, the fourteen f electrons, etc., are also equal to zero.** Secondly, the number of the atomic states which corresponds to the given number of electrons is different and depends on the fact, that these electrons be either equivalent (i.e., having equal values of the quantum numbers n and l) or non-equivalent (i e., having different values at least of one of these quantum numbers).

Let us examine the determination of the multiplicity of electron-

ic states of atoms using the nitrogen at ' as an example. The electron shell of the N atom contains seven electrons, the lowest states of these electrons are two 1s states, two 2s states, and three 2p states; corresponding to this, the nitrogen atom has in its ground state the electron configuration $1s^2 2s^2 2p^3$. The values of L and S are equal to zero for the $1s^2 2s^2$ electrons, and one may take into account only the three p electrons in the nonfilled shell when determining the electron states which correspond to the $1s^2 2s^2 2p^3$ configuration.* These three electrons are equivalent because $\ell = 1$ and $n = 2$ is valid for each of them. As an illustration of the general case, let us examine at first the states which correspond to three non-equivalent p electrons (being possible when the electrons possess different quantum numbers n), and then let us determine, which of these states are possible for equivalent electrons.

TABLE 2

Electron States of Atoms in the Case of Non-equivalent Electrons.

Конфигурация электронной оболочки 1	2 Электронные состояния
s s	^1S, ^3S
s p	^1P, ^3P
s d	^1D, ^3D
p p	^1S, ^1P, ^1D, ^3S, ^3P, ^3D
p d	^1P, ^1D, ^1F, ^3P, ^3D, ^3F
d d	^1S, ^1P, ^1D, ^1F, ^1G, ^3S, ^3P, ^3D, ^3F, ^3G
s s s	^2S, ^2S, ^4S
s s p	^2P, ^2P, ^4P
s s d	^2D, ^2D, ^4D
s p p	^2S, ^2P, ^2D, ^2S, ^2P, ^2D, ^4S, ^4P, ^4D
s p d	^2P, ^2D, ^2F, ^2P, ^2D, ^2F, ^4P, ^4D, ^4F
p p p	$^2S(2)$, $^2P(6)$, $^2D(4)$, $^2F(2)$, ^4S, $^4P(3)$, $^4D(2)$, ^4F
p p d	$^2S(2)$, $^2P(4)$, $^2D(6)$, $^2F(4)$, $^2G(2)$, ^4S, $^4P(2)$, $^4D(3)$, $^4F(2)$, ^4G
p d f	$^2S(2)$, $^2P(4)$, $^2D(6)$, $^2F(6)$, $^2G(6)$, $^2H(4)$, $^2I(2)$, ^4S, $^4P(2)$, $^4D(3)$, $^4F(3)$, $^4G(3)$, $^4H(2)$, ^4I

1) Configuration of the electron shell; 2) electronic states.

In order to determine the quantum numbers of the resultants of the vectors of orbital momenta of three electrons, we first have to find the vector sum of the quantum numbers of two vectors, and then each one of these sums must be added to the quantum number of the third vector. Thus, we have $1 \tilde{+} 1 = 0, 1, 2$ (where $\tilde{+}$ is the sign for the vector addition), and $1 \tilde{+} 1 \tilde{+} 1 = 1; 0, 1, 2$, and $1, 2, 3$. Each one of the found values of L corresponds to states with different values of S. Due to the fact that these states are related to three electrons, the quantum number S may assume the values 1/2, 3/2 and 1/2; and two ^2S, six ^2P, four ^2D, two ^2F, one ^4S, three ^4P, two ^4D and one ^4F states correspond to all three non-equivalent p electrons. In order to simplify the determination of the electronic states formed by each of the configurations of the electron shell of atom, the corresponding data used for the most frequently occurring cases of configurations of non-equivalent electrons are quoted in Table 2. Similar data for equivalent electrons are listed in Table 3.

As shown in Tables 2 and 3, it is evident in the case of equivalence electrons that the number of possible states is essentially smaller than that in the case of non-equivalent electrons, because owing to their having equal values of the quantum numbers n and ℓ, these electrons must have different m_ℓ and m_s quantum numbers. In the case of three equivalent p electrons, for example, the same spatial orientation of the vectors of their orbital momenta is possible because they would have in this case equal values of three quantum numbers (n, ℓ, and m_ℓ), and because the quantum number m_s may assume only two values ($\pm 1/2$), and the atom would have two electrons with equal values of all four quantum numbers. Thus, states with L = 3 (F states) cannot correspond to three equivalent p electrons.

Furthermore, from the seven quartet states which are possible in

the case of three non-equivalent p electrons, one ^4S state only corresponds to three equivalent electrons. Indeed, the quantum numbers m_ℓ of these electrons must be different, equal to 0, +1, and −1, respectively, and, due to this fact, L = 0, because the projections of all electron spins must be parallel (2S + 1 = 4, and S = 3/2) in the quartet state, and the quantum numbers m_s are all equal. Furthermore, out of six D states formed by three non-equivalent p electrons, only one D state is possible with an electron shell containing two p electrons with equal values of the three quantum numbers n, ℓ, and m_ℓ (n = 2, ℓ = 1, m_ℓ = 1 at $m_s = \pm\frac{1}{2}$) and a third electron with another value of the quantum number m_ℓ (m_ℓ = 0).

TABLE 3

Electronic States of Atoms in the Case of Equivalent Electrons.

Конфигурация электронной оболочки	1 2 Электронные состояния
p^1	^2S
p^2	^1S, ^1D, ^3P
p^3	^2P, ^2D, ^4S
p^4	^1S, ^1D, ^3P
p^5	^2P
p^6	^1S
d^1	^2S, ^2D, ^2G, ^2P, ^2F
d^2	^3P, $^3D(2)$, ^3F, ^3G, ^3H, ^1P, ^1F
d^3	$^2S(2)$, $^2D(2)$, ^2F, $^2G(2)$, ^2I, $^2P(2)$, ^2D, $^2F(2)$, ^2G, ^2H, ^2D
d^4	^3S, ^3P, $^3D(3)$, $^3F(2)$, $^3G(2)$, ^3H, ^3I, ^1P, ^1D, ^1F, ^1G, ^1S

1) Configuration of the electron shell;
2) electronic states.

The determination of the number and of the types of states formed by equivalent electrons requires the additionally allowing for the so-called magnetic quantum numbers and deviates from the theme of our Handbook. The data quoted in Table 3 are sufficient for our purpose. According to these data, in the discussed case of three equivalent p electrons, only one ^2P state is possible beside the indicated ^4S and

^2D states. In accordance with Hund's rule (see p. 47) and the experimental data, the ^4S state is the lowest and ground state of these three states.

It must be noted in the case of a part of the electrons of the nonfilled atom shells being equivalent, and the other part non-equivalent, that in order to estimate the corresponding electronic states, we must determine the resultant moments of each electron group separately and then the sums of these resultant moments according to the general rules.

We considered the states of the nitrogen atom with a configuration of the electron shell, in which all electrons have the lowest orbits. The majority of the electronic states of atoms, however, is connected with an excitation of electrons, one or more electrons being in states with values of the quantum numbers n and ℓ which are higher than in the ground state. In order to differentiate between the states which correspond to the various configurations of the electron shell the configuration of the electron shell will be given frequently in front of the term symbol; thus the ground state of the nitrogen atom can be written down as either a $1s^2 2s^2 2p^3\ ^4S$ state, or, when excluding the configuration of the filled shells as a $2p^3\ ^4S$ state.

One or more groups of electronic states or terms originate if one electron of the atom or ion is excited. The number of these groups depends on the configuration of the electron shell of the ion which is formed when the electron is transferred to an infinite distance from the atomic nucleus. Thus, the excitation of a p electron of the nitrogen atom causes three groups of states which may be represented as follows: $2s^2 2p^2 (^3P)\ n\ell$; $2s^2 2p^2\ (^1S)\ n\ell$, and $2s^2 2p^2 (^1D)\ n\ell$, where n and ℓ are the values of the corresponding quantum numbers of the excited electron, $n \geq 3$, and $0 \leq \ell \leq n - 1$. The symbols of states, en-

closed in parenthesis, are the electronic states of the N^+ ion which has the electron configuration* $1s^2 2s^2 2p^2$.

When increasing the quantum numbers n and ℓ, the excitation energies of the corresponding states of the atom increase, and at $n \to \infty$ the excitation energy of the given group tends towards a certain limit, whose magnitude differs for each group. The energy of the lower limit which corresponds to the ground state of the ion is termed ionization potential of the given atom, and it is equal to the energy which is needed to remove to infinity the electron from the ion which is formed by ionization (in the ground electron state). The limit energies of the other states forming at the same time an ion in an excited state which corresponds to the given group. Thus the above-mentioned state groups of the nitrogen atom possess ionization limits with an energy of 117,345; 132,660 and ~ 150,000 cm^{-1} (see § 51) which correspond to the ionization of the nitrogen atom and the formation of the N^+ ion in ^3P, ^1D, and ^1S states, respectively.**

It is obvious that the number and type of the electronic states may be determined for each group of terms on the basis of the rules for the addition of the angular momenta just as it was shown a while ago. Thus the group of the $2s^2 2p^2$ (^3P) $n\ell$ states of the nitrogen atom consists of doublet and quartet terms with the values $L = 1$ at $\ell = 0$, and $L = \ell + 1;\ \ell;\ \ell - 1$ at $\ell \geq 1$.*** The states ^2F, ^4F, ^2G, ^4G, ^2H, and ^4H, for example, correspond to the values $L = 5$ and $S = 4$ (electron configuration $2s^2 2p^2 (^3P) 5g$). The term group $2s^2 2p^2 (^1D)$ $n\ell$ consists of doublet terms (the total spin of the two 2p electrons of the N^+ ion being equal to zero) with the values $L = 2$ at $\ell = 0$; $L = 1, 2, 3$ at $\ell = 1$, and $L = \ell \pm 2,\ \ell \pm 1,\ \ell$ at $\ell \geq 2$, etc.

Aside from the term groups related to the excitation of one of the outer electrons, the atoms possess a great number of state groups

caused by a simultaneous excitation of two or more outer electrons, and also of the electrons of filled shells. Thus the nitrogen atom at excitation of two 2p electrons has the electron configuration $2s^2 2pn_1\ell_1$ ($^{2S_1+1}L$) $n_2\ell_2$; the state groups $2s^2 2p^3 s$ (^1P) $n_2\ell_2$ and $2s^2 2p3s$ (^3P) $n_2\ell_2$ correspond in this case to the values $n_1 = 3$ and $\ell = 0$. Other groups originate from the simultaneous excitation of one 2s and one 2p electrons, etc.; thus six state groups with the configuration $1s^2 2s2p^3$ (^{2S+1}L) $n\ell$, where $^{2S+1}L = {}^3S$, ${}^5S$, ${}^3P$, ${}^5P$, ${}^3D$ and ${}^5D$, correspond to the case $n_1 = 2$, $\ell_1 = 1$.

Determination of the excitation energies of the electronic states of atoms. In evidence of the aforesaid the number of possible electronic states, the type and consequently also the statistical weight p_i can be ascertained without any kind of experimental data, only on the basis of an analysis of the configuration of the electron shells of the given atom. At the same time, a theoretical calculation of the excitation energies of all states of the atoms, which is also possible by application of the methods of quantum mechanics is such an intricate problem in practice, that we can get numerical results only in the most simple cases. Hence all modern data concerning the position of electronic states of atoms are based on the results of the analysis of their spectra.

The examination of the structure of spectra of atoms and the methods of determination of the excitation energies of their electronic states is beyond the purpose of our Handbook (see, for example [150]). Yet it must be noted, notwithstanding the experiments year after year of atomic spectra, that to this day, out of the majority of atoms and ions only the transitions have been investigated amongst a limited quantity of states, which is caused by the low probability of many transitions or by the fact that the corresponding transitions lie in

spectral ranges which are difficult to investigate. The most accurate data concerning electronic states of atoms have been collected in a handbook comprised of three volumes "Atomic Energy Levels" [2941] edited by Moore in the Bureau of Standards of U.S., 1950-1957.* Nevertheless even this handbook which not only refers to data published in periodicals, but also to the results of numerous special investigations carried out in the Bureau of Standards, lacks data in the case of many atoms, concerning states with $L \geq 3$, and also data concerning states connected with the simultaneous excitation of two or more electrons.

It must be noted, however, that experimental data, as a rule, are deficient in electronic states having high excitation energies, i.e., in such states whose contribution to the statistical sum and to the thermodynamic properties of the corresponding gas is trivial and takes place only at very high temperatures. Especially in the case of the atoms of the elements which are treated in this Handbook, the states, connected with the simultaneous excitation of several outer electrons or electrons of filled shells, may remain completely out of consideration.

If experimental data concerning the excitation energies of a part of electronic states of atoms are deficient, the necessary values must be approximately estimated, however at an accuracy which is sufficient to the subsequent calculations. The corresponding evaluations may be made either on the basis of some regularities of the position of the investigated electronic states of the given atom or (with states having high values of the quantum numbers) by referring these states to the ionization limit of the given group of states and putting their excitation energies equal to the ionization energy. The latter is thus made possible, because with an increase value of the quantum numbers r and k the excitation energies of the corresponding electronic states

converge to each other, and their value approaches that of the energy of the ionization limit.

In the above discussed group of states of the nitrogen atom $2s^2 2p^2 (^3P) n\ell$, the handbook by Moore [2941] quotes only data pertaining to states with $\ell = 0, n < 13; \ell = 1, n = 3$ and $4; \ell = 2, n \leq 12$; and there is a lack of data dealing with the states which correspond to values of $\ell \geq 3$ and also with states with $\ell = 1$ and $n \geq 5$. If, on the basis of the rules of vector addition we have determined the types of states which form the given group (see above), then we can estimate, as follows, the excitation energies of states, for which experimental data are not given. Out of the state group $2s^2 2p^2 (^3P)\ n\ell$ the terms with $\ell = 1$ and $n = k$, which were experimentally observed, have excitation energies which resemble the excitation energies of the terms with $\ell = 0$ and $n = k + 1$. For this reason all states of the group with $\ell = 1$ and $n \geq 5$ were ascribed to the known experimental energies of the states with $\ell = 0$ and having a value of n greater than unit. In the same group of states, the terms with $n = 4$ and $\ell = 0$, 1, and 2 have excitation energies in the range of 104,000, 107,000, and 110,000 cm^{-1}, respectively, and the energy of the ionization limit of the group is equal to 117,345 cm^{-1}. Hence excitation energies will be ascribed to the states with $n = 4$ and $\ell = 3$ as well as to all states $n \geq 5$ and $\ell \geq 3$ which are equal to the ionization energy of the nitrogen atom. The maximum error caused by this method of evaluation occurs at states with the configuration $2p^2 (^3P) 4f$ and does not exceed 4000 cm^{-1}; as for the other states, the error is considerably smaller and does not exceed 1000-1500 cm^{-1} on the average.

In order to calculate the thermodynamic functions of monatomic gases, we need data pertaining to the statistical weights and excitation energies of all those states of the gas atoms whose contribution

to the statistical sum (6) in the entire experimental temperature range may not be neglected. Corresponding data assumed for the calculations in this Handbook, are quoted in the special Tables "Energy Levels of the Atom ..." in the Divisions dealing with molecular constants. The values given in these tables are mainly taken according to Moore's Handbook [2941], to the results of approximate evaluations, and also to individual papers published in periodicals in the past years after publication of the handbook [2941]. References to the corresponding sources of information or evaluations are given in the texts of the Divisions dealing with molecular constants.

§3. DIATOMIC MOLECULES*

Unlike atoms or monatomic ions which possess energy states of only one type caused by the motion of the electrons in the electric field of the atomic nucleus, the energy states of diatomic molecules are connected with the motion of the electrons in the electric field of the molecule, the vibration of its atomic nuclei relative to each other, and the rotation of the atoms relative to the center of gravity of the molecule.

The energy of each atomic state is given by the numerical value obtained as a result of the analysis of its spectra or of theoretical calculations. In the case of diatomic molecules which possess a great number of discrete states, the presentation of the excitation energy of each separate state by a numerical value is practically impossible and inexpedient. The energy of a diatomic molecule considering the cases known at present can be represented as the sum of its electron energy T_e^i, vibrational energy $G(v)$ and rotational energy $F_v(J)$ in a sufficiently satisfactory approximation (see Eq. (1.30).

Usually, only the energies of the electronic states are represented by the numerical values. The energies of the rotational and

vibrational states will be expressed always, apart from rare exclusions in the case of the latter, as power functions of the corresponding quantum numbers (see below the Eqs. (1. 4) and (1. 15)) of each electronic state of the molecule.

Systematics of the electronic states of diatomic molecules. The motion of the electrons of a diatomic molecule takes place in an electric field with axial symmetry caused by the presence of two nuclei, where the symmetry axis coincides with the line which connects the two atomic nuclei. Differences in the symmetry of the electric fields of the atom and the molecule cause the essential differences in the peculiarities and systematics of the electronic states. Since the electric field of a diatomic molecule possesses axial symmetry the resulting orbital momentum vector $\vec{L}$ of the electrons in the molecule, owing to its interaction with the electric field, precesses around its axis in such a manner that the projection M_L of the vector on the axis of the field can assume only discrete values equal to L, L − 1, ..., −L, all together 2L + 1 values. The more powerful is the electric field of the molecule, the precession of the vector $\vec{L}$ around the field axis is all the more significant and the difference in the state energies, differing by the value of M_L is all the more greater. It must be noted that in the case of diatomic molecules the value of the orbital momentum of the electrons does not affect the energy of the electronic states of the molecule. We may therefore classify the electronic states of molecules according to the values of the quantum number of the orbital momentum's projection on the connecting line between the atomic nuclei, $\Lambda = |M_L|$, which at a given magnitude of L may assume the values 0, 1, 2, ..., L. When neglecting the rotation of the molecule, the electronic states which differ in the sign of M_L must possess equal energy and therefore all states with $\Lambda \geq 1$ are doubly degenerate.

The states with values of the quantum number Λ equal to 0, 1, 2, 3, ..., are termed Σ, Π, Δ-, and Φ states.

Apart from the value of the quantum number Λ the electronic states of a diatomic molecule are characterized by the total spin $\vec{S}$ of all its electrons, whose quantum number in the same manner as in the case atoms, assumes integral and half-integral values, depending upon whether the total number of the electrons of the molecule is even or odd. The quantum numbers Λ and S determine uniquely the type of the electronic state of the molecule, which may be represented symbolically in the form

$$^{2S+1}\Lambda, \qquad (1.3)$$

where the quan ity $2S + 1$, in the same manner as in the case of atoms, characterizes the multiplicity of the given state.

The spatial position of the vector $\vec{S}$ depends only on the magnetic field of the molecule and does not depend on its electric field. The magnetic field, absent in molecules in Σ state, arises as a result of the orbital motion of the electrons in all states with $\Lambda > 0$. In the presence of this field, the vector $\vec{S}$ precesses around the axis of the molecule in such manner that the projection $(\Sigma)^*$ of the vector on the direction of the axis may have only $2S + 1$ discrete values $\Sigma = S, S - 1, \ldots, -S$. The algebraic sum of the quantum numbers Λ and Σ is equal to Ω, the quantum number of the projection of the total momentum of the electrons of the molecule on the line which connects the nuclei of its atoms. At $\Sigma > 0$, each state is divided into several substates which differ from the values of $\Omega = \Lambda + \Sigma$, where the number of the substates is equal to the multiplicity of the given state, i.e., equal to $2S + 1$. Thus, the electron ground state of the NO molecule is a $^2\Pi$ state composed of the substates $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, of which the quantum numbers Σ, Λ and Ω are equal to 1/2, 1, 1/2 and 1/2, 1, 3/2, respect-

ively.

The system of the electronic state of a molecule may be determined in principle on the basis of the configuration of its electron shell (in the same manner as in the case of atoms) as well as on the basis of the rules for the correlation of the electronic states of the molecule with those of the atoms forming it, or with the electronic states of the so-called unified atom, i.e., the atom which is isoelectronic with the investigated molecule. An exposition of the pertinent problems goes beyond the scope of this Handbook; th. are dealt with in detail in the monograph by Herzberg [151] (see also the original papers by Mulliken [2982], Wigner and Witmer [4267] and others). Yet unlike the atoms, whose all electron states, which are admissible owing to the structure of their electron shells and the Pauli principle, are stable,* only such states of the molecules are stable, whose potential energy of the system passes through a minimum when the distance between their nuclei diminishes. In stable electronic states, the molecules possess systems of vibrational and rotational energy levels. Yet molecules possess in addition to stable electronic states, a great number of unstable repelling states, in which the potential energy of the diatomic system increases continuously when the atom nuclei approach each other.**

Although the methods of quantum mechanics make it fundamentally possible to predict theoretically which electronic states of the given molecule are to be stable and which ones are to be repellent, in practice, however, the corresponding calculations are able to yield numerical results only in the most simple cases, due to the complexity of the mathematical problem. Hence all data concerning the electronic states of diatomic molecules based on the analysis of spectra have been hitherto as a rule, incomplete and very limited. Therefore in the

absence of experimental data, at all events, it is impossible to determine not only the total number and the excitation energies of all electronic states of the molecule but we cannot even get the corresponding data for the lowest excited states. It must be noted that the majority of electronic states of diatomic molecules including the state forming the Rydberg series (i.e., such states in which the principal quantum number of one valence electron passes a series of subsequent values) possesses high excitation energies (see below). * Therefore such states are able to give an essential contribution to the statistical sum only at high temperatures when the corresponding diatomic gases are almost fully dissociated into the atoms.

In a stable electronic state, the potential energy of the molecule passes through a minimum when the atoms approach each other, and tends to zero when the atoms are removed from each other to infinity (if the given state is formed by atoms which are in electron ground states), or it tends to a value which is equal to the sum of the excitation energies of the atoms when the atoms, which form the molecule, are in excited states. The general form of the dependence of the potential energy of the molecule on the distance between the atomic nuclei in stable and in repellent states is shown in Fig. 1. A single several electronic states of the molecule may correspond to two atoms which are in definite electronic states. In such cases, we call this the correlation of the pertinent electronic states of the atoms and of the molecules.

The system of the electronic states of a diatomic molecule may be represented by a series of potential curves; the stable states of the NH molecule, known at present, are shown in Fig. 2. The potential curves of the states which correlate with the same states of the atoms have a common asymptote at $r \rightarrow \infty$ or a common dissociation limit (see

below, p.64). At the same time, the asymptotes of the potential curves of states which correlate with different states of the given atoms, are different. In the latter case, the difference of the energy of the corresponding dissociation limits is equal to the difference of the sum of the excitation energies of the corresponding electronic states of the atoms.

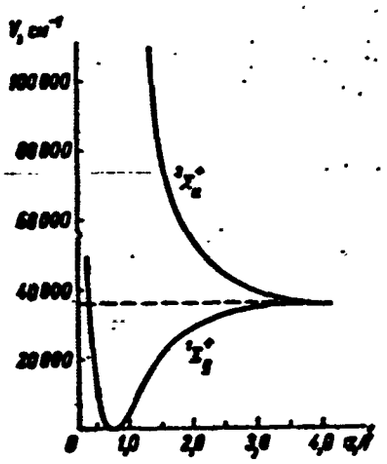


Fig. 1. Potential curves of stable and repellent electronic states of the H_2 molecule (Herzberg [151]).

When investigating the electronic states of molecules, the minimum of the potential energy of the molecular ground state is usually assumed as the zero energy, i.e., as the point of reference and the differences in the energies of the minima of the potential curves of the given and of the ground state, denoted by the symbol T_e, are assumed as the excitation energies. In spectroscopic literature it is usual to denote the lowest or ground state of the molecule by the letters A, B, C, ... according to their increasing excitation energies. Thus, the OH molecule has the ground state $X^2\Pi$ and the first excited state $A^2\Sigma$. It must be noted for light molecules that the states which have a multiplicity differing from the multiplicity of the ground state are denoted by the letters a, b, c, ..., whereas the states whose multiplicity is equal to the ground state, are denoted by the letters A, B, C, ...

Vibrational states of diatomic molecules. In each stable electronic state, a diatomic molecule possesses a system of discrete levels of vibrational energy. The vibrational energy G(v) of the molecule is a function of the magnitude of the vibrational quantum number v, which

in each electronic state assumes the values 0, 1, 2, 3, ... The energy of the vibrational states of a diatomic molecule may be represented as a power function of the values of the vibrational quantum number v:

$$G(v) = \omega_e\left(v+\tfrac{1}{2}\right) - \omega_e x_e\left(v+\tfrac{1}{2}\right)^2 + \omega_e y_e\left(v+\tfrac{1}{2}\right)^3 - \omega_e z_e\left(v+\tfrac{1}{2}\right)^4 + \ldots, \quad (1.4)$$

where G(v) is the energy of the vibrational state relative to the minimum of the potential energy of the given electronic state, ω_e is the oscillation frequency of the molecule, and $\omega_e x_e$, $\omega_e y_e$, ..., – are the anharmonicity constants of the molecular vibrations, where the constants ω_e, $\omega_e x_e$, $\omega_e y_e$, ... of the given molecule are different for each of their electronic states; and $\omega_e \gg \omega_e x_e \gg \omega_e y_e$ ...

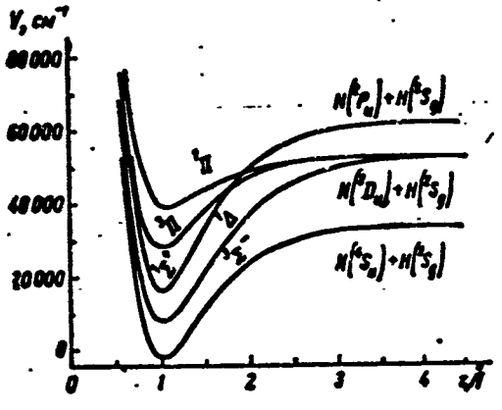


Fig. 2. Potential curves of the observed stable electronic states of the NH molecule (Herzberg [151]).

We note in Eq. (1.4), that corresponding to the experimental data and the deductions of the quantum mechanics, the vibrational energy of a molecule is always greater than zero, and its minimum value (in the state with v = 0) is equal to

$$G(0) = \tfrac{1}{2}\omega_e - \tfrac{1}{4}\omega_e x_e + \tfrac{1}{8}\omega_e y_e - \tfrac{1}{16}\omega_e z_e + \ldots \quad (1.5)$$

If the vibrational energy of the molecule is not related to the minimum of the potential energy but to its lower vibrational state, as is necessary, especially, in the calculation of statistical sums, we get in place of Eq. (1.4):

$$G_0(v) = G(v) - G(0) = \omega_0 v - \omega_0 x_0 v^2 + \omega_0 y_0 v^3 - \omega_0 z_0 v^4 + \ldots \quad (1.6)$$

where

$$\begin{aligned} \omega_0 &= \omega_e - \omega_e x_e + 0{,}75\,\omega_e y_e - 0{,}5\,\omega_e z_e + \ldots \\ \omega_0 x_0 &= \omega_e x_e - 1{,}5\,\omega_e y_e + 1{,}5\,\omega_e z_e - \ldots \\ \omega_0 y_0 &= \omega_e y_e - 2\,\omega_e z_e + \ldots \\ \omega_0 z_0 &= \omega_e z_e - \ldots, \\ &\ldots\ldots\ldots\ldots \end{aligned} \quad (1.7)$$

The constants with the subscripts e in Eqs. (1.4) , (1.6) are called equilibrium constants, and the constants with the subscripts 0 are the zero constants.

When the vibrational quantum number is increased, the vibrational energy of the molecule increases (and also the amplitude of the vibrations of its atomic nuclei), but its absolute value, as a rule, cannot exceed the difference between the potential energy of the molecule at $r = r_\infty$ and $r = r_e$, where r_e is the distance between the nuclei of the atoms at which the potential energy is a minimum. The value equal to the difference of the potential energy of the molecule at $r = \infty$ and $r = r_e$ is denoted by the symbol D_e.

This value is sometimes called the dissociation energy of the molecule. In practice, however, the energy needed to dissociate the molecule into atoms is less than D_e, because the molecules possess always vibrational energy. In this Handbook the term <u>dissociation energy of the molecule</u> will refer to the maximum energy, which is necessary to dissociate the molecule in the given electronic state into its component atoms*; it is denoted as D_0. The values D_e and D_0

are connected by the simple relation:

$$D_e = D_0 + G(0). \qquad (1.8)$$

The differences $\Delta G(v)$ of the vibrational energies decrease with an increasing quantum number v, and the corresponding vibrational levels converge to a definite limit called the dissociation limit of the given electronic state. The total sum of the levels of vibrational energy is finite for all investigated electronic states of diatomic molecules. This coincides with the results of theoretical calculations according to which the molecule AB may possess an infinite number of vibrational levels only if the chemical bond of the molecule is purely ionic, and if the potential energy of the molecule is due to the Coulomb interaction between the ions A^+ and B^- (see [141] p.107, and [2477]), whereas the electronic ground states of all diatomic molecules are correlated to the electronic states of neutral atoms.

The rate of convergence of the vibrational levels of the molecule to the dissociation limit and also the number of vibrational levels and the general type of the dependence of the vibrational energy of the molecule on the value of the quantum number v are determined by the functional dependence of the potential energy of the molecule on the distance between the nuclei of its atoms. If the potential energy of the molecule can be represented by a Morse function (which is a sufficiently satisfactory approximation for several problems)

$$V(r) = D_e\left[1 - e^{-\frac{r-r_e}{r_e}\cdot\frac{\omega_e}{2\sqrt{B_e D_e}}}\right]^2, \qquad (1.9)$$

where D_e is the dissociation energy of the molecule counted from the minimum of the potential curve, ω_e is the oscillation frequency of the molecule, r_e is the equilibrium interatomic distance of the molecule, and B_e is the rotational constant of the molecule (see below), then the levels of the oscillation energy of the molecule may be expressed

as a power function of second order* :

$$G(v) = \omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2. \qquad (1.10)$$

The function (1.9) has a maximum at

$$v_{max} = \frac{\omega_e}{2\omega_e x_e} - \frac{1}{2}, \qquad (1.11)$$

where the maximum value of the vibrational energy of the molecule may be found in this case by the simple relation**

$$G(v_{max}) = \frac{\omega_e^2}{4\omega_e x_e}. \qquad (1.12)$$

Since the vibrational energy of the molecule cannot exceed its dissociation energy in the given state (if the potential energy of the non-rotating molecule does not pass a maximum when the distance between the atomic nuclei decreases) the maximum vibrational energy, therefore, must agree with the dissociation energy of the molecule: If we represent the value of $G(v_{max})$ by the relation (1.8) and the expression (1.12), we get a simplified formula used in the determination of the dissociation energy of the molecule in terms of its oscillation frequency and the anharmonicity constant

$$D_e = \frac{\omega_e^2}{4\omega_e x_e} - \frac{1}{2}\omega_e. \qquad (1.13)$$

This relationship was proposed for the first time by Birge and Sponer [830] (see also [141]). Obviously, it is only sufficient if the potential energy of the molecule may be represented by a Morse function, if $r_e \leq r < \infty$, or, similarly, if Eq. (1.10) describes correctly the energy of the oscillation states of the molecule within the whole range of the values of $\underline{v}$. In the latter case, the difference of the energy of adjacent vibrational states is equal to $\Delta G_{v+1/2} = \omega_e - 2\omega_e x_e - 2\omega_e x_e v$, and, therefore, the intervals between the adjacent states decrease linearly with increasing $\underline{v}$.***

It must be remarked, however, that Eq. (1.10) and the corresponding equation for $\Delta G(v)$ in the most cases describe insufficiently the values of $G(v)$ and $\Delta G(v)$ which were obtained by analysis of molecular spectra. The Morse function, as a rule, gives only a general idea of the dependence of the potential energy of the molecule on the magnitude of the distance between the nuclei of its atoms. Indeed, this dependence is very complex and it has not hitherto been possible, irrespective of various experiments, to obtain such a function which would be sufficient for all circumstances. An analysis of various functions of the potential energy of diatomic molecules is given in the paper by Varshni [4072] (see also [141] and below). Nevertheless, it is wellknown from experimental data as well as on the basis of the assumption that the potential function of the molecule may be expressed in terms of a potential function of an anharmonic oscillator, that, generally, the energy of the vibrational states can be satisfactorily estimated by the power function (1.4) (see [151], p. 69 and ff.). To those cases, in which the application of Eq. (1.10) used for the energy of the vibrational levels of molecules results in considerable differences between the calculated and the experimentally measured values of $G(v)$ (or $\Delta G(v)$), one introduce into the equation of $G(v)$ terms proportional to the third and higher powers of the quantum number v. The constants of such an equation, i.e., the values of the oscillation frequency and the anharmonicity constants, are found by the method of least squares on the basis of the values of $G(v)$ and $\Delta G(v)$. being obtained by analysis of the vibrational or electronic spectrum of the molecule. Since there are not any theoretical considerations as to which order Eq. (1.4) must have, the order of the equation, in each concrete case, depends on the endeavour to obtain an equation of a low order (to facilitate the calculations) and on the demand of a

satisfactory agreement between the values of G(v) calculated from this equation and the experimental data.

Since, in the molecular spectra transitions usually are observed only between a lesser number of vibrational states, mainly between states having low values of v, the equations for G(v), obtained by analysis of spectra cannot sufficiently approximate the energy of all vibrational states of the molecule. Especially, the equations of third and higher powers obtained by this way, as a rule, neither permit the calculation of the energy of vibrational levels in enighborhood of the dissociation limit nor even the approximate, evaluation of the total number of levels in the given state. The vibrational levels calculated by means of such equations, converge either above or below the dissociation limit (which may be judged on the basis of independent data for the dissociation energy) or otherwise do not converge at all to a defined limit.

Since data, concerning the energy of the oscillation levels of the molecules including levels near to the dissociation limit, are necessary in order to calculate the statistical sums of diatomic molecules and the thermodynamic functions of the corresponding gases at high temperatures. It was proposed in paper [177] in determining the constants in Eq. (1.4), to consider two supplementary conditions in addition to the experimental values of G(v) or ΔG(v):

$$G_e(v_{max}) = D_e, \qquad (1.14a)$$

$$\left[\frac{\partial G_e(v)}{\partial v}\right]_{v=v_{max}} = 0, \qquad (1.14b)$$

The condition (1.14a) takes place in cases when a maximum on the potential energy curve is absent. The condition (1.14b) is the condition of the convergence of the vibrational energy levels to the dis-

sociation limit. Both conditions are not completely accurate, because the energy of the last vibrational state of the molecule never coincides exactly with the value of D_0, and the value of $G_0(v)$ is a discrete function of $\underline{v}$. However, the hitherto known experimental data for a series of molecules, shown that the determination of the vibrational constants, in consideration of these additional conditions is by all means admissible. The solution of the system of obtained equations may be carried out as usual by the method of least squares applying successive approximations in order to determine the value of v_{max}.* The number of terms in Eq. (1.4), i.e., the order of this equation, depends only on the required accuracy of the description of the experimental data. As we will point out below (see, for example, the sections on the molecular constants of O_2 and CO), the application of the specified method permits the obtaining of equations which describe satisfactorily the found experimental values of $G_0(v)$ and which results in a convergence of the vibrational levels near to the dissociation limit, and also the determination of the value v_{max} being made possible.

In cases when the experimental data for the values of $G(v)$ or $\Delta G(v)$ are known for $v \leq v_k$, and they described satisfactorily by an equation of n-th power, but these equations give incorrect values of the dissociation energy when extrapolating the equation to values $v > v_k$, more simple methods may be applied to determine the energy of levels with $v > v_k$. Thus, an additional term proportional to $\underline{v}$ in a $n + 1$ or $n + 2$ power may be introduced into the wellknown equation of the n-th power, by choosing a coefficient of this term which does not disturb the agreement of the experimental and the calculated values of $G(g)$ at $v < v_k$ the conditions (1.14a) and (1.14b) remaining satisfied, at the same time.

In the event that it is difficult to get an equation which satisfactorily estimates the energy of the levels in the whole range of the values of $\underline{v}$, we can formulate a second equation for $v > v_k$, conjugated to the first equation in the range $v \approx v_k$ and securing the convergence of the levels near to the dissociation limit. The constants of this equation for $G_0^!(v)$ may be obtained on the basis of the conditions $G_0^!(v_{max}) = D_0$, $[dG_0^!(v)/dv]_{v=v_{max}} = 0$, $G_0^!(v_k) = G_0(v_k)$, $G_0^!(v_{k-1}) = G_0(v_{k-1})$, etc., where the total number of applied relations must be equal to the power of the new equation plus one. When determining the constants of the equation $G_0^!(v)$, the condition of an equality of the functions $G_0^!(v)$ and $G_0(v)$ at $v = v_k$, v_{k-1}, v_{k-2}, etc. may be replaced by the condition that these functions and their derivatives must be equal for the value $v = v_k$.

Rotational states of diatomic molecules. In each oscillation state, the diatomic molecule possesses a system of levels of rotational energy related to the angular momentum $\mathbf{N}$ of the atomic nuclei the relative to the center of gravity of the molecule. Not taking notice of the interaction of this rotation with the motion of the electrons of the molecule, as taken for granted in the xase of the $^1\Sigma$ state, when the quantum numbers A and S are equal to zero, the total angular momentum of the molecule is equal to the momentum $\mathbf{N}$. In this case, the level of the rotation energy of a diatomic molecule may be expressed in terms of the following power function of the quantum number of the total angular momentum J (see [151])* :

$$F_v(J) = B_vJ(J+1) - D_vJ^2(J+1)^2 + H_vJ^3(J+1)^3 - L_vJ^4(J+1)^4 + \ldots, \quad (1.15)$$

where B_v, D_v, H_v, L_v, ... are the constants for the given vibrational and electronic state, and $B_v \gg D_v \gg H_v \gg \ldots$ is valid. These constants depend on the value of the vibrational energy of the molecule. For each electron state of the molecule, the dependence of these con-

stants on the value of the vibrational quantum number v may be represented by the power series.*

$$B_v = B_e - \alpha_1 (v + 1/2) + \alpha_2 (v + 1/2)^2 - \alpha_3 (v + 1/2)^3 + \ldots = B_0 - \alpha_1' v + \alpha_2'' v^2 - \alpha_3' v^3 + \ldots \quad (1.16)$$

$$D_v = D_e - \beta_1 (v + 1/2) + \beta_2 (v + 1/2)^2 - \ldots = D_0 - \beta_1' v + \beta_2' v^2 - \ldots$$

$$H_v = H_e - \gamma_1 (v + 1/2) + \ldots = H_0 - \gamma_1' v + \ldots,$$

where $B_e \gg \alpha_1 \gg \alpha_2 \gg \alpha_3$, $D_e \gg \beta_1 \gg \beta_2$ etc. The constants with the subscripts e and 0 relate to the minimum of the potential energy of the molecule and to its lowest vibrational state, respectively.

It must be mentioned that the constant B_e is donnected with the moment of inertia I_e of the molecule and its interatomic distance r_e by the simple relation

$$B_e = \frac{h}{8\pi^2 c I_e} = \frac{h}{8\pi^2 c \mu r_e^2}, \quad (1.17)$$

where h is the Planck constant, c is the velocity of light (see Supplement 2), $\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$ – is the reduced mass of the molecule (m_1 and m_2 are the masses of the atoms of the molecule).

The values of the constants in Eqs. (1.15) - (1.16) may be found by analysis of the fine structure of vibrational and electronic-vibrational spectra, where a specific set of constants corresponds to each electronic state of the molecule. At the present, however, the values of the constants in the equations of the levels of rotational energy are known only for a small number of molecules and not for all investigated electronic states, due to the insufficient resolving power of the spectral devices and the complex structure of the rotational spectra. Moreover, generally, only the constant B_e and D_e in Eq. (1.15) and the constant α_1 in Eq. (1.16) can be determinedly analysis of the spectrum, because in the molecular spectra transitions can be observed usually between a small number of rotational levels with low values of the

quantum number J, belonging to the lower vibrational states. Although the constants of these equations having higher powers of the quantum numbers can be calculated generally from the oscillation constants and the constants B_v and D_v (see below, p.86), yet, it is impossible to determine the energy of rotational states with high values of the quantum number J (being essentially higher in comparison with those at which transitions in spectra were observed). The situation is rendered more difficult, because, unlike the vibrational levels, the rotational levels of the molecules do not converge to a determined level when increasing the quantum number, whereas the intervals between them increase with increasing J.* The experimental data and the theoretical analysis prove especially, that all molecules possess rotational levels with energies, which exceed the energy of the dissociation level of the given electronic state of the molecule.

It must be noted (see [4322]), in the case of light molecules, H_2, for example, which possess great rotational constants, that the magnitude of $F_v(J)$ at high values of J depends essentially on the number of terms in the power series which approximate this function. In order to eliminate the errors caused by the application of rotational constants obtained by transitions between states with low values of J, Woolley, Scott and Bricwedde [4329] have proposed to add to the expression (1.15) the sum of a geometric progression in which the ratio of the coefficients of the subsequent terms is constant and equal to the ratio of the constants L_v and H_v. Thus the Eq. (1.15) assumes the following form:

$$F_v(J) = B_vJ(J+1) - D_vJ^2(J+1)^2 + H_vJ^3(J+1)^3 - L_vJ^4(J+1)^4 + \frac{[L_vJ^4(J+1)^4]^2}{H_vJ^3(J+1)^3 - L_vJ^4(J+1)^4}. \quad (1.18)$$

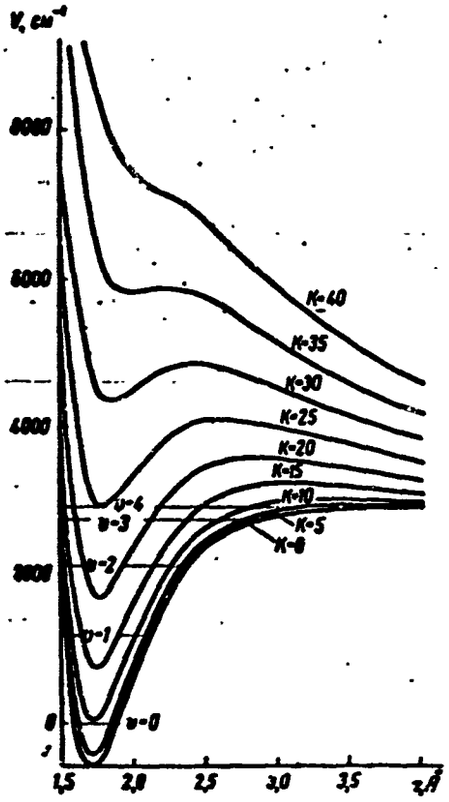


Fig. 3. Effective potential curves of the HgH molecule in electronic ground state (Herzberg [151]).
The levels of the vibrational energy are marked to the lower curve, corresponding to v = 0. For the other curves, the levels of the vibrational energy are shifted upwards by a value which is equal to the difference of the energy of the minima.

At the same time, at least the total number of rotational levels of the molecule in the given electronic and vibrational state must be known in order to calculate the thermodynamic properties of gases at high temperatures. In principle, the determination of the maximum values of the quantum numbers J is made possible by analysing the functions of the potential energy of diatomic molecules. An approximate method of the determination of the corresponding values used for a subsequent calculation of the statistical sums and the thermodynamic functions of diatomic gases was developed as shown in the papers [177, 688, and 401].

The potential energy of the rotating molecule increases at the expense of the kinetic rotational energy which is proportional to $J(J + 1)$. Assuming, according to [177], the Morse function (1.9) to be the potential energy of a nonrotating molecule, and the relation (1.15) to be the energy of the rotational levels, where we restrict ourselves to the first two terms, the effective potential energy will assume the form ($R = r/r_e$)

$$V(r) = D_e\left[1 - e^{-\frac{\omega_e}{2\sqrt{B_e D_e}}(R-1)}\right]^2 + \\ + \frac{B_e^2 J(J+1)}{R^2} - \frac{D_e J^2 (J+1)^2}{R^6}, \quad (1.19)$$

At $J > 0$, potential curves which lie higher than the potential curve of the nonrotating molecule, correspond to the function (1.19) (Fig.3). In addition to a minimum, the pertinent curves possess a maximum at $r > r_e$, where the distance on the ordinate, i.e. the depth of the potential well $\Delta V(r)$, characterizes the stability of the molecule in the given rotational state. The more J increases the smaller becomes the depth of the potential well; for a certain value of J_n the minimum and maximum coincide on the potential curve, and the molecule becomes unstable. Inasmuch as the molecule in any optional stable state must possess discrete levels of the vibrational energy, it is apparent that the depth of the potential well of a stable state cannot be smaller than the value of $G_0(v)$, and the maximum value of J must be smaller than the value of J_n. If, in the given electronic state, the quantum number v increases, the maximum value of J decreases; in this way, the number of rotational levels decreases the more the oscillation energy of the molecule increases.

The depth of the potential well may be determined by calculation of the values of $R = r/r_e$ for the extreme points of the potential curve and introducing them into Eq. (1.19). The values of R_{max} and R_{min}

are determined by the condition $\frac{\partial V(r)}{\partial r} = 0$. Assuming for V(r) the expression (1.19), we obtain from this condition

$$R^3 e^{-a(R-1)}[1 - e^{-a(R-1)}] = bJ(J+1) - \frac{d}{R^6}J^2(J+1)^2, \quad (1.20)$$

where

$$a = \frac{\omega_e}{2\sqrt{B_e D_e}}, \; b = \frac{2B_e}{\omega_e}\sqrt{\frac{B_e}{D_e}}, \; d = \frac{4D_e}{\omega_e}\sqrt{\frac{B_e}{D_e}}.$$

The introduction of the values of R_{max} and R_{min} obtained by solution of Eq. (1.20) into the equation of the effective potential energy (1.19) results in the values of $\Delta V(r) = V_{max} - V_{min}$, which are functions of the quantum number J. The values of ΔV found by this manner may be represented graphically as a function of the quantum number J (Fig. 4). The values of J_{max} for each vibrational state of the molecule may be found when the values of G(v) are plotted on the ordinate axis of Fig. 4, and the direct lines parallel to the abscissa axis are plotted for all values of v and drawn up to intersection with the curve $\Delta V(r) = f(J)$.

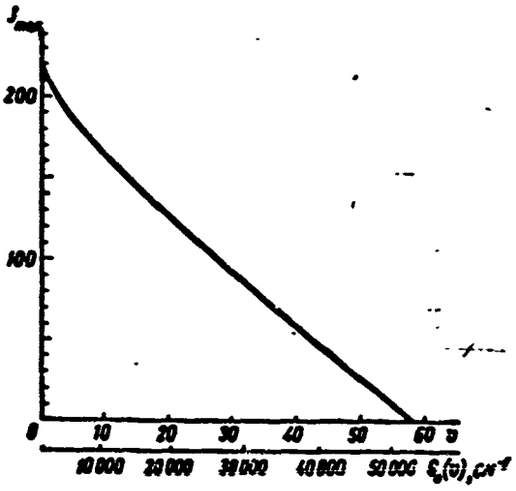


Fig. 4. J_{max} as a function of v for the $X^2\Pi_g$ electronic state of the O_2^+ molecule.

The values for J_{max} calculated from the above described method used for the $X^2\Sigma$ state of HgH (v = 0), the $B^3\Sigma$ state of O_2 (v = 11) and the $B^1\Pi$ state of LiH (v = 0), and also the values of J corresponding to the last lines observed in the spectra of these molecules are compared with in Table 4. For HgH, the value of J_n is also given whereat the minimum vanishes on the potential curve, and J_D, whereat the rotational energy of the molecule is equal

to its dissociation energy. One may assume that the total coincidence of the calculated J_{max} values together with the J values of the last lines observed experimentally is purely accidental, and, that indeed there exist in these molecules still on or more rotational levels. Nevertheless, such accuracy is completely satisfactory to the subsequent application of the corresponding values in the calculation of the statistical sums.

TABLE 4

Comparison of the Calculated Values of J_{max} with the Experimental Data.

J	HgH	LiH	O_2
$J_{max,\ выч}$ 1	30	8	11
$J_{max,\ эксп}$ 2	30	8	15
J_D	20	—	—
J_n	50	—	—

1) Vych; 2) eksp.

Interaction of the motion of the electrons and the nuclei of the molecule. In the event that, in a given electronic state, the quantum numbers Λ and S are not equal to zero, the magnitude of the rotational energy depends not only on the angular momentum $\vec{N}$ of the nuclei of the molecule, but also on the magnitude of the projection of the orbital angular momentum $\vec{\Lambda}$ of the electrons on the axis of the molecule, and on the electron spin $\vec{S}$. The functional dependence of the energy of the rotation levels of the molecule on the value of the quantum number of its total momentum J is determined by the interaction of the vectors $\vec{N}$, Λ, and $\vec{S}$. Five fundamental types of the interaction of these vectors have been investigated by Hund and are termed Hund's coupling cases a, b, c, c, and e. The investigation of the peculiarities of the interaction of the vectors in each case of coupling is beyond the

scope of this Handbook; an accurate discussion of these problems is given in the monographs by Herzberg [151, 2020] and also in the papers by Mulliken [2976, 2981, 2982].

It must be noted in the majority of the electronic states of molecules investigated as yet that the interaction of the vectors $\vec{N}$, $\vec{\Lambda}$, and $\vec{S}$ becomes similar to the Hund coupling cases a or b, or it is intermediate between them. The Hund coupling case a is realized mainly in states with $\Lambda > 0$, i.e., in Π, Δ, ... states. A magnetic field with the direction of the axis of the molecule and proportional to Λ arises in these cases due to the present moment of orbital motion of the electrons. The vector $\vec{S}$ is quantized with regard to the molecule axis as a result of interaction with this field, and Σ is the quantum number of the component of this field in the field direction. The quantum number J of the angular momentum of the molecule is in this case equal to the sum of the quantum numbers Ω (see p. 57) and N, and assumes the values Ω, $\Omega + 1$, $\Omega + 2$, ... (the quantum number Ω assumes integral or half-integral values as a function of the multiplicity of the state, i.e., on the number of the unpaired electrons of the molecules).

Taking into account the interaction of the orbital and spin momenta of the electrons, equal to $A\Lambda\Sigma$, where A is the interaction constant,* the equation for the rotational energy has the following form in the Hund coupling case a [2976]:

$$F_v(J) = A\Lambda\Sigma + [B_v[J(J+1) + S(S+1) - \Sigma^2 - \Omega^2] - D_v J^2(J+1)^2 + \varphi(\Sigma, J). \quad (1.21)$$

In multiplet electronic states (i.e., at $S > 0$) the quantum number Ω assumes $2S + 1$ values. Such states split up into $2S + 1$ substates, each of which is characterized, generally, by its own set of constants B_v and D_v. Thus, all rotational levels of multiplet states are composed of $2S + 1$ components if $J > \Lambda + \Sigma$ is valid, and the difference

of their energies is approximately proportional to the value of $A\Lambda\Sigma$.

At $\Lambda > 0$, an additional small splitting takes place in all rotation levels, and is called the Λ doubling. This splitting is due to the fact that two states (see p. 57) correspond to values $\Lambda > 0$ whose energies are equal in the case of a non-rotating molecule. At rotation the corresponding degeneracy is removed owing to the interaction of the rotational moments of the nuclei and the orbital motion of the electrons of the molecule; this fact is considered in Eq. (1.21) by the component, which possesses for each J two values as follows: $\varphi_a(\Sigma, J)$ and $\varphi_b(\Sigma, J)$. Usually, the corresponding splitting of the rotational levels is small and can always be ignored if the statistical sums and of thermodynamic functions are calculated.

In the Hund case b it is assumed that the interaction of the vectors $\vec{\Lambda}$ and $\vec{S}$ is weak and that the vector $\vec{S}$ is not quantized relative to the molecular axis. This type of interaction is characteristic of states with $\Lambda = 0$, i.e., of Σ states. A resultant moment with the quantum number K which assumes the values Λ, $\Lambda + 1$, $\Lambda + 2$, $\Lambda + 3$, ... is formed generally at such a type of coupling as a result of the interaction of the rotational momentum $\vec{N}$ of the atomic nuclei with the component Λ of the orbital momentum of electrons in the direction of the molecular axis. In this case, the total angular momentum of the molecule is equal to the sum of the vectors $\vec{K}$ and $\vec{S}$, and its quantum number J assumes the values $K + S$, $K + S - 1$, $K + S - 2$, ..., $K - S$. The equation for the rotational levels of the energy has the following form in a Hund coupling case b [2904]:

$$F_v(K) = B_v[K(K+1) - \Lambda] - D_v K^2(K+1)^2 + f(K, J-K) + \varphi_i(K, J). \quad (1.22)$$

Because $2S + 1$ values of J correspond to every value of K, the states with $S > 0$ split just as in the Hund coupling case a into $2S + 1$ components. However, owing to the absence of an interaction of

the vectors $\vec{\Lambda}$ and $\vec{S}$, the splitting is minimized considerably.

Coupling types corresponding to the Hund cases a and b are limiting cases as well as all the other Hund couplings. In actuality the interaction of the angular momenta more or less differs with that which should occur in the Hund cases, and is an intermediate one. Moreover the interaction of the angular momentum $\vec{N}$ with other momenta will be modified if the angular momentum increases, and this result in a change of the type of coupling.

The majority of the electronic states of diatomic molecules dealt with in this Handbook are states of the six types $^1\Sigma$, $^2\Sigma$, $^3\Sigma$, $^1\Pi$, $^2\Pi$ and $^3\Pi$, where the type of coupling in these states (excluding the $^1\Sigma$ states) pertains to the Hund cases a and b or has an intermediate position between them. Expressions for the rotational energy levels in states of the types $^2\Sigma$, $^3\Sigma$, $^2\Pi$ and $^3\Pi$ for ($^1\Pi$ states the expression of the rotational energy coincides with the expression of the $^1\Sigma$ state), will be referred to below.

The equations of the energy levels of molecules in $^2\Sigma$ states, pertaining to the Hund coupling case b, to which belong all states of this type investigated up to date, were developed by Mulliken [2976].

These equations are different from both substates and have the following form:

$$\begin{aligned} F_v^{(1)}(K) &= B_v K(K+1) - D_v K^2 (K+1)^2 - \frac{\gamma}{2}(K+1), \\ F_v^{(2)}(K) &= B_v K(K+1) - D_v K^2 (K+1)^2 + \frac{\gamma}{2} K, \end{aligned} \tag{1.23}$$

where K is the rotational quantum number which assumes the values 0, 1, 2, ... The quantum number J of the total angular momentum is equal to $K \pm S = K \pm 1/2$ and assumes the values 1/2, 3/2, 5/2, ... for the substate $F_v^{(1)}(K)$, and the values 3/2, 5/2, 7/2, ... for the substate $F_v^{(2)}(K)$. For the investigated molecules, $\gamma \ll B_v$, is valid,

and only in the case of HgH the constant γ is commensurable with B_v.

The rotational levels of molecules in $^3\Sigma$ states at a coupling intermediate between the Hund cases a and b are described by equations which were proposed by Schlapp [3623]*:

$$\begin{aligned} F_v^{(1)}(K) &= B_v K(K+1) - D_v K^2(K+1)^2 + B_v(2K+3) - \lambda + \mu(K+1) - \\ &\quad - \sqrt{(2K+3)^2 B_v^2 + \lambda^2 - 2\lambda B_v}, \\ F_v^{(2)}(K) &= B_v K(K+1) - D_v K^2(K+1)^2, \\ F_v^{(3)}(K) &= B_v K(K+1) - D_v K^2(K+1)^2 - B_v(2K-1) - \lambda - \mu K + \\ &\quad + \sqrt{(2K-1)^2 B_v^2 + \lambda^2 - 2\lambda B_v}, \end{aligned} \tag{1.24}$$

where K = 0, 1, 2, ...; the quantum number J assumes the values K+1, K and K − 1 for the substates $F_v^{(1)}(K)$, $F_v^{(2)}(K)$ and $F_v^{(3)}(K)$, and levels with K = 0 are absent in the substates $F_v^{(2)}(K)$ and $F_v^{(3)}(K)$.

The constant λ is commensurable with B_v for all molecules investigated, and $\mu \ll \lambda$.

The rotational levels of molecules in $^2\Pi$ states and a coupling intermediate between the Hund cases a and b may be represented by the Hill and Van Vleck equations [2073]:

$$\begin{aligned} F_v^{(1)}(J) &= -0{,}75 B_v + B_v J(J+1) - D_v J^2(J+1)^2 + \\ &\quad + B_v \sqrt{J(J+1) + \tfrac{1}{4} - \frac{A}{B_v} + \tfrac{1}{4}\left(\frac{A}{B_v}\right)^2}, \\ F_v^{(2)}(J) &= -0{,}75 B_v + B_v J(J+1) - D_v J^2(J+1)^2 - \\ &\quad - B_v \sqrt{J(J+1) + \tfrac{1}{4} - \frac{A}{B_v} + \tfrac{1}{4}\left(\frac{A}{B_v}\right)^2}. \end{aligned} \tag{1.25}$$

For the substate $^2\Pi_{1/2}$, the quantum number J assumes the values 1/2, 3/2, 5/2, ..., and for the substate $^2\Pi_{3/2}$ the values are 3/2, 5/2, 7/2 ... In the Hund case b, the constant A is commensurable with the rotational constant B_v of the molecule, whereas in the Hund case a $A \gg B_v$ is valid.

The energy of the rotational levels of molecules in the $^3\Pi$ state with a spin-orbital coupling intermediate between the Hund

cases a and b is represented by equations obtained by Budó [1005]:

$$F_v^{(1)}(J) = B_v J(J+1) - D_v J^2 (J+1)^2 - B_v \left\{ [y_1 + 4J(J+1)]^{1/2} + \frac{2}{3} \frac{[y_2 - 2J(J+1)]}{[y_1 + 4J(J+1)]} \right\}$$

$$F_v^{(2)}(J) = B_v J(J+1) - D_v J^2 (J+1)^2 + B_v \frac{4}{3} \frac{[y_2 - 2J(J+1)]}{[y_1 + 4J(J+1)]}, \quad (1.26)$$

$$F_v^{(3)}(J) = B_v J(J+1) - D_v J^2 (J+1)^2 + B_v \left\{ [y_1 + 4J(J+1)]^{1/2} - \frac{2}{3} \frac{[y_2 - 2J(J+1)]}{[y_1 + 4J(J+1)]} \right\},$$

where

$$y_1 = Y(Y-4) + \frac{4}{3}, \quad y_2 = Y(Y-1) - \frac{4}{9}, \quad Y = \frac{A}{B},$$

and the quantum number J assumes the values 0, 1, 2, ... for the substate $^3\Pi_0$, the values 1, 2, 3, ... for the substate $^3\Pi_1$, and the values 2, 3, 4, ... for the substate $^3\Pi_2$.

It must be noted, that the splitting constants in the equations (1.21) and (1.22) and in the analogous general equation of the case intermediate between the Hund cases a and b, are, as a rule, unknown in the case of substates which do not belong to the discussed types of electronic states.

On the statistical weights of rotational states of diatomic molecules. The statistical weight of the rotational energy levels of a molecule is equal to 2J + 1, neglecting the spin of the nuclei of the atoms which form the molecule. This value must be multiplied by the product $(2I_1 + 1)(2I_2 + 1)$, where I_1 and I_2 are the spins of the corresponding nuclei in order to take into account the nuclear spins in the case of nonsymmetric molecules, i.e., of molecules whose atomic nuclei differ either in mass or charge. Thus, the statistical weight of the rotational levels of asymmetric molecules is equal to

$$(2I_1 + 1)(2I_2 + 1)(2J + 1). \quad (1.27)$$

In symmetric diatomic molecules, the rotational energy levels which correspond to even and odd values of the quantum number J de-

pend in a different manner on the magnitude of this quantum (see Herzberg [151], p.94). In the one sequence of levels, the statistical weight is equal to

$$p_1 = I(2I+1)(2J+1), \tag{1.28}$$

and in the other it is equal to

$$p_2 = (I+1)(2I+1)(2J+1), \tag{1.29}$$

where I is the spin of the nuclei of the atoms which form the molecule.

If the electronic state of the molecules is characterized by the signs $\bar{u}$ or $\overset{+}{g}$ ($^1\Sigma_g^+$ or $^3\Sigma_u^-$ for example), and the nuclear spin is a half-integer, the rotation levels with odd values of J (or K in the Hund case b) have the statistical weight p_1, and those with even values the statistical weight p_2. If the nuclear spin is an integer, the statistical weights p_1 correspond to the levels with even values of the quantum number J (or K), and the statistical weights p_2 correspond to those with odd values. In the event that the states are characterized by the signs $\overset{+}{u}$ or $\bar{g}$ ($^1\Sigma_g^-$ or $^2\Sigma_g^-$ states, for example), the inverse relationship takes place (see Table 5).

TABLE 5

Statistical Weights of Rotational Levels of Symmetric Molecules

1 Индексы электронного состояния		$\overset{+}{g}$	$\bar{u}$	$\bar{g}$	$\overset{+}{u}$
2 Ядерный спин		3 целый	4 полуцелый	3 целый	4 полуцелый
Статистический вес вращательных уровней 5	6 четных	p_1	p_2	p_2	p_1
	7 нечетных	p_2	p_1	p_1	p_2

1) Indices of the electronic state; 2) nuclear spin; 3) integral; 4) half-integral; 5) statistical weight of the rotational levels; 6) even; 7) odd.

We have seen in the aforesaid that in symmetric diatomic mole-

cules with a nuclear spin equal to zero (as in the case of the O^{16} atom), each second rotational level is lacking (the even or the odd one, depending on the symmetry of the wave function).

In the case of electronic states with values $\Lambda > 0$ (Π, Δ, etc.) each rotational level consists of two components caused by the Λ doubling. These components have the statistical weights p_1 and p_2, respectively; and the statistical weights p_1 and p_2 correspond alternatively to the lower and the upper component at a successive change of the quantum number J.

Choice and estimation of the molecular constants. On the basis of the aforesaid the energy of any state corresponding to the quantum numbers $\underline{v}$ and J (or K) and belonging to the i-th electronic state with the excitation energy $T_e^{(i)}$, may be found by the relation:

$$E^{(i)} = T_e^{(i)} + G^{(i)}(v) + F_v^{(i)}(J). \qquad (1.30)$$

The constants in Eq. (1.30) are determined by analysis of the electronic, vibrational and rotational spectra of the molecules. The methods used to determine these constants, termed molecular constants in this Handbook, are exposed in Herzberg's monograph [151, 2020] (see also [241, 2252, 3825]).

In this Handbook, the choice of the molecular constants is based on the analysis of the results of investigations of the corresponding molecular spectra, published in literature up to 1961. A short summary on the results of spectral investigations of each molecule and the reason for the choice of the constants accepted Handbook, are given in the Divisions on the molecular constants of the corresponding Chapters. It must be noted that the choice of the constants of diatomic molecules was essentially facilitated by the fact that Herzberg [2020] and an author team led by Rosen [649] had published in 1950 and 1951 summaries concerning the recommended values

of diatomic molecules. In these summaries, the entire amount of literature published up to 1949 and 1950, respectively, was discussed thoroughly. Thus, in the case of new investigations of the spectra of a given molecule not being published after publication of these summaries, its constants were assumed in accordance with the recommendations of the authors of the mentioned papers [2020 and 649].

The values of the constants of diatomic molecules chosen in this Handbook, are quoted in separate Tables for the compounds treated in each Chapter. The values of the constants in the equations (1.5), (1.15), and (1.16) for all electronic states of the corresponding molecules having an excitation energy of up to 50,000 cm^{-1} (in cases where the thermodynamic functions of a gas were calculated for $T \leq 20{,}000°K$, all states with $T_e \leq 100{,}000$ cm^{-1} are quoted), and also the excitation energies of these states and their respective equilibrium interatomic distances are quoted in these tables. Besides the choice of constants which were found experimentally, also a determination of the value of J_{max} was carried out, and new equations for G(v) corresponding to the conditions mentioned on p.67 were developed in cases in which this would essentially increase the accuracy of the subsequent calculations (mainly in the case of calculations for temperatures higher than 6000°K).

Previously, it has been noted that owing to the experimental difficulties and the low probability of many of the optical transitions, as well as a number of other reasons, when analyzing the spectra of diatomic molecules, we can determine, even in the most simple cases, only a part of the constants in the equations for G(v) and $F_v(J)$, mainly the constants in the case of low quantum number powers. The rotation structure of the spectra cannot be investigated on account of its complex type and the insufficient resolving power of

present spectroscopic apparatuses, and in such cases, the constants in the equations of the levels of the rotational energy cannot be determined experimentally. Finally, the spectra of a number of diatomic molecules including the ones, treated in this Handbook, have not ben obtained up to date, and, therefore, all molecular constants of these compounds are unknown

In the event that all molecular constants are unknown or only a part of the constants is wellknown, the unknown values may be estimated on the basis of various theoretical or empirical relationships. The constants found by such a manner contain errors, the magnitude of which is determined both by the accuracy of the applied estimation methods and the fact that the constants of the given molecule are wellknown from experimental data. Let us discuss the methods of estimation of constants of diatomic molecules which are compiled in this Handbook.

It was explained on p.59 that the determination of the total number of stable electronic states of a diatomic molecule and their mutual position requires complicated quantum-mechanical calculation methods due to the presence of repelling states, and that these methods give numerical results only for the simplest molecules, such as H_2^+ or H_2. From experimental data it is known that the position of the lower stable electron states is usually the same in the molecules AB and AC, where B and C are elements of the same group of the Periodic system*. When experimental data are missing, this fact permits in a number of cases the prediction of the existence of stable states for some molecules, which were not observed up to date in the spectra, and the evaluation of the excitation energies of such states. The latter may be found on the basis of the relation proposed by Shifrin [463], according to which the ratio of the excitation energies of the i-th state of the molecules AB and AC is inversely proportional to the ratio of the

equilibrium interatomic distances of these molecules in the ground state:

$$\frac{T_e'(AB)}{T_e'(AC)} = \frac{r_{A-C}}{r_{A-B}}. \qquad (1.31)$$

The more analogous are the structures of the electron shells of the atoms B and C, the more valid is this relation.

When the constants ω_e, $\omega_e x_e$ and B_0 are known for a given electronic state of the molecule some other constants in the equations for G(v) and $F_v(J)$ and, primarily, α_1, D_e and H_e may be calculated by means of various approximate relations obtained theoretically. Such relations may be obtained, especially, on the basis of the work by Dunham [1418, 1419] which approximated the potential function of the diatomic molecule by a series of powers of $\xi = \frac{r - r_e}{r_e}$:

$$V(r) = a_0\xi^2(1 - a_1\xi + a_2\xi^2 - \ldots), \qquad (1.32)$$

where $a_0 = \frac{\omega_e^2}{4B_e}$, a_1, a_2, a_3, ... are constants. At $a_1 = a_2 = a_3 \ldots = 0$, this function of the potential energy is identical with the potential function of the harmonic oscillator.

$$V(r) = a_0\xi^2 = \frac{1}{2}hck_e(r - r_e)^2, \qquad (1.33)$$

where

$$k_e = 4\pi^2c^2\mu\omega_e^2 = hca_0\frac{2}{r_e^2}.$$

After substituting the function V(r) into the Schrödinger equation for energy levels of the molecule in a singlet electronic state we obtain the equation

$$\begin{aligned} E = {} & Y_{00} + Y_{10}(v + 1/2) + Y_{20}(v + 1/2)^2 + Y_{30}(v + 1/2)^3 + \ldots + \\ & + [Y_{01} + Y_{11}(v + 1/2) + Y_{21}(v + 1/2)^2 + \ldots]J(J + 1) + \\ & + [Y_{02} + Y_{12}(v + 1/2) + \ldots]J^2(J + 1)^2 + \ldots, \end{aligned} \qquad (1.34)$$

where Y_{-0}, Y_{20}, Y_{30}, ... correspond to the constants ω_e, $\omega_e x_e$, $\omega_e y_e$, ..., and the coefficients Y_{01}, Y_{11}, Y_{02}, ... correspond to the constants B_e, α_1, D_e, ...

Dunham has shown that the constants Y_{ik} in the equation (1.34) may be represented by the oscillation frequency ω_e of the molecule, its rotational constant B_e, and the functions of the coefficients a_1, a_2, ... in Eq. (1.32). Hence, particularly, the following simple relationships for the constants α_1, D_e, and H_e may be obtained in terms of ω_e and B_e:

$$\alpha_1 = \frac{6B_e^2}{\omega_e}, \tag{1.35}$$

$$D_e = \frac{4B_e^3}{\omega_e^2}, \tag{1.36}*$$

$$H_e = \frac{2D_e^2}{B_e} - \alpha_1\omega_e\frac{D_e^2}{6B_e^3}. \tag{1.37}$$

Similar relationships were obtained by a number of authors by application of potential functions of another type. Thus, Pekeris [3212] using the Morse function, obtained the relation

$$\alpha_1 = \frac{6B_e^2}{\omega_e}\left[\sqrt{\frac{\omega_e x_e}{B_e}} - 1\right]. \tag{1.38}$$

Birge (see [2252]) obtained the relation

$$\beta_1 = D_e\left[\frac{\omega_e}{24B_e}\left(\frac{\alpha_1}{B_e}\right)^2 + 5\left(\frac{\alpha_1}{B_e}\right) - 8\frac{\omega_e x_e}{\omega_e}\right]. \tag{1.39}$$

for the constant β_1 in the equations (1.16).

All these relations, however, are approximate. Whereas the values of the constants D_e and H_e calculated on the basis of the relations (1.36) and (1.37) are in good accordance with the experimental

data, analogous evaluations of the constant α_1 (and also of $\omega_e x_e$) give values which may differ from the values found experimentally by tens of percent.*

An analysis of the various relations obtained of various potential functions is given in the reviews by Varshni [4072, 4073, 4074]. In the latter of these papers, an analysis of the diverse semi-empirical formula is given also which may be used to evaluate constants. In this Handbook, the estimations of the constants D_e and H_e were carried out by means of the formulas (1.36), (1.37) and those of the constants α_1 and β_1 by means of Eqs. (1.38) and (1.39), respectively.

Approximate formulas, known also in literature, permit the estimation of the magnitude of the constant $\omega_e x_e$ in terms of ω_e and B_e. The application of these formulas, however, gives insufficient results when the constant $\omega_e x_e$ is estimated for the subsequent calculation of thermodynamic functions at high temperatures, because in the latter case it is necessary that the constants ω_e and $\omega_e x_e$ provide the convergence of the oscillation levels in the range of the dissociation limit. Thus, in the event that the dissociation energy of the molecule is known from independent data, it is more expedient to use the relation (1.12) in the estimation of the constant $\omega_e x_e$. Thus, when the magnitude $\Delta G_{1/2}$ solely may be determined by analysis of the spectrum (which is the fact in all cases when only one band which corresponds to the transition between the states $v = 1$ and $v = 0$ is observable, or in the electron spectrum when only bands are observable which correspond to transitions between both states), the constants ω_e and $\omega_e x_e$ may be found by solution of the following system of two equations:

$$\frac{\omega_e^2}{4\omega_e x_e} = D_e, \qquad \Delta G_{1/2} = \omega_e - 2\omega_e x_e. \tag{1.40}$$

For a number of diatomic molecules treated in this Handbook, ex-

perimental data on their constants are lacking totally. Since, in order to calculate the thermodynamic functions of gases by statistical methods, the values of the oscillation frequency and the rotational constant of the gas molecules in their ground state, at least, must be known (see below p.163), the calculations, when corresponding experimental data are lacking, can be carried out only by means of the estimation of the mentioned constants.

In cases, in which experimental data are lacking the rotational constants of molecules are calculated, in this handbook, on the basis of the relation $B = \frac{h}{8\pi^2 c\mu r^2}$, in which the value of the interatomic distance, when being unknown was estimated approximately. The estimation of the interatomic distance in the diatomic molecule AB may be carried out usually with the aid of the length of the A-B bond in any other molecule (see, for example, the estimation of the length of the Be – Cl in BeCl by means of data for $BeCl_2$ on p.1649). r_{AB} may also be estimated from covalent radii of the atoms, A and B. Finally, in the paper [436] a graphical method for the estimation of the values of B_e was proposed* on the basis of an investigation of the changes of this constant in a series of monotypic compounds of the given period of the Periodic System, of the oxides or fluorides of the corresponding elements, for example.

When experimental data are lacking, the oscillation frequencies of diatomic molecules are usually calculated by means of the relation proposed by Guggenheimer [1880]

$$\omega_e = a\,(z_1, z_2)^{1/6}\,\mu^{-1/6} r_e^{-b}, \qquad (1.41)$$

where z_A, z_B is the number of the valence electrons of the atoms A and B, r_e is the interatomic distance, μ is the reduced mass of the molecule, a and b are constants. In the case of molecules with a predominant covalent bond, a = 2156, and b = 1.23, and in molecules with an ionic type of bond a = 2065, b = 0.92, when ω_e is expressed

in reciprocal centimeters, μ in atomic mass units, and r_e in angstroms. Guggenheimer has shown that this relation permits the calculation of oscillation frequencies of more than 150 molecules with a precision of up to 5%.

The oscillation frequencies of diatomic molecules may also be calculated from the force constants of their bond by making use of the relation (see (1.33))

$$\omega_e = \frac{1}{2\pi c}\sqrt{\frac{k_e}{\mu}} \qquad (1.42)$$

after the value of k_e has been estimated. The latter as well as the constant B_e, may usually be estimated graphically on the basis of the behavior of the k_e values in a number of monotypic compounds of elements of the given period or group of the Periodic System. In some cases, the force constant of the AB molecule may be estimated on the basis of the force constant of the A — B bond in the A_nB_m molecule when the latter is known as a result of investigations of the spectra of the A_nB_m molecule. It must be kept in mind that in this Handbook the estimation of constants has been carried out usually, at the same time, by several methods which allow the approximate determination of the magnitude of the possible errors of the estimated quantities.

Finally, let us discuss the case in which the constants of diatomic molecules can be calculated at a high accuracy without investigation of their spectra. It is known (see [151]) that the constants of two molecules (AB) and $(AB)^i$, which differ in isotopes of the atoms A or B (or of both atoms)* are different. According to the latest theories, the potential energies of isotopic modifications of a molecule, their force constants k_e and the interatomic equilibrium distance r_e are equal because they depend only on the charge of the atomic nuclei and the structure of the electron shell of the molecule and do not

depend on the mass of the nuclei.

It follows from the relations (1.42) and (1.17) that the oscillation frequency ω_e and the rotational constant B_e are proportional to $\mu^{-1/2}$ and μ^{-1}, respectively. Therefore, the relation of the oscillation frequencies of two isotopic modifications of the given molecule is equal to the ratio of their reduced masses in the 1/2 power, and the ratio of the rotational constants is proportional to the ratio of the reduced mass in the a − 1 power. When we denote $\sqrt{\mu/\mu_i}$ by ρ, the ratios of the various constants of the isotopic modifications of the molecule are proportional to the different powers of ρ. The corresponding ratios for the constants of the molecules (AB) and $(AN)^i$ in the equations (1.4), (1.15), and (1.16) may be expressed as follows:

$$\begin{gathered}\omega_e^i = \rho\omega_e,\ \omega_e x_e^i = \rho^3\omega_e x_e,\ \omega_e y_e^i = \rho^5\omega_e y_e,\ \omega_e z_e^i = \rho^7\omega_e z_e, \ldots, \\ B_e^i = \rho^2 B_e,\quad \alpha_1^i = \rho^3\alpha_1,\quad \alpha_2^i = \rho^5\alpha_2,\quad \alpha_3^i = \rho^7\alpha_3, \ldots, \\ D_e^i = \rho^4 D_e,\quad \beta_1^i = \rho^5\beta_1,\quad \beta_2^i = \rho^6\beta_2, \ldots, \\ H_e^i = \rho^6 H_e,\quad \gamma_1^i = \rho^7\gamma_1, \ldots,\end{gathered} \tag{1.43}$$

where $\rho = \sqrt{\mu/\mu_i}$, and μ and μ_i are the reduced masses of the molecules AB and $(AB)^i$, respectively.

The quoted equations are approximate; they were obtained on the basis of a simplified quantum-mechanical theory of diatomic molecules. These equations, however, are satisfied with an accuracy which does not yield to the accuracy of modern experimental data in all molecules not containing hydrogen or its isotopes. The errors caused by the application of the mentioned formulas become essential for hydrogen and its isotopes and also for the hydrides of light elements.

It was shown in the paper [417] on the basis of application of the Dunham relations (see above) that a correcting factor of the form

$$1 \pm \frac{a}{\mu}(1-\rho^2), \tag{1.44}$$

where a is a small constant, must be introduced into the expression (1.43) in second approximation. The relation (1.44) shows that the smaller are the errors of calculations, based on the formulas (1.43), the smaller is the difference between the value of ρ^2 and 1, and the greater is the reduced mass of the AB molecule. Hence, it follows that when estimating the constants of molecules which especially contain the isotope tritium, one must start from the constants of the isotopic modification which contains deuterium, but not protium.

§4. SIMPLE POLYATOMIC MOLECULES

In contrast to the diatomic molecules, the polyatomic molecules, including the most simple considerably possess more complex systems of energy states. These states, as well as those of diatomic molecules, are caused by the motion of the electrons of the molecule, the oscillations of the nuclei of its atoms, and the rotation of the molecule as a whole relative to its center of gravity. If, however, the diatomic molecules have only two principal moments of inertia equal to each other, the polyatomic molecules in the general case possess three principal moments of inertia, a fact that essentially complicates the dependence of the energy of the rotational states on the value of the quantum number of the angular momentum. Moreover, in nonlinear polyatomic molecules which contain atom groups bound by an ordinary chemical bond, an internal rotation takes place (a free or a retarded one). Instead of the one vibrational degree of freedom in the diatomic molecule, a polyatomic molecule containing N atoms possesses $3N - 5$ vibrational degrees of freedom in the case of a linear molecule, and $3N - 6 - k$ in the case of nonlinear molecules, where k is the number of degrees of freedom relative to the internal rotation.

All this causes a complexity of the spectra of polyatomic molecules, particularly of their electronic vibrational-rotational spec-

tra that must be investigated in order to determine the totality of the energy states of the molecule. The complexity of the spectra of polyatomic molecules and the insufficient resolving power of the modern spectral devices are the reason that the spectra of even the most simple polyatomic molecules have not been investigated sufficiently up to date, and that the theoretical conceptions of their energy states, especially of their electronic states, need to be developed furthermore.

A thorough explication of the problems pertaining to the energy states of polyatomic molecules requires the application of the group theory and goes beyond the purpose of this Handbook. Therefore, we shall restrict ourselves, only to the discussion of the problems which are immediately related to the tasks pertaining to the calculations of thermodynamic functions of gases. It must be noted that the small quantity of experimental data on constants of polyatomic molecules generally does not permit the taking into account of the interaction of the different types of motion, the excitation of singular states, the anharmonicity of vibrations and other effects in the calculation of the thermodynamic functions, a fact that justifies the elementary character of the discussion of these problems in this Handbook. In order to familiarize ourselves fully with the corresponding material, we have to study the monograph by Yelliyashevich [186a]*.

It must be noted that the energy states of polyatomic molecules as well as their spectra essentially depend on the structure and symmetry of the molecule. Depending on which elements of symmetry the polyatomic molecule possesses in its equilibrium configuration which corresponds to the minimum of potential energy, it belongs to one or another point group of symmetry. Molecules which belong to the same point group, i.e. which possess equal elements of symmetry, have many features in common

in the type of their electronic, vibrational and rotational states. We shall indicate the fundamental classes of point groups to which belongs the majority of the simple polyatomic molecules.

The molecule belongs to the point group C_p when a symmetry axis of the order $\underline{p}$ is the sole element of symmetry. In cases when in addition to the symmetry axis $\underline{p}$ symmetry planes σ_v are present, the molecule belongs to the point group C_{pv}. The molecules of many substances treated in this Handbook belong to the point groups C_{pv}; nonlinear symmetric molecules as H_2O, NO_2, CF_2 and others belong to the point group C_{2v}, and the tetratomic molecules of the type NH_3 and SiF_3 belong to the point group C_{3v}. All linear molecules, including the diatomic, which do not have a symmetry center, also belong to a point group of this class, marked by the symbol $C_{\infty v}$.

A molecule which has in addition to the symmetry axis of the order $\underline{p}$, a symmetry plane σ_h perpendicular to the symmetry axis, belongs to the point p C_{ph}. When a symmetry axis of the order $\underline{p}$ and $\underline{p}$ axes of symmetry perpendicular to it are present, the molecule belongs to the point group D_p; a molecule which has supplementary $\underline{p}$ symmetry planes going through the symmetry axis of the order $\underline{p}$ and bisecting the angles between the axes of second order, belongs to the point group D_{pd}; and, finally, when the molecule has a symmetry axis of the order $\underline{p}$, $\underline{p}$ symmetry planes σ_v going through the axis and forming with each other angles of 360°/p, and also a symmetry plane σ_h perpendicular to the symmetry axis, it belongs to the point group D_{ph}*.

Among the molecules treated in this Handbook, the plane molecules of the BF_3 type belong to the point group D_{3h}, the molecules C_2H_4, C_2F_4, and C_2C_4 belong to the point group D_{2h}. All linear molecules, including the diatomic ones, which have a symmetry plane perpendicular to the molecular axis, belong to the group $D_{\infty h}$.

Out of the point groups of higher symmetry, the tetrahedral and octahedral groups must be mentioned. Molecules having three symmetry axes of second order perpendicular to each other, for symmetry axes of third order, and six symmetry planes each of which goes through two symmetry axes of third order, belong to the point group T_d. Out of the molecules treated in the Handbook, the molecules P_4 and CH_4 belong to this point group. The molecules which have three mutually perpendicular symmetry axes of fourth order, four symmetry axes of third order, and a symmetry center, belong to the point group O_h. SF_6 is, in this Handbook, the single example of a molecule which belongs to this point group.

Electronic states of polyatomic molecules. The systematics of the electronic states of polyatomic molecules are different from those of linear and nonlinear molecules. The electric field of a linear polyatomic molecule possesses axial symmetry and, in this way, is similar to the electric field of a diatomic molecule. Therefore, the electronic states of linear polyatomic molecules, as well as those of diatomic molecules are characterized by values of the quantum number of the projection of the total orbital momentum Λ of the electrons, which may assume the values 0, 1, 2, ... States with values of Λ equal to 0, 1, 2, ..., are termed Σ, Π, and Δ states, respectively. Electronic states with $\Lambda \neq 0$ are doubly-degenerate and have, therefore, the statistical weight 2.

The electronic states of linear polyatomic molecules as well as those of diatomic molecules are characterized, in addition to the quantum number Λ, by the quantum number S of the total electron spin or the quantum number $\vec{S}$ of the projection of the total spin on the axis of the molecule. It must be noted that the fundamental electronic states of linear polyatomic molecules having filled electron shells are singlet states of the $^1\Sigma$ type.

The total orbital momentum $\vec{L}$ of the electrons, as well as that of diatomic molecules, does not have a definite value in nonlinear polyatomic molecules. However, in contrast to diatomic molecules, its projection on any direction also does not have a definite value, and its mean value is equal to zero. Therefore, the electronic states of nonlinear polyatomic molecules, which belong to definite point groups of symmetry, usually are classified into symmetry types in the same manner as their vibrational states. In the case of groups of lower symmetry (with symmetry axes not higher than second order) only the nondegenerate electronic states A and B are possible. In the case of molecules with a separated symmetry axis, for example belonging, to the point groups D_{ph} and C_{pv}, the electronic states are divided into symmetric and antisymmetric ones with regard to the horizontal axes C_2, the vertical planes σ_v, and the horizontal planes σ_p. As well as in the case of rotational states (see below, p.100), the symmetry of the electron wave function with regard to these symmetry elements is marked by numeral indices and primes on the right side of the state symbol.

If the molecule possesses at least one symmetry axis of the third or a higher order, it must have a doubly degenerate electronic state marked by the symbol E, in addition to the non-degenerated electronic states of the A and B type. Finally, if it has at least three symmetry axes of the third or a higher order, threefold degenerate electronic states F are possible in addition to the nondegenerate and doubly degenerate electronic states. However, in contrast to the linear polyatomic molecules, whose stable electronic states may be both non-degenerate and degenerate due to the Λ doubling, the degenerate electronic states of nonlinear polyatomic molecules are always instable. This fact was proved by Jahn and Teller [2202a] who showed that a nonlinear molecule in degenerate electronic state is instable

molecule in degenerate electronic state is instable with regard to certain incompletely symmetric vibrations. The instability of the degenerate electronic states of nonlinear molecules is essential to the thermodynamic calculations because the type of electronic states of a great number of molecules is unknown due to the lack of corresponding experimental data. Due to the fact that the degenerate states of nonlinear molecules are instable, we can assume in all cases, that the statistical weight of any electronic state (not taking into account its multiplicity) is equal to 1*. The multiplicity of the electronic states of non-linear polyatomic molecules is determined by the value of the quantum number of the total spin of the electrons. In the ground electronic states of molecules having an even number of electrons, the total spin of the electrons, as a rule, is equal to zero, and in molecules having an odd electron number S = 1/2.

The excitation of one of the valence electrons of the molecule may cause both singlet and triplet stable electronic states. The excitation of several valence electrons resulting in states with $S \geq 1$ is also possible in principle; such states, however, are rare exceptions, and at present they are unknown for compounds dealt with in this Handbook.

Vibrational states of simple polyatomic molecules. In classic mechanics, the polyatomic molecule may be represented by a system of matter points which vibrate about their equilibrium positions in the intramolecular force field. The intramolecular potential in first approximation is proportional to the squares of the relative displacements of the atomic nuclei from the positions which correspond to the equilibrium configuration of the molecule. In this case, the potential and kinetic energies may be represented as the sum of the squares of the values termed the normal coordinates (see Supplement 4).

The motion of each particle of the system in normal coordinates fulfils the equation (P4.12), and the corresponding vibrations are termed normal vibrations. Within a system of N particles, the number of normal coordinates and normal vibrations is equal to the number of vibrational degrees of freedom, i.e., $3N - 5$ for a linear system, and $3N - 6$ for a non-linear system. The roots of the secular equation expressed in normal coordinates (see p.2005) are the normal oscillation frequencies of the system. If the particles of the system vibrate with a frequency which corresponds to one of the normal vibrations, each particle performs a simple harmonic oscillation in one and the same phase. Any complicated vibration of the system may be considered as the sum of normal vibrations with corresponding amplitudes.

In the non-linear molecules which do not have symmetry axes of an order higher than second order, the frequencies of all normal vibrations are different. However, in linear and non-linear molecules which have symmetry axes of the third and higher order, some roots of the secular equations, and, therefore, also some frequencies of normal oscillations coincide. Such vibrations are termed degenerate vibrations, and the degree of degeneracy is marked by the symbol d_n.

The normal vibrations of a molecule may be classified on the basis of the changes which are caused by each vibration. According to this, valence, deformational, torsional and mixed vibrations of simple polyatomic molecules are able to be distinguished. The valence vibrations correspond to such dislocations of the atomic nuclei from the equilibrium position which result in a change of the length of the chemical bond between the atoms. The deformational vibrations mainly cause displacements of the atomic nuclei which change the angles between the directions of the chemical bonds of the given atom. The valence and deformational vibrations are divided into symmetric and anti-

symmetric vibrations according to whether the lengths of the bonds and the angles between the bonds change in the same phase or in the opposite phase. the torsional vibrations are caused by displacements of the atomic nuclei which are equivalent to a torsional motion around a certain bond of one group of atoms of the molecule relative to the other group. When the amplitude of the vibrations increases, the torsional vibrations go over into internal rotation.

A more accurate but less evident classification of the normal vibrations is based on the group theory. In this Handbook, the classification of the vibrations of polyatomic molecules is carried out on the basis of the types of symmetry of the normal vibrations in the terms proposed by Herzberg [152]. The symmetry of a vibration is determined by its behavior relative to the operations of symmetry which are allowed due to the geometrical configuration of the molecule. The four types of symmetr A, B, **E**, and F are distinguishable in the case of non-linear molecules. The symmetry types E and F correspond to double and threefold degenerate vibrations, respectively. The vibrations of the symmetry type A remain unchanged if the molecule is turned around its principal symmetry axis C_p at an angle of 360°/p, whereas the vibrations of the symmetry type B are antisymmetric relative to this operation and, therefore, change the sign. The figures 1 and 2 and also the letters u and g, added to the symbols of the symmetry types characterize the symmetry of the given vibration with regard to the other elements of symmetry of the molecule. Thus, for molecules which belong to the point groups D_p and C_{pv}, the A_1 vibrations are symmetrical with regards to rotations of the molecule around an axis of the order p and the axis of second order perpendicular to the former (or the image on the symmetry plane σ_v) whereas the vibrations A_2 are symmetrical with regard to the rotation around the principal symmetry

axis, but antisymmetric with regard to a rotation around an axis of second order (or the image on the symmetry plane σ_v).

In a similar manner, the vibrations which are symmetrical with regard to an inversion in the symmetry center are marked by the subscript g, and those, which are antisymmetric to this operation, by the subscript u; finally, a prime designates vibrations which are symmetrical with regard to the symmetry plane σ_h (perpendicular to the principal symmetry axis) and two primes designate an antisymmetry with regard to this operation.

The classic description of the molecular vibrations is approximative because it does not take into account the discreteness of the vibrational states of the molecule. In fact, the molecule possesses a system of discrete vibrational states in the stable electronic state, i.e., in such a state, in which the molecule's potential energy is at a minimum corresponding to its geometrical equilibrium configuration. If the vibrations of the molecule may be considered as harmonic and independent of each other, which is an adequate approximation and correlates to the supposition tha the potential energy of the molecule is proportional to the squares of the normal coordinates, the energy of the vibrational states of the molecule is described by the equation

$$G(v_1, v_2, v_3, \ldots) = \sum_{n=1}^{n_v} \omega_n \left(v_n + \frac{1}{2}\right), \qquad (1.45)$$

where ω_n is the frequency of the n-th normal vibration of the molecule $v_n = 0, 1, 2, \ldots$ are the values of the quantum number of the n-th vibration, $n_v = 3N - 5$ is valid for linear, and $n_v = 3N - 6$ is valid for non-linear molecules which do not possess an internal rotation.

In the general case, valid for all non-linear molecules which do not have symmetry axes higher than one of a second order, the values

of all normal vibrations ω_n are different when they do not agree accidentally. However, as it was explained above in molecules which possess a higher symmetry, the frequencies of the various normal vibrations are degenerate due to the symmetry of the molecule. Thus, in all linear molecules and molecules which possess one axis of the third r higher order, one or several pairs of normal vibrations have equal frequencies. Molecules which possess several symmetry axes of the third or higher order, i.e., which belong to the tetrahedral and octahedral point groups, possess threefold degenerate vibrations in addition to double-degenerate ones. When a molecule possesses ℓ degenerate vibrations, the number of normal vigrations which have different frequencies n_v' is equal to $3N - 5 - \ell$ in linear molecules, and $3N - 6 \sum_{n=1}^{n=\ell} (d_n - 1)$ in non-linear ones which do not have internal rotations. In this case, the expression for the energy of the vibrational state v_1, v_2, v_3, ... may be represented in the form

$$G(v_1, v_2, v_3, \ldots) = \sum_{n=1}^{n=n_v'} \omega_n \left(v_n + \frac{d_n}{2}\right), \qquad (1.46)$$

where n_v' is the number of normal vibrations of the molecule, which have different frequencies. The vibrational quantum number v_n of the degenerate vibration is equal to the sum of the vibrational quantum numbers of the normal vibrations which have the same frequency.

The vibrational state of a single harmonic oscillator possesses the statistical weight $p_v = 1$; the statistical weight of the n-th double-degenerate vibration is equal to $v_n + 1$, and that of the threefold degenerate oscillation is equal to $(v_n + 1)(v_n + 2) / 2$. The statistical weight of the oscillatory state v_1, v_2, v_3, ..., represented by $\rho_{v_1 v_2 v_3, \ldots}$, is equal to

$$p_{v_1 v_2 v_3 \ldots} = \prod_{n=1}^{n=n_v'} \frac{(v_n + d_n - 1)!}{v_n!\,(d_n - 1)!}. \qquad (1.47)$$

The vibrations of the molecule may not be considered as independent and harmonic in the expression for the potential energy of the molecule (Eq. P4.3), if, besides the terms which are proportional to the squares of the dislocations of the atomic nuclei, the terms are taken into account which are proportional to the third and fourth power of the dislocations. The energy of the vibrational states of a polyatomic molecule may be expressed, in this approximation, by the equation

$$G(v_1, v_2, v_3, \ldots) = \sum_{n=1}^{n_v'} \omega_n \left(v_n + \frac{d_n}{2}\right) + \sum_{n=1}^{n_v'} \sum_{k>n}^{n_v'} x_{nk} \left(v_n + \frac{d_n}{2}\right)\left(v_k + \frac{d_k}{2}\right) + \sum_{n=1}^{n_v'} \sum_{k>n}^{n_v'} g_{nk} l_n l_k, \qquad (1.48)$$

where x_{nk} are the anharmonicity constants of the vibrations, where $x_{nk} \ll \omega_n$ and $x_{nk} \ll \omega_k$, g_{nk} are the constants of the vibrational angular momentum, g_{nk} being different from zero only for double-degenerate vibrations, and $l_n = v_n,\ v_n - 2,\ v_n - 4,\ \ldots,\ 0$ or 1.

The vibrational energy of the molecule in the principal vibrational state ($v_1 = v_2 = v_3 = \ldots = 0$) is equal to

$$G(0, 0, 0, \ldots) = \sum_{n=1}^{n_v'} \omega_n \frac{d_n}{2} + \sum_{n=1}^{n_v'} \sum_{k>n}^{n_v'} x_{nk} \frac{d_n d_k}{4}. \qquad (1.49)$$

The vibrational energy of the molecule related to its principal vibrational state $G_0(v_1, v_2, v_3, \ldots)$, may be represented in the form

$$G_0(v_1, v_2, v_3, \ldots) = \sum_{n=1}^{n_0'} \omega_n^0 v_n + \sum_{n=1}^{n_0'} \sum_{k>n}^{n_0'} x_{nk} v_n v_k + \sum_{n=1}^{n_0'} \sum_{k>n}^{n_0'} g_{nk} l_n l_k, \quad (1.50)$$

where

$$\omega_n^0 = \omega_n + x_{nn} d_n + \frac{1}{2} \sum_{k \neq n}^{n_0'} x_{nk} d_k.$$

It must be observed that, as a rule, it is not possible to determine the frequencies of the normal vibrations of a molecule by investigation of the spectra of polyatomic molecules, and that one must restrict oneself to the determination of the so-called fundamental frequencies ν_n which are equal to the difference between the energy of the vibrational ground state and the state $v_n = 1$ of the given molecule. The values of the fundamental frequency ν_n of the nth vibration and the values of the frequency ω_n of its normal vibration are connected to each other by the relationship

$$\nu_n = \omega_n + x_{nn}(d_n + 1) + \frac{1}{2} \sum_{k \neq n}^{n_0'} x_{nk} d_n + g_{nn} = \omega_n^0 + x_{nn} + g_{nn}. \quad (1.51)$$

Thus, the values of the fundamental frequencies and the frequencies of the normal vibration differ with a value which is proportional to the anharmonicity constants related to the given vibration. It is evident that the difference between the frequencies of the normal vibration becomes meaningless when the vibrations of the molecules are considered as harmonic ones. It must be noted that the fundamental frequency of each vibration possesses a symmetry equal to that of the normal vibration.

In cases when the energies of two or several vibrational states

of a polyatomic molecule, calculated by means of Eqs. (1.45) and (1.46) are similar to each other, the true energy of these states essentially may differ from the calculated values. A corresponding change of the energy of the vibrational states is caused by the resonance interaction between them. Due to the fact that the possibility of resonance interactions between the vibrational states is not taken into account in the Eqs. (1.45) and (1.46), the energy levels calculated by means of these equations are termed non-excited levels. The energy of vibrational states excited due to the resonance interaction may be found by solution of the secular equation

$$\begin{vmatrix} E_k^0 - E & W_{lk} & 0 \\ W_{lk} & E_l^0 - E & W_{lm} \\ 0 & W_{lm} & E_m^0 - E \end{vmatrix} = 0, \qquad (1.52)$$

where E_k^0, E_ℓ^0, E_m^0, ... is the energy of the non-excited states, and $W_{\ell k}$, $W_{\ell m}$, ... is the energy of the resonance interaction between these states.

In cases in which the resonance interaction between the vibrational states is caused by the cubic term of the function of the potential energy of the molecule, it is termed an anharmonic resonance of first order; the interaction caused by terms which are proportional to the fourth power of the displacement of the atoms is termed anharmonic resonance of second order, etc. The anharmonic resonance of first order between states of the types (v_1, v_2, v_3) and ($v_1 - 1$, $v_2 + 2$, v_3) was observed in a number of molecules such as CO_2, COS, HDO, etc.; this resonance is termed Fermi resonance. The energy of the resonance interaction in the case of a Fermi resonance has the form*

$$W_{k'} = W^{v_1 v_2 v_3}_{v_1 - 1,\ v_2 + 2,\ v_3} = \frac{1}{2} W_\Phi \sqrt{v_1 (v_2 + 1)(v_2 + 2)}, \qquad (1.53)$$

where W_Φ is the resonance constant.

Another type of anharmonic resonance, the resonance of second order between the states $(v_1 \geq 2,\ v_2,\ v_3)$ and $(v_1 - 2,\ v_2,\ v_3 + 2)$, which was observed, for example, in H_2O and C_2H_2 molecules, was termed Darling-Dennison resonance. The interaction energy may be found in this case by the relationship

$$W_{kl} = W^{v_1>2,\ v_2,\ v_3}_{v_1-1,\ v_2,\ v_3+2} = \frac{1}{2} W_D \sqrt{v_1 (v_1 - 1)(v_3 + 1)(v_3 + 2)}, \quad (1.54)$$

where W_D is the resonance constant*.

Nielsen [3085] has shown that besides other vibrational types, anharmonic resonances of higher orders are theoretically possible as well as anharmonic resonances of the first and second order. However, as Nielsen has shown, the higher is the order of the resonance, the lower is its effect on the energy of the vibrational states. It must be noted that the sum of the energies of vibrational states excited by resonance interaction is equal to the sum of the energy of these states when neglecting the excitations, and, therefore, the resonance causes, so-to-speak, a mutual repulsion of the corresponding vibrational states.

Rotational states of polyatomic molecules. A polyatomic molecule possesses, in each vibrational state, a system of levels of rotational energy due to the angular momentum of the atomic nuclei of the molecule relative to its center of gravity**. The relations which connect the energy of the rotational states of the polyatomic molecule with the values of the quantum number of the angular momentum of its atomic nuclei depend on the symmetry of the molecule. All polyatomic molecules may be divided into four types as follows:

1) linear molecules,

2) molecules of the type of asymmetric tops, of which the three

principal moments of inertia are different in magnitude;

3) molecules of the type of symmetric tops, of which two principal moments of inertia are equal, the third being greater or lesser than the other two;

4) molecules of the type of spheric tops which have three equal principal moments of inertia.

The linear molecules belong to the point group $D_{\infty h}$ when they possess a symmetry center, and to the point group $C_{\infty h}$ when a symmetry center is absent. The axes of the principal moments of inertia of linear molecules are always perpendicular to the axis of the molecule. When neglecting the angular momentum of the electrons, the levels of the rotational energy of a linear polyatomic molecule may be expressed by an equation similar to that which describes the energy levels of diatomic molecules in the $^1\Sigma$ state:

$$F_{v_1, v_2, v_3, \ldots}(J) = B_{v_1, v_2, v_3, \ldots} J(J+1) - D_{v_1, v_2, v_3, \ldots} J^2(J+1)^2. \quad (1.55)$$

where $B_{v_1, v_2, v_3, \ldots} = \frac{h}{8\pi^2 cI}$ is the rotational constant of the molecule in the vibrational state $v_1, v_2, v_3, \ldots$, $D_{v_1, v_2, v_3, \ldots}$ is the constant of the centrifugal stress in this state, J is the quantum number of the angular momentum, I is the principal moment of inertia of the molecule. The dependence of the constants $B_{v_1, v_2, v_3, \ldots}$ on the vibrational quantum numbers is determined by relations of the following type

$$B_{v_1, v_2, v_3, \ldots} = B_e - \sum_{n=1}^{n_0} \alpha_n \left(v_n + \frac{d_n}{2}\right) + \sum_{n=1}^{n_0} \sum_{k \neq n}^{n_0} \gamma_{nk} \left(v_n + \frac{d_n}{2}\right)\left(v_k + \frac{d_k}{2}\right). \quad (1.56)$$

where B_e is the rotational constant corresponding to the equilibrium configuration of the molecule, α_n and γ_{nk} are the constants of the interaction between rotation and vibration; d_n is the degree of degen-

eracy of the nth vibration. The dependence of the constant $D_{v_1, v_2, v_3, \ldots}$ on the vibrational quantum numbers may also be represented by an equation of the type (1.56).

Molecules which possess one symmetry axis of the third or higher order belong to the molecules of the type of symmetric tops. The axes of the two principal moments of inertia of symmetric tops are perpendicular to the symmetry axis of higher order, and the axis of the third principal moment of inertia always coincides with it. Taking into account the centrifugal stress, the energy levels of the molecules of the type of symmetric tops may be represented by the equation

$$F_{v_1, v_2, v_3, \ldots}(J, K) = B_{v_1, v_2, v_3, \ldots} J(J+1) + (A_{v_1, v_2, v_3, \ldots} - B_{v_1, v_2, v_3, \ldots}) K^2 - D_J J^2 (J+1)^2 - D_{JK} J(J+1) K^2 - D_K K^4, \quad (1.57)$$

where A and B are the rotational constants

$$A = \frac{h}{8\pi^2 c I_A}, \quad B = \frac{h}{8\pi^2 c I_B},$$

I_A is the principal moment of inertia with regard to the axis which coincides with the symmetry axis of the molecule, I_B is the principal moment of inertia with regard to the axis perpendicular to the symmetry axis, K is the quantum number of the component of the momentum J on the symmetry axis of the molecule, and, thus, K assumes values from $-J$ to $+J$. When $A > B$ ($I_A < I_B$) the top is termed a prolate top, when $A < B$ ($I_A > I_B$) the top is termed an oblate one.

The dependence of the constants D_J, D_{JK} and D_K on the vibrational quantum numbers has not been taken into account in Eq. (1.57). The corresponding dependence of the constants $A_{v_1, v_2, v_3, \ldots}$ and $B_{v_1, v_2, v_3, \ldots}$ may be represented by the equations

$$A_{v_1, v_2, v_3, \ldots} = A_e - \sum_n \alpha_n^A \left(v_n + \frac{d_n}{2}\right). \quad (1.58)$$

$$B_{v_1, v_2, v_3, \ldots} = B_e - \sum_n \alpha_n^B \left(v_n + \frac{d_n}{2}\right), \qquad (1.59)$$

where A_e and B_e are the rotational constants of the molecule corresponding to its equilibrium configuration.

It is obvious from (1.57) that all states of a symmetric top with $K > 0$ are doubly-degenerate.

Molecules which possess several axes of symmetry of the third or higher order belong to the molecules of the type of spheric tops. In contrast to the symmetric tops, the molecules of the type of spheric tops do not possess a preferred direction in space. The energy of the rotational levels of spheric tops is described by the equation

$$F_{v_1, v_2, v_3, \ldots}(J) = B_{v_1, v_2, v_3, \ldots} J(J+1) - D_{v_1, v_2, v_3, \ldots} J^2 (J+1)^2, \quad (1.60)$$

which may be obtained directly by (1.57) setting $A = B$. The dependence of the constant $B_{v_1, v_2, v_3, \ldots}$ on the vibrational quantum numbers may be represented, as in the case of linear molecules, by the relation (1.56).*

Molecules which do not possess symmetry axes of a higher than second order belong to the molecules of the type of asymmetric tops.** Not taking into account the centrifugar stress and the interaction between rotation and vibration (i.e., in the case of rigid tops), the levels of the rotational energy of the molecule of the asymmetric top type are described by the equation

$$F(J_\tau) = \frac{1}{2}(A + C) J(J+1) + \frac{1}{2}(A - C) E_{J_\tau}(k), \quad (1.61)$$

where A, B, C are the rotational constants,*** $A = \frac{h}{8\pi^2 c I_A}$, $B = \frac{h}{8\pi^2 c I_B}$, $C = \frac{h}{8\pi^2 c I_C}$, $A \geq B \geq C$; J is the quantum number of the angular momentum; τ is the index which numerates the $2J + 1$ levels of the rotational energy having the same value of the quantum number J; $E_{J_\tau}(k)$ is a composite function of J_τ and the asymmetry parameter $k = \frac{2B - A - C}{A - C}$. The

values of the function $E_{J_\tau}(k)$ are determined by the solution of algebraic equations whose power is the higher the greater J is. The corresponding equations are given, particularly, in the monograph by Herzberg [152]. The values of the function $E_{J_\tau}(k)$ obtained by numerical solution of those equations have been tabulated by a number of authors for values of J from J = 0 to J = 40. An eight-digit table of the $E_{J_\tau}(k)$ functions for J = 0 — 12 and k = 0.00 (0.01) 1.00 is given in the monograph by Townes and Schawlow [416].

The quantum mechanical theory of non-rigid asymmetric tops was developed in a paper by Posner and Strandberg [3311]. The results from this paper may be used in the calculation of corrections for the centrifugal stress in values of F(J) for the levels of the rotational energy of asymmetric tops, when the values of the corresponding constants are found by analysis of the rotational structure of the bonds. The centrifugal stress most significantly affects the levels of the rotational energy of the molecules of hydrides. In the case of such molecules, the corrections calculated theoretically show a sufficient coincidence with the experimental measurement results only in levels having low values of J. A graphic method to determine corrections of the centrifugal stress at higher levels of rotational energy of molecules of the asymmetric top type, which is difficult to investigate by experiment, was proposed in the paper by Kovchiuruzov [444a].

The rotational constants of molecules of the asymmetric top type are different with different vibrational states. The type of dependence of these constants on the vibrational quantum numbers presented by the relations

$$A_{[v]} = A_e - \sum_n \alpha_n^A \left(v_n + \frac{d_n}{2}\right), \qquad (1.62)$$

$$B_{[v]} = B_e - \sum_n \alpha_n^B \left(v_n + \frac{d_n}{2}\right), \qquad (1.63)$$

$$C_{[v]} = C_e - \sum_n \alpha_n^C \left(v_n + \frac{d_n}{2}\right), \qquad (1.64)$$

where $A_{[v]}$, $B_{[v]}$, $C_{[v]}$ are the effective values of the corresponding constants in the vibrational states v_1, v_2, v_3, ...; A_e, B_e, C_e are the values of these constants at the equilibrium configuration of the molecule; α_n^A, α_n^B, α_n^C are the interaction constants which are many times smaller than the values of the corresponding rotational constants.

The statistical weights of rotational states. The statistical weights of rotational states of polyatomic molecules, as well as a number of other properties, depend essentially on the symmetry of the molecule. The determination of the statistical weights of molecules which possess symmetry elements, requires the application of the group theory. However, we may restrict ourselves to the discussion of the statistical weights of rotational states of molecules assuming that the latter do not possess elements of symmetry, because the effect of the symmetry on the statistical weights of rotational states may be taken into account when calculating the thermodynamic functions of gases by means of the symmetry numbers σ (see Table 12). The symmetry number of a molecule is equal to the number of its nondiscernible positions when the molecule rotates as a rigid body.

When neglecting the nuclear spin of the atoms which form the molecule, the statistical weight of the rotational states of asymmetric linear molecules as well as that of diatomic molecules is equal to $2J + 1$. The statistical weight of the level J_τ of molecules of the type of asymmetrical tops, which do not possess symmetry axes is also equal to $2J + 1$. Due to the fact that the index τ of a given J assumes

$2J + 1$ values, the statistical weight of all states with a given value of the quantum number J is equal to $(2J + 1)^2$. In the case of the molecule being of the type of accidental "symmetric" tops, i.e., it possesses two equal principal moments of inertia but does not have symmetry axes, the statistical weight of the rotational states is equal to $2J + 1$ at $K = 0$), and $2(2J + 1)$ at $K > 0$. The statistical weight of the rotational states is equal to $(2J + 1)^2$ in the case of "accidental" spheric tops (with three equal principal moments of inertia and absent symmetry axes). Hence, it follows from this statement that the statistical weights of polyatomic molecules are different and depend on the type of tops to which the molecule belongs.

The spins of the atomic nuclei have not been taken into account in the discussed cases of the statistical weights of rotational states. If the spins of the atomic nuclei of polyatomic molecules which do not possess symmetry axes are taken into account, an increase is required of the quoted statistical weights by $\prod_{i=1}^{i=N} (2I_i + 1)$ times. Here, N is the number of atoms in the molecule, and I_i is the spin of the nucleus of the ith atom.

If the molecule possesses symmetry axes of the second or a higher order, the effect of the symmetry on the statistical weights of the rotational states is regarded by means of the symmetry number; as well as in the case of asymmetric molecules, the spins of the atomic nuclei increase the statistical weights by $\prod_{i=1}^{i=N} (2I_i + 1)$ times.

Choice and estimation of the constants of polyatomic molecules. Data on the energy states, the structure and the constants of polyatomic molecules, may be obtained by investigation of the spectra of the molecules in question. The complexity of the spectra of poly-atomic molecules however, as well as the imperfection of the present spectral devices essentially limit the possibility of determining the constant

of Eqs. (1.45) – (1.64). Especially the electron spectra of polyatomic molecules have been investigated insufficiently, and, due to this fact, data on the excited states of a great number of molecules are lacking and are incomplete only for other ones.

The determination of the vibrational and rotational constants of polyatomic molecules by analysis of the electron spectra, as a rule, is impossible due to the complexity of the electronic-vibrational-rotational spectra of these molecules. Such an analysis was carried out only for some of the most simple molecules of the HCO and ClO_2 type. Thus, the constants in Eqs. (1.45) – (1.64) are determined by analysis of the infrared vibrational-rotational spectra and Raman spectra and also the rotational microwave spectra of the molecules. The determination of the frequencies ω_n of the normal vibrations and of the anharmonicity constants x_{nk} of polyatomic molecules is possible only when all fundamental frequencies ν_n and also the overtones and the composed frequencies combined with each of these constants are observable in the spectrum. Due to the fact that the infrared spectra of polyatomic molecules are usually investigated in absorption, only the fundamental frequencies and, at the best, some of the most intense overtones or composed frequencies are observable therein. Thus, the fundamental frequencies ν_n and not the frequencies ω_n of the normal vibrations are ascertainable in a great number of polyatomic molecules by investigation of the spectra. Particularly, the frequencies of the normal vibrations and the anharmonicity constants are known only for 15 molecules out of the 170 polyatomic molecules dealt with in this Handbook. The results from the investigations of infrared spectra and Raman spectra of simple polyatomic molecules, carried out until 1944, are compiled in the monograph by Herzberg [152]. The results from the numerous investigations carried out after 1944, however, may be found in period-

icals only. Surveys on the investigations of spectra of polyatomic molecules treated in this Handbook and the arguments on the choice of their vibrational constants are given in the corresponding Divisions of the Chapters of the 2nd Part of this Volume.

The determination of the rotational constants and the constants of interaction between rotation and vibration of polyatomic molecules on basis of their infrared spectra and Raman spectra is even more difficult than the determination of the anharmonicity constants and the oscillation frequencies. This is due to the fact that the smaller are the intervals of the rotational structure of the bonds, the greater is the moment of inertia of the molecule, and the resolving power of the recent spectral devices is sufficient only in the resolution of the structure of a small number of the lightest molecules, mainly of 3 and 4 atomic compounds containing hydrogen.

In recent years, significant success has been attained in the determination of the rotational constants of polyatomic molecules in the vibrational ground state due to the development of the radiospectroscopical methods of investigation of rotational absorption spectra of molecules in the microwave range. The application of these methods allowed the determination of the rotational constants of a series of molecules; the results from the investigations of these spectra and the found values of the constants are compiled in the monographs by Gordy, Smith and Trambarulo [164] and Townes and Schavlow [416]. However, it must be noted, that linear symmetric molecules and also molecules of the type of spheric tops do not possess rotational spectra. The rotational constant A of symmetric tops connected with the moment of inertia I_A with regard to the principal axis of symmetry of the molecule also can not be found by analysis of rotational spectra (see, for example [152], p.43). These facts essentially limit the possibility

of determining the rotational constants of polyatomic molecules from their microwave spectra.

However, if the structural parameters of the corresponding molecules are known, the values of these constants may be calculated, due to the fact that the rotational constants are connected by simple relations with their principal moments of inertia. Data on the structural parameters of many tens of polyatomic molecules were obtained by the method of electron diffraction and were compiled in tables by Allen and Sutton [517, 3916]. However, it must be noted that the accuracy of the values of the principal moments of inertia and the rotational constants calculated on the basis of structural parameters determined by electron diffraction is usually less due to the inaccuracy of the electron diffraction method.

Relations connecting the principal moments of inertia of the molecules of various types with the values of their structural parameters are quoted in Supplement 3.

In cases when data on vibrational and rotational constants or structural parameters are lacking, the corresponding values may be estimated on the basis of approximate regularities. The structure of the molecule may be usually estimated on the basis of the general conceptions of directed valences.* The values of the interatomic distance and the angles between the bonds may be estimated on the basis of the value of these parameters in other molecules. An essential increase of the accuracy of the estimations is obtainable, in this case, by taking into account the classification of the bond types proposed by Tatevskiy (see, for example, [409]). It may be pointed out that the estimations of the structure and the structural parameters of a number of molecules (MgF_2, AlF_3, C_2F_2 and some other ones) carried out in the first edition of this Handbook are in good accordance with the results

of experimental investigations carried out in recent years.

When experimental data on oscillation frequencies or fundamental frequencies are lacking, the values of these constants may be calculated by way of an estimation of the force constants of the corresponding molecules. The relations connecting the oscillation frequencies of the molecules of various types with the force constants of the bonds, and the angle between the bonds and the constants for various models of the field of valence forces are quoted in Supplement 4 of this volume of the Handbook. The estimation of the force constants of the bonds and the angles between the bonds may be carried out in the same way as the estimation of the structural parameters, i.e., on the basis of the value of these constants in other molecules.*

The estimation of the force constants and structural parameters of certain molecules on the basis of their values in other molecules in a certain degree is arbitrary because the values of these constants may change essentially from one chemical compound to another, even when a strong classification of the types of bonds is given. This relates essentially to cases in which constants of molecules having free valence electrons (radicals) are estimated on the basis of stable compounds with saturated bonds. Nevertheless, even in these cases, suitable estimations permit the determination of approximate values of the constants necessary to calculate of the thermodynamic function of gases. A thorough explication of the estimations of constants of polyatomic molecules carried out by the authors of this Handbook is given in the Divisions on the molecular constants in the Chapters of the 2nd Part of this Volume.

The geometrical equilibrium configuration and the intramolecular force field of the isotopic modification of polyatomic molecules are identical to each other at a high degree of accuracy. The difference in

the values of the molecular constants (including the moments of inertia and the vibration frequencies) of the different isotopic modifications mainly is caused by the difference in the distribution of the masses. Therefore, the molecular constants of polyatomic isotopic molecules, as well as the constants of diatomic isotopic molecules may be connected together by definite relationships which allow the calculation of the values of these magnitudes by means of experimental data known only for one of the isotopic modifications. Besides the accurate relations, which connect the fundamental oscillation frequencies and the moments of inertia of the molecules (the Teller-Redlich rule of products, the rule for adding squares of oscillation frequencies [362a, 362b], the relations for the oscillation frequency of symmetric nonlinear molecules XY_2 [439], etc.), various approximate relations have been proposed recently which allow the calculation of the molecular constants of isotopic modifications with an accuracy sufficient for the subsequent calculation of the thermodynamic functions [973a, 2193a, 2485a].

Thus, for example, the following relation* may be used in the calculation of the anharmonicity constants of triatomic nonlinear isotopic molecules

$$x'_{ij} = \frac{\omega'_i \omega'_j}{\omega''_i \omega''_j} x''_{ij}, \qquad (1.65)$$

where ω'_i, ω'_j, x'_{ij}, ω''_i ω''_j, x''_{ij} are the oscillation frequencies and the anharmonicity constants of two isotopic modifications: and the constants α_i of the vibrational-rotational interaction of symmetric nonlinear isotopic molecules may be calculated by means of the equation

$$\alpha'_i = \left(\frac{\omega'_i}{\omega''_i}\right)^3 \alpha''_i, \qquad (1.66)$$

which was proposed by Khachkuruzov [417].

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[Footnotes]

43* A more thorough statement of the problems dealt with in this section may be found in the monographs by Herzberg [150], Sommerfield [196], Shopl'skiy [465], Yel'yashevich [186] and Kondrat'yev [242].

43** In the present Handbook, the term atom means atoms and monatomic ions, as well.

44 If $S > L$, J assumes $2L + 1$ values.

46* In the case of a $j - j$ coupling, it is more expedient to use the quantum numbers n, ℓ, j and m_j, where m_j is the quantum number of the component of the total angular momentum of the electron j in the direction of the magnetic field ($m_j = j, j - 1, \ldots, -j$), instead of the quantum numbers n, ℓ, m_ℓ and m_s of the electron. It can be shown that for given values of n and ℓ, the quantum numbers n, ℓ, j and m_j give the same number of possible states of the electron as the quantum numbers n, ℓ, m_ℓ and m_s.

46** A great difference in the energy of states which are components of multiplet states in the case of Russel-Saunders coupling is characteristic of the $j - j$ coupling.

46*** The $j - j$ coupling occurs rarely in a pure form; the Russel-Saunders coupling takes place, as a rule, in the case of lower electronic states, whereas in states connected with the transition of one electron into orbits with higher values of the principal quantum number, a coupling of the $j - j$ type plays the main part.

46**** Frequently, the state energy needed to remove the rest of the atom and the external electron from each other to infinity is assumed as zero energy. In this case, the energy of the ground state is equal to the ionization potential of the atom taken with the inverse sign. It is evident that the excitation energies of all states do not depend on point of reference.

47* Electrons with appropriate values of the quantum number ℓ are frequently termed s-, p-, d-, and f electrons.

47** According to this, the resultant quantum numbers and the number of states formed by x (equivalent) electrons are equal to each other if the number of these electrons is equal to n and $m - n$, where m is the maximum number of electrons with the given value of n and ℓ. Thus, the configurations p^2 and p^4 are identical from this point of view.

48 Similarly, the electrons of the filled shells may not be taken into account when investigating any atoms or monatomic ions.

52* According to Table 3, three electronic states of the N^+ ion: ^3P, ^1D, and ^1S, correspond to the $2p^2$ electron configurations. The lowest of these states, according to Hund's rule and experimental data is the ^3P-state.

52** Thus, atoms (and ions) may possess a great number of discrete states with excitation energies which exceed the ionization potential of the given atom (ion) when two or several electrons are excited simultaneously.

52*** In the discussed case, the total orbital and spin momenta of two 2p electrons are equal to 1. Thus, the resultant spin of three electrons assumes two values: 1/2 and 3/2 (doublet and quartet states). The total orbital momentum of three electrons remains equal to 1 at $L = 0$ and assumes for the three values mentioned above $L \geq 1$.

54 Similar data were compiled earlier by Bacher and Goudsmith in the book "Energy States of Atoms" published in 1932 [594].

56 For a thorough study of the problems dealt with in this section, we recommend the monographs by Herzberg [151, 2020], Kondrat'yev [241, 242], Jevons [2252], Nikol'skiy [320], and also the original papers by Mulliken [2976, 2981, 2982].

58 The quantum number Σ must not be taken mistakenly for the symbol of states with the value $\Lambda = 0$ which is also marked by this letter.

59* The atoms may be in stable states during a time depending only on the probability of the optical transitions from these states (when outer effects are absent).

59** The lifetime of the molecule in repellent state is practically equal to the time of the interaction of atoms in collisions; discrete energy levels are absent in molecules with a repellent state, and these states are not taken into account when the statistical sums are calculated.

60 Some molecules, C_2, MgO, ZrO, or CN, for example, possess excited states with low energies.

63 For the ground state, the dissociation energy D_0 is equal to the thermal effect of the dissociation of the corresponding diatomic gas into monatomic gases at 0°K.

65* Morse [2958] has shown that the expression (1.10) for the energy of the vibrational levels of the molecule may be obtained by solution of the Schrodinger equation assuming the function (1.9) as a potential energy. Recently, Haar [1908] has found that the solution of the Schrodinger equation was carried out inaccurately by Morse, but it is sufficiently

accurate for all the problems which are of interest to us.

65** It is evident, that the relation (1.11) is approximate, and that in the general case, a non-integral value is obtained when v_{max} is calculated using the constants ω_e and $\omega_e x_e$ which were found experimentally.

65*** The magnitude $\Delta G_{1/2} = \omega_e - 2\omega_e x_e$, termed *fundamental frequency* of the molecule, is the frequency of the optical transition from the state with v = 1 into that with v = 0 in the spectrum of the molecule.

68 k + 2 equations are available for the determination of the constants in Eq. (1.4) if experimental data for the magnitude of $G_0(v)$ are given for $\underline{k}$ values of the vibrational quantum number $\underline{v}$.

69 Here, as well as previously, the moment of the spins of the atomic-nuclei of the molecule is not taken into account.

70 Any kind of data on the number of terms in the equations (1.15) - (1.16) or on the power of these equations are lacking at present, as well as for the equations of the vibrational energy.

71 According to (1.15) we have $\Delta F_v(J) = 2B_v(J + 1) - 4D_v(J + 1)^3 + \ldots$, and, because $B_v/D_v \sim 10^6$ is valid, the rotational levels may begin to converge only at $J \sim 10^3$, whereas $J_{max} \leq \leq 1.10^2 - 5.10^2$ is valid for all molecules (see below).

76 The interaction constant A may be a positive or a negative value; corresponding to this fact, we distinguish normal and inverse electronic states; the ground state of the hydroxyl group, for example, is inverse ($X^2\Pi_i$ state), whereas that of the methine is normal ($X^2\Pi_r$ state).

77 The addend f(K, J − K) is caused in the general case as follows: a) by the interaction of the vectors $\vec{S}$ and $\vec{\Lambda}$ which is equal to zero at $\vec{\Lambda} = 0$; b) by the interaction of the vector $\vec{S}$ with the magnetic field of the molecule formed due to the rotation of the nuclei of its atoms and being equal to $\frac{\gamma}{2}$ [J (J + 1) − K(K + 1) − S(S + 1)], where γ is a constant;

c) by interaction of the electron spins, which is not equal to zero S > 1/2.

79 Appropriate equations were proposed by Kramers [2473] for $^3\Sigma$ states similar to the Hund case b; using the symbols of Eq. (1.24), they may be expressed as follows:

$$F_v^{(1)}(K) = B_v K(K+1) - D_v K^2(K+1)^2 - \frac{2\lambda(K+1)}{2K+3} + \mu(K+1);$$
$$F_v^{(2)}(K) = B_v K(K+1) - D_v K^2(K+1)^2; \qquad (1.24a)$$
$$F_v^{(3)}(K) = B_v K(K+1) - D_v K^2(K+1)^2 - \frac{2\lambda K}{2K-1} - \mu K.$$

81 The indices + (plus), − (minus), u and g characterize the symmetry of the electron wave function of the molecule. If the electron wave function reflected on the plane going through the atomic nuclei of the molecule does not change, the corresponding state is called a symmetric one and designated by the index +; if, however, the function changes its sign, the state is called an anti-symmetric one and denoted by −. The states are distinguished additionally on the basis of their parity in the case of molecules which have nuclei with equal charges. If the electron wave function does not change its sign when the sign of the coordinates of all electrons is changed, the corresponding state is termed an even state and marked by the index g. If the wave function changes its sign when the sign of the coordinates of the electrons is changed, the state is an odd state and is marked by the index u.

84 Sometimes, this rule is valid for isoelectronic molecules and even in cases when the atoms A and B and C belong to different groups.

86 The value of D_0 may be calculated by means of the similar relation

$$D_0 = \frac{4B_0^3}{\omega_0^2}. \qquad (1.36a)$$

87 In the case of high powers of the quantum v and J, the determination of the coefficients from the Dunham relations, used in order to improve the approximation of the energy of high vibrational and rotational levels by the aid of Eqs. (1.4) and (1.15), is impossible, because the function (1.32) sufficiently describes the potential energy of the molecule only in the range of its minimum, i.e., at $r \sim r_e$. The function (1.32) is divergent at values $r \gg r_e$ which correspond to great v and J.

88 A distinction between the constants B_e and B_0 is senseless in the case of an estimation of the constants.

89 In the Handbook such molecules will be termed isotopic modifications of the given molecule.

92 See also Herzberg [152], Vol'kenshteyn, Yel'yashevich and Stepanov [128], Wilson, Dashnus and Cross [127a], Towns and Shavlov [416] and also the original papers.

93 Besides the mentioned symmetry elements, the molecules which belong to the point groups D_{ph} possess p second-order symmetry axes which lie on the intersection of the plane σ_h with the plane σ_v.

96 It should be observed that in recent years it was proved that certain monlinear polyatomic molecules, particularly compounds of the type OsF_6, possess stable degenerate electonic states (see, for example, [118a]). However, up to date stable degenerate states are unknown, for the compounds of elements treated in this Handbook.

103 The expressions (1.53) and (1.54) correspond to cases in which anharmonic resonance takes place between the nondegenerate vibrational states. The energy of the Fermi resonance of triatomic molecules with one doubly-degenerate state has the form

$$W_{kl} = W^{v_1, v_2^l, v_3}_{v_1-1, (v_2+2)^l, v_3} = \frac{1}{2} W_{v_1 v_2 v_3} \sqrt{v_1 (v_2 - 2)^l - l^2} \qquad (1.53a)$$

104* The resonance interaction is possible only in cases if the vibrational states with similar energies are described by wave functions of the same symmetry or, in other words, if the appropriate vibrations are of the same symmetry type.

104** The interaction of the angular momentum of the atomic nuclei with the motion of the electrons has not been investigated and will not be discussed further.

107* The expressions for the energy of the rotational levels of linear molecules and of molecules of the type of spherical tops are of the same form; the statistical weights of the rotational states, however, are different (see below, page 109).

107** Molecules which do not possess symmetry axes of the third or higher order may have sometimes two or even three equal principal moments of inertia, i.e., they are "accidental" symmetric or spheric tops.

107*** The axes of the principal moments of inertia coincide with the symmetry axes and lie in the symmetry planes or perpendicularly to them when a molecule of the type of asymmetric tops possess elements of symmetry (a second-order symmetry planes). This essentially facilitates the calculation of the principal moments of inertia of molecules of this type. When the asymmetric top does not possess the mentioned elements

of symmetry, the direction of the axes of the principal moments of inertia may be found only as a direction of the axes of the inertia ellipsoide

113 The simple regularities between the number of valency electron s the structure of the molecule, found by Walsh (see [4139]) on the basis of the method of molecular orbits, may be used in order to predict the structure of simple molecules.

114 The model of the field of intramolecular forces of the molecule of which the vibrational frequencies are known, and of that molecule which estimation is required, must be equal, when carrying out such estimations.

115 Khachkuruzov [440] has shown that the relation (1.65) is valid only for isotopic molecules with an equal symmetry.

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[Transliterated Symbols]

75 выч = vych = vychislitel'nyy = calculated

75 эксп = eksp = eksperimental'nyy = experimental

103 Ф = F = Fermi = Fermi

120 эфф = eff = effektivnyy = effective

Chapter 2

STATISTICAL METHODS OF CALCULATING THE THERMODYNAMIC FUNCTIONS OF IDEAL GASES

§5. INTRODUCTION

In §1 we have remarked that the thermodynamic functions of any gas may be calculated in terms of the statistical sum (partition function) of the system of gas particles (atoms or molecules) and their derivatives with respect to the temperature. We will not discuss in this chapter the theoretical bases of the statistical methods used for calculating the thermodynamic functions of gases, and for deducing the relationships (7) – (10) connecting the values of thermodynamic functions with the statistical sum and its derivatives. These problems are dealt with thoroughly in books on statistical mechanics* and, especially, in Godney's monograph [157] which deals with the general problems involved in calculating thermodynamic functions of gases by means of statistical methods. We will limit ourselves here to the discussion of various methods of calculating thermodynamic functions, with special attention to those problems which are related to the main content of the Handbook. Therefore, several peculiarities in the calculating of thermodynamic functions of gases at low temperatures will not be dealt with, and the methods of calculating the functions of gases, the molecules of which possess an internal rotation, will be discussed only in general terms.

It should be noted however that, apart from the series of papers on methods of calculating the functions of diatomic gases, published

by the author team of the Handbook [105, 106, 107], reviews and monographs, in which the various methods of calculating thermodynamic gas functions are compiled and generalized, are almost nonexistent in modern, up-to-date literature. Fundamental methods, which are widely quoted in literature, are cited in Kassel's wellknown review [2333] and in the previously mentioned monograph by Godnev [157]. An analysis of the accuracy of the methods, however, of their relative advantages, and of the conditions for the expedient application of each of them is lacking in these papers. Moreover, the peculiarities in calculating thermodynamic gas functions at high temperatures, which have acquired especial significance and which have been substantially improved in the past 10 - 15 years, are not examined on their merits in Kassel's review and in Godnev's book.

Almost all fundamental methods of calculating thermodynamic functions of ideal gases at moderate and high temperatures, including the methods developed by the authors of the present Handbook during the last years, are described in this Handbook.

In examining the methods of calculating thermodynamic functions, it is not expedient to discuss all equations for the calculation of all functions. In this section, in principle, the relations for calculating the statistical sum Q, the reduced thermodynamic potential Φ^*_T, and the entropy S°_T are quoted. Similar relations for the calculation of other functions may be developed from Eqs. (8) – (13).

The material under discussion is stated in the following order. First, the division of the statistical sum into components is considered and the general relations for calculating the translational and intramolecular components in terms of thermodynamic functions are cited. Thereupon, the various methods of calculating intramolecular components of the thermodynamic functions of monatomic, diatomic and polyatomic

gases are stated in three separate divisions. All correlations cited in these divisions pertain to individual gases consisting of identical particles and not differing in their isotopic composition. The effect of the isotopic composition of the gases on their thermodynamic functions is stated in the final division of the chapter.

In this Handbook the methods of calculating tables of thermodynamic functions of gases are stated separately; the equations which permit the evaluation of the accuracy of these calculations are listed, and the methods for approximating the tabulated values of thermodynamic properties by polynomials are also quoted.

Division of the statistical sum. Formula for calculating the translational components of thermodynamic functions of gases. The energy of any gas particle (atom or molecule) may be represented as the sum of two independent components, one of which is related to the translational motions of the particle, the other to its internal (intramolecular) motions.

$$\varepsilon_i = \varepsilon_{i,\text{пост}} + \varepsilon_{i,\text{вн}}.$$

Therefore, According to Eq. (6), the sum over the states of the atom (molecule) may be represented as the product of the sum over translational states and the sum over the internal states.

$$Q = Q_{\text{пост}} \cdot Q_{\text{вн}}.$$

In accordance with Eqs. (7) – (10), the thermodynamic functions of a gas may be represented as a sum of two components, in particular, as

$$\Phi_T^\circ = \Phi_{\text{пост}}^\circ + \Phi_{\text{вн}}^\circ, \qquad \text{(II.1)}$$

$$S_T^\circ = S_{\text{пост}}^\circ + S_{\text{вн}}, \qquad \text{(II.2)}$$

where

$$\Phi^{\circ}_{\text{пост}} = R \ln \frac{Q_{\text{пост}}}{N}, \qquad \text{(II.3)}$$

$$S^{\circ}_{\text{пост}} = R \ln \frac{Q_{\text{пост}}}{N} + RT \left(\frac{\partial \ln Q_{\text{пост}}}{\partial T}\right)_{p}, \qquad \text{(II.4)}$$

$$\Phi^{\circ}_{\text{вн}} = R \ln Q_{\text{вн}}, \qquad \text{(II.5)}$$

$$S_{\text{вн}} = R \ln Q_{\text{вн}} + RT \frac{\partial \ln Q_{\text{вн}}}{\partial T}. \qquad \text{(II.6)}$$

The calculation of the sum Q_{post} over the states of translational motion does not present difficulties; the deduction of the appropriate equation

$$Q_{\text{пост}} = \left(\frac{2\pi MkT}{Nh^2}\right)^{3/2} \frac{RT}{p}, \qquad \text{(II.7)}$$

where M is the molecular weight of the gas, p is the pressure, is given in any compendium on statistical mechanics (see, for example, [285], p.127, and also [157], p.53).

On the basis of the numerical values of physical constants assumed in this Handbook (see Supplement 2, Table 302), the following formulas for calculating the translational components Φ^{*}_{post} and S°_{post} (in cal/mole ·degree) are obtained for an ideal gas at a pressure of 1 atm:

$$\Phi^{\circ}_{\text{пост}} = 11{,}43960 \lg T + A_{\Phi}, \qquad \text{(II.8)}$$

$$S^{\circ}_{\text{пост}} = 11{,}43960 \lg T + A_{S}, \qquad \text{(II.9)}$$

$$A_{\Phi} = 6{,}86376 \lg M - 7{,}28355, \qquad \text{(II.10)}$$

$$A_{S} = 6{,}86376 \lg M - 2{,}31535. \qquad \text{(II.11)}$$

The statistical sum over the intramolecular states. Practical and total values of thermodynamic functions. The main difficulties in cal-

culating thermodynamic functions of gases occur in calculating of the statistical sum over intramolecular states and of the corresponding components in the values of the functions. The statistical sum over the intramolecular states is generally the sum over the electronic, vibrational and rotational states and also over the states which are related to the orientation of the spins of the atomic nuclei which form the gas molecules.

The states of atoms and molecules varying from one another by the different orientation of the nuclear spins, possess virtually equal energies, and the nuclear spins remain constant for each isotope of the element as long as there are no nuclear reactions. Therefore, the component in the statistical sum, which is caused by the nuclear spins, is independent of the temperature and comprises an additional statistical weight for states which are related to other intramolecular motions.

It has been shown in Chapter 1 that, depending on the value of the nuclear spins, coefficients enter the statistical weights of the energy states of atoms and molecules (see pages 79, 80 and 109). This coefficient is the same for all states of a given atom or asymmetric molecule, and it is equal to

$$(2I_1+1)(2I_2+1)\dots(2I_n+1),$$

where n is the number of atoms in the molecule. This enables the components $Q_{ya.s.}$ of the nuclear spins to be eliminated from the statistical sum over the intramolecular states of atoms and asymmetric molecules:

$$Q_{a.c.}=\prod_{k=1}^{k=n}(2I_k+1). \qquad \text{(II.12)}$$

In symmetric molecules, however, i.e., in molecules which possess symmetry planes on symmetry axes of second or higher order, the statis-

tical weights of the rotational states depend on the spins of the atomic nuclei which form the molecule. In particular, a part of the rotational states is not realized at all, if the spins are equal to zero (see above, page 82, and also [151] page 10 and [157], page 212). A difference in the energy of two adjacent rotational levels of a symmetric molecule, which is great in comparison to kT, affects the value of the statistical sum over the rotational states in a complex manner, and makes it impossible to eliminate the cofactor $\prod_k (2I_k + 1)$. At normal temperatures, however, the difference between the energies of adjacent rotational states is essentially lower than the value of kT for all molecules, except for the molecule of hydrogen and its isotopic modifications. The errors caused by neglecting the difference in the statistical weights of states with even and odd values of the quantum number J are negligible, even in the case of H_2 (see page 140), at temperatures higher than 293.15°K. Therefore, the statistical sum may be represented as a product of three independent cofactors in the case of all conditions treated in the Handbook, and in regard to all gases:*

$$Q = Q_{\text{пост}} \cdot Q_{\text{вн}} \cdot Q_{\text{я. с.}} \qquad \text{(II.13)}$$

Henceforth Q_{vn}, i.e., the statistical sum of the electronic, vibrational and rotational states will be understood to be the statistical sum over the internal states of atoms and molecules. According to this, the components, in which the spins of the atomic nuclei are not taken into account, will be understood to be the intramolecular components of thermodynamic functions. It should be noted that the appropriate components are usually not included in the values of Φ^*_T and S°_T in modern literature (see [157], page 341) when calculating the thermodynamic functions of gases, due to the fact that the nuclear spins do not change during chemical transformations, and the compo-

nents of the nuclear spins differ from zero only by the values of the thermodynamic potential and of the entropy. The thermodynamic functions calculated without the components of the nuclear spins are sometimes termed *virtual* or *practical functions* in contrast to the total entropy or the thermodynamical gas potential, in which the components of the nuclear spins and some other effects must be included (see below § 15).

Henceforth the practical values of the thermodynamic potential Π^*_T and the entropy S°_T of the gas equal to the sum of the translational and intramolecular components (Eqs. (II.3) and (II.4)) will be understood to be reduced thermodynamical potential and entropy in this Handbook in all cases where no special reservation is made.

Before going over to the discussion of the methods of calculating the statistical sums over the intramolecular states, we should recall (see Chapter 1) that the energy of the electronic, vibrational and rotational levels of atoms and molecules, and also the constants and the equations of molecular energies are expressed in wave numbers (in cm^{-1}). Therefore the corresponding values must be multiplied by hc, where h is the Planck constant and c is the velocity of light, when the corresponding values are to be substituted into the statistical sums. The statistical sum Q_{vn} is in this case equal to

$$Q_{vn} = \sum_i p_i \exp\left(-\frac{\varepsilon_i - \varepsilon_0}{kT}\right) = \sum_i p_i \exp\left[-\frac{hc}{kT}(\nu_i - \nu_0)\right], \quad \text{(II.14)}$$

where ν_i and ν_0 are the energies of the ith and the ground state of the atom or molecule, expressed in reciprocal centimeters.

DIVISION 1. MONATOMIC GASES

§6. CALCULATION OF THE THERMODYNAMIC FUNCTIONS OF MONATOMIC GASES

In the case of monatomic gases, the statistical sum over the internal states is equal to the sum over the electronic states of the atoms (or monatomic ions) of the gas. If we denote the excitation energies of the electronic states of atoms by ν_i (in cm^{-1}), and their statistical weights, which are equal to (2L + 1) (2S + 1), by p_i, the sum over the internal states of an atom may be represented in the form

$$Q_{an} = Q_{at} = \sum_{i=0}^{i} p_i \exp\left(-\frac{hc}{kT}\nu_i\right). \qquad \text{(II.15)}$$

The summation in (II.15) must be carried out in all the electronic states which the atoms of the given gas possess according to the increase of their excitation energy,* each component being considered as a separate state if the excitation energies of the individual components of multiplet states differ essentially from each other. The excitation energies ν_i and the statistical weights p_i of the electronic states of atoms may be determined by examining their spectra or by approximate estimations (see page 54). The sole fundamental problem which arises in calculating the statistical sum over the electronic states of the atom and of its derivatives is to determine the number of states which must be taken into account in the calculation.

The excitation energy of the electronic states of atoms, especially of the atoms of light elements, is relatively great even at temperatures which are not especially high (a problem which has not interested the investigators up to the present time), and the contribution of each individual state $\left(p_i \exp\left[-\frac{hc}{kT}\nu_i\right]\right)$ to the sum (II.15) is small. Therefore, the excited electronic states of atoms were not taken into account in the majority of the published calculations

(see [285], page 140; [157], page 78), a fact which is equal to the assumption

$$Q_{ат}^{e} = \sum_{i=0} p_i \exp\left(-\frac{hc}{kT} \nu_i\right) \cong p_0, \qquad \text{(II.16)}$$

where p_0 is the statistical weight of the ground state of the atom.

In some papers, several low electronic states of atoms were given consideration in the sum (II.15), the contribution of which is comparable to the value of p_0 in the given temperature range. In this case, the number of terms in the sum (II.15) must increase rapidly if the temperature range is extended to include higher temperatures. It was noted in the paper by Veyts, Gurvich and Rtishcheva [126] that all states with $\nu_i \leq 10 \cdot T$ must be taken into account. Kolsky, Gilmer and Gilles [2462] included in the sum (II.15) all states which were observed in the spectra of the investigated atoms (in spite of the fact, that at the same time states with lower excitation energies, not observed experimentally, were not taken into account).

It is evident, that the neglecting in the sum (II.15) of states the contribution of which is small in comparison with the value of p_0, can only be justified on the condition that the total number of terms in the sum is finite. According to Bohr's theory, the number of discrete states in each group of terms becomes infinite at $n \to \infty$. If this were true, however, the statistical sums and thermodynamic functions of monatomic gases would have to become infinite at any temperature. A method is therefore necessary by which the number of states in the sum (II.15) or of the upper limit of the latter can be determined, especially when calculations are to be carried out for high temperatures, where the contribution of states with high excitation energies is significant.

As recently as the Twenties, a number of authors (see [97]) made

attempts to limit the number of possible states of gas atoms in the sum (II.15) in the basis of the assumption that each atom may occupy only a limited volume in space. Due to the fact that the volume of the atom is in first approximation proportional to the sixth power of the principal quantum number n (see Eq. (II.19)), this assumption makes it possible to represent the number of states as a function of the gas pressure and temperature. Particularly Fermi [1554], who carried out a successive calculation of the proper volumes of gas atoms, obtained the expression

$$Q_{ид} = \sum_i p_i \exp\left(-\frac{hc}{kT}\nu_i - \frac{hc}{V}\sum_j N_j U_{ij}\right). \qquad \text{(II.17)}$$

for the statistical sum, where V is the volume of one gas mole, N_j is the number of atoms in the jth state and U_{ij} is the energy of interaction between the atoms i and j.

The supplementary factor in Eq. (II.17) automatically excludes states with high values of n. The values of the principal quantum number n, at which the statistical sum calculated by the Fermi method breaks off, are quoted in Table 6 for p = 1 atm.

TABLE 6

Values of n_{max} at p = 1 atm Calculated by Different Methods

T, °K	298,15	1000	10 000	15 000	20 000
Метод Ферми [1]	7	8	9	9	10
Соотношение (II.18) [2]	6	8	11	12	13

1) Fermi method; 2) equation (II.18).

An essentially new method of approach to this problem was proposed by Baumann [687], based on the application of Heisenberg's uncertainty relation $\Delta t \cdot \Delta E \leq h$ and also taking into account the short lifetime of the atoms in excited states. Due to the fact that the

lifetime τ of atoms in excited states is short, the difference between the excitation energies of adjacent discrete levels cannot be smaller than $\Delta E = \frac{h}{\tau}$, and, therefore, the number of discrete states must be finite even for an isolated atom.*

Assuming the lifetime of an isolated atom in excited state as $\sim 10^{-8}$ sec (a value found experimentally for resolved optical transitions from states with low values of $\underline{n}$) and introducing corrections for the lifetime of the atom in states with high $\underline{n}$ values due to collisions of the external atom electron with the surrounding gas atoms, Baumann has found that the maximum values of $\underline{n}$ in the statistical sum (II.15) are in the order of $8 \cdot 10^3$ and $2.5 \cdot 10^2$, respectively, for the isolated hydrogen atom at T = 10,000°K and the monatomic gaseous hydrogen at a pressure of 1 atm and T = 10,000°K.**

It should be noted that the method proposed by Baumann and also the methods proposed earlier by Fermi, Fowler, Urey and others (see [97]) are, strictly speaking, not applicable to high temperatures when a remarkable ionization of the gas atoms sets in. Shielding fields arise around the atoms and ions at high concentrations of charged particles, and these fields essentially limit the possibility of the existence of atoms and ions in electronic states with high excitation energies. It is evident, that under such conditions, realized in the plasma, the gases may not be considered as being composed from individual components. At the same time, it is impossible to take into account the effect of the Coulomb interaction on the energy of the system and on the value of n_{max} when thermodynamic functions of individual substances are to be calculated. Since the determination of the upper limit of the sum (II.15) is of no importance at temperatures where the ionization degree of the gas is small, and an accurate calculation of the thermodynamic functions of individual gases is impos-

sible at high temperatures (when the ionization degree of the gas is considerable), approximate relations may be used for the estimation of the upper limit of this sum.

Assuming that the gas atoms are rigid spheres, and that the volume of any atom at any temperature cannot exceed the magnitude V/N, where V is the volume of one mole of the gas at T°K and N is the number of atoms in one mole, it is possible to obtain a simple formula for determining n_{max} as a function of the temperature and pressure of the gas:

$$n_{max} = \frac{\left[\left(\frac{3}{4\pi}\frac{kT}{p}\right)^{1/6} 2Rhc\right]^{1/6}}{e} = 2{,}461\left[\frac{T(^\circ K)}{p(\text{atm})}\right]^{1/6}, \qquad \text{(II.18)}$$

where R is the Rydberg constant, h, c, e are the Planck constant, the velocity of light, and the electron charge. This formula was obtained by Gurvich and Kvlividze [171]* assuming that the radius of the atom may be calculated by the equation

$$r_n = \frac{e^2}{2Rhc} n^2, \qquad \text{(II.19)}$$

which, strictly speaking, is valid only for the hydrogen and hydrogen-like atoms. The corrections, however, which take into account the interaction between the electrons in atoms with several electrons in unfilled shells, are essential only for states corresponding to low values of the quantum number ℓ of the orbital momentum of the electron. The corresponding corrections decrease rapidly for states which correspond to values of ℓ different from zero (i.e., states which possess great statistical weights and which give the fundamental contribution to the sum (II.15) of all states with the given quantum number n). The reference to the interaction of atoms changes the value of n_{max} for ℓ = 0 by 1 – 2 units and leaves it practically unchanged at ℓ > 2 even in heavy atoms, for which the corrections for the

interaction of the electrons have maximum values. The values of n_{max} calculated by Eq. (II.18) are quoted in Table 6. As this Table indicates, the values of n_{max} calculated by Eq. (II.18) and by the Fermi method are in a satisfactory accordance with each other at $T \leq 10{,}000°K$ The differences between them increase at higher temperatures. The values calculated by means of Eq. (II.18), however, show a better accordance with those calculated for the hydrogen plasma in the papers by Baumann [687] and Ecker and Weizel [1448] (see also [171]).

In this Handbook, the values of n_{max} were calculated by the formula (II.18). Assuming the expression (II.15) for the statistical sum over the electronic states of the atom, the following equations are valid for the corresponding components in the values of the thermodynamic functions*:

$$\Phi^{\circ}_{эл} = \Phi^{\circ}_{эл} = R \ln \sum_i p_i \exp\left(-\frac{hc}{kT}\nu_i\right), \qquad \text{(II.20)}$$

$$S_{эл} = S_{эл} = R \ln \sum_i p_i \exp\left(-\frac{hc}{kT}\nu_i\right) + R \frac{\sum_i \frac{hc}{kT}\nu_i p_i \exp\left(-\frac{hc}{kT}\nu_i\right)}{\sum_i p_i \exp\left(-\frac{hc}{kT}\nu_i\right)}. \qquad \text{(II.21)}$$

The equations (II.8) – (II.9) and (II.20) – (II.21) give

$$\Phi^{\circ}_{T} = \Phi^{\circ}_{эл} + \Phi^{\circ}_{пост} = \Phi^{\circ}_{эл} + 11{,}43960 \lg T + A_{\Phi}, \qquad \text{(II.22)}$$

$$S^{\circ}_{T} = S_{эл} + S^{\circ}_{пост} = S_{эл} + 11{,}43960 \lg T + A_S, \qquad \text{(II.23)}$$

where A_{Φ} and A_S are calculated by Eq. (II.10) and (II.11). The number of terms in the summation over $\underline{i}$ depends on the temperature at which the calculation is carried out, and on the pressure of the gas.

It has already been noted that the contribution of all levels with high excitation energies is so small at low temperatures that the sums over $\underline{i}$ may be break off at values of $\underline{n}$ which are essentially smaller than n_{max}. The greatest majority of the states corresponding

to high values of $\underline{n}$ possess an excitation energy similar to the energy of the ionization limit of the given group of terms. Hence, the temperature - above which all states with $n \leq n_{max}$, must be taken into account in the statistical sum - is different for different gases and depends on the ionization energy of the given gas. Numerical calculations show, that for $T < 1/15$ it is sufficient to take into account in Q_{el} the states for which $\nu_i \leq 10 \cdot T$, provided that the values of Φ^*_T and S°_T are calculated with an accuracy of the order of $2 \cdot 10^{-3}$ cal/g-atom·degree,* the gas temperature is expressed in °K, and the ionization energy I and the excitation energies ν_i of the electronic states of atoms are represented in cm^{-1}; for $T \geq 1/15$ all states with $n \leq n_{max}$ must be taken into account.

It must be remarked that, calculating the values of n_{max} by Eq. (II.18), the value of n_{max} is obtained as a continuous function of temperature and pressure, whereas the principal quantum number of the electrons of the atom may assume only integral values. If we assume that n_{max} possesses only integral values, the calculated thermodynamic gas functions will show discontinuities at temperatures corresponding to the transition of n_{max} from the value $\underline{a}$ to the value a + 1. In view of the fact that the thermodynamic functions of gases are continuous functions of the temperature, the application of n_{max} values calculated by Eq. (II.18) as a continuous function of the temperature is fully justified. It is expedient to express the value of n_{max} as a sum when carrying out the calculations:

$$n_{max} = n' + \delta, \qquad \text{(II.24)}$$

where $\delta = 2{,}461 \left[\frac{T(°K)}{p(atm)}\right]^{1/6} - n'$, $0 < \delta < 1$; and n' is an integral value, constant within a determined temperature range.

Corresponding to this fact, the statistical sum over the electronic states and its derivatives may be represented in the form of

two sums. For example,

$$Q_{sa} = \sum_{i=0}^{i=a} p_i \exp\left(-\frac{hc}{kT}\nu_i\right) + \delta \sum_{i=a+1}^{i=b} p_i \exp\left(-\frac{hc}{kT}\nu_i\right). \qquad \text{(II.25)}$$

Here, all states corresponding to the values of the quantum number $n \leq n'$ are included into the first sum, and all states with $n = n' + 1$ are included into the second sum.

We have already remarked above that a great number of terms must be taken into account in the statistical sums over the electronic states of electrons and their derivatives at high temperatures since a very considerable number of excited states corresponds to even low values of the principal quantum number of the valence electrons of the atom.* The summation term-by-term in calculating the sums which are components of Eq. (II.25) becomes much too complex a problem when the calculations are carried out for high temperatures, even when electronic computers are used.

In the first edition of this Handbook and in the paper [126] it was proposed to consider states with similar excitation energies as one energy level with a summary statistical weight and an averaged excitation energy, which is equivalent to the condition

$$\sum_{i=a}^{i=b} p_i \exp\left(-\frac{hc}{kT}\nu_i\right) \cong \left(\sum_{i=a}^{i=b} p_i\right) \exp\left(-\frac{hc}{kT}\nu\right), \qquad \text{(II.26)}$$

where

$$\nu = \frac{\sum_{i=a}^{i=b} p_i \nu_i}{\sum_{i=a}^{i=b} p_i}.$$

It may be shown (see [171]) that the error in the value of the statistical sum caused by such a unification of electronic states is in first approximation equal to

$$\exp\left(-\frac{hc}{kT}\nu\right)\sum_{i=a}^{i=b} p_i\left(\frac{\delta\nu_i}{T}\right)^2. \qquad \text{(II.27)}$$

where $\delta\nu_i = |\nu - \nu_i|$.

It follows from Eq. (II.27) that at $\frac{\delta\nu_i}{T} \ll 1$ states with a low $\frac{hc}{kT}\nu$ may be unified into one level, and that at $\frac{hc}{kT}\nu \gg 1$, i.e., states which differ essentially in their energy, may be unified at high electronic states. The latter fact, in particular, makes it possible to attribute the energies of the dissociation limits of the respective state groups to the electronic states of atoms with high values of the quantum number n (see page 54).

Example. Let us examine the calculations of thermodynamic functions of monatomic gases in the example of the calculation of Φ^*_T and $S°_T$ of monatomic nitrogen at temperatures of 5000 and 15,000°K and at pressure of 1 atm. Corresponding to the data cited in Chapter 14 (see page 757), the ionization potential of the N atom is equal to 117,345 cm^{-1}. Thus, at T = 5000°K, we may confine ourselves to the sums which are components of Eqs. (II.20) and (II.21), in order to take into account states for which $\nu_i/T \leq 10$, and, consequently, $\nu_i \leq 50{,}000$ cm^{-1}, whereas, at 15,000°K, all states with $n \leq n_{max}$ must be taken into account, since at this temperature n_{max}, according to (II.18), is equal to 12,222.

a) Calculation of Φ^*_T and $S°_T$ at 5000°K. According to Moore [2941], the N atom possesses two excited electronic states (^2D and ^2P) with energies lower than 50,000 cm^{-1} (see Table 89), and, therefore, the statistical sum is a sum over the states ^4S, ^2D and ^2P and may be represented, according to the data quoted in Table 89, as follows:

$$Q_{ss} = 4 + 10\exp\left(\frac{1{,}43879\cdot 19\,228}{5000}\right) + 6\exp\left(\frac{1{,}43879\cdot 28\,839}{5000}\right) = 4{,}04107.$$

Similarly, we have $T\frac{\partial}{\partial T}Q_{ss} = 0{,}23123$. It follows from this:

$\Phi^{\circ}_{эл} = R \ln Q_{эл} = 2{,}77523$ cal/g-atom·degree, and $S_{эл} = R \ln Q_{эл} + \frac{RT}{Q_{эл}} \frac{\partial}{\partial T} Q_{эл} =$ = 2.88894 cal/g-atom·degree. The transitional components in the values of Φ^{*}_{T} and S°_{T} are calculated by Eqs. (II.8) and (II.9); they are equal to 42.48864 and 47.86784 cal/g-atom·degree (A_{Φ} = 0.58490, and A_{S} = 5.55310 cal/g-atom·degree) if we assume T = 5000°K and M = = 14.008. Thus, we finally find, that Φ_{5000} = 45.67485 cal/g-atom·degree, and that S°_{5000} = 50.75678 cal/g-atom·degree.

b) Calculation of Φ^{*}_{T} and S°_{T} for 15.000°K. The electronic states of the nitrogen atom which correspond to values $n \leq 12.222$ and which belong to five state groups (see page 51 and 663) my be grouped according to the rules stated above into 29 energy levels (Table 89). From these 29 levels, the states with $n \leq 11$ are grouped into 23 levels, and the states with $n \leq 13$ into 6 levels; the energies of the ionization limits of the considered state groups are ascribed to the latter levels. Three statistical weights, p^{a}_{i}, p^{b}_{i} and p^{c}_{i}, are ascribed to each of the six latter levels. These statistical levels correspond to states with the excitation energy of the given level and with the values $n \leq 11$, $n \leq 12$ and $n \leq 13$, respectively.*According to the above statements, the statistical sum for 15,000°K may be represented in the form of two sums:

$$Q_{эл} = \sum_{i=0}^{i=22} p_i \exp\left(-\frac{hc}{kT} \nu_i\right) + \sum_{i=23}^{i=28} \left[p^{b}_{i} + \delta\left(p^{c}_{i} - p^{b}_{i}\right)\right] \exp\left(-\frac{hc}{kT} \nu_i\right),$$

where $\Delta = 2.461\ (15{,}000)^{1/6} - 12 = 0.222$. The corresponding values of $Q_{эл}$, $T \frac{\partial}{\partial T} Q_{эл}$, $\Phi^{\circ}_{эл}$ and S_{vn} are equal to 6.16374; 6.25163 and 3.6142 cal/g-atom·degree and 5.6298 cal/g-atom·degree; the translational components in the values of Φ^{*}_{T} and S°_{T}, calculated by Eqs. (II.8) and (II.9), are equal to 48.3577 and 53.3259 cal/g-atom·degree. Hence, we find $\Phi^{*}_{15,000}$ = 51.9719 cal/g-atom·degree, and $S^{\circ}_{15,000}$ = 59.4569 cal/ /g-atom·degree.

DIVISION 2. DIATOMIC GASES

The methods of calculating the thermodynamic functions of diatomic gases differ from each other mainly in their manner of calculating the statistical sum Q_{vn} over the intramolecular states. As it was stated above, Q_{vn} is the sum over the electronic, vibrational and rotational states, and it may be represented in the case of a diatomic molecule in the following form:

$$Q_{вн} = \sum_i \sum_v^{v_{max}} \sum_J^{J_{max}} \frac{1}{\sigma} (2J+1) \exp\left\{-\frac{hc}{kT}[\nu_{00}^{(i)} + G_0^{(i)}(v) + F_v^{(i)}(J) - F_0^{(X)}(0)]\right\}, \quad \text{(II.28)}$$

and its derivative, with respect to the temperature, is determined by the correlation

$$T\frac{\partial}{\partial T} Q_{вн} = \sum_i \sum_v \sum_J \frac{1}{\sigma} \left\{\frac{hc}{kT}[\nu_{00}^{(i)} + G_0^{(i)}(v) + F_v^{(i)}(J) - F_0^{(X)}(0)]\right\} (2J+1) \cdot \exp\left\{-\frac{hc}{kT}[\nu_{00}^{(i)} + G_0^{(i)}(v) + F_v^{(i)}(J) - F_0^{(X)}(0)]\right\}, \quad \text{(II.29)}$$

where the summation is first carried out over the rotational levels characterized by the quantum number J, then over the vibrational levels characterized by the quantum v, and, finally, over the electronic states of the molecule denoted by the symbol i. In order to facilitate the further statements, we may denote the statistical sum over the rotational levels of the vth vibrational state in the ith electronic state of the molecule by $Q_{v,vr}^{(i)}$:

$$Q_{v,вр}^{(i)} = \frac{1}{\sigma} \sum_J^{J_{max}} (2J+1) \exp\left\{-\frac{hc}{kT}[F_v^{(i)}(J) - F_0^{(X)}(0)]\right\}, \quad \text{(II.30)}$$

and the statistical sum over all rotational and vibrational levels of the ith electronic state by $Q_{кол.vr}^{(i)}$:

$$Q_{кол.вр}^{(i)} = \frac{1}{\sigma} \sum_v^{v_{max}} \sum_J^{J_{max}} (2J+1) \exp\left\{-\frac{hc}{kT}[G_0^{(i)}(v) + F_v^{(i)}(J) - F_0^{X}(0)]\right\}. \quad \text{(II.31)}$$

Then the equation (II.28) for Q_{vn} may be written down in the form:

$$Q_{вн} = \sum_i \sum_v \exp\left\{-\frac{hc}{kT}[\nu_{00}^{(i)} + G_0^{(i)}(v)]\right\} Q_{v,вр}^{(i)} \quad \text{(II.32)}$$

or

$$Q_{вн} = \sum_i \exp\left[-\frac{hc}{kT}\nu_{00}^{(i)}\right] Q_{кол.вр}^{(i)}. \qquad (II.33)$$

The expression (II.33) for Q_{vn} is of special interest when approximate methods of calculating the thermodynamic functions are used, in which the values of $Q_{kol.vr}^{(i)}$ are calculated separately for each electronic state, and the obtained values are multiplied by $\exp\left[-\frac{hc}{kT}\nu_{00}^{(i)}\right]$ and added together.

The zero energy $F_0^{(x)}(0)$, the energy of the lowest rotational level in the ground state, which may differ from zero in the case of diatomic molecules, is introduced into the exponential expressions in Eqs. (II.28) - (II.31). The value σ in these equations is the number of symmetry, equal to 1 in the case of asymmetric molecules, and equal to 2 in that of symmetric ones.

It must be noted, that, strictly speaking, the introduction of the symmetry number in the case of symmetric molecules is a certain approximation. In order to calculate accurately the statistical sum over the intramolecular states of diatomic symmetric molecules the nuclear spin must be taken into account; this results in a splitting off of $Q_{v,vr}^{(i)}$ into two independent sums according to the even and odd rotational states with defferent statistical weights (see Table 5). On the condition that the interval between two adjacent rotational levels is small in comparison to the value of kT (i.e., practically for all gases in the temperature range dealt with in this Handbook), the statistical sum over the even rotational states is equal to the sum over the odd ones, correct to the statistical weight caused by the nuclear spin.* This fact makes it possible to separate totally the factor caused by the nuclear spin, and to calculate $Q_{v.vr}$ for the symmetric molecule by taking one half of the value of $Q_{v.vr}^{(i)}$ calculated over all rotational states, i.e., by assuming $\sigma = 2$.

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§7. Method of Immediate Summation

The calculation of Q_{vn} and $T\frac{\partial Q_{vn}}{\partial T}$ by immediate summation of Eq. (II.28) and (II.29) and a subsequent substitution of the obtained values into Eqs. (II.5) and (II.6) is the most strict and accurate method of calculating the thermodynamic functions of diatomic gases. When calculating Q_{vn}, the energy of each vibrational and rotational level is calculated by the corresponding equations for $G_0^{(i)}(v)$ and $F_v^{(i)}(J)$, or it is given by values taken immediately from the experimental data, whereas the summation over the electronic states is carried out by means of the numerical values of the excitation energy of each electronic state.

The method of immediate summation was first applied in 1926 by Hicks and Mitchell [2066] for calculating the specific heat of HCl up to 600°K according to a suggestion by Tolman. In 1928 Giauque and Wiebe [1721] found an error in the calculation of Hicks and Mitchell and corrected it. Finally, this method was thoroughly developed and introduced into practice by 1930 through the papers by Giauque, Johnston and others [1714, 1721, 1723, 2272, 2278], and the correctness of this method was proved by comparison of the calculated data with data obtained by means of special calorimetric precision measurements.

The method of immediate summation was applied in the thirties for calculating tables of the thermodynamic functions of a number of simple diatomic gases up to 3000-5000°K. The summation over the rotational and vibrational levels of the electronic ground state of the molecule was broken off in these calculations at such values of the quantum numbers v and J, as the corresponding contributions to the statistical sum of the states began to disappear. As regards the excited electronic states of the molecules, they were not taken into

account in these calculations, apart from rare exceptions.

Due to the necessity of compiling tables of thermodynamic gas functions up to 20,000-25,000°K, a series of investigations was undertaken in recent years to prove the method of immediate summation in calculations within a wide temperature range. In particular, such investigations were carried out by Gurvich and Yungman [177], beginning with 1957 during the preparation of this Handbook.*

In 1958, a paper by Baumann [688] was published in which the fundamental principles of calculating the statistical sums over intramolecular states were developed, according in principle with the points of view stated in the paper [177].

The calculation of Q_{vn} and $T\frac{\partial Q_{en}}{\partial T}$ by Eqs. (II.28) and (II.29) requires a great amount of calculating especially for high temperatures. This fact, however, is of no special significance at the present time due to the availability of high-speed electronic computers. Hence, the determination of the upper summation limits, which is especially important in the case of high temperatures, is the main problem in calculating Q_{vn} for diatomic molecules as well as for atoms. As is well-known, the number of rotational and vibrational levels of a molecule is limited. The limit values of v and J, however, are not determined experimentally, with the exception of some few cases. The methods of calculating v_{max} and J_{max}, developed during the preparation of this Handbook, are stated on pages 67 and 74.

The number of electronic states of molecules may be limited in the same manner as in the case of atoms, i.e., by the assumption of a finite volume occupied by each gas molecule in space. Due to the fact, however, that only a small part of the possible electronic states of molecules is stable, the determination of the upper limit of the

statistical sum over the electronic states is, in practice, impossible. Nevertheless, this does not cause essential difficulties and errors in the calculation of the thermodynamic functions of diatomic gases, because the greatest part of the excited electronic states of molecules possess high energies, and the contribution of these states becomes important only at such temperatures at which the gas molecules are almost totally dissociated into atoms. Moreover, the potential curves of the molecules show a weakly expressed minimum at high electronic states. In these electronic states, the molecule possesses a small number of vibrational and rotational energy levels, and the statistical sums over the vibrational-rotational states are small in comparison to the value of $Q_{kol.vr}$ for the electronic ground state. Thus, one may confine oneself to the consideration of states for which $\nu_i/T \leq 5\text{-}8$ (see page 181).

The summation of the rotational levels of multiplet electron states of diatomic molecules becomes complicated depending on the formof the expression $F_v^{(i)}(J)$ which denotes the energy of these levels (see page 76). The corresponding constants of the multiplet splitting, however, are not always determined experimentally. Moreover, they are sufficiently small in a number of cases; the summation over J is then carried out in the same number as in the case of $^1\Sigma$ states, and the multiplicity as well as the Λ doubling (if it takes place) are taken into account by the introduction of an appropriate statistical weight (see Table 7).

The calculations of the thermodynamic functions of diatomic gases based on the calculation of the statistical sums over the intramolecular states and of their derivatives with respect to the temperature by the method of immediate summation, are carried out with the aid of equations similar to those cited for the monatomic gas:

$$\Phi_T^\circ = \Phi_{вн}^\circ + \Phi_{пост}^\circ = R \ln Q_{вн} + 11{,}43960 \lg T + A_\Phi, \qquad \text{(II.34)}$$

$$S_T^\circ = S_{вн} + S_{пост}^\circ = R\left[\ln Q_{вн} + \frac{T}{Q_{вн}} \frac{\partial Q_{вн}}{\partial T}\right] + 11{,}43960 \lg T + A_S, \qquad \text{(II.35)}$$

where Q_{vn} and $T\frac{\partial Q_{вн}}{\partial T}$ are found by Eqs. (II.28) and (II.29), and A_Φ and A_S by Eqs. (II.10) and (II.11).

The approximate calculation methods stated in §10 may be used to calculate $Q_{kol.vr}$ of electronic states which have sufficiently high excitation energies.

Example. Let us consider the calculation of the thermodynamic functions of diatomic nitrogen N_2 at a temperature of 10,000°K by the method of immediate summation. According to the data of Table 92, the electronic states with excitation energies up to 75,000 cm^{-1} must be taken into account i the calculation of the thermodynamic functions of N_2 at 10,000°K.

At a temperature of 10,000°K, almost all nitrogen molecules are distributed among the levels of the ground state $X^1\Sigma^+_g$ and the two first excited states $A^3\Sigma^+_u$ and $B^3\Pi_g$. Assuming the values of the molecular constants of N_2, quoted in Table 92, and limiting the summation over J by values of J_{max} obtained for each vibrational level of these states with the aid of the method stated in §3 (see Fig. 12), we find that

$$Q_{кол.вр}^{(X)} = 13266{,}8;\ T\frac{\partial}{\partial T} Q_{кол.вр}^{(X)} = 25797{,}4;\ Q_{кол.вр}^{(A)} \exp\left(-49756{,}5\frac{hc}{kT}\right) =$$
$$= 26{,}3;\ T\frac{\partial}{\partial T}\left[Q_{кол.вр}^{(A)} \exp\left(-49756{,}5\frac{hc}{kT}\right)\right] = 275{,}4;\ Q_{кол.вр}^{(B)} \exp\left(-59271{,}3\frac{hc}{kT}\right) =$$
$$= 67{,}7;\ T\frac{\partial}{\partial T}\left[Q_{кол.вр}^{(B)} \exp\left(-59271{,}3\frac{hc}{kT}\right)\right] = 605{,}4.$$

The multiplicity of the states $A^3\Sigma$ and $B^3\Pi$ was considered in the values of $Q_{kol.vr}^{(i)}$ by statistical weights equal to 3 and 6, respectively.

Let us denote

$$\Sigma = Q^{(X)}_{\text{кол.вр}} + Q^{(A)}_{\text{кол.вр}} \exp\left(-\frac{hc}{kT}\nu^{(A)}_{00}\right) + Q^{(B)}_{\text{кол.вр}} \exp\left(-\frac{hc}{kT}\nu^{(B)}_{00}\right),$$

we then have: $\Sigma = 13360.8$; $\log \Sigma = 4.12583$, and $R \ln \Sigma = 18.8791$ cal/mole·degree. Adding a correction for the higher excited electronic states, calculated by the equations discussed in §10 and equal to 0.0006 cal/mole·degree, we obtain $\Phi^*_{vn} = 18.8797$ cal/mole·degree. For the entropy we have: $T\frac{\partial}{\partial T} = 26678.2$; $\frac{RT}{\Sigma}\cdot\frac{\partial \Sigma}{\partial T} = 3.9681$ cal/mole·degree; the correction for the higher states is equal to 0.0060 cal/mole·degree. Finally, $RT\frac{\partial \ln Q_{вн}}{\partial T} = 3.9741$ cal/mole·degree. For T = 10,000°K and M = 28.016, we have $\Phi^*_{post} = 47.0320$ cal/mole·degree; $S°_{post} = 52.0002$ cal/mole·degree ($A_\Phi = 1.27363$, $A_S = 6.24183$) and $\Phi^*_{10,000} = 65.9117$ cal/mole·degree, $S°_{10,000} = 74.8540$ cal/mole·degree.

§8. Approximate Methods of Calculating the Vibrational Rotational Components of Thermodynamic Functions.

The calculation of the statistical sum over the intramolecular states and of its derivatives with respect to the temperature by immediate summation over the energy levels of the molecule is the most accurate method of calculation, free from any assumptions and suppositions. The application of this method for calculating the tables of thermodynamic functions within a wide temperature range, has, up to the present, met with a number of important difficulties in practice due to the great amount of calculations requiring the summation of tens, hundreds, and even thousands of addends.* In order to meet this difficulty, various approximate methods of calculations based on certain assumptions were developed in a series of papers; in these methods the sums in Eqs. (II.28) and (II.29) and the appropriate components in the values of Φ^*_T and $S°_T$ are substituted by simple explicit functions of the temperature and molecular constants; the functions may be calculated either immediately or found in auxiliary tables. The main part of the calculating work when calculating ther-

modynamic gas functions is connected with the calculation of the statistical sums over the vibrational and rotational states*, therefore the approximate methods differ from each other in their method of calculating $Q_{kol.vr}$.

Due to the fact that the approximate methods were at first defined for the calculation of thermodynamic gas functions at low and medium temperatures, the existence of excited electronic states was not taken into account in these methods, i.e., it was assumed that $Q_{vn} = Q^{(X)}_{kol.vr}$, where $Q^{(X)}_{kol.vr}$ is the statistical sum over the vibrational and rotational states of the electronic ground state of the molecule. This means that the intramolecular components of the thermodynamic gas functions are equal to the vibrational-rotational components of the ground state:

$$\Phi^{*}_{вн} = R \ln Q^{(X)}_{кол.вр} = \Phi^{*}_{кол.вр},$$

$$S_{вн} = R \ln Q^{(X)}_{кол.вр} + RT \frac{\partial}{\partial T} \ln Q^{(X)}_{кол.вр} = S_{кол.вр}.$$

An appreciation of the excited electronic states may be obtained in this case, if necessary, by the introduction of appropriate corrections into the values of Φ^{*}_{vn} and S_{vn}.

In the preparation of this Handbook, methods for calculating the corrections were developed which, by means of approximate methods, take into account the existence of excited electronic states of molecules in the calculation of thermodynamic functions. These methods will be dealt with after the approximate methods of calculating the statistical sum over the vibrational and rotational states of a single electronic state of the molecule, and after the calculation of the corresponding values in Φ^{*}_{T} and S°_{T} have been discussed.

It must be noted that the equations for calculating $Q_{kol.vr}$ and of the corresponding values in Φ^{*}_{T} and S°_{T} are different depending on

the type of the electronic state of the molecule. Hence, the approximate methods of calculating $Q_{kol.vr}$, $\Phi_{kol.vr}$, and $S_{kol.vr}$ for gas molecules in the $^1\Sigma$ state will be stated first, and then (see page 167) the correlations will follow which make it possible to calculate these values for other types of electronic states.

The Method by Giaugue and Overstreet. The most laborious part in calculating the statistical sum over the intramolecular states and its derivative with respect to the temperature by method of immediate summation is the assumation of the levels of the rotational energy. In order to avoid this operation, Giauque and Overstreet [1718] transformed the sum of the rotational energies by expansion into a series of exponential expressions $\exp\left\{\frac{hc}{kT} D_v J^2 (J+1)^2\right\}$, and $\exp\left\{-\frac{hc}{kT} H_v J^3 (J+1)^3\right\}$. Using the approximate Euler-Maclaurin formula for the substitution of the addition by integration, and assuming $J_{max} = \infty$, Giauque and Overstreet obtained expressions for the statistical sum $Q^{\infty}_{v.vr}$ over the rotational states and of its derivative which are explicite functions of the rotational constants of the gas molecules:

$$Q^{\infty}_{v.sp} = \frac{1}{\sigma}\sum_{J=0}^{\infty}(2J+1)\exp\left\{-\frac{hc}{kT}\left[B_v J(J+1) - D_v J^2 (J+1)^2 + H_v J^2 (J+1)^3\right]\right\} =$$

$$= \frac{q_v}{\sigma}\left(1 + \frac{1}{3q_v} + d_v + 3d_v^2 + f_v + \ldots\right), \qquad \text{(II.36)}$$

$$T\frac{\partial}{\partial T} Q^{\infty}_{v.sp} = q_v(1 + 2d_v + 9d_v^2 + 3f_v + \ldots), \qquad \text{(II.37)}$$

where

$$q_v = \frac{kT}{hcB_v}, \qquad \text{(II.38)}$$

$$d_v = \frac{2D_v}{B_v} q_v, \qquad \text{(II.39)}$$

$$f_v = -\frac{6H_v}{B_v} q_v^2. \qquad \text{(II.40)}$$

The values of $Q^{\infty}_{v.vr}$ and $T\frac{\partial}{\partial T} Q^{\infty}_{v.sp}$, calculated by Eqs. (II.36) and (II.37) for each vibrational state v, are multiplied by

$\exp\left\{-\frac{hc}{kT}G_0(v)\right\}$ when summation is carried out over v. Thus, the statistical sum over the vibrational and rotational states of the ith electronic state and of the derivative of the sum assume the form

$$Q^{(i)\infty}_{\text{кол.вр}} = \sum_v \exp\left[-\frac{hc}{kT}G_0^{(i)}(v)\right]\cdot \gamma^{(i)\infty}_{v,\text{вр}}, \qquad \text{(II.41)}$$

$$T\frac{\partial Q^{(i)\infty}_{\text{кол.вр}}}{\partial T} = \sum_v \exp\left[-\frac{hc}{kT}G_0^{(i)}(v)\right]\left[\frac{hc}{kT}G_0^{(i)}(v)\cdot Q^{(i)\infty}_{v,\text{вр}} + T\frac{\partial}{\partial T}Q^{(i)\infty}_{v,\text{вр}}\right]. \qquad \text{(II.42)}$$

The transformation of the statistical sum over the rotational states, based on the substitution of integration for summation and on the assumption of $J_{max} = \infty$, is very important, and is used in all approximate methods of calculating thermodynamic gas functions.

Brounshteyn [102,104] investigated the properties of this transformation, and obtained an expression for $Q^{\infty}_{V.vr}$ of a more general form, assuming an equation with three constants (B_v, D_v and H_v) for the rotational energy $F_v(J)$ of the molecule:

$$Q^{\infty}_{v,\text{вр}} = \frac{q_v}{\sigma}\left[1 + \frac{1}{3q_v} + \frac{1}{15q_v^2} + \frac{4}{315q_v^3} + \ldots + d_v + \right.$$

$$\left. + 3d_v^2 + f_v + 10d_vf_v + \ldots + \frac{(2n+3m)!}{2^n6^m n!m!}d_v^n f_v^m\right]. \qquad \text{(II.43)}$$

In paper [102] an expression for the general term in an equation of the type of (II.43) was also obtained for the case when terms proportional to higher powers of $J(J+1)$ up to $P_{kv}J^k(J+1)^k$ are taken into account in Eq. (I.15) for the energy of rotational levels.

Partial expressions for $Q^{\infty}_{V.vr}$ obtained earlier by various authors, including Giauque and Overstreet [1718], Johnston and Davis [2274], Woolley [4322], Kassel [2333] and others (see [107]) may easily be derived from the formula (II.43).

It must be noted that the number of terms in the expression (II.43) for $Q^{\infty}_{V.vr}$ cannot be chosen arbitrarily high, because generally the series (II.43) is divergent. At first the terms of the series decrease up to a certain limit value n_{pr} when n increases. At

$n > n_{pr}$, the terms of the series begin to increase with increasing n. It was shown in the paper by Brounshteyn [104] that for $F_v(J) = B_vJ(J+1) - D_vJ^2(J+1)^2 + H_vJ^3(J+1)^3$ the values of n_{pr} may be found by the formula

$$n_{np} = \frac{3B_vH_v + D_v(\sqrt{D_v^2 + 3B_vH_v} - D_v)}{9H_vq_v(D_v + \sqrt{D_v^2 + 3B_vH_v})}.$$

The fundamental errors in calculating thermodynamic functions of gases by the method of Giauque and Overstreet are caused by the fact that the relations (II.36) and (II.37) are obtained under the condition $J_{max} = \infty$. This simplification does not cause errors at low and moderate temperatures when the values of $\exp\left[-\frac{hc}{kT}F_v(J)\right]$, which correspond to high values of J, are negligible. At high temperatures, however, when the contribution of these levels becomes important, it may cause significant errors (see Table 9-10). Particularly, it causes an increase of each term of the series (II.43) at $n > n_{pr}$.

It is evident that the limits of the applicability of the method depend not only on the temperature at which the calculation is carried out, but also on the values of the rotational constants of the gas molecules.

Using the approximate relation

$$G_0(v) + F_v(J) \leqslant D_0,$$

where D_0 is the dissociation energy of the molecule in the given electronic state, Brounshteyn [102] derived formulas for calculating the statistical sum of the rotational states and of its derivative with respect to the temperature, taking into account a finite number of rotational states:

$$Q_{v,sp} = Q^{\infty}_{v,sp} - \frac{q_v}{\sigma}\exp\left\{-\frac{hc}{kT}[D_0 - G_0(v)]\right\}, \qquad \text{(II.44)}$$

$$T\frac{\partial}{\partial T}Q_{v,sp} = T\frac{\partial}{\partial T}Q^{\infty}_{v,sp} - \left\{1 + \frac{hc}{kT}[D_0 - G_0(v)]\right\}\cdot\frac{q_v}{\sigma}\exp\left\{-\frac{hc}{kT}[D_0 - G_0(v)]\right\} \qquad \text{(II.45)}$$

The substitution of the calculation of $Q^{\infty}_{v.vr}$ by the values of the rotational constants of the gas molecules for the immediate summation over the levels of rotational energy in the Giauque-Overstreet method resulted in an essential decrease in the amount of calculations in determining the statistical sums and the thermodynamic gas functions. The inevitable summation over the vibrational energy levels in this method, however, also limits essentially its applicability, as the diatomic molecules generally possess some tens and sometimes more than 100 vibrational levels which must be taken into account for high temperatures in the sums (II.41) and (II.42).

Therefore, methods of a sort are required, which would make possible a total avoidance of the summations over the energy levels in calculating statistical sums over the vibrational and rotational states of molecules, and which would make possible the calculation of the corresponding components in the values of Φ^{*}_{T} and S_{T} of diatomic gases as simple functions of the molecular constants and of the temperature. Such methods were proposed by Gordon and Barnes, Kassel, and some other authors.

Method of Gordon and Barnes. The method of Gordon and Barnes, developed in 1933 [1814], is the most important approximate method for the calculation of $\Phi^{*}_{kol.vr}$ and $S_{kol\ vr}$. The expression (II.36) obtained by Giauque and Overstreet is used in this method for the statistical sum over the rotational states of diatomic molecules, and the determination of a series of values by means of auxiliary tables, compiled by Gordon and Barnes, is substituted for the summation over v Eqs. (II.36) and (II.37) The appropriate equations for calculating $\Phi^{*}_{kol.vr}$ and $S_{kol.vr}$ were obtained on the basis of the transformations and assumptions which are stated below.

If we assume that the dependence of the rotational constant B_v

on the quantum number $\underline{v}$ (see page 70) may be represented by $B_v = B_0 - \alpha_1 v$ (which is sufficiently accurate in the majority of cases), the value of q_v (see(II.38)) in the statistical sum over the rotational states may be written down in the form

$$q_v = q_0 (1 + \beta_1 v + \beta_2 v^2), \tag{II.46}$$

where

$$q_0 = \frac{kT}{hcB_0} \quad \beta_1 = \frac{\alpha_1}{B_0} \quad \beta_2 = \left(\frac{\alpha_1}{B_0}\right)^2.$$

Neglecting in the Giauque-Overstreet Eq. (II 36) the dependence of $1/3q_v$, d_v, and f_v on $\underline{v}$, the expression for $Q^{\infty}_{\text{kol.vr}}$ may be represented as follows:

$$Q^{\infty}_{\text{кол.вр}} = \frac{1}{\sigma} q_0 \left(1 + \frac{1}{3q_0} + d_0 + 3d_0^2 + f_0\right) \cdot \sum_{v=0}^{v_{\max}} \exp\left[-\frac{hc}{kT} G_0(v)\right] (1 + \beta_1 v + \beta_2 v^2). \tag{II.47}$$

Introducing the denotations

$$Q_{\text{кол}} = \sum_{v=0}^{v_{\max}} \exp\left[-\frac{hc}{kT} G_0(v)\right], \tag{II.48}$$

$$\bar{v} = \frac{1}{Q_{\text{кол}}} \cdot \sum_{v=0}^{v_{\max}} v \exp\left[-\frac{hc}{kT} G_0(v)\right], \tag{II.49}$$

$$\bar{v}^2 = \frac{1}{Q_{\text{кол}}} \cdot \sum_{v=0}^{v_{\max}} v^2 \exp\left[-\frac{hc}{kT} G_0(v)\right], \tag{II.50}$$

the equation (II.27) may be transformed into

$$Q^{\infty}_{\text{кол.вр}} = \frac{1}{\sigma} q_0 \left(1 + \frac{1}{3q_0} + d_0 + 3d_0^2 + f_0\right) (1 + \beta_1 \bar{v} + \beta_2 \bar{v}^2) Q_{\text{кол}}. \tag{II.51}$$

Assuming $\beta_1 \bar{v} + \beta_2 \bar{v}^2 \ll 1$ and $\frac{1}{3q_0} + d_0 + 3d_0^2 + f_0 \ll 1$, and logarithming the expression (II.51), Gordon and Barnes obtained the following equations for the rotational-vibrational components of Φ^*_T and S^*_T:

$$\Phi^*_{\text{кол.вр}} = R \left(\ln Q_{\text{кол}} + \ln q_0 + \frac{1}{3q_0} + \beta_1 \bar{v} + \beta_2 \bar{v}^2 + d_0 + 2{,}5 d_0^2 + f_0 - \ln \sigma\right), \tag{II.52}$$

$$S_{\text{кол.вр}} = R \left(\frac{S_{\text{кол}}}{R} + \ln q_0 + 1 + \beta_1 \bar{s} + \beta_2 \bar{s}^2 + 2d_0 + 7{,}5 d_0^2 + 3f_0 - \ln \sigma\right), \tag{II.53}$$

where

$$\frac{S_{кол}}{R} = \ln Q_{кол} + T\frac{\partial}{\partial T}\ln Q_{кол}, \qquad (II.54)$$

$$\bar{s} = \bar{v} + T\frac{\partial \bar{v}}{\partial T}, \qquad (II.55)$$

$$\bar{s}^2 = \bar{v}^2 + T\frac{\partial \bar{v}^2}{\partial T}. \qquad (II.56)$$

In order to calculate the values of $\ln Q_{kol}$; S_{kol}/R; $\bar{v}, \bar{v}^2, \bar{s}, \bar{s}^2$ and $\bar{s}^2$, Gordon and Barnes assumed that the vibrational energy of a diatomic molecule is described by the binomial equation (I.10)

$$G_0(v) = \omega_0 v - \omega_0 x_0 v^2 = \omega_0 v - \omega_e x_e v^2 = \omega_e (1 - x) v - \omega_e x_e v^2,$$

where

$$x = \frac{\omega_e x_e}{\omega_e}.$$

Thus, the values of $\ln Q_{kol}$, S_{kol}/R, $\bar{v}, \bar{v}^2, \bar{s}$ and $\bar{s}^2$ may be represented as functions of the following two parameters:*

$$\frac{\theta}{T} = \frac{hc}{kT}\omega_e, \quad x = \frac{\omega_e x_e}{\omega_e}.$$

Gordon and Barnes compiled tables of these six quantities for the values $0 \leqslant x \leqslant 0{,}025$ with steps of x having a size of 0.005 and for the values $0{,}6 \leqslant \frac{\theta}{T} \leqslant 6{,}0$ with grades of θ/T having a size of 0.1 up to 2.0, and of 0.2 from 2.0 to 6.0.** The upper limit in the sums over v becomes automatically equal to

$$v_{max} = \frac{\omega_e}{2\omega_e x_e} - \frac{1}{2} = \frac{1}{2x} - \frac{1}{2}. \qquad (II.57)$$

(see page 65) when the tables are calculated corresponding to the assumed form of the expression for $G_0(v)$. It must be noted that the values of $\bar{v}$, $\bar{v}^2$, $\bar{s}$, and $\bar{s}^2$ are given immediately in the auxiliary tables compiled by Gordon and Barnes. At the same time, the values of $\ln Q_{kol}$ and S_{kol}/R must be found with the aid of the tables by interpolation as the sum of two components. In the auxiliary tables the values of Q_{kol} (or S_{kol}/R) are quoted as a function of θ/T at $x =$.

i.e., the values of the these magnitudes for the harmonic oscillator are given (see page 165); in the other table, the values of $\Delta \ln Q_{кол}$ (or $\Delta S_{кол}/R$), being differences between the values of $\ln Q_{kol}$ (or S_{kol}/R, respectively), are quoted for a given value of θ/T and x = x and x = 0.*

Developing the Eqs. (II.52) and (II 53), Gordon and Barnes made a number of assumptions which may effect the accuracy of the calculated thermodynamic functions. Some of these simplications are unnecessary for the method, and may be disregarded (especially in calculations for high temperatures) if the corresponding molecular constants are well-known. Thus, the second constant of the interaction in Eq. (1.16), i.e., the constant α_2, may be taken into account in the expression for q_v; the formulas for the calculation of q_0 and β_1 in Eq. (II.46) remain unchanged in this case, whereas β_2 may be found by the equation

$$\beta_2 = \frac{\alpha_1^2 - B_0\alpha_2}{B_0^2}. \qquad \text{(II.58)}$$

In a similar manner, the dependence of the values of d_v and d_v^2 on the quantum number v may be taken into account,etc. In the derivation of Eqs. (II.52) and (II.53) Gordon and Barnes expanded the expressions $\ln(1 + \beta_1\bar{v} + \beta_2\bar{v}^2)$ and $\ln(1 + \frac{1}{3q_0} + d_0 + 3d_0^2 + f_0)$ in series, discontinuing the latter after the first terms.

In cases when the values in parentheses tend to unity, i.e., at high temperatures, the subsequent terms of the corresponding series must be taken into account in Eqs. (II.52) and (II.53), or, the values of $\beta_1\bar{v} + \beta_2\bar{v}^2$ and $\frac{1}{3q_0} + d_0 + 3d_0^2 + f_0$ in these equations must be substituted by $\ln(1 + \beta_1\bar{v} + \beta_2\bar{v}^2)$ and $\ln(1 + \frac{1}{3q_0} + d_0 + 3d_0^2 + f_0)$.

Assumptions over the form of the dependence of the molecular vibrational energy on the values of the quantum number v, and over

the upper limit of the quantum number J, which - as well as in the Glauque-Overstreet method - is assumed to be infinite, are a much more essential simplification. An approximate limitation of the number of rotational states of the gas molecules may be carried out in the calculations according to the Gordon-Barnes method, as well as in the Glauque-Overstreet method, by means of the equations (II.44) and (II.45), proposed by Brounshteyn (see [102]). The appropriate corrections for the values of $\Phi^{*}_{vr.kol}$ and $S_{kol.vr}$, obtained by substitution of these relations into Eqs. (II.52) and (II.53) have the form

$$R \ln (1-a), \tag{II.59}$$

$$R \ln (1-a) + R\frac{a}{1-a}\left(T\frac{\partial}{\partial T}\ln Q^{\infty}_{кол.\,вр} - 1 - \frac{hc}{kT}D_0\right), \tag{II.60}$$

where

$$a = \frac{\sum_{v=0}^{v_{max}} q_v}{gQ^{\infty}_{кол.\,вр}} \exp\left(-\frac{hc}{kT}D_0\right), \tag{II.61}$$

$$\sum_{v=0}^{v_{max}} q_v = q_0\left[1 + v_{max} + \beta_1\frac{v_{max}(1+v_{max})}{2} + \beta_2\frac{v_{max}(1+v_{max})(1+2v_{max})}{6}\right], \tag{II.62}$$

$$Q^{\infty}_{кол.\,вр} = \exp\left(\Phi^{*\infty}_{кол.\,вр}/R\right), \tag{II.63}$$

$$T\frac{\partial}{\partial T}\ln Q^{\infty}_{кол.\,вр} = \frac{1}{R}\left(S^{\infty}_{кол.\,вр} - \Phi^{*\infty}_{кол.\,вр}\right); \tag{II.64}$$

the sign ∞ means that the corresponding values are calculated for $J_{max} = \infty$.

The insertion of corrections in the Gordon-Barnes method, which makes it possible to use the values of vibrational constants in equations of third and higher power of the vibrational energy of the molecule (the second and subsequent anharmonicity constants $\omega_e y_e$, $\omega_e z_e$ etc.), and also to consider the difference between the value of v_{max} and $\frac{1}{2x} - \frac{1}{2}$, is a more difficult problem that requires an important complication of this method.

Relations (see page 161) which permit an estimation of the error in the values of the thermodynamic functions of gases caused by the assumption of a binomial expression for the energy of the vibrational levels are given below.* The corresponding errors do not exceed, generally, the total errors of the method; thus, it is not expedient to introduce the mentioned corrections into the calculations.

Example. Let us examine the calculation of the values of $\Phi^*_{kol.\,vr}$ and $S_{kol.\,vr}$ for the ground state $X^1\Sigma^+_g$ of the diatomic nitrogen N_2 by the method of Gordon and Barnes for the temperatures of 5000 and 10,000°K. According to the values of the molecular constants of this state, quoted in Table 92, we have $\frac{\theta}{T} = \frac{?359.434}{T}$; $x = 0.0063346$; $q_0 = 0.34931 \cdot T$; $\beta_1 = 0.008589$; $\beta_2 = 0.000096884$; $d_0 = 2.11 \cdot 10^{-6} \cdot T$; $\frac{1}{3q_0} = \frac{0,95425}{T}$; and $f_0 = -2.1 \cdot 10^{-12} \cdot T^2$.

For 5000°K $\frac{\theta}{T} = 0.678946$; $q_0 = 1746.6$; $d_0 = 0.0106$; $\frac{1}{3q_0} = 0.0002$; $f_0 = -0.0001$. The values of $\ln Q_{kol} = 0.7076 + 0.0189 = 0.7265$, and $S_{kol}/R = 1.4062 + 0.0403 = 1.4465$ are calculated as the sums of two components, one of which is found by means of the Tables of the values of $\Phi^*_{g.}/R$ and $S_{g.o}/R$ as a function of θ/T, and the other by means of the tables of the values of $\Delta \ln Q_{kol}$ and $\Delta S_{kol}/R$ as a function of θ/T and x. The values $\bar{v} = 1.090$; $\bar{v}^2 = 3,57$; $\bar{s} = 2,$?? ; $\bar{s} = 12.21$ are found in the Tables of these values as a function of ?/T and x. Substituting all the mentioned values into Eqs. (II.52) and (II 53) and considering that the symmetry number $\sigma = 2$ for N_2, we obtain for 5000°K

$$\Phi^*_{кол.\,вр} = 1,98726\,(0,7265 + 7,4654 + 0,0002 + 0,0094 + 0,0003 + 0,0106 + 0,0003 - 0,0001 - 0,6931) = 14,9432 \quad \text{cal/mole·degree}$$

$$S_{кол.\,вр} = 1,98726\,(1,4465 + 7,4654 + 1 + 0,0226 + 0,0012 + 0,0211 + 0,0003 - 0,0003 - 0,6931) = 18,4104 \quad \text{cal mole·degree.}$$

For 10,000°K we have: $\theta/T = 0.339473$; $q_0 = 3493.1$; $d_0 = 0.0211$; $1/3q_0 = 0.0000$; $f_0 = -0.0002$. On the basis of the values of θ/T and x, we find $\ln Q_{kol} = 1.2453 + 0.0416 = 1.2869$; $S_{kol}/R = 2.0852 + 0.0896 = 2.1748$; $\bar{v} = 2{,}756$, $\bar{v}^2 = 19{,}29$; $\bar{s} = 6{,}337$ and $\bar{s}^2 = 66{,}07$ in the same manner as it was made for 5000°K. Finally, we obtain for 10,000°K

$$\Phi^{\circ}_{кол.\,вр} = 1{,}98726\,(1{,}2868 + 8{,}1585 + 0{,}0000 + 0{,}0237 + 0{,}0019 + 0{,}0211 + 0{,}0011 - 0{,}0002 - 0{,}6931) = 17{,}4875 \quad \text{cal/mole·degree}$$

$$S_{кол.\,вр} = 1{,}98726\,(2{,}1748 + 8{,}1585 + 1 + 0{,}0544 + 0{,}0066 + 0{,}0422 + 0{,}0033 - 0{,}0006 - 0{,}6931) = 21{,}3552 \quad \text{cal/mole·degree}$$

In order to calculate the corrections for J_{max} by Eqs. (II.59) and (II.60), we find $v_{max} = 78$, and $D_0 = 91{,}942$. Thus $1 + v_{max} + \beta_1 \frac{(1+v_{max})}{2} + \beta_2 \frac{v_{max}(1+v_{max})(1+2v_{max})}{6} = 121{,}084$. According to Eq. (II.61), a = 0.00000 at 5000°K and 0.00006 at 10,000°K. Thus, the contribution of the rotational states with $J > J_{max}$ to the values of the thermodynamical functions is negligible; at 10,000°K we have $R \ln (1-a) = -0{,}0002$ cal/mole·degree and $R\left[\ln (1-a) + \frac{a}{1-a}\left(T \frac{\partial}{\partial T} \ln Q^{\infty}_{кол.\,вр} - 1 - \frac{hc}{kT} D_0\right)\right] = -0{,}0016$ cal/mole.degree.

The Kassel Method. In contrast to the Gordon-Barnes method, the calculations of the thermodynamic gas functions do not require auxiliary tables in the Kassel method, as we as in the similar Mayer and Goeppert-Mayer methods. The equations for calculating the thermodynamic functions of diatomic gases by the Kassel method may be obtained (see [2333]), assuming for $Q^{\infty}_{v,vr}$ an expression similar to that oroposed by Giauque and Overstreet, representing its dependence on v as a polynomial $\sum_i \gamma_i v^i$, and expanding the function $\exp\left[\frac{hc}{kT}(\omega_e x_e v^2 - \omega_e y_e v^3 + \omega_e z_e v^4 \ldots)\right]$ in the sum (II.41) into a Taylor series. Multiplying the corresponding sums and grouping the similar terms, Kassel obtained the following expression for the statistical sum over the vibrational and rotational states:

$$Q^{\infty}_{\text{кол. ар}} = \frac{q_0}{\sigma(1-z)} \cdot \alpha. \qquad \text{(II.65)}$$

In this expression q_0 and Σ have the same meaning as in the foregoing Divisions;

$$\alpha = \sum_{j=0} A_j f_j, \qquad \text{(II.66)}$$

where

$$A_j = \sum_{k=0}^{k=j} C_k Y_{j-k},$$

C_k are the coefficients of the expansion of the function $\exp\left[\frac{hc}{kT}(\omega_0 x_0 v^2 - \omega_0 y_0 v^3 + \omega_0 z_0 v^4 - \ldots)\right]$ into a Taylor series, i.e., $C_0 = 1$; $C_1 = 0$; $C_2 = \frac{hc}{kT}\omega_0 x_0$, $C_3 = \frac{hc}{kT}\omega_0 y_0$, $C_4 = \frac{hc}{kT}\omega_0 z_0 + \frac{1}{2}\left(\frac{hc}{kT}\omega_0 x_0\right)^2$, ...

$$Y_{j-k} = Y_j = \gamma_j\left[1 + \frac{1}{3q_0} + d_0 + 3d_0^2 + f_0\right] + \gamma_{j-2} l_1 + \gamma_{j-3} l_2,$$

where γ_1 are the coefficients of the polynomial $\frac{1}{B_v} = \frac{1}{B_0}\sum_j \gamma_j v^j$, with $\gamma_0 = 1$; $\gamma_2 = \frac{\alpha_1}{B_0}$, ..., $l_1 = (d_0 + 6d_0^2)s$, $l_2 = 3d_0^2 s^2$ and $s = \beta/D_0$; [β and D_0 are constants of Eq. (I.16)].

The second cofactor in the sum (II.66) is a polynomial of powers of v:

$$f_j = (1-z)\sum_{v=0}^{v_{max}} z^v v^j, \qquad \text{(II 67)}$$

where

$$z = \exp\left(-\frac{hc}{kT}\omega_0\right). \qquad \text{(II.68)}$$

Very cumbersome expressions result when one calculates the sum over v with a finite upper limit according to Eq. (II.67). The problem of the upper limit in this sum was insignificant in calculations for the moderate temperatures which interested the investigators of the Thirties. According to this, Kassel assumed that $v_{max} = \infty$, and he obtained equations for the calculation of the values of f_j and $T\frac{\partial}{\partial T} f_j$ for $0 \leq j \leq 8$ as a function of z.*

On the basis of Eq. (II.65) the following expression for the vibrational-rotational components in Φ^*_T and S°_T are obtained:

$$\Phi^\circ_{\text{кол.вр}} = R\left[\ln q_0 - \ln\sigma - \ln(1-z) + \ln\alpha\right], \tag{II.69}$$

$$S_{\text{кол.вр}} = R\left[\ln q_0 + 1 - \ln\sigma - \ln(1-z) - T\frac{\partial}{\partial T}\ln(1-z) + \ln\alpha + T\frac{\partial}{\partial T}\ln\alpha\right]. \tag{II.70}$$

where

$$T\frac{\partial}{\partial T}\ln\alpha = \sum_{j=0} A_j T\frac{\partial}{\partial T} f_j + \sum_{j=0} f_j T\frac{\partial}{\partial T} A_j,$$

expressions for $T\frac{\partial}{\partial T}A_j$, however, which, as well as those for A_j, have a complex general form, may be obtained in each concrete case.

It must be noted that the number of terms in the sum (II.66) depends on the temperature, for which the calculation is carried out, and on the values of the molecular constants; at high temperatures, the terms with j = 4–6 are comparable with the terms with j = 0, 1 and 2. The method by Godnev [155] ($k \leq 2$, $j \leq 6$) and the methods by Mayer and by Goeppert-Mayer [285] ($k \leq 2$, $j \leq \infty$) are particular cases of the Kassel method.

In comparison to the Gordon-Barnes method, the method in question possesses the advantage of allowing one to take into account any number of anharmonicity and interaction constants of the gas molecules in the calculations, i.e., to use more accurate equations for their vibrational and rotational energy. This advantage, however, which plays an important role in calculations for high temperatures, is not utilized in the Kassel method due to the fact that the upper limit in the sums over v is assumed as infinite. In principle, the last fact invalidates this method for high-temperature calculations and, particularly, it makes inexpedient the introduction of corrections for the limited number of rotational levels into Eqs. (II.69) and (II.70) by means of Eqs. (II.59) and (II.60). Another essential disadvantage is the highly laborious calculations of the values of A_j, f_j and of their derivatives.

The Mayer and the Goeppert-Mayer method. The method in question, being, as has been noted above, a special adaption of the Kassel method, was first proposed in the book by Mayer and Goeppert-Mayer [285]. This method is widely used in ca culating thermodinamical functions of gases in foreign literature published in the last 10-15 years.

The method is based on the assumption that the levels of the vibrational and rotational energy of a diatomic molecule may be described with sufficient accuracy by binomial equations of the type $G(v)=\omega_e(v+{}^1/_2)-\omega_e x_e(v+{}^1/_2)^2$ and $F_v(J)=[B_e-\alpha_1(v+{}^1/_2)]J(J+1)-$ $-D_eJ^2(J+1)^2$, assuming that the constants α_1 and D_e are connected with the values of the three other constants ω_e, $\omega_e x_e$ and B_e by simple relations (see page 86, Eqs. (II.38) and (II.36)). In this case, the statistical sum over the vibrational and rotational states may be transformed (under the condition that $v_{max}=\infty$ and $J_{max}=\infty$) into

$$Q^{\infty}_{\text{кол. вр}}=\frac{q_0}{\sigma(1-e^{-u})}\left[1+\frac{1}{3q_0}+d_0+\frac{1}{(e^u-1)}\beta_1+\frac{2xu}{(e^u-1)^2}\right], \quad \text{(II.71)}$$

where $x=\frac{\omega_e x_e}{\omega_e}$, $u=\frac{hc}{kT}\nu$ and $\nu=\Delta G_{1/2}=\omega_e-2\omega_e x_e$ is the fundamental frequency of the gas olecule.

On the basis of Eq. (II.71), the equation for calculating the vibrational-rotational components in Φ^*_T and S°_T may be written down as follows:

$$\Phi^{\circ}_{\text{кол. вр}}=R\left[\ln q_0-\ln\sigma-\ln(1-e^{-u})+\frac{1}{3q_0}+d_0+\frac{1}{(e^u-1)}\beta_1+\frac{2xu}{(e^u-1)^2}\right], \quad \text{(II.72)}$$

$$S_{\text{кол. вр}}=R\left[\ln q_0+1-\ln\sigma-\ln(1-e^{-u})+2d_0-T\frac{\partial}{\partial T}\ln(1-e^{-u})+\right.$$
$$\left.+\frac{1}{e^u-1}\beta_1+\frac{ue^u}{(e^u-1)^2}\beta_1+\frac{4xu^2e^u}{(e^u-1)^3}\right]. \quad \text{(II.73)}$$

Mayer and Goeppert-Mayer transformed the equations (II.72) and (II.73) by expanding the exponents of the trinomial $d_0+\frac{1}{e^u-1}\beta_1+\frac{2xu}{(e^u-1)^2}$, into a Taylor series and by assuming the Eqs. (I.36) and (I.38) for α_1 and D_e; they obtained

$$\Phi^*_{\text{кол. вр}} = R\left[\ln q_0 - \ln\sigma - \ln(1-e^{-u}) + \frac{1}{3q_0} + u^{-1}(2\gamma + 6\gamma^{1/3}x^{1/3} + 2x) + \right.$$
$$\left. + (3\gamma - 3\gamma^{1/3}x^{1/3} - 2x) + \frac{u}{6}(-3\gamma + 3\gamma^{1/3}x^{1/3} + 5x) - \frac{u^2}{6}x + \frac{u^3}{120}(\gamma - \gamma^{1/3}x^{1/3} + x) + \ldots\right]. \quad \text{(II.74)}$$

$$S_{\text{кол. вр}} = R\left[\ln q_0 + 1 - \ln\sigma - \ln(1-e^{-u}) - T\frac{\partial}{\partial T}\ln(1-e^{-u}) + u^{-1}(4\gamma + 12\gamma^{1/3}x^{1/3} + 4x) + \right.$$
$$\left. + (3\gamma - 3\gamma^{1/3}x^{1/3} - 2x) + \frac{u^2}{6}x - \frac{u^3}{60}(\gamma - \gamma^{1/3}x^{1/3} + x) + \ldots\right]. \quad \text{(II.75)}$$

where $\gamma = \frac{B_e}{\omega_e}$, and, therefore $d_0 = \frac{\delta\gamma}{u}$ and $\beta_1 = 6\gamma^{1/3}x^{1/3} - 6\gamma$.

In these expressions, the values in parentheses are functions of the two constants $\left(\gamma = \frac{B_e}{\omega_e} \text{ and } x = \frac{\omega_e x_e}{\omega_e}\right)$ are independent of the temperature. Therefore, these expressions are very suitable for calculating tables of thermodynamic functions of gases at moderate temperatures (but only, if $u < 1$). It must be noted that the exclusion of a great number of terms from the sum (II.66) and several additional simplifications, which makes this method different from the Kassel method, do not essentially reduce its accuracy. The fundamental errors, important at high temperatures, are caused in both methods by the fact that the upper limits of v and J in the statistical sum over the states are assumed to be equal to infinity.

Example. Let us examine the calculation of the values of $\Phi^*_{\text{kol.vr}}$ and $S_{\text{kol.vr}}$ for the ground state $X^1\Sigma^+_g$ of the molecular nitrogen N_2 by the Mayer and Goeppert-Mayer method Eqs. (II.72)-(II.75) at temperatures of 5000 and 10,000°K. According to the molecular constants of this state, quoted in Table 92, we have: $\nu = \omega_e - 2\omega_e x_e = 2329{,}542$; $\frac{\theta}{T} = \frac{hc}{kT}\nu = \frac{3351{,}72}{T}$; $x = 0.0063346$; $q_0 = 0.34931 \cdot T$; $1/3q_0 = 0.954 \cdot 10^{-6}/T$; $d_0 = 2.11 \cdot 10^{-6} \cdot T$; $\beta_1 = 0.008589$.

At 5000°K, we have: $\theta/T = 0.670344$; $q_0 = 1746.6$; $1/3q_0 = 0.0002$; $d_0 = 0.0106$. By the aid of the Tables for the values $\Phi^*_{k.l}/R$ and $S_{g.o}/R$ we find for the given value of θ/T: $\Phi^*_{g.o}/R = 0.7165$, and $S_{g.o}/R = 1.4185$. Substituting all the required values into the equations (II.72) and (II.73) and taking into account the fact that the symmet-

ry number $\Sigma = 2$ is valid for N_2, we obtain for 5000°K:

$$\Phi^{\circ}_{\text{кол. вр}} = 1{,}98726\,(7{,}4654 - 0{,}6931 + 0{,}7165 + 0{,}0002 + 0{,}0106 + 0{,}0090 + 0{,}0093) = 14{,}9400 \text{ cal/mole·degree}$$

$$S_{\text{кол. вр}} = 1{,}98726\,(7{,}4654 + 1 - 0{,}6931 + 1{,}4185 + 0{,}0211 + 0{,}0090 + 0{,}0123 + 0{,}0256) = 18{,}3996 \text{ cal/mole·degree}$$

At 10,000°K we have: $\theta/T = 0.335172$; $q_0 = 3493.1$; $1/3q_0 = 0.0000$; $d_0 = 0.211$. In the same manner, as it was carried out for 5000°K, we find $\Phi^{*}_{g.o}/R = 1.2560$, and $S_{g.o}/R = 2.0932$, and, finally, for 10,000°K:

$$\Phi^{\circ}_{\text{кол. вр}} = 1{,}98726\,(8{,}1585 - 0{,}6931 + 1{,}2560 + 0{,}0000 + 0{,}0211 + 0{,}0216 + 0{,}0268) = 17{,}4698 \text{ cal/mole·degree}$$

$$S_{\text{кол. вр}} = 1{,}98726\,(8{,}1585 + 1 - 0{,}6931 + 2{,}0932 + 0{,}0422 + 0{,}0216 + 0{,}0254 + 0{,}0630) = 21{,}2851 \text{ cal/mole·degree}$$

If we use the expansion proposed by Mayer and Goeppert-Mayer (Eqs. (II.74) and (II.75)) for the calculation, we obtain $\gamma = 0.0008494$ and we have for 5000°K:

$$\Phi^{\circ}_{\text{кол. вр}} = 1{,}98726\,(7{,}4654 - 0{,}6931 + 0{,}7165 + 0{,}0002 + 0{,}0422 - 0{,}0171 + 0{,}0040 - 0{,}0005 + 0{,}0000) = 14{,}9394 \text{ cal/mole·degree}$$

$$S_{\text{кол. вр}} = 1{,}98726\,(7{,}4654 + 1 - 0{,}6931 + 1{,}4185 + 0{,}0844 - 0{,}0171 + 0{,}0005 - 0{,}0000) = 18{,}3972 \text{ cal/mole·degree}$$

and for 10,000°K

$$\Phi^{\circ}_{\text{кол. вр}} = 1{,}98726\,(8{,}1585 - 0{,}6931 + 1{,}2560 + 0{,}0000 + 0{,}0843 - 0{,}0171 + 0{,}0020 - 0{,}0001 + 0{,}0000) = 17{,}4690 \text{ cal/mole·degree}$$

$$S_{\text{кол. вр}} = 1{,}98726\,(8{,}1585 + 1 - 0{,}6931 + 2{,}0932 + 0{,}1686 - 0{,}0171 + 0{,}0001 - 0{,}0000) = 21{,}2840 \text{ cal/mole·degree}$$

The Method by Brounshteyn and Yurkov. As has already been noted, the fundamental disadvantages of the three approximate methods examined above are caused mainly by the simplifications introduced into the equations for the calculation of $Q_{\text{kol. vr}}$ in order to avoid the immediate summation over the levels of the vibrational energy. These simplifications are not obligatory, and they may be avoided if formulae of the form $\Sigma v^k z^v$, with a finite upper limit are obtainable for the calculation of the sums.

Broursh teyn and Yurkov [110] proposed a novel method of calculating the thermodynamic functions of diatomic gases based on the fact that sums of the type

$$S_k = \sum_{v=0}^{v_{max}} x^v v^k \qquad (II.76)$$

may be calculated for a finite upper limit when the formula for the summation by parts is used (see, for example, [300]).

The authors of the paper [110] developed a new approximate method for calculating thermodynamic function by applying the equations for an approximate limitation of the summation over J in the statistical sum over the rotational states, proposed earlier by Brounshteyn (see page 154). This method is free from the disadvantages inherent in the methods of Kassel, Gordon and Barnes, Mayer and Goeppert-Mayer, caused by the fact that the latter assumed v_{max} as equal to ∞ or to 1/2x; this new method allows the introduction of any equations for the energy of the vibrational and rotational levels of the gas molecules into the calculation. The equations for the vibrational-rotational components of the thermodynamic functions of diatomic gases, developed by the authors of the paper [110], have the following form:

$$\Phi^{\circ}_{\text{кол. вр}} = R\left[\ln q_0 - \ln\sigma + \frac{1}{3q_0} + d_0 + 2{,}5d_0^2 + \ln\sum_{k=0}^{k=n} a_k s_k - \right.$$

$$\left. - \exp\left(-\frac{hc}{kT}D_0\right)\cdot\sum_{v=0}^{v_{max}} q_v \Big/ q_0\sum_{k=0}^{k=n} a_k s_k\right]. \qquad (II.77)$$

$$S_{\text{кол. вр}} = R\left[\ln q_0 + 1 - \ln\sigma + 2d_0 + 7{,}5d_0^2 + \ln\sum_{k=0}^{k=n} a_k s_k + \right.$$

$$\left. + \frac{\sum_{k=0}^{k=n+1} b_k s_k}{\sum_{k=0}^{k=n} a_k s_k} - \frac{\exp\left(-\frac{hc}{kT}D_0\right)\sum_{v=0}^{v_{max}} q_v}{q_0\sum_{k=0}^{k=n} a_k s_k}\cdot\left(2 + \frac{hc}{kT}D_0 - \frac{\sum_{k=0}^{k=n+1} b_k s_k}{\sum_{k=0}^{k=n} a_k s_k}\right)\right] \qquad (II.78)$$

where $a_k = a_k + \beta_1 a_{k-1} + \beta_2 a_{k-2}$ and a_k are the coefficients of the expansion of $\exp\left[\frac{hc}{kT}(\omega_0 x_0 v^2 - \omega_0 y_0 v^3 + \omega_0 z_0 v^4 - \ldots)\right]$ into a Taylor series, being similar to the coefficients C_k in the Kassel method;

$$b_0 = T\frac{\partial}{\partial T}a_0, \quad b_1 = T\frac{\partial}{\partial T}a_1 + a_0\frac{hc}{kT}\omega_0, \ldots,$$

$$b_n = T\frac{\partial}{\partial T}a_n + a_{n-1}\frac{hc}{kT}\omega_0, \quad b_{n+1} = a_n\frac{hc}{kT}\omega_0,$$

$$T\frac{\partial}{\partial T}a_n = T\frac{\partial}{\partial T}a_n + \beta_1 T\frac{\partial}{\partial T}a_{n-1} + \beta_2 T\frac{\partial}{\partial T}a_{n-2},$$

$$s_0 = A\left[\frac{1}{z} - z^{v_{max}}\right],$$

$$s_1 = A\left[s_0 - (v_{max}+1)z^{v_{max}}\right],$$

$$s_2 = A\left[s_0 + 2s_1 - (v_{max}+1)^2 z^{v_{max}}\right],$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$s_k = A\left[s_0 + k\cdot s_{k-1} + \frac{k(k-1)}{2!}\cdot s_{k-2} + \frac{k(k-1)\ldots(k-m)}{m!}\cdot s_{k-m} - (v_{max}+1)^k z^{v_{max}}\right].$$

where

$$A = \frac{z}{1-z}$$

and the other denotations are similar to those which are used in the methods of Kassel, Gordon and Barnes. *

It must . noted that this method has - up to the present - not been applied in calculating tables of thermodynamic functions of gases due to the cumbersome calculations required; moreover, at moderate temperatures, it leads to practically the same results as the Gordon-Barnes method.

Rigid rotator-harmonic oscillator model approximation. All methods of calculating thermodynamic functions of diatomic gases examined above assume that the vibrational and rotational level of the gas molecules have been investigated with sufficient thoroughness and that the equations which sufficiently approximate the energies of these levels in a wide range of the quantum numbers v and J are well known. The latter is possible only on the condition that at least one anharmonicity constant ($\omega_e x_e$), the constant D_e of the centrifugal stress, and the constant α_1 of the vibrational-rotational interaction

in the expressions for $G0(v)$ and $F_v(J)$ are well known or may be estimated. Only if these conditions are fulfilled, can the methods of Gordon-Barnes, Mayer and Goeppert-Mayer and many other methods applied to the calculation of thermodynamic functions. For many gases, however, data on the constants $\omega_e x_e$, D_e, etc., is lacking, and in a number of cases, the values of the oscillation frequencies and rotational constants of the gas molecules are known only approximately. The examined methods become inapplicable in these cases, the calculations of the thermodynamic functions, however, may be carried out by a more simple method which is based on the assumption that the gas molecules correspond sufficiently to the model of a rigid rotator-harmonic oscillator.

It is supposed in this case that:

a) the equilibrium state between the atoms of the molecule does not depend on the values of the quantum numbers v and J and that it remains constant in all vibrational and rotational states of the given electronic state (i.e., $\alpha_1 = \alpha_2 = \ldots = 0$; $D_e = H_e \ldots = 0$):

b) the vibrations of the molecule are harmonical, and, therefore, $\omega_e x_e = \omega_e y_e = \ldots = 0$.

It is evident that $\omega_e = \omega_0 = \nu, B_e = B_0$ is valid the case of a rigid rotator-harmonic oscillator, and that the rotational energy of the molecule does not depend on the vibrational energy of the latter. In this approximation, the expression for $Q_{kol.vr}$ may be written down as follows:

$$Q'_{\text{кол. вр}} = \frac{1}{\sigma} \sum_{v=0}^{\infty} \exp\left(-\frac{hc}{kT}\omega v\right) \cdot \sum_{J=0}^{\infty} (2J+1) \cdot \exp\left[-\frac{hc}{kT} BJ(J+1)\right], \quad \text{(II.79)}$$

where v_{max} and J_{max} are infinite. Due to the fact that the statistical sum over J is independent of v, $Q_{kol.vr}$ is the product of the statistical sum of the vibrators, the statistical sum $Q_{e.o}$ the vibrational statistical sum of har-

monic oscillator, and the statistical sum $Q_{zh.r}$ the rotational states of a rigid rotator; the appropriate components in the values of the thermodynamic functions are calculated as the sum of two independent addends, the components of the harmonic oscillator and the rigid rotator:

$$\Phi^{\circ}_{кол.\,ар} = \Phi^{\circ}_{г.\,о} + \Phi^{\circ}_{ж.\,р}. \qquad \text{(II.80)}$$

$$S_{кол.\,ар} = S_{г.\,о} + S_{ж.\,р}. \qquad \text{(II.81)}$$

If the summation over $\underline{v}$ and J is carried out in Eq. (II.79) taking into account the limits mentioned above, the statistical sum of the rigid rotator and harmonic oscillator has, in the chosen expressions, the following form

$$Q^{\infty}_{кол.\,ар} = \frac{q}{\sigma(1-z)}, \qquad \text{(II.82)}$$

where q/σ is the statistical sum over the states of the rigid rotator, and $1 / (1 - z)$ is the statistical sum over the states of the harmonic oscillator.

Thus we have

$$\Phi^{\circ}_{ж.\,р.\,г.\,о} = R\,[\ln q - \ln\sigma - \ln(1-z)], \qquad \text{(II.83)}$$

$$S_{ж.\,р.\,г.\,о} = R\left[\ln q + 1 - \ln\sigma - \ln(1-z) - T\frac{\partial}{\partial T}\ln(1-z)\right]. \qquad \text{(II.84)}$$

Owing to $Q_{ж.\,р} = \frac{kT}{hcB}$, the components of the rigid rotator may be expressed in terms of thermodynamic functions as the sum of two addends: one which is proportional to ln T, and another, which is constant for the given gas and which depends only on the symmetry of the gas molecules and on their rotational constant (see §11).*

The components of the harmonic oscillator, equal to $-\ln(1 - z)$ and to the derivatives of this value, depend only on the correlation $\frac{\theta}{T} = \frac{hc}{kT}\omega$.

A number of authors have compiled tables of the values of these quantities as functions of θ/T in order to find values of $\Phi^{*}_{g.\,o}$, $S_{g.\,o}$ $(H_T - H_0)_{g.\,o}/T$ and $C_{p_{g.\,o}}$. The components of the harmonic oscilator may be found in

these tables by means of a simple interpolation. Wilson [4291] compiled tables of the values of $\Phi^*_{g.o}$, $(H_T - H_0)_{r.o}/T$, etc., as functions of the values of ω/T, and in the paper of Torkington [4004] these values are expressed as a function of two variables (ω and T).*

The errors in the calculation of the thermodynamic functions of gases carried out by the rigid rotator-harmonic oscillator model approximation are caused by the neglecting of the deviations of the investigated gas molecules from the chosen model, and also by the necessity of restricting the number of vibrational and rotational states in the statistical sum (II.79). The corresponding errors are especially important at high temperatures and also in cases when the molecules of the gas possess low oscillation frequencies or high anharmonicity constants. At low temperatures (at high values of θ/T), however, the application of this method does not cause considerable error (see below, Tables 9 and 10).

Example. Let us examine the values of $\Phi^*_{kol.vr}$ and $S_{kol.vr}$ for the $X^1\Sigma^+_g$ ground state of molecular nitrogen N_2 in the rigid rotator-harmonic oscillator model approximation at 5000° and 10,000°K. On the basis of the values of the molecular constants of this state, quoted in Table 92, we have: $\omega_0 = \omega_e - \omega_e x_e = 2344{,}525$; $\frac{\theta}{T} = \frac{3373.25}{T}$, and $q_0 = 0.34931\ T$.

At 5000°K are valid: $\theta/T = 0.67466$; $q_0 = 1746.6$. We find in the tables of thermodynamic functions of the harmonic oscillator for the given value of θ/T: $\Phi^*_{g.o}/R = 0.7120$ and $S_{g.o}/R = 1.4123$. Substituting all required values into Eqs. (II.83) and (II.84) and taking into account the fact that the symmetry number of N_2 is $\sigma = 2$, we obtain for 5000°K:

$$\Phi^*_{кол.\ вр} = 1{,}98726\ (7{,}4654 - 0{,}6931 + 0{,}7120) = 14{,}8733\ \text{cal/mole·deg}$$

$$S_{кол.\ вр} = 1{,}98726\ (7{,}4654 + 1 - 0{,}6931 + 1{,}4123) = 18{,}2522\ \text{cal/mole·deg}$$

At 10,000°K are valid: $\theta/T = 0.337328$; $q_0 = 3493.1$. Similarly as in the case of 5000°K, we find $\Phi^*_{g.o}/R = 1.2506$ and $S_{g.o}/R = 2.0914$ and we obtain finally for 10,000°K:

$$\Phi^\circ_{r.o} = 1{,}98726\,(8{,}1585 - 0{,}6931 + 1{,}2506) = 17{,}3210 \text{ cal/mole·degree}$$

$$S_{кол.вр} = 1.98726\,(8{,}1585 + 2 - 0{,}6931 + 2{,}0914) = 20{,}9791 \text{ cal/mole·degree}$$

§9. Approximate Calculation Methods Taking Into Account The Multiplicity of the Electronic States of Molecules*

It was assumed in the derivation of the equations for the calculation of thermodynamic functions, carried out in the foregoing section, that the molecules of the investigated gases are in the Σ electronic state, i.e., that the quantum numbers Λ and S are equal to zero and, therefore, the total angular momentum of the molecule is equal to the angular moment of its nuclei. The total number and position of the levels of rotational energy, relative to each other in the diatomic molecule, as well as the form of the equation which describes the energy of these levels depend essentially on the values of Λ and S and on the type of the interaction of the angular momenta when $\Lambda \neq 0$ and $S \neq 0$.

It was mentioned above (see page 58) that at $S > 0$ each rotational level corresponding to the given value of J is split into $2S + 1$ components, and that at $\Lambda > 0$ an additional splitting of each component (the so-called Λ doubling) takes place. The splitting of the levels of rotational energy of the molecule may be approximately taken into account in calculating thermodynamic functions of gases by introducing appropriate satistical weights in the expressions for the statistical sums and in their derivatives with respect to the temperature. These statistical weights are equal to $2S + 1$ at $\Lambda = 0$ and equal to $2(2S + 1)$ at $\Lambda > 0$. The introduction of statistical weights into the expression for $Q_{kol.vr}$ causes additional addends $R\ln(2S + 1)$

or Rln 2(2S + 1) in the formulae for the calculation of Φ_T^* and S°_T. The values of the statistical weights approximately allowing for the multiplicity of the electronic states of different types are quoted in Table 7.

TABLE 7

Statistical Weights of Various Electronic States of Diatomic Molecules

Тип состояния [a]	$^1\Sigma$	$^2\Sigma$	$^3\Sigma$	$^1\Pi$	$^2\Pi$	$^3\Pi$	$^1\Delta$	$^2\Delta$
Статистический вес [b]	1	2	3	2	4	6	2	4

a) Type of the state; b) statistical weight.

The accounting for the splitting of rotational energy levels of molecules in multiplet electronic states, however, by means of statistical weights is, in some cases, a coarse approximation as the energies of the individual components of the level having the given value of the quantum number J may essentially differ from each other (especially states similar to those of the Hund coupling case a), a number of lower levels are missing in the discrete substates, and the quantum number J assumes only half-integral values when the quantum number S possesses nonintegral values. Consequently, the peculiarities of the positions of the energy levels, characteristic for the electronic states of molecules of the given type, must be taken into account in the calculation of the thermodynamic gas functions.*

The scheme of the calculation does not depend on the electronic state in cases when the statistical sums over the vibrational and rotational states are calculated by the method of immediate summation over the energy levels (see page 143). The only change consists in the fact that the energy of the rotational levels, if it is not expressed in numerical values obtained from experimental data, must be calcu-

lated not by means of Eq. (I.15) but by means of Eqs. (I.21)-(I.26) depending on the type of the electronic state and on the type of the interaction of the discrete angular momenta.

At the same time, the form of the equations which join the values of $Q_{kol.vr}$, $\Phi^{*}_{kol.vr}$, $S_{kol.vr}$, etc., with the values of the molecular constants, depends essentially both on the type of the electronic state and on the type of the interaction between the discrete angular momenta, when the calculation of the thermodynamic function of gases is carried out by approximate methods (for example, by the method of Gordon and Barnes or of Kassel).

Equations for approximately calculating the thermodynamic functions of individual concrete gases, taking into account the splitting of the levels into multiplet states, were obtained in a number of papers. Thus, Wtmer [4301] and Gordon and Barnes [1814] derived relations for the calculation of the thermodynamic functions of NO ($^2\Pi_r$ state, and Hund coupling case a), Haar and Friedman [1910] derived equations for calculating the functions of OH ($^2\Pi_i$ state, a coupling, intermediate between the Hund cases a and b). Equations for calculating the thermodynamic functions of O_2 ($^3\Sigma$ state, Hund coupling case b) were stated in papers by Gordon and Barnes [1814] and Woolley [4324]. These equations were obtained in the paper [1814] on the basis of Kramers relationships for the energy of the rotational levels of this molecule, and in paper [4324] on the basis of the Schlapp equations (see page 79). Finally, in Gordon's paper [1808] equations were derived for calculating the thermodynamic functions of gases, the molecules of which are in the $^3\Pi$ state; the deduction was carried out on the example of the C_2 molecule.

The problem of calculating thermodynamic functions of gases, the molecules of which are in multiplet states, was examined in a most

general point of view in papers by Yungman [472] Khachkuruzov and Brounshteyn [445, 446] and Brounshteyn and Yurkov [109] (see also the review [107]). Relations which make possible the calculation of the vibrational-rotational constants of the thermodynamic functions of gases, the molecules of which are in the four most frequently occurring multiplet electronic states: $^2\Sigma$, $^3\Sigma$, $^2\Pi$, and $^3\Pi$,* were obtained in these papers. Since the Gordon-Barnes method is taken as a basis in this Handbook, the corresponding equations were derived, and equations were obtained for the $^2\Pi$ and $^3\Pi$ states which are valid for both the normal and inverse states corresponding not only to the Hund coupling cases a and b, but also to the case intermediate between them.** The relations obtained in these papers are cited above.***

$^2\Sigma$ state. The expression for $Q_{\text{kol.vr}}$ of molecules being in $^2\Sigma$ state was obtained by Yungman [472] on the basis of the equations for the rotational energy derived by Mulliken [2977] (see Eq. (1.23)):

$$Q_{\text{кол. вр}} = 2q_0(1 + \beta_1\bar{v} + \beta_2\bar{v}^2)\left(1 + \frac{1}{3q_0} + d_0 + 3d_0 + f_0\right) \cdot Q_{\text{кол}} \cdot \left[1 + \frac{1}{8}\left(\frac{\gamma}{B_0}\right)^2 \frac{1}{q_0}\right] \cdot \frac{1}{\sigma}. \quad \text{(II.85)}$$

The corresponding equations for the calculation of $\Phi^*_{\text{kol.vr}}$ and $S_{\text{kol.vr}}$ may be obtained from (II.85):

$$\Phi^*_{\text{кол. вр}} = R\left[\ln Q_{\text{г. о}} + \Delta \ln Q_{\text{кол}} + \beta_1\bar{v} + \beta_2\bar{v}^2 + \frac{1}{3q_0} + \ln q_0 + \right.$$
$$\left. + d_0 + 2{,}5d_0^2 + f_0 - \ln\sigma + \ln 2 + \frac{1}{8}\left(\frac{\gamma}{B_0}\right)^2 \frac{1}{q_0}\right], \quad \text{(II.86)}$$

$$S_{\text{кол. вр}} = R\left[\frac{S_{\text{г. о}}}{R} + \frac{\Delta S_{\text{кол}}}{R} + \beta_1\bar{s} + \beta_2\bar{s}^2 + \ln q_0 + 1 + 2d_0 + 7{,}5d_0^2 + 3f_0 - \ln\sigma + \ln 2\right]. \quad \text{(II.87)}$$

where γ is the multiplet splitting constant.

The constant γ is generally very small, and its value is in the order of parts of cm^{-1}. In the case of HgH, in which , possesses the highest value (2.15 cm^{-1}) the value of $\frac{1}{8}\left(\frac{\gamma}{B_0}\right)^2 \frac{1}{q_0}$ is equal to 0.0052 and 0.00015 for T = 298.15 and 1000°K, respectively. Thus, the dif-

ference between the component of the multiplet splitting and the magnitude Rln 2 is equal to 0.0103 and 0.0003 at these temperatures. In the case of other gases, the difference is yet smaller and, therefore, the multiplicity of the $^2\Sigma$ states may be taken into account with sufficient accuracy by the addend Rln 2 in the value of Φ^*_T and $S°_T$ in calculating the thermodynamic functions for temperatures higher than the room temperature.

$^3\Sigma$ state. Formulas for the calculation of thermodynamic functions of ideal gases, the molecules of which are in the $^3\Sigma$ state, were obtained by Yungman [472] on the basis of the Schlapp equations for the rotational energy (see page 79, Eqs. (1.24)):

$$\Phi^{\circ}_{\text{кол. ар}} = R\left[\ln Q_{\text{г. о}} + \Delta \ln Q_{\text{кол}} + \ln q_0 + \beta_1\bar{v} + \beta_2\bar{v}^2 + d_0 + \right.$$
$$\left. + 2{,}5d_0^2 + f_0 + \frac{1}{3q_0} - \ln\sigma + \ln 3 + \frac{hc}{kT}F_0(K_{\min}) + \left(\frac{2}{3}\lambda - \mu\right)\frac{hc}{kT}\right]. \quad \text{(II.88)}$$

$$S_{\text{кол. ар}} = R\left[\frac{S_{\text{г. о}}}{R} + \frac{\Delta S_{\text{кол}}}{R} + \ln q_0 + 1 + \beta_1\bar{s} + \beta_2\bar{s}^2 + 2d_0 + 7{,}5d_0^2 + 3f_0 - \ln\sigma + \ln 3\right]. \quad \text{(II.89)}$$

$^2\Pi$ state. Formulas for the calculation of thermodynamic functions of gases, the molecules of which are in the $^2\Pi$ state, were obtained by Khachkuruzov and Brounshteyn [445] on the basis of the Hill and Van Vleck Eq. (1.25) for rotational energy. The final expressions for the thermodynamic functions may be written down as follows:

$$\Phi^{\circ(r)}_{\text{кол. ар}} = R\left[\ln Q_{\text{г. о}} + \Delta \ln Q_{\text{кол}} + \ln q_0 + \beta_1\bar{v} + \beta_2\bar{v}^2 - \ln\sigma + \ln 4 + \ln z_0 - \frac{hc}{kT}K_0^{(r)}\right] \quad \text{(II.90)}$$

$$\Phi^{\circ(i)}_{\text{кол. ар}} = R\left[\ln Q_{\text{г. о}} + \Delta \ln Q_{\text{кол}} + \ln q_0 + \beta_1\bar{v} + \beta_2\bar{v}^2 - \ln\sigma + \ln 4 + \ln z_0 - \frac{hc}{kT}K_0^{(i)}\right] \quad \text{(II.91)}$$

$$S_{\text{кол. ар}} = R\left[\frac{S_{\text{г. о}}}{R} + \frac{\Delta S_{\text{кол}}}{R} + \ln q_0 + 1 + \beta_1\bar{s} + \beta_2\bar{s}^2 - \ln\sigma + \ln 4 + s_0\right]. \quad \text{(II.92)}$$

where the symbol (r) means the regular (normal) state, and the symbol (i) means the inverse state,

$$\frac{hc}{kT} K_0^{(r)} = \frac{2}{q_0}\left(\frac{A}{4B} - 1\right), \qquad \text{(II.93)}$$

$$\frac{hc}{kT} K_0^{(l)} = \frac{2}{q_0}\left[\sqrt{1 - \frac{A}{B}\left(1 - \frac{A}{4B}\right)} - 2\right]; \qquad \text{(II.94)}$$

z_0 and s_0 are calculated by means of the formulas

$$z_0 = z_0^* - \frac{1}{q_0} \exp\left(-\frac{hc}{kT} \cdot \frac{A}{2}\right), \qquad \text{(II.95)}$$

$$s_0 = \ln z_0 + T\frac{\partial}{\partial T} \ln z_0 = \ln z_0 + \frac{1}{z_0}\left[T \cdot \frac{\partial}{\partial T} z_0^* + \frac{1}{q_0}\left(1 - \frac{hc}{kT} \cdot \frac{A}{2}\right) \exp\left(-\frac{hc}{kT} \cdot \frac{A}{2}\right)\right], \qquad \text{(II.96)}$$

and z_0^* and $T\frac{\partial}{\partial T} z^*$ are calculated by means of the formulas

$$z_0^* = \sum_{n=0}^{\infty} f_n M_n, \qquad \text{(II.97)}$$

$$T\frac{\partial}{\partial T} z^* = \sum_{n=0}^{\infty} f_n \mu_n - m M_n \varphi_n. \qquad \text{(II.98)}$$

The values of f_n and φ_n for $n \leq 4$, which enter into Eqs. (II.97) and (II.98) are found by means of tables compiled by Khachkuruzov and Brounshteyn as functions of the argument

$$m = \frac{\sqrt{-\frac{A}{B_0}\left(1 - \frac{A}{4B_0}\right)}}{q_0}, \qquad \text{(II.99)}$$

and μ_n and M_n are given by the following expressions:

$$\mu_0 = \frac{1}{6q_0} + d_0 + 6d_0^2, \mu_1 = 3\gamma(d_0 + \ldots), \mu_2 = 6\gamma^2(d_0 + \ldots), \mu_3 = \mu_4 = \mu_5 = \ldots = 0.$$

$$M_0 = -\frac{1}{6q_0} + 1 + d_0 + 3d_0^2 + f_0, M_1 = \gamma(1 + 3d_0 + 15d_0^2), M_2 = \gamma^2(1 + 6d_0 + 45d_0^2),$$

$$M_3 = 3\gamma^2(1 + 10d_0 + 105d_0^2), M_4 = 6\gamma^2(1 + 15d_0 + 210d_0^2),$$

where

$$\gamma = \frac{1}{2\sqrt{-\frac{A}{B_0}\left(1 - \frac{A}{4B_0}\right)}}.$$

In the paper by Khachkuruzov and Brounsteyn [446] various special cases of the general formulas (II.90)-(II.92) were examined, which make it possible to simplify essentially the calculations of thermodynamic functions. Thus, for the Hund case a, instead of (II.90)-(II.92), it was obtained

$$\Phi^{\circ(r)}_{\text{кол. вр}} = R\Big[\ln Q_{\text{г. о}} + \Delta \ln Q_{\text{кол}} + \ln q_0 - \ln\sigma + \\ + \beta_1\bar{v} + \beta_2\bar{v}^2 + d_0 + 2{,}5d_0^2 + f_0 + \ln 4 + \frac{5}{6q_0} + \ln\Delta^{(r)}\Big]. \qquad \text{(II.100)}$$

$$\Phi^{\circ(l)}_{\text{кол. вр}} = R\,[\ln Q_{\text{г. о}} + \Delta \ln Q_{\text{кол}} + \ln q_0 - \ln\sigma + \beta_1\bar{v} + \beta_2\bar{v}^2 + d_0 + 2{,}5d_0^2 + f_0 + \\ + \ln 4 + \ln\Delta^{(l)}], \qquad \text{(II.101)}$$

$$S^{(r)}_{\text{кол. вр}} = R\left[\frac{S_{\text{г. о}}}{R} + \frac{\Delta S_{\text{кол}}}{R} + \ln q_0 + 1 - \ln\sigma + \beta_1\bar{s} + \beta_2\bar{s}^2 + \right. \\ \left. + 2d_0 + 7{,}5d_0^2 + 3f_0 + \ln 4 + s^{(r)}_{\Delta}\right]. \qquad \text{(II.102)}$$

$$S^{(l)}_{\text{кол. вр}} = R\left[\frac{S_{\text{г. о}}}{R} + \frac{\Delta S_{\text{кол}}}{R} + \ln q_0 + 1 - \ln\sigma + [\beta_1\bar{s} + \beta_2\bar{s}^2 + \right. \\ \left. + 2d_0 + 7{,}5d_0^2 + 3f_0 + \ln 4 + \bar{s}^{(l)}_{\Delta}\right]. \qquad \text{(II.103)}$$

where

$$\Delta^{(r)} = \frac{1}{2}\left[1 + \frac{B_0}{A} + \left(1 - \frac{B_0}{A}\right)\exp\left(-\frac{hc}{kT}A\right)\right],$$

$$\Delta^{(l)} = \frac{1}{2}\left[1 + \frac{B_0}{|A|} - \frac{2}{q_0} + \left(1 - \frac{B_0}{|A|} + \frac{2}{q_0}\right)\exp\left(-\frac{hc}{kT}|A|\right)\right],$$

$$s^{(r)}_{\Delta} = \ln\Delta^{(r)} + \frac{1}{\Delta^{(r)}}\cdot T\frac{\partial\Delta^{(r)}}{\partial T},$$

$$T\frac{\partial\Delta^{(r)}}{\partial T} = \frac{1}{2}\cdot\frac{hc}{kT}(A - B_0)\exp\left(-\frac{hc}{kT}A\right),$$

$$s^{(l)}_{\Delta} = \ln\Delta^{(l)} + \frac{1}{\Delta^{(l)}}\cdot T\frac{\partial\Delta^{(l)}}{\partial T},$$

$$T\frac{\partial\Delta^{(l)}}{\partial T} = \frac{1}{q_0} + \frac{1}{2}\left[\frac{hc}{kT}(|A| - B_0) - \frac{2}{q_0}\left(1 - \frac{hc}{kT}|A|\right)\right]\exp\left(-\frac{hc}{kT}|A|\right);$$

and for the Hund case b the following expressions were obtained:

$$\Phi^{\circ(r)}_{\text{кол. вр}} = R\Big[\ln Q_{\text{г. о}} + \Delta \ln Q_{\text{кол}} + \ln q_0 - \ln\sigma + \beta_1\bar{v} + \beta_2\bar{v}^2 + \\ + d_0 + 2{,}5d_0^2 + f_0 + \ln 4 + \frac{4}{3q_0} - \frac{1}{2B_0q_0}\Big]. \qquad \text{(II.104)}$$

$$\Phi^{\circ(l)}_{\text{кол. вр}} = R\Big[\ln Q_{\text{г. о}} + \Delta \ln Q_{\text{кол}} + \ln q_0 - \ln\sigma + \beta_1\bar{v} + \beta_2\bar{v}^2 + \\ + d_0 + 2{,}5d_0^2 + f_0 + \ln 4 - \frac{2}{3q_0} + \frac{1}{q_0}\left(\frac{4}{3} - \sqrt{1 + \frac{A^2}{4B_0^2} - \frac{A}{B_0}}\right)\Big]. \qquad \text{(II.105)}$$

$$S_{\text{кол. вр}} = R\left[\frac{S_{\text{г. о}}}{R} + \frac{\Delta S_{\text{кол}}}{R} + \ln q_0 + 1 - \ln\sigma + \beta_1\bar{s} + \beta_2\bar{s}^2 + 2d_0 + 7{,}5d_0^2 + 3f_0 + \ln 4\right]. \qquad \text{(II.106)}$$

$^3\Pi$ state. Formulas for calculating the values of thermodynamic functions of gases, the molecules of which are in the $^3\Pi$ state, were obtained by Brounshteyn and Yurkov [109] on the basis of the Budo equations for rotational energy (1.26). Relations for coupling cases,

corresponding to the Hund cases a, b, and the intermediate case between them, were obtained in the paper [109]. We cite below the relations for the Hund cases a and b.

In the Hund coupling case a, these relations have the form

$$\Phi^{\circ}_{\text{кол. вр}} = R\Big[\ln Q_{\text{г. о}} + \Delta \ln Q_{\text{кол}} + \ln q_0 - \ln\sigma + \beta_1\bar{v} + \beta_2\bar{v}^2 + \\ + d_0 + 2{,}5d_0^2 + \frac{hc}{kT}E_0 + \ln 6 + \ln c_1 + \frac{a_1}{q_0} + \frac{4}{c_1}\cdot\frac{B_0}{|A|}\operatorname{sh}\Big(\frac{hc}{kT}|A|\Big)\Big], \quad \text{(II. 107)}$$

$$S_{\text{кол. вр}} = R\Big[\frac{S_{\text{г. о}}}{R} + \frac{\Delta S_{\text{кол}}}{R} + \ln q_0 + 1 - \ln\sigma + \beta_1\bar{s} + \beta_2\bar{s}^2 + \\ + 2d_0 + 7{,}5d_0^2 + \ln 6 + \ln c_1 - \frac{2}{c_1}\frac{hc}{kT}|A|\operatorname{sh}\Big(\frac{hc}{kT}|A|\Big) + \frac{1}{q_0}\Big(T\frac{\partial a_1}{\partial T} - a_1\Big)\Big], \text{(II. 108)}$$

where

$$c_1 = \frac{1}{3} + \frac{2}{3}\operatorname{ch}\Big(\frac{hc}{kT}|A|\Big),$$

$$a_1 = b_1 - \Sigma',$$

$$b_1 = \frac{1}{3} - \frac{4}{9c_1}\Big[1 - \operatorname{ch}\Big(\frac{hc}{kT}A\Big) + 3\frac{A}{|A|}\operatorname{sh}\Big(\frac{hc}{kT}|A|\Big)\Big],$$

$$T\frac{\partial a_1}{\partial T} = T\frac{\partial}{\partial T} - \frac{1}{3c_1}\Big[T\frac{\partial\Sigma'}{\partial T} + \frac{2}{3c_1}\frac{hc}{kT}|A|\operatorname{sh}\Big(\frac{hc}{kT}|A|\Big)\Sigma'\Big],$$

$$T\frac{\partial b_1}{\partial T} = -\frac{2}{3c_1}\frac{hc}{kT}|A|\Big[(1-b_1)\operatorname{sh}\Big(\frac{hc}{kT}|A|\Big) - 2\frac{A}{|A|}\operatorname{ch}\Big(\frac{hc}{kT}|A|\Big)\Big],$$

$$\Sigma' = \pm\exp\Big(\mp\frac{\sqrt{y_1}}{q_0}\Big) + 3\exp\Big(\frac{\sqrt{y_1}-S}{q_0}\Big),$$

$$T\frac{\partial\Sigma'}{\partial T} = \pm\frac{\sqrt{y_1}}{q_0}\exp\Big(\mp\frac{\sqrt{y_1}}{q_0}\Big) \pm 3\frac{\sqrt{y_1}-S}{q_0}\exp\Big(\frac{\sqrt{y_1}-S}{q_0}\Big),$$

$$y_1 = Y(Y-4) + \frac{4}{3}, \quad Y = \frac{A}{B}.$$

In the expressions for Σ' and $T\frac{\partial\Sigma'}{\partial T}$, the upper signs correspond to the regular states, and the lower signs to the irregular states.

In the Hund coupling case b, the relations have the form

$$\Phi^{\circ}_{\text{кол. вр}} = R\Big[\ln Q_{\text{г. о}} + \Delta \ln Q_{\text{кол}} + \ln q_0 - \ln\sigma + \beta_1\bar{v} + \beta_2\bar{v}^2 + d_0 + \\ + 2{,}5d_0^2 + \frac{hc}{kT}E_0 + \ln 6\Big], \quad \text{(II. 109)}$$

$$S_{\text{кол. вр}} = R\Big[\frac{S_{\text{г. о}}}{R} + \frac{\Delta S_{\text{кол}}}{R} + \ln q_0 + 1 - \ln\sigma + \beta_1\bar{s} + \beta_2\bar{s}^2 + 2d_0 + 7{,}5d_0^2 + \ln 6\Big]. \\ \text{(II. 110)}$$

The quantity E_0 which enters into the relations (II.109) and (II.110) is equal to

$$E_0 = -B_0\left(\sqrt{Y^2 - 4Y + 4/3} + \frac{2}{3}\cdot\frac{Y^2 - Y - 4/3}{Y^2 - 4Y + 4/3}\right). \quad \text{(II.111)}$$

for the regular state and equal to

$$E_0 = -B_0\left(\sqrt{Y^2 - 4Y + 76/3} + \frac{2}{3}\frac{Y^2 - Y - 112/9}{Y^2 - 4Y + 76/3} - 6\right). \quad \text{(II.112)}$$

for the inverse state.

Let us consider the calculation of thermodynamic functions of diatomic gases, the molecules of which possess multiplet states, in the example, of calculation of the $\Phi^*_{kol.vr}$ and $S_{kol.vr}$ of CCl at T = = 3000°K. Due to the fact that the ground state of CCl belongs to the $^2\Pi_r$ type, and A/B ≈ 195 (Hund case a), the calculation may be carried out by Eqs. (II.100) and (II.102). According to the values of the molecular constants of CCl in ground state, quoted in Table 176,* we have: $\theta/T = 1256.93/T$; $x = 0.0080128$; $q_0 = 1.00264 \cdot T$; $d_0 = 5.47 \cdot 10^{-6} T$; $\beta_1 = 9.697 \cdot 10^{-3}$; $\beta_2 = 9.40 \cdot 10^{-5}$, and $5/6q_0 = 0.83114/T$. At 3000°K are valid: $\theta/T = 0.418977$; $q_0 = 3007.92$; $d_0 = 0.0164$; $5/6q_0 = 0.0003$. The values $\Phi^*_{g.o}/R = 1.0722$ and $S_{g.o}/R = 1.8772$ may be found as functions of θ/T in the tables of the thermodynamic functions of the harmonic oscillator, the values of $\Delta \ln Q_{kol} = 0.0424$; $\frac{\Delta S_{kol}}{R} = 0.0922$; $\bar{v} = 2{,}156$; $\bar{v}^2 = 12{,}36$; $\bar{s} = 5{,}066$ and $\bar{s}^2$ 14,32 may be found as functions of θ/T and x in the tables of the corresponding quantities (see footnote to page 152). On the basis of the values $B_0 = 0.6956$ and A = 54.02, quoted in Table 176, we have: $\Delta = 0.96888$ and $\frac{1}{\Delta} T \frac{\partial \Delta}{\partial T} = 0.0311$, from which we have $\ln \Delta = -0.0316$, and $S_\Delta = -0.0005$. Finally, we obtain for $\Phi^*_{kol.vr}$ and $S_{kol.vr}$ at 3000°K from Eqs. (II.100) and (II.102):

$$\Phi^*_{кол.\ вр} = 1{,}98726\ (1{,}0722 + 0{,}0424 + 8{,}0090 - 0{,}0000 + 0{,}0209 + 0{,}0012 + 0{,}0164 + 0{,}0007 + 0{,}0000 + 1{,}3863 + 0{,}0003 - 0{,}0316) = 20{,}9010 \text{ cal/mole·degree}$$

$$S_{кол.\ вр} = 1{,}98726\ (1{,}8772 + 0{,}0922 + 8{,}0090 + 1{,}0000 - 0{,}0000 + 0{,}0491 + 0{,}0042 + 0{,}0328 + 0{,}0020 + 0{,}0000 + 1{,}3863 - 0{,}0005) = 24{,}7460 \text{ cal/mole·degree}$$

TABLE 8

Comparison of the Results of Calculations by Various Methods of the Values of $\Phi^*_{kol.vr}$ and $S_{kol.vr}$ for Gases, the Molecules of which Possess Multiplet States

1 Газ	O_2		NO		OH	
2 Тип состояния	$X^3\Sigma$		$X^2\Pi_r$		$X^2\Pi_i$	
T°, K	298.15	1000	298.15	1000	298.15	1000
3 Метод	4 $\Phi^\circ_{кол.\ вр.}$ *кал/моль·град*					
5 Непосредств. суммирование	10,6894	13,3249	11,8144	14,6825	7,3554	9,9052
Гордона и Барнес 6	10,6940	13,3248	11,8143	14,6823	7,3586	9,9051
7 » » (со стат. весом)	10,6915	13,3242	12,3027	14,8458	7,6164	9,9590
3 Метод	8 $S_{кол.\ вр.}$ *кал/моль·град*					
5 Непосредств. суммирование	12,6798	15,8580	14,2045	17,2181	9,4537	12,0441
Гордона и Барнес 6	12,6835	15,8583	14,2041	17,2180	9,4550	12,0442
7 » » (со стат. весом)	12,6835	15,8583	14,2378	17,2258	9,5047	12,0219

1) Gas
2) type of state
3) method
4) $\Phi^*_{kol.vr}$, cal/mole·degree
5) immediate summation
6) Gordon and Barnes
7) the same (with statistical weight)
8) $S_{kol.vr}$, cal/mole·degree.

In Table 8, the results of calculations of thermodynamic functions of some gases are given, as carried out by the method of immediate summation, by the method of Gordon and Barnes using the approximate relations mentioned above, and also by the method of Gordon and Barnes taking into account the multiplicity of the states by means of statistical weights (see Table 7). It is evident from the Table that the methods of immediate summation and of Gordon and Barnes give almost identical results in all cases.

It must be noted that the relations (II.56)-(II.112) can be used for the calculation of the thermodynamical functions of dissociating gases by any approximate method, including the methods of Kovner, Mayer and Hoeppert-Mayer, and also in the more precise methods

rotator model approximation. It is sufficient, for this purpose, to omit the corresponding terms in Eqs. (II.85)-(II.112) and to change the method of calculation of the vibrational component (see below, page 187).

In concluding this section, it should be noted that the multiplicity of the rotational levels may be taken into account in the calculations in the harmonic oscillator-rigid rotator model approximation for high temperatures (generally, higher than 1000°K) by introduction of the statistical weights quoted in Table 7, as the errors caused by neglecting the anharmonicity of the vibrations are essentially higher. In calculations for temperatures in the range of 500°K and below, however, when the anharmonicity of the oscillations, the centrifugal stree and also the interaction between the vibration and rotation of the molecules hardly affect the thermodynamic functions of diatomic gases, the consideration for the splitting of the states by means of statistical weights results in great errors especially in the values of Φ_T^* (see Table 8). Thus, the calculations by the rigid rotator-harmonic oscillator model approximation for low temperatures must also take into account the splitting of the rotational energy levels in multiplet electronic states, if the splitting constants are well-known or if they may be estimated. The corresponding calculations may be carried out by means of the relations (II.85)-(II.112) assuming in them

$$\beta_1 = \beta_2 = d_0 = f_0 = 0 \text{ and } \ln Q_{\text{кол}} = \ln Q_{\text{г.о.}},\ S_{\text{кол}}/R = \frac{S_{\text{г.о}}}{R}.$$

§10. TAKING INTO ACCOUNT THE EXCITED ELECTRONIC STATES OF THE MOLECULES APPROXIMATE CALCULATION METHODS

It was assumed above, in the examination of approximate methods of calculating the thermodynamic functions of diatomic gases, that the contribution of the excited electronic states of the molecules may be disregarded. Let us examine in which manner the methods may be made more accurate in cases when this assumption does not hold; a fact, which generally takes place at high temperatures.

If the calculation of the thermodynamic functions of gases is carried out using the method of Giauque-Overstreet, the values of $Q_{kol.vr}$ for each electronic state may be found independently of each other as well as in the case where they are calculated by immediate summation. Thus, Q_{vn} and $T\frac{\partial}{\partial T}Q_{вн}$ are found as sums

$$Q_{вн} = \sum_i Q^{(i)}_{кол.вр} \exp\left(-\frac{hc}{kT}\nu^{(i)}_{00}\right). \qquad \text{(II.113)}$$

$$T\frac{\partial}{\partial T}Q_{вн} = \sum_i \left[T\frac{\partial}{\partial T}Q^{(i)}_{кол.вр} + \frac{hc}{kT}\nu^{(i)}_{00}Q^{(i)}_{кол.вр}\right]\exp\left(-\frac{hc}{kT}\nu^{(i)}_{00}\right). \qquad \text{(II.114)}$$

where the summation is carried out over all electronic states which are taken into account in the calculation.

If the thermodynamic functions of gases are calculated by other approximate methods (for example, by the Gordon-Barnes or Kassel methods), the values of $Q_{kol.vr}$ and $T\frac{\partial}{\partial T}Q_{кол.вр}$ are not calculated at all, because the vibrational-rotational components of the thermodynamic functions are calculated immediately by means of the molecular constants. It was shown in the paper [175] by Gurvich and Korobov that this, in principle, presents no obstacle to the calculation of the values of Q_{vn} and $T\frac{\partial}{\partial T}Q_{вн}$ by immediate summation over the electronic states.

The relations (II.113) and (II.114) may be written down in the form:

$$Q_{вн} = \sum_i \exp\left(M_i - \frac{hc}{kT}\nu_{00}^{(i)}\right). \qquad \text{(II.115)}$$

$$T\frac{\partial}{\partial T}Q_{вн} = \sum_i \left(N_i - M_i + \frac{hc}{kT}\nu_{00}^{(i)}\right)\exp\left(M_i - \frac{hc}{kT}\nu_{00}^{(i)}\right). \qquad \text{(II.116)}$$

where

$$M_i = \ln Q_{кол.вр}^{(i)}, \qquad \text{(II.117)}$$

$$N_i = \ln Q_{кол.вр}^{(i)} + T\frac{\partial}{\partial T}\ln Q_{кол.вр}^{(i)}. \qquad \text{(II.118)}$$

The values of M_i and N_i may be calculated on the basis of the molecular constants of the gas in the ith electronic state by any approximate method, for example, by Eqs. (II.52) and (II.53). The calculation of Q_{vn} and $T\frac{\partial}{\partial T}Q_{вн}$ by the relations (II.115) and (II.116) using the approximate methods examined in §8 and 9, in order to determine the values of M_i and N_i, has the advantage that in this case any number of electronic states of the gas molecules may be taken into account in the calculation of the thermodynamic functions, without an immediate summation over v and J is necessary in calculating the statistical sums over the vibrational and rotational states.

The accuracy of the values of Q_{vn} and $T\frac{\partial}{\partial T}Q_{вн}$, calculated by means of Eqs. (II.115)-(II.116) depends on the method of calculating the values of M_i and N_i, i.e., the vibrational-rotational components of the thermodynamic functions. The method of Gordon and Barnes was applied for this purpose in the paper [175].

It is evident that corrections must be introduced in order to limit the number of rotational levels of the molecules in each electronic state, when the calculation of the values of M_i and N_i by Eqs. (II.117) and (II.118) is carried out for cases in which such a provision is necessary, i.e., at high temperatures. If one or several electronic states of the molecule are multiplet states, the values of M_i and N_i for the ground state and the states with low excitation energies may be calculated by Eqs. (II.85)-(II.112), and the addends

in the sums (II.115) and (II.116) must be multiplied by the statistical weights p_i of all these states, corresponding to Table 7, in the case of multiplet states with high excitation energies.

In cases when the number of gas molecules in excited electronic states is low compared to the electronic ground state (i.e., when the $\nu_{00}^{(i)}/T$ are sufficiently high), the excited states may be accounted for simpler methods.

Assuming that the vibrational and rotational constants of the gas molecules are equal in the ground and in the excited electronic states,* the expression for Q_{vn} may be written down in the form

$$Q_{вн} = \sum_i Q_{кол.\,вр}^{(i)} \exp\left(-\frac{hc}{kT}\nu_{00}^{(i)}\right) = Q_{кол.\,вр}^{(X)}\left[1 + \sum_{i=A,\ldots} \frac{p_i}{p_X}\exp\left(-\frac{hc}{kT}\nu_{00}^{(i)}\right)\right], \quad (II.119)$$

where $Q_{кол.\,вр}^{(X)}$ is the statistical sum over the vibrational and rotational states of the ground electronic state of the gas molecules; p_i is the statistical weight which approximately takes into account the multiplicity of the ith state. Thus we have

$$\Phi_T^\circ = \Phi_{пост}^\circ + (\Phi_{кол.\,вр}^\circ)_X + R\ln(1+\delta) = (\Phi_T^\circ)_X + \Delta\Phi_{эл}^\circ, \quad (II.120)$$

$$S_T^\circ = S_{пост}^\circ + (S_{кол.\,вр})_X + R\left[\ln(1+\delta) + \frac{1}{1+\delta}T\frac{\partial\delta}{\partial T}\right] = (S_T^\circ)_X + \Delta S_{эл}. \quad (II.121)$$

where

$$\delta = \sum_{i=A,\ldots} \frac{p_i}{p_X}\exp\left(-\frac{hc}{kT}\nu_{00}^{(i)}\right), \quad (II.122)$$

$$T\frac{\partial\delta}{\partial T} = \sum_{i=A,\ldots} \frac{p_i}{p_X}\cdot\frac{hc}{kT}\nu_{00}^{(i)}\exp\left(-\frac{hc}{kT}\nu_{00}^{(i)}\right). \quad (II.123)$$

$(\Phi_{кол.\,вр}^\circ)_X$ and $(S_{кол.\,вр})_X$ are the vibrational and rotational components of the thermodynamic gas functions calculated by any method without regard for the excited states of the molecules. $\Delta\Phi_{эл}^\circ$ and $\Delta S_{эл}$ are the corrections which take into account the existence of gas molecules in excited electronic states.

The corrections $\Delta\Phi_{эл}^\circ$ and $\Delta S_{эл}$, for excited electronic states,

calculated by Eqs. (II.120) and (II.121), may be made more accurate if the difference of the oscillation frequencies ω_0 and of the rotational constants B_0 of the gas molecules in different electronic states are taken into account. Writing down, according to Eq. (II.82)

$$Q^{(i)}_{\text{к.р.г.о}} = \frac{1}{\sigma} \cdot \frac{kT}{hcB_0^{(i)}} \cdot \frac{1}{1-z_i} \exp\left(-\frac{hc}{kT}\nu_{00}^{(i)}\right). \qquad \text{(II 124)}$$

we obtain an expression for the corrections, which take into account the existence of excited electronic states (see [175]):

$$\delta' = \sum_{i=A,\ldots} \frac{p_i}{p_X} \cdot \frac{(1-z_X)}{(1-z_i)} \cdot \frac{B_0^{(X)}}{B_0^{(i)}} \exp\left(\frac{hc}{kT}\nu_{00}^{(i)}\right), \qquad \text{(II.125)}$$

$$\Delta\Phi^{*}_{\text{вн}} = R \ln (1+\delta'), \qquad \text{(II.126)}$$

$$\Delta S_{\text{вн}} = R\left\{\ln(1+\delta') + \sum_{i=A,\ldots}\left[\frac{(H_T-H_0)^{(i)}_{\text{г.о}}}{RT} - \frac{(H_T-H_0)^{(X)}_{\text{г.о}}}{RT} + \right.\right.$$

$$\left.\left. + \frac{hc}{kT}\nu_{00}^{(i)}\right] \cdot \frac{p_i}{p_X} \cdot \frac{(1-z_X)}{(1-z_i)} \cdot \frac{B_0^X}{B_0^{(i)}} \exp\left(-\frac{hc}{kT}\nu_{00}^{(i)}\right)\right\}, \qquad \text{(II.127)}$$

where $\frac{(H_T-H_0)_{\text{г.о}}}{RT} = T\frac{\partial}{\partial T}\ln(1-z_i)$ may be found using the tables of the thermodynamic functions of the harmonic oscillator.*

The three examined methods for accounting for the excited electronic states of gas molecules in calculating thermodynamic gas functions by approximate methods have a different accuracy. The conditions under which the application of each method is most efficient were studied in the paper [175]. Due to the fact that the contribution of each electronic state to the statistical sum over the intramolecular states is proportional to $\exp\left(-\frac{hc}{kT}\nu_{00}^{(i)}\right)$, it was assumed in the paper [175] that the necessary accuracy of the calculation of the component of a given state depends on the value of $\nu_{00}^{(i)}/T$. In the case $\nu_{00}^{(i)}/T > 8{,}0$, providing that the calculations are carried out with an accuracy of 0.001 cal/mole·degree, the excited states of diatomic molecules may be totally disregarded in calculating the thermodynamic functions of gases.** In the case of $8{,}0 \geqslant \frac{\nu_{00}^{(i)}}{T} \geqslant 4{,}5$ the excited states may be taken into account using Eqs. (II.120) and

(II.121), i.e., disregarding the difference between the molecular constants in the ith and in the ground electronic states. At $\nu_{\infty}^{(i)}/T < 4{,}5$, methods must be applied which take into account the difference between the molecular constats of the gas in the ground and in the excited states; at $\nu_{\infty}^{(i)}/T \geq 3{,}5$, a sufficient accuracy is attainable by calculations with (II.126)-(II.127); in the case of $\nu_{\infty}^{(i)}/T \leqslant 3{,}5$, however, the Eqs. (II.115) and (II.116) must be applied. It should be noted that the values calculated by the latter equations are hardly less accurate than the calculation results by immediate summation, until the application of the approximate method of calculation of $\ln Q_{\text{кол. вр}}$ and $T\frac{\partial \ln Q_{\text{кол. вр}}}{\partial T}$ is justified.

In cases when the gas molecules possess several excited states differing essentially in the value of $\nu_{\infty}^{(i)}$, the components of the various states may be calculated by various methods depending on the value of $\nu_{\infty}^{(i)}/T$. If the components of all excited states must be taken into account, by means of corrections, in the values of $(\Delta_T^\circ)_X$ and $(S_T^\circ)_X$ i.e., by means of Eqs. (II.126)-(II.127), the calculation of Δ^*_{el} and ΔS_{el} by assumption of $(1 - z_1) = (1 - z_X)$ and $B_0^{(i)} = B_0^{(1)}$ for some states does not present difficulties. In similar manner the values of $Q_{\text{кол. вр}}^{(i)} \exp\left(-\frac{\Delta_i}{RT}\nu_{\omega}^{(i)}\right)$ for Q_{vn} and its derivative with respect to the temperature in Eqs. (II.115) and (II.116) may be calculated for some states by immediate summation or by the Glaugue-Gibbert method, and for the other states they may be expressed in terms of M_i and N_i (relations (II.117) and (II.118)), i.e., by application of approximate calculation methods.

Equations (II.126) and (II.127) or (II.130) and (II.131) may be transformed, however, in the cases when the values of $Q_{\text{кол. вр}}^{(i)} \exp\left(-\frac{\Delta_i}{RT}\nu_{\omega}^{(i)}\right)$ and of its derivative must be calculated for several excited states (usually 2-3 lower states) by immediate summation only; Eqs. (

and (II.118) in terms of M_i and N_i; the components of the higher excited states may be taken into account in the form of corrections for $\Delta\Phi^*_{el}$ and ΔS_{el}.

In this case, Q_{vn} may be expressed by the form

$$Q_{вн} = Q^{(X)}_{кол.\,вр} + Q^{(A)}_{кол.\,вр}\exp\left(-\frac{hc}{kT}\nu^{(A)}_{00}\right) + Q^{(B)}_{кол.\,вр}\exp\left(-\frac{hc}{kT}\nu^{(B)}_{00}\right) + \ldots + \\ + \sum_i p_i \cdot \frac{kT}{hcB^{(i)}_0}\cdot\frac{1}{(1-z_i)}\exp\left(-\frac{hc}{kT}\nu^{(i)}_{00}\right), \qquad (II.128)$$

where $Q^{(X)}_{kol.vr}$, $Q^{(A)}_{kol.vr}$, ... are calculated by immediate summation or in terms of M_X, M_A, M_B, ..., and all other electronic states are included into the sum over i.

Let us denote

$$Q^{(X)}_{кол.\,вр} + Q^{(A)}_{кол.\,вр}\exp\left(-\frac{hc}{kT}\nu^{A}_{00}\right) + Q^{(B)}_{кол.\,вр}\exp\left(-\frac{hc}{kT}\nu^{(B)}_{10}\right) + \ldots = \Sigma'. \qquad (II.129)$$

We have then:

$$Q_{вн} = \Sigma'\left[1 + \frac{Q^{(X)}_{кол.\,вр}}{\Sigma'}\cdot\sum_i \frac{p_i}{p_X}\cdot\frac{(1-z_X)}{(1-z_i)}\cdot\frac{B^{(X)}_0}{B^{(i)}_0}\cdot\exp\left(-\frac{hc}{kT}\nu^{(i)}_{00}\right)\right], \qquad (II.130)$$

where the sum Σ' contains all electronic states, the components of which are calculated separately, and where all other states are included into the sum over i. Hence, we have

$$\ln Q_{вн} = \ln\Sigma' + \ln\left(1 + \frac{Q^{(X)}_{кол.\,вр}}{\Sigma'}\delta\right), \qquad (II.131)$$

$$T\frac{\partial}{\partial T}\ln Q_{вн} = \frac{1}{\Sigma'}T\frac{\partial}{\partial T}\Sigma' + \frac{1}{1+\frac{Q^{(X)}_{кол\,вр.}}{\Sigma'}\delta}\times$$

$$\times\left\{\frac{Q^{(X)}_{кол.\,вр}}{\Sigma'}T\frac{\partial}{\partial T}\delta + \frac{\delta}{\Sigma'}T\frac{\partial}{\partial T}Q^{(X)}_{кол.\,вр} - \frac{Q^{X}_{кол.\,вр}\cdot\delta}{(\Sigma')^2}T\frac{\partial}{\partial T}\Sigma'\right\}. \qquad (II.132)$$

where

$$\text{or}\,T\frac{\partial}{\partial T}\Sigma' = T\frac{\partial}{\partial T}Q^{(X)}_{кол.\,вр} + T\frac{\partial}{\partial T}Q^{(A)}_{кол.\,вр}\exp\left(-\frac{hc}{kT}\nu^{(A)}_{00}\right) + \ldots, \qquad (II.133)$$

$$T\frac{\partial\delta}{\partial T} = \sum_i\frac{p_i}{p_X}\cdot\frac{(1-z_X)}{(1-z_i)}\cdot\frac{B^{(X)}_0}{B^{(i)}_0}\cdot\left[\frac{(H_T-H_0)^{(i)}_{г.\,о}}{RT} - \frac{(H_T-H_0)^{(X)}_{г.\,о}}{RT} + \frac{hc}{kT}\nu^{(i)}_{00}\right]\exp\left(-\frac{hc}{kT}\nu^{(i)}_{00}\right). \qquad (II.134)$$

Example. Let us examine the calculation of Φ^*_{vn} and S_{vn} of the gaseous beryllium oxide at T = 5000°K. According to the data quoted

in Table 231, the BeO molecule possesses three excited electronic states with energies lower than 50,000 cm^{-1}. At T = 5000°K, we have $\frac{\nu_{00}^{(A)}}{T} = \frac{9234.8}{5000} = 1,847$; $\frac{\nu_{00}^{(B)}}{T} = \frac{21198.7}{5000} = 4,239$; $\frac{\nu_{00}^{(C)}}{T} = 7,824$.

In accordance with the realtions cited on page 181, the components of the $A^1\Pi$ state must be calculated at 5000°K together with the components of the $X^1\Sigma$ state by Eqs. (II.115) and (II.116): the components of the $B^1\Sigma$ state must be calculated in the form of corrections by Eqs. (II.131) and (II.132), and the $C^1\Sigma$ state must be disregarded in the calculation. On the basis of the constants of BeO quoted in Table 231, we obtain for the calculation of the values of M_X, M_A, N_X and N_A in Eqs. (II.117) and (II.118) by the Gordon-Barnes method: for the $X^1\Sigma$ state: θ = 2319.5°K; x = $7.9539 \cdot 10^{-3}$; q_0 = = 0.42350·T; $\beta_1 = 1.1571 \cdot 10^{-2}$; $\beta_2 = 1.30 \cdot 10^{-4}$; $d_0 = 4.2311 \cdot 10^{-6} \cdot T$; $f_0 = 7.28 \cdot 10^{-12} T^2$; for the $A^1\Pi$ state: p_A = 2; θ = 1646.0°K; x = = $7.3542 \cdot 10^{-3}$; q_0 = 0.511944·T; $\beta_1 = 1.200 \cdot 10^{-2}$; $\beta_2 = 1.49 \cdot 10^{-4}$; $d_0 = 5.90 \cdot 10^{-6} T$; $f_0 = -1.72 \cdot 10^{-12} T^2$. Assuming these values, we find by means of Eqs. (II.117) and (II.118) for T = 5000°K; M_X = 9.2405; M_A = 9.2405; N_X = 10.7119 and N_A = 11.2370. We find the values of Φ_{vn} and $T \frac{\partial}{\partial T} \ln Q_{вн}$ by Eqs. (II.131) and (II.132), where the calculation regarding the $B^1\Sigma$ state is calculated, and assuming for δ the expression (II.135). Then we have: δ = 0.00224; $T \frac{\partial \delta}{\partial T}$ = 0.0150; $\Sigma' = \exp M_X + 2 \exp \left(M_A - \frac{hc}{kT} \nu_{00}^{(A)}\right)$ = 8097.78; $T \frac{\partial \Sigma'}{\partial T}$ = 19421.5; $\Phi_{кол.вр}^{(X)}$ = = 6649.6; $T \frac{\partial}{\partial T} Q_{кол.вр}^{(X)}$ = 12693.9; Φ_{vn}^{*} = 17.8841 + 0.0037 = 17.8878 cal/mole·degree, and S_{vn} = 22.6503 + 0.0272 = 22.6775 cal/mole·degree.

§11. GENERAL RELATIONSHIPS AND COMPARISON OF THE VARIOUS CALCULATION METHODS

In §8, 9 and 10, the approximate methods of calculating the vibrational-rotational components of thermodynamic functions of diatomic gases were examined, as well as methods which make it possible

take into account in the approximate calculations the existence of molecules in excited electronic states. The relationships obtained in §8-10 may be transformed into a generalized form as all approximate methods of calculating the vibrational-rotational components, excluding the Giauque-Overstreet method, differ only in their method of calculating the corrections which take into account the deviation of the gas molecules from the rigid rotator-harmonic oscillator model.

The values of Φ_T^* and S°_T are calculated by Eqs. (II.34)-(II.35) when the thermodynamic functions of diatomic gases are calculated according to the method of Giauque and Overstreet. The values of $Q^{\infty(i)}_{\text{кол. вр}}$ and $T\frac{\partial}{\partial T}Q^{\infty(i)}_{\text{кол.вр}}$ for each electronic state, necessary for the calculation of Q_{vn} and $T\frac{\partial}{\partial T}Q_{вн}$ in Eqs. (II.34) and (II.35), are found by immediate summation over the vibrational levels according to the relations (II.41)-(II.42), where $Q^{\infty(i)}_{v.вр}$ and $T\frac{\partial}{\partial T}Q^{\infty(i)}_{v.вр}$ in turn are calculated by Eqs. (II.36)-(II.37). $Q_{v.vr}$ and $T\frac{\partial}{\partial T}Q_{в.вр}$ are calculated by Eqs. (II.44)-(II.45) if a finite number of rotational states is taken into account.

The thermodynamic functions of diatomic gases must be calculated by (II.34) and (II.35) in cases when the relations (II.115) and (II.116) are used for calculating the components of one or several excited states of the gas molecules. The intermolecular components of the thermodynamic functions in Eqs. (II.34) and (II.35) must be calculated by Eqs. (II.115)-(II.116) or (II.131)-(II.132), depending on whether or not the fraction of the excited states of the gas molecules is taken into account by corrections of the values of Φ^*_{vn} and S_{vn}.

In cases when the vibrational-rotational components of the electronic ground state of the gas molecules are calculated by other

approximate methods (for example the Gordon and Barnes, Kassel, Mayer and Mayer-Goeppert method or in the rigid rotator-harmonic oscillator model approximation) and the excited electronic states are taken into account by corrections of the components of the electronic ground state, the Eqs. (II.34) and (II.35) may be transformed into a simpler form. This is possible since the thermodynamic gas functions calculated by approximate methods are sums of both the appropriate values of the rigid rotator-harmonic oscillator model and of corrections which not only take into account the deviation of the gas molecules from this model but also the splitting of the rotational energy levels in the electronic states. Thus, the equations for the calculations of $\Phi^*_{\text{kol. vr}}$ and $S_{\text{kol. vr}}$ may be represented in the form

$$\Phi^*_{\text{кол.вр}} = R\ln q_0 - R\ln s - R\ln(1-z) + R\ln p_M + R\ln\Sigma + R\ln\Delta_M = \Phi^*_{\text{г.о}} + \Phi^*_{\text{ж.р}} + R\ln p_M + R\ln\Sigma + R\ln\Delta_M, \quad \text{(II.135)}$$

$$S_{\text{кол.вр}} = R(\ln q_0 + 1) - R\ln s - R\left[\ln(1-z) + T\frac{\partial}{\partial T}\ln(1-z)\right] + R\ln p_M + R\left[\ln\Sigma + T\frac{\partial \ln\Sigma}{\partial T}\right] + R\left[\ln\Delta_M + T\frac{\partial \ln\Delta_M}{\partial T}\right] = S_{\text{ж.р}} + S_{\text{г.о}} + R\ln p_M + R\left[\ln\Sigma + T\frac{\partial \ln\Sigma}{\partial T}\right] + R\left[\ln\Delta_M + T\frac{\partial}{\partial T}\ln\Delta_M\right], \quad \text{(II.136)}$$

where $\Phi^*_{\text{zh. r}}$ and $S_{\text{zh. r}}$ are the components of the rigid rotator, and $\Phi^*_{\text{g. o}}$ and $S_{\text{g. o}}$ are the components of the harmonic oscillator, and p_M is the statistical weight of the electronic state (see Table 7).

The values $\ln\Sigma$ and $T\frac{\partial \ln\Sigma}{\partial T}$ in Eqs. (II.135) and (II.136) may be calculated by means of various relations depending upon which method is used in the calculation.

These relations are cited above.

For the Gordon and Barnes method (see page 150) they are

$$\ln \Sigma = \Delta \ln Q_{кол} + \beta_1 \bar{v} + \beta_2 \bar{v}^2 + d_0 + 2{,}5\, d_0^2 + f_e + \frac{1}{3q_0} + \ln (1 - a), \quad \text{(II.137)}$$

$$\ln \Sigma + T \frac{\partial}{\partial T} \ln \Sigma = \frac{\Delta S_{кол}}{R} + \beta_1 \bar{s} + \beta_2 \bar{s}^2 + 2d_0 + 7{,}5\, d_0^2 + 3f_0 + \ln (1 - a) +$$

$$+ \frac{a}{1-a} \left(T \frac{\partial}{\partial T} \ln Q^{\infty}_{кол.\,вр} - 1 - \frac{hc}{kT} D_0 \right). \quad \text{(II.138)}$$

For the Kassel method (see page 156) they are

$$\ln \Sigma = \ln \sum_l A_l f_l. \quad \text{(II.139)}$$

$$\ln \Sigma + T \frac{\partial}{\partial T} \ln \Sigma = \ln \Sigma A_l f_l + \frac{\sum_l A_l T \frac{\partial f_l}{\partial T} + \sum_l f_l T \frac{\partial}{\partial T} A_l}{\sum_l A_l f_l}. \quad \text{(II.140)}$$

For the Mayer and Goeppert-Mayer method (see page 159) they are

$$\ln \Sigma = \frac{1}{3q_0} + u^{-1} (2\gamma + 6\gamma^{1/3} x^{1/3} + 2x) + (3\gamma - \gamma^{1/3} x^{1/3} - 2x) +$$

$$+ \frac{u}{6} (-3\gamma + 3\gamma^{1/3} x^{1/3} + 5x) - \frac{u^2}{6} x + \frac{u^3}{120} (\gamma - \gamma^{1/3} x^{1/3} + x) + \ldots. \quad \text{(II.141)}$$

$$\ln \Sigma + T \frac{\partial}{\partial T} \ln \Sigma = u^{-1} (4\gamma + 12\gamma^{1/3} x^{1/3} + 4x) + (3\gamma - 3\gamma^{1/3} x^{1/3} - 2x) +$$

$$+ \frac{u^2}{6} \ldots - \frac{u^3}{60} (\gamma - \gamma^{1/3} x^{1/3} + x) + \ldots \quad \text{(II.142)}$$

For the rigid rotator-harmonic oscillator model approximation (see page 163) they are

$$\ln \Sigma = 0, \quad \text{(II.143)}$$

$$\ln \Sigma + T \frac{\partial}{\partial T} \ln \Sigma = 0. \quad \text{(II.144)}$$

The expressions $\ln \Sigma$ and $T \frac{\partial}{\partial T} \ln \Sigma$ in the calculation according to the Brounshteyn and Yurkov method and other methods may be expressed in similar manner.

The values of $\ln \Delta_M$ and $T \frac{\partial}{\partial T} \ln \Delta_M$ in Eqs. (II.135) and (II.136) are corrections which take into account the splitting of the rotational levels in the case of multiplet electronic states. The expressions for these values, on the basis of Eqs. (II.85)-(II.112), have the following form:

for $^2\Sigma$ states

$$\ln \Delta_M = \frac{1}{8}\left(\frac{\gamma}{B_e}\right)^2 \frac{1}{q_e}, \qquad \text{(II.145)}$$

$$\ln \Delta_M + T\frac{\partial}{\partial T}\ln \Delta_M = 0; \qquad \text{(II.146)}$$

for $^3\Sigma$ states

$$\ln \Delta_M = \frac{hc}{kT}\left[F_e(K_{min}) + \frac{2}{3}\lambda - \mu\right], \qquad \text{(II.147)}$$

$$\ln \Delta_M + T\frac{\partial}{\partial T}\ln \Delta_M = 0; \qquad \text{(II.148)}$$

for $^2\Pi$ states (the type, intermediate between the Hund a and b cases)

$$\ln \Delta_M = \ln z_e - \frac{hc}{kT}K_e, \qquad \text{(II.149)*}$$

$$\ln \Delta_M + T\frac{\partial}{\partial T}\ln \Delta_M = s_e; \qquad \text{(II.150)**}$$

for $^2\Pi$ states (Hund case a)

$$\ln \Delta_M = \ln \Delta + \frac{5}{6q_e}, \qquad \text{(II.151)***}$$

$$\ln \Delta_M + T\frac{\partial}{\partial T}\ln \Delta_M = s_\Delta; \qquad \text{(II.152)}$$

for $^2\Pi$ states (Hund case b, regular states)

$$\ln \Delta_M = \frac{4}{3q_e} - \frac{A}{2B_e q_e}, \qquad \text{(II.153)***}$$

$$\ln \Delta_M + T\frac{\partial}{\partial T}\ln \Delta_M = 0; \qquad \text{(II.154)}$$

for $^2\Pi$ states (Hund case b, inverse states)****

$$\ln \Delta_M = \frac{1}{q_e}\left(4 - \sqrt{4 + \frac{A^2}{4B_e^2} - \frac{A}{B_e}}\right) - \frac{2}{3q_e}, \qquad \text{(II.155)}$$

$$\ln \Delta_M + T\frac{\partial}{\partial T}\ln \Delta_M = 0; \qquad \text{(II.156)}$$

for $^3\Pi$ states (Hund case a)****

$$\ln \Delta_M = \frac{hc}{kT}E_e + \ln c_1 + \frac{a_1}{q_e} + \frac{4}{c_1}\cdot\frac{B_e}{|A|}\operatorname{sh}\left(\frac{hc}{kT}|A|\right), \qquad \text{(II.157)}$$

$$\ln \Delta_M + T\frac{\partial \ln \Delta_M}{\partial T} = \ln c_1 - \frac{2}{c_1}\cdot\frac{hc}{kT}|A|\operatorname{sh}\left(\frac{hc}{kT}|A|\right) + \frac{1}{q_e}\left(T\frac{\partial a_1}{\partial T} - a_1\right); \qquad \text{(II.158)}$$

for $^3\Pi$ states (Hund case b)

$$\ln \Delta_M = \frac{hc}{kT}\varepsilon_0, \qquad \text{(II.159)}$$

$$\ln \Delta_M + T\frac{\partial}{\partial T}\ln \Delta_M = 0. \qquad \text{(II.160)}$$

The final expressions for the calculation of Φ^*_T and S°_T (in cal/mole·degree) assume, on the basis of Eqs. (II.34), (II.35), (II.120)--(II 127), (II.135), and (II.136), the following form

$$\Phi^\circ_T = 1{,}98726\left(\frac{\Phi^\circ_{r.o}}{R} + \ln\Sigma + \ln\Delta_M\right) + 16{,}01544\lg T + C_\Phi + \Delta\Phi_{\text{эл.}} \quad \text{(II.161)}$$

$$S^\circ_T = 1{,}98726\left(\frac{S_{r.o}}{R} + \ln\Sigma + T\frac{\partial\ln\Sigma}{\partial T} + \ln\Delta_M + T\frac{\partial}{\partial T}\ln\Delta_M\right) + 16{,}01544\lg T + C_S + \Delta S_{\text{эл.}} \quad \text{(II.162)}$$

where $\Phi^*_{g.o}/R$ and $S_{g.o}/R$ may be found with the aid of the tables of thermodynamic functions of the harmonic oscillator as functions of θ/T;

$$C_\Phi = 6{,}86376\lg M - 7{,}28355 + 4{,}57584\lg\frac{k}{hcB_e} - 4{,}57584\lg\sigma + 1{,}57584\lg p_M. \quad \text{(II.163)}$$

$$C_S = 6{,}86376\lg M - 0{,}32809 + 4{,}57584\lg\frac{k}{hcB_e} - 4{,}57584\lg\sigma + 4{,}57584\lg p_M. \quad \text{(II.164)}$$

In cases when the rotational constant of the gas molecules is unknown but their interatomic distance is well known or may be estimated, the values of C_Φ and C_S may be calculated in terms of the moment of inertia of these molecules. We have then for the calculation of C_Φ and C_S:

$$C_\Phi = 6{,}86376\lg M + 4{,}57584\lg(I\cdot 10^{39}) - 4{,}57584\lg\sigma + 4{,}57584\lg p_M - 10{,}0519, \quad \text{(II.165)}$$

$$C_S = 6{,}86376\lg M + 4{,}57584\lg(I\cdot 10^{39}) - 4{,}57584\lg\sigma + 4{,}57584\lg p_M - 3{,}0964, \quad \text{(II.166)}$$

where I is the moment of inertia of the molecule in $g\cdot cm^2$.

In calculating the thermodynamic gas functions by Eqs. (II.161) and (II.162), the values of $\Phi^*_{g.o}/R$ and $S_{g.o}/R$ are calculated by interpolation with the aid of tables of the thermodynamic functions of the harmonic oscillator as functions of θ/T. It is necessary, however, to remember, that the values of θ have a different sense in different methods due to the transformations carried out in the deviation of the corresponding equations for $\ln\Delta$ and $\ln\Delta + T\frac{\partial}{\partial T}\ln\Delta$. Thus, in the Gordon-Barnes method they are $\theta = \frac{hc}{k}\omega_e$; in the Kassel method they are $\theta = \frac{hc}{k}\omega_0$, and in the Mayer and Goeppert-Mayer method they are $\theta = \frac{hc}{k}\nu$. A distinction between the constants ω_e, ω_0 and ν

makes no physical sense when the calculations are carried out in the rigid rotator-harmonic oscillator model approximation. If, however, all three values are well know, they must be assumed in the calculation as equal to ω_0.

TABLE 9

Comparison of the Results of Calculating the Values of $\Phi^*_{kol.vr}$ and $S_{kol.vr}$ for the Electronic Ground State of N_2 by Various Methods.

T, °K	1 Метод непосредственного суммирования	2 Метод Гордона и Барнес [уравнения (II.52)—(II.53)]	Метод Гордона и Барнес с поправкой на J_{max} [уравнения (II.59)—(II.60)] 3	Метод Касселя [уравнения (II.69)—(II.70)] 4	Метод Майера и Гепперт-Майер 5		Приближение модели жесткий ротатор—гармонический осциллятор [уравнения (II.83)—(II.84)] 8
					6 [уравнения (II.72)—(II.73)]	[уравнения (II.74)—(II.75)] 7	
			9 $\Phi^\circ_{кол.вр}$, *кал·моль/град*				
298,15	7,8626	7,8625	7,8625	7,8625	7,8625	7,8160	7,8549
3000	13,2596	13,2595	13,2595	13,2579	13,2587	13,2585	13,2235
5000	14,9430	14,9422	14,9422	14,9421	14,9400	14,9394	14,8733
10000	17,4876	17,4875	17,4873	17,4840	17,4698	17,4690	17,3210
			10 $S_{кол.вр}$, *кал/моль·град*				
298,15	9,8451	9,8448	9,8448	9,8446	9,8448	9,8442	9,8422
3000	16,3700	16,3699	16,3699	16,3675	16,3687	16,3683	16,2859
5000	18,4109	18,4108	18,4108	18,4065	18,3995	18,3972	18,2522
10000	21,3517	21,3552	21,3536	21,3516	21,2851	21,2840	20,9791

1) Method of immediate summation;
2) method of Gordon and Barnes [Eqs. (II.52)-(II.53)];
3) method of Gordon and Barnes with correction for J_{max} [Eqs. (II.59)-(II.60)];
4) method of Kassel [Eqs. (II.69)-(II.70)];
5) method of Mayer and Goeppert-Mayer;
6) [Eqs. (II.72)-(II.73)];
7) [Eqs. (II.74-(II.75)];
8) rigid rotator-harmonic oscillator model approximation [Eqs. (II.83)-(II.84)];
9) $\Phi^*_{kol.vr}$, cal/mole·degree;
10) $S_{kol.vr}$, cal/mole·degree.

TABLE 10

Comparison of the Results of Calculating the Values of $\Phi^*_{kol.vr}$ and $S_{kol.vr}$ for the Electronic Ground State of O_2 by Various Methods.

T, °K	1 Метод непосредственного суммирования	2 Метод Гордона и Барнес [уравнения (II.52)—(II.53)]	3 Метод Гордона и Барнес [уравнения (II.59)—(II.60)]	Метод Касселя [уравнения (II.69)—(II.70)] 4	Метод Майера и Гепперт-Майер 5		8 Приближение модели жесткий ротатор—гармонический осциллятор [уравнения (II.83)—(II.84)]
					6 [уравнения (II.72)—(II.73)]	7 [уравнения (II.74)—(II.75)]	
			9 $\Phi^*_{кол.\ вр.}$, кал/моль·град				
298,15	10,6894	10,6940	10,6940	10,6938	10,6938	10,6672	10,6849
3000	16,6102	16,6115	16,6115	16,6099	16,6069	16,6049	16,5390
5000	18,4321	18,4372	18,4372	18,4356	18,4249	18,4223	18,3001
10000	21,1195	21,1894	21,1832	21,1623	21,1144	21,1071	20,8436
			10 $S_{кол.\ вр.}$, кал/моль·град				
298,15	12,6798	12,6835	12,6835	12,6845	12,6845	12,7564	12,6799
3000	20,0227	20,0230	20,0230	20,0229	20,0107	20,0067	19,8591
[illegible]	22,1622	22,1715	22,1715	22,1663	22,1289	22,1216	21,8599
10000	25,0169	25,4435	25,4038	25,3199	25,1663	25,1504	24,6025

1) Method of immediate summation;
2) method of Gordon and Barnes [Eqs. (II.52)-(II.53)];
3) method of Gordon and Barnes with correction for J_{max} [Eqs. (II.59)-(II.60)];
4) method of Kassel [Eqs. (II.69)-(II.70)];
5) method of Mayer and Goeppert-Mayer;
6) [Eqs. (II.72)-(II.73)];
7) [Eqs. (II.74)-(II.75)];
8) rigid rotator-harmonic oscillator model approximation [Eqs. (II.83)-(II.84)];
9) $\Phi^*_{kol.vr}$, cal/mole·degree;
10) $S_{kol.vr}$, cal/mole·degree.

A comparison between various approximate methods of calculating the thermodynamic functions of diatomic gases leads to the conclusion that the Gordon-Barnes method is the most perfect and convenient method of application in practice; it is essentially more accurate than the Kassel and the Mayer and Goeppert-Mayer methods due to the limitation of the sums over v and also due to the possibility of introducing corrections for the finite value of J; moreover, it is essentially simpler than the methods of Giaque and Overstreet, and Brounshteyn and Yurkov. These circumstances are essential for calcula-

tion of the tables of thermodynamic functions for high temperatures. As an example, the results of the calculations for N_2 and O_2 by different methods are quoted in Tables 9 and 10.

The application of auxiliary tables, compiled during the preparation of this Handbook, for the calculations according to the Gordon-Barnes method make it possible to find the values for $\Delta \ln Q_{кол}$, $\frac{\Delta S_{кол}}{R}$, $\bar{v}$, $\bar{v}^2$, $\bar{s}$ and $\bar{s}^2$ in the whole temperature range by means of a simple interpolation. Owing to this fact, the calculations, according to the Gordon-Barnes method differ little with regard to their extent from these according to the Mayer and Goeppert-Mayer method which, in spite of its lower accuracy, is the fundamental method used in foreign literature.

Division 3. POLYATOMIC GASES

In contrast to the diatomic molecules, the polyatomic molecules dealt with in the Handbook generally possess singlet ground electronic states and excited electronic states with high excitation energies. Hence, one may in most cases assume that the statistical sum Q_{vn} over the intramolecular states of a polyatomic molecule is equal to the statistical sum over the vibrational and rotational states of the ground electronic state:

$$Q_{вн} = Q^{(X)}_{кол.вр} = \sum_{v_1, v_2, v_3, \ldots}^{v_{1m}, v_{2m}, \ldots} p_{v(i)} \exp\left[-\frac{hc}{kT} G_0(v_1, v_2, v_3, \ldots)\right] \sum_{J}^{J_{max}} p_J \exp\left[-\frac{hc}{kT} F_v(J,K)\right]. \quad \text{(II.167)}$$

The summation over $\underline{v}$ in Eq. (II.167) is carried out over all n_v oscillations of the molecule ($n_v = 3N - 5$ for the linear molecule, and $n_v = 3N - 6$ for the nonlinear one, where N is the number of atoms in the molecule), and the statistical weight of the state $v_1, v_2, v_3, \ldots$ is equal to $\prod_{n=1}^{n_v} \frac{(v_n + d_n - 1)!}{v_n!\,(d_n - 1)!}$ (see page 101).* The summation over J is carried out for each value $\underline{v}$ of all $\underline{n}$ vibrations. The energy of the vibrational levels $G_0(v_1, v_2, v_3 \ldots)$ may be represented by Eqs. (I.50),

and the energy of the rotational levels $F_v(J, K)$ by one of the Eqs. (1.55), (1.57), (1.61) or (1.60), depending on the type of the molecule, symmetric, asymmetric, and spherical top).

On the basis of Eqs. (II.167), the intramolecular components of the thermodynamic functions of polyatomic gases may be assumed to be equal to the vibrational-rotational components calculated for the ground electronic states of the molecules of the given gas. Appropriate corrections must be inserted in the rare cases where the multiplicity of the ground electronic state or the presence of excited electronic states must be taken into account. The methods of calculating these corrections are examined on page 210.

The immediate summation over the energy levels of the polyatomic molecule is, in principle, as well as in the case of diatomic molecules, the most accurate method for calculating Q_{vn}. The application of this method, however, is impossible in the case of polyatomic molecules primarily, because data on the energy of the levels are lacking, with the exception of a small number of levels with low values of v_n and J, and, secondly, due to the total lack of both experimental data and any well founded conceptions on the upper limits of v_n and J. Immediate summation may therefore be applied for the calculation of Q_{vn} only at low temperatures, when the summation in (II. 167) may be broken off at low values of v_n and J owing to the fact that the contributions of the higher states to the statistical sum are sufficiently small; and it can be applied only to a small number of molecules, whose spectra have been investigated sufficiently. The application of immediate summation at these temperatures, however, is inexpedient, because the approximate methods under these conditions give sufficiently accurate results. The calculations of tables of thermodynamic functions of polyatomic gases are, therefore, always

carried out by approximate methods, and the method based on the rigid rotator-harmonic oscillator model approximation is applied in most of the cases, due to the fact that data on the anharmonicity constants, on the interaction between rotation and vibrations, on the centrifugal stress, etc., are lacking. Owing to the wide prevalence of this method, the explanation of the approximate methods of calculating the vibrational-rotational components of the thermodynamic functions of polyatomic gases begins with this method, and then follows the discussion of the methods which allow for the anharmonicity of the vibrations, the interaction between vibrations and the rotation, and also the centrifugal stress, it is assumed in examination of these methods that such effects as inversion doubling, internal rotation and excitation of vibrational and rotational states are absent. The methods of calculating the corrections for the values of the thermodynamic functions with regard to these effects, and also the formulas for the calculation of corrections due to the multiplicity of the electronic states and the presence of excited electronic states of the molecules are described after the statement of the approximate calculation methods. General correlations for the calculations of Φ^*_T and S°_T by various approximate methods are quoted at the end of this division.

§12. APPROXIMATE METHODS OF CALCULATION OF THE VIBRATIONAL-ROTATIONAL COMPONENTS OF THERMODYNAMIC FUNCTIONS

Rigid rotator-harmonic oscillator. The model of the rigid rotator-harmonic oscillator in the case of polyatomic molecules, as well as in that of the diatomic ones, is identical with the assumption that the interatomic equilibrium distances do not depend on the vibrational and rotational quantum numbers, and also that no anharmonicity of

vibration and no interaction between vibrations and rotations take place. Moreover, the vibrations do not dependon each other in the approximation in question. The statistical sum over the vibrational and rotational states in the rigid rotator-harmonic oscillator model approximation ($Q_{zh.r.g.o}$) may be written down, as well as in the case of diatomic molecules, as a product of the sum over the vibrational states $Q_{g.o}$ and the sum over the rotational states $Q_{zh.r}$:

$$Q_{m.p.r.o} = Q_{m.p}\, Q_{r.o}. \qquad \text{(II.168)}$$

The value $Q_{g.o}$ of a polyatomic molecule may be written down in a general form as follows:

$$Q_{r.o} = \sum_{v_1 v_2 \ldots} p_{v_1 v_2 \ldots} \exp\left[-\frac{hc}{kT} G_0(v_1, v_2, v_3, \ldots)\right]. \qquad \text{(II.169)}$$

where

$$p_{v_1 v_2 v_3 \ldots} = \prod_n \frac{(v_n + d_n - 1)!}{v_n!\,(d_n - 1)!}.$$

In the approximation in question, the vibrations do not depend on each other, and therefore, $Q_{g.o}$ may be expressed as the product of the sums over the states of the individual harmonic oscillators:

$$Q_{r.o} = \sum_{v_1}^{v_{1\max}} p_{v_1} \exp\left[-\frac{hc}{kT}\omega_1 v_1\right] \cdot \sum_{v_2}^{v_{2\max}} p_{v_2} \exp\left[-\frac{hc}{kT}\omega_2 v_2\right] \cdot \sum_{v_3}^{v_{3\max}} p_{v_3} \exp\left[-\frac{hc}{kT}\omega_3 v_3\right] \cdot \ldots \qquad \text{(II.170)}$$

The number of sums in Eq. (II.170) will be smaller than the number of normal vibrations, 3N − 6, of the molecule by $\sum_{k=1}^{k=a} (d_k - 1)$, where a is the number of the degenerate vibrations of the molecule, and d_k is the degree of degeneracy of the kth vibration, due to the fact that the expression for $G_0(v)$ contains only vibrations with different values of frequencies. As was noted in §3, the statistical weights of the nondegenerate, two and threefold degeneral vibrations are equal to 1, $v_k + 1$, and $\frac{(v_k+1)(v_k+2)}{2}$, respectively.

If we assume, that the upper limits of the sums over v_n are in-

finite, the sum over the vibrational states of a polyatomic molecule, equal to the product of the sums over the states of harmonic oscillation, will have the form

$$Q_{r.o} = \prod_n (1 - z_n)^{-d_n}, \qquad \text{(II.171)}$$

where

$$z_n = \exp\left(-\frac{hc}{kT}\omega_n v_n\right), \qquad \text{(II.172)}$$

and d_n is the degree of degeneracy of the nth vibration.

The appropriate components of the thermodynamic functions will have the form

$$\Phi^*_{r.o} = -R\sum_n d_n \ln(1 - z_n), \qquad \text{(II.173)}$$

$$S_{r.o} = -R\sum_n d_n\left[\ln(1 - z_n) + T\frac{\partial}{\partial T}\ln(1 - z_n)\right]. \qquad \text{(II.174)}$$

Thus, each of the values of $\Phi^*_{g.o}$ and $S_{g.o}$ is a sum of the corresponding components for n harmonic oscillators. These components may be found by means of the tables for the thermodynamic functions of the harmonic oscillator (see page 165).

The expression for $Q_{zh.r}$ will be different depending on the type of the molecule.

For linear molecules, it is

$$Q_{m.p} = \frac{1}{\sigma}\frac{kT}{hcB}, \qquad \text{(II.175)}$$

i.e., it is identical with the expression for $Q_{zh.r}$ for a diatomic molecule (see page 165), and, in the case of nonlinear molecules,* it is

$$Q_{m.p} = \frac{1}{\sigma}\sqrt{\frac{\pi}{ABC}\cdot\left(\frac{kT}{hc}\right)^3}, \qquad \text{(II.176)}$$

where Σ is the symmetry number of the molecule, and A, B, C, are the rotation constants.

Let us keep in mind that in the case of nonlinear molecules of

the type of the assymmetric tops, all three rotational constants are different, in the case of molecules of the type of symmetric tops, two of the three constants are equal to each other, and in the case of molecules of the spherical top type, all three rotational constants are equal to each other. In the derivation of Eqs. (II.175) and (II.176) it was assumed that $J_{max} = \infty$.

The symmetry numbers Σ of the various point groups, to which polyatomic molecules may belong, are quoted in Table 11.

TABLE 11

Symmetry Numbers of Molecules of Various Point Groups

Точечная группа симметрии [1]	Число симметрии [2]	Точечная группа симметрии [1]	Число симметрии [2]	Точечная группа симметрии [1]	Число симметрии [2]
C_1, C_i, C_s	1	C_4, C_{4v}, C_{4h}	6	S_6	3
C_2, C_{2v}, C_{2h}	2	D_3, D_{3d}, $D_{3h}(=V_h)$	4	$C_{\infty v}$	1
C_3, C_{3v}, C_{3h}	3	D_3, D_{3d}, D_{3h}	6	$C_{\infty h}$	2
C_4, C_{4v}, C_{4h}	4	D_4, D_{4d}, D_{4h}	8	T, T_d	12
C_5, C_{5v}, C_{5h}	5	D_6, D_{6d}, D_{6h}	12	O_h	24

1) Point group of the symmetry; 2) symmetry number.

The components of the rigid rotator in the thermodynamic functions may be calculated for linear molecules by the formulas

$$\Phi^{\circ}_{\text{м.р}} = 4{,}57584 \lg T - 4{,}57584 \lg B - 4{,}57584 \lg \sigma + 0{,}7230, \qquad \text{(II.177)}$$

$$S_{\text{м.р}} = 4{,}57584 \lg T - 4{,}57584 \lg B - 4{,}57584 \lg \sigma + 2{,}2643 \qquad \text{(II.178)}$$

and for nonlinear molecules by the formulas

$$\Phi^{\circ}_{\text{м.р}} = 6{,}86376 \lg T - 2{,}23792 \lg (ABC) - 4{,}57584 \lg \sigma + 0{,}0528, \qquad \text{(II.179)}$$

$$S_{\text{м.р}} = 6{,}86376 \lg T - 2{,}26792 \lg (ABC) - 4{,}57584 \lg \sigma + 3{,}0339. \qquad \text{(II.180)}$$

In the case in which the calculation is carried out using the values of the moments of inertia and not those of the rotational constants, the formulas (II.177)-(II.180) may be represented as follows:

for linear molecules

$$\Phi^{\circ}_{\text{м.р}} = 4{,}57584 \lg T + 4{,}57584 \lg (I \cdot 10^{39}) - 4{,}57584 \lg \sigma - 2{,}7683, \quad \text{(II.181)}$$

$$S_{\text{м.р}} = 4{,}57584 \lg T + 4{,}57584 \lg (I \cdot 10^{39}) - 4{,}57584 \lg \sigma - 0{,}7810; \quad \text{(II.182)}$$

for nonlinear molecules

$$\Phi^{\circ}_{\text{м.р}} = 6{,}86376 \lg T + 2{,}28792 \lg (I_A I_B I_C\, 10^{117}) - 4{,}57584 \lg \sigma - 3{,}0152, \quad \text{(II.183)}$$

$$S_{\text{м.р}} = 6{,}86376 \lg T + 2{,}28792 \lg (I_A I_B I_C\, 10^{117}) - 4{,}57584 \lg \sigma - 0{,}0341, \quad \text{(II.184)}$$

where I, I_A, I_B, I_C are the principal moments of inertia of the molecule, expressed in $g \cdot cm^2$.

Example. Let us examine the calculation of the values of $\Phi^{*}_{\text{kol.vr}}$ and $S_{\text{kol.vr}}$ for CO_2 and H_2O at 5000°K in the rigid rotator-harmonic oscillator model approximation.

According to the values of the molecular constants of CO_2, quoted in Table 132, we have ν_1 = 1341.54 cm^{-1}; ν_2 = 667.26 cm^{-1}; ν_3 = = 2349.16 cm^{-1}; B_{000} = 0.39021 cm^{-1}, and σ = 2. On the basis of these values we have $\frac{\theta_1}{T} = \frac{1930.19}{T}$; $\frac{\theta_2}{T} = \frac{960.047}{T}$; $\frac{\theta_3}{T} = \frac{3379.95}{T}$. By means of the tables of thermodynamic functions of the harmonic oscillator we find: $\frac{\Phi^{\circ}_1}{R} = 1{,}1385$; $\frac{\Phi^{\circ}_2}{R} = 1{,}7447$; $\frac{\Phi^{\circ}_3}{R} = 0{,}7106$; $\frac{S_1}{R} = 1{,}9580$; $\frac{S_2}{R} = 2{,}6517$; $\frac{S_3}{R} = 1{,}4104$ and we calculate by Eqs. (II.177)-(II.178) $\Phi^{*}_{\text{zh.r}}$ = 18.1416 cal/mole·degree, and $S_{\text{zh.r}}$ = 19.6829 cal/mole·degree, and finally, for CO_2 at 5000°K:

$$\Phi^{\circ}_{\text{кол. вр}} = 1{,}99726\,(1{,}1385 + 2 \cdot 1{,}7447 + 0{,}7106) + 18{,}1416 = 28{,}7508 \text{ cal/mole·degree}$$

$$S_{\text{кол. вр}} = 1{,}99726\,(1{,}9580 + 2 \cdot 2{,}6517 + 1{,}4104) + 19{,}6829 = 36{,}9160 \text{ cal/mole·degree}$$

According to the values of the molecular constants of H_2O, quoted in Table 33, ν_1 = 3656.65 cm^{-1}; ν_2 = 1594.78 cm^{-1}; ν_3 = 3755.79 cm^{-1}, ABC = 3755.36 cm^{-3}, and σ = 2. By means of the tables of thermodynamic functions of the harmonic oscillator we find: $\frac{\Phi^{\circ}_1}{R} = 0{,}4295$; $\frac{\Phi^{\circ}_2}{R} = 0{,}9995$; $\frac{\Phi^{\circ}_3}{R} = 0{,}4145$; $\frac{S_1}{R} = 0{,}9940$; $\frac{S_2}{R} = 1{,}7876$; $\frac{S_3}{R} = 0{,}9696$; we calculate by means of Eqs. (II.179)-(II.180) $\Phi^{*}_{\text{zh.r}}$ = 15.8856 cal/mole·degree, $S_{\text{zh.r}}$ = 18.8667 cal/mole·degree, and we finally obtain for H_2O at 5000°K:

$$\Phi^{\circ}_{кол.\,вр} = 1{,}98726\,(0{,}4295 + 0{,}9936 + 0{,}4145) + 15{,}8856 = 19{,}5493 \text{ cal/mole·degree}$$

$$S_{кол.\,вр} = 1{,}98726\,(0{,}9940 + 1{,}7876 + 0{,}9395) + 18{,}8637 = 26{,}3213 \text{ cal/mole·degree}$$

The Gordon method.* A method similar to the Gordon and Barnes method for diatomic molecules (see page 150), in which corrections for the anharmonicity of the vibration and the interaction between the rotation and the vibrations are calculated by means of auxiliary tables, may be used for the calculation of the thermodynamic functions if the constants of the anharmonicity and of the vibrational-rotational interaction of polyatomic molecules are well known. The corresponding formulas for the calculation of the vibrational-rotational components of the thermodynamic functions of gases whose molecules do not have degenerate vibrations, were obtained by Gordon [1800]:

$$\Phi^{\circ}_{кол.\,вр} = R\left\{\sum_{s=1} \ln Q_{кол\,(s)} + \ln q'_0 - \ln\sigma + \sum_{s=1} a_s\bar{v}_s + \sum_{s=1} b_{ss}\bar{v}_s^2 + \sum_{s=1}\sum_{m>s} c_{ms}\bar{v}_s\bar{v}_m + \right.$$

$$\left. + \sum_{s=1}\sum_{m>s} y_{ms}\bar{v}_s\bar{v}_m + \frac{1}{12}\left(2\sigma_A + 2\sigma_B + 2\sigma_C - \frac{\sigma_A\sigma_B}{\sigma_C} - \frac{\sigma_B\sigma_C}{\sigma_A} - \frac{\sigma_A\sigma_C}{\sigma_B}\right)\right\}. \quad \text{(II.185)}$$

$$S_{кол.\,вр} = R\left\{\sum_{s=1} \frac{S_{кол\,(s)}}{R} + \ln q'_0 + \frac{3}{2} - \ln\sigma + \sum_{s=1} a_s\bar{s}_s + \sum_{s=1} b_{ss}\bar{s}_s^2 + \right.$$

$$\left. + \sum_{s=1}\sum_{m>s} c_{sm}(\bar{s}_s\bar{v}_m + \bar{s}_m\bar{v}_s - \bar{v}_s\bar{v}_m) + \sum_{s=1}\sum_{m>s} y_{ms}(\bar{s}_s\bar{v}_m + \bar{s}_m\bar{v}_s - 2\bar{v}_s\bar{v}_m)\right\}. \quad \text{(II.186)}$$

The values $\ln Q_{кол\,(s)}$; $\frac{S_{кол\,(s)}}{R}$; $\bar{v}_s$; $\bar{v}_s^2$; $\bar{s}_s$, and $\bar{s}^2$ are found for each vibration by interpolation, using the tables by Gordon and Barnes in the same manner as in the case of diatomic molecules, as functions $\frac{\theta_s}{T} = \frac{hc}{kT}(\omega_s - x_{ss}) = \frac{hc}{kT}\omega^{\circ}_s$ and $x_s = \frac{x_{ss}}{\omega_s - x_{ss}}$ (the values of $\ln Q_{кол\,(s)}$ and $S_{кол\,(s)}/R$ are found by means of two tables for each one (see page 152).**

The other values entering into Eqs. (II.185)-(II.186) are found by the formulas

$$q_0' = \sqrt{\frac{\pi}{A_0 \cdot B_0 \cdot C_0}\left(\frac{kT}{hc}\right)^3}, \qquad \text{(II.187)}$$

$$a_n = \frac{1}{2}\left[\frac{\alpha_n^A}{A_0} + \frac{\alpha_n^B}{B_0} + \frac{\alpha_n^C}{C_0}\right], \qquad \text{(II.188)}$$

$$b_{nn} = \frac{1}{4}\left\{\frac{\alpha_n^A \alpha_n^B}{A_0 B_0} + \frac{\alpha_n^A \alpha_n^C}{A_0 C_0} + \frac{\alpha_n^B \alpha_n^C}{B_0 C_0} + \frac{3}{2}\left[\left(\frac{\alpha_n^A}{A_0}\right)^2 + \left(\frac{\alpha_n^B}{B_0}\right)^2 + \left(\frac{\alpha_n^C}{C_0}\right)^2\right]\right\}, \qquad \text{(II.189)}$$

$$c_{nm} = \frac{1}{4}\left\{\frac{\alpha_n^A \alpha_m^B + \alpha_m^A \alpha_n^B}{A_0 B_0} + \frac{\alpha_n^A \alpha_m^C + \alpha_m^A \alpha_n^C}{A_0 C_0} + \frac{\alpha_n^B \alpha_m^C + \alpha_m^B \alpha_n^C}{B_0 C_0} + 3\left[\frac{\alpha_n^A \alpha_m^A}{A_0^2} + \frac{\alpha_n^B \alpha_m^B}{B_0^2} + \frac{\alpha_n^C \alpha_m^C}{C_0^2}\right]\right\}, \qquad \text{(II.190)}$$

$$y_{nm} = -\frac{hc}{kT} x_{nm} \quad (n < m), \qquad \text{(II.191)}$$

$$\sigma_A = \frac{hc}{kT} A_0, \qquad \text{(II.192)}$$

$$\sigma_B = \frac{hc}{kT} B_0, \qquad \text{(II.193)}$$

$$\sigma_C = \frac{hc}{kT} C_0. \qquad \text{(II.194)}$$

The symbols in these formulas mean: ω_n is the oscillation frequency x_{nm} are the anharmonicity constants; A_0, B_0, C_0 are the rotational constants, α_n^A, α_n^B, α_n^C are the constants of the vibrational-rotational interaction (see §4).

On the basis of Gordon's paper [1803], formulas may also be obtained for the calculation of the vibrational-rotational components of thermodynamic functions of gases whose molecules are linear and, therefore, possess degenerate vibrations (neglecting the centrifugal stress):

$$\Phi^*_{\text{кол. ар}} = R\left[\sum_{n=1} \ln Q_{\text{кол.}(n)} + \ln q_0 + \frac{1}{3q_0} - \ln\sigma + \sum_{n=1} a_n \bar{v}_n + \sum_{n=1} b_{nn} \bar{v}_n^2 + \right.$$
$$\left. + \sum_{n=1}\sum_{m>n} c_{nm} \bar{v}_n \bar{v}_m + \sum_{n=1}\sum_{m>n} y_{nm} \bar{v}_n \bar{v}_m + \sum_n \frac{y_{ln}}{3}(\bar{v}_n^2 + 2\bar{v}_n)\right], \qquad \text{(II.195)}$$

$$S_{\text{кол. ар}} = R\left[\sum_{n=1} \frac{S_{\text{кол.}(n)}}{R} + \ln q_0 + 1 - \ln\sigma + \sum_{n=1} a_n \bar{s}_n + \sum_{n=1} b_{nn} \bar{s}_n^2 + \right.$$
$$+ \sum_{n=1}\sum_{m>n} c_{nm}(\bar{s}_n \bar{v}_m + \bar{s}_m \bar{v}_n - \bar{v}_n \bar{v}_m) + \sum_{n=1}\sum_{m>n} y_{nm}(\bar{s}_n \bar{v}_m + \bar{s}_m \bar{v}_n - 2\bar{v}_n \bar{v}_m) +$$
$$\left. + \sum_n \frac{y_{ln}}{3}(\bar{s}_n^2 - \bar{v}_n^2 + 2\bar{s}_n - 2\bar{v}_n)\right]. \qquad \text{(II.196)}$$

The following denotations are used in these formulas:

$$a_n = \frac{\alpha_n}{B_{000}}, \qquad \text{(II.197)}$$

$$b_{nn} = a_n^2, \qquad \text{(II.198)}$$

$$c_{nm} = \frac{\alpha_n \alpha_m}{B_{000}^2}, \qquad \text{(II.199)}$$

$$y_{ln} = -\frac{hc}{kT}(g_{nn} + B_{000}). \qquad \text{(II.200)}$$

The values $\ln Q_{kol(n)}$, $\frac{S_{kol(n)}}{R}$, $\bar{v}_n$, $\bar{v}_n^2$, $\bar{s}_n$ and $\bar{s}_n^2$ for nondegenerate vibrations may be found by means of interpolation, using the same tables as in the case of monatomic and diatomic molecules, as a function of θ/T and x. Gordon [1803] compiled for double degenerate vibrations tables of the values of $\ln Q_{kol}$, $\bar{v}$, and $\bar{v}^2$ for the range $0{,}6 \leqslant \frac{\theta}{T} \leqslant 4$ with 0.1 intervals; for the range $0 \leqslant x \leqslant 0{,}020$ with 0.0025 intervals, to $\theta/T = 1.0$ and for the range $1{,}0 \leqslant \frac{\theta}{T} \leqslant 4$ with 0.005 intervals.* The values of S_{kol}/R, $\bar{s}$ and $\bar{s}^2$ for twice generate vibrations are not listed in Gordon's Tables. The values of Q_{kol}, $\bar{v}$, and $\bar{v}^2$ were calculated again on an electronic computer and completed by the values of S_{kol}/R $\bar{s}$, and $\bar{s}^2$ during the preparation of the present Handbook. These tables are compiled in 0.01 steps in the range $0{,}05 \leqslant \theta/T \leqslant 6$, and in 0.001 steps in the range $0 \leqslant x \leqslant 0{,}025$.** The values of $\ln Q_{kol(n)}$ and $S_{kol(n)}/R$ for twice degenerate vibrations as well as those for nondegenerate ones may be found, using the new tables, as a sum of two components: The component of the harmonic oscillator, and the corrections for anharmonicity. In contrast to nondegenerate vibrations, the double values of the components of the harmonic oscillator must be taken in the case of double degenerate vibrations.

The method by Gordon for the calculation of thermodynamic functions of polyatomic gases assumes that the sums over the vibrational states in the expression for $Q_{kol.vr}$ possess finite upper limits, and that the maximum values of the vibrational quantum numbers are determined, as well as in the case of diatomic molecules, for each vibration

by the relation

$$v_{n,\max} \approx \frac{1}{2x_n} \qquad \text{(II.201)}$$

$J_{max} = \infty$ is assumed in the statistical sums over the rotational states.

Example. Let us examine the calculation of the values of $\Phi^*_{kol.vr}$ and $S_{kol.vr}$ for CO_2 at 5000°K using the Gordon method. According to the values of the molecular constants of CO_2 quoted in Table 132, we have: $\omega_1^* = 137.26\ cm^{-1}$; $\omega_2^* = 667.77\ cm^{-1}$; $\omega_3^* = 2374.07\ cm^{-1}$; $\frac{\theta_1}{T} = \frac{1936,03}{T}$; $\frac{\theta_2}{T} = \frac{960,59}{T}$;

$\frac{\theta_3}{T} = \frac{3415,10}{T}$; $x_1 = 0,0016329$; $x_2 = 0,0011231$; $x_3 = 0,0052484$; $q_0 = 1,781568 \cdot T$; $\frac{1}{3q_0} = \frac{0,18710}{T}$; $d_0 = 1,096 \cdot 10^{-6} T$; $y_1 = -\frac{2,0298}{T}$; $y_{12} = -\frac{5,40376}{T}$; $y_{13} = \frac{26,66979}{T}$; $y_{23} = \frac{17,95248}{T}$; $a_1 = 2,79344 \cdot 10^{-3}$; $a_2 = -1,87084 \cdot 10^{-3}$; $a_3 = 7,86776 \cdot 10^{-3}$; $b_{11} = 7,80331 \cdot 10^{-6}$; $b_{22} = 3,50004 \cdot 10^{-6}$; $b_{33} = 6,19016 \cdot 10^{-5}$; $c_{12} = -1,04521 \cdot 10^{-3}$; $c_{13} = 4,39562 \cdot 10^{-3}$; $c_{23} = -2,94386 \cdot 10^{-5}$.

At 5000°K, we have $q_0 = 8907,9$; $\frac{1}{3q_0} = 0,0000$; $d_0 = 0,0055$; $y_1 = -0,00041$; $y_{12} = -0,00109$; $y_{13} = 0,00533$; $y_{23} = 0,00359$.

In the tables of the thermodynamic functions of the harmonic oscillator we find: $\frac{\Phi_1^*}{R} = 1,1353$; $\frac{\Phi_2^*}{R} = 1,7442$; $\frac{\Phi_3^*}{R} = 0,7034$; $\frac{S_1}{R} = 1,9540$; $\frac{S_2}{R} = 2,6512$ and $\frac{S_3}{R} = 1,4004$ as functions of θ/T. In the tables of the values of $\Delta \ln Q_{kol}$, $\frac{\Delta S_{kol}}{R}$, $\bar{v}$, $\bar{v}^2$, $\bar{s}$, $\bar{s}^2$ (as functions of θ/T and x) for nondegenerated vibrations we find: $\Delta \ln Q_{kol\,(1)} = 0,0035$; $\Delta \ln Q_{kol\,(3)} = 0,0154$; $\bar{v}_1 = 2,158$; $\bar{v}_3 = 1,059$; $\bar{v}_1^2 = 11,60$; $\bar{v}_3^2 = 3,43$; $\frac{\Delta S_{kol\,(1)}}{R} = 0,0175$; $\frac{\Delta S_{kol\,(3)}}{R} = 0,0327$; $\bar{s}_1 = 4,800$; $\bar{s}_3 = 2,581$; $\bar{s}_1^2 = 34,45$; $\bar{s}_3^2 = 11,67$. In similar tables for double degenerate vibrations, we find: $\Delta \ln Q_{kol\,(2)} = 0,0346$; $\bar{v}_2 = 9,838$; $\bar{v}_2^2 = 157,57$, $\frac{\Delta S_{kol\,(2)}}{R} = 0,0732$; $\bar{s}_2 = 21,058$; $\bar{s}_2^2 = 503,47$. If we substitute all the required values into Eqs. (II.195) and (II.196), we finally obtain for 5000°K:

$$\Phi^{\circ}_{\text{кол. вр}} = 1{,}98726\,(1{,}1438 + 3{,}5230 + 0{,}7188 + 9{,}0947 + 0{,}0000 - 0{,}6931 + 0{,}0055 + 0{,}0050 + 0{,}0084 - 0{,}0184 + 0{,}0001 + 0{,}0006 + 0{,}0002 - 0{,}0002 + 0{,}0001 - 0{,}0003 - 0{,}0229 + 0{,}0123 + 0{,}0378 - 0{,}0248) = 27{,}4075 \text{ cal/mole·degree}$$

$$S_{\text{кол. вр}} = 1{,}98726\,(1{,}9715 + 5{,}3756 + 1{,}4331 + 9{,}0947 + 1 - 0{,}6931 + 0{,}0110 + 0{,}0134 - 0{,}0394 + 0{,}0203 + 0{,}0003 + 0{,}0018 + 0{,}0007 - 0{,}0007 + 0{,}0004 - 0{,}0011 - 0{,}0542 + 0{,}0324 + 0{,}0965 - 0{,}0523) = 36{,}1898 \text{ cal/mole·degree}$$

The Kassel Method. Kassel [2332] proposed the following equation

$$Q_{\text{кол. вр}} = \frac{1}{\sigma} \frac{q_0}{(1-z_1)(1-z_2)^2(1-z_3)} \alpha. \qquad \text{(II.202)}$$

for the calculation of the vibrational-rotational sum of triatomic linear molecules. The correction α may be calculated by the formula

$$\alpha = \sum_{i,j,k} Y_{ijk} \Pi_{i;k} \quad (i + j + k \geqslant 0). \qquad \text{(II.203)}$$

where

$$Y_{ijk} = \sum_{\alpha=0,\ \beta=0,\ \gamma=0} C_{\alpha\beta\gamma} \Gamma_{i-\alpha,\ j-\beta,\ k-\gamma}; \qquad \text{(II.204)}$$

$C_{\alpha\beta\gamma}$ are the coefficients for the expansion of the exponentials, which contain the anharmonicity constants, into a Taylor series:

$$\exp\left[\sum_{n}\sum_{m>n}\left(-\frac{hc}{kT} x_{nm} v_n v_m\right)\right] = \sum_{\alpha,\beta,\gamma} C_{\alpha\beta\gamma} v_1^{\alpha} v_2^{\beta} v_3^{\gamma}; \qquad \text{(II.205)}$$

thus,

$$C_{000} = 1,$$

$$C_{100} = C_{010} = C_{001} = 0,$$

$$C_{200} = -\frac{hc}{kT} x_{11},$$

$$C_{020} = -\frac{hc}{kT} x_{22},$$

$$C_{002} = -\frac{hc}{kT} x_{33};$$

the values of Γ are determined by the following relation:

$$\Gamma_{\phi,\psi,\xi} = \sum_{x=0}^{x=4} M_x L_{\phi,\psi,\xi}. \qquad \text{(II.206)}$$

where

$$M_1 = -\frac{10k_1 + 8k_2}{15},$$

$$M_2 = -\frac{5k_1 - 8k_2}{15},$$

$$M_3 = \frac{4}{5}k_2; \quad M_4 = \frac{1}{5}k_2,$$

$$k_1 = g + \frac{1}{q_0}, \quad k_2 = \frac{g^2}{2} + \frac{g}{q_0},$$

$$g = \frac{hc}{kT}g_{22}.$$

The quantities L in Eq. (II.206) are coefficients of the series obtained after expansion of $B_{v_1v_2v_3}$ with respect to the powers of $\underline{v}$:

$$L_{\phi,\varphi,\xi} = \frac{(\psi+\varphi+\xi)!}{\psi!\,\varphi!\,\xi!} \cdot \frac{\alpha_1^{\psi}\cdot\alpha_2^{\varphi}\cdot\alpha_3^{\xi}}{B_{000}^{(\psi+\varphi+\xi)}}, \qquad \text{(II.207)}$$

i.e., $L_{000} = 1, L_{100} = \frac{\alpha_1}{B_{000}}, L_{110} = \frac{\alpha_1\alpha_2}{B_{000}^2}$, etc.

The quantity Π_{ijk} in the expression (II.203) has the form

$$\Pi_{ij} = f_i^{(1)}F_j^{(2)}f_k^{(3)}, \qquad \text{(II.208)}$$

where $f_i^{(1)}$ and $f_k^{(3)}$ (the upper symbol to the right denotes the number of vibrations) correspond to nondegenerate vibrations and are calculated by means of the equations cited on page 157 for diatomic molecules; $F_j^{(2)}$ corresponds to the degenerate vibration and is equal to

$$F_j^{(2)} = (f_{j+1}^{(2)} + f_j^{(2)})(1 - z_2). \qquad \text{(II.209)}$$

The definitive formulas for the calculation by the Kassel method of the vibrational-rotational components of the thermodynamic functions of gases consisting of triatomic linear molecules may be represented as follows:

$$\Phi^{\circ}_{\text{кол. вр}} = \Phi^{\circ}_{\text{ж. р. г. о}} + R\ln\alpha, \qquad \text{(II.210)}$$

$$S_{\text{кол. вр}} = S_{\text{ж. р. г. о}} + R\left(\ln\alpha + T\frac{\partial}{\partial T}\ln\alpha\right), \qquad \text{(II.211)}$$

where $\Phi^{*}_{\text{zh.r.g.o}}$ and $S_{\text{zh.r.g.o}}$ are the corresponding components calculated in the rigid rotator-harmonic oscillator model approximation,

and

$$T\frac{\partial}{\partial T}\ln\alpha = T\frac{\partial}{\partial T}\Delta + \ldots, \qquad \text{(II.212)}$$

where $\Delta = 1 - \alpha$.

In the Kassel method, the upper limits in the sums over v and J, as well as in diatomic molecules, are assumed as infinite.

The method of Pennington and Kobe. The method of Pennington and Kobe [3221] for the calculation of thermodynamic functions of polyatomic gases is applicable for both linear molecules and for molecules of the type of symmetric, asymmetric and spherical top, and it allows for the anharmonicity of the vibrations and also for the interactions between the vibrations and the rotation. The formula for $\Phi^{*}_{\text{kol.vr}}$ for the calculation by the Pennington-Kobe method has the form

$$\Phi^{\circ}_{\text{кол. вр}} = \Phi^{\circ}_{\text{м. р. г. о}} + R\left[\sum_n d_n r_n {}^{1}\varphi_n + \frac{1}{2}\sum_n d_n (d_n + 1) X_{nn} {}^{2}\varphi_n + \sum_{n<m} d_n d_m X_{nm} {}^{1,1}\varphi_{n,m}\right], \qquad \text{(II.213)}$$

where d_n is the degree of degeneracy of the nth vibration,

$$X_{nn} = -\frac{x_{nn} + g_{nn}\frac{B}{\nu_n}}{\nu_n}, \qquad \text{(II.214)}$$

$$X_{nm} = -\frac{x_{nm}}{\sqrt{\nu_n \nu_m}}. \qquad \text{(II.215)}$$

${}^{k}\varphi_n$ are the functions $\frac{\theta_n}{T} = \frac{hc}{kT}\nu_n$; ν_n is the fundamental frequency (in cm^{-1}) of the nth vibration; the values of ${}^{k}\varphi_n$ are tabulated in the paper by Pennington and Kobe for the values of $\frac{\theta_n}{T} = \frac{hc}{kT}\nu_n$ from 0.20 to 10.00 and for k from 1 to 11; r_n is the function of the constants of interaction between the rotations and the vibration; the values of r_n for molecules of different types are determined by the following relations:

I. Linear molecules: $r_n = b_n + b_n^2$. (II.216)

II. Spherical tops: $r_n = \frac{3b_n}{2} + \frac{15b_n^2}{8}$. (II.217)

III. Symmetrical tops: $r_n = \frac{3b_n}{2} + \frac{15b_n^2}{8}$. (II.218)

IV. Asymmetrical tops: $r_n = \frac{a_n + b_n + c_n}{2} + \frac{a_n^2 + b_n^2 + c_n^2}{4} + \frac{(a_n + b_n + c_n)^2}{4}$. (II.219)

a_n, b_n, c_n in the formulas (II.216)-(II.219) are the coefficients of the developments

$$A_{v_1v_2\ldots} = A_{000} - \Sigma a_n v_n, \qquad B_{v_1v_2\ldots} = B_{00} - \Sigma b_n v_n,$$
$$C_{v_1v_2\ldots} = C_{000} - \Sigma c_n v_n,$$

i.e.,

$$a_n = \frac{a_n^A}{A_{000}}; \quad b_n = \frac{a_n^B}{B_{000}}; \quad c_n = \frac{a_n^C}{C_{000}}.$$

The formulas cited made it evident that the Pennington-Kobe method is essentially an expansion of the Mayer and Goeppert-Mayer method on polyatomic molecules and, therefore, it does not possess advantages with regard to accuracy of the calculation in comparison with the Kassel method, and, moreover, with the Gordon method.

Allowing for centrifugal stress. It was assumed in the approximate methods of calculation of the vibrational-rotational components of the thermodynamic functions of polyatomic gases, cited above, that a centrifugal stress of the molecules caused by rotation is absent. The effect of this phenomenon on the energy of the rotational states is insufficiently investigated.

A method to take into account the centrifugal stress of polyatomic gases was for the first time developed in a general form by Wilson [4287], who proposed for the statistical sum over the states of a nonrigid molecule an expression of the form

$$Q_{zp} = Q_{zh.r}(1 + \rho_1 T), \qquad (II.220)$$

where $Q_{zh.r}$ is the statistical sum over the states of the rigid rotator, ρ_1 is a constant which characterizes the centrifugal stress of the given molecule during rotation.

Khachkuruzov and Milevskaya [448] have shown that the equation (II.220) is a first approximation, and that the expression in the parentheses must be completed by terms which are proportional to a higher power of T:

$$Q_{вр} = Q_{вн.р}\,(1 + \rho_1 T + \rho_2 T^2). \qquad \text{(II.221)}$$

Based on Eq. (II.221), the corresponding components of the thermodynamic functions have the form

$$\Phi^{\circ}_{вр} = \Phi^{\circ}_{вн.р} + R \ln (1 + \rho_1 T + \rho_2 T^2), \qquad \text{(II.222)}$$

$$S_{вр} = S_{вн.р} + R\left[\ln (1 + \rho_1 T + \rho_2 T^2) + \frac{\rho_1 T + 2\rho_2 T^2}{1 + \rho_1 T + \rho_2 T^2}\right]. \qquad \text{(II.223)}$$

In the case of linear molecules and of molecules of the type of spherical top, as well as in the case of diatomic molecules we have

$$\rho_1 = \frac{d_0}{T}, \qquad \text{(II.224)}$$

$$\rho_2 = \frac{3d_0^2}{T}, \qquad \text{(II.225)}$$

where d_0 is immediately referred to the constant D_0 of the centrifugal stress of the molecule:

$$d_0 = \frac{2D_0}{B_0^2} \cdot \frac{kT}{hc}.$$

Substituting (II.224) and (II.225) into the Eqs. (II.222) and (II.223) and expanding the expression $\ln (1 + \rho_1 T + \rho_2 T^2)$ into a power series, one may obtain more simple formulas for allowance for the centrifugal stress in the case of linear molecules or of molecules of the type of spherical top:

$$\Phi^{\circ}_{вр} = \Phi^{\circ}_{вн.р} + R\,(d_0 + 2{,}5d_0^2), \qquad \text{(II.226)}$$

$$S_{вр} = S_{вн.р} + R\,(2d_0 + 7{,}5d_0^2). \qquad \text{(II.227)}$$

Yungman [474] has shown that in the case of symmetrical tops the constants ρ_1 and ρ_2 may be expressed by the constants D_J, D_{JK} and D_K of the centrifugal stress:

$$\rho_1 = \frac{1}{4}\frac{k}{hc}\left[\frac{8}{B_0^2}D_J + \frac{4}{B_0C_0}\left(D_J + \frac{1}{2}D_{JK}\right) + \frac{3}{C_0^2}(D_J + D_{JK} + D_K)\right], \quad \text{(II.228)}$$

$$\rho_2 = \frac{3}{32}\left(\frac{k}{hc}\right)^2\left[\frac{128}{B_0^4}D_J^2 + \frac{32}{B_0^3C_0}(6D_J^2 + D_JD_{JK}) + \frac{8}{B_0^2C_0^2}(6D_J^2 + 2D_JD_K + 6D_JD_{JK}) + \right.$$

$$\left. + \frac{20}{B_0C_0^3}(2D_J^2 + D_{JK}^2 + 2D_JD_K + 3D_JD_{JK} + D_{JK}D_K) + \frac{35}{C_0^4}(D_J + D_{JK} + D_K)^2\right]. \quad \text{(II.229)}$$

The constants of the centrifugal stress are unknown for molecules of the type of asymmetric top. Wilson [4287] proposed a method of calculating the constant ρ_1 in Eq. (II.220) in terms of the values of the fundamental oscillation frequencies and the moments of inertia of the molecule. Khachkuruzov and Milevskaya [448] improved and generalized the Wilson method and developed similar relations for the calculation of the constant ρ_2. These are not cited in this Handbook due to their cumbersome form, and they may be found in the papers [4287, 448, 449].

§13. ALLOWING FOR THE INTERNAL ROTATION OF MOLECULES IN THE CALCULATION OF THERMODYNAMIC FUNCTIONS OF GASES

There exist a great number of molecules in which internal rotation of separate atom groups (CH_3, NH_2, OH, for example) takes place around the single bonds which connect these groups with the remaining part (the frame) of the molecule. Such a rotation is termed internal rotation, and the rotating atom group is termed a top. The internal rotation is rarely absolutely free: in most cases a deceleration takes place due to the interaction between the atoms of the top and of the frame, and this retardation is so intense at low temperatures that the top performs torsional oscillations around the equilibrium instead of rotation. At high temperatures, the internal rotation of the separate groups is almost free.

The potential function of the internal rotation must be known in order to calculate the thermodynamic functions in the presence of a retarded internal rotation. Pitzer and Gwinn [3259] had shown that in

the case of a symmetrical top this function may be represented in good approximation in the form

$$V = \frac{1}{2} V_0 (1 - \cos n\varphi), \qquad \text{(II.230)}$$

where V_0 is the height of the potential barrier, n is the number of maxima on the potential curve, and φ is the deflection angle of the top with respect to the frame. The form of the potential function must be considerably more complex in the case of asymmetrical tops because the height of the diverse maxima is, in general, unequal in this case. The lack of complete investigations of this problem, however, forces the application of Eq. (II.230) as a potential function of the internal rotation of asymmetric tops under the condition that V_0 is the effective height of the potential barrier.

Let us examine the method of calculation of thermodynamic functions of a gas which consists of molecules in which a retarded internal rotation of one asymmetric top takes place, developed in the papers by Pitzer and Gwinn [3259] and Pitzer [3255].* (In the case of several tops, the same method is applied to each of them as in the case of a single top, and the components of the thermodynamical functions caused by the presence of internal rotations are summed over the tops). The calculation is carried out in the harmonic oscillator - rigid rotator model approximation with the exception that one vibrational degree of freedom, which corresponds to the torsional oscillation, is substituted by the rotational degree of freedom; the corresponding contribution to the thermodynamical functions is denoted as $\Phi^*_{zat.vr}$ and $S_{zat.vr}$.

The values of $\Phi^*_{zat.vr}$ and $S_{zat.vr}$ are determined by means of special tables compiled by Pitzer and Gwinn [3259]. The differences $\Phi^*_{sv.vr} - \Phi^*_{zat.vr}$ and $S_{sv.vr} - S_{zat.vr}$ between the components of the free and retarded internal rotation in the values of the thermodyna-

mic functions are quoted in these tables. These values are listed in the tables by Pitzer and Gwinn as a function of the arguments V_0/RT and $1/Q_{sv.vr}$, where V_0 is the height of the potential barrier (in cal/mole·degree), and $Q_{sv.vr}$ is the statistical sum over the states of free internal rotation, equal to

$$Q_{св.вр} = \frac{i}{n} \frac{2\pi (2kTI_{пр})^{1/2}}{h}; \qquad \text{(II.231)}$$

where n is the number of maxima on the potential curve; I_{pr} is the reduced moment of inertia of the top.

The corresponding components of the thermodynamic functions have the form

$$\Phi^{\circ}_{св.вр} = 2{,}28792 \lg T + 2{,}28792 \lg (I_{пр} \cdot 10^{40}) - 4{,}57584 \lg n - 2{,}5346. \qquad \text{(II.232)}$$

$$S_{св.вр} = 2{,}28792 \lg T + 2{,}28792 \lg (I_{пр} \cdot 10^{40}) - 4{,}57584 \lg n - 1{,}5410. \qquad \text{(II.233)}$$

The method of calculating the reduced moment of inertia of the asymmetric top is developed by Pitzer in the paper [3255].

One must find the major central axes of inertia 1, 2, and 3, and the principal moments of inertial I_A, I_B and I_C with respect to these axes for the whole molecule with the mass M, including the rotating group in the equilibrium state; then the coordinate axes of the top are drawn in such a manner that the z axis coincides with the rotation axis of the top, the x axis goes through the center of gravity of the top and is perpendicular to the z axis, and the y axis goes through the point of intersection of the x and z axes and is perpendicular to them. The atoms of the top lying on the rotation axis z are excluded from the following consideration.

If m_k is the mass of the kth atom of the top, than $A = \sum_k m_k (x_k^2 + y_k^2)$ is the moment of inertia of the top with respect to the z axis;

$B = \sum_k m_k x_k z_k$ and $C = \sum_k m_k y_k z_k$ are the products of inertia,

$U = \sum_k m_k x_k$ is the unbalance factor of the top.

Then the direction cosines of the axes x, y, and z with respect to the axes 1, 2, and 3 must be found:

$$\alpha^{1x}\ \alpha^{2x}\ \alpha^{3x}$$

$$\alpha^{1y}\ \alpha^{2y}\ \alpha^{3y}$$

$$\alpha^{1z}\ \alpha^{2z}\ \alpha^{3z}$$

The direction of the axes is chosen in such a manner that both systems are either right or left systems. The determinant formed by the direction cosines is equal to +1 in this case, which fact may be used to check the correctness of the calculation of the direction cosines.

Let us denote the vector from the gravity center of the molecule to the gravity center of the top by $\vec{r}$, and its projections on the axes of inertia of the molecule by $r^{(1)}$, $r^{(2)}$, and $r^{(3)}$. Thus, the reduced moment of inertia of one asymmetric top has the following form:

$$I_{ap} = A - \sum_{i=1,2,3} \left[\frac{(\alpha^{iy} U_i)^2}{M} + \frac{(\beta^{(i)})^2}{I_i} \right], \qquad \text{(II.234)}$$

where $\beta^{(i)} = \alpha^{iz} A - \alpha^{ix} B - \alpha^{iy} C + U\,(\alpha^{i-1,y} r^{(i+1)} - \alpha^{i+1,y} r^{(i-1)})$.

The indices i, i - 1, and i + 1 may assume the values 1, 2, and 3 (in a cyclic sequence), thus, the index i - 1 is equal to 3 if i= 1, and i + 1 is equal to 1 if i = 3.

It must be noted that in the case of a balanced asymmetric top (i.e., if the rotation axis of the top coincides with one of the principal axes of inertia) and also in that of a symmetric top, the expression (II.234) obtains a more simple form:

$$I_{ap} = A\left[1 - \sum_{i=1,2,3} \frac{A}{I_i} (\alpha^{iz})^2\right]. \qquad \text{(II.235)}$$

This equation is given by Pitzer and Gwinn in the paper [3259].

The formulas for the calculation of the components of the internal rotation in the values of Φ_T^* and S_T° in the case of a molecule with a single top have the form

$$\Phi^{*}_{\text{вн. вр}} = \Phi^{*}_{\text{св. вр}} - (\Phi^{*}_{\text{св. вр}} - \Phi^{*}_{\text{заг. вр}}) + 4{,}57584 \lg \frac{n}{\sigma_i}. \qquad \text{(II.236)}$$

$$S_{\text{вн. вр}} = S_{\text{св. вр}} - (S_{\text{св. вр}} - S_{\text{заг. вр}}) + 4{,}57584 \lg \frac{n}{\sigma_i}. \qquad \text{(II.237)}$$

σ_i is in Eqs. (II.236) and (II.237) the symmetry number of the top with respect to the rotation axis. We must remember that the components of the torsional oscillation are neglected in the values of $\Phi^{*}_{g.o}$ and $S_{g.o}$ in this method of allowance for internal rotation.

§14. ALLOWANCE OF MULTIPLICITY AND EXICTED ELECTRON STATES OF MOLECULES IN APPROXIMATE CALCULATION METHODS! GENERAL RELATIONS

Above we have discussed the various methods of calculation of the vibrational and rotational components of the thermodynamic functions of polyatomic gases. The corresponding equations were obtained by assuming that the ground states of the gas molecules are singlet states, and the existence of excited states may be neglected. A number of polyatomic molecules, however, including such which are dealt with in this Handbook, possess free electrons, and, therefore, must possess multiplet electronic states. This circumstance was not sufficiently taken into account up to lately calculations of thermodynamic gas functions, and the calculations were carried out in the majority of the papers as if the ground states of the polyatomic molecules were singlet states.

The most simple method to allow for the multiplicity of the electron states of polyatomic gases is, as well as in the case of diatomic gases, the inclusion of the addends R ln p_M into the equation for the calculation of Φ^{*}_{T} and S°_{T} where p_M is the statistical weight of the corresponding electronic state. As was noted above (see page 94), the same systematics is chosen for linear polyatomic molecules as for diatomic ones. Therefore, the values of p_M for different electronic states of linear polyatomic molecules may be found in Table 7.

The statistical weights of some types of electronic states of nonlinear polyatomic molecules are quoted in Table 12. It must be noted, however, that the electronic spectra of almost all polyatomic radicals which possess free electrons are not investigated, and the type of the ground electronic state is not determined. The statistical weight 2 is in this Handbook ascribed to all electronic states of molecules which possess one free electron (with exlucion of BO_2).

TABLE 12

Statistical Weights of Several Electronic States of Nonlinear Polyatomic Molecules.

Тип состояния A	$^1A_1$	$^2A_1$	$^3A_1$	$^1A_2$	$^2A_2$	$^3A_2$	$^1B_1$	$^2B_1$	$^3B_1$
B Статистический вес	1	2	3	1	2	3	1	2	3

A) Type of the state; B) statistical weight.

Several investigators assumed that ground electronic states with two or more free electrons are possible in several polyatomic molecules or radicals, as, for example, in CH_2 or C_3. This assumption has not been proved to be valid up to the present for the compounds which are dealt with in the Handbook. In this Handbook it is assumed that the ground electronic states of polyatomic molecules, which possess an even number of electrons, are singlet states. The statistical weights of the ground states pf nonlinear molecules with an even number of electrons is equal to 1 because stable electronis states of nonlinear molecules can not be degenerate.

The constants of the multiplet splitting of polyatomic molecules are generally unknown, thus, one must restrict oneself to inclusion of the values of $R \ln p_M$ into the values of Φ_T^* and S_T° when calculating the thermodynamic functions. If the constants of the multiplet splitting of the polyatomic molecule are well known, the effect

of the splitting of the rotational levels on the thermodynamic functions may be taken into account by transformating the equations for the calculation of Q_{vn}, as it was carried out in the case of diatomic gases. In particular, calculation of the values of $\Phi^*_{kol.vr}$ and $S_{kol.vr}$ may be carried out immediately by means of the equations cited in §9 in the case of gases with linear molecules.

Data on excited electronic states are missing or uncoordinated for the majority of simple polyatomic molecules. The vibrational and rotational constants of molecules in excited states are usually unknown (with the exclusion of some simple molecules of the type HCN, C_2H_2, HCO, and ClO_2), and the energies of these states possess values in the order of 15,000-20,000 cm^{-1} and higher. Taking into account that the accuracy of the calculation of thermodynamic functions of polyatomic gases is generally lower than in the case of diatomic ones, a method may be used to allow for the excited states of polyatomic molecules at all temperatures, which is based on the assumption that the vibrational and rotation constants of the molecule are equal in all electronic states.

Thus, (in the same manner as for diatomic gases, see Eqs. (II.120) and (II.121), we have

$$\Phi^*_{эл} = \Phi^*_{кол.\ вр} + \Delta\Phi^*_{эл} = \Phi^*_{кол.\ вр} + R \ln (1 + \delta),$$

$$S_{эл} = S_{кол.\ вр} + \Delta S_{эл} = S_{кол.\ вр} + R\left[\ln (1 + \delta) + \frac{\delta}{1+\delta} T \frac{\partial}{\partial T} \delta\right],$$

where, (see page 180)

$$\delta = \sum_i \frac{p_i}{p_x} \exp\left(-\frac{hc}{kT} \nu^{(i)}_{\omega}\right),$$

$$T \frac{\partial}{\partial T} \delta = \sum_i \frac{p_i}{p_x} \cdot \frac{hc}{kT} \nu^{(i)}_{\omega} \exp\left(-\frac{hc}{kT} \nu^{(i)}_{\omega}\right).$$

The formula cited for δ may be made more accurate for cases in which the transition of the molecule into the excited state is accom-

panied by a change of its structure and a change of the number of rotational degrees of freedom, as well as was done for diatomic gases (Eq. II.125) taking into account the differences of the constants of the gas molecules in the ground and in the excited state. We then have

$$\delta = \sum_i \frac{p_i}{p_X} \frac{\prod_n (1-z_X)_n^{d_n}}{\prod_n (1-z_i)_r^{d_n}} \cdot \frac{Q_{\text{кл. р}}^{(i)}}{Q_{\text{кл. р}}^{(X)}} \exp\left(-\frac{hc}{kT} \nu_{00}^{(i)}\right), \qquad \text{(II.238)}$$

where $\frac{1}{(1-z_i)_n}$ is the component of the nth vibration of the molecule in the ith electronic state; d_n is the degree of degeneracy of the nth vibration; the upper limits of the derivatives with respect to n may be different for the given molecule if the latter possesses a linear structure in one and a nonlinear structure in other states, or if the number of degenerate states changes; $Q_{\text{кл. р}}^{(i)} = \frac{kT}{hcB_0}$ is valid for linear molecules and $Q_{\text{кл. р}}^{(i)} = \sqrt{\frac{\pi}{ABC}\left(\frac{kT}{hc}\right)^3}$ is valid for molecules of the other types.

Based on these statements, the relations for the calculation of the thermodynamic functions of gases may be written down as follows:

$$\Phi_T^\circ = \Phi_{\text{пост}}^\circ + \Phi_{\text{г. о}}^\circ + \Phi_{\text{кл. р}}^\circ + R \ln \Sigma + R \ln (1 + \rho_1 T + \rho_2 T^2) + R \ln p_M + \Delta\Phi_{\text{эл}}^\circ + \Phi_{\text{эл. яр.}}^\circ \qquad \text{(II.239)}$$

$$S_T^\circ = S_{\text{пост}}^\circ + S_{\text{г. о}} + S_{\text{кл. р}} + R\left[\ln \Sigma + T\frac{\partial}{\partial T} \ln \Sigma\right] + R \ln p_M + R\left[\ln (1 + \rho_1 T + \rho_2 T^2) + \frac{\rho_1 T + 2\rho_2 T^2}{1 + \rho_1 T + \rho_2 T^2}\right] + \Delta S_{\text{эл}} + S_{\text{эл. яр.}} \qquad \text{(II.240)}$$

where R ln Σ and $RT\frac{\partial}{\partial T} \ln \Sigma$ are corrections for the vibrational anharmonicity and the interaction between rotation and vibrations. These corrections may be calculated, in accordance with the chosen method of calculation, by means of the relations (II.185), (II.186); (II.195), (II.196); (II.210), (II.211) or (II.213); $R \ln (1 + \rho_1 T + \rho_2 T^2)$ and $R \ln (1 + \rho_1 T + \rho_2 T^2) + \frac{\rho_1 T + 2\rho_2 T^2}{1 + \rho_1 T + \rho_2 T^2}$ are corrections of the centrifugal stress: R ln p_M, $\Delta\Phi_{el}^*$ and ΔS_{el} are corrections of the multiplicity of the ground state and the presence of excited electronic states of the

gas molecules; $\Phi^*_{vn.vr}$ and $S_{vn.vr}$ are corrections of the internal rotation of the molecules.

It must be remembered that, as well as in the case of diatomic molecules, the values of θ_n/T, necessary for finding $\Phi^*_{g.o}$ and $S_{g.o}$ in the tables of the harmonic oscillator, are calculated on the basis of different frequencies, depending on the method chosen to calculate Φ^*_T and S^o_T: thus, $\theta_n/T = \frac{hc}{kT}(\omega_n - x_{nn})$, holds true for the Gordon method; $\theta_n/T = \frac{hc}{kT}\omega^0_n$ holds for the Kassel method, and $\theta_n/T = \frac{hc}{kT}\nu_n$ holds for the Pennington-Kobe method. The constants ω_n and ω^0_n are unknown if the calculations are carried out in the rigid rotator-harmonic oscillator model approximation, and the calculation of $\theta/T = \frac{hc}{kT}\nu_{...}$ is carried out assuming $R \ln \Sigma$, $R \ln (1 + \rho_1 T + \rho_2 T^2)$ and their derivatives as equal to zero.

The relations (II.239)-(II.240) may be transformed by unification of the translational components and the components of the rigid rotator.

Thus, for linear molecules we have

$$\Phi^*_T = \Phi^*_{r.o} + 16{,}01544 \lg T + C_\Phi + 1{,}98726 (\ln \Sigma + \rho_1 T + 2{,}5\rho_2 T^2) + \Delta\Phi^*_{an}. \quad \text{(II.241)}$$

$$S^*_T = S_{r.o} + 16{,}01544 \lg T + C_S + 1{,}98726 \left(\ln \Sigma + T\frac{\partial}{\partial T}\ln \Sigma + 2\rho_1 T + 7{,}5\rho_2 T^2\right) + \Delta S_{an}, \quad \text{(II.242)}$$

and for nonlinear molecules

$$\Phi^*_T = \Phi^*_{r.o} + 18{,}30336 \lg T + C'_\Phi + 1{,}98726 (\ln \Sigma + \rho_1 T + 2{,}5\rho_2 T^2) + \Delta\Phi^*_{an} + \Phi^*_{an.sp}. \quad \text{(II.243)}$$

$$S^*_T = S_{r.o} + 18{,}30336 \lg T + C'_S + 1{,}98726 \left(\ln \Sigma + T\frac{\partial}{\partial T}\ln \Sigma + 2\rho_1 T + 7{,}5\rho_2 T^2\right) + \Delta S_{an} + S_{an.sp}. \quad \text{(II.244)}$$

where

$$C_\Phi = 6{,}86376 \lg M + 4{,}57584 \lg \frac{\varphi_0}{T} + 4{,}57584 (\lg p_M - \lg \sigma) - 7{,}2836, \quad \text{(II.245)}$$

$$C_S = 6{,}86376 \lg M + 4{,}57584 \lg \frac{\varphi_0}{T} + 4{,}57584 (\lg p_M - \lg \sigma) - 0{,}3281, \quad \text{(II.246)}$$

$$C_{\Phi}^{\circ} = 6{,}86376 \lg M + 4{,}57584 \lg \frac{q_0^{\circ}}{T^{3/2}} + 4{,}57584 (\lg p_M - \lg \sigma) - 7{,}2836. \quad \text{(II.247)}$$

$$C_S^{\circ} = 6{,}86376 \lg M + 4{,}57584 \lg \frac{q_0^{\circ}}{T^{3/2}} + 4{,}57584 (\lg p_M - \lg \sigma) + 0{,}6655. \quad \text{(II.248)}$$

If the rotational constants of the gas molecules are unknown and the calculation is carried out in terms of the principal moments of inertia, the Eqs. (II.245)-(II.248) assume the form (according to the values of the physical constants accepted in the Handbook):

$$C_{\Phi} = 6{,}86376 \lg M + 4{,}57584 \lg (I \cdot 10^{39}) + 4{,}57584 (\lg p_M - \lg \sigma) - 10{,}0519, \quad \text{(II.249)}$$

$$C_S = 6{,}86376 \lg M + 4{,}57584 \lg (I \cdot 10^{39}) + 4{,}57584 (\lg p_M - \lg \sigma) - 3{,}0964, \quad \text{(II.250)}$$

$$C_{\Phi}^{\circ} = 6{,}86376 \lg M + 2{,}28792 \lg (I_A \cdot I_B \cdot I_C \cdot 10^{117}) + 4{,}57584 (\lg p_M - \lg \sigma) - 10{,}2986. \quad \text{(II.251)}$$

$$C_S^{\circ} = 6{,}86376 \lg M + 2{,}28792 \lg (I_A \cdot I_B \cdot I_C \cdot 10^{117}) + 4{,}57584 (\lg p_M - \lg \sigma) - 2{,}3495. \quad \text{(II.252)}$$

Finally, it must be remembered that, if internal rotation is lacking, we have

$$\Phi_{r.\,e}^{\circ} = \sum_{n=1}^{n=a} d_n (\Phi_{r.\,e}^{\circ})_n, \qquad S_{r.\,e}^{\circ} = \sum_{n=1}^{n=a} d_n (S_{r.\,e})_n,$$

where $a = 3N - 5 - \sum_{k=1}^{k=b} (d_k - 1)$, is valid in the case of linear molecules, $a = 3N - 6 - \sum_{k=1}^{k=b} (d_k - 1)$ is valid for nonlinear molecules, b is the number of degenerate vibrations; and in the case of molecules with internal rotation we have $a = 3N - 6 - \sum_{k=1}^{k=b} (d_k - 1) - g$; g is the number of the degrees of freedom for the internal rotation. The values of q_0/T and $q_0^{\circ}/T^{3/2}$ in the equations (II.245)-(II.248) are equal to $\frac{k}{hcB_0}$ and $\sqrt{\frac{\pi}{A_0 B_0 C_0}\left(\frac{k}{hc}\right)^3}$, or $\frac{1}{1{,}43879 \cdot B_0}$ and $\sqrt{\frac{\pi}{A_0 B_0 C_0}\left(\frac{1}{1{,}43879}\right)^3}$, respectively.

Division 4. CALCULATION OF THE TABLES OF THERMODYNAMIC GAS FUNCTIONS

§15. ALLOWING FOR THE ISOTOPIC COMPOSITION AND FOR THE NUCLEAR SPINS IN THE CALCULATION OF THERMODYNAMIC FUNCTIONS

In the derivation of the formulas for the calculation of the thermodynamic functions of gases, carried out in the foregoing Divisions it was assumed, that the molecules of the given gas are similar, in particular, that they consist of the same isotopes of elements which form these molecules. In fact, a great number of elements possess two or more stable isotopes, and the relative content of the minor isotope is in many cases (Cl, Br, etc., for example) important (see Supplement 1) and may not be neglected. The natural percentage of the various stable isotopes of an element is almost constant. Gases consisting of molecules formed by elements which possess several isotopes have also an almost constant composition which corresponds to the percentage of the isotopes in question in nature. Gases with such a composition are termed a natural mixture of isotopic molecules.

All gases with the exclusion of the deuterium and tritium compounds are considered in this Handbook as natural mixtures. Therefore, the formulas deduced in the foregoing divisions, strictly speaking, may not be applied immediately for the determination of the thermodynamic functions of these gases. It is necessary to calculate, by means of these formulas, the separate thermodynamic functions of each gas which consists of identical isotopic molecules, to multiply the calculated values with the corresponding molecular parts (proportional to the percentage of the isotopic molecules), to sum up the obtained contributions and to add to the sum found a value, which is constant for the given isotopic mixture and which takes into account the mixture of nonidentical molecules (the so-called mixing entropy) when the thermodynamic functions of a gas must be determined which is

a natural mixture of isotopic molecules. The described way of calculation is cumbersome and, therefore, inconvenient for the application in the practice of calculation of tables of thermodynamic functions of gases. It is possible, however, to use certain simplifications which do not lower substantially the accuracy of the calculations and which make it possible to reduce the calculation to simpler computations similar to those which are used for gases consisting of identical molecules.

If the masses of the individual isotopes are comparable to each other, a fact which is valid for all elements with the exclusion of the lightest (hydrogen, helium and some others) or if the percentage of one of the isotopes is prevalent (which happens in the case of the light elements mentioned above), the thermodynamic functions of the natural mixture of isotopic molecules may be calculated in terms of thermodynamic functions of a gas which consists of identical molecules with a molecular weight and other constants which are "averaged" values of the constants of the molecules which form the given mixture.

Thus, for example, the molecular weight of a gas which consists of molecules with a different isotopic composition, having the molecular weights M_1, M_2, M_3, ... and the molecular parts x_1, x_2, x_3, ... ($\Sigma x_i = 1$), is equal to $M = \sum_i x_i M_i$. In the general case, we have

$$\lg\left(\sum_i x_i M_i\right) \neq \sum_i x_i \lg M_i. \qquad \text{(II.253)}$$

The substitution of the left part of the inequation (II.253) by the right part, however, does not cause errors in the values of Φ^*_{post} and S°_{post} which exceed 0.0005 cal/mole·degree, under the conditions mentioned above ($M_1 \cong M_2 \cong M_3 \cong M_4 \ldots$ or $x_i \cong 1$), which are valid in essence for all elements. Thus, the translational components of the thermodynamic functions of a gas consisting of different isotopic mo-

lecules may be calculated with an accuracy which is sufficient for any problems in practice by means of the averaged molecular weight of the mixture which is equal to the molecular weight of the gas.

The components of the intramolecular degrees of freedom may also be calculated by means of the averaged values of the molecular constants. The energies of the electronic states of atoms and molecules do hardly at all depend on the mass of their nuclei and, therefore, the averaged values are equal to the energies of the electronic states of any isotopic modifications.

The averaged values of the rotational and vibrational constants of diatomic molecules may be calculated by Eqs. (1.43). The constants of the conventional molecule which possesses the mean molecular weight of the isotopic mixture are calculated in terms of ρ on the basis of the constants of any of its isotopic modifications. Thus, for example, the averaged constants of the isotopic BCl mixture are the constants of the conventional molecule $B^{10.82}Cl^{35.457}$ which consists of the hypothetical boron atoms with the atomic weight 10.82, and chlorine with the atomic weight 35.457. Having calculated the reduced mass of this molecule (μ = 8.290181), one may find the averaged values of the constants of BCl, using the value ρ = 1.005014, the Eqs. (1.43) and the constants of the real $B^{11}Cl^{35}$ molecule (μ = 8.373518).

The calculation of the components of the intramolecular degrees of freedom by means of averaged vibrational and rotational constants as well as the calculation of the transitional components, is not fully accurate. In all cases, however, which are dealt with in this Handbook, the corresponding error in the values of the thermodynamic functions does not exceed 0.007 cal/mole·degree in Φ_T^* and S_T°, which may be considered to be satisfactory.

In cases when the thermodynamic functions of gases are calcu-

lated in the rigid rotator-harmonic oscillator model approximation, the gas molecules may be considered as having the same constants and the same molecular weight, i.e., the average molecular weight of the isotopic mixture of gas molecules. This simplification does not cause errors in the values of the thermodynamic functions which exceed the total error of the method. It must be noted, however, that in the present Handbook the atomic weights of the elements are chosen corresponding to the natural mixture of their isotopes for the estimation of the molecular constants and, in particular, for the calculation of the oscillation frequencies and the products of the moments of inertia on the basis of the relations quoted in Supplements 3 and 4. It is evident that the values obtained in this way are averaged constants for the natural mixture of isotopic molecules.

The values of the reduced thermodynamic potential and of the entropy of the gas, calculated by means of averaged molecular constants, are the practical values of these functions (see page 127). The total values of the thermodynamic functions of a gas consisting of isotopic molecules differ from the practical values, apart from the components of nuclear spins, by values caused by the mixing of the isotopic molecules and also by the difference in their symmetry numbers. The difference between the total and the practical values of the thermodynamic functions will in this Handbook be termed the nuclear component. This component (S_{yad}) has the same value in Φ_T^* and in S_T° and is equal to zero in the $H_T^\circ - H_0^\circ$ values.

According to the definition, we have

$$S_{ax} = S_{см.из} + S_{и.с} + S_{см.}. \qquad (II.254)$$

The entropy $S_{sm.iz}$ of isotope mixing may be calulated by the relation

$$S_{см.\,из} = -\sum_i x_i \ln x_i, \qquad \text{(II.255)}$$

where x_i is the molar part of the ith isotopic modification of the gas molecule. The entropy $S_{ya.s}$ of the nuclear spins may be calculated by the formula

$$S_{я.с} = R\sum_i x_i \ln \alpha_i, \qquad \text{(II.256)}$$

where α_i is the statistical weight of the ith isotopic molecule caused by the spins of its nuclei.

In the case of a monatomic gas, we have

$$\alpha_i = 2I_i + 1, \qquad \text{(II.257)}$$

where I is the nuclear spin of the ith isotope. In the case of a diatomic gas, we have

$$\alpha_i = \alpha_1\alpha_2, \qquad \text{(II.258)}$$

where $\alpha_1 = 2I_1 + 1$, $\alpha_2 = 2I_2 + 1$, and I_1, I_2 are the nuclear spins of the atoms which form the molecule. In the case of a polyatomic gas, we have

$$\alpha_i = (\alpha_1^{n_1}\cdot\alpha_2^{n_2}\cdot\alpha_3^{n_3}\cdot\ldots), \qquad \text{(II.259)}$$

where $\alpha_1 = 2I_1 + 1$, $\alpha_2 = 2I_2 + 1$, ..., I_1 is the nuclear spin of the isotope 1, n_1 is the number of atoms of the isotope 1, etc.

The value of S_{sim} which takes into account the difference in the symmetry number of the isotopic modifications of the molecules, may be calculated by the formula

$$S_{сим} = -R(\Sigma x_i \ln \sigma_i - \ln \sigma), \qquad \text{(II.260)}$$

where σ_i is the symmetry number of the ith isotopic molecule, σ is the symmetry number of the hypothetic molecule with averaged values of the molecular constants.

The nuclear component of the thermodynamic functions of gases hardly changes at all in the temperature range in question. This component is equal to the initial and the end products of chemical re-

actions and does not affect the values of the equilibrium constant of the reaction.

Due to this fact, the nuclear component S_{yad} is not included into the values of Φ_T^* and S_T° when calculating the practical values of the thermodynamic function of gases, irrespective of disregarding the composition of the gases which may consist of molecules or of mixtures of isotopes.

Since the nuclear component is equal for the initial substances and for the products of any reaction, its value may easily be calculated for any gas by the relation

$$S_{\text{яд}} = R\sum_A n_A\left[\sum_i x_{A,i}\ln(2I_{A,i}+1) - \sum_i x_{A,i}\ln x_{A,i}\right]. \quad \text{(II.261)}$$

where, in contrast to Eqs. (II.255)-(II.260), n_A is the number of atoms of the element A in the molecules, $x_{A.i}$ and $I_{A.i}$ are the molar part and the nuclear spin of the ith isotope of the element A. Summation is carried out over all elements and isotopes which are part of the composition of the molecule of the given gas.

Let us examine the calculations of S_{yad} on a number of examples.

1. Monatomic chlorine

Isotope	x_i	I_i	α_i
Cl^{35}	0,754	3/2	4
Cl^{37}	0,246	3/2	4

$$S_{\text{я.с}} = 4{,}57584\,(0{,}754\cdot 0{,}60206 + 0{,}246\cdot 0{,}60206) = 2{,}7546 \text{ cal/g-atom·degree}$$

$$S_{\text{см. яд}} = -4{,}57584\,[0{,}754\,(-0{,}12263) + 0{,}246\,(-0{,}60901)] = 1{,}1087 \text{ cal/g-atom·degree}$$

Due to the fact that $S_{sim} = 0$ for a monatomic gas, we have $S_{yad} = S_{ya.s} + S_{sm.iz} = 3.8636$ cal/g-atom·degree.

2. Diatomic chlorine.

Isotopic molecule	x_i^2	α_i	σ_i
$Cl^{35}\ Cl^{35}$	0,5685	16	2
$Cl^{35}\ Cl^{37}$	0,3710	16	1
$Cl^{37}\ Cl^{37}$	0,0605	16	2

a) The values of x_i are calculated as terms of the binomial $(x_{Cl^{35}} + x_{Cl^{37}})^2$ assuming $x_{Cl^{35}} = 0,754$ and $x_{Cl^{37}} = 0,246$.

$$S_{n.c} = 4,57584\ (0,5685 \cdot 1,20412 + 0,3710 \cdot 1,20412 + 0,0605 \cdot 1,20412) = 4,57584 \cdot 1,20412 = 5,5098 \text{ cal/mole·degree}$$

$$S_{см.вз} = -4,57584\ [0,5685\ (-0,2453) + 0,3710(-0.4306) + 0,0605\ (-1,2182)] = 1,7037 \text{ cal/mole·degree}$$

$$S_{сим} = -4,57584\ [0,5685 \cdot 0,30103 + 0,0605 \cdot 0,30103 - 0,30103] = 0,5110 \text{ cal/mole·degree}$$

$$S_{яд} = S_{n.c} + S_{см.вз} + S_{сим} = 7,7275.$$

It is easily noticeable that the obtained value $S_{yad} = 7.7275$ is accurately the doubled value of the S_{yad} for atomic chlorine.

3. Carbon tetrachloride.

Isotopic molecule	x_i^2	α_i	σ_i
CCl_4^{35}	0,3232	256	12
$CCl_3^{35}Cl^{37}$	0,4216	256	3
$CCl_2^{35}Cl_2^{37}$	0,2065	256	2
$CCl^{35}Cl_3^{37}$	0,0449	256	3
CCl_4^{37}	0,0037	256	12

a) The values of x_i are calculated as terms of the binomial $(x_{Cl^{35}} + x_{Cl^{37}})^4$.

$$S_{n.c} = 4,57584\ (0,3232 \cdot 2,40824 + 0,4216 \cdot 2,20824 + 0,2065 \cdot 2,40824 + 0,0449 \cdot 2,40824 + 0,0037 \cdot 2,40824) = 4,57584 \cdot 2,40824 = 11,0197 \text{ cal/mole·degree}$$

$$S_{см.вз} = -4,57584\ [0,3232\ (-0,4905) + 0,4216\ (-0,3751) + 0,2065\ (-0,6851) + 0,0449\ (-1,3478) + 0,0037\ (-2,4318)] = 4,57584 \cdot 0,2577 = 2,4146 \text{ cal/mole·degree}$$

$$S_{сим} = -2,57584\ (0,3232 \cdot 1,07918 + 0,47712 + 0,2065 \cdot 0,30103 + 0,0449 \cdot 0,47712 + 0,0037 \cdot 1,07918 - 1,07918) = 4,57584 \cdot 0,44165 = 2,0209 \text{ cal/mole·degree}$$

$$S_{яд} = S_{n.c} + S_{см.вз} + S_{сим} = 15,4552 \text{ cal/mole·degree}$$

Thus, S_{yad} for CCl_4 is accurately the quadruplicated value of S_{yad} for atomic chlorine.

§16. ESTIMATION OF THE ACCURACY OF THE TABLES OF THERMODYNAMIC FUNCTIONS. APPROXIMATION OF THE TABLES BY EQUATIONS. REFERENCE LITERATURE ON THERMODYNAMIC FUNCTIONS OF GASES

The thermodynamic functions of gases, cited in the Tables of the IInd volume of this Handbook, are calculated for the natural mixture of isotopes (with exclusion of D, T and their compounds) using the methods stated in the foregoing sections. The values of Φ_T^* and S_T° have been calulated (in cal/mole·degree) immediately by the equations cited in these sections, and the values of $H_T^\circ - H_0^\circ$ (in cal/mole) have been found by means of the relation

$$H_T^\circ - H_0^\circ = T(S_T^\circ - \Phi_T^\circ). \qquad \text{(II.262)}$$

The values of Φ_T^* and S_T° of monatomic gases have been calculated with five significant digits after the decimal point and have then been rounded off to four significant digits. The calculations of the values of di- and polyatomic gases were carried out with four significant digits, and a subsequent rounding off to three significant digits following the decimal point.*

This accuracy is excessive in most cases, and the quotation of superfluous significant digits in the values of the thermodynamic functions is justified only from the point of view of facilitating the interpolation and also to provide the internal coordination of the subsequent calculations. In fact, the accuracy of the calculated values of thermodynamic functions depends on the method of calculation and also on the accuracy and completeness of the molecular constants which are used for calculation.

In the 2nd part of the 1st volume of the present Handbook, the method of calculating the functions is stated for each gas in the sections dealing with the calculation of the thermodynamic functions of gases, and also the magnitudes of uncertainty in the values of Φ_T^* are given for 198.15, 3000 and 6000°K. The uncertainties in the values of S_T° are generally by 2-3 times greater than those for Φ_T^* at the same temperature. The class of accuracy determined by the magnitude of uncertainty in the value of Φ_{3000}^* for each given gas is indicated in each table of thermodynamic properties in volume II (see introduction to the second volume).

Estimation of the accuracy of values of thermodynamic functions. In the case of monatomic gases, at $T < I/10$, where I is the ionization potential of the atom in cm^{-1}, the uncertainties in the values of the thermodynamic functions, caused by the inaccuracy of the calculation method, are negligible in comparison with the uncertainties caused by the inaccuracy of the fundamental physical constants. At $T < I/10$ the uncertainties caused by an inaccurate determination of the n_{max} values become more important. It is assumed in the present Handbook that the n_{max} value is determined with an uncertainty of ± 1. The corresponding uncertainties in the Φ_T^* values may be estimated by comparing the results of the calculation of the sum (II.15) at the values $n_{max} = k$ and $n_{max} = k + 1$. The uncertainties caused by the joining of electronic states and the approximate estimation of the unknown v_i value is essentially lower than the uncertainty caused by the incorrectness of n_{max}, and they may be calculated by means of Eqs. (II.27).

The uncertainty in the Φ_T^* value of a monatomic gas, caused by the inaccuracy of the excitation energy of the ith electronic state, is estimated in the Handbook by the formula

$$\delta\Phi_T^* = \mathcal{R}\frac{\frac{p_i}{p_0}\exp\left(-\frac{hc}{kT}\nu_i\right)}{1+\frac{p_i}{p_0}\exp\left(-\frac{hc}{kT}\nu_i\right)}\cdot\frac{hc}{kT}\nu_i. \qquad \text{(II.263)}$$

The Gordon-Barnes method was the fundamental method of calculating the thermodynamic functions of diatomic gases. The application of this method may result in errors in the values of the thermody a-mic functions, caused by the following sources of errors.

a) Incorrectness of the values of molecular constants assumed in the calculation. The uncertainties in the Φ_T^* values caused by incorrectness of the oscillation frequency ω_e and the rotational constant B_e were estimated by the formula

$$\delta\Phi_T^* = R\left[\frac{(H_T-H_0)_{r.o}}{RT}\cdot\frac{\Delta\omega_e}{\omega_e}+\frac{\Delta B_e}{B_e}\right]. \qquad \text{(II.264)}$$

The uncertainties caused by the incorrectness of the interaction constant α_1 and the constant D_0 of the centrifugal stress were estimated by the formula

$$\delta\Phi_T^* = R\left[\frac{\Delta\alpha_1}{B_e}\bar{v}+\frac{2\Delta D_0}{B_e}q_0\right]. \qquad \text{(II.265)}$$

The uncertainties caused by the incorrectness of the constant of anharmonicity $\omega_e x_e$ were estimated as being a difference of the values

$$R(\Delta\ln Q_{кол}+\beta_1\bar{v}+\beta_2\bar{v}^2), \qquad \text{(II.266)}$$

which correspond to the maximum and minimum values of this constant. The uncertainty caused by the incorrectness of the value of the excitation energy of the ith electronic state was estimated by the formula (II.263).

b) Uncertainties in the Φ_T^* values, caused by neglection of the second and higher constants of anharmonicity, may be estimated on the basis of the Brounshteyn and Yurkov method (see page161). If the available constants of anharmonicity do not conform with the known value of the dissociation energy of the molecule, a new value of the se-

cond anharmonicity constant may be found by the relation

$$\omega_0 y_0 = \frac{2\omega_0 x_0 v_{max} - \omega_0}{3v_{max}^2}, \qquad \text{(II.267)}$$

where

$$v_{max} = \frac{\omega_0}{\omega_0 x_0} - \sqrt{\left(\frac{\omega_0}{\omega_0 x_0}\right)^2 - \frac{3D_0}{\omega_0 x_0}}, \qquad \text{(II.268)}$$

and the uncertainty of Φ_T^* may be estimated on the basis of this value of $\omega_0 y_0$ by the Brounshteyn and Yurkov method.*

c) Uncertainties in the Φ_T^* values caused by neglection of the splitting of the rotational levels in the multiplet electronic states may be estimated according to the equations cited in §9, if the constant of the multiplet splitting is known. In particular, for $^2\Pi$ states.

$$\delta\Phi_T^* = R\exp\left(-\frac{hc}{kT}A\right). \qquad \text{(II.269)}$$

is valid.

The errors caused by inaccurate initial constants for the calculation of the thermodynamic functions of diatomic gases by the rigid rotator-harmonic oscillator model approximation were determined by means of the Eq. (II.264). Uncertainties caused by the deviation of the properties of the gas molecules from the rigid rotator-harmonic oscillator model may be determined if the constants $\omega_e x_e$, α_1 and D_e are known or when they may be estimated by approximate relations.**

Then we have, on the basis of Eq. (II.52):

$$\delta\Phi_T^* = R(\Delta \ln Q_{kon} + \beta_1 \bar{v} + d_0). \qquad \text{(II.270)}$$

The thermodynamic functions of biatomic gases have been computed to 20,000°K by the direct summation method. The errors of the values calculated by this method depend only on the errors of the starting constants.

The thermodynamic functions of the great majority of polyatomic

gases have been calculated in the rigid rotator-harmonic oscillator model approximation due to the missing data on the anharmonicity constants, the constants of interaction between vibration and rotation, and the constants of the centrifugal stress.

The uncertainties in the Φ_T^* values of polyatomic gases, calculated in this approximation, caused by the uncertainty of the assumed values of oscillation frequencies and rotational constants (or principal moments of inertia) are estimated by the relation

$$\delta\Phi_T^* = R\left\{\sum_{n=1}^{n=a} d_n \left[\frac{(H_T - H_0)_{r.o}}{RT}\right]_n \frac{\Delta\omega_n}{\omega_n} + \frac{\Delta(I_A I_B I_C)}{2 I_A I_B I_C}\right\}. \quad \text{(II.271)}$$

The uncertainties of the thermodynamic functions of polyatomic gases caused by the application of the rigid rotator-harmonic oscillator model approximation may not be estimated with a sufficient accuracy because a substantiate estimation of the constants which allow for the deviation of the gas molecules from this model is impossible. A comparison of the calculation of the thermodynamic functions of some gases in the rigid rotator-harmonic oscillator model approximation with more accurate calculations in which the anharmonicity of the vibrations, the interaction between rotation and vibration and the centrifugal stress were taken into account, has shown that the corrections for the three letter effects do not exceed 10% of the $\Phi_{g.o}^*$ value. Due to this fact, it was assumed in the present Handbook, that when the accuracy of the thermodynamic functions of polyatomic gases, calculated in the rigid rotator-harmonic oscillator model approximation was estimated, the uncertainties in the Φ_T^* values, caused by the neglection of the anharmonicity of the vibrations, etc., amount to 10% of the $\Phi_{g.o}^*$ value at the given temperature.

Derivation of equations approximating the tabulated values of thermodynamic functions. The results of calculations of thermodynamic

functions of gases are represented in modern literature, as a rule, in the form of tables similar to the Tables 1-380 in the volume II of the present Handbook. The utilization of tabulated values of thermodynamic functions, however, is inconvenient for the solution of a number of problems, in particular, for the calculation of the composition of complex mixtures of reacting gases by means of electronic computers. In these cases it is more convenient to use analytical functions which describe the values of thermodynamic magnitudes in a certain temperature range.

Even in the first years of development of statistical methods of calculation of thermodynamic functions of gases, some authors (see [1098a, 3821] proposed to calculate the values of the appropriate magnitudes only for discrete reference points, in order to reduce the extent of the calculations, and then to describe them by equations of the type

$$C_p = a + bT + cT^2, \qquad \text{(II.272)}$$

$$C_p = a + bT + c'T^{-2}, \qquad \text{(II.273)}$$

which make it possible to calculate these values for intermediate temperatures, Godnev [155] proposed to calculate the corrections for the anharmonicity of the vibrations, the centrifugal stress and the rotational-vibrational interaction only for a number of reference temperatures and then to approximate their values by interpolation equations.

The temperature range, however, for which analytic equations were deduced in the papers cited, was small and the requirements as to the accuracy of the approximation of the values of thermodynamic functions by these equations were low.

In the present Handbook, analytical equations were derived on the basis of the values of thermodynamic functions tabulated in the

Tables of Volume II, which describe the thermodynamic properties of gases at temperatures from 293.15 to 6000°K with an accuracy of 0.002-0.005 cal/mole·degree for Φ_T^* and S_T°. It must be noted that the approximation of the Φ_T^* and S_T° values with the accuracy mentioned above in such a wide temperature range by power series of the type $f(T) = \sum_{n=-3} a_n T^n$ requires the inclusion of terms up to n = 15-17 into the series of powers of T.

The relations discussed in the foregoing divisions made it obvious that the equations for the calculation of Φ_T^* and S_T° values by means of the statistical sum and its derivatives must contain terms proportional to ln T and T^{-1} besides values proportional to T^n at $n \geq 0$. Thus, introducing terms proportional to ln T, T^{-1} and T^{-2} in the equation of f(T), the number of terms may essentially be diminished in comparison with the usual power series $\sum_{n=0} a_n T^n$. It may be shown that at $293 \leq T \leq 6000°C$ the accuracy mentioned above is attainable by breaking off the series of T powers at n = 7, if addends proportional to ln T, T^{-1}, and T^{-2} are introduced in the equations for the approximation of the Φ_T^* and S_T° values. Correspondingly, the values of Φ_T^*, S_T°, and $H_T^\circ - H_0^\circ$ were approximated in the present Handbook by the equations

$$\Phi_T^* = \varphi \ln x + \sum_{n=-2}^{n=7} \varphi_n x^n, \qquad \text{(II.274)}$$

$$S_T^* = s \ln x + \sum_{n=-2}^{n=7} s_n x^n, \qquad \text{(II.275)}$$

$$H_T^* - H_0^* = h \ln x + \sum_{n=-1}^{n=5} h_n x^n, \qquad \text{(II.276)}$$

where $x = T \cdot 10^{-4}$.

Due to the fact that the values of Φ_T^*, S_T°, and $H_T^\circ - H_0^\circ$ are simple functions of ln Q and $T \frac{\partial}{\partial T} \ln Q$, the coefficients in Eqs. (II.274)-(II.276) are conjointed with the following relations:

$$s = \varphi_1,\ s_0 = \varphi + \varphi_0,\ s_n = (n+1)\varphi_n \text{ at } n \neq 0; \qquad \text{(II.277)}$$

$$h = 0,\ h_1 = \varphi \cdot 10^4,\ h_n = (n-1)\varphi_{n-1} \cdot 10^4 \text{ at } n \neq 1. \qquad \text{(II.278)}$$

Thus, when the coefficients of these equations must be determined, it is sufficient to calculate the coefficients in the equation of one function, and after this the coefficients of the other functions may be found by means of equations of the type (II.277) and (II.278). The coefficients in Eqs. (II.274)-(II.276) have been determined in the present Handbook in terms of the coefficients of the equation which describes the S_T° values.

The coefficients of Eq. (II.275) for each gas were found by means of the method of the least squares as the result of the solution of a system of 59 normal equations** by a highspeed electronic computer. The coefficients of Eq. (II.274) were found by means of Eqs. (II.277), after the S_n coefficients of Eq. (II.275) have been determined. This method did not permit determination of the value of φ_{-1} because $s_{-1} = 0$. In order to find the φ_{-1} values, the Φ_T^* values were calculated on the basis of the calculated φ_n values and Eq. (II.274) for 10 temperatures in the range of from 400 to 2000°K, i.e., for that temperate range in which the contribution of the $\varphi_{-1}x^{-1}$ addend possesses the maximum value. The Φ_T^* values found in this way differ from the values quoted in the corresponding table of thermodynamic functions by the magnitude $\varphi_{-1}x^{-1}$. Thus, the constant φ_{-1} may be calculated by means of the relation $\varphi_{-1} = \frac{\Delta(\Phi_T^*)}{x^{-1}}$, where $\Delta(\Phi_T^*)$ is the difference between the tabulated values of Φ_T^* and those calculated by means of the approximate equation at $\varphi_{-1} = 0$. The average of the ten calculated values of φ_{-1} was assumed to be a constant in Eq. (II.274).

The coefficients of Eq. (II.276) may be found in terms of the coefficients of Eqs. (II.274) and (II.275) using the relations (II.279). The values of the constants in the Eqs. (II.274)-(II.276) for

the gases dealt with in the Handbook, are quoted in the Tables 381-383 of the IInd Volume.

Reference literature on thermodynamic functions of gases. A large number of Handbooks containing tables of thermodynamic functions of various gases in a wide temperature range was published in recent years. The most important of these Handbooks are cited in Table 13, where a short characteristic of them is given (authors, title, scope of the investigated compounds, etc.) A large groups is formed by Handbooks on thermodynamic functions of hydrocarbons and their derivatives (Rossini et a. [3507], Vvedenskiy [119,119a], Korobov and Frost [249, the Handbook edited by Tilicheyev [425-427], etc.) In the main, these Handbooks are compiled on the basis of data published in periodicals.

The Handbooks compiled by Zeise [4384] and Kelley [2363] are the most complete among the Handbooks on thermodynamical properties of inorganic substances available at present. The other Handbooks treat only discrete groups of compounds, simple gases (Hilsenrath et al. [2076]) for example, elements (Stull and Sinke [3894]), halides (Brewer et al. [1093]) etc. A number of the Handbooks is compiled for special purposes, which in a definite manner effects the selection of the investigated compounds. To these papers belong the Handbooks compiled by Huff, Gordon and Morrell [2142] and Ribaud [3426] for purposes of rocket engineering.

It must be noted that tables of thermodynamic functions, adopted from various Handbooks (see [197, 229, 376a], etc.) are often given in a number of manuals and monographs dealing with various heat-engineering processes. Such publications are not included in Table 13.

The existing Handbooks of thermodynamic properties of gases are, with rare exclusions, compilations. The authors transferred in

most cases the tables of thermodynamic functions mechanically from the original papers into the Handbooks, not taking into account the change of the physical and molecular constants duruing the time after the publication of these papers. This concerns above all the Handbook compiled by Zeise [4384]. The lack of an analysis of the accuracy of the cited tables of thermodynamic functions (with the exclusion of the Handbook by Hilsenrath et al. [2076]) is of great disadvantage to all Handbooks.

TABLE 13

The Fundamental Handbooks on Thermodynamic Functions of Gases

A № п/п	B Справочник	C Авторы	D Год издания	E № ссылки	F Рассмотренные соединения и температурный интервал	G Откуда взяты таблицы
1	«Физико-химические свойства индивидуальных углеводородов», вып. I, II и III	ред. М. Д. Тилличеев	1945, 1947, 1951	[426], [427], [428]	Различные углеводороды до 1500° К	Заимствованы из оригинальных работ
2	«Selected Values of Chemical Thermodynamic Properties», Series III		1947—1954	[3680]	Точно список таблиц неизвестен. Верхний предел температур до 5000°К	Главным образом рассчитаны заново
3	«Термодинамические расчеты процессов топливной промышленности»	А. А. Введенский	1949	[119]	Простые газы (O_2, N_2, CO, CO_2, H_2O, CH_4) — до 5000° К; алканы, алкены — до 1500°К	Заимствованы из оригинальных работ
4	«High-Temperature Heat-Content, Heat-Capacity and Entropy Data for Inorganic Compounds»	К. К. Kelley	1949	[2363]	Ряд неорганических соединений почти всех элементов до 2000° К	Заимствованы из оригинальных работ и частично рассчитаны
5	«Свободные энергии органических соединений»	В. В. Коробов, А. В. Фрост	1949	[249]	Алканы, алкены, алкины и ряд простых газов до 1000°, 1500°, 3000° и 5000° К	Заимствованы из оригинальных работ
6	«The Chemistry and Metallurgy of Miscellaneous Materials. Thermodynamics»	Ed. by L. L. Quill	1950	[1093]	Элементы и простые газы до 2000° К, галогениды всех элементов — до 1500° К	Частично заимствованы, частично рассчитаны заново
7	«General Method and Thermodynamic Tables for Computation of Equilibrium Composition and Temperature of Chemical Reactions»	V. N. Huff, S. Gordon, V. E. Morrell	1951	[2142]	Al, B, C, Cl, F, Li, N, O, H, Ar и их соединения до 6000° К	Главным образом рассчитаны заново
8	Constantes thermodynamiques des gaz aux temperatures élevées»	M. G. Ribaud	1952	[3426]	H, Cl, C, N, H_2, O_2, N, OH, NO, CO, CO_2 — до 4000° К; CH, CH_2, CH_3, — до 3500°К; Cl_2 — до 3000° К; HCN, NO_2, NH_3 — до 2000° К; H_2S, CS_2, COS — до 1800° К; N_2O, H_2O_2 — до 1500°К, C_2H_2 — до 1000° К; а также ряд алканов и алкенов до 1500° К	Заимствованы из оригинальных работ и частично рассчитаны заново

№ п/п	Справочник	Авторы	Год издания	№ ссылки	Рассмотренные соединения и температурный интервал	Откуда взяты таблицы
					b	c
9	«Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds»	F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, G. C. Pimentel	1953	[3507]	Простые газы (O, H, N, C, O_2, H_2, OH, H_2O, N_2, NO, CO, CO_2) — до 5000° K; углеводороды — до 1500° K	В основном заимствованы из оригинальных работ
					d	L
10	«Thermodynamik», Band III/1, III/2	H. Zeise	1954, 1957	[4384]	Неорганические и простейшие органические соединения, для которых в литературе до 1954 г. были опубликованы таблицы термодинамических свойств	Заимствования из оригинальных работ
					e	c
11	«Tables of Thermal Properties of Gases»	J. Hilsenrath, C. Beckett, W. Benedict, L. Fano, H. Hoge, J. Masi, R. Nuttall, Y. Touloukian, H. Woolley	1955	[2076]	Ar, CO, CO_2, H_2, N_2, O_2 до 5000° K	В основном заимствованы из оригинальных работ
					f	g
12	«Thermodynamic Properties of the Elements»	D. R. Stull, G. C. Sinke	1956	[3597]	Простые вещества до 3000° K	То же
					h	
13	«Thermodynamic Functions of Gases»	Ed. by F. Din	1956	[1350]	NH_3, CO_2, CO, C_2H_2, C_2H_4, C_3H_8, Ar, воздух до температур не выше 1000° K	» »
14	«Physico-Chemical Measurements at High Temperatures», p. 353	Ed. by J. Bockris, J. L. White, J. D. Mackenzie	1959	[2775]	Элементы от H до U, простые вещества и большое число окислов, галогенидов, гидридов и нитридов до 5000° K	» »
					i	m
15	«Термодинамические и теплофизические свойства веществ»	А. Ф. Брюханов	1960	[1196]	Ряд органических и неорганических соединений до ~1500 и 5000° K соответственно	Заимствованы из литературных данных, опубликованных до 1958 г.

A) Serial number;

B) handbook;
C) authors;
D) year of publication;
E) number of reference:
F) investigated compounds and temperature range;
G) source of the tables;
H) "Fiziko-khimicheskiye svoystva individual nykhuglevodorodov" [Physiochemical Properties of Individual Hydrocarbons], Vols. I, II, and III;
I) editor M.D. Tilicheyev;
K) various hydrocarbons up to 1500°K;
L) Adopted from original papers;
M) the list of the tables is not completely known. The upper temperature limit is 5000°K.
N) mainly calculated anew;
O) "Termodinamicheskiye raschety protsessov toplivnoy promyshlennosti" [Thermodynamical Calculations of Processes of Fuel Industry];
P) A.A. Vvedenskiy;
Q) simple gases (O_2, N_2, CO, CO_2, H_2O, CH_4) up to 5000°K; alkanes and alkenes up to 1500°K;
R) a series of inorganic compounds of almost all elements up to 2000°K;
S) adopted from original papers and partially recalculated;
T) "Svobodnyye energii organicheskikh soyedineniy" [Free Energies of Organic Compounds];
U) V.V. Korobov, A.V. Frost;
V) alkanes, akenes, alkines, and a number of simple gases up to 1000°, 1500°, 3000°, and 5000°K;
W) elements and simple gases up to 2000°K, halides of all elements up to 1500°K;
X) partially adopted, partially calculated anew;
Y) Al, B, C, Cl, F, Li, N, O, H, Ar, and their compounds up to 6000°K;
Z) mainly calculated anew;
a) H, Cl, C, N, H_2, O_2, N, OH, NO, CO, CO_2 up to 4000°K; CH, CH_2, CH_3 up to 3500°K; Cl_2 up to 3000°K; HCN, NO_2, NH_3 up to 2000°K; H_2S, CS_2, COS up to 1800°K; N_2O, H_2O_2 up to 1500°K; C_2H_2 up to 1000°K and also a series of alkanes and alkenes up to 1500°K;
b) simple gases (O, H, N, C, O_2, H_2, OH, H_2O, N_2, NO, CO, CO_2) up to 5000°K; hydrocarbons up to 1500°K;
c) mainly adopted from original papers;
d) inorganic and simplest organic compounds for which tables of thermodynamic properties were published up to 1954;
e) Ar, CO, CO_2, H_2, N_2, O_2 up to 5000°K;
f) simple substances up to 3000°K;
g) the same;
h) NH_3, CO_2, CO, C_2H_2, C_2H_4, C_3H_8, Ar, and air up to temperatures not higher than 1000°K;
i) elements from H to U, simple substances and a great number of oxides, halides, hydrides and nitrides up to 5000°K;
k) "Termodinamicheskive raschety neftekhimicheskikh protsessov" [Ther-

modynamic Calculations of Petrochemical Processes];
l) a series of organic and inorganic compounds up to ~ 1500 and 5000°K, respectively;
m) adopted from literature data published up to 1958.

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[Footnotes]

122 See, for example, the monographs by Mayer and Goeppert-Mayer [285], Landau and Lifshits [272], Fowler and Guggenheim [423], and Sommerfeld [197].

127* The fact that some rotational levels are missing and the difference in the statistical weights of the rotational levels of symmetric molecules is taken into account by introduction of a constant factor, the so-called symmetry number σ, in the statistical sum over the rotational states.

127** Due to the fact that $\Pi(2I_k + 1) = \text{const}$, the component of the nuclear spins in the derivatives of ln Q, and, therefore, in $H^\circ_T - H^\circ_0$, C°_p, etc., is equal to zero.

129 The summation may also be carried over the principal quantum numbers of the electrons of the atoms; in this case, each term of the statistical sum is in turn a sum over the states with the given value of the quantum number $\underline{n}$.

132* According to Bohr's theory, the difference between the excitation energies of discrete states with the principal quantum number $\underline{n}$ and $n + 1$ become arbitrarily small at $n \to \infty$.

132** It was noted in the paper by Gurvich and Kvlividze [171] that evidently excessive values of n_{max} were obtained by Baumann due to the presumption that the continuous spectrum of electronic states begins at the state where energy differs from ionization energy by a magnitude of the order h/τ. If we assume that the latter quantity is the upper limit for the difference between the energies of two adjacent discrete states, we obtain, instead of the values found by Baumann, 400 and 40, respectively. Lower values of n_{max} may be obtained if one takes into account, that not one, but several states correspond to the given value of $\underline{n}$. The lack of data on the excitation energies of the majority of high states and on the lifetime of these states makes this method inapplicable for concrete calculations.

133 It seems, that a similar method for the determination of n_{max} was proposed by Bethe in 1942, but it was never published (see [687]).

In calculating the statistical sum in Eqs. (II.16), the summation over $\underline{i}$ is subsequently carried out in accordance with the increasing energy of the electronic states and independently of the value of $\underline{n}$; the sums must be discontinued on states for which $n \leq n_{max}$. The summation may also be carried out over the values of the quantum number $\underline{n}$; in this case each term of the sum is a sum over the states with the given value of the quantum number $\underline{n}$. This method of calculation, however, is less convenient for practical purposes.

135 This is equal to the magnitude of the error in the functions due to the inaccuracy of the well-known values of physical constants.

136 For example, 4032 electronic states correspond to the value $n \leq 12$ in the nitrogen atom with $2p^2(^3P)nl$ and $2p^2(^1D)nl$ state groups.

138 Excluding these states of each group which refer to levels with lower excitation energies.

140 The diatomic hydrogen and its isotopic varieties are an exclusion; the stipulated condition is not fulfilled in their case up to 1000°K. The corresponding error, however, in the values of the thermodynamic functions of H_2 and of its isotopic varieties is negligible (see page 358) even at T = = 293.15°K, i.e., at the lowest temperature for which tables of thermodynamic properties are compiled in this Handbook.

142 The results of this investigations were reported at the Conference of the Young Scientific Coworkers of the Institute of Mineral Fuels of the Academy of Sciences USSR, October 23, 1957 [178].

145 It is sufficient to recall that only in the $X^1\Sigma_g^+$ electronic state does the N_2 molecule possess about $\sim 7 \cdot 10^3$ vibrational and rotational energy levels, and that at high temperatures all these levels must be taken into account in the calculations.

146 The number of stable electronic states of the molecule is always small in comparison to the number of vibrational and rotational levels. Thus, the calculation of the sums $\sum_i Q^{(i)}_{кол.вр} \exp(-hc/kT \cdot \nu^{(i)}_e)$ does not cause an essential increase in the amount of calculating.

152* The magnitude $\theta = \frac{hc}{k} \omega_e$ is termed <u>characteristic temperature</u>.

152** Smirnova and Frost [386] accomplished these tables for the values of $0{,}2 < \frac{\theta}{T} < 0{,}6$ c in intervals of 0.1, i.e., in the range of values of θ/T which corresponds to high temperatures. The tables compiled in the paper [386] are inapplicable, however, for sufficiently accurate calculations because the intervals between the values of θ/T and $\underline{x}$ are too large for a satisfactory interpolation. Due to this fact, the

tables of the values of $\Delta \ln Q_{кол}$, $\frac{\Delta S_{кол}}{R}$, $\bar{v}$, $\bar{v}^2$, $\bar{s}$ и $\bar{s}^2$ and $\bar{s}^2$ were calculated anew on an electronic computer when this Handbook was prepared. The tables are calculated for the values $0.000 \leq x \leq 0.025$ in 0.001 steps, and for the values $0{,}05 < \frac{\theta}{T} < 6{,}0$ in 0.01 steps in order to facilitate the interpolation and to increase its accuracy. These tables, as well as the other auxiliary tables prepared by the authors of the Handbook, will be published separately.

153 At $x = 0$, we have, according to (II.57) $v_{max} = \infty$ and $Q_{кол} = \sum_{v=0}^{v_{max}} \exp\left[-\frac{hc}{kT} G_0(v)\right] = \sum_{v=0}^{\infty} \exp\left(-\frac{hc}{kT}\omega\right)$; the latter expression is the statistical sum of the harmonic oscillator.

155 The application of the equation $G_0(v) = \omega_0 v - \omega_0 x_0 v^2$ for the energy of the vibrational levels in the Gordon-Barnes method is equivalent to the assumption that the potential energy of the molecule is described by a Morse function.

157 According to Kassel [2333], the following functions are valid:

$$f_0 = 1,$$
$$f_1 = z(1-z)^{-1},$$
$$f_2 = z(1+z)(1-z)^{-2},$$
$$f_3 = z(1+4z+z^2)(1-z)^{-3},$$
$$f_4 = z(1+11z+11z^2+z^3)(1-z)^{-4},$$
$$f_5 = z(1+26z+66z^2+26z^3+z^4)(1-z)^{-5},$$
$$f_6 = z(1+57z+302z^2+302z^3+57z^4+z^5)(1-z)^{-6},$$
$$f_7 = z(1+120z+1191z^2+2416z^3+1191z^4+120z^5+z^6)(1-z)^{-7},$$
$$f_8 = z(1+247z+4293z^2+15619z^3+15619z^4+4293z^5+247z^6+z^7)(1-z)^{-8},$$

$$T\frac{\partial}{\partial T} f_0 = 0,$$
$$T\frac{\partial}{\partial T} f_1 = \frac{hc}{kT}\omega_0 z(1-z)^{-2},$$
$$T\frac{\partial}{\partial T} f_2 = \frac{hc}{kT}\omega_0 z(1+3z)(1-z)^{-3},$$
$$T\frac{\partial}{\partial T} f_3 = \frac{hc}{kT}\omega_0 z(1+10z+7z^2)(1-z)^{-4},$$
$$T\frac{\partial}{\partial T} f_4 = \frac{hc}{kT}\omega_0 z(1+25z+55z^2+15z^3)(1-z)^{-5},$$
$$T\frac{\partial}{\partial T} f_5 = \frac{hc}{kT}\omega_0 z(1+56z+276z^2+236z^3+31z^4)(1-z)^{-6},$$
$$T\frac{\partial}{\partial T} f_6 = \frac{hc}{kT}\omega_0 z(1+119z+1134z^2+2114z^3+889z^4+63z^5)(1-z)^{-7},$$
$$T\frac{\partial}{\partial T} f_7 = \frac{hc}{kT}\omega_0 z(1+246z+4173z^2+14428z^3+13203z^4+3102z^5+127z^6)(1-z)^{-8},$$
$$T\frac{\partial}{\partial T} f_8 = \frac{hc}{kT}\omega_0 z(1+501z+14361z^2+83941z^3+140571z^4+72615z^5+$$
$$+10315z^6+255z^7)(1-z)^{-9}.$$

163 Relations similar to those proposed by Brounshteyn and Yurkov [110] were obtained also by Arvym [75a] in 1960; with regard to the errors committed in [75a], see [110a].

165 A more strict approximation gives $Q_{v.r} = \frac{kT}{hcB} + \frac{1}{3} + \ldots$, and then an additional term R 1/3q, which is valid only at low temperatures, appears in Eq.(II.83).

166 During the preparation of this Handbook, tables of the values $\Phi^{\circ}_{r.o}/R$, $S_{r.o}/R$, $(H_T - H_0)_{r.o}/R$, $C_{p_{r.o}}/R$ were calculated on electronic computer as functions of θ/T for the range $0.0000 \leqslant \frac{\theta}{T} \leqslant 0.1300$ in 0.0001 steps; for the range $0.1300 \leqslant \frac{\theta}{T} \leqslant 1.300$ in 0.001 steps; for the range $1.300 \leqslant \frac{\theta}{T} \leqslant 7.00$ in 0.01 steps, and for the range $7.00 \leqslant \frac{\theta}{T} \leqslant 15.0$ in 0.1 steps in order to obtain the components of the harmonic oscillator for the calculation according to the rigid rotator-harmonic oscillator model, and also according to the Gordon-Barnes method (R ln Q_{kol} and S_{kol} at x = 0). These tables as well as other auxiliary tables will be published separately.

167 States with S > 0 or Λ > 0 are termed multiplet electronic states in this Handbook.

168 The lower the temperature for which the thermodynamic functions are calculated, and the greater the splitting of the components of levels with the given value of J, the greater the difference between the components which take into account the splitting of the rotational levels of the multiplet electronic states, and the values calculated by means of the statistical weights quoted in Table 7. It must be noted that this effect may be taken into account by the statistical weight 2 due to the fact that the splitting of the levels caused by the Λ doubling is always very small.

170* The splitting of the rotational levels in $^1\Pi$ state, caused by the Λ doubling, may in all cases be taken into account with sufficient accuracy by the statistical weight 2.

170** Papousek obtained 1961 formulas for the calculation of $Q_{v.vr}$ of molecules in the states $^3\Pi$ [3183a] and $^2\Pi$ [3183b]. These formulas are similar to those obtained earlier in the papers [109, 445, 446].

170*** The relations cited above are obtained on the assumption that $J_{max} = \infty$; if it is necessary, corrections may be introduced in those equations which take into account the limitation of the number of rotational levels by means of the Eqs. (II.59) and (II.60).

175 The calculation was carried out on the basis of the "effective" values of the constants of $CCl^{35.457}$ molecule (see page 220).

180 This assumption is sufficiently fulfilled in a number of

cases.

181* Recently

$$b' = \sum_{i=A,\dots} \frac{p_i}{p_X} \frac{\omega_0^{(X)}}{\omega_0^{(i)}} \cdot \frac{B_0^{(X)}}{B_0^{(i)}} \exp\left(-\frac{hc}{kT} \nu_\omega^{(i)}\right).$$

was assumed instead of the relation (II.125) in the paper [714]. This expression may be obtained from (II.125) expanding in the latter z_i and z_X into Taylor series and breaking off the series on the terms with hc/kt ω_0. It is evident that such an expansion is accurate only at hc/kT $\omega_0 \ll 1$.

181** Here and in the following, $\nu_\omega^{(i)}$ is expressed in cm^{-1}, and T in °K.

188* In this case, the terms $d_0 + 3d_0^2 + f_0$ must not be taken into account in the expression for ln Σ.

188** In this case, the terms $2d_0 + 7{,}5d_0^2 + 3f_0$ must not be taken into account in the expression for $\ln \Sigma + T \frac{\partial}{\partial T} \ln \Sigma$.

188*** In this case, the term $1/3q_0$ must not be taken into account in the expression for ln Σ.

188**** In this case, the term $1/3q_0$ must not be taken into account in the expression for ln Σ.

192 We remember that the statistical weight of a single vibrational state is equal to 1 in the case of nondegenerate vibrations, equal to $v_n + 1$ in the case of doubly degenerated, and equal to $(v_n + 2)(v_n + 1)/2$, in that of triply degenerate vibrations.

196 Stripp and Kirkwood [3888] obtained for the statistical sum over the rotational states of a rigid nonlinear molecule an expression of the following form

$$Q_{\text{вр}} = \sqrt{\frac{\pi}{ABC}\left(\frac{kT}{hc}\right)^3}\left\{1 + \frac{1}{12}\frac{hc}{kT}\left[2A + 2B + 2C - \frac{AB}{C} - \frac{BC}{A} - \frac{AC}{B}\right] + \right.$$

$$+ \frac{1}{480}\left(\frac{hc}{kT}\right)^2\left[10(A^2 + B^2 + C^2) + 12(AB + BC + AC) - 12\left(\frac{A^2B + AB^2}{C} + \frac{B^2C + CB^2}{A} + \frac{C^2A + CA^2}{B}\right) + \right.$$

$$\left.\left. + 7\left(\frac{A^2C^2}{B^2} + \frac{B^2C^2}{A^2} + \frac{C^2A^2}{B^2}\right)\right] + \dots\right\},$$

where the correction terms are effective only at low temperatures.

199* A number of equations which are absent in the original papers by Gordon and Kassel are cited in this and in the following divisions. These equations were obtained by L.V. Gurvich during the preparation of the first edition of the pre-

paration of the first edition of the present Handbook.

199** The last term in Eq.(II.185) is a correction of the statistical sum of a rigid asymmetrical top (see footnote on page 362). The less accurate expression

$$\frac{\sigma_{BC}}{3} - \frac{1}{12}\frac{\sigma_B\sigma_C}{\sigma_A}, \text{ где } \sigma_{BC} = \sqrt{\sigma_B\sigma_C}$$

was used instead of this term in the similar formula in Gordon's original paper.

201* In Gordon's tables, the value of $\ln Q_{кол}$ for doubly degenerate vibrations is calculated only by means of one table and not by two tables, as in the case of diatomic molecules.

201** These tables, together with other auxiliary tables, will be published separately.

209 The methods of allowing for the internal rotation in molecules when calculating the thermodynamic functions of gases are stated in detail in the monograph by Godnev [157].

225 In the tables concerning thermodynamic functions of diatomic gases calculated by immediate summation, the values of Φ_T^* and S_T° are given up to 10,000°K with four significant digits after the decimal point.

228* The relations (II.267) and (II.268) are applicable for the estimation of $\omega_e y_e$ only under the condition $\left(\frac{\omega_0}{\omega_e x_e}\right)^2 > \frac{3D_0}{\omega_e x_e}$, i.e., when the dissociation energy of the molecule exceeds the value obtained by linear extrapolation by more than 25%.

228** Approximate values of these constants for the estimation of uncertainties may be calculated by means of the equations $\omega_e x_e = \frac{\omega_e^2}{4D}$, $\alpha_1 = \frac{\ldots}{\omega}$, and $D = \frac{4B^3}{\omega^2}$ (see page 86).

232* The coefficients in the equation for S_T° may be calculated in terms of the coefficients in the equation for Φ_T^*. In this case, however, the accuracy of the approximation of the S_T° values proves to be insufficient on the borders of the temperature interval.

232** The thermodynamic functions of gases have been calculated in the Handbook for 59 temperatures in the range of from 293.15 to 6000°K.

Manuscript Page No.	[Transliterated Symbols]
124	пост = post = postupatel'nyy = translational
124	вн = vn = vnutrenniy = internal
126	я.с. = ya.s. = yadernyy spin = nuclear spin
129	эл = el = elektronnyy = electronic
139	вр = vr = vrashchatel'nyy = rotational
139	кол.вр = kol.vr = kolebatel'nyy-vrashchatel'nyy = vibration--rotational
149	пр = pr = predel'nyy ' limit
151	кол = kol = kolebatel'nyy = vibrational
164	г.с. = g.o. = garmonicheskiy ostsillyator = harmonic oscillator
165	ж.р. = zh.r. = zhestkiy rotator = rigid rotator
165	ж.р.г.о. = zh.r.g.o. = zhestkiy rotator-garmonicheskiy astsillyator = rigid rotator-harmonic oscillator.
209	зат.вр = zat.vr = zatormozhennoye vrashcheniye = retarded rotation
209	св.вр = sv.vr = svobodnoye vrashcheniye = free rotation
210	пр = pr = privedennyy = reduced
221	ядл = yad = yadernyy = nuclear
221	см.из = sm.iz = smesheniye izotopov = mixing of isotopes
221	я.с = ya.s = yadernyy spin = nuclear spin
221	сим = sim = simmetriya = symmetry

Chapter 3

METHODS OF CALCULATION OF THE THERMODYNAMIC FUNCTIONS OF SUBSTANCES IN SOLID AND LIQUID STATES

§17. GENERAL RELATIONSHIPS

Attempts to apply statistical methods for the calculation of the specific heat and of other thermodynamic functions of crystalline substances date back to the beginning of the XXth century, i.e., to the time of the origin of the quantum theory. One did not succeed, however, to develop practical methods of calculation of the thermodynamic functions of substances in the solid state, in which results of experimental measurements of the specific heat were not applied, in spite of the series of fundamental investigations by Einstein, Nernst and Lindeman, Debye, Born and Karman, and the subsequent development of these works by Blackman, Tarasov, Lifshits and others. The existent theories of specific heat were applied only to a limited extent, mainly as methods of extrapolation of the data on specific heat to the absolute zero.

The determination of thermodynamic functions of substances in solid and liquid states at high temperatures on the basis of theoretical calculations is also practically impossible due to the lack of any reliable methods for the calculation of the temperatures and heats of the phase transitions and of the specific heats of substances in the liquid state.

Thus, the calculation of tables of thermodynamic functions of substances in solid and liquid states may at present be carried out

only on the basis of the results of experimental measurements of the specific heat and the heats of the phase transitions, using the relations based on the third law of thermodynamics.

A thorough statement of the calorimetric methods of measuring the specific heat and of the enthalpy of substances, of the melting and transformation heats, etc., may be found in a number of special monographs.* In this chapter, only several properties of the existing methods of measurement of these values and methods of processing experimental data will be discussed, which is necessary for a critical analysis of the experimental material discussed in the 2nd Part of the I volume of the Handbook.

It must be noted that the thermodynamical properties of many substances are up to now insufficiently investigated, especially at high temperatures. The available date on a number of substances are unreliable, and the thermodynamic values are totally unknown for many other substances. Nevertheless, the various approximate methods based on empirical and semi-empirical regularities make it possible, in many cases to estimate the unknown thermodynamic values with sufficient accuracy.

Therefore, the approximate methods of calculating and estimating thermodynamic values will also be stated in this chapter beside the methods of processing of experimental data.

Theory of the specific heat of solids.** Einstein [1471] in 1907 applied the classic Boltzmann statistics on the theory of the specific heat of crystalline substances. Einstein's theory was based on the assumption that the vibrations of atoms in a monatomic solid may be considered as vibrations of harmonic quantum oscillators with the same frequen y ω and with the energy levels

$$\varepsilon_v = \varepsilon_0 + vhc\omega, \qquad \text{(III.1)}$$

where ε_v and ε_0 are the energies of the oscillator on the vth and zero levels; h is the Planck constant, c is the velocity of light, and v is the quantum number.

Substituting Eq.(III.1) into the equation for the statistical sum over the states (6) and denoting $hc\omega/k$ by θ_E (the "characteristic Einstein temperature"), one may obtain the following relation for the specific heat of 1 gram-atom of substances at a constant volume:

$$C_v = \frac{3R(\theta_E/T)^2 \exp(\theta_E/T)}{[\exp(\theta_E/T)-1]^2} = 3E(\theta_E/T). \qquad \text{(III.2)}$$

The quantity $E(\theta_E/T)$ is the Einstein function for the specific heat of a onedimensional harmonic oscillator.

This equation satisfies the conditions $\lim(C_v)_{T \to \infty} = 0$ and $\lim(C_v)_{T \to \infty} = 3R$ which result from the third law of thermodynamics and the Dulong and Petit law, respectively. Eq.(III.2) satisfactorily describes the specific heat of substances at relatively high temperatures; at low temperatures, however, the values calculated by Eq. (III.2) are essentially lower than the values found experimentally.

Nernst and Lindeman [3045] (in 1911) found a somewhat better conformity with the experiment using the empirical equation

$$C_v = \frac{3}{2} E(\theta/T) + \frac{3}{2} E(\theta/2T). \qquad \text{(III.3)}$$

which assumes the existence of two characteristic frequencies differing by two times from each other.

In Debye's theory [1281] (in 1912), the monatomic crystalline body is considered to be a continuous isotropic elastic medium having an infinitely great number of natural vibrations with frequencies from 0 to ω_{max}, assuming that the distribution function of these frequencies over this interval has the form

$$f(\omega) = C\omega^2 \qquad \text{(III.4)}$$

(if $\omega > \omega_{max}$, the function is $f(\omega) = 0$).

The quantity $\theta_D = hc\omega_{max}/k$, the characteristic Debye temperature,* enters into the Debye equation for the specific heat of 1 gram-atom substance at a constant volume:

$$C_v = 3R\left[12(T/\theta_D)^3 \int_0^{\theta_D/T} \frac{\left(\frac{hc\omega}{kT}\right)^3 e^{\left(\frac{hc\omega}{kT}\right)}}{\exp\left(\frac{hc\omega}{kT}\right)-1} - \frac{3(\theta_D/T)}{\exp(\theta_D/T)-1}\right] = 3D(\theta_D/T) \quad \text{(III.5)}$$

At low temperatures ($T \ll \theta_D$), Eq.(III.5) assumes a simpler form:

$$C_v = \frac{12}{5}\pi^4\left(\frac{T}{\theta_D}\right)^3 = aT^3, \quad \text{(III.6)}$$

corresponding to which the specific heat of a monatomic body is proportional to the third power of the temperature at low temperatures.

Equations (III.5) and (III.6) are in better accordance with experimental data than the Eqs. (III.2) and (III.3) obtained by Einstein and Nernst and Lindeman. A more thorough study, however, shows that even in the case of isotropic simple substances a significant deviation from the T^3 rule occur, caused, in particular, by the assumption of the Debye theory that it is possible to consider the crystal lattice as a continuous elastic medium.

In the dynamic theory of the crystal lattice, developed by Born and Karman [869a, 870] (1912-1915), the crystal is considered to be a sustem of harmonic oscillators whose frequencies correspond to the natural frequencies of the crystal. The inner energy and the specific heat of complex compounds whose molecules consist of p atoms, may be expressed, according to this theory, as combinations of the Debye and Einstein functions (see [93a]):

$$C_v = \sum_{i=1}^{3} D(\theta_{D_i}/T) + \sum_{i=4}^{3p} E(\theta_{E_i}/T), \quad \text{(III.7)}$$

where θ_{D_1}, θ_{D_2}, and θ_{D_3} are the characteristic Debye temperatures representing the elastic properties of the anisotropic crystal lattice,

and Θ_{E_1} are the characteristic Einstein temperatures related to the natural oscillations of the lattice.* Attempts were made in a number of works to combine the values of the characteristic Debye and Einstein temperatures with various thermal, mechanical and optical properties, in particular, with the frequencies of the residual radiation of Rubens [3546a] (the spectral bands in the far infrared range of crystal spectra). In some cases, the calculations of characteristic temperatures by means of the various empiric equations succeeded in a sufficient coincidence with values calculated on the basis of experimental measurements of the specific heat.

The theory of the specific heat of crystalline substances was developed in two fundamental directions during the past two to three decades. In the papers by Blackman [834a], Houston [2132a] and many other investigators, it was attempted to improve the Debye theory by substituting the postulated parabolic distribution function of the frequencies (III.4) by another function which describes the real distribution of frequencies of crystal lattices of various types much better. Rational methods were not to be found, however, up to now, to determine this function; thus, only the inverse problem was treated in practice: to find the distribution function on the basis of the experimental values of the specific heat.

Another direction in the development of the theory of specific heat of solids is represented in the papers by Tarasov (see the review [456], Lifshits [277, 278] and some other investigators dealing with the development of the theory of the specific heat of laminar and chainlike crystal lattices. These theories, however, as well as Debye's theory, find practical application only by the extrapolation of experimental data on the specific heat to 0°K (see page 253).

Equations for the calculation of thermodynamic functions. Accu-

ing to the general relationships (see §1), the thermodynamic functions of substances in solid and liquid states may be calculated by the equations:

$$H_T^\circ - H_0^\circ = (H_{298.15}^\circ - H_0^\circ) + \int_{298.15}^{T_1} C_p^{(1)} dT + \Delta H_{T_1}^\circ + \int_{T_1}^{T_2} C_p^{(2)} dT + \ldots$$
$$\ldots + \Delta H_{T_i}^\circ + \int_{T_i}^{T} C_p^{(i+1)} dT, \qquad \text{(III.9)}$$

$$S_T^\circ = S_{298.15}^\circ + \int_{298.15}^{T_1} \frac{C_p^{(1)}}{T} dT + \frac{\Delta H_{T_1}^\circ}{T_1} + \int_{T_1}^{T_2} \frac{C_p^{(2)}}{T} dT + \ldots \frac{\Delta H_{T_i}^\circ}{T_i} + \int_{T_i}^{T} \frac{C_p^{(i+1)}}{T} dT, \qquad \text{(III.10)}$$

$$\Phi_T^\circ = S_T^\circ - \frac{H_T^\circ - H_0^\circ}{T}. \qquad \text{(III.11)}$$

where $H^\circ_{298.15} - H^\circ_0$ is the change of the enthalpy of the substance from 0 to 298.15°; $S^\circ_{298.15}$ is the entropy of the substance at 298.15°K; $C_p^{(1)}$, $C_p^{(2)}$, ..., $C_p^{(i+1)}$ are the specific heats of the substance in different phase states, determined as functions of the temperature; T_1, T_2, ..., T_i are the temperatures of the phase transitions, including the melting point*; $\Delta H^\circ_{T_1}$, $\Delta H^\circ_{T_2}$, ..., $\Delta H^\circ_{T_i}$ are the heats of the phase transitions including the melting heat.

The quantities on the right side of Eqs. (III.9) and (III.10) are starting values for the calculation of the thermodynamic functions of substances on solid and liquid states. The values of these quantities for the individual substances accepted in the Handbook, are quoted in the corresponding sections of the 2nd Part of Volume I.

§18. DETERMINATION OF THE THERMODYNAMIC VALUES OF SUBSTANCES IN SOLID AND LIQUID STATES ON THE BASIS OF THE EXPERIMENTAL DATA AND ON EMPIRICAL ESTIMATES

Entropy at 298.15°K and change of the enthalpy $H^\circ_{298.15} - H^\circ_0$. The values of these magnitudes for substances in solid and liquid states may be determined with high accuracy on the basis of experimental measurements of the specific heat from absolute zero to 298.15°K, and

also by means of the temperatures and heats of phase transitions if they take place at these temperatures. The measurements of specific heats at low temperatures are carried out in the intervals between room temperature and the so-called "nitrogen" temperature (about 55°K), "hydrogen" temperature (about 12°K) and, in some cases, the "helium" temperature (1-4°K).

The accuracy of the measurements of the specific heat at low temperatures depends on a number of factors: the accuracy of the dosage of the energy supplied for heating, the degree of avoidance of heat loss, the accuracy of the measurement of small heatings due to the supplied energy portions, and the accuracy of the temperature measurement (see [395, 398]). Accordance between the temperature scale and the thermodynamic scale used acquires an important part in the exact measurements of the specific heat at low temperatures. The international temperature scale between 90 and 298°K, and also the practical temperature scales used in the U.S. [2096] and the USSR [94] in the 20-90°K interval differ from the thermodynamic scale by not more than ±0.5-0.1%. This difference increases below 20°K and may reach ±5% at 10-15°K.*

An analysis of the sources of errors and a comparison of the data obtained by various investigators lead to the conclusion that the error of the most accurate measurement of the specific heat amounts to ±0.1-0.2% within the interval from room temperature to 20°K, and increases up to ±0.5-1% below 20°K.

Due to the fact that for the excessively high majority of simple substances and inorganic and organic compounds in the crystalline state the entropy values at 298.15°K lie between 3 and 40 cal/mole·degree,** the error of the measurements of the specific heat mentioned above results in uncertainties in the values of $S^\circ_{298.15}$ of the order 0.01-0.1

cal/mold·degree. Thus, for example, accurate measurements of the specific heat of benzoic acid, recommended as standard substance for the low temperature calorimetry, were carried out by two investigator teams: Furukawa, McCoskey and King [1633] (14-300°K) and Strelkov, Sklyankin and Kostryukov [50a, 378a, 399] (4-300°K). The recommended values 40.055 [1633] and 40.04 ± 0.08 cal/mole·degree [399] differ only by 0.015 cal/mole·degree, i.e., by less than 0.05%.

Among the substances treated in the present Handbook, the following have an uncertainty in the entropy value at 298.15°K of the order of ±0.2-0.3% (the $S^\circ_{298.15}$ values given in cal/mole·degree): Al_2O_3 (12.175 ± 0.02), KCl (19.70 ± 0.05), Li_2O (9.056 ± 0.03), K (15.46 ± 0.05), Mg (7.78 ± 0.03), Al (6.77 ± 0.02), Pb (15.49 ± 0.05), PbO (cryst., yellow) (16.42 ± 0.03).

It must be noted that an essential error in the calculation of the $S^\circ_{298.15}$ values on the basis of experimental data is frequently caused by the large extrapolation of the specific heat to 0°K. The extrapolation may be carried out accurately only at the lowest temperatures, when the specific heat obeys Debye's rule (III.6). This occurs, however, even in the case of the simplest crystalline lattices, at temperatures of the order of $(0.02\text{-}0.01)\theta_D$ (θ_D is the characteristic Debye temperature). Complex and anisotropic lattices (laminated, etc) show frequently a curve of the specific heat which may not be described even approximately by Debye's equation. Combinations of the Debye and Einstein functions (Eqs. (III.7) and (III.8) are used in these cases for the extrapolation to zero, adjusting them to the lower section of the experimental curve. Kelley [2364] assumed that the error in the entropy obtained by such an extrapolation of the specific heat to 0°K may be approximately 10%. Taking into account, however, the possibility of anomalies of the specific heat and the reduced accuracy

of its determination at its lowest temperatures, the magnitudes of the possible error of the entropy must be increased to 20-30% of the value obtained by extrapolation to 0°K.*

In cases where the investigation of the specific heat is carried out in order to calculate the thermodynamic functions of substances, it is expedient to determine the lower temperature limit of the experimental measurements by that amount which contributes to the extrapolation of the specific heat below this limit up to 0°K to the value of the entropy. In this case it is desirable that the entropy value, which is determined by extrapolation of the specific heat to 0°K, does not essentially exceed the value of the total error in $S^{\circ}_{298.15}$, i.e., that it is not greater than 0.01-0.10 cal/mole·degree.

The criterion indicated above may be joined, in the case of simple substances, with the characteristic Debye temperature. As Table 14, shows, the entropy values at low temperatures depend very strongly on the characteristic temperature; for example, the entropy of substances with θ_D = 300 at 12°K is equal to 0.01 cal/g-atom·degree, while in the case of θ_D = 50, the entropy at 12°K exceeds 1.4 cal/g-atom·degree. A study of the Table shows that one may restrict oneself to measurements of the specific heat in the interval of from 298°K to "nitrogen" temperature (about 55°K) only in the case of a low number of substances having a characteristic Debye temperature of the order of 1000° and above, when reliable entropy values at 298.15°K are to be obtained. The measurement of the specific heat must be expanded to "hydrogen" temperatures (10-12°K) in the case of substances with characteristic temperatures of 150-200°K, and for substances with much lower characteristic temperatures the measurement must be extended up to the "helium" temperatures (1-4°K).

In the present Handbook, data were used which were compiled in

the last edition of Kelley's Handbook [2364] (which takes into account the literature published up to November 1948) and also later publications issued up to the end of 1959, when selecting the values of $S^\circ_{298.15}$ and $H^\circ_{298.15} - H^\circ_0$ based on experimental measurements of the specific heat. The values of $S^\circ_{298.15}$ and $H^\circ_{298.15} - H^\circ_0$ were generally calculated by numerical integration of the smoothened values of C°_v/T and C°_p, respectively, in the interval of 0-100°K with steps of 5°K, and in the interval of 100-298.15°K with steps of 10°K.

Data on the specific heat at low temperatures are totally lacking for a number of substances treated in the Handbook (BeF_2, $BeCl_2$, PbF_2, AlN), and for some other substances ($AlCl_3$, Sr, Ba), these data are available only for a narrow temperature interval. In these cases, the authors of the Handbook carried out estimations of the entropy value at 298.15°K by means of various empirical methods proposed by Kireyev [224], Karapet'yants [219, 222], Drozin [180], Venner [127], and Latimer [273].

TABLE 14

Entropy Values (in cal/g-atom·degree) for Substances with Different Characteristic Debye Temperatures

T°,K \ θ°,K	50	70	100	150	200	300	500	700	1000	1500
1	0,001	—	—	—	—	—	—	—	—	—
3	0,033	0,012	0,004	0,001	—	—	—	—	—	—
5	0,15	0,056	0,019	0,006	0,002	—	—	—	—	—
10	0,98	0,42	0,16	0,046	0,019	0,006	0,001	—	—	—
12	1,44	0,68	0,27	0,079	0,033	0,010	0,002	—	—	—
15	2,16	1,14	0,48	0,16	0,065	0,019	0,004	0,001	—	—
20	3,32	1,99	0,98	0,35	0,16	0,046	0,010	0,004	0,001	—
25	4,37	2,84	1,55	0,61	0,30	0,089	0,019	0,007	0,002	—
30	5,30	3,65	2,16	0,98	0,49	0,16	0,033	0,012	0,004	0,001
40	6,85	5,05	3,32	1,75	0,98	0,35	0,079	0,029	0,010	0,003
50	8,10	6,23	4,37	2,56	1,55	0,61	0,16	0,056	0,019	0,005
55	8,64	6,75	4,85	2,94	1,86	0,80	0,21	0,075	0,026	0,008

The methods of estimating the entropy of solid inorganic sub-

stances indicated above, are in principle, semi-empirical relations between the entropies of these compounds and any others of their properties. Thus, according to Drozin [180], the entropy of a compound is equal to the half-sum of the entropies of the neighbored compounds, if monotypical compounds of elements of one group of the periodic system are arranged according to the increasing molecular weight. According to Venner [127], the entropy of monotypical compounds is a linear function of the logarithm of their molecular weights. According to Kireyev [224], the entropy of the formation of compounds from atomic ions is an approximately constant value (or magnitude varying regularly within a limited range). The additive scheme by Latimer [73] is based on the method of ascribing constant entropy values to the cations and several values to the anions depending on the value of the anionic charge. The accuracy of the calculation according to Latimer amounts to ± 3 cal/mole·degree, but the introduction of empirical corrections for monotypical compounds make it possible to reduce the error of the calculation by two or three times. As Kireyev has shown [224a], simpler additive schemata are inapplicable to calculation of entropies.

The methods of comparative calculations proposed by Karapet'yants [219] are the most accurate for estimating the entropy of crystalline substances:

$$(S^\circ_{298.15})_I = a + b\,(S^\circ_{298.15})_{II}, \qquad \text{(III.12)}$$

$$(S^\circ_{298.15})_I = A + B\,(S^\circ_{298.15})_{III}, \qquad \text{(III.13)}$$

where the indices I and II refer to the series of related compounds, and a, b, A, B are empirical constants of the given series.

The estimations were carried out, as a rule, by means of different methods. The probable uncertainty of the $S^\circ_{298.15}$ values obtained in this way depends both on the reliability of the applied meth-

estimation as well as on the accuracy of the experimental values used in the estimation, and changes within the range from ±0.5 (BeF_2) to ± cal/mole·degree (PbF_2).*

Specific heat of substances in the solid state at temperatures from 298°K to melting point. A statement of the existing experimental methods of determination of the specific heat and enthalpy of substances in solid and liquid states at high temperatures may be found in the monographs by Popov [332], Kubaschewski and Evans [267], Kelley [2363, 98] and others. The methods of immediate measuring of the true specific heat at a temperature higher than room temperature are used at relatively low temperatures (not higher than 1000°) due to the experimental difficulties. The accuracy of the values of specific heat obtained by these methods is usually slight (in the order of 1%).**

The majority of the data on temperatures above 298°K was obtained by using the mixing methods which make it possible to measure the enthalpy of substances in a wide temperature range (from room temperature to 2000-2500°C) with a sufficient accuracy.*** The specific heats may be obtained from these data only by differentiation of the enthalpy-versus-temperature curve:

$$C_p = \frac{\partial H}{\partial T}. \qquad \text{(III.14)}$$

Various equations are used to represent analytically the dependence of the specific heat of solid substances on the temperature at temperatures higher than room temperature. The most frequently used equation is

$$C_p = a + bT - cT^{-2}, \qquad \text{(III.15)}$$

which was at first proposed by Maier and Kelley [2745]. This equation reproduces the curvature of the specific heat - temperature function

at relatively low temperatures and the almost linear character of this function at high temperatures well. The parabola

$$C_p = a + bT + cT^2 \qquad \text{(III.16)}$$

applied in a number of papers, possesses, in contrast to Eq.(III.15), a greater curvature at high temperatures, which is not characteristic of the specific heat of solids. Applying this equation, one may frequently find that the term cT^2 possesses a negative sign, i.e., the specific heat of the substance passes through a maximum at a certain temperature, a fact which does not make physical sense. Trinomial equations of other types for the specific heats, for example,

$$C_p = a + bT - cT^{-1/2}, \qquad \text{(III.17)}$$

or

$$C_p = a + bT - cT^{-2}, \qquad \text{(III.18)}$$

are used very rarely. The application of four or five-membered equations is justified only in exceptional cases (see, for example [1387]) because the accuracy of the experimental data is generally insufficient for this purpose.

The derivation of the trinomial equation for the specific heat on the basis of experimental measurements of the enthalpy is carried out either by means of the value of the specific heat on the lower limit of the investigated temperature range (usually at 298.15°K) and of two enthalpy values for high temperatures chosen experimentally. In the second case, the derived equation for the specific heat is adjusted to the data obtained by investigation of the specific heat in the low-temperature range. In order to determine the coefficients a, b, and c of Eq.(III.15) by means of the second method, the following system of three equations

$$C_p = a + 298.15b - \frac{c}{(298.15)^2}; \qquad \text{(III.19)}$$

$$H^\circ_{T_1} - H^\circ_{298.15} = (T_1 - 298{,}15)\,a + \frac{T_1^2 - 298{,}15^2}{2}\,b + \left(\frac{1}{T_1} - \frac{1}{298{,}15}\right)c, \qquad \text{(III.19)}$$

$$H^\circ_{T_2} - H^\circ_{298.15} = (T_2 - 298{,}15)\,a + \frac{T_2^2 - 298{,}15^2}{2}\,b + \left(\frac{1}{T_2} - \frac{1}{298{,}15}\right)c.$$

must be solved.

Shomate [3711] proposed another method to determine the coefficients of the trinomial equation of the type (III.15) taking into account the value of $C_{p_{298.15}}$. Based on the experimental values of $H^\circ_T - H^\circ_{298.15}$ the values of the function*

$$y = \frac{\{(H^\circ_T - H^\circ_{298.15}) - C_{p_{298.15}}(T - 298{,}15)\}\,T}{(T - 298{,}15)^2} = bT + \frac{c}{(298{,}15)^2}. \qquad \text{(III.20)}$$

are calculated by this method. If the specific heat may be represented by a trinomial equation of the (III.15) type, and the change of the enthalpy by the corresponding equation

$$H^\circ_T - H^\circ_{298.15} = aT + \frac{b}{2}T^2 + cT^{-1} + d, \qquad \text{(III.21)}$$

the function (III.20) is a linear function of the temperature. In this case the coefficient b may be found from the slope of the straight line (III.20), and c by the relation $c = (298.15)^2 \cdot y_0$, where y_0 is the ordinate of Eq.(III.20) at T = 0, $a = C_{p_{298.15}} - 298.15b + y_0$, and $d = (298.15)^2 b/2 - 298.15 C_{p_{298.15}} - 596.3\,y_0$. This method was used for the derivation of equations of the specific heat in Kelley's Handbook [2363] and is at present widely in use.

The extrapolation of the values of specific heat by means of empirical equations to the range of high temperatures, for which experimental data on specific heat and entropy are lacking, is very unreliable and frequently leads to excessive values. The method proposed by Kelley ([2363], page 206), based on the comparison of the specific heats of solids at the melting point (or at the points of the first polymorphous transformation) gives more reliable results. According to Kelley, the specific heat of elements is approximately equal to 7.3 cal/g-atom·degree at the indicated temperatures, and the specific heat

of compounds is 7n cal/mole·degree, where n is the number of atoms in the compound. A linear equation of the type $C_p = a + bT$ is derived on the basis of the value of the specific heat at the melting point estimated in this way and one value of the specific heat at the lower limit of the temperature interval for which the estimation was carried out.

Heats and temperatures of phase transitions. The calculations of the thermodynamic functions of substances in the solid state were carried out for the equilibrium modifications of these substances. When the temperature rises, the solids may undergo phase transitions accompanied by thermal effects. One distinguishes phase transitions of first order in which the inner energy (and density) of the substances changes suddenly, and phase transitions of second order in which no jumplike change of these values occurs, but their partial derivatives, the specific heat, the compressibility and the coefficient of thermal expansion, change suddenly at the point of transformation.

It is expedient that the heat of the phase transformation of second order does not refer to the temperature interval but to one temperature when calculating the thermodynamic functions of solids. Thus, Kelley [2363] recommends a binomial and trinomial equation, respectively, for the calculation of the thermodynamic functions of the α and β quartz modifications and the values of the heat of transformation equal to 290 cal/mole, related to the temperature of 843°K.

It must be noted that the internal concordance of the heats of transformation with the data on the enthalpy and specific heat of the low and high-temperature phases must be provided when choosing these values.

The existence of polymorphous transformations was in several cases not taken into account in this Handbook when calculating the thermo-

dynamic functions, due to the fact that either the transformation heats are small and that they were not determined during the measurement of the enthalpy (in LiF and LiOH, for example), or experimental data on the specific heat and enthalpy of these substances are unknown at present. Thus, the polymorphous transformations determined by thermography, were not taken into account in the estimation of the specific heats of BeF_2 and $BeCl_2$, although the transformations heats, especially in BeF_2, are obviously of significant value.

The values of the melting points of almost all substances dealt with in the Handbook are chosen on the basis of experimental measurements. The accuracy of these measurements is very different, and depends not only on the errors in the measurement of the temperature but also on the purity of the investigated preparation and, in some cases, on the reaction of the substance with the vessel material at temperatures near the melting point. The probable error in the values of the melting point usually does not exceed 1-2° for substances melting below 1000°K, for higher melting substances (up to 2000°K) the error rises in some cases to 5-10°, and at temperatures above 2000°K, the error may attain 20-50°. The melting points of the nitrides of aluminum and boron are assumed on the basis of insufficiently reliable data [1614] with a possible error of ±100-200°. Reliable data on the melting points of boron, aluminum trifluoride and graphite are lacking in the literature. The values of these quantities assumed in the Handbook, must be considered to be roughly indicative.

The melting heats may be determined with the highest accuracy on the basis of calorimetric data. Unfortunately, such data are available only for part of the substances treated in the Handbook. The values of the melting heats calculated by Kelley [2356] using the Schroeder equation and the data of the state diagrams of bicomponent

systems were assumed for a number of compounds (MgO, SiO_2, etc.). The values obtained in this way are rather approximative, their uncertainty may achieve ±20-30% and more. Melting heats of substances may also be calculated in terms of the heats of evaporation and sublimation found as a result of measurements of the pressure of saturated vapors.

Data on melting heats are totally lacking for a number of substances, and it was necessary, therefore, to estimate them. There do not exist any general regularities concerning melting heats. For separate groups of related substances, however, the value of the melting entropy is an approximately constant magnitude. Thus, according to Kubaschewski and Evans [267], the mean value of the melting entropy of "true" metals (with a dense structure and a high coordination number, from 8 to 12) and of their non-ordered alloys is equal to 2.2 cal/g-atom·degree and that of the ordered alloys is 3.5 cal/g-atom·degree. Compounds having an ionic lattice of the NaCl type, for example, have a mean melting entropy of 3-3.5 cal/g-atom·degree, substances with a laminar lattice as, e.g., one of about 2.5 cal/g-atom·degree, and substances with molecular or particularly molecular lattices having a melting entropy of from 1 to 2 cal/g-atom·degree. It must be noted that the values indicated above are rather approximative and many significant deviations arise from these mean values.

The melting heats of a number of substances contained in this Handbook (Li_2O, BeO, BN, B, AlN, graphite) have been estimated on the basis of a comparison of the melting entropy of analogous compounds having the same or a similar type of crystalline structure. The possible error of the values of the melting heats obtained in this way is 20-40%.

Specific heat of substances in liquid state. Data on the specific

heat of molten inorganic substances at high temperatures are available only for a limited number of substances in a relatively narrow interval of temperatures. The accuracy of the values of specific heats obtained by differentiationof the curves of the enthalpy change $H^{\circ}_{T} - H^{\circ}_{298.15}$ is generally not high. Discussion of the available experimental material results in the following conclusions.

1) The specific heats of various high-melting substances (elements and their inorganic compounds) in the liquid state differ slightly from the specific heats of these substances in the solid state close to the melting points (as a rule by not more than 10-15%).

2) The specific heat of substances in the liquid state changes insignificantly at rising temperature. According to the data obtained in the Bureau of Standards of the U.S. (see the paper by Douglas [1385], the specific heat of seven substances (Li, Na, K, Pb, Hg, NaOH, and LiCl) decreases slightly at rising temperature, on an average by 0.02% per 1°, in a certain temperature range above the melting point (300-500°).

Among the substances treated in the Handbook, regularities in the change of the specific heat of the smelt at changing temperature may be determined only for the substances mentioned above (Li, Na, K, Pb, and LiCl). The experimental data for the other substances available at present are determined only for a limited interval of temperatures. This fact, and also the insufficient accuracy of the measurements disturbs the determination of the temperature dependence of the specific heat, and, therefore, the specific heats of these substances in the liquid state are assumed as being constant in the Handbook.

In the present Handbook, the estimations of the specific heats of substances in the liquid state were carried out in accordance with the approximate empiric regularities stated by Kelley [2363], accord-

ing to which the specific heat of molten elements is on the average, equal to 7.5 cal/g-atom·degree, and the specific heat of inorganic compounds in the liquid state is 8n cal/mole·degree, where n is the number of atoms in the molecule of the given compound.*

In conformity with this fact, the specific heats of substances in the liquid state were assumed to be equal to 7.5 cal/g-atom·degree for elements, and to be equal to 16, 24, 32 and 40 cal/mole·degree for three-, four- and five-atomic compounds, respectively in cases where experimental data on the specific heat or enthalpy of the substances in the liquid state were lacking or doubtful.

The specific heat at higher temperatures has been assumed to be constant and equal to the value of the specific heat in the investigated temperature range (or to the value at the upper limit of this range) in cases where experimental data on the specific heat of substances in the liquid state are known for part of the temperature interval in question.

Reference literature on the thermodynamic properties of solid and liquid substances. Kelley's Handbook, published as separate issues beginning with 1932 (see [2354-2358, 2360, 2363-2365]), is the most fundamental Handbook on the thermodynamic quantities of inorganic substances at low and high temperatures.

The Handbook "Entropies of Inorganic Substances" [2364], gives a critical analysis of the experimental data on the specific heat and the heats of phase transitions of inorganic substances in the 0-298.15°K temperature range,** smoothened values of the specific heat are quoted (for temperatures of 10, 25, 50, 100, 150, 200 and 298.15°K), the values of the entropies at 298.15°K are calculated, and the accuracy of the recommended $S^{\circ}_{298.15}$ values is estimated. In the Handbook "High temperature Heat Content, Heat-Capacity and Entropy Data for In-

organic Compounds" [2363, 2364a] the corresponding data at temperatures above 298.15°K are analyzed, recommended equations for the specific heat, change of enthalpy ($H^\circ_T - H^\circ_{298.15}$) are given, and also tables of the values of ($H^\circ_T - H^\circ_{298.15}$) and ($S^\circ_T - S^\circ_{298.15}$) in the temperature range from 400°K and above, up to the maximum temperature at which the measurements were carried out are quoted for each 100°K.

Besides the Handbooks mentioned, Kelley published a series of Handbooks on the melting heats of inorganic substances [2356], the pressure of saturated vapors [2355], and also the thermodynamic properties of carbonates [2365], of sulfur and its inorganic compounds [2357], of metal carbides and nitrides [2358].

The 2nd and 3rd parts of the Handbook "Termicheskiye kanstanty neorganicheskihk veshchestv" [Thermal Constants of Inorganic Substances] [98] have been compiled on the basis of the values, recommended by Kelley in the Handbooks [2360, 2354a], and of the results of investigations published up to 1940-1941.

In the reviews by Brewer [1093] dealing with the thermodynamic properties of elements, halides and other classes of compounds, besides the experimental data, the results of an estimation of the thermodynamic functions ($H^\circ_T - H^\circ_{298.16}$, S°_T, and Φ^*_T) are given in the temperature range up to 2000°K (elements) and up to 1500°K (halides).

Tables of thermodynamic functions of 60 substances in solid and liquid states are quoted in the third volume of Zeise's book [4384]. These tables are adopted without any changes from papers published in periodicals after the publication of Kelley's Handbooks [2363, 2364].

In the Handbook of the National Bureau of Standards of the U.S. [3508], besides the heats of formation of inorganic substances, the values of $S^\circ_{298.16}$, $C_{p298.16}$, and temperatures and heats of phase transitions are given.

In the third series of this Handbook, published in the form of separate tables beginning with 1947 [3680], tables of thermodynamic functions of some tens of substances in solid and liquid states are given; a part of these tables was subsequently reprinted with supplements in a number of other editions.

In the monographs by Kubaschewski and Evens "Metallurgische Thermochemie" [Thermochemistry in Metallurgy] published in several issues (see [2495]), reference material on the thermodynamic properties of the most important inorganic substances is compiled, and results are given of the estimation of some unknown values. The values of the entropies at 298.15°K, of the temperatures and heats of phase transitions, the equations for the specific heats of substances at high temperatures the pressures of saturated vapors, the isobaric potentials of formation and of reactions are cited in this book. It must be noted that Kubaschewski and Evans made sufficient use of the papers published in the last years.

In the Handbook by Stull and Sinke "Thermodynamic Properties of the Elements" [3894], a thorough analysis of all data on the thermodynamic properties of elements, available in literature (including publications in 1955), is given, the lacking values are estimated and tables are calculated on the thermodynamic functions of all elements (from hydrogen to uranium) in the interval from 298 to 3000°K in 100°K steps. The calculations of the thermodynamic functions (C_p°, $H_T^\circ - H_{298}^\circ$, S_T°, and Φ_T^*) are expanded up to boiling (sublimation) points of these substances.

§19. ESTIMATION OF THE ACCURACY OF THE THERMODYNAMIC FUNCTIONS OF SUBSTANCES IN SOLID AND LIQUID STATES

The estimation of the thermodynamic values measured experimentally was carried out allowing for the accuracy of the methods used for

their determination, the purity of the investigated samples, and, in some cases, for the phase state of the latter, the perfection of the crystal lattice, the degree of dispersity, etc. A comparison of data obtained by different methods is also important because the authors frequently overestimate the accuracy of their measurements, not allowing for the possibility of systematic errors.

Estimation of the value of $H^\circ_{298.15} - H^\circ_0$ for solid substances, obtained on the basis of experimentally found values of the specific heat, does not meet with significant difficulties, because the relative error of the value of $H^\circ_{298.15} - H^\circ_0$ does not exceed the weighted mean of the relative error of the values of specific heat in the indicated temperature range. If we divide the temperature interval from 0 to 298.15°K into n intervals, and if we denote the relative error of the specific heat in the nth interval by δC_{p_n}; the weighed mean relative error of $H^\circ_{298.15} - H^\circ_0$ in the temperature interval of from 0 to 298.15°K is determined by the formula

$$\delta (H^\circ_{298.15} - H^\circ_0) = \sum_{n=1}^{n} \left[\delta C_{p_n} \frac{H^\circ_{T_n} - H^\circ_{T_{n-1}}}{H^\circ_{298.15} - H^\circ_0} \right]. \qquad \text{(III.22)}$$

A more difficult problem is the estimation of the accuracy of $S^\circ_{298.15}$ values because the maximum of the C°_p/T function used for the calculation of the entropy lies usually below 298°K. A calculation and an estimation of the accuracy of the $S^\circ_{298.15}$ value is given, as a rule, by investigators which measured the specific heat at low temperatures. It must be noted that the amount of the error of $S^\circ_{298.15}$ depends mainly on the accuracy of the extrapolation of the specific heat to 0°K.

The value of Φ^* at 298.15°K is approximately equal to the half value of $S^\circ_{298.15}$ (from 30 to 70%) for solid substances. The absolute amount of the error of $\Phi^*_{298.15}$ usually does not exceed 2/3 of the

error of the value of $S^{\circ}_{298.15}$; in cases, however, in which the error in the value of $S^{\circ}_{298.15}$ is in principle due to an inaccurate extrapolation of the specific heat to 0°K, the error of $\Phi^{*}_{298.15}$ may attain the magnitude of the error of $S^{\circ}_{298.15}$. In the given Handbook, the error of $\Phi^{*}_{298.15}$ was adjusted to the error of the $S^{\circ}_{298.15}$ value.

The accuracy of the calculation of thermodynamic functions of substances in solid and liquid states at high temperatures depends on the accuracy of all initial thermodynamic values used for the calculation, e.g., the enthalpy and entropy at 298.15°K, the data on the specific heat of the substances above 298°K (or data on the enthalpy change $H^{\circ}_{T} - H^{\circ}_{298.15}$), the values of the temperatures and the heats of the phase transitions.

Estimation of the values of the specific heat calculated on the basis of the results obtained by experimental changes of the enthalpy $H^{\circ}_{T} - H^{\circ}_{298.15}$ is not a simple problem. Due to the fact that the specific heat is the first derivative of the enthalpy with respect to the temperature, errors in the values of C_p may significantly exceed the errors in the initial values of $H^{\circ}_{T} - H^{\circ}_{298.15}$. In order to diminish these errors in the values of the specific heats, the derivation of equations for C_p is carried out in accordance with the results of low-temperature measurements of the specific heat. It must be noted that a partial compensation of the errors takes place in the calculation of the thermodynamic functions by means of equations for the specific heat derived in this manner, and that the relative accuracy of the S°_{T} and Φ^{*}_{T} values exceeds the mean accuracy of the values of the specific heat.

Estimation of the accuracy of the Φ^{*}_{T} values of solid and liquid substances was carried out in the Handbook at temperatures of 298.15; 1000, 1500, 2000, and 3000°K. The increments of Φ^{*}_{T} between the indicated temperatures were calculated, and the relative errors of these

increments $(\Phi^*_{T_2} - \Phi^*_{T_1})$ were assumed to be equal to the relative errors in the values of the specific heat at the same temperature intervals (from T_1 to T_2).

The correctness of the latter assumption in first approximation may easily be proved in the case in which the specific heat in the investigated temperature interval $T_1 - T_2$ is assumed to be constant:

$$C_p = a = \text{const.} \qquad \text{(III.23)}$$

We have then

$$H^*_T - H^*_0 = aT - b, \qquad \text{(III.24)}$$

$$S^*_T = a \ln T - c \qquad \text{(III.25)}$$

and

$$\Phi^*_T = a \ln T + \frac{b}{T} - (c - a). \qquad \text{(III.26)}$$

The increments of the Φ^*_T function in the temperature interval $T_1 - T_2$ are equal to

$$\Phi^*_{T_2} - \Phi^*_{T_1} = a(\ln T_2 - \ln T_1) + b\left(\frac{1}{T_2} - \frac{1}{T_1}\right). \qquad \text{(III.27)}$$

The value of the first term on the right side of Eq.(III.27) exceeds, as a rule, that of the second term at least by one order; hence, one may assume with a sufficient accuracy, that the error in the value of $(\Phi^*_{T_2} - \Phi^*_{T_1})$ depends on the relative error in the value of $C_p = a$.

The error caused by the second term on the right side of Eq. (III.27) may be neglected in cases where Eq.(III.24) was derived on the basis of experimental data, and the errors in the coefficients a and b of Eq.(III.24) are connected with each other. If, however, the values of a and b are determined independently from each other (for example, by estimation of the melting heat and specific heat of the molten substance), the accuracy of the term $b\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$. must be taken into account when calculating the error of the value of $(\Phi^*_{T_2} - \Phi^*_{T_1})$.

The errors obtained or the values of $(\Phi^*_{T_2} - \Phi^*_{T_1})$ for different

temperature ranges were added and then rounded off. Thus, the error limits quoted in the Handbook determine the maximum possible errors in the value of Φ_T^*.

It must be noted that the estimation of the accuracy of the Φ_T^* values are only of a roughly indicating nature, mainly owing to the unreliability of the estimation of the accuracy of the specific heats, especially of specific heats of substances in the liquid state.

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[Footnotes]

246* See, for example, M.M. Popov, Termometriya i kalorimetriya [Thermometry and Calorimetry] [332]; Kubaschewski and Evans, Metallurgische Thermochemie (Thermochemistry in Metallurgy [267]); Roberts, Teplota i termodinamika [Heat and Thermodynamics] [345].

246** For greater detail with regard to the theory of the specific heat of solids see the monographs by Born and Goeppert-Mayer [93a], and Born and Huang-K'un [93b], and also the books by A.I. Brodskiy [99], and V.M. Gryaznov and A.V. Frost [167a].

248 With regard to tables of the Debye functions for specific heat at constant volume, $C_v = 3D(\theta_D/T)$, and also the corresponding functions for the internal energy, entropy and the reduced thermodynamic potential, see the editions [261a, 208a].

249 Kelley [2364] used the Eq.(III.7) for the extrapolation of the specific heat to 0°K in the following simplified form

$$C_v = 3D(\theta_D/T) + 3\sum_{i=1}^{i=1} E(\theta_{E_i}/T), \qquad \text{(III.8)}$$

where θ_D and θ_{E_i} are the averaged values of the characteristic Debye and Einstein temperatures.

250 T_i in some cases indicates the temperature at which the analytical equation for the specific heat of the given substance changes.

251* For details with regard to the accuracy of temperature scales at low temperatures see the review by Strelkov [394].

251** An entropy value at 298.15°K lower than 3 cal/mole·degree possesses diamond (0.566 ± 0.005); graphite (1.29 ± 0.01); boron (1.403 ± 0.005), and beryllium (2.28 ± 0.02).

253 For substances with anisotropic (lamellar or chain) structures, the extrapolation of the specific heat to 0°K may be carried out by means of appropriate Tarasov functions. Itskievich [198a] on the example of CdI_2 and $CdBr_2$ has proved that the accuracy of such an extrapolation amounts to approximately 25% (the calculated values of $S_{11.0}$ for CdI_2 and $CdBr_2$ are equal to 0.49 and 0.31 cal/mole·degree, and the experimentally found values are 0.39 and 0.25 cal/mole·degree, respectively).

256* The different empirical equation for the calculation of the standard entropies of groups of compounds, cited in literature, must be applied with precautions. Thus, the calculation for metal halides by means of Eq.(72), cited in the monograph by Kubaschewski and Evans [267], results in values which are strongly underrated in comparison with the true values (the appropriate difference attains 10 cal/mole·degree in the case of $S^\circ_{298.15}$ for some fluorides and chlorides of light metals).

256** In the paper by Krauss [2480], published recently, a method of measuring the true specific heat of metals at a higher temperature (1300°C) is developed. The accuracy of the measurement of the specific heat amounts, according to the estimation by Krauss [2480], to ±0.7% at 700°C, ±1% at 1000°C, and ±2% at 1300°C.

256*** To the disadvantages of the mixing method belong the insensitivity of the method to the determination of heats of phase transitions and the possibility of errors caused by the equilibrium of the final state in the case of a rapid quenching of the samples during the experiment.

258 The derivation of Eq.(III.20), see Kelley [2363].

263* Douglas [1385] recently carried out a thorough examination of all experimental data on the specific heat of inorganic substances in the liquid state and he obtained mean values very close to the values recommended by Kelley [2363]. For molten metals and alloys Douglas recommends the value of 7.4 cal/g-atom·degree, and for molten salts, 8.1 n cal/mole·degree. The salts of some oxygen acids (nitrates, sulfates) possess a lower specific heat, from 5n to 7n cal/mole·degree, and hydroxides and silicates have an average of about 7n cal/mole·degree. The salts of other oxygen acids, borates, titanates, chromates, etc., possess a specific heat in the liquid state from 7.5n to 9n cal/mole·degree.

263** In this edition, the literature published up to November 1948 is taken into account.

Chapter 4

THERMOCHEMICAL QUANTITIES

In the Tables of Volume II of the present Handbook, the values of the equilibrium constants of the dissociation of gases into atoms, of the dissociation constants of ions, of the vapor pressure of the substances above the condensed phase, and of the total enthalpies are cited. The values of a number of thermochemical quantities are necessary for calculating these data: the heat of formation ($\Delta H°f$) from the elements, the sublimation heat (ΔH_s), the dissociation energy (D), the ionization energy (I)*, and the electron affinity (A)

A review on the data in literature and the reason for the choice of the thermochemical quantities enumerated above are given in the corresponding sections of the chapters in the 2nd part of Volume I. Tables of the accepted values of the thermochemical quantities are given at the end of each section. The values of the dissociation energy (at 0°K) of gaseous substances into monatomic gases, the heats of sublimation of crystalline substances at 0°K, the ionization energy of certain atoms, molecules and ions at 0°K, the heats of formation of the substances at 0°, 293.15° and 298.15°K are listed therein. In both of the last colums of the tables, the values of $H°_{293.15} - H°_0$ and $H°_{298.15} - H°_0$ of the corresponding substances are quoted. The thermochemical quantities accepted in the Handbook on the basis of an analysis of the data in literature are marked in the text of the sections and in the tables of the accepted thermochemical quantities by bold type.

The thermal effects of exothermic reations (i.e., of reactions which proceed with release of energy) are considered to be negative ones, and the effects of endothermic reaction (proceeding with absorption of energy) as positive effects.

§20. GENERAL RELATIONSHIPS BETWEEN THE THERMOCHEMICAL QUANTITIES. COORDINATION OF THE VALUES AND THEIR UNCERTAINTIES

The thermochemical quantities dealt with in the Handbook are coordinated to each other. The equations which express this coordination are based on the Hess law, a particular case of the energy conservation law. Corresponding to this law, the thermal effect (or the change of enthalpy, ΔH_T) of the process which is connected with chemical transformations, changes of the phase state, ionization etc., and which is determined by the equation

$$\nu_1 X_1 + \nu_2 X_2 + \dots = \nu_1' X_1' + \nu_2' X_2' + \dots, \qquad (IV.1)$$

where ν_i is the number of moles of the substances X_i, may be calculated by the formula

$$\Delta H_T^\circ = [\nu_1' \Delta H^\circ f_T(X_1') + \nu_2' \Delta H^\circ f_T(X_2') + \dots] - [\nu_1 \Delta H^\circ f_T(X_1) + \nu_2 \Delta H^\circ f_T(X_2) + \dots]. \qquad (IV.2)$$

Here, $\Delta H^\circ f_T$ is the heat of formation of the substance at the temperature T, equal to the change of enthalpy during its formation from the elements at this temperature, the elements being taken in their standard states (the definition of the standard state is given on page 29).

The standard states of elements, at which the formation heats of the latter are assumed to be equal to zero, are quoted in Table 15 and stipulated in each of the sections dealing with the choice of the thermochemical quantities. The electron gas with a volatility equal to unit is in the standard state, and its heat of formation is assumed as being equal to zero at any temperature.

TABLE 15

The Standard States of the Chemical Elements Accepted in the Handbook.

1 Элемент	2 Стандартное состояние	1 Элемент	2 Стандартное состояние
Кислород . 3.	34 Двухатомный газ	Ртуть . . 19. .	36 Жидкость
Водород . . 4.	» »	Цирконий 20. .	Кристаллическое состояние
Гелий . . . 5.	35 Одноатомный газ	Свинец . 21. .	» 37 »
Неон . . 6. .	» »	Бор . . . 22. .	» »
Аргон . . . 7. .	» »	Алюминий 23. .	» »
Криптон . . 8.	» »	Бериллий 24. .	» »
Ксенон . . 9.	» »	Магний . 25. .	» »
Фтор . . . 10.	34 Двухатомный газ	Кальций . 26. .	» »
Хлор . . . . 11.	» »	Стронций 27. .	» »
Бром . . . 12.	16 Жидкость 37	Барий . . 28. .	» »
Йод . . . 13. .	Кристаллическое состояние	Литий . . 29. .	» »
Сера 14. . . .	Ромбическая сера (крист.)	Натрий . . 30. .	» »
Азот . 15. .	34 Двухатомный газ	Калий . . 31. .	» »
Фосфор . 16. .	39 Белый фосфор (крист.)	Рубидий . 32. .	» »
Углерод . 17. .	40 Графит	Цезий . . 33. .	» »
Кремний . . . 18	Кристаллическое состояние 37		

1) Element;
2) standard state;
3) oxygen;
4) hydrogen;
5) helium;
6) neon;
7) argon;
8) krypton;
9) xenon;
10) fluorine;
11) chlorine;
12) bromine;
13) iodine;
14) sulfur;
15) nitrogen;
16) phosphorus;
17) carbon;
18) silicon;
19) mercury;
20) zirconium;
21) lead;
22) boron;
23) aluminum;
24) beryllium;
25) magnesium;
26) calcium;
27) strontium;
28) barium;
29) lithium;
30) sodium;
31) potassium;
32) rubidium;
33) cesium;
34) diatomic gas;
35) monatomic gas;
36) fluid;
37) crystalline state;
38) rhombic sulfur (crystalline);
39) white phosphorus (crystalline);
40) graphite.

Using the general relationship (IV.2), equations may be found which connect all thermochemical quantities dealt with in the Handbook with one another.

1. Heat of Sublimation

The heat of sublimation is the thermal effect of the process

$$X(\text{ cryst. }) \rightarrow X(\text{ gas }). \qquad \text{(IV.3)}$$

Hence

$$\Delta Hs_T(X, \text{ cryst. }) = \Delta H^\circ f_T(X, \text{ gas }) - \Delta H^\circ f_T(X, \text{ cryst. }). \qquad \text{(IV.4)}$$

For example,

$$\Delta Hs_T(MgO, \text{ cryst. }) = \Delta H^\circ f_T(MgO, \text{ gas }) - \Delta H^\circ f_T(MgO, \text{ cryst. }).$$

2. Dissociation Energy

The dissociation energy is the thermal effect of the process

$$X_{\nu_1}Y_{\nu_2}\ldots(\text{gas}) \rightarrow \nu_1 X(\text{gas}) + \nu_2 Y(\text{gas}) + \ldots. \qquad \text{(IV.5)}$$

Hence

$$D_T(X_{\nu_1}Y_{\nu_2}\ldots) = \nu_1\Delta H^\circ f_T(X, \text{ gas }) + \nu_2\Delta H^\circ f_T(Y, \text{ gas }) + \ldots - \Delta H^\circ f_T(X_{\nu_1}Y_{\nu_2}\ldots, \text{ gas }). \qquad \text{(IV.6)}$$

For example,

$$D_T(Al_2O_3) = 2\Delta H^\circ f_T(Al, \text{ gas }) + 3\Delta H^\circ f_T(O, \text{ gas }) - \Delta H^\circ f_T(Al_2O_3, \text{ gas })$$

or

$$D_T(Al_2O_3) = 2\Delta H^\circ f_T(Al, \text{ gas }) + 3\Delta H^\circ f_T(O, \text{ gas }) - \Delta H^\circ f_T(Al_2O_3, \text{ cryst. }) - \Delta Hs_T(Al_2O_3, \text{ cryst. }).$$

3. Ionization Energy

The ionization energy is the thermal effect of the process

$$X(\text{gas}) \rightarrow X^+(\text{ }) + e^-(\text{gas}). \qquad \text{(IV.7)}$$

Hence

$$I(X) = \Delta H^\circ f_0(X^+, \text{ gas }) + \Delta H^\circ f_0(e^-, \text{ gas }) - \Delta H^\circ f_0(X, \text{ gas }). \qquad \text{(IV.8)}$$

For example,

$$I(NO) = \Delta H^\circ f_0(NO^+, \text{ gas }) + \Delta H^\circ f_0(e^-, \text{ gas }) - \Delta H^\circ f_0(NO, \text{ gas })$$

The values of ionization energy given in the Handbook are related to 0°K.

4. Electron Affinity

The electron affinity is the thermal effect of the process

$$X(\text{gas}) + e^-(\text{gas}) \rightarrow X^-(\text{gas}). \qquad \text{(IV.9)}$$

Hence

$$A(X) = \Delta H^\circ f_0(X^-, \text{gas}) - \Delta H^\circ f_0(X, \text{gas}) - \Delta H^\circ f_0(e^-, \text{gas}). \qquad \text{(IV.10)}$$

In literature, a positive sign is usually ascribed to the values of the electron affinity, although the addition of an electron is accompanied by release of energy. In order to conserve the uniformity of the signs of the thermochemical magnitudes, the values of electron affinity are given with negative signs in the Handbook, as follows from Eq.(IV.10).

The values of the equilibrium constants quoted in the Handbook correspond to the reactions of dissociation, inoization and evaporation of substances, i.e., to processes accompanied by energy absorption. Thus, in order to conserve the uniformity in the Tables of thermodynamic properties in Vol. II of the Handbook, the values are given for the equilibrium constants which correspond to the reaction

$$X^-(\text{gas}) \rightarrow X(\text{gas}) + e^-(\text{gas}), \qquad \text{(IV.11)}$$

i.e., for the process of detachment of an electrom from the ion, for which

$$I(X^-) \equiv -A(X) = \Delta H^\circ f_0(X, \text{gas}) + \Delta H^\circ f_0(e^-, \text{gas}) - \Delta H^\circ f_0(X^-, \text{gas}). \qquad \text{(IV.12)}$$

is valid. For example,

$$I(O^-) \equiv -A(O) = \Delta H^\circ f_0(O, \text{gas}) + \Delta H^\circ f_0(e^-, \text{gas}) - \Delta H^\circ f_0(O^-, \text{gas}).$$

The values of electron affinity (and, respectively, of the detachment of an electron from the ion), quoted in the Handbook, are related to 0°K.

The reduction of the heat affects of a reaction from one temperature to another is carried out by equation

$$\Delta H_{T_2} = \Delta H_{T_1} - \nu_1 (H^\circ_{T_1} - H^\circ_{T_2})_{x_1} - \nu_2 (H^\circ_{T_2} - H^\circ_{T_1})_{x_2} - \ldots + \\ + \nu'_1 (H^\circ_{T_2} - H^\circ_{T_1})_{x'_1} + \nu'_2 (H^\circ_{T_2} + H^\circ_{T_1})_{x'_2} + \ldots, \quad \text{(IV.13)}$$

based on Kirchhoff's law. Carrying out such reductions, it must be taken into account that the heats of phase transitions between crystalline modifications and the melting heats are allowed for in the compilation of the tables of the enthalpy of substances in the condensed state (see Eq.(III.9)). Thus, the thermal effect of a reaction calculated by Eq. (IV.13) corresponds always to the thermodynamical equilibrium state of the substances at the temperature T_2.

Coordination. The mutual connection between the thermochemical quantities makes their coordination necessary. The thermochemical quantities quoted in the Handbook are a system of values coordinated to each other. In order to provide for this coordination, only thermal effects of reactions measured immediately in the papers were used when choosing the thermochemical quantities. A number of other thermochemical quantities is needed in order to calculate the heats of formation, the dissociation energies, etc. by means of these data. The calculations were in all cases carried out on the basis of the data accepted in the Handbook. In a number of cases, the values of certain thermochemical quantities were needed which are not dealt with in the Handbook (for example, the integral and differential heats of dissolution of hydrogen chloride or fluoride in water, the heat of alkali halides, etc.). These values were assumed according to the data of the Handbook of the Bureau of Standards of the U.S. [3508].

Attention was also paid to the coordination between the thermochemical quantities and the values of the thermodynamic functions accepted in the Handbook. In connection with this fact, the results of all measurements of thermal effects at high temperatures and also the results of investigation of equilibria and measurements of vapor

pressures were converted, using the values of enthalpy and of the reduced thermodynamic potential of the reaction components accepted in the Handbook.

Estimation of Inaccuracies. The estimation of inaccuracies of the accepted thermochemical quantities in many cases causes great difficulties. The authors of experimental work, as a rule, quote inaccuracies which characterize the random errors of the experiment. The results of measurements, beside the random errors, may include systematic errors caused by the presence of side reactions, by systematic errors of the measuring devices, the inaccuracy of the conditions under which the measurements are carried out, etc. A correct estimation of these errors is, with rare exceptions, not possible. Thus, the values of inaccuracies of some thermochemical quantities (especially of the estimated ones) accepted in the Handbook are, in a number of cases to a certain extent arbitrary.

The results of the individual experimental investigations are usually given in the text of the Handbook with that inaccuracy which the authors of the investigations ascribe to them. The values of inaccuracies of the heats of sublimation or reactions, quoted in the text, obtained by recalculation of the experimental data on the basis of the values of thermodynamical functions accepted in the Handbook, are arithmetic mean inaccuracies.

Together with the value of the thermochemical quantity accepted in the Handbook, that inaccuracy is given which the authors of the Handbook consider to be the most justified one and which is used in the subsequent calculations (these values are given in bold type). The inaccuracies of derivative quantities are calculated on the basis of the inaccuracies of all quantities used for calculation. It was assumed that the inaccuracy of a derivative quantity is equal to the

square root of the sum of squares of the inaccuracies of the individual measurements. This explains the fact that the inaccuracies of derivative quantities sometimes possess an unjustifiably large number of significant digits (the number of significant digits in inaccuracies of derivative quantities does not reflect the degree of reliability of their estimation).

The values of inaccuracies of thermochemical quantities accepted in the Handbook differ in many cases from those cited in the original papers, because the choice of the inaccuracies was carried out allowing for the peculiarities of the experimental investigation (or the method of estimation), for the results of other measurements of the same quantity, the comparison of the given quantity with quantities obtained for other compounds, of the uncertainties used in calculating supplementary data (heats of formation, thermodynamic functions), etc. The values of uncertainties ascribed to the given quantity by authors of other Handbooks, monographs or reviews, have also been taken into account.

§21. EXPERIMENTAL METHODS OF THE DETERMINATION OF THERMOCHEMICAL QUANTITIES

The majority of the values of heats of formation accepted in the Handbook is based on the results of calorimetric measurements of the thermal effects of reactions. A thorough description of methods of calorimetric measurements is given in the monographs by Popov [332], Rossini [3502] and Kubaschewski and Evans [267]. Among the other methods of determination of thermochemical magnitudes, the calorimetric methods belong to the most accurate ones. The technique of the calorimetric measurements is at present perfect and provides accurate results. The main sources of measurement errors in these methods are side reactions, insufficient accuracy in the determination of the com-

position (including the phase composition) of the reaction products, and the presence of impurities in the initial substances.

The determination of the heat of formation of organic substances is mainly carried out by measuring the heat of combustion. Heats of hydration, halogenation and hydrohalogenation of organics are more rarely determined by calorimetric methods. The accuracy of measuring the combustion heat of organics containing carbon, hydrogen, oxygen and nitrogen achieved in contemporary works, is very high; thus, for example, the results obtained in a number of works, are reproducible within 0.02-0.05%. The calculation of the heat of formation of organics on the basis of the measured heats of combustion offers no great difficulties because the composition of the combustion products is usually relatively simple and may be reliably determined by analysis, and the heats of formation of the main products of combustion (CO_2, H_2O) are determined very accurately.

Difficulties in the determination of the final composition of the combustion products arise when combusting organics which contain sulfur, chlorine and bromine, because these elements are present in the combustion products in the form of several compounds. In these cases the accuracy of the determination of the heat of combustion and the accuracy of the calculation of heat of formation on the basis of these data is not always satisfactory.

The combustion of compounds containing chlorine and bromine is usually carried out in the presence of reducing agents (an aqueous solution of As_2O_3, for example). Under these conditions, chlorine and bromine are found totally in the form of the corresponding hydrogen halide acid. Good results are achieved when combusting halide-containing compounds by the methods of the rotating bomb and "quartz wool".* Many halide-containing compounds burn with difficulties and must be

burned together with other substances, which fact reduces the accuracy of the measurement. More accurate values of formation heats of halogen derivatives of methane and ethylene have been obtained by other methods, for example, by measuring the heat of the reaction with alkali metals.

The application of calorimetric methods for the determination of the heats of formation of inorganics is, as a rule, a more difficult problem. In many cases, the heats of formation of inorganics may be calculated on the basis of the measurement of the heats of combustion; this method, however, in this case is not of such an universal importance as in that of organics. Beside measurements of heats of combustion, measurements of the heats of solution, hydrolysis, chlorination, substitution, reduction, etc., are widely used. The final composition of the products of reactions used for the determination of the heats of formation of inorganics is in many cases complex, and their chemical analysis cannot always be carried out with sufficient accuracy. These circumstances make it necessary to use for the calculation of the heat of formation of inorganics data on the thermal effects of several reaction, and the accuracy of the obtained values is reduced.

An important source for data on heats of formation of various compounds, including compounds which are not stable at room temperature, are the measurements of the equilibrium constants. A description of the various methods of the investigation of equilibria is given in the reviews by Kubaschewski and Evans [267], Vvedenskiy [119], and Cottrell [255].

A particular case of the investigation of equilibria are the measurements of vapor pressures above solid and liquid substances. The most important method of measuring vapor pressures are: the effusion

method by Knudsen, the method of evaporation on an open surface by Langmuir, and the method of measuring influr (dynamic method). A description of these methods is given in the Handbook by Nesmeyanov [308b] and in the monograph by Vvedenskiy [119a].

The molecular composition of the products of the investigated reaction must be known in order to determine the value of the equilibrium constant. The results of various thermodynamic investigations, in the first place of mass-spectrometric ones, have shown that the composition of the products of chemical reactions is very complex in many cases, especially at high temperatures.* The problems related to the complication of the molecular composition of substances in gaseous and condensed states at high temperatures are thoroughly dealt with in the review by Brewer and Searcy [95].

Besides the equilibrium constants, also the heats of formation of the other reaction components and the values of the thermodynamic functions of all reaction components must be known when calculating the heat of formation of one component of reaction under standard conditions. The authors of the original investigations on equilibria used for the calculation of heats of formation values of thermodynamic functions, which in many cases differ essentially from those accepted in the present Handbook. In order to provide a coordination of the data quoted, the results of the original works have been recalculated on the basis of the values of thermodynamic functions and heats of formation of the reaction components accepted in the Handbook. The latest data on the reaction products have been taken into account when carrying out such calculations. This recalculation led in a number of cases to a higher accuracy and, sometimes to a total alteration of the results of the calculations of the authors of original papers.

The calculation of the values of reaction heats on the basis of

the measurement of equilibrium constants (including the measurement of the sublimation heat on the basis of vapor pressures) may be carried out in two ways. The first one, usually applied in older papers, is based on the IInd rule of thermodynamics, in particular on the van't Hoff equation for the isobar of the reaction

$$R \ln K_p = -\frac{\Delta H_T}{T} + \text{const.} \qquad \text{(IV.14)}$$

Data on the equilibrium constants at two temperatures (two unknown quantities, ΔH_T and const, enter into the equation) are necessary and sufficient in order to determine the heat of reaction by this method. In practice, the heat of reaction is determined on the basis of the values of equilibrium constants in a certain temperature interval by plotting a graph or by analytical determination of the slope of the straight line expressing $\ln K_p$ as a function of $1/T$.

The second method, recently widely in use, is based on Eq.(I.15), according to which

$$\Delta H_0 = T(\Delta \Phi_T^* - R \ln K_p). \qquad \text{(IV.15)}$$

The values of Φ_T^* of all substances, taking part in the reaction, and at least one value of the equilibrium constant is necessary for the calculation of the heat of reaction by Eq.(IV.15). Calculation by this method has a number of essential advantages in comparison with the calculation based on the temperature dependence of $\ln K_p$. In particular, scattering of the experimental data frequently hinders reliably to determine the slope of the straight line $\ln K_p = f(1/T)$, which causes errors in the thermal effect of the reaction up to 10-20 kcal/mole. At the same time, even the use of relatively inaccurate values of the reduced thermodynamic potentials Φ_T^*, having an inaccuracy equal to ± 1 cal/mole·degree, leads to an error of ± 1 kcal/mole if the measurements are carried out at 1000°C, and $\pm$ 2 kcal/mole at 2000°K.

An important advantage of the calculation method based on Eq. (IV.15) is the fact that it makes it possible to allow for a complex composition of the reaction products, including the complex composition of vapors (see [296]). Thus, in the present Handbook, the calculations of the heats of reaction on the basis of data or equilibria were carried out, as a rule, by Eq.(IV.15).

The method of explosion in a spherical bomb [169, 297] and the method of investigation of equilibria in flames [122] may be used for the investigation of equilibria at high temperatures. The method of explosion in a spherical bomb consists of measuring the pressure developed in an adiabatic explosion of a gas mixture in a closed vessel. The value of the explosion pressure found in the experiment makes it possible to calculate the heat of formation of one of the combustion products. This method was successfully applied for the determination of the heat of formation and energies of dissociation of F_2, ClF, OH, SiO, SiO_2 (gas), COF_2, and some halogen derivatives of methane.

The intensity of spectral emission of one of the reaction components is measured when determining the equilibrium constants on the basis of equilibrium in flames. This method was applied with great success in the determination of dissociation energies of the oxides of alkali earth metals.

The method of explosion in a spherical bomb and the spectroscopical investigation of equilibria in flames make it possible to determine the values of heats of formation and dissociation energies of substances which are formed only at high temperatures. The main difficulties arising when investigations are carried out by these methods are caused by the determination of the composition of the reaction products at high temperatures.

The mass-spectrometric method becomes more and more widely spread

in recent years for the determination of thermochemical magnitudes. A description of this method may, for example, be found in the monographs by Bernard [90] and Cottrell [255]. The results of mass-spectroscopical investigations are measurement of the potentials of occurrence and ionization, and also of the intensity of the currents of the ions formed. If, as the result of an electronic impact, the bond in the molecule is broken, the experimentally found potentials of occurrence and ionization make it possible to calculate the dissociation energy of this bond. In this case, it is necessary, to know the energy of the electron excitation and the kinetic energy of the fragments of the molecule. In many cases, however, it is difficult to ascribe the measured potential of the occurrence of an ion to a concrete process. The temperature at which the dissociation ionization takes place must also be known when calculating the dissociation energy of the bond. As Tal'roze and Frankevich [407] have shown, a temperature equilibrium occurs between the walls of the chamber and the gas in the ionization chamber of a mass spectrometer having a source of the Nier type. Taking this fact into account, it was assumed in the Handbook, when recalculating the results of mass spectroscopical investigations, where the temperature of the molecular beam is not explicitly mentioned, that the process of the dissociation ionization take place at the temperature of the ion source. The temperature of the walls of the ion source was approximately assumed to be equal to 500°K.

The application of the mass-spectrometrical method for measuring vapor pressures of substances in the condensed state has proved itself to be very productive. In contrast to the usual methods of the measurment of vapor pressures, the mass-spectrometrical method makes it possible to determine the molecular composition of the products of evaporation and to obtain data which characterize each component of the

saturated vapor. A great number of examples may be cited, in which especially the mass-spectrometrical method enabled the investigator to clear up the composition of vapors and to find the correct values of the heat of sublimation. The intensity of the ion current of the given vapor component as a function of the temperature is measured when such investigations are carried out. Owing to the fact that the intensity of the ion current is proportional to the pressure, the heat of sublimation of the given vapor component (or the heat of reaction between gaseous substances, if the intensities of the corresponding ion current have been measured) may be calculated by Eq.(IV.14). More accurate values of the thermal effects may be obtained by Eq.(IV.15), the values of the partial pressures, however, must be known for this calculation, and their determination requires estimation of the ionization cross sections of the atoms and molecules.

The heats of formation of several substances may be calculated on the basis of measurement of the emf of galvanic cells (PbO) and also on the basis of measurements of the solubility product of difficulty soluble substances (PbF_2). These methods are discussed in the papers by Kubaschewski and Evans [267] and Brewer [1093]. A review of the methods to determine bond energies, based on investigations of the reaction kinetics, may be found in the papers by Szwarc [3912] and Cottrell [255]. These methods have been used successfully in the determination of the formation heats of a number of radicals.

The dissociation energies of diatomic molecules may be found as a result of the investigation of their spectra.* A thorough statement of the various spectroscopical methods of determination of the dissociation energy is given in Gaydon's monograph [1668] (see also the papers by Herzberg [2020] and Cottrell [255]).

The spectroscopical determination of the dissociation energy of a

molecule requires finding of the energy of the dissociation limit with respect to the lower level (v = 0, J = 0) of the ground state and the determination of the electronic states of the dissociation products. The energy of the dissociation limit may be determined: 1) on the basis of the boundary where the bands join the continuous spectrum in the absorption spectrum; 2) on the basis of the predissociation in the spectrum; 3) on the basis of the long-wave edge of the continuous absorption spectrum, and 4) by investigation of the atomic fluorescence. The energy of the dissociation limit may also be estimated approximately by extrapolation of the observed vibrational energy levels.

Frequently, the energy states cannot be determined on the basis of data obtained by the investigation of spectra. The determination of the state of dissociation products may in a number of cases be carried out theoretically on the basis of the correlation rules of electronic states of molecules, and of their atoms, proposed by Wigner and Witmer [4267]. In cases of a unique interpretation of the electron states of the dissociation products, the spectroscopic investigations make it possible to determine the values of dissociation energies with the highest accuracy owing to the high accuracy in the measurement of the energies of dissociation limits. In particular, such data were obtained for 20 molecules dealt with in the Handbook (O_2, H_2, Cl_2, Br_2, I_2, CO, N_2, and others).

For a number of diatomic molecules, whose spectra are insufficiently investigated, the dissociation energies may be estimated only approximately by extrapolation of the vibrational energy levels, observed experimentally, to the dissociation limit. It is possible to carry out this extrapolation by various methods. The simplest method is the linear extrapolation, which was for the first time proposed by

Birge and Sponer [830] and based on the use of Morse's potential function (see page 65).* The linear extrapolation is usually carried out analytically by means of Eq.(1.12). The extrapolation of the vibrational energy levels, observed experimentally, to the dissociation limit may also be carried out graphically. It must be noted that various types of graphical extrapolation are possible: design of graphs of the functions $\Delta G(v + 1/2)$ from $G(v)$, $\Delta G(v + 1/2)$ from $v + 1/2$, and also of the total energy of each vibrational level $T_v = \nu_0 + G(v)$ from $\Delta G(v + 1/2)$.

In the present Handbook, the dissociation energies of 18 diatomic molecules (SiCl, MgF, MgCl, NH, NS, etc.) have been estimated by means of various methods of extrapolation. The accuracy of the values of the dissociation energy obtained in this way depends on the type of bond in the molecule, the number of vibrational levels determined in the experiment, and, to a certain degree, on the method of extrapolation. The problems of accuracy and applicability of the methods of extrapolation of vibrational levels for the determination of the dissociation energy are thoroughly discussed in Gaydon's papers [1668, 141, 1665].

It must be emphasized that the extrapolation is correct only in those cases where the potential curve has a form which is described with sufficient satisfaction by a Morse function. It was shown in a number of papers [2996, 2995, 643, 2037] that for certain molecules, AlF and AlCl, for example, the potential curves of the excited electronic states possess maxima lying higher than the dissociation levels of these states. The extrapolation of the vibrational levels of these states results in overrated values of the dissociation energy. Moreover, the linear extrapolation results in essentially underrated values in cases where the type of the bond in the molecule is to a sig-

nificant degree caused by ionic forces (in AlF or LiF, for example).

The dissociation energies of molecules whose spectra have not been investigated at all and for which thermochemical data are not given (the dissociation energies of NF, MgN, BeN, PCl, PF, SF, etc., for example) were estimated in the present Handbook by means of various approximate relations and regularities which make it possible to obtain orientating values of the unknown dissociation energies.

§22. APPROXIMATE ESTIMATIONS OF THERMOCHEMICAL QUANTITIES

Experimental data which make it possible to determine the heats of formation or dissociation energies with sufficient reliability are lacking for many of the substances dealt with in the Handbook. In such cases, various empirical or half-empirical methods of calculation were used for the determination of the thermochemical quantities and for checking their concordance with other thermochemical quantities accepted in the present Handbook.

The method of "comparative calculation" proposed by Karapet'yants [220, 221, 215, 216, 217, 218] is widely used in the Handbook. This method is based on the principle of the similar behavior of properties in a series of compounds which are similar in chemical properties and in molecular structure. Based on numerous examples, Karapet'yants in particular showed that the heats of formation of similar series of compounds (for example, KF, KCl, KBr, KI, and NaF, NaCl, NaBr, NaI) show a mutual linear dependence. A linear dependence is also observable between different properties of the same series of similar compounds (for example, between ΔHs and ΔHf, $S_{298.15}$ and D_0; etc.). Plotting the corresponding graphs, the values of the thermodynamic quantities may be estimated with a certain accuracy. It must be noted, however, that the method by Karapet'yants gives good results only if data on compounds are used which are sufficiently similar to each other. Calculations

carried out by the authors of the Handbook proved that the method by Karapet'yants is applicable not only for stable compounds but makes it possible to estimate also the heats of formation of radicals. The method by Karapet'yants was used in the Handbook in a number of cases to check the agreement of thermochemical quantities and to estimate their inaccuracies.

The method of determining the dissociation energy of substances based on the principle of additivity of the mean bond energies, is widely used in literature. It is assumed, if carrying out such calculations, that the energy of a bond with the same multiplicity remains constant in all compounds of a given pair of atoms. This relatively simple scheme has been widely used in a number of papers [357, 358, 199, 127, 471, 255] (the values of mean bond energies calculated in accordance with recent thermochemical data are quoted in paper [468]). However, carrying out calculations by means of this most simple method, the effect on the bond energy of neighbored atoms and atom groups remains totally neglected. The problem of the connection between the dissociation energy of a molecule and the structure of the latter has been thoroughly discussed in the papers by Tatevskiy [409] and Tatevskiy and Papulov [411, 412, 413]. It has been shown in these papers that accurate calculations are possible only in combination with a detailed classification of the chemical bonds, and such a classification is given for some homologous series. The most thorough classification of the bonds in alkanes, developed by the authors, includes the classifications, proposed earlier in other papers, as particular cases. Tatevskiy and Papulov [412] also investigated the method of representing the dissociation energies of molecules as the sums of the interactions of their atoms developed by Bernstein [761], and they have shown that this method gives definite

equations which do not differ in principle from the equations derived on the basis of classification of the bonds.

It must be noted that, in the case of inorganics, the method of determining the dissociation energy of compounds by means of the dissociation energies of the individual bonds does not yield such accurate results as in the case of homologous series of organic compounds. This may be explained by the significantly higher specifity of the bonds in inorganics which do not allow for the statement of a general and, at the same time, detailed classification of the bonds and to ascribe to the individual bonds values of dissociation energy which remain constant for a sufficiently large group of substances.

In some cases, the method of estimating the heats of combustion of organics, proposed by Kharasch [2392] (see also [468, 471, 214, 271]), and the method of "half-sums" proposed by Berkenheim [89] (see also [470]), was used in the Handbook.

Experimental investigations on the heats of formation or on dissociation energies make it possible, as a rule, to determine the values of these quantities for one of the isotopic modifications of the molecules of the substance in question. In most cases, the difference of the formation heats of the different isotopic modifications of molecules does not exceed the inaccuracy of the measurements. In cases, however, where this is needed, the dissociation energies and, therefore, also the formation heats of all isotopic modifications of a given substance may be calculated if the dissociation energy of any modification is wellknown. Owing to the fact that the intramolecular field of force does almost not depend on the isotopic composition of the molecule, the value of the quantity D_e (see page 64) also does not depend on the isotopic composition of the molecules. Thus, the difference between the dissociation energies of two isotopic modifications

of the ABCD molecule may be calculated by the equation

$$D_0(A'B'C'D') - D_0(A''B''C''D'') = G(0, 0, 0, \ldots)_{A'B'C'D'} - G(0, 0, 0, \ldots)_{A''B''C''D''}, \quad \text{(IV.16)}$$

where $G(0, 0, 0, \ldots)_{A'B'C'D'}$ and $G(0, 0, 0, \ldots)_{A''B''C''D''}$ are the vibrational energies of these molecules in ground states (see Eqs.(1.5) and (1.49)).

If the vibrational constants are determined with sufficient accuracy, the error of the calculation of the difference of the dissociation energies by Eq.(IV.16) does not exceed the errors of the best experimental measurements.

§23. REFERENCE LITERATURE ON THERMOCHEMICAL QUANTITIES

The authors of the Handbook were guided in the choice of the thermochemical quantities mainly by original papers. Moreover, the materials of various Handbooks have been widely used. The Handbook by Bichowsky and Rossini [813] is of great value because the results of a vast number of thermochemical investigations, beginning with the papers by Berthelot and Thompson, and ending with 1934, are compiled and estimated. This Handbook served as a basis for the majority of later publications.

The Handbook "Termicheskiye konstanty neorganicheskikh veshchestv" [Thermal Constants of Inorganic Substances], compiled by Britske, Kapustinskiy, Veselovskiy, Shamovskiy, Chentsova and Anvayer [98] on the basis of the work by Bichowski and Rossini [813] was the first publication of this type in the Russian language. The paper [813] is extended by material taken from the Landolt-Bernstein Handbook and the monographs by Kelley [2355, 2365, 2356, 2357, 2358, 2360] and also by data taken from original papers published in 1936-1940. However, being useful as a whole, the Handbook [98] possesses grave disadvantages. Thus, correcting numerical data, the authors committed an internal discordance among some data. For example, they changed essentially the heats

of formation of aluminum oxide and boron oxide, the heats of formation of a number of other substances, however, which are usually calculated by means of these values, have been left without correction.

The Handbook of the National Bureau of Standards of the U.S. [3508] may be considered to be the fundamental modern reference publication of heats of formation of phase transitions. This Handbook is unique with regard to the number of compounds dealt with and the totality of the literature material included. Unfortunately, in the case of some compounds, the literature is utilized only up to 1947-1950, and the Handbook does not contain texts which explain the choice of the quantities, and thus, in some cases, may cause difficulties.

Of great value are the reviews by Brewer et al. on the thermodynamic properties of elements, nitrides, carbides, sulfides, silicides, borides, phosphides, usual gases, and halogen compounds [1093 and oxides [917]. A short substantiation of the accepted values is given in these reviews, and the original estimations are quoted.

In the papers by Kubaschewski and Evans [267, 2494, 2495], the heats of formation and sublimation of a number of compounds are cited. The fact that estimations of the inaccuracies of the accepted values are given, is an important merit of these papers. Coughlin [1193] compiled a review on the heats of formation of oxides and also estimated the errors of the accepted values. Papers published up to September 1953 were utilized in this review. The paper by Cottrell [255] and the review by Kondrat'yev [243] are dealing with the choice of the values of mean bond energies and dissociation energies of bonds, the latter being of particular value for the calculation of the heats of formation of radicals and molecules instable under usual conditions.

A review of the results and methods of measurement of the electron affinity is given in the papers by Pritchard [3330] and Buchel'-

nikova [116].

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[Footnotes]

271 The ionization energy is frequently also named ionization potential.

279 The essence of the "quartz wool" method lies in the fact that the combustion is carried out in a calorimetric bomb whose inner walls are covered by quartz wool moistened with the solution of a reducing agent. The great area of contact provides for the total transformation of the free halide into a solution of the corresponding hydrogen halide acid.

281 Under certain conditions, such "unusual" molecules as Ba_2O Ba_2O_3, Ba_2O_2, Al_2O, AlO, Mo_3O_9, Mo_4O_{12}, Al_2C_2, Be_3O_2, B_2O_2, etc., are the main products of evaporation or important components of the saturated vapor. Moreover, the composition of the condensed phases becomes also complex at high temperatures: thus, for example, phases of varying composition and such compounds as AlO (solid) and Al_2O (solid) may exist under certain conditions.

285 With rare exceptions, the dissociation energy of polyatomic molecules cannot be determined by spectroscopical methods owing to the complexity of the corresponding spectra.

287 Other, more complex relations may be obtained when using more complex expressions for the potential energy of the molecule (see, for example, the papers by Lippincott and Schroeder ([2624, 2625], Varshni [4072] and others).

Part Two

CHOICE OF THE INITIAL CONSTANTS AND CALCULATION OF THE TABLES OF THERMODYNAMIC PROPERTIES

Chapter 5

OXYGEN

(O, O^+, O^-, O_2, O_2^+, O_3)

In the present chapter, the monatomic oxygen and its positive and negative ions, the diatomic oxygen and its positive ion, and ozone are dealt with. The data cited make it possible to calculate the composition and the thermodynamic properties of oxygen and its dissociation and ionization products with a sufficiently high accuracy up to 20,000°K. Even at a temperature of 20,000°K, multicharge ions of monatomic oxygen are formed in negligible quantities and, with the exclusion of special cases, it is not necessary to take them into account.

The compounds of oxygen with other elements are dealt with in the subsequent chapters of the Handbook.

§24. MOLECULAR CONSTANTS

O. In the ^3P ground state, the oxygen atom possesses a $1s^2 2s^2 2p^4$ electron configuration to which two other states, ^1D and ^1S, still correspond. Three series of terms are formed by excitation of one 2p electron: $1s^2 2s^2 2p^3(^4S)n\ell$; $1s^2 2s^2 2p^3(^2D)n\ell$ and $1s^2 2s^2 2p^3(^2P)n\ell$, whose limits lie at 109,837; 136,650, and 150,304 cm^{-1} higher than the under $^3P_2$ level of this atom. The first series consists of triplet and quintet states with $L = \ell$, the second one of singlet and triplet states with $L = 2$ (at $\ell = 0$); $L = 1, 2, 3$ (at $\ell = 1$) and $L = \ell$; $\ell \pm 1$, $\ell \pm 2$ (at $\ell \geq 2$); the third series consists of singlet and triplet states with $L = 1$ (at $\ell = 0$) and $L = \ell$, $\ell \pm 1$ (at $\ell \geq 1$). The first

excited states of these series (n = 3) possess energies of 73,767.81 cm^{-1}; 101,143 cm^{-1}, and 113,910 cm^{-1}, respectively.

Besides the states which correspond to the electron configuration $1s^2 2s^2 2p^3 n\ell$, the oxygen atom possesses a great number of states corresponding to the excitation of one 2s electron ($1s^2 2s 2p^4 n\ell$ configuration), the simultaneous excitation of two electrons, etc. However, the energies of these levels are very high (higher than 200,000 cm^{-1}), and, therefore, with the exclusion of the levels of the $1s^2 2s 2p^4 (^4P) n\ell$ series, they are not dealt with in the present Handbook.

The energy levels of the oxygen atom, corresponding to the $1s^2 2s^2 2p^4$, electron configuration, to the three $1s^2 2s^2 2p^3 n\ell$ series and to the $1s^2 2s 2p^4 (^4P) n\ell$ series, accepted on the basis of values recommended by Moore [2941] are listed in Table 16. It must be noted that data on only a small part of the levels of the series mentioned, mainly on terms with $L \leq 2$, are given in this review. Transitions between the other levels were not observed experimentally in the spectrum of the monatomic oxygen. Thus, only the excitation energies for levels with $\ell \leq 2$ and $n \leq 11$ are known for the $1s^2 2s^2 2s^3 (^4S) n\ell$ series, and the P terms are known only for $n \leq 6$ (with the exception of the $5p^5 P$- and $6p^5 P$- levels), and the D terms are known only for $n \leq 10$. Data on states belonging to the three other series are even more limited: there are some P and D terms with n = 3 for the $1s^2 2s^2 2p^3 (^2P) n\ell$ series and, finally, the $2p^5\ ^3P$ and $2p^5\ ^5P$ terms for the $1s^2 2s 2p^4 (^4P) n\ell$ series.

Owing to this fact, the excitation energies of these states of the series in question, for which experimental data are missing, have been estimated corresponding to the rules formulated in §2 (see page 53) and on the basis of certain regularities observed in the position of the electronic states of the oxygen atom. Thus, in the $1s^2 2s^2 2p^3 (^4S)$

$n\ell$ series, the excitation energy of the corresponding triplet terms was ascribed to the $5p^5P$ and $6p^5P$ terms (the error caused by this fact amounts to approximately 200 cm^{-1}); all terms of this series with $L \geq 3$ have been related to the energy of the series boundary, i.e., to 109,837 cm^{-1}. The maximum error in the estimation of the terms of this series is committed for the $4f^3F$ and $4f^5F$ states and amounts to about 4000 cm^{-1}. Owing to the high excitation energy of the states of this series (higher than 102, 102,000 cm^{-1}), however, the inaccuracy mentioned does not cause essential errors in the results of the subsequent calculations (see below, page 316). A similar situation is given for the levels of the other series owing to the fact that all states for which experimental data are missing, lie by about 100,000--120,000 cm^{-1} higher than the $^3P_2$ ground state of the oxygen atom. The estimated excitation energies of the levels of the four series mentioned are quoted in Table 16. States having energies similar in value are unified into one level with a mean excitation energy and a summarized statistical weight. The levels of these series with values of the principal quantum number $n \leq 13$ are listed in Table 16.

O^+. The positively charged ion of monatomic oxygen possesses the $1s^2 2s^2 2p^3$ electron configuration in the ground state, to which three terms correspond: ^4S, ^2D and ^2P. The terms connected with the excitation of 2s and 2p electrons possess an energy which exceeds 100,000 cm^{-1} and are not delat with in the Handbook. The excitation energies and the statistical weights of the ^4S, ^2D and ^2P states of the O^+ ion, accepted according to Moore [2941], are quoted in Table 17.

TABLE 16

Energy Levels of the Oxygen Atom

Номер уровня A	B Состояние: C электронная конфигурация	D терм	Статистический вес E	Энергия, $F^{см^{-1}}$
0	$1s^2 2s^2 2p^4$	$^3P_2$	5	0,0
1	$1s^2 2s^2 2p^4$	$^3P_1$	3	158,5
2	$1s^2 2s^2 2p^4$	$^3P_0$	1	226,5
3	$1s^2 2s^2 2p^4$	^1D	5	15867,7
4	$1s^2 2s^2 2p^4$	^1S	1	33792,4
5	$1s^2 2s^2 2p^3 (^4S) 3s$	^5S	5	73767,8
6	$1s^2 2s^2 2p^3 (^4S) 3s$	^3S	3	76794,7
7	$1s^2 2s^2 2p^3 (^4S) 3p$	^5P	15	86629
8	$1s^2 2s^2 2p^3 (^4S) 3p$	^3P	9	88630
9	$1s^2 2s^2 2p^3 (^4S) 4s$	^5S	5	95476
10	$1s^2 2s^2 2p^3 (^4S) 4s$	^3S	3	96226
11	$1s^2 2s^2 2p^3 (^4S) 3d$	^3D, ^5D	40	97446
12	$1s^2 2s^2 2p^3 (^4S) 4p$	^3P, ^5P	24	99250
13	$1s^2 2s^2 2p^3 (^2D) 3s$	^3D	15	101143
14	$1s^2 2s^2 2p^3 (^4S) 4d$ $1s^2 2s^2 2p^3 (^4S) 5s$ $1s^2 2s^2 2p^3 (^2D) 3s$	^3D, ^5D ^3S, ^5S ^1D	53	102800
15	$1s^2 2s^2 2p^3 (^4S) 5p$	^3P, $^5P^*$	24	103870
16	$1s^2 2s^2 2p^3 (^4S) 5d$ $1s^2 2s^2 2p^3 (^4S) 6s$ $1s^2 2s^2 2p^3 (^4S) 6p$	D S ^3P, $^5P^*$	72	105500
17	$1s^2 2s^2 2p^3 (^4S) 6d$ $1s^2 2s^2 2p^3 (^4S) 7s, 7p, 7d$ $1s^2 2s^2 2p^3 (^4S) 8s$	D S, P^*, D S	120	107200
18	$1s^2 2s^2 2p^3 (^4S) 8p, 8d$ $1s^2 2s^2 2p^3 (^4S) 9s, 9p, 9d$ $1s^2 2s^2 2p^3 (^4S) 10s, 10p, 10d$ $1s^2 2s^2 2p^3 (^4S) 11s$	P^*, D S, P^*, D S, P^*, D S	216	108400
19	$1s^2 2s^2 2p^3 (^4S) 11p, 11d$ $1s^2 2s^2 2p^3 (^4S) n = 12, 13, l = 0,1,2$ $1s^2 2s^2 2p^3 (^4S) 4 \leqslant n \leqslant 13, 3 \leqslant l \leqslant 12$	P^*, D^* S^*, P^*, D^* F^*-R^*	3424[a] a 4576[b] b 5928[c] c	109837
20	$1s^2 2s^2 2p^3 (^2D) 3p$ $1s^2 2s^2 2p^3 (^2P) 3s$ $1s^2 2s^2 2p^3 (^2D) 3p$ $1s^2 2s^2 2p^3 (^2P) 3s$	^3D, ^3F, ^1F ^3P ^1D ^1P	60	114100
21	$1s^2 2s^2 2p^3 (^2D) 4s$	^1D, $^3D^*$	20	122800
22	$1s^2 2s^2 2p^3 (^2D) 3p$ $1s^2 2s^2 2p^3 (^2D) 3d$	$^1P^*$, $^3P^*$ S^*, P^*, D^*, F, G	112	124000

A Номер уровня	B Состояние: C электронная конфигурация	D терм	E Статистический вес	F Энергия, $см^{-1}$
23	$1s^2 2s^2 2p^3 (^2D) 4p$ $1s^2 2s 2p^5$	^2D ^2P	24	126000
24	$1s^2 2s^2 2p^3 (^2P) 3p$	$^2P, ^2P^*, ^2D$	27	127500
25	$1s^2 2s^2 2p^3 (^2P) 3p$ $1s^2 2s^2 2p^3 (^2D) 5s$ $1s^2 2s^2 2p^3 (^2D) 4p$ $1s^2 2s^2 2p^3 (^2D) 4d$	^2D $^2D, ^2D^*$ P^*, D^*, F^* S^*, P^*, D^*, F, G	170	129600
26	$1s^2 2s^2 2p^3 (^2P) 3p$ $1s^2 2s^2 2p^3 (^2D) 6s$	$^2S, ^2S^*$ $^2D, ^2D^*$	24	131700
27	$1s^2 2s^2 2p^3 (^2D) 5p$ $1s^2 2s^2 2p^3 (^2D) 5d$	P^*, D^*, F^* S^*, P^*, D^*, F, G	160	132200
28	$1s^2 2s^2 2p^3 (^2D) 6p$ $1s^2 2s^2 2p^3 (^2D) 6d$ $1s^2 2s^2 2p^3 (^2D) 7s$	P^*, D^*, F^* S^*, P^*, D^*, F^*, G^* $^2D, ^2D^*$	180	133600
29	$1s^2 2s^2 2p^3 (^2D) 4 \leqslant n \leqslant 13, 3 \leqslant l \leqslant 12$ $1s^2 2s^2 2p^3 (^2D) 7p - 13p$ $1s^2 2s^2 2p^3 (^2D) 7d - 13d$ $1s^2 2s^2 2p^3 (^2D) 8s - 13s$	$L = l; l \pm 1; l \pm 2$ P^*, D^*, F^* S^*, P^*, D^*, F^*, G^* D^*	9280[a] a 12160[b] b 15540[c] c	136650
30	$1s^2 2s^2 2p^3 (^2P) 3d$ $1s^2 2s^2 2p^3 (^2P) 4 \leqslant n \leqslant 13, 0 \leqslant l \leqslant 12$	P^*, D^*, F^* $L = l; L = l \pm 1$	5832[a] a 7882[b] c 9720[c]	150300
31	$1s^2 2s 2p^3$ $1s^2 2s 2p^4 (^4P) 3 \leqslant n \leqslant 13, 0 \leqslant l \leqslant 12$	$^1P^*$ $L = l; l \pm 1$	12027[a] a 15483[b] b 19335[c] c	229700

+This level has not been observed experimentally

a) At $n \leq 11$. b) at $n \leq 12$. c) at $n \leq 13$. A) Number of the levels; B) state; C) electron configuration; D) term; E) statistical weight; F) energy, cm^{-1}.

O^-. The negatively charged ion of the monatomic oxygen possesses the electron configuration $1s^2 2s^2 2p^5$ in the ^2P ground state. Similar to the isoelectronic F atom and the Ne^+, Na^{++}, etc., ions, the excited states of the O^- ion must have energies higher than 100,000 cm^{-1}, exceeding almost by one order its ionization potential, a fact which allows for the assumption that the O^- ion does not possess stable excited states. This assumption is proved by the missing

of spectra of the negatively charged oxygen ion.

TABLE 17

Energy Levels of the O^+ and O^- Ions

A Ион	B Номер уровня	C Состояние: D электронная конфигурация	C Состояние: E терм	Статистический вес F	Энергия, $см^{-1}$ G
O^+	0	$1s^2 2s^2 2p^3$	$^4S_{3/2}$	4	0
	1	$1s^2 2s^2 2p^3$	^2D	10	26 817
	2	$1s^2 2s^2 2p^3$	^2P	6	40 467
O^-	0	$1s^2 2s^2 2p^5$	$^2P_{3/2}$	4	0
	1	$1s^2 2s^2 2p^5$	$^2P_{1/2}$	2	180

A) Ion; B) number of the level; C) state; D) electron configuration; E) term; F) statistical weight; G) energy, cm^{-1}.

The doublet splitting of the ^2P ground state into the $^2P_{3/2}$ and $^2P_{1/2}$ components is assumed to be equal to 180 cm^{-1} on the basis of the extrapolation of this quantity in the series of isoelectric atoms and ions: F, Ne^+, Na^{++}, Mg^{+++}, etc., according to the data cited by Moore [2941] (see Table 17). Similar to the isoelectric ions and the F atom, the ^2P ground state of the O^- ion must be an inversed state.

O_2. According to theoretical conceptions in [2933, 1627], the oxygen molecule must have 9 stable states (including the ground state) which correspond to the two lower electron configurations and possess an excitation energy lower than 100,000 cm^{-1}. The seven first states ($X^3\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$, $c^1\Sigma_u^-$, $A^3\Delta_u$, $B^3\Sigma_u^+$, $C^3\Sigma_u^-$) have been identified in oxygen spectra. The two last (the $d^1\Delta_u$- and $e^1\Sigma_u^+$ state) may, possibly, be identified with the states observed by Tanaka [3930].*

A scheme of the electronic states of the O_2 molecule with indication of the transitions observed in spectra is shown in Fig.5. It

must be noted that the majority of the transitions between the known electronic states of the O_2 are forbidden by the selection rules; owing to this fact, the majority of the states was observed only in the absorption spectrum of oxygen using thick absorption layers.

The most accurate values of the molecular constants of O_2 in the ground state may be determined by an analysis of the bands of the Schumann-Runge system which corresponds to the $C^3\Sigma_u^- \rightleftarrows X^3\Sigma_g^-$ transition and which lies in the 1750-4400 A region. The other band systems in the oxygen spectrum have been obtained mainly by absorption, and their analysis allows for the determination of the constants of O_2 only for the first vibrational levels of the ground state.

An analysis of the rotational structure of a great number of bands of the Schumann-Runge system, obtained in absorption and emission spectra by devices with a high dispersion, was carried out in the papers [3150, 2635, 1234]; Lochte-Holtgreven and Dieke [2635] investigated the bands of this sytem up to $v'' = 21$. Curry and Herzberg [1234] on the basis of their own and the data obtained by [3150, 2635] determined the rotational and vibrational constants of O_2 in the $X^3\Sigma_g^-$ state. The values for the vibrational constants proposed by these authors very accurately describe the energy of levels, for which experimental data are available (see Table 18), and these data are cited in the monograph by Herzberg [2020] and in the Handbook [649].

After the papers by Curry and Herzberg had been published, the bands of O_2 related to the Schumann-Runge system have been investigated by Feast [1540, 1538], Herczog and Wieland [1996], Millon and Herman [2919] and Lal [2545]. A discussion of these results showed that, within the error limits of the measurement, they are in accordance with the molecular constants of O_2 recommended by Curry and Herzberg in the paper [1234]. Nevertheless, the vibrational constants of O_2 found by

Curry and Herzberg approximate with insufficient accuracy the energy and number of vibrational states of this molecule near the dissociation limit of the ground state because, according to these constants, the levels of the vibrational energy converge at 45,975 cm^{-1}, whereas the dissociation energy of O_2 is equal to 41,260 ± 15 cm^{-1} (see §26).

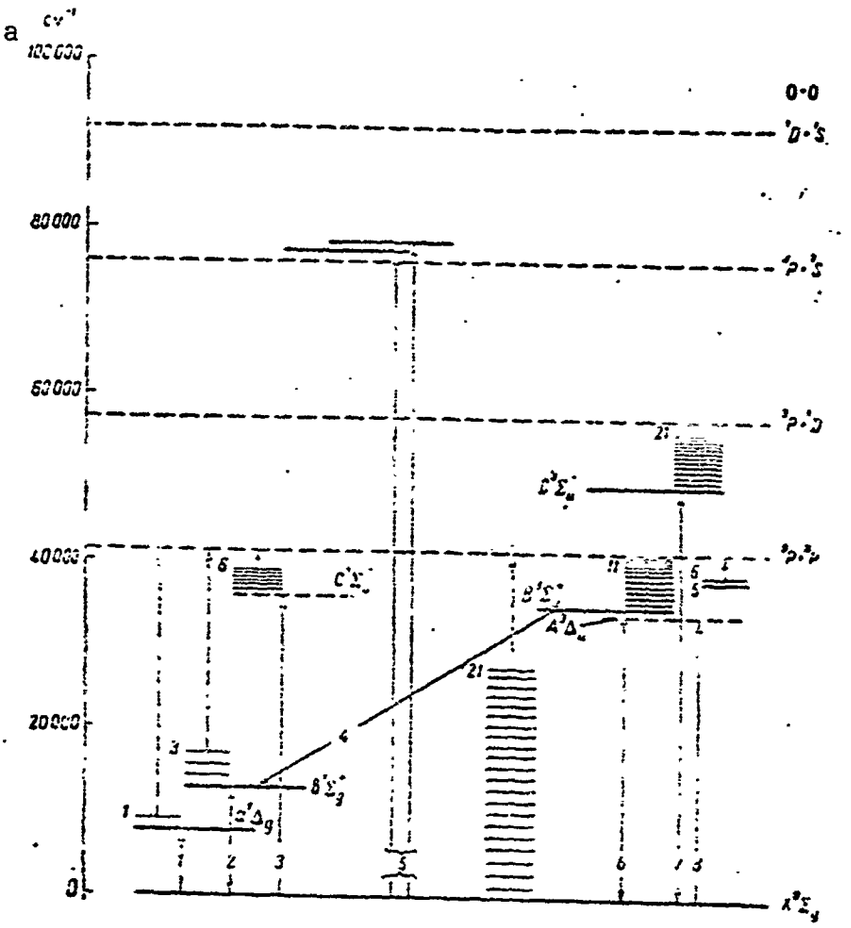


Fig.5. Scheme of the energy levels of the O_2 molecule. The electronic states are marked by bold horizontal lines. The thinner lines correspond to the vibrational levels. The figure at the left denotes the number of levels observed in the given state. The dotted arrows indicate the dissociation limits of the electronic states. These limits are denoted by dotted horizontal lines. Electron transitions, observed in the O_2 spectrum, are denoted by solid arrows, where 1) is the $a^1\Delta_g - X^3\Sigma_g^-$ band system; 2) is the $b^1\Sigma_g^+ - X^3\Sigma_g^-$ band system (atmospheric bands); 3) is the $c^1\Sigma_u^- - X^3\Sigma_g$ band system; 4) is the $B^3\Sigma_u^- - b^1\Sigma_g^+$ band system (Broida-Gaydon bands); 5) is the Tanaka band system; 6) is the

$B^3\Sigma_u^+ - X^3\Sigma_g^-$ band system (Herzberg bands); 7) is the $C^3\Sigma_u^- - X^3\Sigma_g^-$ band system (Schumann-Runge bands); 8) is the $A^3\Delta_u - X^3\Sigma_g^-$ band system; a) cm^{-1}.

TABLE 18

Energies (in cm^{-1}) of the $G_0(v)$ Vibrational Levels of the O_2 Molecule in the $X^3\Sigma_g^-$ state

v	A Экспериментальные данные [1234]	B Расчет по постоянным [1234]а	B Расчет по постоянным табл. 19
1	1556,4	1556,4	1556,37
2	3089	3089	3089,34
3	4608	4620,3	4620,07
4	6084	6084,4	6085,34
5	7540	7547,4	7548,38
6	--	8987,5	8988,70
7	10400,-	10404,9	10406,66
8	11800,5	11798,7	11800,60
9	13172,3	13171,3	13172,49
10	14522,1	14521,3	14521,89
11	15848,5	15848,3	15848,59
12	17152,2	17152,6	17152,80
13	18434,3	18434,2	18434,56
14	19695,0	19695,3	19695,58
15	20935,6	20935,6	20935,72
16	22156,3	22156,0	22156,74
17	23358,3	23358,-	23358,82
18	24542,0	24542,5	24542,75
19	25708,0	25708,0	25708,70
20	26854,0	26854,1	26854,33
21	27983,1	27983,3	27983,55
v_{max}	41280 ± 15	45075	42181б b

a) $G_0(v) = 1568.33v - 11.993v^2 + 0.0517v^3 - 0.00143v^4$, $v_{max} = 51$. b) $v_{max} = 42$. A) Experimental data; B) calculation on the basis of the constants.

In order to approximate more accurately the energies of the high vibrational levels of the ground state, the authors of the Handbook developed a new equation assuming as an additional condition the convergence of the levels near the dissociation limit. The details of the

corresponding calculations are published in the paper [173]. The values found for the constants in the five-power equation are quoted in Table 19. It must be noted that the equation of G(v) with the new values of the constants describes the energies of the experimentally observed vibrational levels of oxygen in no worse manner than the equation proposed by Curry and Herzberg (see Table 18) but it has the advantage that the levels converge at 41,261 cm^{-1}.

TABLE 19

Accepted Values of the Molecular Constants of O_2

A Состояние	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	$\omega_e z_e \cdot 10^4$	B_e	$\alpha_1 \cdot 10^3$	$\alpha_2 \cdot 10^3$	$D_e \cdot 10^6$	$\beta_1 \cdot 10^6$	r_e
	B $см^{-1}$										
$X^3\Sigma_g^-$	0[a]	1579,78	12,099	—0,0724	—0,2448[b]	1,44567	2,579	—	4,957	0,88[c]	1,207
$a^1\Delta_g$	7917,46	1510,2	12,8	—0,0672	—	1,4304	2,71	—	4,86	0,07	1,213
$b^1\Sigma_g^+$	13196,38	1430,44	12,896	—0,127	—	1,43042	2,817	—0,043	5,356	—0,77	1,217
$A^3\Delta_u$	34660	802,2	19,42	—0,537	—	0,974	2,6	—	4,54	—[d]	1,491
$B^3\Sigma_u^-$	35374,96[e]	825,959	22,574	1,088	9,15	0,91062	2,416	—0,57	4,63	3,0[f]	1,521
$c^1\Sigma_u^-$	36695,26	2,144	10,666	—0,3491	—2,80	0,8261	2,055	—0,83	10,5	—0,96	1,597
$C^3\Sigma_u^-$	49782,42[e]	,478	14,620	0,6246	6,72[e] f	0,891	0,651	1,079[e] g	4,38	—3,2	1,621
$d^1\Delta_u$	77042,2	1500,97	18,22	—	—	—	—	—	—	—	—
$e^1\Sigma_u^+$	78123,2	1890,50	29,41	—	—	—	—	—	—	—	—

a) $\lambda = 1.984\ cm^{-1}$, $\mu = -0.00837$

b) $\omega_e t_e = -8.211 \cdot 10^{-5}\ cm^{-1}$.

c) $\lambda = 5.08\ cm^{-1}$, $\mu = -0.0034\ cm^{-1}$.

d) $\beta_2 = 0.1 \cdot 10^{-6}\ cm^{-1}$.

e) $\lambda = 2.34\ cm^{-1}$, $\mu = -0.18\ cm^{-1}$.

f) $\omega_e t_e = 0.00165\ cm^{-1}$.

g) $\alpha_3 = 5.1 \cdot 10^{-6}\ cm^{-1}$.

A) State; B) cm^{-1}.

On the basis of an analysis of the rotational structure of individual bands, the authors of the papers [3150, 2635, 1234] determined the B_v constants of the O_2 molecule in the $X^3\Sigma_g^-$ state corresponding to various values of the vibrational quantum number up to v = 21.

Using these data and the results of their own measurements, Curry and Herzberg [1234] calculated the values of the rotational constants in the Kramer's Equation (see page 119) for the ground electronic state of O_2.

Babcock and Herzberg [593], in 1948, carried out a thorough investigation of the fine structure of seven bands in the red $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$ system in the spectrum of atmospheric absorption of solar radiation. The investigation was performed by devices having a high dispersion (up to 0.12 A/mm), and it was possible to determine the wave numbers of the observed lines with high accuracy; the interpretation of the rotational structure of the bands was carried out according to Schlapp's formula (see Eqs. (1.24)) for the rotational energy of the molecules in the $^3\Sigma$ state. The values of the rotational constants of O_2 in the ground state, quoted in Table 19, have been determined by Babcock and Herzberg [593] on the basis of the values of B_0 and B_1 found by them, and of the values of B_v obtained in papers [3150, 2635, 1234].*

The molecular constants of O_2 in the first excited $a^1\Delta_g$ state have been determined by L. Herzberg and G. Herzberg [2053] as a result of an investigation of the fine structure of bands of the infrared absorption spectrum of atmospheric oxygen, corresponding to the forbidden $a^1\Delta_g \rightarrow X^3\Sigma_g^-$ transition. Due to the fact, however, that the authors of paper [2053] observed only two bands of this system, 0-0 and 1-0, they coud, for the $a^1\Delta_g$ state, only determine the values of $\Delta G_{1/2}$ and the rotational constants. Since the values found for $\Delta G_{1/2}$, B_e and α_1 of the $^1\Delta_g$ state lie between the values of these constants for the $X^3\Sigma_g^-$ and $b^1\Sigma_g^+$ states (see Table 19), and, as all three states correspond to the same electron configuration of the O_2 molecule, L. Herzberg and G. Herzberg assumed that the constant $\omega_e x_e$ of the $a^1\Delta_g$

state possesses a value between the values of this constant for the $X^3\Sigma_g^-$ and $b^1\Sigma_g^+$ states. Assuming $\omega_e x_e = 12.9$ cm^{-1} on the basis of these considerations and using the experimentally found value for $\Delta G_{1/2}$, L. Herzberg and G. Herzberg obtained the vibrational constants of O_2 in the $a^1\Delta_g$ state, which are recommended in the monograph [2020] and in the Handbook [649]. These values may be considered to be only approximate one, because equations with two constants (ω_e and $\omega_e x_e$) insufficiently describe the energy even of the lower vibrational levels of the O_2 molecule in all electronic states. The vibrational levels of the $a^1\Delta_g$ state, calculated on the basis of these constants, converge in the range of 52,000 cm^{-1} ($v_{max} = 58$). In order to achieve convergence of the vibrational levels in the region of the dissociation limit, the value of the constant $\omega_e y_e$ was calculated on the occasion of the compilation of the Handbook. The accepted values of the vibrational and rotational constants of O_2 in the $a^1\Delta_g$ state are quoted in Table 19.

The molecular constants of O_2 in the second excited $b^1\Sigma_g^+$ state have been determined by Babcock and L. Herzberg [593] on the basis of an analysis of the $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$ band system. Individual bands of this system were observed in emission by R. Herman and L. Herman [2002] and also by R. Herman and Weniger [2006], an analysis of these bands, however, was not carried out in these investigations. Babcock and L. Herzberg [593] observed transitions into the four first vibrational levels of the $b^1\Sigma_g^+$ state and determined the constants in the cubic equation for the vibrational energy($\omega_e = 1432.6874$; $\omega_e x_e = 13.95008$, and $\omega_e y_e = -0.01075$ cm^{-1}) and also the rotational constants quoted in Table 19. Since the vibrational levels calculated in the terms of the constants mentioned converge essentially above the dissociation limit of the $b^1\Sigma_g^+$ state (at 45,400 cm^{-1} and $v_{max} = 36$), new constants

were calculated for this equation on the occasion of the compilation of the Handbook, which satisfy the condition of a convergence of the levels near 41,200 cm^{-1}. The constants found in this way are cited in Table 19. They also describe satisfactorily the experimental data for v' = 0-3, they cause, however, a convergence of the levels at 42,160 cm^{-1} and $v_{max} = 36$.

The next singlet state of oxygen is the $c^1\Sigma_u^-$ state, observed for the first time by G. Herzberg [2024] during the investigation of the absorption spectrum of oxygen using thick layers of absorbing gas. In the paper [2024], six bands of the $c^1\Sigma_u^- \rightarrow X^3\Sigma_g^-$ system in the 2800 A region were found by means of a high-dispersion device, which correspond to transitions into the six subsequent vibrational levels of the upper state; an analysis of the rotational structure of all bands was also carried out. Herzberg mentions that the low intensity of the lines of this system (this is a forbidden transition) essentially reduced the accuracy of the determination of the constants. Moreover, the data obtained were not sufficient to enumerate the bands uniquely. Herzberg assumes that the bands observed correspond to values of v' from 1 to 6, with the reservation, however, that the real values of v' may be higher than the assumed ones. The values of the rotational constants of O_2 in the $c^1\Sigma_u^-$ state, which Herzberg found to be corresponding to the numbering of the bands assumed in paper [2024], are listed in Table 19. Herzberg also determined the vibrational constants of the molecule in this state. The values of the energy of the vibrational levels, however, calculated by means of these constants, are in poor accordance with experimental data. Thus, the difference between the measured and calculated energy amounts to 26 cm^{-1} for the v' = 6 level. Hence, the authors of the present Handbook calculated new values of the constants in the 4th power equation; the vibrational level

calculated by means of these constants converge about 41,300 cm^{-1} (at v = 17) and the level energy calculated in the terms of this equation conforms with the energy calculated on the basis of the experimental data with an accuracy of 1 cm^{-1}.

Investigating the $c^1\Sigma_u^- \rightarrow X^3\Sigma_g^-$ band system, Herzberg obtained two bands which he ascribed to the $A^3\Delta_u \rightarrow X^3\Sigma_g^-$ transition. Assuming that the diffuse band at 2913 A observed by L. Herman [1997] is a 0-0 band of the $A^3\Delta_u \leftarrow X^3\Sigma_g^-$ system, Herzberg interpreted the bands found by him as 5-0 and 6-0 bands and supposed that the $A^3\Delta_u$ state and the $X^3\Sigma_g^-$ state possess a common dissociation limit. On the basis of an analysis of the rotational structure of these bands, he found the values $B_5 = 0.823$ and $B_6 = 0.794$ cm^{-1}, and also $\Delta G_{5.5} = 611.1$ cm^{-1}. The authors of the present Handbook calculated the values of the O_2 constants in the $A^3\Delta_u$ state, quoted in Table 19; according to [2024], the wave numbers of the beginning of the 5-0 and 6-0 bands were assumed to be equal to 38,768 and 38,157 cm^{-1}, the wave number at the beginning of the 0-0 band was assumed to be equal to 34,319 cm^{-1}, and the B_5 and B_6 values found by Herzberg were used for the calculation of the rotational constants.

The next excited state of O_2 is the $B^3\Sigma_u^+$ state. It was observed for the first time by Herzberg [2016] during the investigation of the band system in the 2400-2600 A region in the absorption spectrum, corresponding to the forbidden $B^3\Sigma_u^+ \leftarrow X^3\Sigma_g^-$ transition. Later, this system was investigated by L. Herman [1997] who found in it some new bands and who carried out an approximate analysis of their fine structure. The system was studied anew by Herzberg [2023] in 1952 by means of a high-dispersion device and using a multipass cell which made it possible to extend the path of absorption up to 800 m. Herzberg carried out a thorough analysis of the rotational structure of 11 bands

corresponding to transitions into 11 subsequent, rapidly converging levels of the $B^3\Sigma_u^+$ state, and he determined the values of the rotational constants of O_2 in these vibrational states. Assuming that the highest of the observed levels is the last level of the $B^3\Sigma_u^+$ state, Herzberg found the energy of the dissociation limit to be equal to $41,219 \pm 40$ cm^{-1}. However, the author of the paper [2023] did not succeed in finding a unique numbering of the observed bands owing to the low intensity of the bands which correspond to transitions into the lower vibrational levels of the $B^3\Sigma_u^+$ state. Assuming that the largest longwave λ 2794 A band is a 0-0 band, Herzberg calculated the values of the constants of O_2 in the $B^3\Sigma_u^+$ state, mentioning that these values may change essentially if the assumed coordination proves to be incorrect.

In 1954, Broida and Gaydon [974, 975] obtained the $B^3\Sigma_u^+ - X^3\Sigma_g^-$ system in emission and found a series of new bands which were sufficiently described by the constants proposed by Herzberg, if the numbering chosen by him was changed by one unit. This induced Broida and Gaydon to come to the conclusion that the λ 2794 A band is a 1-0 band. The assumption made by Broida and Gaydon was corroborated by the recent investigation of the spectrum of air luminescence carried out by Chamberlain [1082, 1083]. The values of the constants of O_2 in the $B^3\Sigma_u^+$ state, quoted in Table 19, were calculated by the authors of the Handbook on the basis of the data given by G. Herzberg, and the numbering of the bands was adopted from the paper [974].

The molecular constants of O_2 in the $C^3\Sigma_u^-$ state were determined on the basis of an analysis of the system of Schumann-Runge bands (see above). Curry and Herzberg determined the values of the vibrational and rotational constants of O_2 in this state on the basis of an analysis of the structure of bands with the values $v' = 7$, carried

out in the papers [3150, 2635]. Knauss and Ballard [2446] obtained in the absorption spectrum a series of new bands of the Schumann-Runge system corresponding to the values $v' \leq 15$, and they succeeded in a more accurate determination of the constants found in the paper [1234]. Brix and Herzberg [952], in 1954, carried out a thorough investigation of the $C^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ system in the absorption spectrum of oxygen in order to define more accurately the dissociation energy of O_2, and they performed the analysis of the fine structure of bands with $v' \leq 21$. These authors have shown that only one vibrational level with $v = 22$ is still possible in the $C^3\Sigma_u^-$ state, and they determined with high accuracy the energy of the dissociation limit of this state (see §26). However, the values of the vibrational constants and also the equilibrium values of the rotational constants of O_2 in the $C^3\Sigma_u^-$ state have not been determined in the paper [952]. The values of these constants, quoted in Table 19, were calculated by the authors of the Handbook on the basis of the data of [3150, 2635, 1234, 952].

O_2^+. The spectrum of the molecule of ionized oxygen consists of two band systems referring to transitions between two doublet, $^2\Pi_u - ^2\Pi_g$, and two quartet, $^4\Sigma - ^4\Sigma$, states. Intercombination transitions were not observed in the O_2^+ spectrum, the relative position of the doublet and quartet states, however, may be determined on the basis of data on the Rydberg series of the O_2 molecule [3323], the energy of the $b^4\Sigma_g^- (O_2^+) \leftarrow X^3\Sigma_g^- (O_2)$ transition [3941, 3939] and the value of the ionization potential of O_2 (see page 328), if one assumes that the lower observable $^2\Pi_g$ state of O_2^+ is the ground state as well as for the case of the isoelectronic NO molecule.

The band system $A^2\Pi_u - X^2\Pi_g$ lies in the near ultraviolet region and is easily observable in the emission spectrum of such sources as glow and high-frequency discharges. The analysis of this band system

was carried out for the first time by Ellsworth and Hopfield [1479], who obtained a formula for the wave numbers of the band edges. Stevens [3850, 3851] obtained four bands of the system on a device with a 1.32 A/mm dispersion and carried out the analysis of their fine structure. On the basis of the data obtained, Stevens proved that these bands belong to the $^2\Pi - {}^2\Pi$ transition, and that the lower state is regular and similar to the Hund case a with a doublet splitting of ~ 195 cm^{-1}. It must be taken note of that an incorrect numbering of the 0_2^+ bands, proposed earlier by Mulliken [2975] was used in Stevens' papers, differing from the numbering accepted by Ellsworth and Hopfield. Later on, the band series of 0_2^+ was obtained by a spectrograph with an 1.2 A/mm dispersion by Bozoky [883] who carried out the analysis of their rotational structure and determined the rotational constants of 0_2^+ in the $X^2\Pi_g$ and $A^2\Pi_u$ states. Mulliken and Stevens [3004] investigated the 0_2^+ spectrum on a device having a mean dispersion using a discharge tube as a source, and observed a series of new bands up to $v'' = 14$ and $v' = 15$. Later, Lal [2546] and Feast [1541] still obtained some bands of the $A^2\Pi_u - X^2\Pi_g$.

The vibrational constants of 0_2^+ in the $X^2\Pi_g$ and $A^2\Pi_u$ states, found by Ellsworth and Hopfield [1479], being in good accordance with the data of later investigations, were accepted in the Handbook [649] and by Herzberg [2020]. It must be noted that the vibrational levels of 0_2^+ in the $X^2\Pi_g$ state, calculated on the basis of these constants, converge in the 52,330 cm^{-1} region, whereas the dissociation limit of the $X^2\Pi_g$ state lies at 53,670 cm^{-1} higher than the $v = 0$ level. Owing to this fact, the authors of the Handbook introduced a second constant of anharmonicity into the binomial equation for the energy of the vibrational levels, proposed by Ellsworth and Hopfield, in order to describe more accurately the energy of the 0_2^+ level near the dissociation

limit of the state. The introduction of this constant changes the energy of the experimentally observed last level (v = 15), by 24 cm^{-1}, which is permissible because the vibrational constants were determined on the basis of the band edges; the vibrational levels of O_2^+, calculated by a trinomial equation, converge at $G_0(58) = 53{,}672$ cm^{-1}, i.e., near the dissociation limit. The corresponding values of the vibrational constants of O_2^+ in the $X^2\Pi_g$ state are quoted in Table 20. The vibrational constants of O_2^+ in the $A^2\Pi_u$ state, found by Ellsworth and Hopfield [1479], the rotational constants in the $X^2\Pi_g$ and $A^2\Pi_u$ states, found by Bozoky [883], and the band constants found by Stevens [3851] are here cited too.

TABLE 20

Accepted Values of the Molecular Constants of O_2^+

A Состояние	T_e	ω_e	$\omega_e x_e$	B_e	$\alpha_e \cdot 10^3$	$D_e \cdot 10^6$	r_e
	B $см^{-1}$						Å
$X^2\Pi_g$	0[a]	1870,4	16,82[b]	1,0722	1,634	6,85	1,1227
$a^4\Pi_u$	32639[a] [c]	1085,65	10,31	1,0203	1,575	4,58[d]	1,13126
$A^2\Pi_u$	38538[a] [e]	868,9	13,7	1,033.7	1,630[f]	—	1,1030
$^2\Pi$	44000[a] [g]	—	—	—	—	—	—
$b^4\Sigma_g^-$	49467[a] [h]	1183,77	17,05	1,05729	2,203	5,81[d] [i]	—

a) $A = 195$ cm^{-1}.
b) $\omega_e y_e = 0.0072$ cm^{-1}.
c) $A_0 = 47.97$. $Y_0 = 43.74$ cm^{-1}.
d) $\beta = 0.095 \cdot 10^{-6}$ cm^{-1}.
e) $A = 8.2$ cm^{-1}.
f) $\alpha_2 = 1.95 \cdot 10^{-4}$ cm^{-1}.
g) Estimated on the basis of the perturbations in the O_2^+ spectrum. It was shown in the paper [2465a], on the basis of an analysis of the perturbations in the O_2^+ spectrum, that this $^2\Pi$ state must lie by 5700 cm^{-1} higher than the $A^2\Pi$ state.
h) $\varepsilon = 0.1487$, $\gamma = -0.00033$ cm^{-1}.

i) $\beta_1 = 0.185 \cdot 10^{-6}$ cm^{-1}.
A) State; B) cm^{-1}.

The band system $b^4\Sigma - a^4\Pi$ of the O_2^+ molecule was investigated in a number of papers. Frerichs [1606] carried out the analysis of the rotational structure of some bands of this sytem. Later on, Mulliken and Stevens [3004] and Bozoky and Schmid [884] obtained a series of new bands with the values $v' \leq 4$ and $v'' \leq 3$. Singhand Lal [3748] extended the investigations up to $v' \leq 7$ and $v'' \leq 5$. The most thorough analysis of this system was carried out by Nevin [3058, 3059, 3060] and Nevin and Murphy [3061], who obtained the O_2^+ spectrum on a device with a concave 21-feet grating, determined the rotational constants and the constants of the quartet splitting of both states, and also calculated the values of the vibrational constants on the basis of the band edges.

The constants found in these investigations are adopted by the Handbook [649] and the monograph [2020] and are cited on Table 20.

It must be noted that Budo and Kovacz [1007], investigating the perturbations in the $a^4\Pi$ state, drew the conclusion that these perturbations are caused by two $^2\Pi$ states, one of which is an $A^4\Pi$ state and the other an unknown state having an excitation energy in the range of 40,000-41,000 cm^{-1}.

O_3. A great number of investigations of the infrared ozone spectrum, having three intense bands at 4.75; 9.57 and 14.2 microns [2103, 1045 and 704 cm^{-1}) and weak bands at 3.28; 3.57 and 5.75 microns (3049, 2801 and 1739 cm^{-1}), is well known. An analysis of the infrared spectra of O_3, obtained up to 1945, is given in the papers by Adel and Dennison [491], Simpson [3741] and in the monograpy by Herzberg [152]. Later on, the infrared spectrum of O_3 was investigated in papers [4295, 2910, 3064] and in others, whose results are discussed below. Attempts to obtain the Raman spectrum of O_3 were not crowned with success up to the end of 1960. Thus, in spite of the numerous investigations of the infrared spectrum of O_3, one succeeded only recently in correlating the fundamental frequencies of this molecule and to determine the accurate values of its structural parameters.

The study of the rotational and vibrational-rotational spectra and also the results of the electron-diffraction investigations led to the conclusion that the O_3 molecules possesses the structure of an isosceles triangle and belongs to the C_{2v} point group of symmetry. However, the difficulties in the interpretation of the infrared spectra for a long time hampered the determination of the true values of the structural parameters, and two models of the O_3 molecule have been discussed in literature; the "acute" and the "obtuse" model, depending on the value of the angle between the bands.

A correct interpretation of the infrared ozone spectrum was for the first time given in 1948 in the paper by Wilson and Badger [4295] who investigated the ozone spectrum in the 6700-670 cm^{-1} (1.5-15 microns) region and who found a new band in the 1110 cm^{-1} region closely adjoining the 9.57 microns band. Wilson and Badger succeeded in the partial resolution of the rotational structure of the band, which, as well as the 14.2 microns band, does not possess a Q branch, and has an intensity similar to that of the latter. On the basis of the data obtained, they came to the conclusion that the intensity of the 9.57 microns or 1043 cm^{-1} band corresponds to the antisymmetrical vibration ν_3, and that both the other frequencies, ν_1 and ν_2, are equal to 1110 and 705 cm^{-1}.

In recent years, a number of ozone bands was investigated by devices with high dispersion [2910, 3064, 2323, 4108]. The frequencies of the beginning of the ν_2 and ν_3 bands, quoted in Table 21, have been accurately determined in papers by Newsen [3064] and Kaplan, Migeotte and Neven [2323]. Up to now, one has not succeeded accurately to determine the position of the beginning of the ν_1 band. In paper [4108] it is mentioned that it swave number is smaller than 1114 cm^{-1}. The value found in the paper by Wilson and Badger [4295]*is accepted

for the ν_1 frequency in Table 21. On the basis of new spectral data, Wilson and Badger showed that the ozone molecule must have an "obtuse" structure. This conclusion was proved by numerous investigations of the microwave spectrum of ozone, published in recent years [4012, 4310 1798, 2146, 3247, 2145]. In the papers mentioned, the spectra of four isotopic modifications of the ozone molecule have been investigated, which correspond with transitions at a number of J values up to J = 50. On the basis of the data obtained, it was possible to determine the structural parameters of the O_3 molecule with high accuracy: r_{O-O} = = 1.278 ± 0.002 A, and $\angle$ O − O − O = 116°45' ± 30 . It must be mentioned that it is reported in paper [2146] that a new electron diffraction study of the structure of the ozone molecule, carried out by Jones, Hedberg and Schomaker [2304] resulted in almost the same value for the structural parameters. The most accurate values for the rotational constants of O_3 have been calculated by Pierse [3247], who processed the experimental data obtained by Trambarulo [4012], Hughes [2146, 2145] and others. The values found by Pierse and converted into inverse centrimeters are given in Table 21.*

TABLE 21

Accepted Values of the Molecular Constants of O_3

ν_1	ν_2	ν_3	A_{00}	B_{00}	C_{00}	σ
A cm^{-1}						
1110	701,42	[illegible]	3,55301	0,44527	0,35475	2

A) cm^{-1}.

Ozone possesses a number of absorption regions in the visible and ultraviolet spectral region, which, to all appearances, are related to transitions between the electronic states of this molecule. In spite of the numerous investigations of these spectra, it was not possible up

to now to interpret them, although some attempts have been made to carry out the corresponding analysis (see [975, 4140]). On the basis of the data available in literature, only the assumption may be made that the ozone molecule must possess at least one excited electronic state with an excitation energy of the order of 10,000-15,000 cm^{-1}.

§25. THERMODYNAMIC FUNCTIONS OF GASES

The thermodynamic functions of the substances dealt with in the present chapter are calculated without allowing for the intramolecular interaction on the basis of the constants accepted in the foregoing section, and are quoted in the Tables 1-6 of the IInd volume of the Handbook. The calculations for four gases (O, O^+, O_2 and O_2^+) are carried out up to 20,000°K, those for the two others (O^- and O_3), up to 6000°K. The differences of the constants of the individual isotopic modifications of the gas molecules have not been taken into account owing to the low content of the O^{17} and O^{18} isotopes in the natural mixture.

O. The thermodynamic functions of the monatomic oxygen, quoted in Table 1(II) are calculated for the 293.15-20,000°K temperature range. The translational components are calculated by Eqs. (II.8) and (II.9), assuming $A_\Phi = 0.98124$ and $A_S = 5.94244$ cal/g-atom·degree, the electronic components are calculated by Eqs. (II.20) and (II.21) on the basis of the values quoted in Table 16. The sum over the electronic states, and its derivative with respect to temperature are calculated on a high-speed electronic computer by immediate summation over the energy levels. The calculation is carried out, allowing for a finite number of states of the oxygen atom in accordance with the method expounded in §6 (see page 133, Eq.(II.18)). In order to simplify the calculation, all energy levels with values of the principal quantum number $n \leq 11$ are taken into account at temperatures below 8000°K.

Owing to the high excitation energies of all electronic states of the oxygen atom with $n > 7$, the error caused by this simplification is negligible, and its maximum value does not exceed 0.0003 cal/g-atom·degree in the values of Φ_T^*. Energy levels with $n \leq n_{max}$ are taken into account in the calculations for temperatures higher than 13,600°K (n_{max} increases steadily when the temperature rises from 13,600 to 20,000°K, see page 135).

The inaccuracy of the values of the thermodynamic functions of the atomic oxygen at temperatures below 10,000°K, calculated in that way, is caused mainly by the inaccuracy of the physical constants and does not exceed 0.002-0.003 cal/g-atom·degree. At higher temperatures, the errors become essential, which are caused by the approximate method of determination of the maximum value of the principal quantum number. An error of ± 1 (at $n = 13$) in this value results in errors of the order of 0.01 and 0.1 cal/g-atom·degree in the values of $\Phi^*_{15,000}$ and $\Phi^*_{20,000}$, respectively. It must be noted that the inaccuracies in the values of the thermodynamic functions caused by an inaccurate estimation of the energy of individual levels is lower by one order of magnitude than these values.

The thermodynamic functions of atomic oxygen have been calculated in a number of papers, from which the calculation by Huff, Gordon and Morrell [2142] (up to 6000°K), by the Bureau of Standard of the U.S. [3680] (up to 5000°K) and by Kolsky and coauthors [2462] (up to 8000°K) carried out in recent years, are worth mentioning. The results of all calculations conform to each other and to the data quoted in the present Handbook with an accuracy which is determined by the difference of the physical constants.

The thermodynamic functions of the monatomic oxygen up to 20,000°K have been calculated on the occasion of the calculation of the thermo-

dynamic functions of the air by Predvoditelev and coworkers [335]. Owing to the fact that electronic states of the O atom, not observed experimentally, have not been taken into account in these calculations, the values of S°_{T}, quoted in paper [335] and at T > 12,000°K essentially lower than those calculated in the Handbook. The corresponding difference amount to almost 4 cal/g-atom·degree at 20,000°K.

O^{+}. The thermodynamic functions of the positive monatomic oxygen ion, quoted in Table 2(II), are calculated for the 293.15-20,000°K temperature range. The calculation of the translational components is carried out by the same formulas as are used for the monatomic oxygen, and the calculation of the electronic components is carried out by Eqs.(II.20) and (II.21) on the basis of the values quoted in Table 17. The sum on the electronic states and its derivative with respect to the temperature is obtained by immediate summation over the energy levels.

The inaccuracy of the thermodynamic functions of the positive monatomic oxygen ion is a sum of the errors caused by the inaccuracy of the assumed values of the physical constants and neglection of the electronic states of the O^{+} ion with excitation energies higher than 100,000 cm^{-1}. These errors do not exceed 0.005 cal/g-atom·degree in the values of Φ^{*}_{T} at temperatures up to 20,000°K. The thermodynamic functions of O^{+} have been calculated in papers [335] (S°_{T}, E°_{T}, and C°_{p} up to 20,000°K), and [185a] (Φ^{*}_{T} up to 50,000°K); the results of both calculations are in conformity with the data of Table 2(II) within a range of 0.02 cal/g-atom·degree. Other calculations of tables of thermodynamic functions of O^{+} are unknown in literature.

O^{-}. The thermodynamic functions of the negative monatomic oxygen ion, quoted in Table 3(II), are calculated for the 293.15-6000°K temperature range. The calculation of the translational components was

carried out by the same formulas as in the case of monatomic oxygen, the splitting of the components of the ground state of the O^- ion has been taken into account in calculating the electronic components. It was assumed that the O^- ion does not possess excited electronic states (see page 298).

The inaccuracy of the values of thermodynamic functions of the negative monatomic oxygen ion calculated in this way is caused mainly by the inaccurately estimated value of the splitting of the $^2P_{3/2}$ and $^2P_{1/2}$ ground-state components of O^-. Since the inaccuracy of the assumed value amounts to about 20-50 cm^{-1}, the inaccuracies of the calculated $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000} values lie in the range of 0.1, 0.03 and 0.01 cal/g-atom·degree, respectively. Other calculations of the thermodynamic functions of the O^- ion are unknown in literature.

O_2. The thermodynamic functions of the diatomic oxygen, quoted in Table 4(II), are calculated for the 293.15-20,000°K temperature range. Eqs.(II.8) and (II.9), assuming $A_\Phi = 3.04744$ and $A_S = 8.01564$ cal/mole·degree, were used for the calculation of the translational components, and Eqs. (II.131) and (II.132) and the constants quoted in Table 19, for the intramolecular compounds. The partition functions of the vibrational and rotational levels of the $X^3\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$, $c^1\Sigma_g^-$, $A^3\Delta_u$, $B^3\Sigma_u^+$ and $C^3\Sigma_u^-$ states and their derivatives with respect to temperature have been calculated by immediate summation on a high-speed electronic computer. The energy values of each vibrational and rotational level of these states, put in for the calculation, are obtained by means of equations, being functions of the corresponding quantum numbers, and by the constants quoted in Table 19. The maximum values of the quantum number $\underline{v}$ and J are shown in Fig.6. Calculating the partition functions of the vibrational-rotational levels of the $X^3\Sigma_g^-$, $B^3\Sigma_u^+$ and $C^3\Sigma_u^-$ states, the summation of the F_1, F_2 and F_3 com-

ponents over the energy levels was carried out separately; the energy of the rotational levels was calculated by the Schlapp formulas (see page 79).

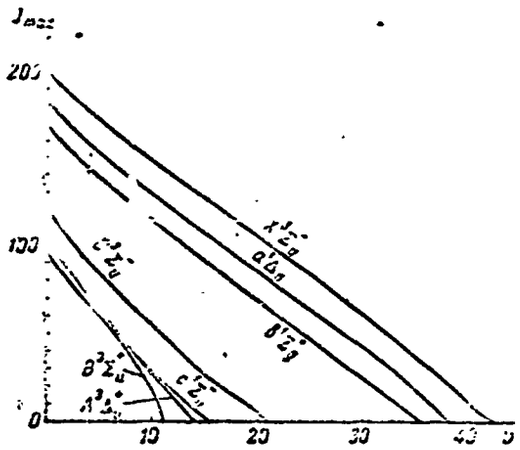


Fig.6. J_{max} as a function of v for the electronic states $X^3\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$, $A^3\Delta_u$, $B^3\Sigma_u^+$, $c^1\Sigma_u^-$ and $C^3\Sigma_u^-$ of the O_2 molecule.

The accuracy of the thermodynamic functions of diatomic oxygen at temperatures up to 3000-5000°K, calculated by this way, depends the accuracy of the physical constants, and the inaccuracy in the Φ_T^* and S_T° values does not exceed 0.005 cal/mole·degree. At higher temperatures, the lack of sufficiently reliable data on the vibrational and rotational energy of the O_2 molecule in the $a^1\Delta$ state (see page 305) and, further, in the subsequent electronic states of this molecule begins to affect the results. A comparison of the results of calculation carried out, allowing for the possible inaccuracy of the molecular constants of O_2 in the $X^3\Sigma_g^-$, $a^1\Delta_g$, $A^3\Delta_u$ and $B^3\Sigma_u^+$ states, leads to the conclusic that the error does not exceed $\pm$0.03 cal/mole·degree in the $\Phi^*_{10,000}$ value and $\pm$0.15 cal/mole·degree in the $\Phi^*_{20,000}$ value.

The molecular constants, quoted in Table 19 and used in the cal-

culation, correspond to the O_2^{16} molecule. Owing to the low content of the other isotopic modifications of the O_2 molecule in the natural isotopic oxygen mixture, the errors caused by this simplification do not exceed 0.001-0.002 cal/mole·degree.

A number of calculations of the thermodynamic functions of molecular oxygen including those for high temperatures is well known in literature. A bibliography of the corresponding papers published up to 1940, is given in the review by Wilson [4291]. Among these calculations, the papers by Johnston and Walker [2282, 2283, 2284] ($T \leq 5000°$), in which the thermodynamic functions of O_2 have been calculated by immediate summation over the levels of the vibrational energy, using the formulas by Kramers for the rotational energy of the O_2 molecule in triplet states, may be mentioned. The data obtained by Johnston and Walker have been converted to the recent values of the universal constants in the paper by Warman et al.[4122] and are cited in a number of reference books. The most accurate calculation of the thermodynamic functions of diatomic oxygen have been carried out by Woolley [4324] for temperatures up to 5000°K by immediate summation over the levels of the vibrational energy on the basis of molecular constants similar to those accepted in the present Handbook. The divergences between the values of the functions quoted in Table 4(II) and the calculation results obtained by Woolley do not exceed 0.005 cal/mole·degree. An approximate extrapolation of the thermodynamic functions of O_2 for temperatures of from 6000 to 12,000°K was carried out in the paper [1556]. The authors of this paper performed the calculation by means of the Mayer and Goeppert-Mayer method and extrapolated the differences obtained up to 12,000°K, after having compared the calculation results up to 5000°K with the values recommended by the Bureau of Standards of The U. S. [3680]. The values obtained in

this way contain significant errors. In particular, the $S^{\circ}_{12,000}$ value differs from the value quoted in Table 4(II) by 0.6 cal/mole·degree. Predvoditelev et al.[336] calculated some thermodynamic functions of a number of air components, including O_2, up to 20,000°K. The calculation was performed by immediate summation over the electronic and vibrational states. In the sum over the rotational states, the summation was substituted by integration, taking into account the upper limit of the change of the quantum number J. The values of J_{max} have been calculated by a method similar to that stated above (see page 74), but differing from the latter by the fact that in the equation of the effective potential curve the term proportional to $J^2(J + 1)^2$ was not taken into account. The calculated S°_T values differ from those quoted in Table 4(II) by not more than 0.15 cal/mole·degree.

In the paper by Beckett and Haar [714], the thermodynamic functions of O_2 were calculated for various degrees of temperatures up to 25,000°K. In order to avoid the difficulties caused by the divergence of the series when using approximate calculation methods at high temperatures, the authors of the paper [714] used a method fundamentally differing from the traditional methods to calculate the thermodynamic gas functions, which are expounded in Chapter II and operate with the quantum-mechanical sum over the states. In the method used by them, the gas molecules were considered to be groups consisting of atoms bound to each other by interaction forces. Using the classic expression for the sum over the states (see [285], Eq.(6.12)) and transforming it into an equation connected with virial coefficients, the authors of the paper [714] obtained for $Q_{kol.vr}$ of diatomic molecules an expression containing group integrals. The calculation of the group integrals was carried out in paper [714] by an electronic computer, the energy of the interaction of the atoms was approximated by a Morse

function. The values of the thermodynamic functions of O_2, calculated in this way, differ essentially from the values quoted in Table 4(II), and the difference increases rapidly at rising temperature. These divergences amount to 0.19 and 1.8 cal/mole·degree for Φ_T^* and to 0.7 and 3.8 cal/mole·degree for S_T° at 10,000 and 20,000°K, respectively. The application of the Morse function for the potential energies of gas molecules and of an approximate method of taking into account the excited electronic states apparently causes the insufficient accuracy of the calculation of the authors of paper [714].

O_2^+. The thermodynamic functions of the positively charged ionized diatomic oxygen, quoted in Table 5(II), have been calculated for the 293.15-20,000°K temperature range. The calculation of the translational components was performed by means of the same formulas which are used for the calculation of the translational components of the functions of O_2, the intramolecular compounds were calculated by Eqs. (II.28) and (II.29), using the constants quoted in Table 20.

The partition function of the vibrational and rotational energy levels of the $X^2\Pi_g$ state of O_2^+ and its derivative with respect to the temperature have been calculated by immediate summation on a high-speed electronic computer. The values of the energies of the individual levels, put in for the calculation, are obtained by means of equations which are functions of the corresponding quantum numbers, using the constants quoted in Table 20. The maximum values of the quantum numbers $\underline{J}$ and J are given in Fig.4. When calculating the sum over the states and its derivative, the summation over the energy levels of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ substates was performed separately.

The components of the $a^4\Pi$-, $A^2\Pi$- and $b^4\Sigma$- states of O_2^+ in the expressions for Φ_T^* and S_T° have been calculated by Eqs.(II.126) and (II.127), i.e., taking into account the difference of the constants of

the O_2^+ molecule in these and in the $X^2\Pi_g$- states; the components of the $B^2\Pi$- states, for which the constants of O_2^+ are unknown, have been calculated by Eqs.(II.120)-(II.121). The approximate method of taking into account the excited states of O_2^+ may cause essential errors in the values of the thermodynamic functions only at temperatures higher than 10,000-15,000°K. The inaccuracy of the calculated thermodynamic functions of O_2^+ at temperatures up to 8000-10,000°K does not exceed 0.005-0.01 cal/mole·degree.

The thermodynamic functions of O_2^+ have been calculated in papers [336] (S_T° up to 20,000°K) and [714] (Φ_T^* and S_T° up to 25,000°K). The difference between the values quoted in Table 5(II) and the values obtained in these papers increases with rising temperature. At 20,000°K the S_T° value cited in Table 5(II) exceeds the value calculated in the paper [336] by 1.6 cal/mole·degree and is by 1 cal/mole·degree lower than the value found in paper [714].

O_3. The thermodynamic functions of ozone quoted in Table 6(II) have been calculated in the harmonic oscillator-rigid rotator approximation for the temperature range of from 293.15 to 6000°K, using the constants quoted in Table 21. The values of C_Φ' and C_S' in Eqs. (II.243) and (II.244), serving for the calculation of the translational-rotational components of the thermodynamic functions of O_3, are given in Table 22. In the same table, the values of θ_n are cited which were used for calculating the vibrational components.

The ozone molecules obviously possesses electronic states with low excitation energies (see Page 314). The lack of data necessary for taking into account these states and also for allowing for the anharmonicity of the vibration, the interaction between rotation and vibrations and the centrifugal stress of the O_3 molecule causes high errors in the calculated thermodynamic functions of ozone. The errors

in the values of $\Phi^*_{298.15}$ and Φ^*_{3000} amount to about 0.03 and 0.7 cal/ /mole·degree, respectively. The calculations of the thermodynamic functions of ozone, performed up to 1950, are based on incorrect values of the oscillation frequencies and moments of inertia. After the values of the molecular constants have been determined more accurately, the thermodynamic functions of ozone have been calculated in the Bureau of Standards of the U.S. [3680] (up to 1500°K) and by Cleveland and Klein [1129, 2430] (up to 1000°K). The results of the calculations mentioned are in conformity with the values of the functions quoted in Table 6(II) within a range of ±0.02 cal/mole·degree.

TABLE 22

Values of the Constants for the Calculation of the Thermodynamic Functions of O_3

θ_1	θ_2	θ_3	C'_Φ	C'_S
A *град*			B *кал/моль·град*	
1597,06	1009,20	1499,36	3,3991	11,3482

A) Degree; B) cal/mole·degree.

§26. THERMOCHEMICAL QUANTITIES

O_2 (gas) is the standard state of elementary oxygen.

O (gas). According to the assumed value of $D_0(O_2)$ (see below), the heat of formation of monatomic oxygen is equal to

$$\Delta H^\circ f_0(O, \text{gas}) = 58{,}987 \pm 0{,}025 \text{ kcal/g-atom.}$$

O^+ (gas). The value of the ionization potential of the oxygen atom was assumed according to Moore's recommendation [2941] (see page 295) as

$$I(O) = 314{,}052 \text{ kcal/g-atom.}$$

The inaccuracy of this value amounts to ±1 cal/g-atom. According to the assumed ionization potential, we have

$$\Delta H^\circ f_0(O^+, \text{gas}) = 373{,}039 \pm 0{,}025 \text{ kcal/g-atom.}$$

O^- (gas). In literature published up to 1948, values of from -46 ± 9 kcal/g-atom [1946] up to -70.8 ± 2 kcal/g-atom [4106] have been obtained for the quantity of the electron affinity A(0) of the oxygen. The results of these investigations have been discussed in the papers by Metlay and Kimball [2861] who also carried out their own measurements. For the A(0) quantity they recommended the value -53.8 ± 0.8 kcal/g-atom.* The same value is recommended in Pritchard's review [3330].

Branscomb and Smith [902] in 1955, carried out the first direct determination of the quantity A(0) by measuring the photodissociation threshold of the O^- ion, and obtained an essentially lower value, equal to -1.45 ± 0.15 ev or -33.4 ± 4 kcal/g-atom. Later, in the paper by Branscomb and coworkers [901], the wavelength of the emission corresponding to the photodissociation threshold of the O^- ion was determined more accurately and being found equal to 8460 ± 30 A, which gives a value of the electron affinity of the oxygen atom equal to -33.80 ± 0.12 kcal/g-atom.

Owing to the fact that in the investigations carried out by the method of electronic impact, significantly higher values have been obtained for the A(0) quantity; Hagstrum [1930] carried out an analysis of these papers and, based on a new interpretation of the experimental data, drew the conclusion that they conform with the results of measurements by the method of photo-ionization. The corresponding values calculated on the basis of the most reliable data by Clarke [1125] and Lagergren [2517] are equal to -32.7 ± 1 1 kcal/g-atom and 33.9 ± ± 1.1 kcal/g-atom, respectively. It must be noted that the new interpretation of the results of investigation of the A(0) quantity by the method of electronic impact made it possible to obtain values for the

dissociation energy of CO, and the sublimation heat of carbon, which is in conformity with these, obtained by other methods and have been accepted in the present Handbook. Recently, the measurements of the A(0) quantity by means of the method of electronic impact have been repeated by Tozer [4011a] who obtained the value of -35.05 ± 2.3 kcal/g-atom.

According to the data of [901], the value

$$A(0) = -33{,}80 \pm 0{,}12 \text{ kcal/g-atom}$$

is accepted in the Handbook for the electron affinity of the oxygen atom, and the expression

$$\Delta H^\circ f_0(O^-, \text{gas}) = 25{,}187 \pm 0.12 \text{ kcal/g-atom}.$$

corresponds to this value.

On the basis of an earlier paper by Smith and Branscomb [3795], the value -34.1 ± 2.3 kcal/g-atom of the A(0) quantity has been accepted in the review by Buchel'nikova [116].*

O_2 (gas). During several years, the value of 41,000 cm^{-1}, calculated by Herzberg [151] and Gaydon [141] on the basis of the extrapolation of the bands of the Schumann,Runge series has been assumed in literature. In 1952, however, Herzberg [2023] found (see page 312) that the last vibrational level of the $B^3\Sigma_u^+$ state having a common dissociation limit with the $X^3\Sigma_g^-$ ground state, possesses an energy of 41, 157 cm^{-1}, and, therefore, the value of the dissociation energy, assumed earlier, is underestimated. On the basis of an analysis of the rotational structure of the 11-0 band of the $B^3\Sigma_u^+ \leftarrow X^3\Sigma_g^-$ system and extrapolation of the observed vibrational levels of the $B^3\Sigma_u^+$ state, Herzberg came to the conclusion that the dissociation energy of oxygen is equal to 41,219 ± 40 cm^{-1}.

Later, Brix and Herzberg [952] determined a number of new bands in the Schumann-Runge system, which fact proved the inaccuracy of the value of 41,000 cm^{-1}, assumed earlier. A short extrapolation (to 13 cm^{-1}) of

the vibrational levels of the $C^3\Sigma_u^-$ state enabled the authors significantly to increase the accuracy of the determination of the dissociation limit of this state which they have found to be equal to 57,127 ± 5 cm^{-1}; a value of $D_0(O_2)$ = 57, 127 − 15,867 = 41,260 ± 5 cm^{-1} corresponds to this fact. On the basis of a new analysis of the data obtained by Herzberg [2023] during the investigation of the bands of the $B^3\Sigma_u^+ - X^3\Sigma_g^-$ system, and on the basis of the value of $D_0(O_2)$ found from the dissociation limit of the $C^3\Sigma_u^-$ state, Brix and Herzberg recommend the value

$$D_0(O_2) = 41\,260 \pm 15\ см^{-1} = 117{,}973 \pm 0{,}050 \text{ kcal/mole},$$

which is accepted in the present Handbook.

O_2^+ (gas). The ionization potential of the molecular oxygen has recently been investigated by the photoionization method in papers by Inn [2175] and Watanabe and Marmo [4177]. The photoionization limit of the O_2 molecules was found to be equal to 1029 and 1030.8 A, respectively, in these papers. Taking into account the distribution of the oxygen molecules on the energy levels of the $X^3\Sigma_g^-$ state, and studying the yield of photoionization as a function of the wavelength, Watanabe and Marmo assume for the 0-0 transitions $X^2\Pi_g(O_2^+) \leftarrow X^3\Sigma_g^-(O_2)$ λ = 1026.5 ± 0.01 A, to which corresponds an $I(O_2)$ value equal to 97,418 ± 10 cm^{-1}, or

$$I(O_2) = 12{,}077 \pm 0{,}001\ эв = 278{,}545 \pm 0{,}03 \text{ kcal/mole}.$$

This value has been accepted in the present Handbook. Almost the same value (12,075 ev) is recommended in the review [4176] on the basis of the ionization potentials of a series of molecules. Older measurements (see [141]) have given values for the ionization potential of O_2 from 12.2 to 12.5 ev.

The function

$$\Delta H^\circ f_0(O_2^+,\ газ) = 278{,}545 \pm 0{,}03 \text{ kcal/mole}.$$

corresponds to the accepted ionization potential of O_2.

The investigation of O_2^+ spectra makes it impossible to obtain a reliable value of the dissociation energy of this molecule. The value

$$D_0(O_2^+) = 153{,}48 \pm 0{,}05 \text{ kcal/mole.}$$

corresponds to the values of $I(O_2)$, $D_0(O_2)$ and $I(O)$, assumed above.

O_3 (gas). Measurement of the heats of interaction between O_3 and As_2O_3 and the catalytical decomposition of O_3 on platinum and soda lime have been carried out in papers by Berthelot [775, 776], Mulder and Van der Meulen [2966, 2967], Jahn [2203] and Kailin and Jahn [2319] in order to determine the heat of formation of O_3. The data obtained by these authors have been analyzed critically by Bichowski and Rossini [813], who recommended the value of 34.5 kcal/mole for the heat of formation of ozone at 293.15°K. Later, the same value has been obtained by Gunther, Wassmuth and Schryver [1891] on the basis of measurements of the decomposition heat of O_3 in explosion. Corresponding to this data,

$$\Delta H^\circ f_{293.15}(O_3, \text{ газ}) = 34{,}5 \pm 0{,}5 \text{ kcal/mole.}$$

is accepted in the present Handbook.

$$D_0(O_2) = 141{,}828 \pm 0{,}5 \text{ kcal/mole.}$$

corresponds to the accepted value.

TABLE 23

Accepted Values of Thermochemical Quantities (in cal/mole) of Oxygen and its Compounds in the Gaseous State

A Вещество	D_0	$\Delta H^\circ f_0$	$\Delta H^\circ f_{293.15}$	$\Delta H^\circ f_{298.15}$	$H^\circ_{293.15} - H^\circ_0$	$H^\circ_{298.15} - H^\circ_0$
O	—	58 987	59 548	59 558	1581	1608
O^+	314 052[a]	373 039	374 931	374 963	1456	1481
O^-	33 800[a,b]	25 187	24 256	24 240	1545	1571
O_2	117 973	0	0	0	2040	2075
O_2^+	278 545[a]	278 545	280 149	280 176	2188	2225
O_3	141 828	35 132	34 500	34 496	2428	2476

a) The value of the ionization potential of the corresponding neutral ion or molecule is given.
b) the energy of electron detachment from the O^- ion is given.
A) Substance.

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[Footnotes]

299 A uniform system of denomination of the excited electronic states of O_2 is lacking in literature; in the Handbook, the designations a, b, c are chosen for singlet states, and A, B, C, for triplet states (in the sequence of their rising excitation energies).

304 In the papers [2929, 2916, 1026] the microwave spectra of oxygen have been investigated. The data obtained by analysis of the microwave spectra have been used mainly for checking the validity of the Schlapp's equations for the rotationsl levels of the $X^3\Sigma_g^-$ state of the O_2 molecule. The values of the rotational constants B_e and α_1, close to those cited in Table 19 (1.4457 and 0.0158 cm^{-1}), and also $\Delta G_{1/2}$ = = 1556.26 cm^{-1} have been obtained in 1960 during the investigation of the Raman spectrum of gaseous oxygen by Weber and McGinnis [4189a].

313 It must be noted that in the paper by Gutowsky and Peterson [1905] the attempt was made to interpret the ν = 1110 cm^{-1} band as a $\nu_1 - \nu_2$ difference and to assume the "acute model" for the O_3 molecule. Badger and Wilson [603] proved the unfitness of this assumption, on the basis of an investigation of the ozone spectrum at low temperatures.

314 After the calculations of the thermodynamic functions of ozone had been finished, the paper by Gora [1798a] has been published, who, on the basis of a new processing of the experimental data, obtained almost the same values of the rotational constants of O_3 (A_{000} = 3.55360; B_{000} = 0.44527, and C_{000} = 0.39475 cm^{-1}). It must be noted that the structure of the rotational spectrum of O_3, investigated in 1959-1960 [1260, 1674a] is also well described by equations having these constants.

325 The value A(0) = -53.8 ± 0.8 kcal/g-atom was obtained by Metlay and Kimball on the basis of the measurement of the current of negative ions formed due to the dissociation of

N_2O on an incandescent tungsten filament. Recently, Branscomb [900], investigating the dependence of the negative ion current, observed in the work by Metlay and Kimball on the temperature of the incandescent filament, has shown that these ions are Cl^- ions and not O^- ions. Owing to the fact that in the commercial nitrous oxide used by Metlay and Kimball, chlorine must be present as an impurity, the conclusion drawn by Branscomb is sufficiently substantiated.

326 A value A(O) = -33.5 kcal/g-atom, almost similar to the value accepted above, had been obtained in 1961 by Page [3163a] by measuring the current of negative ions ionizing O_2, NO and H_2O on an incandescent filament.

[Translitérated Symbol]

321 кол.вр = kol.vr = kolebatel'nyy-vrashchatel'nyy = vibrational-rotational.

Chapter 6

HYDROGEN AND ITS ISOTOPES

(H, H^+, H^-, H_2, D, HD, D_2, T, HT, DT, T_2)

Three isotopes of hydrogen are well known: protium (H^1), deuterium (H^2 or D) and tritium (H^3 or T). Natural hydrogen consists of 99.9851% protium and 0.0149% deuterium. In nature, tritium occurs in insignificantly small quantities. In contrast to protium and deuterium, tritium is radioactive and has a half-life of 12.262 years [3889].

Owing to the fact that natural hydrogen consists almost entirely of protium, its thermodynamic properties practically do not differ from the thermodynamic properties of pure protium. Thus, the difference between the Φ_T^* value of monatomic natural hydrogen and that of pure protium amounts to 0.0004 cal/g-atom·degree, i.e., it is lower than the error caused by the inaccuracy of the values of physical constants. Therefore, in the present Handbook, a difference between the compounds of protium and natural hydrogen is not quoted, as a rule, with the exclusion of cases, in which compounds of individual hydrogen isotopes with one another, as well as with oxygen or halogens, are dealt with.

In the present chapter, the monatomic hydrogen isotopes (H^1, D, T), the ions H^+ and H^-, and the diatomic compounds (H_2^1, HD, D_2, HT, DT, T_2)* are dealt with. The thermodynamic functions of the monatomic protium and its ions and also that of the diatomic protium are calculated for the temperature range of from 293.15 to 20,000°K, and the

thermodynamic functions of deuterium, tritium and their compounds, up to 6000°K. The D^+ and T^+ ions are not dealt with in the Handbook, because an ionization of hydrogen does not take place practically up to 6000°K. The excitation energies of the H, D, and T atoms and of the H_2, HD, D_2, HT, DT, and T_2 molecules are very high. Thus, the contribution of these states to the values of thermodynamic functions of the corresponding gases are negligible at temperatures up to 10,000-15,000°K and become essential only up to 20,000°K. Owing to this fact, mainly the results of investigations of the ground electronic states of the H_2 molecule and of its isotopic modifications are dealt with in the Division "Molecular Constants".

The spectra of the isotopic modifications of hydrogen are similar to each other. In particular, the system of excited electronic states is similar. As Stoicheff [3875] has shown, the interatomic equilibrium distance r_e is equal for all isotopic modifications of the H_2 molecules with an accuracy of up to ± 0.0001 A. It must be noted, however, that the value of $r_e(H_2^1) = 0.74130 \pm 0.00006$ A, found by Stoicheff differs somewhat from the value found by Herzberg and Howe [2032], $r_e(H_2) = 0.741116$ A, and, in connection with this fact, repeated determinations of the r_e values of each isotopic modification of the H_2 molecule are necessary.

§27. MOLECULAR CONSTANTS

H^1. The protium atom possesses in the ground state an 1s electron configuration, to which the $^2S_{1/2}$ state corresponds. The excitation energies and statistical weights of all electronic levels of the protium atom, corresponding to the values of the principal quantum number $n \leq 13$, accepted on the basis of the values recommended by Moore [2541], are quoted in Table 24. States having energies which are similar in their values, are unified into one level with a mean exci-

tation energy and a summarized statistical weight.

TABLE 24

Energy Levels of the H^1, D and T Atoms

A Атом	B Номер уровня	C Состояние: электронная конфигурация D	C Состояние: E терм	F Статистический вес	G Энергия, $см^{-1}$
H^1	0	1s	$^2S_{1/2}$	2	0
	1	2s, 2p	^2S, ^2P	8	82259,1
	2	3s, 3p, 3d	^2S, ^2P, ^2D	18	97492,3
	3	4s,...4f	^2S,...,^2F	32	102824
	4	5s,....5g	^2S,...,^2G	50	105292
	5	6s,...,6h	^2S....,^2H	72	106632
	6	7s,....7i	^2S,...,^2I	98	107440
		s,...,8k	^2S,...,^2K	128	107965
	8	9s,...,9l	^2S,...,^2L	162	108325
	9	10s,...,10m	^2S,...,^2M	200	108582
	10	11s,...,11n	^2S,...,^2N	242	108772
	11	12s,...,12q	^2S,...,^2Q	288	108917
	12	13s,...,13r	^2S,...,^2R	338	109030
D	0	1s	$^2S_{1/2}$	2	0
T	0	1s	$^2S_{1/2}$	2	0

A) Atom; B) number of the level; C) state; D) electron configuration; E) term; F) statistical weight; G) energy, cm^{-1}.

D, T. The deuterium and tritium atoms, as well as the protium atom, possess the electron configuration 1s in the ground state $^2S_{1/2}$. The energies of the excited electronic states of these atoms possess values similar to those of the energies of the corresponding states of the protium atoms.

In Table 24, only the data of the ground states of D and T atoms are given, because the excited electronic states of these atoms possess energies exceeding 82,000 cm^{-1} [2541] and are not dealt with in the present Handbook.

H^+. The positive ion of the protium atom (the proton) is the nucleus of this atom, devoid of the electron shell.

H^-. The negative ion of the monatomic protium possesses in the

ground state the $..s^2$ electron configuration, to which one ^1S state corresponds. The energies of the excited electronic states of the H^- ion must be high and, according to theoretical calculations (see [233a]) they must exceed essentially the ionization potential of this ion. Thus, it is assumed in the present Handbook that the H^- ion does not possess discrete excited electronic states.

H_2. The ground state of the H_2 molecule is a state of the $^1\Sigma_g^+$ type. All excited states of H_2 possess excitation energies higher than 90,000 cm^{-1} and they are, therefore, not dealt with in the present Handbook; the results of the numerous investigations on these states may be found in the monograph by Herzberg [2020] and in the Handbook [649].

Exactly as all symmetrical diatomic molecules, hydrogen does not possess a dipole vibrational-rotational spectrum and the molecular constants of H_2 in the ground electronic state may be found only on the basis of an investigation of the quadrupole vibrational-rotational spectrum, the Raman spectrum, and the electron spectrum.* The quadrupole spectrum of H_2 lying in the photographic infrared region, has been investigated by Herzberg [2021]. The Raman spectrum of H_2 has been studied by several investigators [828, 3399, 3875, 3957]. This spectrum was obtained with a maximum resolution in the works of Teal and McWood [3957] and Stoicheff [3875]. Transitions only between low vibrational and rotational levels ($v \leq 3$, and $J \leq 5$) have been observed in the quadrupole spectrum and Raman spectrum. Although the accuracy of the measurement of these spectra is very high, the values of the molecular constants of H_2 found in the corresponding papers, describe insufficiently the high vibrational and rotational levels of the ground state. Transitions corresponding to these higher levels have been observed in the electron spectrum of H_2.

TABLE 25

Energies (in cm^{-1}) of the Vibrational Levels $G_0(v)$ of the H_2 Molecule in the $X^1\Sigma_g^+$ state

v	A Экспериментальные данные	B Расчет по постоянным				
		[3957][a]	[4013][b] b	[2021][c] c	[3875][d] d	табл. 26
1	4161,14 [3875]-	4160,4	4162,4	4160,3	4161,1	4161,14
2	8087,11 [3875]‖	8084,4	8085,0	8087,0	8087,1	8088,68
3	11782,35 [3875]	11778,4	11777,2	11782,2	11782,3	11785,22
4	15250,36 [2032]	15251,7	15244,2	15247,5	15251,2	15253,23
5	18491,92 [2032]	18487,4	18486,4	18484,5	18497,9	18494,13
6	21505,65 [2032]	21501,[illegible]	21499,8	21495,3	21526,9	21507,37
7	24287,83 [2032]	24283,8	24275,4	24281,3	24342,5	24289,55
8	26830,97 [2032]	26827,0	26800,0	26841,4	26949,0	26833,49
9	29123,93 [2032]	29120,3	29056,9	29186,3	29351,0	29127,32
10	31150,19 [2032]	31152,0	31022,4	31308,7	31552,6	31153,58
11	32386,85 [2032]	32906,6	32670,2	33213,5	33558,0	32888,30
12	34301,83 [2032]	34356,8	33968,6	34902,1	35371,9	34300,11
13	35351,01 [2032]	35508,9	34881,9	36376,5	36998,5	35349,29
14	35972,97 [2032]	36312,6	35369,4	37638,6	38442,1	35986,91
v_{max}	36116±6[A][e]	36794,3	35385,7	40845,2	43925,2	35986,91[e][f]

a) $G_0(v) = 4281,4v - 122.573v^2 + 1.722v^3 - 0.11265v^4$; $v_{max} = 16$.

b) $G_0(v) = 4286.68v - 126.813v^2 + 2.7369v^3 - 0.19v^4$; $v_{max} = 15$.

c) $G_0(v) = 4277.46v - 117.560v^2 + 0.29v^3$; $v_{max} = 20$.

d) $G_0(v) = 4280.12v - 119.7285v^2 + 0.72419v^3$; $v_{max} = 22$.

e) See the footnote to page 358.

f) $v_{max} = 14$.

A) Experimental data; B) calculation on the basis of the constants.

Two most thoroughly studied band systems of the electron spectrum of H_2, related to the electronic ground state, lie in the vacuum-ultraviolet spectral range, where the accuracy of the measurement of the wave numbers of the lines was mediocre up to recent times. These are the systems $B^1\Sigma_u^+ \rightleftarrows X^1\Sigma_g^+$ (Lyman bands) [801, 2032, 2161, 2239, 2242, 3928] and $C^1\Pi_u \rightleftarrows X^1\Sigma_g^+$ (Werner bands) [2239, 2242, 3928]. The most thorough investigation of the Lyman bands has been published in 1959 by Herzberg and Howe [2032], who, using a device with high dispersion,

obtained results which significantly exceed, as to accuracy, all the works performed earlier. In particular, the energies of the vibrational levels of the electronic ground state of H_2 were determined in paper [2032] up to $v'' = 14$, and it was shown that the assumption made by Beutler [801] concerning the possible existence of an additional level ($v'' = 15$) below the dissociation limit is erroneous.

A number of equations proposed by various authors, which approximate the energy of the vibrational levels of the electronic ground state of H_2 is well known in literature. In Table 25 the results of the calculation by means of these formulas are given for comparison with the most accurate experimental data. The vibrational constants of H_2, found by Teal and McWood [3957] and Urey and Teal [4043] are calculated on the basis of insufficiently accurate data for $v'' = 0$-12, especially on the basis of data obtained by Jeppesen [2239, 2242] investigating the ultraviolet spectrum of H_2. Thus, the calculation of the values of $G_0(v)$ on the basis of the constants found in the papers [3957, 4031] gives inaccurate results for all values of v, especially for levels near the dissociation limit. The constants found by Herzberg [2021] (and cited in Herzberg's monograph [2020] and in the Handbook [649]) from the quadrupole spectrum, and by Stoicheff [3875] from the Raman spectrum, describe satisfactorily, only the energies of the lower vibrational levels of H_2. Only the constants, found by Herzberg and Howe [2032], as Table 25 shows, describe satisfactorily all vibrational levels of H_2 and let them converge near the dissociation limit of H_2. These vibrational constants are accepted in the present Handbook and quoted in Table 26.*

The rotational constants of the electronic ground state of the H_2 molecule have been calculated by several authors. Herzberg [2021] calculated the constants on the basis of an analysis of the fine struc-

ture of the 2-0 and 3-0 bands of the quadrupole spectrum of H_2. Stoicheff [3875], using the data obtained by Herzberg [2021], and also the results of his own measurements of the 1-0 band in the Raman spectrum, calculated anew the rotational constants of H_2. However, the rotational constants found by these two authors possess the same deficiency as the vibrational constants, being accurate only for low values of v. Jeppesen [2239] calculated the rotational constants, using the data for $v'' \leq 12$ and $J \leq 7$ obtained by him from the electron spectrum. Later, these data have been accepted as being a basis by Woolley, Scott and Bricwedde [4329], who calculated anew the values of the rotational constants of H_2 in the electronic ground state. The calculation performed in paper [4329] must be acknowledged to be the more correct one because the authors of this paper endeavored to develope such an equation which gives reasonable values for the energy of rotational levels at great values of J. In particular, the Eq. (1.18) instead of the polynomial (1.15) has been used for the energy of the rotational levels of the H_2 molecule.

TABLE 26

Accepted Values of the Molecular Constants of H_2 in the Electronic Ground State (in cm^{-1})

A Постоянная	B Значение	Постоянная A	B Значение	Постоянная A	B Значение
ω_e	4333,331	D_e	60,8433	D_e	$4,8435 \cdot 10^{-2}$
$\omega_e x_e$	117,9723	α_1	3,06335	β_1	$1,4004 \cdot 10^{-2}$
$\omega_e y_e$	0,24360	α_2	$3,3331 \cdot 10^{-2}$	β_2	$3,3478 \cdot 10^{-5}$
$\omega_e z_e$	−0,3302	α_3	$3,5 \cdot 10^{-3}$	H_e	$4,53203 \cdot 10^{-5}$
$\omega_e t_e$	−0,037581	α_4	$3,7217 \cdot 10^{-4}$	γ_1	$2,8 \cdot 10^{-7}$

A) Constant; B) value.

In the present Handbook, the values of the rotational constants are accepted, which are recommended in the paper [4329] by Woolley,

Scott and Bricwedde (see Table 26). The energies of the rotational levels of H_2 calculated by using these constants, differ somewhat from the experimental data found with high accuracy by Herzberg [2021], Stoicheff [3875] and Herzberg and Howe [2032]. However, these differences are negligible and do not exceed 0.1 cm^{-1} in the values of $F_v(J)$ at low J.

HD. The molecular constant of the $^1\Sigma_g^+$ electronic ground state of protodeuterium were for the first time found by Jeppesen [2240], Mie [2900] and Fujioka and Wada [1626] as the result of the analysis of the $C^1\Pi \rightarrow X^1\Sigma_g^+$ and $B^1\Sigma \rightarrow X^1\Sigma_g^+$ band systems in the ultraviolet spectrum of HD.

The $C^1\Pi \rightarrow X^1\Sigma_g^+$ band system was investigated by Jeppesen [2240], who obtained the absorption spectrum of HD in the 800-1375 A region by means of a vacuum spectrograph with a diffraction grating whose revolving power was 30,000. The spectrum consists of 12 bands corresponding to $v' = 0$-3 and $v'' = 1$-7, in which Jeppesen measured the wave numbers of about 2500 lines. Using the isotopic relations (1.43), Jeppesen calculated the vibrational and rotational constants of HD on the basis of the molecular constants of H_2 which he found earlier [2239]; the values obtained for the molecular constants well describe the observed positions of the lines in the HD spectrum.

Mie [2900] investigated the $B^1\Sigma \rightarrow X^1\Sigma_g^+$ and $C^1\Pi \rightarrow X^1\Sigma_g^+$ band systems with a spectrograph having a dispersion of 17.5 A/mm and observed transitions into the 12 lower levels of the electronic ground state of HD. On the basis of the analysis of the spectra obtained, Mie came to the conclusion that the cubic equation for ΔG_v obtained by Jeppesen [2239] is sufficient for describing the transitions into the lower levels of the ground state ($v'' = 0, 1, \ldots, 6$). Mie supplemented the equation for ΔG_v, obtained by Jeppesen [2239] by the term +0.005

$(v + 1/2)^4$, in order to describe the transitions into higher vibrational levels ($v'' = 7, 8, \ldots, 12$).

Later, the $B^1\Sigma \rightarrow X^1\Sigma_g^+$ and $C^1\Pi \rightarrow X^1\Sigma_g^+$ band systems were investigated by Fujioka and Wada [1626] by a device having a lower dispersion, and they confirmed the analysis results of Mie [2900].

The Raman spectrum of protodeuterium has been investigated for the first time by Teal and McWood [3957] who measured 8 lines of HD corresponding to pure rotational transitions ($J = 0, 1, \ldots, 6$) and 5 lines of the vibrational-rotational 1-0 band. On the basis of these measurements, Teal and McWood found $\Delta G_{1/2} = 3631.4 \pm 0.2$ cm^{-1}. Combining this value with the results of the measurements of the ultraviolet band systems of HD, obtained by Jeppesen [2240] and Mie [2900], Teal and McWood calculated the values of the vibrational constants of the electronic ground state of HD, quoted in the second column of Table 27.

The infrared spectrum of HD was obtained by Herzberg [2022], who measured 7 lines of the 3-0 band ($\sim$ 9650 A) and 6 lines of the 4-0 band ($\sim$7400 A). Combining the results obtained by the investigation of the infrared spectrum with the results of the investigation of the Raman spectrum [3957], Herzberg [2022] calculated the values of the molecular constants of HD, quoted in the third column of Table 27.

Stoicheff [3875], in 1957, obtained the Raman spectrum of HD by means of a device with a dispersion of 1.2 A/mm and measured 5 lines of the purely rotational transitions and 4 lines of the Q branch of the 1-0 band with an accuracy of from ± 0.02 to ± 0.05 cm^{-1}. The results of these measurements and those of the measurement of the infrared spectrum obtained by Herzberg [2022] enabled Stoicheff to calculate the molecular constants of HD, quoted in the fourth column of Table 27.

Later on, Durie and Herzberg [1426a] obtained in the infrared spectrum of HD the 1-0, 2-0, 3-0, and 4-0 bands with a very high resolution, and they determined anew, on the basis of an analysis of the rotational structure of these bands, the values of the molecular constants of HD in the electronic ground state (see Table 27). The data obtained by Durie and Herzberg are in good agreement with those of Stoicheff, but they exceed the latter with regard to accuracy and completeness. The values of the rotational constants of HD, found in paper [1426a], are similar to the values recommended by Woolley, Scott and Bricwedde [4329].

The molecular constants of HD found in papers [3875] and [1426a] made it possible to calculate the energy of the four lower vibrational levels of HD with high accuracy. The values of the molecular constants of HD, recommended by Woolley, Scott and Bricwedde [4329], determine the lower levels of the vibrational and rotational energy of HD with a practically equal accuracy as the constants found by Durie and Herzberg [1426a]. The higher levels, however, are determinable by these values with higher accuracy. Therefore, the values of the molecular constants of HD, recommended by Woolley, Scott and Bricwedde in paper [4329] have been accepted in the present Handbook for the electronic ground state. Woolley, Scott and Bricwedde adopted the values of the vibrational constants of the HD from the paper of Teal and McWood [3957]. The rotational constants B_e, α_1, α_2, α_3 have been calculated anew by the authors of paper [4329] on the basis of the data obtained by Jeppesen [2240].* The constants D_e, β_1, β_2, β_3, H_e, λ_1 and L_e have been calculated by Woolley, Scott and Bricwedde [4329] by means of the Dunham formulas (see page 85), using the constants entering into the expressions for $G(v)$ and B_v.

TABLE 27

Values of the Molecular Constants (in cm^{-1}) of the Electronic Ground State of HD According to the Data of Various Investigators

A Постоянная	B Вулли, Скотт и Брикведе [4329][a]	C Герцберг [2022]	D Стойчев [3875]	E Дьюри и Герцберг [1426a]
ω_e	3817,09	3809,745	3811,924	3812,293
$\omega_e x_e$	94,958	89,7668	90,7113	90,906
$\omega_e y_e$	1,4569	0,36567	0,47759	0,504
$\omega_e z_e$	0,07665	—	—	—
B_e	45,6549	45,6385	45,6378	45,6627
α_1	1,992721	1,9503	1,95004	2,0034
α_2	0,038482	0,0140	0,01402	0,03972
α_3	0,00316885	—	—	0,0034
D_e	$26,136 \cdot 10^{-3}$	$25,90 \cdot 10^{-3}$	$26,341 \cdot 10^{-3}$	$26,67 \cdot 10^{-3}$
β_1	$0,72661 \cdot 10^{-6}$	$0,84 \cdot 10^{-3}$	$0,857 \cdot 10^{-3}$	$0,78 \cdot 10^{-3}$
β_2	$0,0268773 \cdot 10^{-3}$	$0,044 \cdot 10^{-3}$	$0,033 \cdot 10^{-3}$	—
H_e	$20,827 \cdot 10^{-6}$	—	$22,4 \cdot 10^{-6}$	$22 \cdot 10^{-6}$ [6] b
γ_1	$0,1024 \cdot 10^{-6}$	—	—	—
L_e	$21,295 \cdot 10^{-9}$	—	—	—

a) Woolley, Scott and Bricwedde adopted the values of the vibrational constants of HD from the paper by Teal and McWood [3957].
b) Assumed in paper [1426a] according to the data by Stoicheff [3875].
A) Constant; B) Woolley, Scott and Bricwedde; C) Herzberg; D) Stoicheff; E) Durie and Herzberg.

The values of the molecular constants of HD for a number of excited electronic states are quoted in the book by Herzberg [2020] and in the Handbook [649].

D_2. The molecular constants of the $X\,^1\Sigma_g^+$ electronic ground state of the diatomic deuterium have been determined in the papers [3957, 3875, 4329, 2241, 417, 420] on the basis of the results obtained by the investigation of the Raman spectrum [3957, 3875] and the $^1\Sigma_u^+ \rightarrow X\,^1\Sigma_g^+$; $^1\Pi_u \rightarrow X\,^1\Sigma_g^+$ band systems lying in the ultraviolet region [2241].

The Raman spectrum of D_2 was obtained for the first time by Teal

and McWood [3957], who measured a number of lines of the purely rotational spectrum and of the 1-0 band and found $\Delta G_{1/2} = 2993.5 \pm 0.2$ cm^{-1}. A repeated investigation of the Raman spectrum of D_2 was carried out by Stoicheff in 1957 [3875] by a spectrograph with a 1.2 A/mm dispersion. Stoicheff measured 5 lines of the purely rotational spectrum and 5 lines of the Q branch of the 1-0 band. The results of the investigation of the Raman spectrum enabled Stoicheff to determine the following values (in cm^{-1}) of the molecular constants of D_2; $\Delta G_{1/2} = 2993.56_1$, $D_0 = 1.134 \cdot 10^{-2}$, $B_0 = 29.9105$, $D_1 = 1.075 \cdot 10^{-2}$, $B_1 = 28.8482$, $H_1 = 3.6 \cdot 10^{-6}$.

TABLE 28

Values (in cm^{-1}) of the Molecular Constants of the Electronic Ground State of D_2

Постоянная A	Вулли, Скотт и Брикведе [4329] B	Твердовский, Хачкурузов и др. [417] C	Постоянная A	Вулли, Скотт и Брикведе [4329] B	Твердовский, Хачкурузов и др. [417] C
ω_e	3118,46	3118,46	α_2	0,00027486	0,00115141
$\omega_e x_e$	64,10	64,10			
$\omega_e y_e$	1,2514	1,2514	D_e	$11,586 \cdot 10^{-3}$	$11,627 \cdot 10^{-3}$
$\omega_e z_e$	0,10612	0,10612	β_1	$0,151 \cdot 10^{-3}$	$0,26401 \cdot 10^{-3}$
$\omega_e t_e$	0,00034	0,003427	β_2	$0,0066 \cdot 10^{-3}$ [a]	$0,0079705 \cdot 10^{-3}$
B_e	30,4286	30,5422	H_e	$6,22 \cdot 10^{-6}$	$6,17945 \cdot 10^{-6}$
α_1	1,04917	1,085534	γ_1	$0,105 \cdot 10^{-6}$	$0,02465 \cdot 10^{-6}$
α_2	0,0057934	0,017121			
			L_e	$4,42 \cdot 10^{-9}$	$4,2141 \cdot 10^{-9}$

a) The corrected value of the β_2 constant is cited. A wrong value of the constant β_2^2, equal to $-0.058 \cdot 10^{-3}$ cm^{-1} is given in paper [4329].
A) Constant; B) Woolley, Scott and Bricwedde; C) Tverdovskiy, Khachkuruzov et al.

Jeppesen [2241] investigated 37 bands of the $^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ system and 29 bands of the $^1\Pi_u \rightarrow X^1\Sigma_g^+$ system of the D_2 molecule by a spectrograph having a 2.4 A/mm dispersion. The analysis of the rotational structure of the observed bands enabled him to determine the energy of

the vibrational and rotational levels of the electronic ground state of D_2, corresponding to $v'' = 0, 1, \ldots, 8$, and to calculate the vibrational and rotational constants of the electronic ground state, using for this purpose the results of the investigation of the Raman spectrum of D_2, obtained by Teal and McWood [3957]. Calculating the vibrational constants, Jeppesen [2241] used an erroneous value for ΔG_v, and thus the values of the vibrational constants of D_2 obtained by him, are incorrect.* Therefore, Woolley, Scott and Bricwedde [4329] calculated anew the vibrational constants of D_2 on the basis of the experimental data by Jeppesen [2241] and Teal and McWood [3957]. The values of the rotational constants of D_2 (B_e, α_1, α_2, α_3, D_e), calculated by Jeppesen [2241], have been accepted without alterations by the authors of paper [4329] and also by Herzberg [2020] and the Handbook [649]. In addition to these constants, Woolley, Scott and Bricwedde [4329], by the Dunham formulas [1418], calculated the constants β_1, β_2, H_e, γ_1 and L_e. The values of the molecular constants of D_2, obtained in this way in the paper [4329], are quoted in Table 28.

The vibrational constants of D_2 recommended in the paper [4329] however, sufficiently describe only the lower levels of the vibrational energy of this molecule, corresponding to the values of $v \leq 7$. The following interpolation formula

$$G_v(v) = 3071{,}8v - 66{,}769\,v^2 + 0{,}78927\,v^3 - 0{,}029535v^4 \qquad \text{(VI.1)}$$

was obtained for the calculation of the levels of the vibrational energy of D_2 at $v > 7$ in the first edition of the Handbook. The values of the levels of the vibrational energy of D_2 (at $v > 7$) calculated by this formula agree satisfactorily with the experimental data by Jeppesen [2241] and also with the value of $D_0(D_2)$ accepted in the present Handbook.

The calculation of the molecular constants of D_2, performed by

Woolley, Scott and Brickwedde [4329] have been repeated in the paper [4329]. These calculations showed that an erroneous value of the constants $\omega_e t_e$, and also inaccurate values of the rotational constants of D_2 differing from those calculated in terms of the isotopic (1.43) on the basis of the corresponding constants of H_2 accepted in the paper [4329], are given in the latter. The values of the constants B_e, α_1, α_2, and α_3, assumed in the paper [417] for the D_2 molecule, have been calculated by means of the isotopic relations (1.43) on the basis of the corresponding constants of HD.* The values of a number of rotational constants of D_2, calculated by Stoicheff [3875]** on the basis of the results of an accurate investigation of the Raman spectrum, are similar to the values of the corresponding constants of D_2 accepted in the paper [417]. This proves that the values of the rotational constants of D_2 obtained in the paper [417] are more satisfactorily for the calculation of the thermodynamic functions as those found in the paper [4329].

The values of the molecular constants of D_2 recommended in the paper [417] are quoted in Table 28. They were used in the present Handbook for determining the molecular constants of DT and T_2.

The vibrational constants recommended in the paper [4329] (see Table 28) are accepted in the present Handbook for the description of the lower levels of the vibrational energy of the D_2 molecule ($v \leq 7$), and the constants of Eq. (VI.1) are used to describe the upper levels of the vibrational energy ($v > 7$). The values calculated in paper [4329] and the corrected value of the constant β_2, quoted in Table 28, are accepted in the Handbook for the rotational constants of D_2.

HT, DT, T_2. Only band systems related to transitions between excited electronic states have been observed in the spectra of the HT, DT and T_2 molecules [1347, 1348, 1338]. Similar band systems are well

known in the spectra of the H_2, HD and D_2 molecules.

Although experimental data on the electronic ground states of the HT, DT and T_2 molecules were not obtained, it is indubitable that, as well as in the case of the H_2 HD and D_2 molecules, they must be $^1\Sigma_g^+$ states, and that the values of the molecular constants of the electronic ground state of HT, DT, and T_2 may be calculated by means of the isotopic relations on the basis of the molecular constants of H_2, HD and D_2 with approximately the same accuracy as the latter were determined on the basis of experimental data. Calculations of this type have been performed for the first time by Libby [2607, 2608] and Jones [2306, 2307] in the case of the vibrational constants of HT, DT, and T_2. The calculations of these authors, however, were based on obsolete values of the molecular constants.

In the paper by Tverdovskiy, Khachkuruzov et al.[417], it was shown that, using the isotopic relations (1.43) for the calculation of the molecular constants of HT, DT and T_2, the experimental data of the corresponding constants of the HD and D_2 molecules and not of the H_2 molecule must be applied (see page 90). The molecular constants of HD (see Table 27) were used in paper [417] for the calculation of the molecular constants of HT, and the corresponding constants of D_2 for the calculation of the molecular constants of DT and T_2 (see Table 28]. It must be noted that, besides the isotopic relations (1.43), also Eqs. (1.14a) and (1.14b) have been applied in the paper [417] for the calculation of the vibrational constants of the HT, DT and T_2 molecules; the latter equations made it possible to determine such values of the vibrational constants of the HT, DT and T_2 molecules, which satisfactorily describe the high vibrational levels near the dissociation limits of the corresponding molecules.

The values of the vibrational and rotational constants of the HT,

DT and T_2 molecules, calculated in paper [417] are accepted in the present Handbook and are quoted in Table 29.

TABLE 29

Accepted Values (in cm^{-1}) of the Molecular Constants of HT, DT and T_2 in the $X^1\Sigma_g^+$ Electronic Ground State

A Постоянная	HT	DT	T_2
ω_e	3599,43	2847,74	2548,36
$\omega_e x_e$	84,437	53,454	42,806
$\omega_e y_e$	1,2216	0,95315	0,68293
$\omega_e z_e$	0,06061	0,074045	0,047382
$\omega_e l_e$	—	0,02327	0,001297
$\omega_e s_e$	—	0,00003362	-0,00001601
B_e	40,5967	25,394	20,3358
α_1	1,67090	0,826633	0,59239
α_2	0,030427	0,011905	0,0076350
α_3	0,0023627	0,00073116	0,0004196
D_e	$20,664 \cdot 10^{-3}$	$8,0852 \cdot 10^{-3}$	$5,1851 \cdot 10^{-3}$
β_1	$0,54175 \cdot 10^{-2}$	$0,16765 \cdot 10^{-3}$	$0,096212 \cdot 10^{-3}$
β_2	$0,018884 \cdot 10^{-3}$	$0,00[illegible]19 \cdot 10^{-3}$	$0,0023736 \cdot 10^{-3}$
H_e	$14,6408 \cdot 10^{-6}$	$3,58334 \cdot 10^{-6}$	$1,8403 \cdot 10^{-6}$
γ_1	$0,06743 \cdot 10^{-6}$	$0,01305 \cdot 10^{-6}$	$0,005999 \cdot 10^{-6}$
L_e	$13,310 \cdot 10^{-9}$	$2,0378 \cdot 10^{-9}$	$0,83806 \cdot 10^{-9}$

A) Constant.

§28. THERMODYNAMIC FUNCTIONS OF GASES

The thermodynamic functions of the gaseous hydrogen and its isotopes (monatomic neutral and charged gases, and diatomic gases) calculated without allowing for the intramolecular interaction, are quoted in the Tables 7-10, 17-20 and 26-29 of the IInd volume of the Handbook. The thermodynamic functions of H, H^+, H^- and H_2 are calculated for the temperature range of from 293.15 to 20,000°K, and those of the other substances for the range from 293.15 to 6000°K.

In the introduction to the present chapter it was noted that the difference in the values of the thermodynamic functions of the corresponding compounds of protium and natural hydrogen lies beyond the limits of the accuracy of the determination of these functions. Owing to this fact, separate tables for diatomic protium and for the natural mixture of diatomic hydrogen are not given in the IInd volume of the Handbook, as well as there are no separate given tables for H_2^1O and H_2O, OH^1 and OH, but only tables for H_2, H_2O and OH. Nevertheless, a table of the thermodynamic properties of monatomic protium (Table 17), besides the table of the thermodynamic properties of monatomic natural hydrogen (Table 7) is given in the IInd volume. The thermodynamic properties of protium are used for calculating the equilibrium constants of the dissociation reactions of H^1T, H^1DO, H^1TO and H^1D.

For the purpose of taking into account the intramolecular interaction in the values of the thermodynamic functions of the diatomic hydrogen, the values of the virial coefficients of H_2 and of their derivatives with respect to temperature are given in Table 387(II).

H. The thermodynamic functions of the monatomic hydrogen, quoted in Table 7(II), are calculated by Eqs. (II.22) and (II.23) for the temperature range from 293.15 to 20,000°K. The values of the constants A_Φ and A_S, quoted in Table 30, have been assumed for the calculation of the translational components of the thermodynamic functions of H; the electronic components have been calculated on the basis of the values quoted in Table 24 by immediate summation over the energy levels on a high-speed electronic computer. The calculation has been carried out taking into account a finite number of hydrogen states corresponding to the method stated in §6.

In order to simplify the calculation, below 13,600°K, all energy levels with values of the principal quantum number $n \leq 12$ have been

taken into account. Owing to the high excitation energies of the hydrogen atom levels with $n > 6$, the error casued by alllowing for additional levels, corresponding to n = 10, 11, and 12, is negligible at $T < 13{,}600$ °K; its maximal value does not exceed 0.00002-0.00003 cal/g-atom·degree in the Φ_T^* values. At temperatures higher than 13,600°K, all energy levels with values $n \leq 13$ have been taken into account.

The inaccuracies of the values of thermodynamic functions of monatomic hydrogen calculated this way, are, at temperatures below 10,000°K caused mainly by the inaccuracy of the physical constants and do not exceed 0.002 cal/g-atom·degree in the Φ_T^* values. At higher temperatures the errors become effective, caused by the approximate method of determination of the maximum of the principal quantum number. An error of ± 1 (at n = 13) results in inaccuracies of the Φ_T^* values equal to 0.02 and 0.12 cal/g-atom·degree at 15,000 and 20,000°K, respectively.

The thermodynamic functions of monatomic hydrogen have been calculated earlier in a number of papers, from which the recently performed calculations by Huff, Gordon and Morrell [2142] (up to 6000°K), of the Bureau of Standards U.S. [3680] (up to 5000°K) and of Kolsky and coauthors [2462] (up to 8000°K) may be mentioned. The results of all these calculations are conform with each other and also with in the values quoted in Table 7(II) with an accuracy depending on the difference of the physical constants.

H^1, D, T. The thermodynamic functions of monatomic protium, deuterium and tritium, quoted in Tables 17(II), (18(II) and 26(II), are calculated for the temperature range of from 293.15-6000°K.

The values of the const ants A_Φ and A_S, assumed in the calculation of the translational components of the thermodynamic functions of these gases, are quoted in Table 3C. Only the statistical weight of the electronic ground state of the corresponding atoms has been taken

into account when calculating the electronic components of the thermodynamic functions of H^1, D and T, because the contributions of the excited electronic states of H^1, D and T to the partition functions and their derivatives with respect to the temperatures are negligible at $T \leq 6000°K$.

TABLE 30

Values of the Constants A_Φ and A_S for the Calculation of the Translational Components of the Thermodynamic Functions of H, H^1, H^+, H^-, D, T, H_2, HD, D_2, HT, DT, and T_2

A Вещество	A_Φ	A_S	A Вещество	A_Φ	A_S
	B кал/г-атом·град			C кал/моль·град	
H	—7,2598	—2,2916	H_2	—6,5711	—1,6029
H^1	—7,2602	—2,2921	HD	—3,9856	0,9823
H^+	—7,2618	—2,2937	D_2	—3,1288	1,8391
H^-	—7,2583	—2,2901	HT	—3,1320	1,8359
D	—5,1962	—0,2281	DT	—2,4667	2,5012
T	—3,9926	0,9755	T_2	—1,9253	3,0426

A) Substance; B) cal/g-atom·degree; C) cal/mole·degree.

The difference in the values of the thermodynamic functions of monatomic hydrogen (natural mixture of isotopes) and protium in the temperature range of from 293.15 to 6000°K is caused by the difference of the atomic weights of H and H^1 and amounts to 0.0004 cal/g-atom·degree for Φ^*_T.

The thermodynamic functions of the monatomic protium and deuterium have been calculated earlier by Goff, Gratch and van Voorhis [1787] for temperatures of from 55.5 to 2777.8°K. The difference between the values of S°_{1000} for H and D, calculated in paper [1787] and those quoted in Tables 17(II) and 18(II) amounts to 0.024 cal/g-atom·degree and is caused mainly by the difference in the assumed values of the physical

constants.

H^+. The thermodynamic functions of proton gas, quoted in Table 8(II) are calculated for the temperature range from 293.15 to 20,000°K. The thermodynamic functions of this gas are practically identical with the translational components of the neutral monatomic protium because the proton does not possess an electron shell.

The thermodynamic functions of proton gas are published for the first time.

H^-. The thermodynamic functions of the negative ion of the monatomic hydrogen, quoted in Table 9(II), are calculated for the temperature range from 293.15 to 20,000°K. The values of the constants A_Φ and A_S, assumed for the calculation of the translational components of the thermodynamic functions of H^-, are quoted in Table 30. The electronic components of the thermodynamic functions of H^- are equal to zero, because the H^- ion obviously does not possess discrete excited electronic states, and the ^1S state is its ground state (see page 333).

The thermodynamic functions of the negative hydrogen ion are published for the first time.

H_2. The thermodynamic functions of the diatomic hydrogen, quoted in Table 10(II), are calculated by Eqs. (II.34) and (II.35) for the temperature range of from 293.15 to 20,000°K.

The values of the constanta A_Φ and A_S assumed for the calculation of the translational components of the thermodynamic functions of H_2 are quoted in Table 30. The partition function of the vibrational- rotational states and its derivative with respect to the temperature is calculated for the electronic ground state of the H_2 molecule by means of immediate summation over the levels of the vibrational and rotational energy on a BESM electronic computer. The experimental values of the energy of vibrational levels of H_2, quoted in Table 25, are used

for these calculations. The values of the levels of the rotational energy are calculated for each vibrational state of H_2 by means of Eq. (1.18) using the values of rotational constants assumed in Table 26. The maximum values of J for each $\underline{v}$ are adopted from the paper by Woolley, Scott and Bricwedde [4329] in which an analysis of the effective potential curves of the H_2 molecule is performed, and the J versus $\underline{v}$ graph is given (Fig.7). Calculating the partition function of the vibrational-rotational states and its derivative with respect to temperature, the summation was carried out over the levels of the rotational energy of H_2 corresponding to $J = 0, 1, 2, \ldots, J_{max}$. The symmetry of the molecule is taken into account in the Φ_T^* and S_T° values by the addend R ln 2.

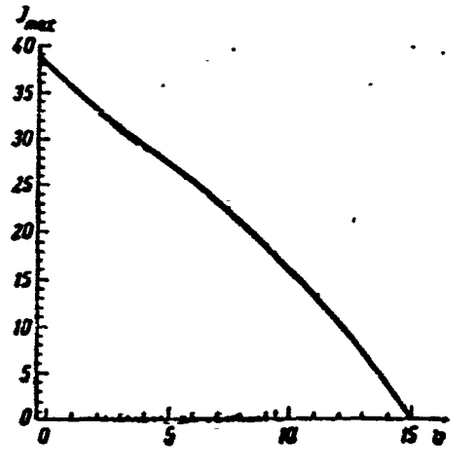


Fig.7. J_{max} as a function of v^2 for the $X^1\Sigma_g^+$ electronic state of the H_2 molecule.

Owing to the fact that the excitation energies of the excited states of the H_2 molecule are very high (they exceed 90,000 cm^{-1}), the excited electronic states are not taken into account in the calculation of the thermodynamic functions of diatomic hydrogen, quoted in Table 10(II). The contribution of these states to the Φ_T^* value however, amounts to 0.07 cal/mole·degree at 20,000°K owing to the great number of excited electronic states of H_2.

The inaccuracies of the Φ_T^* values quoted in Table 10(II) do not exceed 0.01 cal/mole·degree at $T \leq 8000$°K. They are caused mainly by the inaccuracy of the physical constants, and, at low temperatures, by the neglection of the ortho and para states of H_2. Above 8000°K, the

uncertainties of the calculated values of the functions increase and obtain 0.1-0.2 cal/mole·degree at 20,000°K. These inaccuracies are caused mainly by the neglection of the excited electronic states of the H_2 molecule in the calculations.

The tables of the thermodynamic functions of H_2 have been calculated for the first time by the method of immediate summation by Giauque [1709] (S°_T) and Davis and Johnston [1274] (Φ^*_T) up to 5000°K. Obsolete values of the physical constants have been used in the calculations undertaken by these authors. Moreover, the molecular constants of H_2, used for the calculation in the papers [1709, 1274] unsatisfactorily describe the higher vibrational and rotational levels of the ground state. Wagman et al. [4122] recalculated in 1945 the thermodynamic functions of H_2, given in the papers [1709, 1274] on the basis of the new values of the physical constants. The results of the calculations by Wagman et al. at temperatures of 3000°K are conforming satisfactorily (within 0.01 cal/mole·degree) with the values quoted in Table 10(II). At higher temperatures, the divergences increase and obtain 0.1 cal/mole·degree in the S°_{5000} values. This accounts for the fact that an accurate allowing for the energy levels near the dissociation limit plays an essential part at high temperatures. The best calculation of the thermodynamic functions of H_2 in this respect, published in literature, is that by Woolley, Scott and Brickwedde [4329] for temperatures up to 5000°K. The authors of paper [4329] calculated the thermodynamic functions of H_2 by immediate summation, taking into account a finite number of levels of the vibrational and rotational energy.* Choosing the molecular constants of H_2 for the calculation of the thermodynamic functions in paper [4329], their suitability for the approximation of the energy of levels with high values of the quantum numbers $\underline{v}$ and J was taken into account. The

values of the thermodynamic functions of H_2, quoted in Table 10(II) and in the paper [4329], do not differ more than by 0.002 cal/mole·degree within the whole temperature interval up to 6000°K (with exclusion of the S°_T values at the lowest temperatures*). The thermodynamic functions of H_2 quoted in the Handbook of the Bureau of Standards of the U.S. [3680] and in the review [2142] are almost similar to those calculated by Woolley, Scott and Bricwedde [4329].

Fickett and Cowan [1555] performed an approximate calculation of the thermodynamic functions of H_2 up to 12,000°K. The significant divergences between the thermodynamic functions of H_2 given in the paper [1555] and in Table 10(II) (up to 0.2 cal/mole·degree) are explained first of all by the approximate character of the calculations in paper [1555] (see page 320).

HD, D_2. The thermodynamic functions of the protodeuterium and diatomic deuterium, quoted in Tables 19(II) and 20(II), are calculated by Eqs. (II.34) and (II.35) for the temperature range of from 293.15 to 6000°K.

The values of the constants A_Φ and A_S assumed for the calculation, are quoted in Table 30. The partition functions of the vibrational-rotational states of the electronic ground state of HD and D_2 and their derivatives with respect to the temperature are calculated by immediate summation over the levels of the vibrational and rotational energy for T = 298.15, 400 (100), 1000, 1500, and 2000°K by Woolley, Scott and Bricwedde [4329], and for T = 293.15, 2000, 2500, 3000, 4000, 5000, and 6000°K by the authors of this Handbook. The tables 19(II) and 20(II) are compiled on the basis of the results of these calculations by means of interpolation.

Both calculations take into account a finite number of levels of the vibrational and rotational energy of HD and D_2, identical values of

the molecular constants of HD and similar values of the molecular constants of D_2 are used. The levels of the rotational energy are calculated by Eq.(I.18) and the constants are quoted in Tables 27 and 28. The levels of the vibrational energy of HD are calculated on the basis of the constants recommended by Woolley, Scott and Bricwedde [4329] (see Table 27). The levels of the vibrational energy of D_2 with $v \leq 7$ are calculated by means of the vibrational constants assumed in paper [4329] (see Table 28). The levels of the vibrational energy of D_2 with $v \geq 8$ are calculated by using the interpolation formula (VI.1). The same values of the rotational constants as in paper [4329], with exclusion of the constant β_2 (see footnote to Table 28), are used for the calculation of the levels of the rotational energy of D_2.

In spite of the difference in the assumed values of the vibrational constants of D_2, the values of the partition functions of the vibrational-rotational states and of their derivatives with respect to temperature, calculated in the present Handbook, coincide fully at $T = 2000°K$ with the values given in the paper by Woolley, Scott and Bricwedde [4329].

The excited electronic states of the HD and D_2 molecules are not taken into account in the calculation of the thermodynamic functions, because their contribution is very small at $T \leq 6000°K$.

The inaccuracies of the calculated thermodynamic functions of HD and D_2 are caused by the inaccuracy of the values of physical and molecular constants of these gases, used in the calculation. The inaccuracies of the Φ_T^* values amount to approximately 0.001; 0.01 and 0.03 cal/mole·degree at 298.15, 3000 and 6000°K, respectively..

The thermodynamic functions of HD and D_2 have been calculated earlier by Urey and Rittenberg [4041] (Φ_T^*, $T \leq 700°K$), Johnston and Long [2281] ($T \leq 3000°K$), Libby [2607] (Φ_T^*, $T \leq 773.15°k$), and Woolley,

Scott and Bricwedde [4329] ($T \leq 2000°K$). The latter paper, as was mentioned above, was used for the compilation of the Tables 19(II) and 20(II). The differences between the values of thermodynamic functions obtained in papers [4041, 2281]* and the values quoted in Tables 19(II) and 20(II) do not exceed 0.02 cal/mole·degree and may be explained by a certain difference of the values of molecular and physical constants assumed in the calculations. The divergences between the Φ_T^* values obtained by Libby [2607] and those quoted in Tables 19 and 20 of volume II of the Handbook lie between 0.03 and 0.15 cal/mole·degree and may be explained by the approximate nature of the calculations in [2607]. The thermodynamic functions of HD and D_2 calculated by Johnston and Long [2281] are cited in the Handbooks by Yusti [4370] and Zeiss [4384] The $S^\circ_{298.15}$ values of gaseous HD and D_2, based on the results of calorimetric measurements in [2364], coincide within the error limits of their determination with the values of these quantities quoted in Tables 19 and 20 of Volume II of the Handbook.

HT, DT, T_2. The thermodynamic functions of prototritium, deuterotritium and diatomic tritium, quoted in Tables 28(II), 29(II) and 27(II) are calculated by Eqs. (II.34) and (II.35) for temperatures of from 293.15 to 6000°K.

The values of the constants A_Φ and A_S, used in the calculations, are quoted in Table 30. The partition functions of the vibrational and rotational states of the electronic ground state of the HT, DT and T_2 molecules, and their derivatives with respect to temperature are calculated by immediate summation over the levels of the vibrational and rotational energy for T = 293.15; 298.15; 400; 500; 600; 800; 1000 (500); 4000; 5000, and 6000°K in the paper [417]. The values of the vibrational and rotational energy levels are calculated by Eqs.(1.6) and (1.18), using the molecular constants quoted in Table 29. The va-

lues of the thermodynamic functions of HT, DT and T_2 at the other temperatures are found by means of interpolation formulas.

The inaccuracies of the thermodynamic functions of HT, DT and T_2 quoted in the II volume of the Handbook are caused mainly oy the inaccuracy of the assumed values of molecular constants. They may be estimated as being equal to 0.005; 0.02 and 0.05 cal/mole·degree at 298.15°; 3000 and 6000°K, respectively, for the Φ_T^* value.

At an earlier date, the thermodynamic functions of HT, DT and T_2 have been calculated by Libby [2607] (Φ_T^* up to 773.15°K) and Jones [2306, 2307] (up to 2500°K, allowing for the nuclear components). The values of the thermodynamic functions of HT, DT and T_2 obtained in the papers [2607, 2306, 2307] conform with the values of the corresponding quantities in Tables 27-29 of the II volume of the Handbook within the limits of differences caused by differences in the assumed values of molecular and physical constants.

§29. THERMOCHEMICAL QUANTITIES

In the thermochemical calculations, H_2(gas)*, D_2(gas) and T_2(gas) are assumed to be the standard states of hydrogen and its isotopes.

H(gas), D(gas) and T(gas). The values of the heats of formation of the monatomic gases H, D, and T, assumed in the Handbook, are calculated on the basis of the assumed (see below) values of the dissociation energy of the corresponding diatomic gases:

$$\Delta H^\circ f_0(H, gas) = 51{,}632 \pm 0{,}010 \text{ kcal/g-atom},$$
$$\Delta H^\circ f_0(D, gas) = 52{,}537 \pm 0{,}012 \text{ kcal/g-atom},$$
$$\Delta H^\circ f_0(T, gas) = 52{,}938 \pm 0{,}012 \text{ kcal/g-atom}.$$

H^+(gas). The value of the ionization potential of the hydrogen atom equal to 109,678.788 cm^{-1} or

$$I(H) = 313{,}600 \text{ kcal/g-atom},$$

recommended by Moore [2941], is assumed in the Handbook. This value is

calculated with a very high accuracy on the basis of the analysis of the spectrum of monatomic hydrogen; its inaccuracy amounts to about 1 cal/g-atom. The expression

$$\Delta H^\circ f_0(H^+, \text{gas}) = 365{,}232 \pm 0{,}010 \text{ kcal/g-atom.}$$

corresponds to the assumed value of the ionization potential.

H^-(gas). The value of the electron affinity of the hydrogen atom was determined by a number of investigators on the basis of quantum-mechanical calculations. The analysis of the results published up to 1958, enabled Buchel'nikova [116] to recommend the value A(H) = -0.747 ev, obtained by Henrich [1992a]. This value of A(H) is also cited in a number of reference books. It corresponds well with the value of A(H) = 0.8 ± 0.1 ev, obtained by Khvostenko and Dukel'skiy [449a] by the method of surface ionization, measuring the dependence of the ion current of H^- on the temperature of a tungsten filament.

In the present Handbook, the value of -0.747 ± 0.005 ev, or

$$A(H) = -17{,}2 \pm 0{,}1 \text{ kcal/g-atom.}$$

is assumed for the electron affinity of hydrogen. The value of the heat of formation of H^- ions is, corresponding to this, equal to

$$\Delta H^\circ f_0(H^-, \text{gas}) = 34{,}432 \pm 0{,}1 \text{ kcal/g-atom.}$$

H_2(gas). The dissociation energy of the H_2 molecule was determined by a number of investigators on the basis of a study of chemical equilibria in gases [2055, 851], measurement of the explosion pressure of a $H_2 + Cl_2$ mixture [4305], measurement of the heat of recombination of H atoms [812], investigation of the H_2 spectrum [4300, 1340, 1342, 825 3436, 3435, 802, 803, 1339] and as the results of quantum-mechanical calculations [2207, 2208]. These investigations have been analyzed by Beutler [802, 803].*

The most accurate value of $D_0(H_2)$ was obtained by Beutler [803] on the basis of the edge of continuous absorption in the H_2 spectrum cor-

responding to the photochemical decomposition into the $H(1s^2S_{1/2})$ + + $H(2s^2S_{1/2})$ atoms. A thorough analysis of the absorption spectra of para hydrogen and of the normal mixture of ortho with para hydrogen in the region of from 950 to 750 A enabled Beutler to determine the edge of continuous absorption in the H_2 spectrum corresponding to the transition from the lowest energy state v" = 0, K" = 0, equal to 118,376 cm^{-1}. Subtracting the excitation energy of the state of the H atom from this value, Beutler obtained $D_0(H_2) = 36,116 \pm 6$ cm^{-1}, to which correspond

$$D_0(H_2) = 103,264 \pm 0,020 \text{ kcal/mole}$$

The cited value of $D_0(H_2)$ is assumed in the present Handbook. It is veryfied by the results of a thorough investigation of the system of electronic bands of H_2 carried out by Herzberg and Howe [2032].*

TABLE 31

Assumed Values (in cal/mole) of the Thermochemical Quantities of Gaseous Hydrogen and Its Isotopes

1 Вещество	D_0	$\Delta H^\circ_f{}_0$	$\Delta H^\circ_f{}_{293,15}$	$\Delta H^\circ_f{}_{298,15}$	$H^\circ_{293,15}-H^\circ_0$	$H^\circ_{298,15}-H^\circ_0$
H	—	51 632	52 096	52 104	1456	1481
D	—	52 537	52 987	52 990	1456	1481
T	—	52 938	53 383	53 390	1456	1481
H^+	313 600[a]	365 232	367 152	367 185	1456	1481
H^-	17 200[b]	34 432	33 440	33 423	1456	1481
H_2	103 264	0	0	0	1984	2019
HD	104 090	79	80	75	1999	2034
D_2	105 074	0	0	0	2013	2057
HT	104 395	175	176	175	2004	2038
DT	105 454	21	21	17	2018	2053
T_2	105 876	0	0	0	2023	2058

a) The value of the ionization potential of the H atom is given.
b) The value of the energy of electron detachment from the H^- ion is given.
1) Substance.

HD(gas) D_2(gas), HT(gas), DT(gas), T_2(gas). The values of the dissociation energies of the HD, D_2, HT, DT and T_2 molecules, accepted in the Handbook, are calculated by Eq.(IV.17) using the assumed values of $D_0(H_2)$ and the molecular constants of these molecules (see§27):

$$D_0(HD) = 104{,}090 \pm 0{,}023 \text{ kcal/mole*}$$
$$D_0(D_2) = 105{,}074 \pm 0{,}023 \text{ kcal/mole*},$$
$$D_0(HT) = 104{,}395 \pm 0{,}023 \text{ kcal/mole},$$
$$D_0(DT) = 105{,}454 \pm 0{,}023 \text{ kcal/mole},$$
$$D_0(T_2) = 105{,}876 \pm 0{,}023 \text{ kcal/mole}.$$

The following values of heats of formation of HD, DT and T_2 correspond to the cited values of the dissociation energies:

$$\Delta H°f_0(HD, \text{ газ}) = 0{,}079 \pm 0{,}030 \text{ kcal/mole},$$
$$\Delta H°f_0(HT, \text{ газ}) = 0{,}175 \pm 0{,}030 \text{ kcal/mole},$$
$$\Delta H°f_0(DT, \text{ газ}) = 0{,}021 \pm 0{,}030 \text{ kcal/mole}.$$

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[Footnotes]

331 Compounds of hydrogen isotopes are also dealt with in Chapter 7 (oxygen compounds) and in Chapter 12 (compounds with halogens).

334 In recent years, a number of pages was published dealing with the investigation of the vibrational-rotational spectrum of H_2 arising in electric fields, under pressure, etc., (see, for example [3957a, 2379]). These papers, however, are not interesting from the point of view of the calculation of the molecular constants of H_2.

336 It must be noted that Herzberg and Howe [2032 recommend in their paper values of the vibrational constants of H_2 calculated by Stoicheff [3875] (see Table 25), because the authors of paper [2032] assume that the value $\omega_e = 4403.39$ cm^{-1}, found by Stoicheff, comes nearer the true value.

340 The recalculation of the constants was caused by the fact that Jeppesen applied in paper [2240] the evolution of $F_v(J)$ with respect to $(J + 1)^2$ and not $J(J + 1)$.

343 Jeppesen assumed in the paper [2241] $\Delta G_v = \omega_e - 2\omega_e x_e$

$(v + 1/2) + 3\omega_e y_e (v + 1/2)^2$, the correct expression for ΔG_v, however, is

$$\Delta G_v = A_\omega - A_x(v+1) + A_y(v+1)^2 - A_z(v+1)^3 + \ldots,$$

where

$$A_\omega = \omega_e + \frac{1}{4}\omega_e y_e + \frac{1}{16}\omega_e l_e + \ldots, \quad A_x = 2\omega_e x_e + \omega_e z_e + \ldots, \quad A_y = 3\omega_e y_e + 2{,}5\omega_e l_e + \ldots$$
$$A_z = 4\omega_e z_e + \ldots$$

344* It was shown in paper [417] that, using the isotopic relations (1.43) for the calculation of the molecular constants of one isotopic variety of the diatomic hydrogen by means of the corresponding constants of another isotopic variety, the calculation results are the more accurate, the lower the difference between the masses of the isotopic H_2 varieties in question (see page 90).

344** $^1\ \alpha_e \cong B_0 - B_1 = 1{,}0623\ cm^{-1};\ \beta_e \cong D_0 - D_1 = 0{,}00059\ cm^{-1};$

$B_e = 30{,}442\ cm^{-1};\ D_e = 0{,}01164\ cm^{-1}$

352 In the calculations carried out by immediate summation for $T > 2000°K$ in paper [4329], the levels lying higher than 25,000 cm^{-1} were unified for each 2000 cm^{-1} to one level with a mean energy and a summarized statistical weight.

353 This is explainable, obviously, by the englect of the difference between the ortho and para states of the H_2 molecule.

355 If the nuclear spin components, taken into account in these papers, are excluded from the thermodynamic functions of HD and D_2.

356 The difference between the thermochemical quantities of the isotopic hydrogen mixture and of the pure protium is very small and it is not taken into account in this section.

357 The quantity $D_0(H_2)$ was also determined on the basis of an investigation of the dissociating ionization of the H_2 molecules under the effect of electron impacts [3984]. The obtained value (4.4 ± 0.3 ev) conforms with those found by other methods, but has a lower accuracy.

358 After the preparation of the Handbook has been finished, the results of accurate determinations of the dissociation energy of the H_2, HD and D_2 molecules, obtained by Herzberg and Monfils [2036a], were published. The edge of the continuous absorption in the H_2 spectrum at 850 Å, found by Beutler [803], was investigated anew for H_2, HD and D_2 by Herzberg

and Monfils in the sixth order of a vacuum spectrograph, which enabled them to measure the positions of the individual lines with an accuracy of up to 0.002 A. It was found in the paper [2036a] that the upper state of H_2 corresponding to this continuum, is stable and does not possess a maximum on the curve of the potential energy. The dissociation limit of the H_2 molecule in this state is, according to [2036a], equal to 118,372.1 $\pm$ 0.2 cm^{-1} and corresponds to the $H(1s^2S) + H(2s^2P)$ state. Hence $D_0(H_2)$ = 36,113.0 $\pm$ 0.3 cm^{-1} was obtained, which corresponds to $D_0(H_2)$ = 103.2565 $\pm$ $\pm$ 0.0009 kcal/mole. This value of $D_0(H_2)$ is based on the assumption that the upper state of the continuum investigated in paper [2036a] is a $C^1\Pi_u$ state of the H_2 molecule. Herzberg and Monfils, however, do not exclude the possibility, that this is a $B'^1\Sigma_u^+$ state. In this case, the value of $D_0(H_2)$ must be increased by 0.6 cm^{-1} (resulting in $D_0(H_2)$ = 103.2582 $\pm$ 0.0009 kcal/mole).

359 After the preparation of the Handbook has been finished, Herzberg and Monfils [2036a] found values for $D_0(HD)$ and $D_0(D_2)$ based on the investigation of the edge of the continuous absorption of HD and D_2 at 850 A, equal to $D_0(HD)$ = 36,399.9 $\pm$ 1 cm^{-1} and $D_0(D_2)$ = 36743.6 $\pm$ 0.5 cm^{-1} or $D_0(HD)$ = 104.077 $\pm$ 0.003 kcal/mole, and $D_0(D_2)$ = 105.059 $\pm$ $\pm$ 0.002 kcal/mole (see also the second footnote to page 358).

[Transliterated Symbols]

350 БЭСМ = BESM = bystrodeystvuyushchaya elektronnaya schetnaya mashina = high-speed electronic computer.

Chapter 7

COMPOUNDS OF HYDROGEN AND ITS ISOTOPES WITH OXYGEN

(H_2O, HDO, D_2O, HTO, DTO, T_2O, H_2O_2, HDO_2, D_2O_2, HO_2, OH, OD, OT, OH^+, OH^-)

In the present chapter, the oxygen compounds of hydrogen are dealt with: water, hydrogen peroxide and their dissociation products: the OH and HO_2 radicals and the OH^+ and OH^- ions in gaseous state. The isotopic modifications of water (HDO, D_2O, HTO, DTO, T_2O) and of hydrogen peroxide (HDO_2, D_2O_2), and their main dissociation products, the OD and OT radicals, are also dealt with.

The existence of several very unstable and insufficiently investigated oxygen compounds of hydrogen, such as the higher hydrogen peroxide H_2O_4 [339, 308, 307, 233, 344, 203, 3453, 452] and the ozone-like compounds HO_4 [4227, 3454, 3792] and H_2O_3 [2478], which are not dealt with in the Handbook is known.* Likewise the ions $(H_2O)^+$ and $(H_2O)^{++}$ of the water molecule, and the oxonium ion $(H_3O)^+$, all of which are known to exist on the basis of data derived from spectroscopic and mass-spectroscopic investigations (see [3403, 2255, 1622]), are not dealt with.

The organization of the material in this chapter differs somewhat from the order used in the other chapters: first, the saturated oxygen compounds of hydrogen (H_2O, H_2O_2) and their isotopic modifications are dealt with, and then follow the dissociation products of these compounds, i.e., the radicals HO_2, OH, OD, OT, and the ions OH^+ and OH^-.

§30. MOLECULAR CONSTANTS

H_2O. The spectrum of the water molecule is thoroughly investiga-

ted from the microwave up the center of the visible region (4-17,500 cm^{-1}) and in the ultraviolet region from 2000 A up to the ionization limit at 980 A. The pure rotational spectrum and the bands corresponding to vibrational-rotational transitions in the electronic ground state lie in the 4-17,500 cm^{-1} region. A system of bands corresponding to transitions from electronic states close to the ionization limit into the electronic ground state lies in the ultraviolet range (from 2000 to 980 A). The intermediate spectral range, from 5700 to 2000 A, is not investigated. This spectral range corresponds to transitions into higher vibrational levels of the electronic ground state.

The results of the investigations of the vibrational-rotational and rotational spectrum of H_2O, carried out up to 1944, are discussed in the monograph by Herzberg [152]. In the following years, however, more accurate and complete data was obtained in the near infrared region owing to the development of the technique of infrared spectroscopy, a fact which caused a revision of the values of the vibrational and rotational constants of the water molecule. The values of these quantities, obtained by allowing for the new spectral data, are quoted in the papers by Friedmann and Haar [1615], and Benedict, Gailar und Plyler [727]. There are systematic divergences, however, between the experimentally found values of the vibrational energy levels of the H_2O molecule and the values calculated on the basis of the constants found in the papers [1615, 727]. These divergences are caused by the fact that the vibrational level energies of H_2O are approximated in [1615, 727] by a square-law expression with respect to the vibrational quantum numbers. It was shown, however, in the paper [438] that even the lower levels of the vibrational energy of the water molecule cannot be described sufficiently without taking into account the cubic terms.* Owing to this fact, Khachkuruzov [438, 437] recalculated anew

all the vibrational constants of H_2O, which enter into the total cubic expression for the vibrational energy levels on the basis of an analysis of the most comprehensive and accurate results of the investigation of the vibrational-rotational spectrum of H_2O, consecutively taking into account the Darling-Dennison resonance between the ($v_1 \geq 2$, v_2, v_3) and ($v_1 - 2$, v_2, $v_2 + 2$) states.

The analysis of the rotational structure of the H_2O bands, obtained by devices with a high dispersion, was carried out the first time by Mecke and co-workers [2831, 690, 1605]. These authors analyzed 5 bands,* lying in the near infrared region, using the results of the insufficiently accurate measurements by Plyler and Sleator [3284, 3267] (who used low-sensitive heat-bolometers for the recording of the spectrum) and 12 bands, ** lying in the "photographic" infrared region (8750-17,500 cm^{-1}), using the very accurate measurements of the spectrum of atomospheric absorption of sunlight, obtained by Rowland et al. [2256a], and the results of the measurements of the lines of the $v_1 + v_3$ band, obtained by Lueg and Hedfeld [2671]. The experimental data obtained in the papers [2256a, 2671] and the results of their analysis [690, 1605] have retained their importance up to the present. Later on, they were verified and somewhat supplemented by the investigations of Yeropkin, Kondrat'yev and Yel'yashevich [188, 184].

In the following years, the rotational structure of the bands in the vibrational-rotational spectrum of H_2O was investigated by Nielsen [3083, 3082], Mohler and Benedict [2934], Nelson and Benedict [3039], Benedict and Plyler [730, 722, 731], Benedict, Classen and Show [724], Dalby and Nielsen [1255], and Benedict [721]. The results of the analysis of the structure of 34 bands of H_2O observed in absorption spectra,*** and of the structure of 22 H_2O bands obtained in emission

spectra have been published. Table 32, which quotes the most accurate values of the vibrational level energy of the H_2O molecule in the electronic ground state, is compiled on the basis of an analysis of these data, carried out in paper [438].

The values of the vibrational constants of the H_2O molecules, calculated in the papers [438, 437] for unperturbated levels of the vibrational energy, and also the values of the constant W of the Darling-Dennison resonance, accepted in the present Handbook, are quoted in Table 33. The experimental values of the energy of 25 vibrational levels of H_2O (see Table 32) are used in these calculations.

It was shown in the papers [438, 437] that the levels of the vibrational energy of H_2O which correspond to v_1, v_2, $v_3 \leq 5$, are determined by the vibrational constants, quoted in Table 33, with the same accuracy as the experimental values of these quantities, quoted in Table 32.

When determining the vibrational constants of H_2O on the basis of experimental data, some authors (see [500, 508]) suggested that, in the case of H_2O, the constant W of the Darling-Dennison resonance depends on the vibrational quantum numbers in the same manner as the constant of the Fermi resonance in the case of CO_2 (see page 891). It was also suggested in the papers [4326, 727] that besides the Darling-Dennison resonance a Fermi resonance also takes place between the vibrational states of H_2O. Khachkuruzov [438, 437] showed that both these suggestions do not correspond to the facts because they are superfluous when the complete cubic expression for $G_0(v_1, v_2, v_3)$ is used.

The analysis of the rotational structure of a great number of bands, obtained by devices with high resolving power, made it possible to determine the experimental values of the energy of the rotational

levels of H_2O for the vibrational ground state as well as for many of the excited vibrational states.

TABLE 32

Experimental Values (in cm^{-1}) of the Energy of Vibrational Levels of the H_2O Molecule in Ground Electronic State

v_1, v_2, v_3	$G_0(v_1, v_2, v_3)$	v_1, v_2, v_3	$G_0(v_1, v_2, v_3)$
000	0	121	10328,85 [438, 731, 721]
010	1594,78[a] [1255]	022	10523 [438, 731]
020	3151,53[a] [724]	300	10599,7[a] [438, 731]
100	3656,65[a] [727, 730]	201	10613,12[a] [690]
001	3755,79[a] [730]	102	10868,8[a] [438, 731, 721]
030	4666,65[a] [438, 2934, 731]	003	11032,3[a] [690]
110	5235,0[a] [3039]	051	11248,4 [438, 731]
011	5331,19[a] [722]	131	11813,44 [721]
040	6136,4 [438, 731]	032	12012 [438, 731]
120	6775,0[a] [2934]	211	12151,22[a] [690]
021	6871,65[a] [722]	112	12407,65 [721]
200	7201,4[a] [3039]	013	12565,01[a] [690]
101	7249,8[a] [3039]	221	13652,65 [721]
002	7445,0[a] [3039]	301	13830,92[a] [1605]
130	8273,98[a] [721]	103	14318,77[a] [1605]
031	8373,6[a] [438, 731]	311	15347,91[a] [1605]
210	8761,5 [721]	113	15832,47[a] [1605]
111	8807,05[a] [2831]	321	16821,61 [1605]
012	9000,10 [722]	401	16899,01 [1605]
041	9833,5 [438, 731]	203	17495,48 [1605]

a) Used for calculating the vibrational constants of H_2O, quoted in Table 33.

The levels of the rotational energy of the vibrational ground state of H_2O* were determined the first time by Mecke and coworkers [2831, 690, 1605] on the basis of an analysis of the rotational structure of bands in the vibrational-rotational spectrum of H_2O. Later on, Randall and coworkers [4335, 3366] investigated by high resolving power the purely rotational spectrum of water vapor in the region from 17.8 to 555 cm^{-1}, which allowed the authors of the papers [3366, 1754]

to determine 230 levels of rotational energy of H_2O from J = 0 to $J_\tau = 14_{14}$. In 1952 Benedict, Claasen and Show investigated by means of a high-dispersion spectrometer the rotational structure of the ν_2 band laying in the 770-2222 cm^{-1} region, and determined very accurately the position of 255 levels of rotational energy of H_2O up to $J_\tau = 18_{-11}$. Taylor, Benedict and Strong [3951], using a multipass high-temperature cell, obtained a purely rotational spectrum of water vapor heated to 500°C in the region from 67 to 400 cm^{-1}, and determined on the basis of these data the position of 83 rotational levels from $J_\tau = 18_8$ to $J_\tau = 20_{-9}$, a part of which was more accurately determined in the paper [724].* Subsequent investigations of the purely rotational level of water vapor in the infrared region [2696, 1679, 484] corroborated the values of the energy of rotational levels of H_2O in the vibrational ground state, obtained by Benedict, Claassen and Show [724].

In the microwave range, the frequencies of only two lines of the purely rotational spectrum of water vapor, corresponding to the $5_{-1} - 6_{-5}$ [712, 4008, 1792] and $2_2 - 3_{-2}$ [2405] transitions,** were successfully recorded and measured with great accuracy.

Information is also published in literature dealing with the energy of the rotational levels of 20 excited vibrational states of the H_2O*** molecule, for which the effective values of the rotational constants have been determined in the corresponding papers. Besides, the analysis of the rotational structure of a series of weak bands of H_2O was carried out, and the values of the rotational constants of the vibrational states (030), (110), (120), (200), (130), (031), (210), (041), (121), (102), (131), (112), and (221) were determined in the papers [2934, 3039, 721] In these papers, however, the values of the energy of rotational levels of H_2O in the cited vibrational state are

not quoted.

TABLE 33

Accepted Values (in cm^{-1}) of the Molecular Constants of H_2O in the Electronic Ground State ($\sigma = 2$)

Constant	Value	Constant	Value
ω_1	3835,37	A_{000}	27,87
ω_2	1647,59	α_1^A	−0,89
ω_3	3938,74	α_2^A	+2,68
x_{11}	−45,18	α_3^A	−1,26
x_{22}	−17,04	α_{11}^A	+0,16
x_{33}	−44,62	α_{22}^A	+0,44
x_{13}	−15,14	α_{33}^A	+0,03
x_{23}	−19,99	α_{12}^A	−0,08
x_{12}	−165,48	α_{23}^A	−0,29
y_{111}	+0,47	α_{13}^A	−0,04
y_{222}	−0,60	α_{222}^A	+0,04
y_{333}	−0,45	B_{000}	14,52
y_{112}	−0,10	α_1^B	−0,20
y_{122}	−0,10	α_2^B	+0,16
y_{223}	+1,55	α_3^B	−0,11
y_{233}	−0,81	C_{000}	9,28
y_{113}	+0,68	α_1^C	−0,18
y_{123}	−1,72	α_2^C	−0,14
y_{133}	+1,17	α_3^C	−0,12
W	76,02		

In the papers of Mecke and coworkers [2831, 690, 1605], the effective values of the rotational constants of H_2O were determined for 20 vibrational states on the basis of the quantum-mechanical theory of the rigid asymmetric top. Later on, Darling and Dennison [1263] calculated the values of the effective moments of inertia, allowing for the correction for centrifugal stress, on the basis of the experimental data of Mecke and his coworkers. The results of the calculations by Darling and Dennison [1263], supplemented by the corresponding results of Nielsen [3082, 3083] for other vibrational states, were used by Herzberg [152] in the calculation of the constants of the vibrational-rotational interaction, the equilibrium values of the rotational

constants, and the structural parameters of the water molecule.

After the monograph by Herzberg [152] was published, many of the H_2O bands were obtained with high resolving power, making it possible to analyze their rotational structure. The microwave spectra of H_2O, HDO and D_2O have also been studied. On the basis of an analysis of all these data, and taking into account all the results obtained earlier, Benedict, Gailar and Plyler [727] determined anew the values of the rotational constants of H_2O in the vibrational ground state, the values of the constants of the vibrational-rotational interaction and also the equilibrium values of the moments of inertia and of the structural parameters. In the paper [727], however, the effective values of the rotational constants of H_2O, used to find the constants of the vibrational-rotational interaction, are not given, and the complete set of the latter is also not quoted. The following values (in cm^{-1}) of the rotational constants of the vibrational ground state of H_2O are given in the paper [727]: $A_{000} = 27.8778 \pm 0.005$; $B_{000} = 14.5092 \pm \pm 0.003$, and $C_{000} = 9.2869 \pm 0.003$.* On the basis of the cited values of the rotational constants for the vibrational ground state, the values of the constants of the vibrational-rotational interaction, and corrections for gyromagnetic effects of the electron motion, Benedict, Gailar and Plyler calculated the equilibrium values of the principal moment of inertia and equilibrium values of the structural parameters of H_2O: $r_e(O - H) = 0.95718$ A; $\angle H - O - H = 104°31'23''$, the uncertainty being determined as ± 0.0003 A and $\pm 3'$, respectively.

Khachkuruzov [444] calculated anew the effective values of the rotational constants of H_2O for these vibrational states for which the experimental values of the levels of rotational energy are known,** allowing for a more strict and accurate correction with regard to the centrifugal stress as it was made earlier. On the basis of the results

of these calculations, and also taking into account all values of effective rotational constants of H_2O, the values of the vibrational-rotational constants have been calculated in paper [444], and are quoted in Table 33 and accepted in the present Handbook. These values together with the values of the rotational constants for the vibrational ground state, quoted in Table 33, determine the effective values of the rotational constants of H_2O for 34 vibrational states within the error limits of their experimental determination.

The electron spectrum of H_2O in the region from 2000 A to the ionization limit at 980 A* was investigated by Leifson [2587], Rathenau [3403], Price [3321], Wilkinson and Johnston [4278], Hopfield [2120], Watanabe and Zelikoff [4179]. These investigators determined that two groups of bands are observable in the H_2O lectron spectrum: the first lying in the region from 1770 to 1540 A [3403, 2587, 4278, 2120], and the second in the region from 1370 to 980 A [3403, 3321, 2120]. The spectral region occupied by the first group of bands was investigated in devices with mean and small dispersion, and thus it was impossible to analyze the structure of this group of bands. The second group of bands was analyzed thoroughly by Price [3321] in a device with a 2.3 A/mm dispersion. Price found that these bands form a series similar to the series in atomic spectra, and he suggested a formula similar to the formulas for the Rydberg series for atomic spectra. Corresponding to this formula, the edge of the H_2O bands in the 1370-980 A region is equal to 101,780 cm^{-1} or 12.62 ev, which concurs with the values of the ionization potential of H_2O, determined by the method of electron impact [3791, 1622], and by measuring the efficiency of the photoionization of water vapor [4128]. The comparison of the H_2O terms in the Rydberg series formula with the terms of oxygen allowed Price to prove that the bands in the electron spectrum

of H_2O investigated by him are caused by transitions from a series of excited electronic states corresponding to the excitation of the electron which does not take part in the formation of the O-H bond and which is localized on the oxygen atom. The existence of such electronic states of the water molecule was predicted earlier by Mulliken [2988] who showed that these must be triplet-singlet $^{3.1}A_1$ states corresponding to the electron configurations $(2\,sa_1)^2[p_yb_2]^2\,[p_xa_1]^2\,(2p_zb_1)(nsa_1)$* where n = 3, 4, 5, ... Price [3321] observed bands corresponding to the mentioned excited electronic states of H_2O with n = 4, 5, 6, 7, 8 and 9. The band corresponding to n = 3 lies obviously within the bands of the first group which was not investigated by Price.

It must be assumed that aside from the electron which does not take part in the formation of bonds, the H_2O molecule possesses yet a series of electronic states caused by the excitation of electrons which take part in the formation of the O-H bonds. Apparently, the minimum excitation energies of these states must be lower than the minimum excitation energies of the electronic states investigated by Mulliken [2988, 2985] and Price [3321]. Indeed, if the excitation energy of the $(2p_zb_1)(3sa_1)\ ^{3.1}A_1$ state may be estimated as equal to about 60,000-70,000 cm^{-1}, the minimum energy of the electronic state, caused by the excitation of the bonding electron, must in its order of magnitude be equal to the energy of the first excited state of the OH radical, i.e., it must be equal to about 30,000 cm^{-1}.

The energy of the levels of electronic states of H_2O caused by the excitation of the valence electrons, both participating in the O-H bonds and not taking part in the formation of these bonds, was calculated by Niira [3095] on the basis of the method of atom orbits. These calculations were carried out in order to explain the anomalous rotation of the OH radicals formed by dissociation of H_2O molecules in

the electric discharge under the effect of electron impacts. The results of the calculations by Niira allowed a quantitative interpretation of this phenomenon as well as a prediction of its particularities which were not observed earlier. It must be noted that according to Niira's calculations, the energy of the first excited electronic state of H_2O was found to be of the same order as that of the OH radical.* For the excited electronic states of the type $(2sa_1)^2[p_yb_2]^2[p_xa_1]^2(2p_zb_1)(nsa_1)^{3,1}A_1$, Niira obtained excitation energies similar to the experimental values found by Price [3321]. Thus, the data on the excited electronic states of the water molecule, found in the paper [3095] on the basis of approximate theoretical calculations, are in accordance with the results of the experimental investigations. Thus, these data, together with the experimental data by Price [3321] on the excited electronic states of H_2O, are accepted in the present Handbook and quoted in Table 34.

TABLE 34

Levels of the Electron Energy of the H_2O Molecule

Электронные состояния A	Статистический вес B	Энергия, C $см^{-1}$	Электронные состояния A	Статистический вес B	Энергия, C $см^{-1}$
$^1A_1$	1	0	$^3B_2$	3	81 220 [3095]
$^3B_2$	3	30 650 [3095]	$^3A_2$; $^3B_1$	6	87 600 [3095]
$^3A_2$; $^3B_1$	6	33 800 [3095]	$^3A_1$; $^1A_1$	4	89 170 [3321]
$^3A_1$	3	38 560 [3095]	$^1B_1$; $^1A_2$	2	91 870 [3095]
$^1A_2$; $^1B_1$	2	48 960 [3095]	$^3A_1$; $^1A_1$	4	94 780 [3321]
$^3A_1$; $^3B_1$; $^3A_2$	15	58 080 [3095]	$^3A_1$; $^1A_1$	4	97 320 [3321]
$^3A_1$; $^1B_1$	4	62 830 [3095]	$^3A_1$; $^1A_1$	4	98 690 [3321]
$^1A_1$; $^3B_2$	4	72 590 [3095]	$^3A_1$; $^1A_1$	4	99 500 [3321]
$^3B_1$; $^3A_2$	6	77 590 [3095]	$^3A_1$; $^1A_1$	4	100 040 [3321]

A) Electronic states; B) statistical weight.

The uncertainty of the values of excitation energies of the ex-

cited electronic states of H_2O, quoted in Table 34 and calculated by Niira [3095], may be estimated by ± 500 cm^{-1}, and the uncertainty of the experimental values, found by Price [3321] may be ± 10 cm^{-1}.

HDO. The HDO molecule belongs to the symmetry class C_1. A great number of papers has been published dealing with the investigation of the vibrational-rotational spectrum of HDO in the infrared region (from 7 to 1 micron or from 1400 to 10,000 cm^{-1}) and the purely rotational spectrum in the microwave region. The investigation of the Raman spectrum of HDO vapor is also known [3376].

The earlier investigations of the vibrational-rotational spectrum of HDO [3376, 667, 668, 2050, 2052, 639], carried out mainly by devices with a low dispersion,* are discussed by Herzberg [152].

Later on, Benedict, Gailar and Plyler [726, 727] investigated the vibrational-rotational spectrum of HDO in the region from 1.5 to 4.2 microns (2400-6800 cm^{-1}) by devices with a high dispersion. In the paper [727], the results of a thorough investigation of the rotational structure of 9 bands of HDO are given, and the levels of the rotational energy of the HDO molecule are determined in the vibrational states (000), (100), (020), (001), (030), (011), (200), (101), (021) for J_τ from 0_0 to 15_{-15}. In the paper [726], the wave numbers of the zero lines of the corresponding bands, and the effective values of the rotational constants of HDO in the mentioned states are given. Moreover, in this paper the wave numbers of the zero lines of the ν_2 and $\nu_2 + 2\nu_3$ bands are quoted, obtained by the authors using both earlier investigations of the infrared HDO spectrum [639, 2052], and also the effective values of the rotational constants of HDO in the (012) state.

The vibrational constants of the HDO molecule have been determined earlier in the papers [2607, 1615, 727]. An analysis of these calculations was carried out by Khachkuruzov [440], who calculated anew

the vibrational constants of HDO.

Just as in the case of H_2O, the complete cubic expression for $G(v_1, v_2, v_3)$ must be used for the description of the vibrational energy levels of the HDO molecule. The results of investigations of the vibrational-rotational spectrum of HDO, however, are insufficient for determining the vibrational constants which enter into the cubic equation for the levels of the vibrational energy.* In the paper by Kachkuruzov [440], the values of the vibrational constants of HDO, entering into the quadratic equation for the vibrational energy levels, are determined anew on the basis of the experimental data on the energy of the vibrational states of HDO and the frequencies of the normal oscillations of these molecules, calculated by him in the paper [438].** The values of the vibrational constants of HDO, found in the paper [440], are adopted in the present Handbook and quoted in Table 35. These constants determine the unperturbed levels of the vibrational energy of the HDO molecule. The constant W_Φ of the Fermi resonance between the vibrational states of HDO of the form (v_1, v_2, v_3) and $(v_1 - 1, v_2 + 2, v_3)$ is equal to 14.5 ± 1.5 cm^{-1}, according to the calculations in [440].

The values of the rotational constants, the constants of the vibrational-rotational interaction and the centrifugal stress, and also the structural parameters of the HDO molecule are calculated by Benedict, Gailar and Plyler [727] on the basis of an analysis of the rotational structure of the HDO bands and the results of investigations of microwave spectra of this compound (see below). The values of the rotqtional constants of HDO for the vibrational ground state, and the values of the constants of vibrational-rotational interaction, found in the paper [727], are accepted in the present Handbook and quoted in Table 35. The uncertainty of the A_{000} value in the paper [727] is es-

timated to be ± 0.01 cm^{-1}, and the uncertainties of B_{000} and C_{000} to be ± 0.003 cm^{-1}. The uncertainties of the accepted values of the constants of vibrational-rotational interaction of the same order of magnitude.

TABLE 35

Accepted Values (in cm^{-1}) of the Molecular Constants of HDO in the Electronic Ground State ($v = 1$)

A Постоянная	B Значение	A Постоянная	B Значение	A Постоянная	B Значение
ω_1	2823,19	x_{33}	−20,06	α_1^B	0,199
ω_2	1444,53	x_{13}	−12,91	α_2^B	−0,147
ω_3	3888,63	A_{000}	23,3786	α_3^B	0,0125
x_{11}	−41,51	α_1^A	0,253	C_{000}	6,4173
x_{22}	−11,90	α_2^A	−1,798	α_1^C	0,1098
x_{33}	−82,34	α_3^A	1,087	α_2^C	0,0710
x_{12}	−16,98	B_{000}	9,1020	α_3^C	0,0681

A) Constant; B) value.

Benedict, Gailar and Plyler [727] have shown that the equilibrium values of the structural parameters of the HDO molecule concur within the error limits with the values corresponding parameters of the H_2O molecule.

A considerable part of the pure rotational spectrum of HDO lies in the microwave region. A number of lines of the purely rotational spectrum of HDO was observed by Fuson, Randall and Dennison [1636] in the infrared region. The frequencies of 18 rotational transitions in the vibrational ground state of the HDO molecule are calculated with great accuracy on the basis of microwave spectra in the papers [4008, 3883, 3881, 2684, 699, 4196, 2222, 716, 1822, 3311, 1494].* Posener and Strandberg [3311] attempted to use the results of these measurements for the determination of the values of rotational constants and constants of centrifugal stress of the HDO molecule. The authors of

the paper [3311] based their calculations on the formulas of second approximation of the quantum-mechanical theory of perturbation for the rotational energy levels of polyatomic molecules. However, more accurate theoretical bases for the numerical calculations than those assumed by Ponsener and Strandberg [3311] are required for the determination of the rotational constants and the constants of the centrifugal stress of the HDO molecule on the basis of the frequencies of rotational transitions in the microwave spectrum.

The electron spectrum of HDO was not investigated.

D_2O. Just as the H_2O molecule, the D_2O molecule also belongs to the symmetry class C_{2v}. The vibrational-rotational absorption spectrum of D_2O vapor was investigated with devices having a high dispersion by Barker and Sleator [639], Dickey and coworkers [1331-1334], Innes, Cross and Giguere [2178], and Benedict, Gailar and Plyler [725 727]. The analysis of the rotational structure of the observed bands allowed the determination of the energy levels of the D_2O molecule in the vibrational states (000), (010), (100), (001), (011), (021), (200) (101), (210), (111), (300) and (201). The most thorough investigation of the D_2O bands was carried out by Benedict, Gailar and Plyler [725, 727], who obtained the absorption spectrum of D_2O vapor in the wavelength region from 1.25 to 4.2 microns, using spectrometers which provided a resolving power of 0.2 cm^{-1}.

The vibrational constants of D_2O, found by analysis of the vibrational-rotational spectrum of this molecule, were first quoted in the paper by Friedman and Haar [1615] in 1954. Earlier, the vibrational constants of D_2O had been calculated in the papers [863, 2404, 1263] by means of isotopic relations on the basis of the vibrational constants of H_2O. In the following years, Benedict, Gailar and Plyler [727] and Khachkuruzov [440] calculated the vibrational constants of

D_2O on the basis of the results of the investigation of spectra of this molecule.*

It was shown in paper [440] that the available experimental data must be complemented by two theoretical relations between the frequencies of the normal oscillations of D_2O and H_2O, when calculating the values of D_2O vibrational constants, which enter into the complete quadratic equation for unperturbed vibrational energy levels, and also when calculating the constant of the Darling-Dennison resonance between the vibrational states $(v_1 \geq 2, v_2, v_3)$ and $(v_1 - 2, v_2, v_3 + 2)$.** In this paper, the experimental values of the energy of vibrational levels of D_2O, found by Benedict, Gailar and Plyler [725, 727], and the values of the frequencies of normal oscillations according to [439] are used in order to calculate the vibrational constants of D_2O. The values of the vibrational constants of D_2O found in the paper [440], are similar to the values of the corresponding constants quoted in the papers [1615, 727]. The value of 42.5 ± 1.0 cm^{-1} was found for the Darling-Dennison resonance constant of D_2O in [440].

The values of the vibrational constants of D_2O, calculated by Khachkuruzov [440] are accepted in the present Handbook and quoted in Table 36.***

The purely rotational spectrum of D_2O in the far infrared range (23-135 microns) was investigated by Fuson, Randall and Dennison [1636]. On the basis of the measurement results obtained by these investigators, the levels of the rotational energy of D_2O in the vibrational ground state up to $J_\tau = 15$ were determined in the papers [1636, 1754]. It must be noted that the frequencies of the purely rotational transitions**** in the vibrational ground state of D_2O are determined in the papers [699, 1822, 3311, 1494, 1219] with great accuracy on the basis of microwave spectra.

Benedict, Gailar and Plyler [727] determined the levels of the rotational energy of the D_2O molecule in the vibrational ground state and in mine excited vibrational states* up to $J_\tau = 15_{-15}$ on the basis of an analysis of the fine structure of the D_2O bands obtained by them on devices with high dispersion. More accurate values of the vibrational ground state are obtained in paper [727] than in the papers [1636, 1754]. The analysis of the rotational structure of the bands allowed Benedict, Gailar and Plyler to determine the effective values of the rotational constants of D_2O in the vibrational ground and excited states and also the values of the constants of rotational-vibrational interaction.

TABLE 36

Accepted Values (in cm^{-1}) of the Molecular Constants of D_2O in the Electronic Ground State ($\sigma = 2$)

A Постоянная	B Значение	A Постоянная	B Значение	A Постоянная	B Значение
ω_1	2762,84	x_{22}	—10,17	α_1^B	0,0938
ω_2	1206,72	x_{12}	—85,76	α_2^B	—0,0823
ω_3	2885,99	A_{000}	15,3946	α_3^B	0,0418
x_{11}	—21,94	α_1^A	0,246	C_{000}	4,8458
x_{33}	—9,46	α_2^A	—1,161	α_1^C	0,0768
x_{23}	—24,99	α_3^A	0,593	α_2^C	0,0495
x_{13}	—8,77	B_{000}	7,2716	α_3^C	0,0538

A) Constant; B) value.

In Table 36, the values of the rotational constants and the constants of the vibrational-rotational interaction of the D_2O molecule are quoted, accepted in the present Handbook, and calculated by Benedict, Gailar and Plyler [727] on the basis of the corresponding spectral data. They estimate the uncertainty of A_{000} by ± 0.01 cm^{-1} and those of B_{000} and C_{000} by ± 0.003 cm^{-1}.

It was shown in paper [727] that the equilibrium values of the structural parameters of the D_2O molecule concur within the error limits with the values of the corresponding parameters of the H_2O and HDO molecules.

The electron spectrum of D_2O was not investigated.

HTO, DTO, T_2O. The information on the HTO, DTO and T_2O spectra was exhausted by the results of investigations on the infrared spectra of the vapors of these compounds within the region from 700 to 7000 cm^{-1}, obtained by Staats, Morgan and Goldstein [3831] on a low-dispersion spectrometer. The frequencies of the centers of the ν_2 and ν_3 bands are quoted in paper [3831] for HTO, the frequency of the center of the ν_3 band, for DTO, and the frequencies of the centers of the ν_2 and ν_3 bands and also the wave numbers of the maxima of the Q branch for the $\nu_2 + \nu_3$ and $\nu_1 + \nu_3$ bands, for T_2O.

Libby [2607] calculated for the first time the vibrational constants of HTO, DTO and T_2O by means of the isotopic relations (1.65) on the basis of the vibrational and force constants of H_2O obtained by Darling and Dennison [1263]. In the paper [440], however, the inadmissibility of using the relation (1.65) for the calculation of the anharmonicity constants of asymmetric isotopic molecules on the basis of the corresponding constants of the symmetric molecule is proved on the example of the HDO molecule. Thus, the values of the anharmonicity constants of HTO and DTO molecules, calculated by Libby, are incorrect. Libby's T_2O vibrational constants and HTO and DTO normal vibration frequencies are inaccurate, as the values of the H_2O constants used by him [1263] are obsolete.

The values of the vibrational constants of H_2O are determined more accurately in the papers [438, 437]. On the basis of these constants, Khachkuruzov [439] calculated the force constants of the water molecule and the frequencies of the normal oscillations of its isotopic modifications. The frequencies were used by him in the paper [440]

to calculate the anharmonicity constants of HTO, DTO and T_2O by means of Eq. (1.65). The anharmonicity constants of T_2O are calculated on the basis of the values of the corresponding constants of D_2O, and the anharmonicity constants of HTO and DTO on the basis of the corresponding constants of HDO, similar to the manner used by Friedman and Haar [1615].

The values of the vibrational constants of HTO, DTO and T_2O, determined in this way, are quoted in Table 37. The levels of the vibrational energy of the HTO, DTO and T_2O molecules, calculated on the basis of these constants [440], are in good accordance with the results of the measurements carried out by Staats, Morgan and Goldstein [3831].

Benedict, Gailar and Plyler [727] showed on the basis of the analysis of the well known spectral data for H_2O, HDO and D_2O that the equilibrium values of the structural parameters of the water molecule are not changed by isotopic substitution and are equal to: $r_e(O - H) = 0.9572 \pm 0.0003$ A; $\angle H - O - H = 104°31 \pm 3'$. This makes it possible to calculate the moments of inertia of the HTO, DTO and T_2O molecules and the corresponding values of the rotational constants, which are quoted in Table 37.

In Table 37, the values of the constants of vibrational-rotational interaction of HTO, DTO, T_2O are also given, calculated by Eq. (1.66). The calculations for HTO and DTO are based on the values of the corresponding HDO constants, accepted in the Handbook (see Table 35), and those for T_2O on the corresponding D_2O constants (see Table 36).

TABLE 37

Accepted Values (in cm^{-1}) of the Mclecular Constants of HTO, DTO and T_2O in the Electronic Ground State

A Постоянная	B Молекула		
	HTO ($\sigma=1$)	DTO ($\sigma=1$)	T_2O ($\sigma=2$)
ω_1	2367,90	2359,26	2298,76
ω_2	1370,17	1115,65	1015,84
ω_3	3887,44	2833,00	2436,91
x_{11}	—29,20	—28,99	—15,19
x_{22}	—10,71	—7,10	—6,70
x_{33}	—82,29	—43,70	—17,81
x_{12}	—13,51	—10,96	—6,14
x_{23}	—19,04	—11,30	—7,23
x_{13}	—10,82	—7,86	—60,25
A_e	22,300	13,565	11,211
α_1^A	0,149	0,148	0,142
α_2^A	—1,534	—0,828	—0,693
α_3^A	1,086	0,420	0,357
B_e	6,642	5,762	4,877
α_1^B	0,117	0,116	0,055
α_2^B	—0,125	—0,068	—0,049
α_3^B	0,012	0,005	0,025
C_e	5,118	4,044	3,399
α_1^C	0,065	0,064	0,044
α_2^C	0,061	0,033	0,030
α_3^C	0,088	0,034	0,032

A) Constant; B) molecule.

H_2O_2. In the hydrogen peroxide molecule consisting of two OH groups joined by an O-O bond, a retarded internal rotation around this bond takes place. Penney and Sutherland [3218] showed on the basis of quantum-mechanical calculations that the position of the O-H bonds on two planes (gauche configuration) is characteristic for the stable H_2O_2 configuration, the angle φ between the planes being similar in magnitude to the O-O-H angle and equal to about 100°. The authors of the paper [3218] showed also that the plane (cis and trans) configura-

tions of the H_2O_2 molecule must be unstable, and that the heights V_c and V_t of the cis and trans barriers on the curve of the potential energy of internal rotation (see Fig. 8, curve 1) are unequal ($V_c > V_t$). Thus, two isomeric gauche configurations of H_2O_2 exist, and the transition between them may be realized by a tunnel effect through the trans barrier V_t. This effect causes the line doubling in the H_2O_2 spectrum similar to the inversion doubling in the NH_3 spectrum. The subsequent results of spectroscopic [616, 4392, 1729, 1732, 624, 3952, 3731, 3954, 3732, 1543, 1542, 2794], X-ray diffraction [2669, 486] and electron diffraction [1739] investigation, the measurements of the dipole moment [2623, 2794] and also repeated theoretical calculations [2563] corroborated the assumption of Penney and Sutherland with regard to the stable configuration of the H_2O_2 molecule and made it possible to reject all the other forms which had been assumed (for detail see [460]).

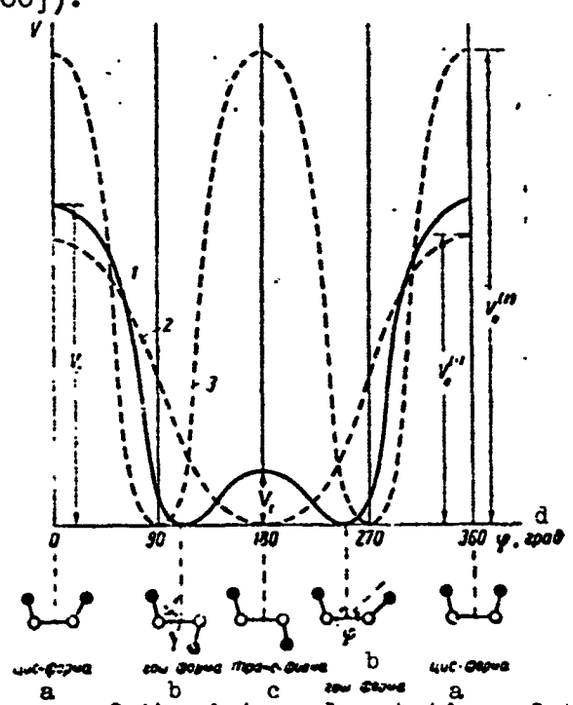


Fig.8. Potential curve of the internal rotation of the H_2O_2 molecule. 1) Theoretical calculation; 2) and 3) approximate forms of the cosine curve corresponding to n = 1 and 2. a) cis form; b) gauche form; c) trans form; d) degree.

The values of the structural parameters of the stable H_2O_2 configuration are determined by electron diffraction [1739], X-ray diffraction [2669, 486] and spectroscopical [4392, 1729, 1732] investigations.

The following values of the structural parameters, recommended by Shumb, Setterfield and Wentworth [460] and also by Giguere and Liu [1736], are adopted in the present Handbook: $r_{O-O} = 1.49 \pm 0.03$; $r_{O-H} = 0.965 \pm 0.005$ A; $\angle O - O - H = 100 \pm 5°$, and $\varphi = 95 \pm 10°$. The values of the principal moments of inertia, quoted in Table 38 and being in accordance with the values of the rotational constants determined in the papers [4392, 1729] on the basis of the analysis of the rotational structure of the infrared $2\nu_1 + \nu_5$ and $\nu_1 + \nu_5$ bands,* correspond to these parameters. In the same Table, the value of I_{pr} is given, equal to $I/4I_A$, according to Giguere and Liu [1736].

The stable gauche configuration of the H_2O_2 molecule belongs to the C_2 point group of symmetry and, correspondingly the molecule possesses six nondegenerate fundamental oscillation frequencies which are active both in the infrared and in the Raman spectrum. The frequencies ν_1, ν_2, ν_3 and ν_4 of the symmetrical vibrations of the class A correspond to the stretching of the O-H bonds (ν_1), to the deformation of the O-O-H angle (ν_2), to the stretching of the O-O bond (ν_3) and to the torsion of OH groups around the O-O bond (ν_4). The frequencies ν_5 and ν_6 of the antisymmetric oscillations correspond to the stretching of the O-H bonds (ν_5) and to the deformation of the O-O-H angle (ν_6). The infrared absorption spectrum of hydrogen peroxide vapor was investigated by Bailey and Gordon [616] (770-4000 cm^{-1}); Zunwalt and Giguere [4392] (835-1340 cm^{-1}), Giguere [1729] (665-5000 cm^{-1}), Giguere and Bain [1732, 624] (400-6650 cm^{-1}) and Chin and Giguere [1098a] (300-400 cm^{-1}). The infrared spectrum of the liquid hy-

drogen peroxide in the 400-5000 cm^{-1} region was investigated in the papers [616, 1727, 1729, 624]. The infrared spectrum of crystalline supercooled liquid hydrogen peroxide was investigated by Taylor [3952] in the 455-4750 cm^{-1} region. Giguere and Harvey [1734] investigated the spectrum of crystalline and amorphous hydrogen peroxide in the 400-4000 cm^{-1} region. In all the investigations, the infrared H_2O_2 spectrum was obtained on prisma spectrometers with a low or mean dispersion. The papers [· . 2, 1729] are an exception, where, owing to the application of a vacuum spectrometer with a concave 21-foot diffraction grating, it was possible to resolve the rotational structure of a number of bands.

The Raman spectrum of the gaseous H_2O_2 is not investigated. Investigated are the Raman spectra of liquid hydrogen peroxide [3731, 3954, 3732], of its aqueous solutions [4079, 1258, 4082, 3954] and of crystalline hydrogen peroxide (see [460], page 241, and also [9353 3732]).

The spectrum of H_2O_2 vapor in the microwave region was obtained by Massey and Bianco [2794]..

The attempt to interpret the vibrational spectrum of H_2O_2 on the basis of the two-plane model of the molecule, proposed by Penney and Sutherland [3218], was first carried out by Bailey and Gordon [616]. These authors, however, had at their disposal very scanty experimental data, and the interpretation of the frequencies proposed by them is erroneous, a fact which was pointed out by Feher [1543] at the time. Feher proposed another interpretation of the H_2O_2 frequencies, using only the results of the investigation of Raman spectra of liquid H_2O_2 [3731] and D_2O_2 [1542], and assuming also $\nu_1 \cong \nu_5$ and $\nu_2 \cong \nu_6$ on the basis of a comparison of the fundamental frequencies of the symmetric and antisymmetric vibrations of H_2O, H_2S, H_2CO, C_2H_2 and CH_2Cl_2. Later

on, the values of the fundamental frequencies of H_2O_2 were determined accurately by the investigations of Giguere and his coworkers [4392, 1729, 624, 1734, 1098a].

In Table 38, the values of the fundamental oscillation frequencies of H_2O_2 are quoted as they are accepted in the present Handbook. The values of the fundamental frequencies of the symmetric vibrations (ν_1 and ν_2) are not determined experimentally, and they are quoted in Table 38 on the basis of an estimation made by Khachkuruzov and Kokushkin [447]. The uncertainties of the accepted values of ν_1 and ν_2 are estimated as ± 20 cm^{-1}. The value of the fundamental frequency ν_3 is accepted according to the data obtained by Taylor and Cross [3954] from the Raman spectrum of liquid hydrogen peroxide. The values of the fundamental frequencies ν_5 and ν_6 of the asymmetric vibrations listed in Table 38, are determined by Giguere and Bain [1732, 624] when investigating the infrared spectrum of H_2O_2 vapor. The uncertainties of these values may be estimated as equal to ± 5 cm^{-1}. The value of the ν_4 frequency of the torsional vibration of the H_2O_2 molecule, quoted in Table 38, was obtained by Chin and Giguere [1098a] who determined an intense infrared band with a center at 314 cm^{-1} in the 300-400 cm^{-1} (23-33 microns) region. The band at 575 cm^{-1}, earlier referred to ν_4 [1729, 1728, 1732, 1736], is its first overtone.

Many of the investigators have attempted to determine the form of the potential energy curve of the internal rotation of the H_2O_2 molecule on the basis of theoretical calculations as well as on that of investigation of spectra. Penney and Sutherland [3218] were the first to calculate the values 0.5 and 1.0 ev (11.5 and 23 kcal/mole) for V_t and V_c, respectively, by the method of electron pairs. Later on, these authors [3219] performed a more accurate calculation, according to which $V_t = 6$ and $V_c = 10$ kcal/mole. Lassetre and Dean [2563] obtained

values of V_t and V_c of the same order of magnitude on the basis of theoretical calculations. Luft obtained by calculation the values V_t = 1.8, and V_c = 6.9 kcal/mole [2672, 2675, 2680] and V_t = 0.9, V_c = 15 kcal/mole [2679]. Massey and Bianco [2794] found V_0 = 323 cal/mole on the basis of the doubling of the lines in the microwave spectrum, assuming that the potential curve of the internal rotation in the molecule is described by a curve of the form (II.230). Massey and Hart [2795] attempted to interpret the same experimental data [2794] using the asymmetric curve $V(\varphi)$ proposed by them. It was found that the microwave data alone was not sufficient to determine simultaneously the values of V_c and V_t. Thus, Hirrota [2079] utilized besides the microwave data also the results of investigations of the vibrational-rotational spectra [4392, 1729, 624]. He obtained the values V_c = 1.29 kcal/mole, and V_t = 0.59 kcal/mole. As the author noted, the uncertainty of the obtained V_c value is very high.

TABLE 38

Accepted Values of the Molecular Constants of H_2O_2, D_2O_2 and HDO_2

A Молекула	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	I_A	I_B	I_C	$I_{пр}$	V_0	G
	$см^{-1}$ B						10^{-40} г·см² C				ккал/моль D	
H_2O_2	3580	1320	880	314	3610	1266	0,2785	3,40	3,38	0,0696	4422	2
D_2O_2	2650	970	880	(230)[a]	2661	947	0,514	3,83	3,79	0,1285	4422	2
HDO_2	3595	1290	880	(270)[b]	2655	960	0,398	3,59	3,6	0,0995	4422	1

a) Estimated on the basis of the relation $\frac{\nu_6(H_2O_2)}{\nu_6(D_2O_2)} = 1,36$. b) Estimated on the basis of the relation $\nu_6(HDO_2) = \frac{\nu_6(H_2O_2) + \nu_6(D_2O_2)}{2}$. A) Molecule. B) cm^{-1}. C) $g.cm^2$. D) kcal/mole.

It follows from the foregoing that a unique choice of the V_t and V_c values on the basis of the data available at present is impossible. Owing to this fact, one may assume that the potential curve of the in-

ternal rotation of the H_2O_2 molecule can be described approximately by a simple cosine line of the form (II.230). In this case, the effective height of the potential berrier V_0 may be determined on the basis of the value $S^\circ_{298.15}$ (H_2O_2, gas) = 55.66 ± 0.12 cal/mole·degree, found by Giguere, Liu, Dugdale and Morrison [1737, 1730] by calorimetric measurements. Assuming n = 1 (see curve 2 in Fig.8) the authors of [1737, 1730] found V_0 = 3.5 kcal/mole. Giguere and Liu [1736], assuming n = 2 (see curve 3 in Fig.8), found V_0 = 4.45 kcal/mole. The assumption of n = 2 is, obviously, more justified, because in this case the two minima on the curve of the potential energy are miantained. Thus, it is assumed in the present Handbook that the potential curve of the internal rotation of the H_2O_2 molecule is described by Eq.(II.230), at n = 2. Using the values of the fundamental oscillation frequencies, the principal moments of inertia and the reduced moment of inertial of the H_2O_2 molecule, quoted in Table 38, V_0 = 4422 cal/mole was found by the Pitzer and Gwinn method [3259, 3255] (see Eqs.(II.236) and (II.237)). This value was accepted in the present Handbook, and it is quoted in Table 38.

According to Mulliken [2989] the $^1A_1$ state is the electronic ground state of the H_2O_2 molecule. Data on excited electronic states of H_2O_2 are not available. It is only known that a continuous absorption is observed in the region of 3750-1850 A, but it can not be identified with any excited states of H_2O_2. A survey on the investigation of the ultraviolet H_2O_2 spectrum is given by Shumb, Setterfield and Wentworth [460].

D_2O_2. The molecule of the deuterium peroxide D_2O_2, similar in its structure to that of the H_2O_2 molecule, belongs to the same C_2 point group of symmetry and possesses also six fundamental oscillation frequencies. Similar to H_2O_2, an internal rotation of the OD groups around the O-O bond is characteristic for D_2O_2.

The infrared absorption spectrum of D_2O_2 vapor was investigated by Bain and Giguere [1732, 624] in the region from 400 to 5000 cm^{-1}. These authors determined the fundamental oscillation frequencies of ν_2 (unreliably), ν_5 and ν_6, and also the combined frequencies $\nu_2 + \nu_6$ and $\nu_1 + \nu_5$. They succeeded in investigating the rotational structure of the ν_5 band.

The infrared absorption spectrum of liquid and solid deuterium peroxide was investigated by Taylor [3952] and Bain and Giguere [624]. These investigations made it possible to determine the fundamental frequencies ν_3, ν_4, ν_5 and ν_6 and also a number of combined frequencies.

The Raman spectrum of liquid deuterium peroxide was investigated by Feher [1542], Taylor [3953] (see also [460], page 256]) and Taylor and Cross [3954]. These investigations made it possible to determine the fundamental frequencies ν_1, ν_2, and ν_3 of D_2O_2 in liquid state. The Raman spectrum of deuterium peroxide vapor was not obtained.

The microwave D_2O_2 spectrum was obtained by Massey and Bianco [2794] in the region from 0.3 to 1.333 cm^{-1}. These authors, however, did not succeed in making a sufficient interpretation of the observed lines.

The values of the fundamental oscillation frequencies of the D_2O_2 molecule, adopted in the present Handbook, are quoted in Table 38. The values of the ν_1 and ν_2 frequencies cited in this Table were obtained by Khachkuruzov and Kokushkin [447] from the analysis of the available data on the spectra of vaporous and liquid hydrogen and deuterium peroxide. The uncertainties in the values of the ν_1 and ν_2 frequencies of the D_2O_2 molecule, cited in Table 38, are assumed in the paper [447] as equal to ± 20 cm^{-1}. The ν_3 oscillation frequency of the D_2O_2 molecule, referred to the stretching of the O-O bond, is known

from the infrared spectra [624, 3952] and Raman spectra [3954, 1543] of solid and liquid deuterium peroxide. Just as in the case of H_2O_2 a value of 880 cm^{-1} was found for the ν_3 frequency in all these investigations. Taking into account the low dependence of the ν_3 frequency of the H_2O_2 and D_2O_2 molecule on the aggregate state, the same value was assumed in Table 38 for H_2O_2 and D_2O_2. The uncertainty of the cited value of the ν_3 frequency may be estimated as equal to ± 10 cm^{-1}. The values of the ν_5 and ν_6 frequencies of the D_2O_2 molecule, obtained by Bain and Giguere [624] as the result of the investigation of the infrared spectrum of hydrogen peroxide vapor, are contained in Table 38. The uncertainties of the values of the ν_5 and ν_6 frequencies, cited in Table 38, may be estimated as equal to ± 5 and ± 3 cm^{-1}, respectively.

The values of the torsional vibration frequency ν_4 of the D_2O_2 molecule is not determined. The values $\nu_4 = 538$ cm^{-1} [3952] and 480 cm^{-1} [1736] belong obviously to the overtone $2\nu_4$ because the value of 314 cm^{-1} was found in the paper [1098a] for the ν_4 frequency of the H_2O_2 molecule. The value $\nu_4 = 230$ cm^{-1}, cited in Table 38 for D_2O_2, was estimated by the authors of the Handbook on the basis of empirical regularities obtained by Khachkuruzov and Kokushkin [447] for the oscillation frequencies of the H_2O_2 and D_2O_2 molecules.

The curve of the potential energy of the internal rotation of the OD groups in the D_2O_2 molecule possesses a form similar to that of the curve of the potential energy of internal rotation of the OH groups in the H_2O_2 molecule (see Fig.8). Undoubtedly, it is not a simple sinusoidal curve but possesses two maxima corresponding to the unstable plane trans and cis forms of the D_2O_2 molecule, and $V_c > V_t$ as well as in the case of H_2O_2. The values of V_c and V_t of the D_2O_2 molecule are obviously similar to the values of the corresponding quantities of the

H_2O_2 molecule.

In the present Handbook, it is assumed for D_2O_2 (as well as H_2O_2) that the potential curve of the internal rotation may be approximated by a simple cosine function with two minima. Analogically to H_2O_2, it is also assumed in the Handbook that $V_0 = 4422$ cal/mole (see Table 38). Experimental data on the structure of the D_2O_2 molecule is missing. In the present Handbook, the same values as those for H_2O_2 are assumed for the structural parameters of D_2O_2: $r_{O-O} = 1.49 \pm 0.01$ A; $r_{O-D} = 0.965 \pm 0.005$ A; $\angle O - O - D = 100 \pm 5°$; $\varphi = 95 \pm 10°$. These values are used for the calculation of the moments of inertia of the D_2O_2 molecule, quoted in Table 38. The same values of the structural parameters and moments of inertia of the D_2O_2 molecule are accepted by Shumb, Setterfield, Wentworth [460] and also by Giguere and Liu [1736]. The value of I_{pr} (see Table 38) is assumed as equal to $1/4I_A$, as well as in the case of H_2O_2.

HDO_2. The HDO_2 molecule is similar in its structure to the H_2O_2 and D_2O_2 molecules, but, in contrast to them, it possesses a lower symmetry owing to the presence of two different hydrogen isotopes in it. Just as H_2O_2 and D_2O_2, HDO_2 possesses six fundamental frequencies.

The spectra of HDO_2 were investigated by Feher [1542], and Bain and Giguere [624]. Feher [1542] obtained the Raman spectrum of a liquid mixture of H_2O_2, D_2O_2 and HDO_2 containing the corresponding components in the ratio 1 : 1 : 2. Analyzing the obtained spectrum, Feher proposed the following values (in cm^{-1}) for the fundamental frequencies of HDO_2: $\nu_1 = 3407$; $\nu_2 = 1406$; $\nu_3 = 877$; $\nu_5 = 2510$, and $\nu_6 = 1009$. The comparison of vibrational spectra of H_2O_2 HDO_2 and D_2O_2 led Feher to the conclusion that the HDO_2 spectrum is composed additively from the H_2O_2 and D_2O_2 spectra. Bain and Giguere [624] investigated the infrared spectrum of a solution of the mixture of H_2O_2, D_2O_2 and HDO_2 in

CCl_4 containing H_2O, D_2O and HDO. They found for the HDO_2 molecule that the values of both frequencies $\nu_1 = 3554$ and $\nu_5 = 2628$ cm^{-1} coincide respectively with the oscillation frequences of the H_2O_2 and D_2O_2 molecules. Moreover, Bain and Giguere found that the frequency of the valence vibration of the HDO molecule, referred to the stretching of the O-H bond, is equal to the arithmetic mean of the ν_1 and ν_3 frequencies of the H_2O molecule, and the frequency of the valence vibration of HDO, referred to the stretching of the O-D bond, is equal to the arithmetic mean of the ν_1 and ν_3 frequencies of the D_2O molecule. This gave cause for Bain and Giguere to suggest that analogical reations must be valid also between the corresponding frequencies of the H_2O_2, D_2O_2 and HDO_2 molecules. It must be noted that Bain and Giguere [624], investigating the infrared spectrum of D_2O_2 vapor, observed a band with the center at 981 cm^{-1} which they ascribed to the ν_6 frequency of the HDO_2 molecule.

Calculating the thermodynamic functions of gaseous HDO_2, Giguere and Liu [1736] assumed the following values of the fundamental frequencies (in cm^{-1}): ($\nu_1 = 3610$; $\nu_2 = 1310$; $\nu_3 = 880$; $\nu_4 = 450$; $\nu_5 = 2660$, and $\nu_6 = 980$. The cited values of the frequencies ν_1, ν_2, ν_4 and ν_5 were obtained by Giguere and Liu as arithmetic means of the corresponding frequencies of symmetric and antisymmetric vibrations of the H_2O_2 and D_2O_2 molecules. For the ν_3 frequency, referred to the stretching of the O-O bond, Giguere and Liu assumed the same value as for H_2O_2 and D_2O_2, and for the ν_6 frequency they assumed the value ascribed to this frequency by Bain and Guguere [624] owing to an investigation of the infrared spectrum of D_2O_2 vapor.

The values of the fundamental frequencies of the HDO_2 molecule, accepted in the present Handbook, are quoted in Table 38. These values were obtained on the basis of the same consideration as in the paper

[1736] and in accordance with the accepted values of the fundamental frequencies of the H_2O_2 and D_2O_2 molecules. In contrast to paper [1736], the arithmetic mean of the frequencies ν_2 and ν_6 of the D_2O_2 molecule is accepted for the ν_6 frequency of the HDO_2 molecule.

Just as for H_2O_2 and D_2O_2, the magnitude of the potential barrier of the internal rotation of HDO_2 is accepted as equal to $V_0 = 4422$ cal/mole.

In the present Handbook, the same values as those for the H_2O_2 and D_2O_2 molecules (see pages 383 and 389) are accepted for the structural parameters of the HDO_2 molecule. The corresponding values of the principal moments of inertia and of the reduced moment of inertia ($I_{pr} = 1/4I_A$) of the HDO_2 molecule are quoted in Table 38.

HO_2. The first direct proof of the existence of the HO_2 radical was obtained by Robertson [3452, 346] and Foner and Hudson [1574], who carried out mass-spectrometric investigations of the dissociation ionization of H_2O_2 by electron impact.* Attempts to obtain the spectrum of the HO_2 radical have also been made (see [1740, 1731, 405, 1069]). However, not one of them may be regarded as successful. It was assumed at one time [1740, 1731] that the band at 1305 cm^{-1}, observed in the absorption spectrum of condensed dissociation products of H_2O and D_2O, belongs to the HO_2 radical. Later on, however, Giguere and Harvey [1733] showed that this band belongs to the nitrogen exides which arise during the dissociation of water vapor by electric discharge.**

According to Walsh [4141], it is assumed in the present Handbook that the HO_2 radical possesses a nonlinear structure in the electronic ground state. The conclusion of the nonlinear structure of HO_2 was drawn by Walsh [4141] on the basis of a systematic study of the correlation between the number of valence electrons in polyatomic molecules and the geometrical structure of the latter. According to Walsh, the

angle between the bonds in HO_2 must be smaller than in HNO.* The angle between the directions of the bonds in HNO was found as 109° by investigation of the electron spectrum of this molecule (see page 713). On the other hand, the angle between the bonds in the HO_2 radical may not be smaller than the angle between the bonds in the H_2O and H_2O_2 molecules. Thus, it is assumed in the present Handbook that $\angle O - O - H$ in the HO_2 radical is equal to $110 \pm 10°$. With regard to the lengths of the O-O and O-H bonds, it is assumed that they have the same values as in th H_2O_2 molecule: $r_{O-O} = 1.49$; $r_{O-H} = 0.97$ A (see page 383). The uncertainty of the accepted values for the lengths of the O-O and O-H bonds is estimated as equal to ± 0.1 and ± 0.05 A, respectively. The product of the principal moments of inertia, quoted in Table 39, is calculated on the basis of these structural parameters of HO_2.

TABLE 39

Accepted Values of the Molecular Constants of HO_2 in the Ground Electronic State

ν_1	ν_2	ν_3	$I_A I_B I_C$	σ
cm^{-1} A			10^{-117} $g^3 \cdot cm^6$ B	
3600	1300	900	1,3	1

A) cm^{-1}; B) $g^3 \cdot cm^6$.

The frequencies of the fundamental oscillations of HO_2, quoted in Table 39 and used in the Handbook, are calculated by Eqs. (P4.27) assuming the force constants of HO_2 as equal to the corresponding force constants of the hydrogen peroxide molecule, found by Giguere and Bain [1732] and Hirota [2079]. The possible error of the oscillation frequencies of HO_2, calculated in this way, may amount to 10-15%.

The energy of the transition of the HO_2 radical from the electronic ground state into the first excited electronic state is estimated, on the basis of kinetic data obtained by Burgess and Robb [1022], as equal to 14,250 cm^{-1}.

OH. The electronic ground state of the hydroxyl molecule is the inversed $^2\Pi$ state. Three excited electronic states of OH are also known: $A^2\Sigma^+$, $B^2\Sigma^+$ and $C^2\Sigma^+$. Three band systems, lying in the visible and ultraviolet regions, $A^2\Sigma^+ - X^2\Pi_i$, $B^2\Sigma^+ - A^2\Sigma^+$ and $C^2\Sigma^+ - A^2\Sigma^+$, are investigated in the OH spectrum.

The bonds of the $A^2\Sigma^+ \rightleftarrows X^2\Pi_i$ system have been investigated repeatedly. The work of Johnston, Dawson and Walker [2277, 1277] of Tanaka and coworkers [3923, 3925] and also of Dieke and Crosswhite [1340] are among the most thorough investigations.

On the basis of an analysis of the papers published up to 1950, the constants found by Tanaka and Koana [3924] are recommended for the electronic ground state of OH in the Handbook [649] and the constants found by Dieke and Crosswhite [1340] are recommended in the monograph by Herzberg [2020] owing to the fact, however, that in the above-mentioned papers the bands of the $A^2\Sigma^+ - X^2\Pi_i$ system have been observed only up to the values $v'' \leq 3$, these constants describe the high levels of the vibrational energy with insufficient accuracy.

More reliable values of the molecular constants of OH in the electronic ground state may be obtained by an analysis of the vibrational-rotational spectrum, lying in the region from 2440 to 14,300 cm^{-1}. The investigation of this spectrum began in 1950 by Meinel [2838-2841] who observed in the spectrum of the night sky the 4-0, 5-1, 6-2, 7-3, 7-2, 8-3 and 9-4 bands on a device with a dispersion of 50 A/mm. Cabannes, J. Dufay and M. Dufay [1040, 1411] and also Jones and Gush [2290] also observed a number of OH bands in the night sky spectrum.

Chamberlain and Oliver [1085] obtained the same bands in the northern lights on a device with a dispersion of 138 A/mm. Measurements of the vibrational-rotational spectrum of OH in the 11,110-14,300 cm^{-1} region have been carried out also under laboratory conditions using oxyacetylene and oxyhydrogene flames. Thus, Herman and Hornbeck [2125-2127, 2005] investigated the 4-0, 5-1 and 6-2 bands, Dejardin, Janin and Peyron [1291, 1294-1296, 3232] investigated the 4-0, 5-1 and 6-2 bands Benedict, Plyler and Humphreys [736-738] and also Rogge, Yarger and Dickey [3473a] investigated the 2-0, 3-1 and 4-2 bands, and Allen, Blaine and Plyler [501] investigated the 3-2, 2-1 and 1-0 bands. In all these works, an analysis of the rotational structure of the OH bands was carried out.

TABLE 40

Energies (in cm^{-1}) of the Vibrational Levels $G_0(v)$ of the OH Molecule in the $X^2\Pi_i$ State.

v	A Экспериментальные данные	B Расчет по постоянным				
		[1340]a	[3923]b	[2665]c	[1086]d	Стабл. 41
1	3569,63 [1340]	3569,6	3568,41	3569,63	3569,63	3569,63
2	6973,58 [1340]	6973,6	6971,52	6973,51	6973,57	6973,57
3	10215,83 [2005]	10211,9	10203,33	10213,76	10213,8[illegible]	10213,83
4	13291,50 [2005]	13284,6	13257,84	13291,48	13291,54	13291,52
5	16206,74 [2005]	16191,7	16129,05	16206,61	16206,74	16206,97
6	18958,17 [2005]	18933,2	18810,96	18958,07	18958,18	18958,71
7	—	21509,1	21297,57	21543,63	21543,12	21544,02
8	23957,5 [1086]	23919,4	23582,88	23960,02	23957,16	23958,11
9	26193,9 [1086]	26164,0	25660,89	26202,83	26194,00	26194,00
v_{max}	35450±100	40277,6	34102,	36815,1	36181,3	35450,2[illegible] e

a) $G_0(v) = 3652.4\ v - 82.8\ v^2$; $v_{max} = 22$.

b) $G_0(v) = 3649.06\ v - 79.65\ v^2 - 1.00\ v^3$; $v_{max} = 17$.

c) $G_0(v) = 3653.22\ v - 84.47\ v^2 + 0.63\ v^3 - 0.05\ v^4$; $v_{max} = 18$.

d) $G_0(v) = 3653.33\ v - 84.182\ v^2 + 0.5022\ v^3 - 0.02083\ v^4 - 0.001637\ v^5$; $v_{max} = 17$

e) $v_{max} = 17$.

A) Experimental data; B) Calculation of the basis of the constants.

Chamberlain and Roesler [1086] observed the vibrational-rotational spectrum of OH in the luminescence of the night sky on a device which made it possible to determine the wave numbers of the bands with an accuracy of 0.1-0.3 cm^{-1}. Moreover the 5-1 and 6-2 bands were obtained observed earlier in flame spectra, and also the 8-3 and 9-4 bands, not observed in flame spectra. Chamberlain and Roesler proved the identity of both spectra and determined the accurate values of the levels of the vibrational energy with v = 8 and 9.

McKinley and coworkers [1077, 2719], Krauss [2479], and Garwin, Broida and Kostkowski [1655b] observed a number of bands of OH in the infrared emission spectrum accompanying the $H + O_3$ reaction. Krauss was the first to obtain the 10-5 band under these conditions.

The experimental values of the vibrational energy levels of OH in the electronic ground state, recommended by Chamberlain and Roesler [1086] on the basis of their own investigations as well as on the results of the investigations by Herman and Hornbeck [2005] and the results of the analysis of the $A^2\Sigma^+ - X^2\Pi_i$ band system, obtained by Dieke and Crosswhite [1340], are quoted in Table 40. *

On the basis of the experimental data, several authors determined the values of the vibrational constants of OH in the equations for $G_0(v)$ of third, fourth and fifth order with respect to $\underline{v}$. Besides the most accurate values of the vibrational energy levels of OH, found experimentally, the values of the corresponding levels, calculated by equations proposed in the papers [1340, 3924, 2005, 1086], are also given in the Table 40.

The study of the data given in Table 40 proves that the equation of fifth order, obtained by Chamberlain and Roesler [1086], describes with the greatest accuracy the experimental data. However, even this equation obviously does not describe accurately enough the levels of the vibrational energy of OH close to the dissociation limit, because the extrapolation of the vibrational levels by the equation of Chamberlain-Roesler let these levels converge at 36,188 cm^{-1}, whereas the experimental value of the dissociation energy of OH is equal to 35,450 $\pm$ 100 cm^{-1}.

Owing to the fact that the dissociation limit of OH calculated by the equation proposed by Chamberlain and Roesler [1086] differs from the true value by 730 cm^{-1}, two terms proportional to v^6 and v^7 were added to this equation when compiling this Handbook. This equation hardly changes the energy of levels with $v \leq 9$ and gives the correct value of the dissociation energy of OH at $v_{max} = 17$.

The values of $G_0(v)$, calculated by the new equation accepted in this Handbook, are quoted in the last column of Table 40.

The rotational constants of OH in the $X^2\Pi_i$ state are determined only for vibrational states corresponding to $v \leq 6$, because the bands referring to higher vibrational states are obtained by devices with a low dispersion, a fact which makes a thorough resolution of the rotational structure impossible. The values of the rotational constants calculated by various authors (Tanaka and coworkers [3923-3925], Dieke and Crosswhite [1340], Herman and Hornbeck [2125-2127, 2005], Dejardin, Janin and Peyron [1291-1296, 3232] are similar to each other. In particular, the differences of the B_e values do not exceed 0.01-0.02 cm^{-1}. In the Handbook, the values of the constants B_e, α_1, α_2 and A are accepted, as found by Herman and Hornbeck [2005], and the values of D_e and β_1, as determined by Dieke and Crosswhite [1340]. The values of

D_v, found by Herman and Hornbeck [2005], are satisfactorily described by the accepted values of the constants D_e and β_1. All rotational constants are calculated on the basis of an analysis of the OH bands by the equation of Hill and Van vleck [Eq.(1.25)], because the spin-orbital coupling in the electronic ground state of OH belongs to a type intermediate between the Band coupling causes a and b.

In papers dealing with the study of the microwave spectrum of OH (see, for example, [1391-1393], etc.) the superfine structure of the lines of rotational transitions was mainly investigated. It must be noted that Dousmanis, Sanders and Townes [1393] found for $O^{16}H$ the value $A/B = -7.444 \pm 0.017$, whereas the analysis of the rotational structure of the bands of the $A^2\Sigma - X^2\Pi$ system gives the value $A/B = -7.404$. This difference is caused by the fact that the analysis of the rotational structure of the ultraviolet OH bands yields the effective value of this ratio, including the effect of the centrifugal stress of the molecule.

The first excited electronic state $A^2\Sigma^+$ of the OH molecule was investigated in the papers [2277, 1277, 3923, 3924, 3925, 1340] on the basis of an analysis of the $A^2\Sigma^+ - X^2\Pi_i$ band system. However, studying the $A^2\Sigma^+ - X^2\Pi_i$ band system, it was possible to observe only transitions from the four first vibrational levels of the $A^2\Sigma^+$ state ($v' \leq 3$). It was shown in the papers by Barrow [645, 646, 652], that the band system in the 4200-6000 A region, investigated earlier by Schuler and coworkers [3657, 3654, 3656], Benoist [748, 749] and Leach [2576], belongs to the OH radical and is caused by a transition between the earlier unknown $B^2\Sigma^+$ electronic state and the $A^2\Sigma^+$ electronic state. A thorough analysis, carried out in the papers [645, 646, 652], showed that the bands of the $B^2\Sigma^+ - A^2\Sigma^+$ system are coupled with the vibrational levels $5 \leq v' \leq 9$ of the $A^2\Sigma^+$ state. The data for the vibrational

levels $5 \leq v' \leq 9$, obtained in these papers, is based on the analysis of the $B^2\Sigma^+ - A^2\Sigma^+$ band system supplemented by the data of Schuler and Michel [3653] for $v' = 4$ of the same band system, and the data of Dieke and Crosswhite [1340] for the levels $0 \leq v' \leq 3$ of the $A^2\Sigma^+$ state found in the analysis of the $A^2\Sigma^+ - X^2\Pi_i$ system, enabled Barrow [645] to calculate with great accuracy the vibrational and rotational constants of OH in the $A^2\Sigma^+$ state.* Barrow [645] used equations of the fourth and fifth order to approximate the levels of the vibrational energy of OH in the $A^2\Sigma^+$ state. The most accurate description of the experimental values of the levels up to the dissociation limit ($v_{max} = 10$) has been obtained by Barrow by means of the fifth order equation. The values of the vibrational constants of OH in the $A^2\Sigma^+$ state, corresponding to this equation, are accepted in the present Handbook and quoted in Table 41. The values of the rotational constants of OH in the $A^2\Sigma^+$ state, quoted in Table 41, are also calculated by Barrow [645].

The levels of the vibrational energy of OH in the $B^2\Sigma$ state converge to the dissociation limit already at $v = 2$, because, according to [645], the curve of the potential energy of OH possesses a very flat minimum in this state. The molecular constants of OH in the $B^2\Sigma$ state, calculated by Barrow [645] on the basis of the analysis of the $B^2\Sigma - A^2\Sigma$, band system, are quoted in Table 41.

The $C^2\Sigma^+$ state is the highest electronic state of OH which has been experimentally. It was identified by Michels [2871] who suggested that the hydroxyl is dissociated in this state into $O^-(^2P) + H^+(^1S)$. This interpretation made it possible to resolve the problem of the reference of the bands observed earlier by Benoist [749] and also by Schuler and Michel [3653] in the 2300-2500 A region. The analysis of these bands [2871] proved that they are 0-7, 0-8, 1-6 and

1-7 bands of the $C^2\Sigma^+ - A^2\Sigma^+$.

The molecular constants of OH in the $C^2\Sigma^+$ system, calculated by Michels [2871] are cited in Table 41.

TABLE 41

Accepted Values of the Molecular Constants of OH

A Состояние	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	$\omega_e z_e$	$\omega_e t_1$	B_e	α_1	α_2	$D_e \cdot 10^3$	r_e
	B $см^{-1}$										Å
$X^2\Pi_i$	0[a]	3737,90	84,965	0,5397	0,01659	—0,001759[b]	18,867	0,708	0,00207	1,87[c]	0,9707
$A^2\Sigma^+$	32683,2	3178,86	92,917	—1,7915	—0,32362	—0,03585	17,358	0,7868	—0,016	2,04[c]	1,012
$B^2\Sigma^+$	69775	939,95	105,04	—21,5	—	—	5,54	0,653	—0,16	—[d]	1,791
$C^2\Sigma^+$	90105	2339	32	—	—	—	4,207	0,167	—	—	2,056

a) $A_0 = -139.7$ cm^{-1}. b) $\omega_e s_e = -4.732 \cdot 10^{-5}$; $\omega_e u_e = -3.786 \cdot 10^{-6}$ cm^{-1}. c) $\beta_1 = -3 \cdot 10^{-5}$ cm^{-1}. d) The value of D_0 is given. A) State; B) cm^{-1}.

OD. Two band system, $A^2\Sigma \rightarrow X^2\Pi_i$ and $B^2\Sigma^+ \rightarrow A^2\Sigma^+$, lying in the wavelength regions from 2500 to 3600 and 4200 to 6000 A, respectively, are investigated in the deuteroxyl spectrum. The results of the first investigations of the $A^2\Sigma^+ \rightarrow X^2\Pi_i$ band system [2276, 2268, 3695, 3151] were not applicable to the determination of the molecular constants of OD because the band structure was insufficiently resolved. Later on, the $A^2\Sigma^+ - X^2\Pi_i$ band system was investigated on devices with high dispersion by Ishaq [2185-2190], Sastry and Rao [3395, 3396, 3585-3591], Narayan [3022] and Oura [3154-3156]. In the works of these authors, the fine structure of 12 bands (0-0, 0-1, 1-0, 1-1, 2-0, 3-0, 3-1, 2-1, 1-2, 2-2, 3-2, 3-3) was studied and the values of the molecular constants of OD in the $X^2\Pi_i$ and $A^2\Sigma^+$ states were determined.

The vibrational constants of OD in the $X^2\Pi_i$ and $A^2\Sigma^+$ states have been calculated by Sastri and Rao [3591]* and Oura [3154, 3155]** on the basis of the zero lines of the bands of the $A^2\Sigma^+ - X^2\Pi_i$ system corresponding to $v' \leq 3$ and $v'' \leq 2$. The values of the vibrational con-

stants of OD, however, obtained by these authors, could not lay claim to having a high accuracy because they were found on the basis of transitions between low vibrational levels which were determined with an accuracy up to some reciprocal centimeters.

It must be noted that the vibrational constants of OD in the $A^2\Sigma$ state, found in the papers [3591, 3154, 3155] on the basis of an analysis of the bands of the $A^2\Sigma - X^2\Pi_i$ system differ essentially from the values of the corresponding constants found by Barrow [645] on the basis of an analysis of a great number of bands of the $B^2\Sigma - A^2\Sigma$ system. This permits us to assume that the vibrational constants of OD in the $X^2\Pi$ state, found in the papers [3591, 3154, 3155], are inexact. Moreover, these vibrational constants do not give a satisfactory extrapolation of the high levels of the vibrational energy, because the levels calculated by them converge far from the dissociation limit of OD.

Thus, the vibrational constants of OD in the electronic ground state are determined in the present Handbook by means of the relations (1.43) and the vibrational constants of the $X^2\Pi_i$ state of OH^1, quoted in Table 41 (see Table 42). The limit value of the vibrational energy of OD calculated by this vibrational constants coincides with the experimental value of the dissociation limit of OD within the error limits of its determination.

The values of the rotational constants of OD for a number of vibrational states of the $X^2\Pi_i$ and $A^2\Sigma^+$ electronic states were determined by the investigation of the fine structure of the bands of the $A^2\Sigma^+ - X^2\Pi_i$ system. Herzberg [2020] calculated the constants B_e, α_1 and D_0 for the $X^2\Pi_i$ and $A^2\Sigma^+$ states of OD on the basis of data obtained in the papers [2268, 2186, 2189, 2190, 3591, 3585-3590, 3156]. Very similar values of the corresponding constants are found in the papers by

Oura [3154, 3155]. The calculation of the rotational constants of OD by means of the Eqs. (1.43) on the basis of the rotational constants of OH^1 also gives values similar to those found by Herzberg.

It must be noted that the rotational constants of the $A^2\Sigma$ state of OD, determined on the basis of the bands of the $A^2\Sigma - X^2\Pi$ system [2020] differ little from the values found in paper [645] on the basis of the $B^2\Sigma - A^2\Sigma$ band system. Thus, in the present Handbook, the values of the rotational constants calculated by Herzberg [2020] are accepted for the $X^2\Pi_i$ state of OD. The comparison of the values of the rotational constants of the $X^2\Pi_i$ state of OD, calculated by different data, makes it possible to estimate the uncertainty of the accepted B_e value as equal to ± 0.01 cm^{-1}, and that of α_1 as equal to ± 0.04 cm^{-1}.

In the papers [2186, 2189, 3586, 3587], values from -139.1 to -140.0 cm^{-1} are obtained for the constant of the coupling between the orbital and spain angular momenta A in the $X^2\Pi_i$ state of OD. The most accurate value $A = -139.6 \pm 0.2$ cm^{-1} was found by Ishaq [2189] by an analysis of the structure of the 1-1 band obtained on a device with an 1.3 A/mm dispersion. The same value of the constant A was obtained by Sastri [3586] by analysis of the fine structure of the 3-0 band. The investigation of the superfine structure of purely rotational transitions of OD in the microwave spectrum carried out by Dousmanis, Sanders and Townes [1393] showed that the value $A = -139.6$ cm^{-1} determined on the basis of the analysis of the fine structure of the $A^2\Sigma - X^2\Pi_i$ band system is the effective value of this constant allowing for the centrifugal stress of the molecule. The proper value of the constant A of OD is equal to -137.7 cm^{-1}, according to the investigations in [1393]. In the present Handbook, the effective value of the constant A, found in the papers [2189, 3586], is accepted for the $X^2\Pi_i$ state of OD.

Barrow and Downie [652] showed that the band system in the wavelength region from 4200 to 6000 A, observed by Schuler and coworkers [3657, 3654, 3656] and by Benoist [749] in the discharge spectrum in water vapor is caused by the $B^2\Sigma^+ \rightarrow A^2\Sigma^+$ transition in the OH and OD radicals. The molecular constants of the $A^2\Sigma^+$ and $B^2\Sigma^+$ states of the OD radical were calculated by Barrow [645] on the basis of experimental data obtained in the papers [3657, 3654, 3656, 749] for bands with $7 \leq v'' \leq 11$.

The values of the molecular constants of the $A^2\Sigma^+$ and $B^2\Sigma^+$ states of OD, obtained in the paper [645] are quoted in Table 42.

The value of the excitation energy of the $A^2\Sigma^+$ state of the OD radical, accepted in Table 42, is based on the value $\nu_{00} = 32477.14$ cm^{-1} of the $A^2\Sigma^+ - X^2\Pi_i$ band system, calculated by Almy and Horsfall [523]. The excitation energy of the $B^2\Sigma^+$ state of OD is accepted according to the data by Barrow [645].

In analogy to the radical OH, one may expect that OD must possess an excited state with an energy of ~90,000 cm^{-1}.

OT. The spectrum of the OT radical was not observed. Undoubtedly, however, it must be similar to the spectra of OH[1] and OD. The molecular constants of OT may be calculated with sufficient accuracy by means of the Eqs. (1.43) on the basis of the corresponding constants of OH and OD.

The values of the molecular constants of OT for the $X^2\Pi_i$, $A^2\Sigma^+$ and $B^2\Sigma^+$ states. quoted in Table 42, are calculated on the basis of the corresponding constants for OD, quoted in the same table. It must be noted that the vibrational constants of the $X^2\Pi_i$ state of OT, given in Table 42, make possible a satisfactory extrapolation of the vibrational energy levels up to the dissociation limit. The probable uncertainty of the accepted values of the constants ω_e and $\omega_e x_e$ of the

$X^2\Pi_1$ state may be estimated as ± 2 cm^{-1}, and that of the values of the rotational constants B^e and α_1 as ± 0.05 cm^{-1}. The T_e value for th $A^2\Sigma^+$ and $B^2\Sigma^+$ states of OT is accepted as equal to this value for the corresponding states of OD. The uncertainty of these values may be estimated as ± 30 cm^{-1}. Owing to the fact that the coupling constants of OH and OD are almost similar, the same value as for OD is accepted for the constant A of the spin-orbital coupling of the OT radical in the $X^2\Pi_1$ state.

TABLE 42

Accepted Values of the Molecular Constants of OD and OT

A Молекула	B Состояние	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_1	D_e	r_e
		C $см^{-1}$							Å
OD	$X^2\Pi_i$	0[a]	2721,39	45,036	0,2083[b]	10,016	0,295d	$4,2\cdot10^{-4}$	0,97
	$A^2\Sigma^+$	32680	2322,6	55,45	−1,0365[a c]	9,198	0,3224[f]	—	1,012
	$B^2\Sigma^+$	69790	684,3	55,67	−8,295	2,91	0,252[a e]	—	1,8
OT	$X^2\Pi_i$	0[a]	2284,90	31,748	0,1233[e f]	7,061	0,1745	$2,1\cdot10^{-4}$	0,97
	$A^2\Sigma^+$	32680	1950,1	39,09	−0,6135[a g]	6,484	10,191[a]	—	1,012
	$B^2\Sigma^+$	69790	574,5	39,24	−4,910 g	2,05	10,15[a h]	—	1,8

a) $A = -139.6$ cm^{-1}.

b) $\omega_e z_e = 4.70\cdot10^{-3}$; $\omega_e t_e = -3.55\cdot10^{-4}$, $\omega_e s_e = -7.05\cdot10^{-6}$, $\omega_e u_e = -4.10\cdot10^{-7}$ cm^{-1}.

c) $\omega_e z_e = 9.333\cdot10^{-2}$, $\omega_e t_e = -6.78\cdot10^{-4}$ cm^{-1}.

d) $\alpha_5 = -4.5\cdot10^{-6}$ cm^{-1}.

e) $\alpha_2 = -0.045$ cm^{-1}.

f) $\omega_e z_e = 2.32\cdot10^{-3}$, $\omega_e t_e = -1.50\cdot10^{-4}$, $\omega_e s_e = -2.47\cdot10^{-6}$, $\omega_e u_e = -1.21\cdot10^{-7}$ cm^{-1}.

g) $\omega_e z_e = -4.638\cdot10^{-2}$, $\omega_e t_e = -2,83\cdot10^{-4}$ см$^{-1}$.

h) $\alpha_5 = -1.32\cdot10^{-6}$ cm^{-1}.

i) $\alpha_2 = -0.025$ cm^{-1}.

A) Molecule; B) state; C) cm^{-1}.

OH^+. Two bands (0-0 and 1-0) belonging to the OH^+ molecule were determined for the first time by Rodebush and Wahl [3470] in the near ultraviolet spectral region of an electrodeless discharge in presence of water vapor. Later on, Loomis and Brandt [2646] obtained under the same conditions two other bands (0-1 and 1-1) with a resolved fine structure on a device with 1.25 A/mm dispersion. On the basis of the analysis of the rotational structure and the analogy with the iso-electronic NH molecule, Loomis and Brandt drew the conclusion that these bands correspond to the $A^3\Pi - X^3\Sigma^-$ transition, where the $^3\Pi$ state is an inversed state in which the spin-orbital coupling is of the intermediate type between the Hund cases a and b. Loomis and Brandt determined the rotational constants B_0 and D_0 in both states and estimated also the vibrational constants on the basis of the experimentally found values of $\Delta G_{1/2}$ and the relation (1.36) ($\omega''_e = 3111$, $\omega''_e x''_e = 73$, $\omega'_e = 2387$, $\omega'_e x'_e = 200$ cm^{-1}). Moreover, the constants of the multiplet splitting of the $^3\Sigma^-$ ground state are found in the paper [2646]. The molecular constants of OH^+, found by Loomis and Brandt [2646], are cited in the Handbook [649] and in the monograph by Herzberg [2020].*

In 1958, Weniger and Herman [4204] repeated the investigation of the OH^+ spectrum on a device with 2 A/mm dispersion. Besides the earlier known 1-1 band, two new bands were obtained in the paper [4204], the bands 2-2 and 3-3 of the A-X system with a well developed rotational structure. On the basis both of the obtained data and also of the investigations by Loomis and Brandt [2646], Weniger and Herman calculated the rotational constants of OH^+ in both states and, just as in the paper [2646], estimated the vibrational constants of this molecule ($\omega''_e = 3229$; $\omega''_e x''_e = 131$, $\omega'_e = 2202$ $\omega'_e x'_e = 108$ cm^{-1}).

The great difference between the values of the vibrational constants of OH^+, obtained in the papers [2646, 4204], points out the insufficienc reliability of the method used for their determination in these papers. It must be noted that the linear extrapolation of the vibrational energy levels of OH^+, on the basis of the constants calc - lated by Loomis and Brandt [2646], leads to the value $D_0(OH^+)$ = 31,608 cm^{-1}, and on the basis of the constants calculated by Weniger and Herman [4204], to the value $D_0(OH^+)$ = 18,316 cm^{-1}. In reality, $D_0(OH^+)$ = 38,819 or 38,977 cm^{-1} according as to whether the OH^+ molecule dissociates into $O(^3P) + H^+$ or $O^+(^4S) + H(^2S)$.* Owing to this fact, Yungman [473] carried out the calculation of the vibrational constants of OH^+ on the basis of the equations

$$\Delta G_{1/2} = \omega_0 - \omega_0 x_0; \quad \frac{\omega_0^2}{4\omega_0 x_0} = D_0,$$

using the two possible values of $D_0(OH^+)$ (see above) and the values ν_{00} = 27956 ± 3; $\Delta G'_{1/2}$ = 1985 ± 5 and $\Delta G''_{1/2}$ = 2970 ± 5 cm^{-1}, found by experimental data for the 0-0, 0-1 and 1-0 bands [2646] and the 1-1 band [4204]. The result was that the vibrational constants ω''_0 = 3029, $\omega''_0 x''_0$ = 59, ω'_0 = 2012 and $\omega'_0 x'_0$ = 27 cm^{-1}, calculated on the assumption that the $X^3\Sigma^-$ state correlates to the $O^+(^4S) + H(^2S)$ atoms, and the $A^3\Pi$ state to the $O^+(^2D) + H(^2S)$ atoms, best describe the experimental data for the 2-2 and 3-3 bands measured by Weniger and Herman [4204].

The values of the molecular constants of OH^+, accepted in the present Handbook, are quoted in Table 43. In this Table, the values of the vibrational constants of OH^+, calculated in the paper [473], are given. The rotational constants are accepted according to Weniger and Herman [4204], and the constants of the multiplet splitting of the $X^3\Sigma^-$ state according to Loomis and Brandt [2646].

In the papers [2646, 1081, 4204], attempts were made to determine

the constant A of the spin-orbital coupling for the $A^3\Pi_1$ state of OH^+ but apparently, owing to the difficulties in determining the zero lines of the bands, they did not give unique results.

In analogy to the isoelectronic NH molecule,* the OH^+ molecule must possess a series of singlet electronic states with excitation energies in the order of 10,000-20,000 cm^{-1}, transitions into which has not yet been observed in the OH^+ spectrum.

TABLE 43

Accepted Values of the Molecular Constants of OH^+ and OH^-

A Молекула	B Состояние	T_e	ω_e	$\omega_e x_e$	B_e	α_1	$D_e \cdot 10^3$	r_e
		C $см^{-1}$						A
OH^+	$X^2\Sigma^-$ [a]	0	3088	59	16,774	0,727	1,802 [b] [c]	1,0295
	$A^3\Pi_i$	28472,5	2039	27	13,742	0,853	2,120 [a]	1,1374
OH^-	$X^1\Sigma$	0	4200 [c] [d]	—	21,0 [c] [d]	—	—	0,92 [c] [d]

a) $\varepsilon = 0.763$, $\gamma = -0.132$ cm^{-1}.
b) $\beta_1 = 1.5 \cdot 10^{-5}$ cm^{-1}.
c) $\beta_1 = 4.0 \cdot 10^{-5}$ cm^{-1}.
d) estimate.
A) Molecule; B) state; c) cm^{-1}.

OH^-. The spectrum of the OH^- molecule in gaseous state was not observed.** For several years, some authors (Schuler and coworkers [3657, 3654, 3656] and Leach [2576]) ascribed to this molecule bands in the visible and ultraviolet region, excited by discharges in water vapor. However, Barrow [652, 645, 646] and Michels [2871] proved that these bands are caused by transitions between excited electronic states of the OH molecule.

The OH^- molecule is isoelectronic with the HF molecule; therefore, it may be assumed that the constants of these molecules are similar to each other. On the basis of the values of ω_e and B_e (see Table 74)

accepted for the HF molecule, the values of these quantities quoted in Table 43 are accepted for OH^-.

The comparison of these values of the constants ω_e and B_e, accepted for the ground electronic state of the OH^- molecule, with the values of the corresponding constants of OH and OH^+ (in cm^{-1}): $\omega_e(OH^+)$ = = 3088, $\omega_e(OH)$ = 3737.90, $\omega_e(OH^-)$ = 4200, $B_e(OH^+)$ = 16.774, $B_e(OH)$ = = 18.867, $B_e(OH^-)$ = 21.0, may corroborate the rightness of the accepted values. The uncertainties of the accepted ω_e and B_e values of the OH^- ion may be estimated as ± 200 and ± 0.5 cm^{-1}, respectively.

Just as in the case of the HF molecule, the $^1\Sigma$ state must be the ground state of the OH^- molecule. Analogously to the HF (see page 559) the stable excited electronic states of OH^- must possess excitation energies higher than 55,000 cm^{-1}.

§31. THERMODYNAMIC FUNCTIONS OF GASES

The thermodynamic functions of the compounds of hydrogen and its isotopes with oxygen in gaseous state, dealt with in this chapter, are calculated without taking into account the intermolecular interaction and are quoted in the Tables 11-16, 21-25, and 30-33 of the second volume of the Handbook. The thermodynamic functions are calculated for H_2O, OH and OH^+ for the temperature range 293.15-20,000°K (Tables 15, 11, 12), and for the other compounds for the temperature interval from 293.15 to 6000°K.

It must be noted that the difference in the values of the thermodynamic functions of the compounds of natural hydrogen and the corresponding compounds of protium lies beyond the accuracy limit of the determination of these functions. It may be sufficient to point out that the difference between the values of $\Phi_T^*(H_2O)$ and $\Phi_T^*(H_2^1O)$ amounts to 0.0004 kcal/mole·degree. Owing to this fact, in this Handbook the Tables of the thermodynamic properties of H_2O, OH, OH^+, OH^- and H_2O_2 give

values calculated for the natural isotopic mixture of hydrogen (M_H = = 1.0080) on the basis of the molecular constants of the corresponding protium compounds.

In the IInd volume of the Handbook, the values of the virial coefficients and of their derivatives for water vapor are also quoted, thus making it possible to take into account the deviation of the properties of this gas from the ideal state [see Table 393 (II)]. The virial coefficients are calculated on the basis of the values of the force constants of the intermolecular potential of H_2O, accepted in Supplement 5. The values of the critical constants of water are given in Supplement 6.

H_2O. The thermodynamic functions of gaseous H_2O, quoted in Table 15(II), are calculated for the temperature interval from 293.15 to 20,000°K.

A_Φ = +1.3350 cal/mole·degree and A_S = +6.3031 cal/mole·degree are assumed for the calculation of the translational components of the thermodynamic functions of H_2O. The partition function of the vibrational-rotational states of the H_2O molecule is calculated by immediate summation over the levels of the vibrational energy $G_0(v_1, v_2, v_3)$ using the formula*

$$Q_{\text{кол. эр}} = \sum_{v_1=0}^{v_{1m}} \sum_{v_2=0}^{v_{2m}} \sum_{v_3=0}^{v_{3m}} Q_{\text{вр}}^{(v_1, v_2, v_3)} \cdot e^{-\frac{hc}{kT} G_0(v_1, v_2, v_3)},$$

where v_{1m}, v_{2m}, v_{3m} are the limit values of the vibrational quantum numbers; and $Q_{vr}^{(v_1, v_2, v_3)}$ is the partition function of the rotational levels of the vibrational state (v_1, v_2, v_3). The levels of the vibrational energy are calculated by the formula

$$G_0(v_1, v_2, v_3) = G_0^0(v_1, v_2, v_3) + \Delta G_{v_1, v_2, v_3}$$

where $G_0^0(v_1, v_2, v_3)$ are the unperturbed values of the vibrational en-

ergy levels of H_2O determined by a polynomial of third order with respect to v_1, v_2, v_3, the coefficients of which are quoted in Table 33; $\Delta G_{v_1, v_2, v_3}$ are the corrections for the Darling-Dennison resonance. These corrections are taken into account for the first hundred levels. The limit values of the vibrational quantum numbers v_{1m} and v_{3m} are determined from the conditions $G_0(v_1, 0, 0) \leq D_0(HO - H)$, $G_0(0, 0, v_3) \leq D_0(HO - H)$, $G_0(v_1, 0, v_3) \leq D_0(HO - H)$, where $D_0(HO - H)$ 41,269 cm^{-1}. It was found on the basis of this condition: $v_{1m} = 12$; $v_{3m} = 13$, and $v_1 + v_3 \leq 12$. The value of v_{2m} was determined by the maximum of the function $G_0(v_1, v_2, v_3)$ at fixed values of v_1 and v_3, and variable values of v_2. Corresponding calculations proved that the function $G_0(v_1, v_2, v_3)$ possesses a stable maximum at $v_2 = 22$ which coincides with the magnitude of the energy of dissociation of H_2O into atoms; this fact makes it possible to accept the value $v_{2m} = 22$ for the calculation of $Q_{kol.vr}$.

The partition function $Q_{vr}^{(v_1, v_2, v_3)}$ could not be calculated for the whole temperature range by immediate summation over the levels of the rotational energy of H_2O owing to the impossibility of satisfactorily determining the rotational levels near by the dissociation limit. Thus the values of $Q_{vr}^{(v_1, v_2, v_3)}$ are calculated using the approximate relation (II.221) and the expression (II.176a) (see footnote to page 196) is used for $Q_{zh.r}$. The effective values of the rotational constants of H_2O are calculated on the basis of the values of the constants in Table 33, with allowance for the Darling-Dennison resonance by the formulas obtained in the paper [444]. The constants ρ_1 and ρ_2, accepted in the calculations of the thermodynamic functions of H_2O, are calculated by Khachkuruzov and Milevskaya [449] for the ground vibrational state of the H_2O molecule; they are equal to:

$$\rho_1 = 2{,}24 \cdot 10^{-5} deg^{-1}, \rho_2 = 0{,}36 \cdot 10^{-8} deg^{-2},$$

Calculating the thermodynamic functions, the components of the excited states of the H_2O molecule have been calculated by Eqs.(II.120) and (II.121) on the basis of this values of the statistical weights and excitation energies quoted in Table 34, and assuming, that the partition functions of the vibrational-rotational levels are identical for all electronic states of H_2O.

The uncertainties in the values of the thermodynamic functions of H_2O, wyoted in Table 15(II), are - at temperatures below 3000°K - caused mainly by the inaccuracy of the accepted values of the molecular and physical constants. At higher temperatures, the primary sources of errors are as follows: 1) errors in the values of the energy of vibrational levels corresponding to $v_1, v_2, v_3 > 5$, calculated on the basis of the vibrational constants of H_2O accepted in the Handbook*; 2) application of the approximate expression (II.221) for $Q_{vr}^{(v_1,v_2,v_3)}$ which is derived without allowing for the necessity of limiting the number of levels of the rotational energy; 3) inaccuracies in the accepted values of the excitation energies of the electronic states of the H_2O molecule and the statistical weights corresponding to them. The total errors of the Φ_T^* values quoted in Table 15(II) and corresponding to T = 298.15; 3000; 6000; 10,000 and 20,000°K may be estimated as 0.01; 0.05; 0.15; 1.5, and 3.0 cal/mole·degree.

The thermodynamic functions of gaseous H_2O were calculated for the first time in the papers by Gordon and Barnes [1811] (S_T° and C_P° from 400 to 1200°K), Giauque and Ashley [1712] ($S_{298.15}^\circ$) and Gordon [1799] (Φ_T^* from 298.15 to 3000°K). These papers, based on early, very imperfect and inaccurate results of investigation of the infrared spectrum of the H_2O molecule are only of historical interest. The results of these calculations have not been utilized later on, because the calculations by Gordon [1800, 1801], carried out by a significantly

more accurate method and based on more perfect and accurate results of the analysis of the infrared H_2O spectrum, have subsequently been published.

Gordon [1800, 1801] calculated the thermodynamic functions of H_2O, taking into account the anharmonicity of the vibrations and the vibrational-rotational interaction of the molecules in the temperature range from 298.1 to 3000°K on the basis of the method of calculating the thermodynamic functions of polyatomic gases, developed by him (see page 199). The molecular constants of H_2O, found by Freudenberg and Mecke, [1605] are used in the calculations.* Methodic shortcomings of Gordon's calculations are: failure to make allowance for the centrifugal stress of the molecule, and using of an approximate expression for the partition function of the levels of the rotational energy. The values of the thermodynamic functions of H_2O, calculated by Gordon [1800, 1801], are cited in the Handbooks by Justic [2312] and Chernobayev and Zhivotovskiy [355].

Later on, the values of the thermodynamic functions of H_2O, calculated by Gordon [1800, 1801] were corrected for the centrifugal stretching of the molecules by the method proposed by Wilson [4287] (see page 206). This was done for the first time by Gordon himself [1810] for the specific heat of H_2O on the basis of the value $\rho_1 = 2.04 \cdot 10^{-5}$ degree^{-1}, calculated by Wilson [4287]. In the paper by Wagman et al. [4122], corrections were introduced into the values of thermodynamic functions of H_2O calculated by Gordon [1800, 1801], taking into account the changed values of the physical constants and corrections for the centrifugal stretching of the molecules calculated by the method of Wilson [4287]. The values of the thermodynamic functions of H_2O, obtained in the paper [4122], were subsequently extrapolated up to 4000°K [2681], 5000°K [3680] and 6000°K [2142] and also used for

the compilation of thermotechnical tables of the thermodynamical properties of water vapor [137]. In the Handbooks [3426, 3507], the same values of the thermodynamic functions of H_2O are quoted as in the Handbook of the U. S. Bureau of Standards [3680].

After the publication of Gordon's papers [1800, 1801], calculations of the thermodynamic functions of H_2O were carried out by Trautz and Adler [4013], Stephenson and McMahon [3847], Libby [2607], Friedman and Haar [1615], Fichett and Cowan [1555, 1556], Glatt, Adams and Johnston [1759], and when the first edition of the present Handbook was being prepared.

Trautz and Adler [4013] and Stephenson and McMahon [3847] calculated the values of the rotational constant of the specific heat of the ortho and para modifications of H_2O (up to 50 and 300°K, respectively) by immediate summation over the rotational levels of the water molecule, found in the papers [690, 3366]. The calculations by Stephenson and McMahon showed that the thermodynamic functions of the ortho and para modifications of H_2O practically coincide at temperatures higher than 100°K. Moreover, a checking of the method of taking into account the centrifugal stretching of molecules in the calculation of the thermodynamic functions of gases, proposed by Wilson [4287], was carried out in the paper [3847].*

Libby [2607] calculated the Φ_T^* values for temperatures from 298.15 to 773.15°K, taking into account the anharmonicity of the oscillations and the vibrational-rotational interaction on the basis of the values of the molecular constants of H_2O, cited in the monograph by Herzberg [152]. The same values of molecular constants of H_2O were accepted in the first edition of the Handbook, in which the thermodynamic functions of H_2O are calculated for temperatures from 293.15 to 6000°K by Gordon's method [1800], and taking into account the centri-

fugal stress of the molecules by Wilson's method [4287] ($\rho_1 = 2.33.10^{-}$ degree^{-1} was accepted according to [3847].

Friedman and Haar [1615] calculated the thermodynamic functions of H_2O for temperatures from 270 to 5000°K on the basis of somewhat more accurate values of the present Handbook. This calculation was carried out by the Mayer and Goeppert-Mayer method [285] (extended by Stockmayer, Kavanagh and Mickely [3871] on polyatomic gases), which is less accurate than Gordon's method (see page 206).

The differences in the values of S°_{500} and S°_{5000}, quoted in Table 15(II) and in the paper by Friedman and Haar [1615], and also in the first edition of the Handbook and Table 15(II), are equal to 0.009 and 0.492 cal/mole·degree in the first case, and 0.002 and 0.077 cal/mole·degree in the second case, respectively. The satisfactory agreement of the results of calculation of the thermodynamic functions of H_2O in the first and the present edition of the Handbook proves the advantage of Gordon's method over the other approximate methods.

The thermodynamic functions of H_2O calculated by Friedman and Haar [1615] are cited in the Handbook [2076].*

Pickett and Cowan [1555, 1556] calculated the thermodynamic functions of H_2O from 300 to 12,000°K in the harmonic oscillator-rotator model approximation,** very roughly taking into account the anharmonicity of the vibrations, the vibrational-rotational interaction, the centrifugal stress and the excited electronic states of the H_2O molecules. The correction for the anharmonicity of the vibrations, the vibrational and rotational interaction and the centrifugal stress of the H_2O molecules were found in the papers [1555, 1556] by graphical extrapolation of the differences between the values of the thermodynamic functions of H_2O quoted in the Handbook [ ] to $T \leq$ [illegible] the values calculated [illegible] the harmonic oscillator-rigid rotator [illegible]

approximation. In the calculations [1555, 1556] a very imperfect attempt was also made to take into account the excited electronic states of H_2O.

In Table 44, the results of calculations of thermodynamic functions of H_2O, carried out by statistical methods by various authors, are quoted for comparison.

The thermodynamic functions of H_2O were also calculated in a number of investigations on the basis of calorimetric measurements and measurements of the pressure of explosion of hydrogen-oxygen mixtures. These calculations, however, could be carried out only for a limited temperature range and with a lower accuracy than that based on molecular constants.

In the Handbooks [2354, 2360, 98] the values of $S^\circ_{298.15}(H_2O, gas)$ are given, calculated on the basis of the results of calorimetric measurements at low temperatures obtained in the papers [3734, 3042, 3290, 3512, 1336, 1337, 1720]. Giaque and Stoud [1720] found in this way a more accurate value $S^\circ_{298.15}(H_2O, gas) = 44.28 \pm 0.05$ cal/mole·degree, which is 0.8 cal/mole·degree lower than the value calculated on the basis of spectroscopical data. According to Pauling [3201], this difference is caused by disordered orientation of the hydrogen bonds in ice. The calculation of $S^\circ_{298.15}(H_2O, gas)$, carried out by Giauque and Archibald [1711], indirectly corroborated this explanation.

Calorimetric measurements of the specific heat of water vapor were carried out in a number of investigations. Keyes [2386] made a comparison of the results of measurements of the specific heat of H_2O, obtained at the temperatures from 273.15 to 773.15°K and pressures of ≤ 5 atm, making use of the results of Gordon's calculations [1800] that were carried out allowing for the centrifugal stress of the molecules according to Wilson's method [4287]. McCullogh et al. [2699]

measured the specific heat of water vapor in the pressure interval 0.125 atm at t mperatures from 361 to 487°K (with an error not exceeding 0.2%). The values of C_p, found in paper [2699] and extrapolated to the zero pressure, coincided with the $C°_p$ values calculated from the molecular constants.

TABLE 44

Results of Calculations of Thermodynamic Functions of H_2O

T,°K	Φ_T°, кал/моль·град A					
	B Настоящий Справочник	C Уагман и др. [4122]	D Хафф и др. [2142]	Справочник Бюро стандартов США E [3680]	F Фридман и Хар [1615]	G Первое издание Справочника
298,15	37,167	37,172	37,165	37,165	—	37,173
1000	47,023	47,018	47,0100	47,010	47,0157	47,023
2000	53,392	53,38	53,3643	53,322	53,3644	53,383
3000	57,624	57,59	57,5341	57,47	57,5048	57,606
4000	60,892	—	60,7093	60,70	60,7877	60,863
5000	63,583	—	63,2876	63,31	63,4195	63,542
6000	65,885	—	65,4566	—	—	65,841

T, °K	S_T°, кал/моль·град A						
	B Настоящий Справочник	C Уагман и др. [4122]	D Хафф и др. [2142]	E Справочник Бюро стандартов США [3680]	F Фридман и Хар [1615]	G Первое издание Справочника	H Фиккетт и Кауан [1555, 1556]
298,15	45,108	45,106	45,106	45,106	—	45,108	—
1000	55,614	55,598	55,6180	55,618	55,5919	55,607	—
2000	63,314	63,26	63,2010	63,137	63,2343	63,287	—
3000	68,594	68,45	68,2661	68,19	68,4209	68,542	—
4000	72,640	—	72,0420	72,04	72,3307	72,326	—
5000	75,951	—	75,0359	75,08	75,4588	75,454	75,083
6000	78,787	—	77,5175	—	—	78,742	—
8000	83,598	—	—	—	—	—	81,710
12000	91,376	—	—	—	—	—	87,636

A) cal/mole·degree;
B) the present Handbook;
C) Wagman et al.;
D) Huff et all.;
E) Handbook of the U.S. Bureau of Standards;
F) Friedman and Haar;
G) first edition of the Handbook;
H) Fickett and Cowan

Investigations of the thermodynamic equilibria of hydrogen-oxygen mixtures were carried out by means of explosions in a spherical bomb

within the temperature range of 2100 to 2800°K [3242-3244,832, 432, 4306, 4307, 2601, 282, 1551]. The values of enthalpy and the mean specific heat of water vapor in the cited temperature range have been calculated by these data. The allowance for the heat loss is the main difficulty in these calculations. The heat loss was taken into account by Fenning and Wiffin [1551] and Medvedev [295, 297]. Medvedev's calculations showed that the thermodynamic functions of H_2O, based on the data of the explosion method, conform to the values calculated by means of the molecular constants, but they are less accurate.

HDO, D_2O, HTO, DTO, T_2O. The thermodynamic functions of the gaseous HDO, D_2O, HTO, DTO and T_2O, quoted in the Tables 23, 22, 32, 33 and 31 of the second volume of the Handbook, are calculated for the temperature range from 293.15 to 6000°K with allowance for the anharmonicity of the vibrations, the vibrational-rotational interaction, and the centrifugal stress of the corresponding molecules. The calculations are carried out by the Gordon method (Eqs.(II. 185) and (II. 186) on the basis of the molecular constants quoted in the Tables 35, 36 and 37. The expression by Stripp and Kirkwood (II.176a) for the partition function of the rotational levels was used in the calculations, and the centrifugal stress of the molecules was taken into account by the generalized Wilson's formula (II.221) in which the same values are accepted for the constants ρ_1 and ρ_2, as in the calculation of the thermodynamic functions of H_2O.* The values of the constants in the Eqs. (II.185)-(II.186), accepted for the calculation of the thermodynamic functions of HDO, D_2O, HTO, DTO, and T_2O, are quoted in Table 45.

The errors in the values of the thermodynamic functions of HDO, D_2O, HTO, DTO and T_2O, quoted in the Tables of the 2nd volume of the Handbook, are at $T < 3000$ °K caused mainly by the inaccuracy of the ac-

cepted values of physical and molecular constants. At high temperatures, additional errors are caused by using the approximate method of calculation, in which the necessity of limiting the number of levels of the rotational energy was not taken into account, and the number of levels of vibrational energy was limited with an insufficient accuracy. The total errors in the Φ_T^* values of these compounds are estimated as equal to 0.01; 0.05 and 0.15 cal/mole·degree for the temperatures of 298.15, 3000 and 6000° , respectively.

TABLE 45

Values of the Constants for the Calculation of the Thermodynamic Functions of HDO, D_2O, HTO, DTO, and T_2O.

Постоянная A	HDO	D_2O	HTO	DTO	T_2O
θ_1, *град* B	4040,47	3907,15	3389,42	3380,94	3259,66
θ_2, *град* B	2051,71	1722,59	1947,98	1589,17	1451,97
θ_3, *град* B	5571,20	4083,31	5571,73	4062,31	3457,66
x_1	0,014782	0,008079	0,012395	0,012337	0,006705
x_2	0,008345	0,007901	0,007910	0,006428	0,006639
x_3	0,021265	0,008805	0,021250	0,015478	0,007411
y_{12}:T, *град* B	24,431	12,618	19,428	15,769	8,8342
y_{13}·T, *град* B	18,575	123,39	15,568	11,309	86,687
y_{23}·T, *град* B	28,891	1[illegible],632	27,395	16,258	10,402
C_0', *град* B	3,076	2,323	2,402	1,908	1,604
ρ_1, *град*$^{-1}$ B	$2,24\cdot10^{-5}$	$2,24\cdot10^{-5}$	$2,24\cdot10^{-5}$	$2,24\cdot10^{-5}$	$2,24\cdot10^{-5}$
ρ_2, *град*$^{-2}$ B	$0,36\cdot10^{-8}$	$0,36\cdot10^{-8}$	$0,36\cdot10^{-8}$	$0,36\cdot10^{-8}$	$0,36\cdot10^{-8}$
$q_0\cdot T^{-5/2}$, *град*$^{-5/2}$	0,027793	0,044119	0,037577	0,058697	0,075729
a_1 B	0,024898	0,022506	0,018594	0,023572	0,018561
a_2	−0,040997	−0,038284	−0,037540	−0,032033	−0,031265
a_3	0,030799	0,027698	0,033908	0,020051	0,023218
b_{11}	0,000532	0,000[illegible]4	0,000303	0,000474	0,000288
b_{12}	0,002415	0,002214	0,001996	0,001479	0,001472
b_{22}	0,001062	0,000734	0,001238	0,000455	0,000549
c_{12}	−0,001518	−0,001461	−0,001012	−0,001135	−0,000964
c_{13}	0,001151	0,001057	0,000921	0,000716	0,000723
c_{23}	−0,002986	−0,002491	−0,002839	−0,001540	−0,001676
A_Φ, *кал/моль·град* C	1,4970	1,6507	1,6500	1,7962	1,9349
A_S, *кал/моль·град* C	6,4651	6,6188	6,6181	6,7643	6,9030

A) Constants; B) degree; C) cal/mole·degree.

Earlier, the thermodynamic functions of gaseous HDO, D_2O, HTO, DTO, and T_2O were calculated on the basis of the molecular constants

by Libby [2607] (Φ_T^* from 298.15 to 773.15°K), Friedman and Haar [1615] (from 270 to 5000°K), and during the compilation of the first edition of the present Handbook [from 293.15 to 6000°K). These calculations differ significantly from each other and from the calculations carried out for the present edition of the Handbook, both as to the chosen molecular constants and as to the methodics. The calculations, carried out by Libby and in the first edition of the Handbook, were based on the molecular constants of D_2O, obtained by Darling and Dennison [1263] and on the molecular constants of HDO, HTO, DTO and T_2O calculated by Libby [2607]. Libby carried out the calculations in the harmonic oscillator-rigid rotator model approximation, and in the first edition of the Handbook, the thermodynamic functions were made by Gordon's method, taking into account the centrifugal stress of the molecules by Wilson's method. Later on, it was shown in paper [440] (see page 379) that the values of the anharmonicity constants of HDO, HTO and DTO accepted in Libby's paper and in the first edition of the Handbook were erroneous. In this paper, the values of the other molecular constants of these compounds and of D_2O and T_2O are improved. Thus, the thermodynamic functions of HDO, D_2O, HTO, DTO and T_2O were calculated anew for the present edition of the Handbook.

The differences in the accepted values of the molecular constants and some differences in the calculation methodics,* caused differences in the values of the thermodynamic functions of HDO, D_2O, HTO, DTO and T_2O quoted in the first and in the present edition of the Handbook. These differences are relatively low at T < 2000°K, but increase significantly at higher temperatures amounting to 0.23 cal/mole·degree for Φ_{6000}^* and ~0.75 cal/mole·degree for S_{6000}°.

Friedman and Haar [1615] carried out the calculation of the thermodynamic functions of HDO, D_2O, HTO and T_2O on the basis of molecu-

cular constants similar to those accepted in the present Handbook, but using the less accurate method of Mayer and Goeppert-Mayer. This explains the great divergences between the values of the thermodynamic functions of HDO, D_2O, HTO, DTO and T_2O obtained in paper [1615] and in the present edition of the Handbook. The differences are approximately equal to 0.02 and 0.3; 0.1 and 0.9 cal/mole·degree for the values of Φ^*_{1500} and Φ^*_{5000}, S°_{1500} and S°_{5000}, respectively.

Long and Kemp [2641] measured the specific heat of D_2O from 15 to 298°K and calculated $S^\circ_{298.15}(D_2O, \text{gas})$ by means of the obtained data. The difference between the values of $S^\circ_{298.15}(D_2O, \text{gas})$ found in paper [2641] and those calculated by the molecular constants is equal to $R \ln 3/2 = 0.802$ cal/mole·degree and conforms to the theoretical suggestions by Pauling [3201] with regard to the structure of ice.

H_2O_2. The thermodynamic functions of gaseous hydrogen peroxide, quoted in Table 16(II), were calculated for temperatures from 293.15 to 6000°K in the rigid rotator-harmonic oscillator model approximation using the Eqs. (II.243)-(II.244) in which the components $R \ln \Sigma$, $R(\rho_1 T \Gamma 2.5\rho_2 T^2)$, $R(2\rho_1 T + 7.5\rho_2 T^2)$, $R(\ln \Sigma + T\, d \ln \Sigma/dT)$, $\Delta\Phi^*_{el}$ and ΔS_{el} were assumed as being equal to zero, and the components of the internal rotation $\Phi^*_{vn.vr}$ and $S_{vn.vr}$ were found by means of Eqs.(II.236) and (II.237). The values of ϑ_i, C'_Φ, C'_S (see Table 46), necessary for the calculation by means of Eqs. (II.243)-(II.244), were calculated on the basis of the molecular constants of H_2O_2 quoted in Table 38. The values of $\Phi^*_{sv.vr} - \Phi^*_{vn.vr}$ and $S_{sv.vr} - S_{vn.vr}$ in Eqs.(II.236) -(II.237) were found by using the Tables of Pitzer and Gwinn [3259] and the arguments $1/Q_{sv.vr} = 8.584/\sqrt{T}$ and $V_0/RT = 2225/T$. Calculating $Q_{sv.vr}$ by Eq. (II.231), it was assumed $n = 2$, and $\Sigma_i = 1$ was assumed in the Eqs. (II.236)-(II.237).

The errors in the values of the thermodynamic functions of H_2O_2,

quoted in Table 16(II), are at temperatures below 1000°K caused mainly by the inaccuracy of the accepted value of the potential barrier V_0 of the internal rotation, and at higher temperatures by neglecting the centrifugal stress and the vibrational-rotational interaction. Moreover, a noticeable error in the values of the thermodynamic functions of H_2O_2 was caused throughout the whole temperature range by the inaccuracy of the accepted structural parameters and fundamental frequencies of the molecule. The total error of the values of Φ_T^* is estimated as equal to 0.20, 0.75 and 1.50 cal/mole·degree at 298.15, 3000 and 6000°K, respectively.

The thermodynamic functions of gaseous hydrogen peroxide were calculated earlier by Zeise [4382], Mickley [2898], Giguere [1728], Giguere, Liu, Dugdale and Morrison [1737] and Giguere and Liu [1736]. All these authors carried out calculations in the temperature range from 298.15 to 1500°K in the rigid rotator-harmonic oscillator model approximation, taking into account the retarded internal rotation of the H_2O_2 molecule using the tables of Pitzer and Gwinn [3259]. The values of the thermodynamic functions of H_2O_2, cited in the papers mentioned above, differ significantly from one another (up to 1.4 cal/ /mole·degree); a fact which is mainly caused by differences in the functions which approximate the potential curve of the retarded internal rotation, and also by differences in the accepted values of the molecular constants of H_2O_2.

Zeise [4382] used a cosinusoidal form of the potential curve with n = 2 for the calculation of the thermodynamic functions of H_2O_2; he accepted the quantity V_0 as equal to 6000 cal/mole corresponding to the theoretical calculations of Penney and Sutherland [3219], and he calculated the moments of inertia on the basis of the underestimated value r_{O-O} = 1.4 A. This explains the fact that the Φ_T^* and S_T° values

given in the paper [4382] are by 0.4 cal/mole·degree lower than those calculated in the present Handbook. The thermodynamic functions of H_2O_2, calculated by Zeise, served as a basis for the compilation of the tables in the Handbook [4384] and in the paper [3426].

The calculations of thermodynamic functions of H_2O_2, carried out by Mickley [2898], are based on an incorrect interpretation of the vibrational spectrum of H_2O_2, proposed by Bailey and Gordon [616], and are, therefore, erroneous. Also incorrect are the values of thermodynamic functions of H_2O_2 calculated by Giguere [1728], who, assuming $\sigma = 2$ and $n = 2$, did not allow for the correcting term $R \ln n/\sigma_i$ in the equations for the calculation of Φ_T^* and S_T° [see Eqs. (II.236) and (II.237)].

Giguere, Liu, Dugdale and Morrison [1737] calculated the thermodynamic functions of H_2O_2 approximating the potential curve by a cosine function with one minimum ($r = 1$), and assuming $V_0 = 3500$ cal/mole. The difference between the Φ_T^* values at T = 298.15; 1000 and 1500°K quoted in the paper [1737] and in Table 16(II) amounts to 0.62; 0.01 and 0.07 cal/mole·degree, respectively. The great discrepancies at low temperatures are caused by the fact that the approximation of the potential curve by a function with one minimum very approximately describes the lower part of the potential curve (see Fig.8), the form of which significantly effects the values of the thermodynamic functions at these temperatures.

Later on, Giguere and Liu [1736] repeated the calculation of the thermodynamic functions of H_2O_2, assuming $n = 2$ in the same manner as was done in the present Handbook. The small differences in the values of the thermodynamic functions quoted in the paper [1736] and in Table 16(II) are caused mainly by some differences in the accepted values of the molecular constants.

D_2O_2, HDO_2. The thermodynamic functions of D_2O_2 and HDO_2, quoted in Tables 24(II) and 25(II) respectively, were calculated for temperatures from 293.15 to 6000°K in the rigid rotator-harmonic oscillator model approximation using the Eqs. (II.243)-(II.244) in which the components R ln Σ, $R(\rho_1 T + 2.5_{\rho_2} T^2)$, $\Delta\Phi^*_{el}$, $R(\ln \Sigma + T\, d\ln\Sigma/dT)$, $R(2_{\rho_1} T + 7.5_{\rho_2} T^2)$ and ΔS_{el} were accepted as being equal to zero, and the components of the internal rotation $\Phi^*_{vn.vr}$ and $S_{vn.vr}$ were found from (II.236) and (II.237). The values of θ_1, C'_Φ and C'_S (see Table 46) necessary for the calculation by means of Eqs. (II.243)-(II.244) were calculated on the basis of the molecular constants of D_2O_2 and HDO_2, cited in Table 38. The quantities $(\Phi^*_{sv.vr} - \Phi^*_{vn.vr})$ and $(S_{sv.vr} - S_{vn.vr})$ in the Eqs.(II.236) and (II.237) are found using the tables of Pitzer and Gwinn [3259] and the arguments $V_0/RT = 2225/T$; $1/Q_{sv.vr} = 6.317/\sqrt{T}$ and $7.179/\sqrt{T}$ for D_2O_2 and HDO_2, respectively. Calculaging $Q_{sv.vr}$ by Eq.(II.231), it was assumed n = 2, and, therefore, $\sigma_i = 1$ was accepted in the Eqs. (II.236)-(II.237).

The errors in the values of thermodynamic functions quoted in Tables 24(II) and 25(II) were caused by the same sources of errors as were the corresponding calculations for H_2O_2. Thus, the same estimates as those for H_2O_2 (see page 421) may be assumed for the errors in the Φ^*_T values of these compounds at 298.15; 3000 and 6000°K.

Earlier, the thermodynamic functions of HDO_2 and D_2O_2 were calculated by the same method by Giguere and Liu [1736] for the temperatures from 298.15 to 1500°K. The difference between the corresponding values of the thermodynamic functions of HDO_2 and D_2O_2, quoted in the paper [1736] and in the Tables 24(II) and 25(II) is mainly caused by a certain difference in the accepted values of the molecular constants.

HO_2. The thermodynamic functions of hydrosuperoxyl, quoted in Table 14(II), were calculated by Eqs. (II.243) and (II.244) for temperatures from 293.15 to 6000°K. The calculation was carried out in

rigid rotator-harmonic oscillator model approximation. The values of θ_i, used for the calculation of the vibrational components of the thermodynamic functions, and the constants C_Φ' and C_S', accepted for the calculation of the components of translational motion and of the rigid rotator are given in Table 46. Owing to the fact that the HO_2 molecule must have a doublet electronic ground state, the addends R ln 2 are included into the values of C_Φ' and C_S'. The excited electronic states of HO_2 are not taken into account in the calculation of the thermodynamic functions of the hydrosuperoxyl.

TABLE 46

Values of the Constants for the Calculation of the Thermodynamic Functions of H_2O_2, D_2O_2, HDO_2 and HO_2.

A Вещество	θ_1	θ_2	θ_3	θ_4	θ_5	C_C'	C_S'
	B *град*					C *кал/моль·град*	
H_2O_2	5151	1899	1266	5194	1822	—0,0071	7,9420
D_2O_2	3813	1396	1266	3829	1363	1,0052	8,9543
HDO_2	5172	1856	1266	3820	1381	1,9452	9,8943
HO_2	5180	1870	1295	—	—	1,7630	9,7121

A) Substance; B) degree; C) cal/mole·degree.

The main errors in the values of thermodynamic functions quoted in Table 14(II) were caused by the lack of reliable data on the constants of the HO_2 molecule (see page 392), by the neglect of the anharmonicity of the vibrations, as well as of the vibrational-rotational interaction and the centrifugal stress in the calculation of the thermodynamic functions, and also by neglect of excited electronic states of HO_2. The errors of the calculated Φ_T^* values amount to 0.3; 1.2 and 2 cal/mole·degree at 298.15; 3000 and 6000°K.

Other calculations of thermodynamic functions of hydrosuperoxyl have not been published.

OH. The thermodynamic functions of OH, quoted in Table 11(II), were calculated by Eqs. (II.34) and (II.35) for temperatures from 293.15 to 20,000°K. Only the electronic states $X^2\Pi_i$, $A^2\Sigma^+$ and $B^2\Sigma^+$ of the OH molecule are taken into account in the calculation; the $C^2\Sigma^+$ state, having an excitation energy of about 90,000 cm^{-1}, was neglected because the contribution of this state to the thermodynamic functions is negligible up to 20,000°K (it amounts to ~0.001 cal/mole·degree in the $\Phi^*_{20,000}$ value).

The calculation of the values of $Q_{kol.vr}$ and $T\,\partial Q_{kol.vr}/\partial T$ in Eqs. (II.28) and (II.29) was carried out for each of the three states by a BESM. Programming the electronic computer, the levels of the vibrational and rotational energy are given by equations with constants quoted in Table 41, with exclusion of the vibrational energy levels of the ground state with quantum numbers v = 0-9, for which the experimental values of $G_0(v)$ quoted in Table 40 are programmed. The levels of the rotational energy of OH in the $X^2\Pi_i$ state were calculated by the Hill and Van Vleck Eq. (1.25) with separate summation over the levels of the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ substates. The multiplicity of the excited $A^2\Sigma^+$ and $B^2\Sigma^+$ states was taken into account by the factor 2 in the expression for $Q^{(i)}_{kol.vr}$, as the splitting of the energy levels is negligible. J_{max} as a function of $\underline{v}$ is given in Fig. 9 for each state. A_Φ = 1.16336 and A_S = 6.13156 cal/mole·degree are accepted for the calculation of the translational components of the thermodynamic functions.

The error of the values of thermodynamic functions of OH, calculated in this way, amounts to approximately 0.01 cal/mole·degree at T < 12,000°K. It is caused mainly by the inaccuracy of the physical constants. At T > 12,000°K, the inaccuracy of the determination of the rotational energy levels with great J values by the equations with the accepted constant values begins to play a part. In particular, the ne-

glect of the rotational constant H_e in the ground state of the OH molecule manifests itself. This causes a total error of the order of 0.1 cal/mole·degree in the $\Phi^*_{20,000}$ value. Owing to the fact that the excited electronic states of OH possess relatively high excitation energies, and the levels of the vibrational energy of OH in these states are determined experimentally up to the convergence limit, the error caused in the calculation by the inaccuracy of the molecular constants of the excited states is insignificant.

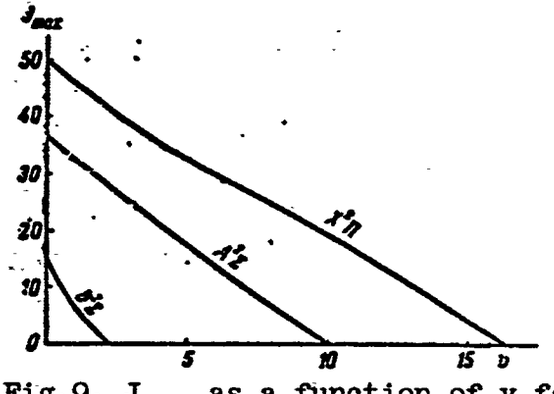


Fig.9. J_{max} as a function of $\underline{v}$ for the electronic states $X^2\Pi_i$, $A^2\Sigma^+$ and $B^2\Sigma^+$ of the OH molecule.

The first table of the thermodynamic functions of OH up to 5000°K was compiled by Johnston and Dawsey in 1933 [2275] on the basis of a calculation by immediate summation over the vibrational and rotational energy levels of the $X^2\Pi_i$ and $A^2\Sigma^+$ electronic states, using recurrence formulas. The recalculation of this table for the new values of the physical constants (as it was made, obviously, in the Handbooks [3680, 3507, 2142, 3426]) leads to values of the thermodynamic functions of OH conforming to the corresponding values of Table 11(II) within the limits of some thousandths of cal/mole·degree. The calculation of the thermodynamic functions of OH up to 5000°K was carried out also by Haar and Friedman [1910] on an electronic computer.

The differences between the values of the thermodynamic functions of OH in Table 11(II) and the calculation results by Haar and Friedman increase with rising temperatures and amount to 0.028 cal/mole·degree in the Φ^*_{5000} value. This is explained mainly by the fact that Haar and Friedman based their calculation on the Mayer and Goeppert-Mayer method (see page 159) which leads to incorrect results at high temperatures. In the first edition of the Handbook, the calculation of the thermodynamic functions of OH was carried out by the tabular method of Gordon and Barnes up to 6000°K. The differences in the Φ^*_T values of the hydroxyl in the first and the present editions of the Handbook do not exceed 0.004 cal/mole·degree.

After the calculations for the present Handbook were finished, the paper by Baumann [688] was published dealing with the calcu ation of the partition function of the intermolecular states of the OH molecule. Baumann [688] developed a new equation (in the same manner as it is used in the present Handbook) for the vibrational levels converging to the dissociation limit, calculating the values of v_{max} and J_{max} for each $\underline{v}$ using the potential function of Gulbert and Hirschfelder, and calculating Φ^*_T/R by immediate summation on an electronic computer for the temperatures of 2000, 5000, 6000 and 10,000°K. The results obtained by Baumann confirm admirably to the values of thermodynamic functions of OH quoted in the present Handbook (the divergence in Φ^*_T amounts to 0.008 cal/mole·degree at 10,000°K).

OD, OT. The thermodynamic functions of deuteroxyl and tritoxyl, quoted in Tables 21(II) and 30(II) for temperatures from 293.15 to 6000°K, were calculated by Eqs.(II.161) and (II.162) using the molecular constants of OD and OT accepted in Table 42. The values of $\ln\Sigma$ and $T\,\partial/\partial T$ in these equations were calculated by the Gordon and Barnes method (the Eqs.(II.137) and (II.138); the values of $\ln\Delta_M$ and

$T\,\partial/\partial T\,\ln\Delta_M$ were calculated using the relations obtained by Khachkuruzov and Brounshteyn for diatomic gases, the molecules of which are in the $^2\Pi$ state (see Eqs. (II.149) and (II.150)). A correction for the limited summation over J in Eqs. (II.137) and (II.138) was not taken into account. The components of the first excited electronic state $A^2\Sigma$ of the OT and OD molecules were taken into account by means of Eqs. (II.120) and (II.121), i.e., without differentiating between the constants of the ground and the excited state. The values of C_Φ, C_S, θ and $\underline{x}$ and also of the constants in Eqs. (II.137) and (II.138), accepted in the calculation of the thermodynamic functions of OD and OT, are quoted in Table 47.

TABLE 47

Values of the Constants for the Calculation of the Thermodynamic Functions of OD, OT and OH^-

A Вещество	B Состояние	θ	$x\cdot10^2$	$\beta_1\cdot10^3$	$\beta_2\cdot10^4$	$\frac{q_0}{T}$	$\frac{d_0\,10^4}{T}$	C_Φ	C_S
		град C	—	—	—	C град$^{-1}$		D кал/моль·град	
OD	$X^2\Pi_i$	3914,0	16,245	2,9834	9,80	0,070447	5,96	—1,1810	5,7749
OT	$X^2\Pi_i$	3386,2	13,66	2,502	5,5	0,09968	6,00	1,4970[a]	6,4649[a]
OH^-	$X^1\Sigma$	6042,92	—	—	—	—	—	—5,6099	1,3456

a) The values of A_Φ and A_S, respectively, are given. A) Substance; B) state; C) degree; D) cal/mole·degree.

The errors in the values of the thermodynamic functions of OD and OT are caused at $T < 4000°K$ mainly by the inaccuracy of the accepted values of the molecular constants. At higher temperatures, the errors in the thermodynamic functions of OD and OT, quoted in Tables 21(II) and 30(II) increase owing mainly to the lack of a limited summation over J in the calculations. The errors in the Φ_T^* values of deuteroxyl and tritoxyl are estimated as 0.003; 0.015 and 0.04 cal/mole·degree at 298.15; 3000 and 6000°K, respectively.

The thermodynamic functions of OD were calculated for the first time by McDonald [2700] in the harmonic oscillator-rigid rotator model approximation (Φ_T^* for T = 1000-3000°K). Haar and Friedman [1910] calculated the thermodynamic functions of OD and OT within 250-5000°K using a method similar to the Mayer and Goeppert-Mayer method [285].

The Φ_T^* values of deuteroxyl, obtained by McDonald for 1000 and 3000°K, differ from the corresponding values in Table 21(II) by 0.08 and 0.30 cal/mole·degree owing to the neglect of the anharmonicity of the vibrations of OD and other simplifications in the calculations in [2700]. The differences between the values of the thermodynamic functions of OD and OT quoted in the paper by Haar and Friedman [1910] and in the present Handbook are at T < 3000°K essentially lower. These differences increase at rising temperatures and attain 0.011 and 0.072 cal/mole·degree in the values of Φ_{5000}^* and S_{5000}°, respectively, owing to the inaccuracy of the Mayer and Goeppert-Mayer method.

OH^+. The thermodynamic functions of the gas consisting of OH^+ ions and quoted in Table 12(II) were calculated by Eqs. (II.34) and (II.35) in the temperature range from 293.15 to 20,000°K, using the molecular constants accepted in Table 43. The calculation of the values of $Q_{kol.vr}^{(X)}$ and $T\,\partial/\partial T\, Q_{kol.vr}^{(X)}$ for the electronic ground state $X^3\Sigma$ was carried out on an electronic computer* by immediate summation over the levels of the vibrational and rotational energy, programmed by means of the corresponding equations, and taking into account finite values of $\underline{v}$ and J. As an approximate calculation has shown, the allowance for the multiplet splitting of the rotational levels in the electronic ground state of OH^+ by means of the accepted values of the quantities ε and γ (see Table 43) leads even at room temperature to almost the same results as when the splitting is neglected. Thus, the multiplicity of the $X^3\Sigma^+$ state was taken into account by introduction of

the statistical weight of 3 into the expression for $Q^{(X)}_{kol.vr}$.

The $A^3\Pi$ state was taken into account in the calculation by Eqs. (II.120) and (II.121), i.e., the difference between the vibrational and rotational constants of the $X^3\Sigma^-$ and $A^3\Pi$, states were neglected, thus causing noticeable errors above 10,000°K. However, the magnitudes of these errors are unimportant in comparison with the total error of the thermodynamic functions of OH^+ at these temperatures.

The constants A_Φ and A_S are accepted as being equal to 1.16336 and 6.13156 cal/mole·degree, respectively, in the calculation of the translational components of the thermodynamic functions of OH^+.

As it was shown in §30, the molecular constants of OH^+ contain noticeable errors owing to the difficulties in determining the zero lines of the bands and also owing to the insufficient number of investigated vibrational levels. The uncertainties in the values of the thermodynamic functions of OH^+, caused by these errors, increase rapidly with rising temperatures. Taking also into account the uncertainty caused by the lack of data on excited electronic states (see page 407), the total uncertainty of Φ^*_T may amount to 0.03 cal/mole·degree at 3000°K and to 1.0 cal/mole·degree at 20,000°K.

Information on other calculations of the thermodynamic functions of OH^+ is missing in literature.

OH^-. The thermodynamic functions of the negative hydroxyl ion, quoted in Table 13(II), were calculated by Eqs. (II.161) and (II.162) in the rigid rotator-harmonic oscillator model approximation, using the molecular constants of OH^- accepted in Table 43. The values of the constants C_Φ and C_S in the formulas for the calculation of the thermodynamic functions of OH^- and also the values of θ are quoted in Table 47.

The uncertainties of the calculated values of thermodynamic func-

tions of OH^- are caused by the inaccuracy of the accepted values of molecular constants and the approximate character of the calculation. They amount to 0.05; 0.15 and 0.25 cal/mole·degree in the Φ_T^* values for 298.15; 3000 and 6000°K, respectively.

Information on other calculations of the thermodynamic functions of OH^- is missing in literature.

§32. THERMOCHEMICAL QUANTITIES

The difference between the thermochemical quantities of compounds of the natural isotopic mixture of hydrogen and of the protium compounds is not taken into account in this section because this difference is significantly smaller than the uncertainties of the quantities in question.

H_2O (gas). A thorough analysis of the results of calorimetric measurements of the heat of combustion of hydrogen in oxygen, carried out up to 1931, is given in the papers by Bichowsky and Rossini [813] and Rossini [3491].

The most accurate measurement of the heat of formation of liquid water was carried out by Rossini [3491]. The quantity $\Delta H°f_{298.15}$ (H_2O liqu.) = -68.313 ± 0.010 kcal/mole, found in the paper [3491], was subsequently improved by Rossini [3499, 4122] taking into account the nonideality of the investigated system and improving the values of the atomic weights and physical constants. The value of $\Delta H°f_{298.15}$ (H_2O, liqui) = -68.317 ± 0.010 kcal/mole obtained by Rossini in [4122] was accepted in the Handbook of the U. S. Bureau of Standards [3508]. The most accurate value of the heat of evaporation of water, $\Delta H°v_{298.15}$ (H_2O, liqu.) = 10,519 ± 0.002 kcal/mole, was found by Osborne, Stimson and Ginnings [3149].

The value of the heat of formation of water vapor accepted in the present Handbook is based on the values of heat of formation of liquid

water and its heat of evapo.ation, cited above:

$$\Delta H^{\circ}f_{298.15}\ (H_2O,\ gas) = -57{,}798 \pm 0{,}010\ \text{kcal/mole},$$

The value of the dissociation energy, corresponding to this value, is equal to

$$D_0(H_2O) = 219{,}361 \pm 0{,}035\ \text{kcal/mole}.$$

D_2O (gas). Flood an Tronstad [1568] determined for the first time in 1935 the ratio between the heats of formation of D_2O (liqu.) and H_2O (liqu.) by measuring the heat of explosion of $D_2 + O_2$ and $H_2 + O_2$ mixtures in a calorimetric bomb. Flood and Tronstad found that this ratio is equal to 1.027 ± 0.003 at 298.15°K.

Rossini, Knolton and Johnston [3506] also determined the ratio of the heats of formation of D_2O (liqu.) and H_2O (liqu.) combusting hydrogen and deuterium in an oxygen flow at constant pressure. A value equal to 1.03068 ± 0.00029 was found as the result of the measurements carried out. Using the value of formation of H_2O (liqui.' accepted in the present Handbook and the ratio of the heats of formation of D_2O and H_2O, obtained by Rossini, Knowlton and Johnston, we find: $\Delta H^{\circ}f_{298.15}$ (D_2O, liqu.) = -70.413 ± 0.023 kcal/mole.

In the paper [3506], besides the ratio of the heats of formation of D_2O and H_2O, the ratio of the heats of evaporation of D_2O and H_2O was also found, equal to 1.03145 ± 0.00075 at 298.15°K, the value of which -together with the cited value of the heat of evaporation of H_2O - leads to the value $\Delta H^{\circ}v_{298.15}$ (D_2O) = 10.850 ± 0.009 kcal/mole.

The value of the heat of formation of gaseous deuterium oside, based on the results of the calorimetric measurements in [3506],

$$\Delta H^{\circ}f_{298.15}(D_2O,\ gas) = -59{,}563 \pm 0{,}025\ \text{kcal/mole},$$

is accepted in the present Handbook. The energy of dissociation, corresponding to this value, is

$$D_0(D_2O) = 222{,}911 \pm 0{,}040 \text{ kcal/mole},$$

and corresponds excellently to the value of 222.925 ± 0.037 kcal/mole, calculated by Eqs.(IV.17) on the basis of the values of $D_0(H_2O)$ and the vibrational constants of H_2O and D_2O, accepted in the Handbook.

HDO (gas), HTO (gas), DTO (gas), T_2O (gas). The heats of formation of HDO, HTO, DTO and T_2O have not been determined experimentally. We give below the values of the dissociation energies of these compounds calculated by Eqs. (IV.17) using the accepted values of $D_0(H_2O)$ and the vibrational constants of H_2O, HDO, HTO, DTO and T_2O:

$$D_0(HDO) = 221{,}083 \pm 0{,}040 \text{ kcal/mole},$$
$$D_0(HTO) = 221{,}833 \pm 0{,}040 \text{ kcal/mole},$$
$$D_0(DTO) = 223{,}672 \pm 0{,}040 \text{ kcal/mole},$$
$$D_0(T_2O) = 224{,}469 \pm 0{,}040 \text{ kcal/mole}:$$

These values of the dissociation energies are accepted in the present Handbook. The following values of heats of formation correspond to them:

$$\Delta H°f_0(HDO, \text{ gas}) = -57{,}927 \pm 0{,}050 \text{ kcal/mole},$$
$$\Delta H°f_0(HTO, \text{ gas}) = -58{,}276 \pm 0{,}050 \text{ kcal/mole},$$
$$\Delta H°f_0(DTO, \text{ gas}) = -59{,}210 \pm 0{,}050 \text{ kcal/mole},$$
$$\Delta H°f_0(T_2O, \text{ gas}) = -59{,}606 \pm 0{,}050 \text{ kcal/mole}.$$

H_2O_2 (gas), D_2O_2 (gas), HDO_2 (gas). The results of measurements of the heat of formation of liquid hydrogen peroxide, obtained in earlier papers [1536, 1537, 3980, 3981, 774, 782, 783, 1581, 2504, 1992] are insufficiently accurate. The most accurate values of the heat of formation of hydrogen peroxide were obtained by measuring the heat of decomposition of liquid H_2O_2.* Matheson and Maas [2802] measured the heat of decomposition of 97.15 and 38.05% solutions of hydrogen peroxide and calculated on the basis of these measurements the heat of decomposition of a 100% hydrogen peroxide as equal to ΔH_{293} = -23.45 kcal/mole. Roth, Grau and Meichsner [3527] obtained by the same method the value ΔH_{293} = -23.48 kcal/mole, practically coincident with the

foregoing value. Fontana [1579] measured the heat of decomposition of a diluted hydrogen peroxide solution ($H_2O_2 \cdot 8880\ H_2O$) and obtained a value which proves the measuring results of Roth et al. [3527]. On the basis of measurement data cited in the papers [2802, 3527], Giguere [1728] recommended the value $\Delta H_{293} = -23.47$ kcal/mole. A significantly different value, $\Delta H_{298} = -24.3$ kcal/mole, was obtained by Medard [2834]. However, the details of this experimental investigation and, therefore, the reliability of the value recommend by Medard, remain obscure.

Thorough investigations of the thermodynamic properties of hydrogen peroxide and deuterium peroxide including the determination of the heats of their formation were carried out by Giguere and coworkers [1728, 1573, 1737, 1736, 1738]. In the paper by Giguere, Morrissette, Olmos and Knop [1738], the heats of decomposition of pure H_2O_2 and D_2O_2 and of their solutions are measured. In the same paper, the heats of evaporation of the peroxides, the heats of their mixing with water and the specific heats of the solutions of the peroxides are measured. Thus, all data necessary for the calculation of the heats of formation of gaseous hydrogen and deuterium peroxide under standard conditions were obtained in one series of experiments. Moreover, in this paper the heats of decomposition not only of solutions but also of 100% peroxides were for the first time investigated. Giguere et al. [1738] obtained the following values for the heats of decomposition of liquid H_2O_2 and D_2O_2: -23.44 ± 0.02 kcal/mole and -23.41 ± 0.02 kcal/mole, to which correspond:

$$\Delta H^\circ f_{298.15}(H_2O_2,\ \text{liquid}) = -44{,}88 \pm 0{,}03 \text{ kcal/mole},$$
$$\Delta H^\circ f_{298.15}(D_2O_2,\ \text{liquid}) = -47{,}02 \pm 0{,}06 \text{ kcal/mole}.$$

The heats of evaporation of H_2O_2 and D_2O_2 at 298.15°K are, corresponding to [1738], equal to 12.34 ± 0.03 and 12.51 ± 0.05 kcal/mole,

respectively.

On the basis of these values, we obtain the following values for the heats of formation of gaseous peroxides H_2O_2 and D_2O_2:

$$\Delta H^\circ f_{298,15}(H_2O_2,\ gas) = -32{,}54 \pm 0{,}04 \text{ kcal/mole},$$
$$\Delta H^\circ f_{298,15}(D_2O_2,\ gas) = -34{,}51 \pm 0{,}08 \text{ kcal/mole},$$

which are accepted in the Handbook. To these values correspond

$$D_0(H_2O_2) = 252{,}282 \pm 0{,}07 \text{ kcal/mole},$$
$$D_0(D_2O_2) = 256{,}137 \pm 0{,}09 \text{ kcal/mole}.$$

The dissociation energy calculated by Eq. (IV.17), using the accepted values of $D_0(H_2O_2)$ and the vibrational constants of H_2O_2 and D_2O_2, is equal to 256.10 ± 0.20 kcal/mole, the value of which conforms admirably to the value accepted in the Handbook.

The value, accepted in the Handbook is

$$D_0(HDO_2) = 254{,}15 \pm 0{,}26 \text{ kcal/mole},$$

it was calculated by Eq. (IV.17) using the accepted values of $D_0(H_2O_2)$ and the vibrational constants of H_2O_2 and HDO_2. The value of the heat of formation, which corresponds to it, is

$$\Delta H^\circ f_{298,15}(HDO_2,\ gas) = -32{,}007 \pm 0{,}28 \text{ kcal/mole}.$$

HO_2 (gas). Several authors made attempts to calculate the dissociation energy $D_0(H - O_2)$. The results of estimations of $D(H - O_2)$, carried out by various authors, are thoroughly analyzed in the papers by Walsh [4137] and Foner and Hudson [1575]. In the present Handbook, only the fundamental works dealing with this problem are discussed.

Bodenstein and Schenck [855], studying the reaction of chlorine with hydrogen in presence of oxygen, drew the conclusion that the retardation of this reaction was caused by the formation of the HO_2 radical, and they estimated the value of $D_0(H - O_2)$ as equal to 40 kcal/mole. Haber and Weiss [1914] found from the results of an investigation of the $Fe^{++} - Fe^{+++} - H_2O_2$ system, that $D_0(H - O_2) \cong 50$ kcal/mole.

Bray [913] estimated $D_0(H - O_2)$ as equal to 51 kcal/mole by comparison of HO_2 with HOCl.

Walsh [4137] carried out a thorough analysis of the estimated values of $D_0(H - O_2)$ and came to the conclusion that the dissociation energy of the $H - O_2$ bond must be significantly higher than 50 kcal/mole, the found using various data for halogens, O_2, H_2O, OH and H_2O_2, that $D_0(H - O_2)$ must be approximately equal to 60 kcal/mole.

Thus, the values of $D_0(H - O_2)$ estimated by various authors, lie within 40-60 kcal/mole.

In 1955 Foner and Hudson [1575] determined the potential of occurrence of the HO_2^+ ion from H_2O_2 (15.41 ± 0.1 ev) and the ionization potential of HO_2 (11.53 ± 0.1 ev). These investigators showed that in the case of the dissociative ionization of H_2O_2 the kinetic energy of the reaction products may be assumed as being equal to zero, and they calculated $D_0(H - HO_2) = 3.88$ ev = 89.5 kcal/mole. Using this value and the well known thermochemical data for H_2O_2 [3854], Foner and Hudson [1575] found $D_0(H - O_2) = 2.04 \pm 0.1$ ev = 47 ±2 kcal/mole and the later estimation by Robertson [3452] (46 ± 7 kcal/mole) based on the results of the ionization of H_2O_2 by electron impact,* conform admirably to this value. The calculation, based on the thermochemical data accepted in the present Handbook and on the value of $D_0(H - O_2)$ calculated by Foner and Hudson [1575] leads to the value

$$D_0(HO_2) = 165 \pm 3 \text{ kcal/mole},$$

which is accepted in the present Handbook. The value

$$\Delta H^\circ f_0(HO_2, g) = 4{,}606 \pm 3 \text{ kcal/mole}.$$

corresponds to the accepted value of the dissociation energy of HO_2.**

OH (gas). The dissociation energy of the hydroxyl was repeatedly determined by various methods. The results of the determination of this quantity, published up to 1950, are thoroughly analyzed by Dam-

kohler and Edse [1259, 1464]. However, new data has been obtained after the publication of these surveys, making it possible to determine the value of $D_0(OH)$ with much greater accuracy. A short review of the values of $D_0(OH)$, obtained by various authors up to 1960, is given in Table 48.

The most accurate results, obtained by investigations of the photolysis of water vapor under the effect of excited mercury atoms, were reported in the paper by Richemeier, Senftleben and Pastorff [3439]. Damkohler and Edse [1259, 1464] showed that the data quoted in paper [3439] allows the determination of the upper limit of the possible values of the dissociation energy of hydroxyl as being equal to 104.8 kcal/mole, and found that the lower limit $D_0(OH)$ is 101.8 kcal/mole, may be determined on the basis of the results of investigation of the photochemical dissociation of hydrogen peroxide vapor [4039].

In the papers [4307, 282, 295, 299], the pressures of explosions of hydrogen-oxygen mixtures are measured. A comparison of the calculated values of the explosion pressures with the experimentally found values allows the determination of the thermal effect of the dissociation reaction $H_2O \rightarrow OH + 1/2H_2$. A deviation of the experimental conditions from the adiabatic ones in the works [4307, 282] resulted in overevaluated values of $D_0(OH)$ (see [295, 299]). In the works by Medvedev, Korobov and Baybuz [295, 299] the experiments were carried out under conditions which were similar to adiabatic ones, and it was found $D_0(OH) = 102.2 \pm 1.0$ kcal/mole.

Bonhoeffer and Reichardt [861], Avramenko and Kondrat'yev [59], Dwyer and Oldenberg [1433], and Purmal' and Frost [340] measured the intensity of the absorption spectrum of hydroxyl formed in the reaction $H_2O + 1/2O_2 = 2OH$, and calculated by means of Van'Hoff's isochore equation the thermal effect of this reaction. The work by Dwyer and Olden-

berg [1433], in which the value $D_0(OH) = 100.7 \pm 65$ kcal/mole was obtained, was for a long time reputed to be the most accurate one. Purmal' and Frost [340] allowed for the effect of the temperature gradient along the length of the reaction tube, which was an essential improvement on the results in comparison with the paper by Dwyer and Oldenberg [1433].

TABLE 48

Results of the Determination of the Dissociation Energy of Hydoxyl [a].

	A Авторы	B Год опубликования	C Метод определения	D $D_0(OH)$, ккал/моль
1	Зенфтлебен, Ререн [3683]	1926	Фотолиз паров воды под действием возбужденных атомов ртути [17]	~106
2	Гавиола, Вуд [1660]	1928	То же [18]	~99
3	Бонхёффер, Рейхард [861]	1928	Измерение концентрации OH, образующегося при реакции $H_2O + \frac{1}{2}O_2 = 2OH$, по спектрам поглощения [19]	103,3±2,5
4	Юри, Дауси, Райс [4039]	1929	Фотохимическая диссоциация перекиси водорода $H_2O_2 \rightleftarrows 2OH$ [20]	102,7±0,9
5	Бейтс [678]	1931	Экстраполяция уровней колебательной энергии OH по спектральным данным [21]	~117
6	Воль и Мага [4307]	1932	Метод взрыва [22]	103,7
7	Ричмейер, Зенфтлебен, Пасторф [3439]	1934	Фотолиз паров воды под действием возбужденных атомов ртути [17]	103,8±1,0[b]
8	Танака, Кояма [3924]	1934	Экстраполяция уровней колебательной энергии OH по спектральным данным [21]	103,9±6,4
9	Льюис, Эльбе [282]	1935	Метод взрыва [22]	104,7±1,0
10	Авраменко, Кондратьев [59]	1937	Измерение концентрации OH, образующегося при реакции $H_2O + \frac{1}{2}O_2 = 2OH$, по спектрам поглощения [19]	103,3±0,5
11	Дуайр, Олденберг [1433]	1944	То же [18]	100,7±0,65
12	Пурмаль и Фрост [340]	1952	» »	103,3±1,0
13	Гейдон [1668]	1953	Экстраполяция уровней колебательной энергии OH по спектральным данным [21]	103,0±4,5
14	Медведев Коробов, Байбуз [295, 299]	1954	Метод взрыва [22]	102,2±1,0
15	Хорнбек [2125]	1955	Экстраполяция уровней колебательной энергии OH по спектральным данным [21]	106,8
16	Барроу [645]	1956	То же [18]	101,36±0,3

a) The individual results contain corrections which take into account the values of the heat of formation of monatomic hydrogen and oxygen, accepted in the present Handbook.
b) Recalculated by Camkohler and Edse [1259, 1464].

A) Authors;
B) year of publication;
C) method of determination;
D) kcal/mole;
1) Senftleben, Rehren;
2) Gaviola, Wood;
3) Bonhoeffer, Reichardt;
4) Urey, Dawsey, Rice;
5) Bates;
6) Wohl and Magat
7) Richemeier, Senftleben, Pastoriff;
8) Tanaka, Koana;
9) Lewis, Elbe;
10) Avramenko, Kondrat'yev;
11) Dwyer, Oldenberg;
12) Purmal and Frost
13) Gaydon;
14) Medvedev, Korobov, Baybuz;
15) Hornbeck;
16) Barrowl
17) photolysis of water vapor under the effect of excited mercury atoms;
18) the same;
19) measurement of the concentration of OH formed in the reaction $H_2O + 1/2O_2 = 2OH$ on the basis of the absorption spectra;
20) photochemical dissociation of hydrogen peroxide $H_2O_2 \rightleftarrows 2OH$;
21) extrapolation of the levels of the vibrational energy on the basis of spectral data;
22) explosion method.

Till recently, no data was available in literature which allowed a sufficiently accurate extrapolation of the vibrational energy levels of hydroxyl and the calculation in this way, of its dissociation energy. This circumstance explains the low accuracy of the values obtained by means of extrapolation in the papers by Bates [678], Tanaka and Koana [3924] Gaydon [1668] and Hornbeck [2125].

In 1956 Barrow [652, 645] carried out a thorough investigation of the bands of the $B^2\Sigma^+ - A^2\Sigma^+$ system in the hydroxyl spectrum. He studied the transitions into the high vibrational levels of the $A^2\Sigma^+$ state with values of the vibrational quantum number $4 \leq v' \leq 9$. A short extrapolation (about 280 cm^{-1}) leads to a dissociation limit at $v'_{max} = 10$. Owing to the fact that the $A^2\Sigma^+$ state correlates with

$O(^1D) + H(^2S)$, this data allows the determination of the dissociation energy of OH in the electronic ground state, resulting in 35450 ± 100 cm^{-1} or 101.36 ± 0.3 kcal/mole. The data obtained by Barror for the $B^2\Sigma^+$ state leads to the same value of the dissociation energy. The value

$$D_0(OH) = 101{,}36 \pm 0{,}3 \text{ kcal/mole},$$

recommended by Barrow [645] is the most accurate published in literature and it was accepted in the Handbook. To this accepted value of the dissociation of OH corresponds

$$\Delta H^\circ f_0(OH, \text{gas}) = 9{,}259 \pm 0{,}32 \text{ kcal/mole}.$$

OD (gas), OT (gas). The extrapolation of the vibrational energy levels of the OD radical allows the derivation of only a very approximate value of $D_0(OD)$ because the available data determines only the energy of the first four vibrational levels of OD in the $X^2\Pi_i$ state (see page 400). Oura [3154, 3155] calculated in this way $D_0(OD) \approx$ ≈ 98 kcal/mole. More reliable values of the dissociation energy of the OD and OT radicals are as follows:

$$D_0(OD) = 102{,}785 \pm 0{,}3 \text{ kcal/mole},$$
$$D_0(OT) = 103{,}4 \pm 0{,}3 \text{ kcal/mole}.$$

These values were calculated by Eq. (IV.17), using the values of $D_0(OH)$ accepted in the Handbook and those of the vibrational constants of OH, OD and OT. The mentioned values of $D_0(OD)$ and $D_0(OT)$ are accepted in the present Handbook. The values of the heats of formation, which correspond to them are

$$\Delta H^\circ f_0(OD, \text{gas}) = 8{,}739 \pm 0{,}3 \text{ kcal/mole},$$
$$\Delta H^\circ f_0(OT, \text{gas}) = 8{,}525 \pm 0{,}3 \text{ kcal/mole}.$$

OH^+ (gas). Mann, Hustrulid and Tate [2762] measured the potential of occurrence of the OH^+ hydroxyl ion in dissociative ionization of H_2O molecules under the effect of electron impacts. An ionization po-

tential of the hydroxyl I(OH) = 13.38 ev* corresponds to the value of the potential of occurrence of the OH^+ ion (18.7 ± 0.2 ev) found in the paper [2762]. Lindemann and Guffy [2616] obtained in a similar investigation a very similar value of the potential of occurrence of the OH^+ ion, equal to 18.59 ± 0.08 ev, to which the value I(OH) = = 13.31 ev ** corresponds.

Foner and Hudson [1576] measured the ionization potential of OH by a direct method. The molecules of the hydroxyl, formed by a dis-, charge in water vapor, entered into the ionization chamber of a mass-spectrometer. The comparison of the intensity of the ion currents of OH^+ and of Ar^+ as a standard at different electron energies led to a value of the ionization potential of hydroxyl equal to 13.18 ± 0.1 ev or 304 kcal/mole. In the paper [1576], the potential of occurrence of the OH^+ ion in dissociative ionization of H_2O molecules was also measured. The found value (18.19 ± 0.1 ev) differs significantly from the values in the paper [2762, 2616].

In the Handbook, the value

$$I(OH) = 13{,}18 \pm 0{,}2\ эв = 304 \pm 5\ \text{kcal/mole}$$

is accepted as the value of the ionization potential of hydroxyl, obtained by Foner and Hudson [1576]. This value conforms, within the error limits, to the values found in the papers [2762, 2616]. The heat of formation of the OH^+ ions

$$\Delta H°f_0(OH^+, газ) = 313{,}259 \pm 5\ \text{kcal/mole},$$

and the dissociation energy of the OH^+ ion into $O^+ + H$

$$D_0(OH^+) = 111{,}412 \pm 5\ \text{kcal/mole}.$$

corresponds to the accepted value of I(OH).

OH^- (gas). Until recently, the value of the electron affinity of hydroxyl was known only by various estimates made on the basis of calculation of the energy of crystal lattices [1828, 1832] or on the basis

of hypotheses with regard to a coherency between the absorption maxima of hydrated ions and the corresponding values of the electron affinity [3346], and regularities in the values of the electron affinity of various atoms and radicals (see the review by Pritchard [3330]).

In works by Sugden and coworkers [3780, 3781, 3163] attempts were made to determine experimentally the value of A(OH) by measuring the concentration of free electrons in flames containing alkali metals and calculating the equilibrium constants of the reaction $OH^- \rightleftarrows OH + e^-$. Page [3163], who carried out the majority of these measurements, processed the data obtained by him together with the results of the foregoing investigations [3780, 3781] and found for A(OH) the value -65 ± 1 kcal/mole. As a result of the analysis of the indirect determinations of the value of A(OH), Page showed that the inaccuracy of these estimates allows only the conclusion that the value of A(OH) lies between -45 and -85 kcal/mole, the value of -65 kcal/mole being the most possible one. It must be noted, however, that the value of A(OH) found in the papers [3780, 3781, 3163] depends essentially on the correctness of the determination of the mechanism of formation of electrons in the flame and also on the magnitude of the partial pressure of hydroxyl in the flame.

Smith and Branscomb [3796] made the attempt to determine the value of A(OH) using the method of photodetachment of electrons from negative molecular gaseous ions, developed by them. In a short publication in 1955 [3796], they reported on the value of the photoionization threshold of OH^- found by investigation of the dependence of the photocurrent on the wavelength in the 4000-8000 A region in a OH^- beam obtained from the anode of a glowing discharge at low pressure in H_2O vapor. The threshold found by Smith and Branscomb corresponds to an energy of 1.75 ev (or approximately 40 kcal/mole). As far as the authors of

the Handbook know, these investigators did not publish a detailed statement of their work and nowhere give the value of A(OH) obtained on the basis of this investigation.

It must be noted that the example of the O_2 molecule shows [1018] that the coherency of the threshold of photodetachment with the magnitude of the electron affinity is ambiguous owing mainly to the total lack of spectroscopical data on the energy levels of gaseous molecular negative ions. Thus, on the basis of the published data, it is difficult to judge to what degree the value of A(OH), corresponding to the threshold of photoionization found by Smith and Branscomb, is reliable. It must be noted, however, that Sugden's paper [2447a], published in 1960, dealing preference to the lower value of A(OH) which corresponds to the measurements by Smith and Branscomb.

In the present Handbook

$$A(OH) = -40 \pm 5 \text{ kcal/mole},$$

is accepted to which $\Delta H^\circ f_0(OH^-, \text{gas}) = -30.741 \pm 5$ kcal/mole, corresponds, and an energy of the dissociation of OH^- into O^- + H of

$$D_0(OH^-) = 107.56 \pm 5 \text{ kcal/mole}.$$

TABLE 49

Accepted Values (in cal/mole) of the Thermochemical Quantities of Oxygen Compounds of Hydrogen and its Isotopes in Gaseous State.

A Substance	B or	$\Delta H^\circ f_0$	$\Delta H^\circ f_{298.15}$	$\Delta H^\circ f_{298.15}$	$H^\circ_{298.15} - H^\circ_0$	$H^\circ_{298.15} - H^\circ_0$
H_2O	219 33[illegible]	−57 110	−57 786	−57 753	2328	2333
HDO	221 [illegible]	−57 927	−58 [illegible]	−58 631	2332	2372
D_2O	222 [illegible]	−58 [illegible]	−59 543	−59 582	2340	2381
H^3HO	221 [illegible]	−58 [illegible]	−58 935	−58 976	2334	2373
D^3HO	223 [illegible]	−58 [illegible]	−59 903	−59 919	2345	[illegible]
T_2O	224 [illegible]	−59 [illegible]	−60 296	−60 308	2353	2394
H_2O_2	252 282	−31 044	−32 521	−32 549	2547	2588
HDO_2	254 [illegible]	−32 [illegible]	−33 439	−33 459	2037	2681
D_2O_2	256 [illegible]	−33 [illegible]	−34 486	−34 510	2656	2711
HO_2	165 000	4 006	3 942	3 933	2368	2411
OH	101 380	9 259	9 [illegible]18	9 319	2071	2107
OD	102 785	9 790	9 828	9 824	2115	2151
OT	103 [illegible]	9 525	9 627	9 628	2133	2169
OH^+	304 [illegible]	313 259	314 744	314 [illegible]	2041	2075
OH^-	40 [illegible]	−33 741	−32 170	−32 195	2039	2074

a) The value of the ionization energy of OH is given.
b) The value of the energy of electron detachment from the OH^- ion is given.
A) Substance; B) or.

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[Footnotes]

362 The problem of the thermodynamic stability of H_2O_4 and H_2O_3 is discussed by Benson [750a].

363 In the paper [727], the quadratic expression for $G_0(v_1, v_2, v_3)$ is accomplished by the cubic term $y_{222}v^3$ without, however, improving essentially the approximation of the vibration energy levels.

364* v_2, $2v_2$, v_3, $v_2 + v_3$, $v_1 + v_3$.

364** $v_1 + v_2 + v_3$, $2v_1 + v_3$, $3v_3$, $2v_1 + v_2 + v_3$, $v_2 + 3v_3$, $3v_1 + v_3$, $v_1 + 3v_3$, $3v_1 + v_2 + v_3$, $v_1 + v_2 + 3v_3$, $3v_1 + 2v_2 + v_3$, $4v_1 + v_3$, $2v_1 + 3v_3$.

364*** After the calculation of the molecular constants of H_2O was

completed, we came to know the very thorough review paper by Regula [3481a] in which a table is given of the wave numbers of zero lines of 44 H_2O bands which have been observed by various investigators in the vibrational-rotational absorption spectrum of water vapor. Besides the H_2O bands discussed in the paper [438], Regula's review lists also data on bands whose wave numbers of the zero lines are equal to 1556, 2057, 2161, 10,284, 10,600, 12,140, 13,828, 14,221, 16,898 and 18,394 cm^{-1}. These bands are referred, respectively, to the vibrational transitions (010) → (020); (010) → (100); (010) → (001); (000) → (220); (000) → (300); (000) → (310); (000) → (202); (000) → (400); (000) → (302), and (000) → → (411). The results, however, obtained, in the papers [724, 727, 730, 1255], were not taken into consideration in the review [3418a]. In this review, the results of investigations of the vibrational-rotational emission spectra of H_2O are also not taken into account. A comparison of the values of the levels of vibrational energy of H_2O - between which a triple resonance interaction takes place, and which are calculated in paper [438] - with the experimental values of some of them, listed in the review [3418a], shows that the referring of the zero lines of the bands at 13,828; 14,221, and 16,898 cm^{-1} to the vibrational transitions (000) → (202); (000) → (400) and (000) → (302) is erroneous. The correct attribution of these bands is as follows: (000) → (400); (000) → (202) and (000) → (500). In connection with this fact the correctness of the attribution of the band at 18,394 cm^{-1} to the (000) → (411) transition needs to be verified.

366 42 levels up to $J_\tau = 10_{-10}$.

367* Khachaturuzov [444a] showed how the values of all levels of the rotational energy of the vibrational ground state of H_2O, which correspond to $J \leq 25$, may be determined.

367** The frequency of the pure rotational transition $2_2 - 3_{-2}$ was also observed in the infrared absorption spectrum of water vapor [483, 485] in the region from 4 to 7.2 cm^{-1}.

367*** (010) [724, 3951, 1255]; (020) [724]; (100), (001) [730]; (011), (021), (012) [722]; (101) [3083]; (111) [2831]; (201), (003), (211), (013), (301) [690]; (113) [1605, 188]; (103), (311), (321), (401), (203), [1605].

369* It appears that the authors of the paper [727] applied not only the results of the analysis of infrared spectra but also the results of measurements of microwave spectra of water vapor when determining the mentioned values of the rotational constants.

369** I.e., for the (000) state and states listed in the third footnote to page 367.

370 The bands observed in the absorption spectrum of water vapor, and lying in the region of shorter wavelengths (up to 100-50 A), belong to the H_2O^+ and H_2O^{++} ions.

371 $2sa_1$ are the inner electron orbits of the O atom in the H_2O molecule; $[p_x b_2]$ and $[p_x a_1]$ are the orbits which take part in the formation of the O-H bands; $(2p_2 b_1)$ is the orbit which does not take part in the formation of the bond. The electron configuration $(2sa_1)^2[p_y b_2]^2[p_x a_1]^2(2p_z b_1)^2$ corresponds to the ground electronic state ^1A of the water molecule, when using this notation.

372 A similar correspondence is observed, for example, for CO_2 and CO [3002].

373 A sole exception is the paper by Barker and Sleator [639], in which the rotational structure of the ν_1 and ν_2 bands was resolved.

374* The value of the constant y_{222} for HDO is given in the paper [727]. However, as was shown in paper [440], the value of this constant may not be determined solely on the basis of experimental data on the energy of the vibrational levels of HDO.

374** In the paper [440], the results of investigations of the rotational structure of the ν_2 bands, obtained by Gailar [1638] were not taken into account when calculating the virational constants of HDO. Repeated calculations of the vibrational constants of HDO, carried out later and taking into account the data in [1638] gave, in particular, a value of the constant x_{23} which is greater (in its absolute value) than in the case of H_2O. Thus, the value of the wave number of the zero line of the ν_2 band, used in paper [440], is more reliable than the value given in the paper [1638].

375 1_1-1_0; 2_1-2_0; 2_{-1}-2_{-2}; 3_0-3_1; 3_2-3_3, 4_1-4_2; 4_{-3}-3_{-1}; 4_0-5_{-5}; 5_0-5_1; 6_1-6_2; 6_{-2}-7_{-6}; 7_0-7_1; 8_{-1}-8_0; 9_0-9_1; 10_{-1}-10_0; 11_{-2}-11_{-1}; 12_{-1}-12_0.

377* In the paper [440], the obtained values of the vibrational constants of D_2O were compared to the values found by the authors of the papers [863, 2404, 1263, 1615, 727].

377** In the paper [727] the values of the constant k_{122} of the Fermi resonance and the constant y_{222} of the anharmonicity of second order are also given for D_2O. There is, however, no reason to assume a Fermi resonance in D_2O, because it was

shown in the paper [438] that it is missing in H_2O. As regards the constant y_{222}, it was obviously calculated by the authors of [727] on the basis of some additional assumptions, because the data known for D_2O is insufficient for the determination of this constant.

377*** Carrying out the calculation of the vibrational constants, of D_2O, Khachkuruzov [440] did not take into account the results of the investigation of the rotational structure of the ν_2 band obtained by Dickey and Hoffman [1332]. Repeated calculations, carried out by taking into account these data, hielded the following values (in cm^{-1}) of the vibrational constants: $\omega_1 = 2762.42$; $\omega_2 = 1206.90$; $\omega_3 = 2885.99$; $x_{11} = 21.54$; $x_{22} = -9.46$; $x_{33} = -24.96$; $x_{12} = -8.77$; $x_{33} = -10.29$; $x_{13} = -85.76$.

377**** 2_2-3_{-2}; 4_3-5_1; 3_2-4_{-1}; 3_3-4_1; 5_0-4_4; $5_{-1}-6_{-5}$; 5_1-4_3.

378 (100), (001), (011), (021), (200), (101), (111), (201).

383 A report on the analysis of the fine structure of the $\nu_2 + \nu_6$ band in the H_2O_2 spectrum, carried out by Olson [3134a], was published in 1960. According to Olson's data, $I_A = 0.2779 \cdot 10^{-39}$ g·cm^2, $I_B = 3.33 \cdot 10^{-39}$ g·cm^2 and $I_C = 3.21 \cdot 10^{-39}$ g·cm^2; these data are in sufficient accoracnce with the values accepted in the present Handbook (see Table 38).

392 The assumption of the existence of the HO_2 radical has been expressed by Bakh [86]. Further, it was again suggested by Haber [1916] in order to explain the mechanism of the reaction between hydrogen and oxygen, and this assumption has been used by many authors in the study of the kinetics of gas reactions (see, for example, [240, 304, 244]). Many investigators made attempts to find proofs of the existence of the HO_2 radical. The paper by Minkoff [2924] gives a review on the suggested proofs for the existence of the HO_2 radical based on the analysis of chemical investigations and on the results of theoretical calculations. Minkoff gives in this paper a theoretical evidence of the stability of the HO_2 radical based on the semi-empirical method by Glasston, Laidler and Eyring [154] for the study of the interaction between the H atom and the O_2 molecule. In the paper [2924], the attempt is also made to estimate the fundamental oscillation frequencies and the values of the structural parameters of the linear model of the HO_2 radical. At the same time, Minkoff noted that the assumption of a nonlinear structure of the HO_2 radical is more substantial.

392** Tagirov [405] stated that he observed in the infrared spectrum of a hydrogen flame bands with a maximum corresponding to the frequency of 1305 cm^{-1}, which he ascribed to the HO_2 radical. Later on, however, this assumption was not confirmed. It must be noted that Cashion and Polanyi [1069], who investigated the infrared spectrum of the chemiluminescence of the $H + O_2$ reaction, did not observe this band.

393 Walsh [4141] predicted, with regard to the angle in the HNO radical, that it must be smaller than the angle between the bonds in the HCO radical. this was later on confirmed when the spectra of the HNO and HCO radicals had been obtained and analyzed (see pages 713 and 898).

396 After the choice of the molecular constants of the ground electronic state of OH and the calculation of the thermodynamic functions had been made, the papers by Blackwell, Ingham and Rundle [834b] and Wallace [4132b] were published in which the values of B_v and $G_0(v)$ for v = 7, 8 and 9 were found by investigation of the infrared spectrum of the afterglow of the night sky. The accepted values of $G_0(v)$ listed in Table 40, conform to the date obtained in the papers [834b, 4132b] within the experimental error limits.

399 The rotational constants of OH in the $A^2\Sigma^+$ state for v' = = 6-9, conforming to the values obtained by Barrow [645], were also found in the papers [2871, 1997a].

400* According to [3591], the following values are valid: ω'_e = = 2319.9, $\omega'_e x'_e$ = 52.0, ω''_e = 2720.9, $\omega''_e x''_e$ = 44.2 cm^{-1}.

400** According to [3154, 3155] the following values are valid: ω'_e = 2313.50, $\omega'_e x'_e$ = 49.18, $\omega'_e y'_e$ = -0.373, ω''_e = 2716.13, $\omega''_e x''_e$ = 42.15, $\omega''_e y''_e$ = -0.386 cm^{-1}.

405 In Herzberg's monograph the rotational constants of the $A^3\Pi_i$ state are given; these were improved by Challacombe and Almy [1081] by calculation of the rotational constants of the upper $^3\Pi_i$ state by Gilbert's method [1741], using the experimental data obtained by Loomis and Brandt [2646].

406 Calculated on the basis of the values of $D_0(OH)$ and I(OH) accepted in the Handbook. The error in the obtained values of $D_0(OH^+)$ does not exceed ± 1800 cm^{-1}.

407* This analogy is also corroborated by the existence of the $A^3\Pi$ state, which has a dissociation limit difference from that of the ground state, and an excitation energy almost to that of NH.

407** Johnston [2298], investigating the spectrum of solid LiOH and $LiOH \cdot H_2O$, calculated the vibrational constants of the

OH^- ion in the crystal lattice and found:

$$\omega_e(OH^-) = 3839 \pm 10\ cm^{-1} \text{ в LiOH и } \omega_e(OH^-) = 3735 \pm 10\ cm^{-1} \text{ в LiOH}\cdot H_2O.$$

409 The calculations are carried out on a BESM electronic computer.

411 The mentioned cause gives rise also to the inaccuracy in the accepted values of v_{1m}, v_{2m} and v_{3m}.

412 Owing to the fact that the results of these calculations are entered into a series of reference books, we cite the values of the vibrational constants of H_2O (in cm^{-1}) accepted by Gordon: $\omega_1 = 3740$; $\omega_2 = 1635$; $\omega_3 = 3834$; $x_{11} = 70$; $x_{22} = 20$; $x_{33} = 39$; $x_{12} = 20$; $x_{23} = 20$; $x_{13} = 109$; and also the expressions for the effective moments of inertia (in 10^{-40} $g\cdot cm^2$):

$$I_A = 0{,}996 + 0{,}026\cdot v_1 - 0{,}098\cdot v_2 + 0{,}045\cdot v_3,$$
$$I_B = 1{,}908 + 0{,}033\cdot v_1 - 0{,}034\cdot v_2 + 0{,}014\cdot v_3,$$
$$I_C = 2{,}981 + 0{,}062\cdot v_1 + 0{,}062\cdot v_2 + 0{,}047\cdot v_3.$$

413 In the paper [3847], $\rho_1 = 2.33\cdot10^{-5}$ $degree^{-1}$ was found on the basis of the values of the rotational component of the specific heat of H_2O calculated by immediate summation, whereas the calculations by Wilson [4287] give $\rho_1 = 2.04\cdot10^{-5}$ $degree^{-1}$. This difference was explained by Khachkuruzov and Milevskaya [449] as the influence of the zero vibrations of H_2O molecules.

414* In the paper [1615] and in the Handbook [2076], a calculation of the thermodynamic functions is reported which was carried out by Glatt, Adams and Johnston [1759] in the temperature range from 100-5000°K by immediate summation over the levels of the rotational energy. However, these calculations have not been published, and it is therefore impossible to criticize their quality and to compare them with the results of the calculations carried out during the compilation of the present Handbook.

414** On the basis of the same values of the molecular constants as those in Gordon's papers [1800, 1801] (see footnote on page 412).

417 The values of the constants ρ_1 and ρ_2 for D_2O and T_2O differ insignificantly from the values of the corresponding constants of H_2O, as the calculations which have been carried out during the preparation of the present Handbook have shown.

419 These differences are caused by allowing for the centrifugal stress of the molecules and the application of Eq.(II.176a) for Q_{vr}.

429 Since the molecular constants of OH^+ are known with but little accuracy, the use of an electronic computer is, in this case, justified only by the necessity of applying the immediate summation for the calculation of the thermodynamic functions at high temperatures.

433 The results of the determination of the heat of formation of hydrogen peroxide by other methods are cited in the Handbook by Bichowsky and Rossini [813]. A review on the papers dealing with determination of the heat of formation of H_2O_2 is also given in the book by Shumb, Setterfield and Wentworth [460].

436* The data by Skorokhodova et al. [379], who determined the thermal effect of the reaction: $H_2O_4(liqu.) \rightarrow H_2O_2(liqu.) + O_2(gas)$, also conform to the value of $D_0(H - O_2)$ obtained by Foner and Hudson.

436** In Grey's review [1846] the value $\Delta H°f_0$ (HO_2, gas) = 4.9 ± ± kcal/mole is accepted on the basis of data by Foner and Hudson.

441* In the paper [2762] the value I(OH) = 13.6 ev is given, which is also recommended in the reviews by Gaydon [1668] and Pritchard [3330]. The value of I(OH), cited in the text, is calculated on the basis of the measurements by Mann, Hustrulid and Tate [2762], taking into account the value of $D_0(OH)$ accepted in the Handbook.

441** According to the calculations by the authors of the Handbook, the value I(OH) = 13.53 ev is given in the paper [2616].

[Transliterated Symbols]

383 пр = pr = privedennyy = reduced

393 П = P = prilozheniye = supplement

409 кол.вр = kol.vr = kolebatel'nyy-vrashchatel'nyy = vibrational-rotational.

410 ж.р = zh.r. = zhestkiy rotator = rigid rotator

420 эл = el = elektronnyy = electronic

420 вн.вр = vn.vr. = vnutrenneye vrashcheniye = internal rotation

420 св.вр = sv.vr. = svobodnoye vrashcheniye = free rotation

425 БЭСМ = BESM = bystrodeystvuyushchaya electronnaya schetnaya mashina = high-speed electronic computer.

CHAPTER 8

FLUORINE AND ITS OXYGEN COMPOUNDS

(F, F^-, F_2, FO, F_2O)

The present chapter deals with monatomic and diatomic fluorine, the fluorine ion (F^-) and the oxygen compounds of fluorine (FO and F_2O) in the gaseous state. According to literature data the following oxygen compounds of fluorine may exist under certain conditions: F_2O, FO, F_2O_2 and F_2O_3. All these compounds are of little stability, under reducing conditions they decay rapidly in an explosion. The most stable oxygen compound of fluorine at room temperature is fluorine dioxide, F_2O, whose chemical and physical properties were studied in great detail [356]. The compounds F_2O_2 and F_2O_3 are only stable at low temperatures: F_2O_3 disintegrates at 121°K into F_2O_2 and O_2, F_2O_2 disintegrates into its elements at 190°K [2410].

Among the fluorine-oxygen compounds mentioned above, the Handbook deals with FO and F_2O, since the other fluorine-oxygen compounds are unstable. The data given in the Handbook are sufficient to calculate the thermodynamic properties of the $F_2 - O_2$ system, particularly at high temperatures. It should be mentioned that the oxygen compounds of fluorine are not characteristic of these elements and at high temperatures or when other elements are present they are thermodynamically unstable.

Tne compounds of fluorine with Cl, Br, J, H, S, N, P, C, Si, Pb, B, Al, Be, Mg, Hg, Li, Na and K are dealt with in the following chapters.

TABLE 50

The Energy Levels of the F-Atom and the F^--Ion

Atom	State		statistical weight	energy, cm^{-1}
	Electron configuration	term		
F	$1s^2\,2s^2\,2p^5$	$^2P_{3/2}$	4	0
	$1s^2\,2s^2\,2p^5$	$^2P_{1/2}$	2	404
F^-	$1s^2\,2s^2\,2p^6$	^1S	1	0

§33. MOLECULAR CONSTANTS

F. In its ground state ^2P the fluorine atom has the electron configuration $1s^2 2s^2 2p^5$. The energy corresponding to a transition of the flurorine atom from its ground state ^2P to an excited electron level exceeds 100,000 cm^{-1}; these levels are therefore not considered in the Handbook. Table 50 gives the excitation energies and statistical weights of two components of the fluorine atom's ground state, taken from Moore [2941].

F^-. The negative ion of monatomic fluorine in the ground state has the electron configuration $1s^2 2s^2 2p^6$, which corresponds to one ^1S term. In analogy to the isoelectronic Ne atom, the energy of a transition to an excited state of the F^- ion must exceed 100,000 cm^{-1}. Since the F^- ionization potential is much lower than this value (cf. p. 463) we may assume that the ion considered, like the negative ions of the other halogens, has no stable excited states. This assumption is corroborated by the failure of attempts aiming to obtain spectra of negative monatomic ions of halogens.

F_2. The F_2 molecule has an electron ground state of the type $^1\Sigma$. A determination of the F_2 constants in the electron ground state entails essential difficulties which are due to the fact that the absorption spectrum of fluorine in the visible and the near ultraviolet ranges (in contrast to the absorption spectra of other halogens) does not show a

band structure; the vacuum ultraviolet absorption spectrum is caused by transitions to high excited states

TABLE 51

Values of the F_2 and FO Molecular Constants Used

1 Молекула	2 Состояние	ω_e	$\omega_e x_e$	B_e	α_1	$D_0 \cdot 10^6$	r_e
		$см^{-1}$					Å
F_2	$X^1\Sigma$	924[a]	16[a]	0,891	0,017[b]	3,3[c]	1,418
FO	$X^2\Pi^r$ [d]	900[e]	—	1,0[e]	—	—	1,4

1) Molecule; 2) state.

a) Calculated from $\Delta G_{\frac{1}{2}}$ and $D_0(F_2)$.

b) Calculated from Eq. (1.38).

c) Calculated from Eq. (1.36a).

d) In analogy with ClO.

e) Estimate.

from the $v'' = 0$ level, the emission spectrum is connected with transitions between high excited states. The data on the molecular constants of F_2 in the $X^1\Sigma$ state are therefore mainly bases on data obtained in studying the Raman spectrum of gaseous fluorine.*

The Raman spectrum of F_2 was obtained by Andrychuk [559, 560]; it consists of the fundamental frequency ($\Delta G_{\frac{1}{2}} = 891,85 \pm 0,4$ cm^{-1}) and a pure rotation spectrum. As a result of analyzing the rotation spectrum, Andrychuk [560] determined the values of the rotational constants of the F_2 molecule in the $X^1\Sigma$ state: $B_0 = 0,8828 \pm 0,0010$ cm^{-1} [560]. The interatomic distance amounts to $r_{F-F} = 1,4177 \pm 0,001$ Å, the corresponding value of the rotational constant is in good agreement with that obtained by the electron diffraction method [3473].

The results of investigating the Raman spectrum do not permit a determination of the constant of anharmonicity $\omega_e x_e$ of the vibrations (and thus also of the vibrational frequency ω_e) and also of the constant α_1 of interaction between rotation and vibration. Owing to this a series of researchers estimated these quantities for a subsequent

calculation of the thermodynamic functions of fluorine. Since for the Cl_2 and ClF molecules a linear extrapolation with repect to the vibrational energy levels of the ground state leads to values of dissociation energies which are close to those found by way of experiment, the constant of anharmonicity and the vibrational frequency of F_2 may be calculated by a consistent solution of Eq. (1.40).

First estimations of the quantity $\omega_e x_e$, bases upon these relationships, were made by Butkov and Rozenbaum [114]. The authors of these papers, however, used in their calculation an incorrect value of the F_2 dissociation energy. Khachkuruzov [436] and later Rees [3414] calculated the values of ω_e and $\omega_e x_e$ using the values $\Delta G_{\frac{1}{2}} = 891.85$ cm^{-1} and $D_0(F_2) = 37$ kcal/mol (cf. p. 467) and obtained virtually coincident values (in cm^{-1}): $\omega_e = 924$, $\omega_e x_e = 16$ [436] and $\omega_e = 923$, $\omega_e x_e = 15$[3414].

Evans et al. [1514] and Potter [3313], in order to calculate the thermodynamic functions of F_2, used the values $\omega_e = 919$ and $\omega_e x_e = 13.6$ cm^{-1} calculated by Haar and Beckett.* In the Handbook we use (cf. Table 51) the values for the vibrational frequency and the anharmonicity constant suggested by Khachkuruzov [436] since the method of estimation, used by Haar and Beckett, is unknown and the quantities, found by Rees [3414] are in good agreement with those used. The errors of the used values of ω_e and $\omega_e x_e$ were estimated to ± 2 and ± 5 cm^{-1}, respectively.

The constant α_1 of oscillation-vibration interaction and the equilibrium value of the rotational constant B_e, given in Table 51, were calculated by the authors of the Handbook from formula (1.38) the values used for ω_e and $\omega_e x_e$ and the quantity B_0 were found by Andriychuk [560]. In their work [1514] Evans et al. used the values $B_e = 0.8901$ and $\alpha_1 = 0.0146$ cm^{-1}, calculated by Haar and Beckett.

In the F_2 electron spectra we may observe transitions between elec-

tron states of high excitation energies [1642] and also transitions, constituting a Rydberg series [2163].

In analogy with Cl_2, Br_2 and I_2 it may be assumed that the first excited electron state of the F_2 molecule is a $^3\Pi_u$ state whose energy does not exceed the value of $D_o(F_2) \cong 13{,}000$ cm^{-1}. The existance of a stable $^3\Pi_u$ state of F_2 could not be verified by experiment. None the less Rees [3414] interpreted the continuous absorption in the F_2 spectrum as partly connected with a transition to the repulsive branch of the potential energy curve of the $^3\Pi_{0_u^+}$ state.

FO. The spectrum of the FO molecule has not been observed so far and attempts to obtain it in pulsed photolysis of a F_2+O_2 mixture, i.e., under conditions where absorption spectra of ClO, BrO and IO could be obtained, failed (cf. [1428]).

Khachkuruzov [436] estimated graphically the rotational constant and the vibration frequency of FO according to the dependence of the values of these constants for the diatomic fluorides of elements of the 2nd column on the number of valence electrons. The values he obtained, $B_e \sim 1.08$ and $\omega \sim 1100^{-1}$ were used in the first edition of our Handbook. But an estimation of the molecular constants other diatomic fluorides may lead us to incorrect values since experimental data are only known for the fluorides of elements of the groups II, III, IV, whose bons are of essentially different nature compared with the bonds in such molecules as FO, F_2, NF and SF. More reliable estimates of the FO molecular constants may obviously be obtained on the basis of wellknown data on the structure and vibration frequencies of the F_2O molecule. Comparison of the interatomic distances in diatomic and triatomic fluorides of a number of elements indicates that the former are 0.02-04 A smaller than the latter. Since the length of the F-O bond in the F_2O molecule is 1.418 A (cf. p. 457), the rotational constant of FO, given in Table 51, was calculated for $r_{FO} = 1.4$ A. The errors of the used values of B and r_{FO} are of the order of 0.1 cm^{-1} and 0.05 A, respectively.

The force constants of the F_2O molecule for a potential function

with four constants was calculated by Bernstein and Powling [763], who found that the force constant k_1 of the F – O bond in the F_2O molecule must satisfy the following condition: $3.21 \cdot 10^5$ dyne$\cdot$cm$^{-1} \leq k_1 \leq 5.23 \cdot 10^5$ dyne$\cdot$cm^{-1}. If we assume that $k_e(FO) = k_1(F_2O)$ we find that, according to Eq. (1.42), $\omega_e(FO) = 900 \pm 100$ cm^{-1}.* This value of the FO vibration frequency was accepted in the present Handbook and entered Table 51.

The electron ground state of the FO molecule must be a doublet since it has one unpaired electron. On analogy to ClO, BrO and IO it was assumed in the Handbook that the FO ground state is a $^2\Pi^3$ state. The energy of the first excited state of FO was estimated to amount to 30,000 cm^{-1}.

$\underline{F_2O}$. The F_2O molecule has a symmetrical nonlinear structure (point group of symmetry C_{2v}). The F_2O absorption spectrum was obtained by Hettner, Pohlman and Schumacher [2059] but part of the bands observed in this paper, as was shown in the following, belong to impurities. In Herzberg's monograph [152] the values of the fundamental frequencies of F_2O were chosen in agreement with suggestions by Sutherland and Penney [3906] on the interpretation of the infrared spectrum of F_2O obtained in paper [2059]. In the subsequent investigations of the F_2O infrared spectrum [736, 2294] it was shown that the relationships were incorrect as part of the bands attributed to F_2O actually belonged to CF_4.

Later on the infrared spectrum of F_2O was again investigated in the papers by Bernstein and Powling [763] and Jones et al. [2294] in the range from 400 to 5000 cm^{-1}. Apart from spectroscopic studies with prism spectrometers, in paper [2294] the F_2O spectrum was investigated additionally by means of a grating instrument which made it possible partly to resolve the rotational structure of the bands. In both papers series of bands of the F_2O molecule were obtained, among them the

harmonics and composite frequencies. The authors of papers [763, 2294] give the same interpretation of the frequencies, with the exception of several composite frequencies. The values of the fundamental frequencies of F_2O which were chosen in agreement with these papers, are given in Table 52.

TABLE 52

Values of the Molecular Constants of F_2O Used

ν_1	ν_2	ν_3	$I_A I_B I_C$	σ
cm^{-1} 1			10^{-117} $(g \cdot cm^2)^3$ 2	
928	461	831	104,4	2

1) cm^{-1}; 2) $(g - cm^2)^3$.

The structure of the F_2O molecule was studied by the electron diffraction method [964, 857, 2162]. The values of r_{F-O} obtained in these papers lie within the limits of 1.36 and 1.42 Å and the values of $\angle F - O - F$ within the limits of 100 and 105°. In paper [763], when studying the F_2O infrared spectrum, the rotational structure of the ν_1 – band was partly resolved. On the basis of their analysis Bernstein and Powling obtained: $r_{F-O} = 1{,}38 \pm 0{,}03$ Å and $\angle F - O - F = 101{,}5 \pm 1°{,}5$. Ibers and Shomaker [2162] who analyzed carefully the electron diffraction pictures they obtained and compared the values found with the results of an analysis of the rotational structure of the ν_1 – band in the F_2O spectrum, recommend the following values for the structural parameters: $r_{F-O} = 1{,}418 \pm 0{,}019$ Å and $\angle F - O - F = 103{,}2 \pm 1°{,}5$. The products of the fundamental moments of inertia of F_2O given in Table 52, were calculated on the basis of these values.*

§ 34. THE THERMODYNAMIC FUNCTION OF GASES

The thermodynamic functions of fluorine and its compounds considered

in the present chapter, in the state of perfect gas, were calculated for the temperatures 293.15-6000°K and are complied in Tables 39-43 of Vol. II of the Handbook. For diatomic fluorine Appendix 5 gives data on the intermolecular potential constants and Table 394 (II) gives the values of the virial coefficients and their derivatives. For the remaining gases, considered in the present chapter, analogous data are not known.

F. The electron components of the thermodynamic functions of monatomic fluorine were calculated from the constants given in Table 50, and the progressive components from the relations (II.8) and (II.9) with $A_s = 1.4935$ and $A_\Phi = 6,4617$ cal/g – atom·deg. The errors of the calculated functional values were practically determined by the inaccuracy of the physical constants alone and did not exceed 0.005 cal/g – atom·deg for the values of Φ_T^* and S_T°.

The thermodynamic functions of monatomic fluorine were previously calculated by many authors for various temperature intervals. Among these calculations we should mention the papers by Butkov and Rozenbaum [114], Potter [3313], Cole et al. [1149], Evans et al. [1514], Kolsky et al. [2462], Huff, Gordon and Morrell [2142] in which the thermodynamic functions of F were calculated up to 5000 - 6000°K. Divergences between the values given in Table 39 (II) and the results of preceding calculations are mainly explained by differences in the chosen values of the physical constants and amount to 0.001 – 0.002 cal/g – atom·deg for papers [3313, 1514, 2142] and to about 0.01 – 0.015 cal/g – atom·deg for papers [1149, 2462]. The deviations from the results of the Butkov-Rozenbaum calculations [114] are much greater and reach 0.03 cal/g – atom·deg and are, obviously, to be explained by the errors admitted in this paper. The thermodynamic functions of monatomic fluorine given in Zeise's book [4384] were obtained from calculations in [114]; Stull and

Sinke [3894] and the Handbook of the Bureau of Standards, USA, [3680] use the functions obtained from data of [1514]. The divergences between the values of thermodynamic functions of monatomic fluorine given in the first and the present Editions of the Handbook lie within the limits that are caused by variations of the values of the physical constants.

$\underline{F^-}$. The progressive components of the thermodynamic functions of the negative ion of monatomic fluorine are calculated according to the same relationships as in the case of the monatomic fluorine. The electron components of the thermodynamic functions of F^- are equal to zero since the F^- ion has no stable excited states and its ground state is a ^1S state (see page 452).

Previously it was Huff et al. [2142] who calculated the thermodynamic functions of F^-. The divergence between the values of the thermodynamic functions of F^-, given in paper [2142], in the first and in the present edition of the Handbook is due to the fact that different values of the physical constants were used, and does not exceed 0.005 cal/g – atom·deg.

$\underline{F_2}$. The thermodynamic functions of diatomic fluorine, given in Table 41 (II) were calculated from Eqs. (II, 161), (II, 162). The values of $\ln \Sigma$ and $T\partial/\partial T \ln \Sigma$ in these equations were calculated according to the method of Gordon and Barnes, on the basis of constants, given in Table 51. Table 53 shows the values of the constants C_Φ and C_s and the coefficients in Eqs. (II, 137), (II, 138) calculated with the accepted values of the molecular constants.

The F_2 molecule has a low dissociation energy. The corrections for the limitatio of the number of rotational levels of the F_2 molecule in calculating the thermodynamic functions of fluorine accord..g to the method of Gordon and Barnes must therefore be considerable. In the present

Handbook the corresponding corrections are not taken into account since they are compensated by the contribution of the excited $^3\Pi_u$ state of F_2 which has the opposite sign and is likewise not considered in the calculation. Moreover, the absence of experimental data on the vibrational constants and the constant α_1 of the interaction between rotation and vibration of this molecule render impossible a sufficiently accurate calculation of the thermodynamic functions of diatomic fluorine. The calculated value of Φ^*_{3000} exhibits an error which amounts to about 0.1 cal/mole·deg.*

TABLE 53

Values of the Constants used for Calculating the Thermodynamic Functions of F_2 and FO.

1 Вещество	0	$x \cdot 10^2$	$\beta_1 \cdot 10^3$	$\beta_2 \cdot 10^6$	$\frac{q_0}{T}$	$\frac{d_0 \cdot 10^{-6}}{T}$	$C\Phi$	Cs
	2 *град*				3 *град*$^{-1}$		4 *кал/моль·град*	
F_2	1329,4	17,316	1,9264	3,711	0,787569	5,89	1,7077	8,6631
FO	1294,9	—	—	—	—	—	5,3464	13,3019

1) Substance; 2) deg.; 3) deg^{-1}; 4) cal/mole·deg.

The thermodynamic functions of diatomic fluorine were previously calculated for a wide temperature interval in the papers by Butkov and Rozenbaum [114], Potter [3313], Cole et al. [1149] (up to 5000°K), Huff, Gordon and Morrell [2142] (up to 6000°K) and Evans et al. [1514] (up to 3000°K) and Evans et al. [1514] (up to 3000°K). In the papers [3313, 1514, 1149] the calculations were made according to the method by Mayer and Goeppert-Mayer and molecular constants recommended by Haar and Becket. (see p. 454). The divergence between the values of the thermodynamic functions of F_2 given in papers [3313, 1514, 1149] and in Table 41 (II) (up to 0.3 cal/mole·deg Φ^*_{5000} value) are almost entirely to be explained by the difference in the calculating methods. In the paper by Butkov and Rozenbaum [114] the thermodynamic functions of F_2 were also

calculated according to the method by Mayer and Göppert-Mayer but the values of the molecular constants of F_2 used in this paper were incorrect (see page 454). The divergence between the values of the thermodynamic functions of F_2 given in paper [114] and in Table 41 (II) is therefore greater than with other papers.

In the summary of [2142] and also in the first edition of the present Handbook the thermodynamic functions of fluorine were calculated in the approximation of the rigid rotator – harmonic oscillator model. In Zeise's book [4384] the thermodynamic functions of F_2 are tabulated which have been calculated in the papers [114, 1149]; results of calculations by Evans et al. [1514] may be found in the paper by Stull and Sinke [3894] and in the Handb ok [3680].

FO and F_2O. The thermodynamic functions of fluorine oxide and difluorine oxide given in Tables 42 (II) and 43 (II) were calculated in the approximation of the rigid rotator – harmonic oscillator model, using the constants given in Tables 51 and 52. In Tables 53 and 54 we find the values of the quantities C_Φ (C'_Φ) and C_S(C'_S) of Eqs. (II.161), (II.162) and (II.243), (II.244) needed to calculate the thermodynamic functions of FO and F_2O, and also the values of the constants θ with which the vibrational components were calculated. The terms R ln 4 are are comprised in the values of C_Φ and C_S for FO since the ground state of the FO melecule was assumed to be a $^2\Pi$ state.

At low temperatures the principal errors of the values of the thermodynamic functions of FO are due to the inaccuracy of the value taken for the rotational constant (about 0.2 cal/mole·deg) and the approximate consideration of the multiplet character of the ground state (up to 0.7 cal/mole·deg for the $\Phi^*_{298.15}$ value). At high temperatures the errors due to the absence of experimental data on the FO vibration frequency and the fact that the calculations were made in the approximation

of the rigid-rotator – harmonic-oscillator model become considerable (up to 0.5 cal/mole·deg for Φ^*_{3000}). Besides this, the errors due to the approximate consideration of the multiplet nature of the ground state diminish as the temperature rises. The total error of the values of Φ^*_{3000} have the order of 0.8 cal/mole·deg.

The main errors of the calculated values of the F_2O thermodynamic functions at low temperatures are caused by the fact that inaccurate values were used in calculating the molecular constant (0.02 cal/ mole. deg $\Phi^*_{298.15}$) while at high temperatures it is due to the approximate method of calculating (0.7 cal/mole.deg Φ^*_{3000}). The error of the calculated value of Φ^*_{3000} amounts to 0.6-0.8 cal/mole.deg.

TABLE 54

The Values of the Constants Used in Calculating the Thermodynamic Functions of F_2O.

θ_1	θ_2	θ_3	C'_Φ	C'_S
1 град			2 кал/мол·град	
1335,2	663,28	1195,6	4,8332	12,7823

1) Deg.; 2) cal/mole·deg.

The thermodynamic functions of F_2O were previously calculated by Potter [3312] and Evans et al. [1514], up to 1500°K. Both calculations were made with inaccurate values for the products of the moments of inertia; in paper [3312], moreover, the frequency values used for the calculations were incorrect. In the Handbook of the US Bureau of Standards [3680] the thermodynamic functions of F_2O were taken according to data of [1514], those in Zeise's book [4384] according to paper [3312]. The divergence between the values of the thermodynamic functions given in Table 3 (II) and the results of the preceding calculations are explained by the difference of the molecular constants used (in the first

edition of the Handbook the thermodynamic functions of F_2O were not calculated).

The thermodynamic functions of FO given in the first and the present editions of the Handbook differ by an amount of from 0.2 (at 293.15°K) to 0.5 cal/mole·deg (at 6000°K), owing to the fact that in the first edition the values of the molecular constants of FO were taken from paper [436]. Other calculations of the thermodynamic functions of FO are unknown in literature.

§35. THE THERMODYNAMIC QUANTITIES

The fluorine standard state is that of F_2 (gas).

F (gas). The heat of formation of monatomic fluorine, corresponding to the applied value of $D_0(F_2)$ (see below), is equal to

$$\Delta H^\circ f_0 = 18{,}5 \pm 0{,}5 \text{ kcal/g-atom}$$

F^- (gas). In literature the electron affinity of the fluorine atom, A(F), was for a long time given too high a value (about 98 kcal/g-atom), which had been obtained by Mayer and Helmholtz in paper [2821] and was based upon a calculation according to the Born-Haber cycle with an incorrect value of $D_0(F_2)$. In 1948 Metlay and Kimball [2862] obtained the first experimental data on the quantity A(F) by measuring the F^- ion concentration appearing when F_2 molecules dissociate on an incandescent tungsten wire. Since the value of A(F) obtained in paper [2862] was much lower than that calculated by Mayer and Helmholtz according to Born's cycle, the authors of paper [2862] devoted their main interest to analyzing the causes of possible experimental errors. Evans, Warhurst and Whittle [1512] however, showed that the high values of A(F), suggested in paper [2821], are incorrect since wrong values of $D_0(F_2)$ had been used in the calculations; the electron affinity of the fluorine atom must amount to -81.7 ± 4 kcal/g-atom. This value is in good agreement with that calculated according to the experimental data, obtained by Metl

and Kimball; A(F) = −82.1±3.9 kcal/g-atom (see [770]).

In Pritchard's review article [3330] in which the data on the energy values of the electron affinity of various atoms were subject to a critical analysis, for A(F) a value of −83.5 kcal/g-atom was recommended, a value that was also accepted in the first edition of the present Handbook.

Following Pritchard's review, three experimental study reports were published which dealt with the determination of the value of A(F) and a series of theoretical and semiempirical estimates of this quantity (see [2768]). In the papers of Bakulina and Ionov [83,84] a mass spectrometer was used to measure the ratios of the negative ion currents of two halogens produced in a simultaneous surface ionization of the vapors of their alkali salts. The measurements in [84] of the ion-current ratios, with an introduction of KF, KCl, KBr and KI in pairs, resulted in a high-accuracy determination of the differences (in kcal/g-atom) of the electron affinities of the atoms of all halogens:

$$A(\mathrm{Cl}) - A(\mathrm{Br}) = -5{,}77 \pm 1{,}38,$$
$$A(\mathrm{Cl}) - A(\mathrm{I}) = -12{,}22 \pm 0{,}69,$$
$$A(\mathrm{Cl}) - A(\mathrm{F}) = -4{,}61 \pm 0{,}69,$$
$$A(\mathrm{Br}) - A(\mathrm{I}) = -6{,}23 \pm 0{,}46,$$
$$A(\mathrm{F}) - A(\mathrm{Br}) = -0{,}46 \pm 0{,}46,$$
$$A(\mathrm{F}) - A(\mathrm{I}) = -6{,}69 \pm 0{,}92.$$

In order to determine the absolute values the authors of paper [84] used the value A(Br) = −3.56 ev = −82.1 kcal/g-atom as the most reliable magnitude and obtained: A(F) = −82.6 kcal/g-atom. The value of A(Br) = −81 kcal/g-atom we used in the present Handbook corresponds to A(F) = −81.5 kcal/g-atom.

In Bailey's paper [623] the quantity A(F) was obtained with the help of two methods: on the basis of a mass-spectrometrical determination of the ion concentration in the dissociation of KF and RbF on in-

candenscent tungsten wires and on the basis of a mass-spectometrical determination of the Cl and F ion concentrations in the dissociation of ClF_3 under like conditions, using the A(Cl) value obtained in paper [623].*

On the basis of the data obtained, Bailey recommended A(F) = −82.1 ± 2.1 kcal/g-atom which is in good agreement with the data of [3330, 83, 623]. Virtually the same value, namely A(F) = −82 ± 2 kcal/g-atom was obtained in the paper by Jortner, Stein and Treinin [2308] from the UV absorption maximum of solutions containing F^- anions. Finally, in Cubicciotti's paper [1229] the electron affinity of the fluorine atom (and also that of the other halogens) was calculated according to the Born-Haber cycle, after a theoretical calculation of the lattice energy of the halide salts of alkali metals. The corresponding value of A(F) was equal to −80.2 ± 1 kcal/g-atom. A calculation of this value on the basis of the values of the thermodynamic quantities accepted in the present Handbook results in a somewhat higher value: A(F) = −80.7 ± 1 kcal/g-atom.**

In the present Handbook for the electron affinity of the fluorine atom, obtained on the basis of experimental data [770, 84, 623 and 2308], we accept the value

$$A(F) = -82.1 \pm 2 \text{ kcal/g-atom}$$

to which corresponds

$$\Delta H°f_0(F^-, \text{gas}) = -63. \pm 2.1 \text{ kcal/g-atom.}$$

F_2(gas). In older papers [1990, 3832, 4173, 2583, 850, 1123, 1317] too high values were assumed for the F_2 dissociation energy, which were equal to or higher than 63 kcal/mole. These values were calculated from indirect experimental data or estimated by means of approximation methods.

Wahrhaftig [4127] was the first who established that the high val-

Wahrhaftig [4127] was the first who established that the high values of the fluorine dissociation energy are in contradiction with the data on the dissociation energy and the heat of formation of ClF and Gaydon [141] showed that they are also in contradiction with the HF dissociation energy as calculated on the basis of a linear extrapolation of the vibrational levels of this molecule. Schmitz and Schumacher [3640] repeated Wahrhaftig's investigations of the ClF absorption spectrum and also measured the heat of formation of ClF [3641]; they found that the F_2 dissociation energy is equal to 33.4 or 30.6 kcal/mole according to the quantity $D_0(ClF)$ (see p. 506). Caunt and Barrow studied thermodynamic cycles including the dissociation energy, the heats of formation, dissolution and evaporation of RbF, CsF [1073] and TlF [1074] and found that $D_0(F_2)$ amounts to 50 ± 6 kcal/mole [1073] or less than 45 kcal/mole [1074]. A detailed survey of these and other papers, with an analysis of the accuracy of the data obtained, was published by Evans, Warhurst and Whittle [1512] who showed that $D_0(F_2)$ must lie within the limits of 37 ± 8 kcal. Analogous results as to the inaccuracy of the high values of the fluorine dissociation energy were obtained by Riss [355] who analyzed the literature published until 1951.

In 1953 Barrow and Caunt [648] carried out additional studies on the dissociation energy of the fluorides of alkali metals and obtained $D_{298}(F_2) = 37{,}6 \pm 3{,}5$ kcal/mole (or $D_0(F_2) = 36{,}6 \pm 3{,}5$ kcal/mole).

In 1948 Wicke [4251, 4252] studied the thermal conductivity of fluorine by means of the method of the incandescent wire and arrived at the result that fluorine does not dissociate up to temperatures of 1000°, a fact that speaks in favor of the value $D_0(F_2) = 63$ kcal/mole. Analogous measurements were made in 1951 by Frank and Wicke [1594] who found that $D_0(F_2)$ must amount to at least 45 kcal/mole. More precise results of measurements of the thermal conductivity of fluorine showed that $D_0(F_2)$

lies in the interval of 40 – 45 kcal/mole [4253]. Later on Wicke and coworkers [4255, 4254] established that under experimental conditions [4251, 4252] equilibrium is not achieved so that the results of the measurements cannot be used in order to determine $D_0(F_2)$.

The pressure that establishes when fluorine is heated in a closed container was measured by Doesher [1358, 1359] (nickel container, temperature 753 – 1115°, 24 measurements) and Gilles and Margrave [1745] (copper container, temperature 300 – 860°, three measurements). On the basis of the values found in papers [1358, 1359, 1745] for the equilibrium constants of the F_2 dissociation reaction, the authors of the present Handbook calculated the values $D_0(F_2)$ = 36.7* and 32 kcal/mole, respectively.

Milne and Gilles [2923] determined the values of the equilibrium constants of fluorine dissociation when fluorine was heated in a container of Monel metal up to a certain temperature. The authors of paper [2923] measured the quantity of fluorine atoms in a molecular beam emerging from an opening in the container and hitting a target which was coated with a thin tellurium layer. It was established beforehand that it was only the fluorine atoms and not its molecules that reacted with the tellurium. The values of the equilibrium constants of the F_2 dissociation reaction and also the temperature dependence of the equilibrium constants of this reaction found in paper [2923] correspond to a dissociation energy of fluorine equal to 41.3 ± 0.5 kcal/mole. But Milne and Gilles assume that in their work systematic errors may have occurred.

Wise [4298, 4299] studied the dissociation of fluorine by means of an effusion method and obtained $D_{298}(F_2)$ = 37,6 ± 0,8 kcal/mole (or $D_0(F_2)$ = 36.6 kcal/mole). A calculation of the dissociation energy of F_2 from the values of the equilibrium constants of fluorine dissociation

as found by Wise [4298, 4299] and the thermodynamic functions of F and F_2 as accepted in the present Handbook result in the value $D_o(F_2)$ = 37.6 ± 1.0 kcal/mole. The results of two measurements in Wise's experiments at very high temperatures are considerably lower which might be explained by a more powerful interaction between fluorine and the material of the effusion cell. If we ignore these two experiments, Wise's data result in $D_o(F_2)$ = 37.0 ± 0.5 kcal/mole.

Wicke and Fritz [4255] measured the explosion pressure of mixtures of $F_2 + Cl_2$ and $H_2 + F_2 + Ar$ in a spherical bomb and found $D_o(F_2)$ = 37 ± 2 kcal/mole.* Wray and Hornig [4334] studied the speed of shock waves in gas mixtures containing different quantities of fluorine and obtained $D_o(F_2)$ = 31 ± 4.3 kcal/mole.

In the past years attempts were made to determine the dissociation energy of F_2 molecules on the basis of studying their spectra. Iczkowski and Margrave [2163] investigated the fluorine absorption spectrum in vacuum ultraviolet and, via a short linear extrapolation of the levels of the high excited state, they obtained $D_o' = 3800\ cm^{-1}$. In this state the dissociation products of fluorine molecules must be fluorine atoms in the ^2P_g and ^2P_u states. Since these states of the fluorine atom are both doublets, four values are possible for the dissociation energy of F_2 in the ground state. Iczkowski and Margrave recommend the mean value of them, which is equal to 37.5 ± 2 kcal/mole. Rees [3414], on the basis of data on the continuous absorption spectrum of F_2 in the visible range of the spectrum, obtained in paper [3849a], and estimated values of the vibrational constants of F_2 in the state $X^1\Sigma$ (see p. 453), constructed the potential curve of the repulsive excited state $^1\Pi_u$, possessing the same dissociation limit as the ground state of the F_2 molecule. Comparing the potential energy curve of the $^1\Pi_u$ state obtained in this way with the curves obtained by theoretical calculations from the

Born-Mayer formula for different values of $D_0(F_2)$, Rees came to the conclusion that the F_2 dissociation energy is equal to 37.1 ± 0.85 kcal/mole.

The contradiction between the comparatively low value of the dissociation energy of the fluorine molecule ($D_0(F_2)$ = 37 kcal/mole) and the high value of its force constant ($k_e = 4.78 \cdot 10^5 \cdot dynes \cdot cm^{-1}$) was explained by Brown [987] on the basis of a conception on the valent states.

Thus, most of the studies made in the past years, with the help of different methods, led to similar values of $D_0(F_2)$. The most accurate values were obtained in the papers [1359, 4255, 4299, 3414], according to which we accepted in the Handbook the value

$$D_0(F_2) = 37.0 \pm 1.0 \text{ kcal/mole}$$

The quantities recommended in the Handbook editions and in review articles [1668, 255, 2585, 4384, 2494] agree virtually with those accepted in the present Handbook.*

FO (gas). Dibeler, Reese and Franklin [1329] studied the dissociation of F_2O by the method of electron impact and found that the F^- ionization potential is equal to 1.2 ± 0.2 ev. The authors of paper [1329] related this value with the following process:

$$F_2O \text{ (gas)} + e^- \rightarrow FO \text{ (gas)} + F^- \text{ (gas)}, \qquad (8.1)$$

which permitted them to calculate $D_0(FO - F)$ = 2,8 ev = 64.5 kcal/mole (where the kinetic energy of FO and F^- is taken into account which, according to measurements carried out in paper [1329], is equal to 2 ev). The value of $D_0(FO - F)$ obtained in paper [1329], corresponds to D_0 (FO) = 24 kcal/mole. The great difference between the values of $D_0(FO)$ D_0 (FO − F), found in paper [1329], is not plausible; it may be due to an erroneous interpretation of the process of F^- ion production accepted in this paper.

In Gaydon's monograph [1668] we find the value $D_0(FO)$ = 35 kcal/mole,

calculated by Glockler [1762] under the assumption that $D_o(FO) = \frac{1}{2} D_o(F_2O)$* and $D_o(F_2) = 60$ kcal/mole. Since F – O bond in FO and F_2O molecules is of the same type (see p. 455), the method of estimating the quantity D_o (FO) suggested by Glockler is admissible. A calculation according to this method, using the values of the thermodynamic quantities accepted in the Handbook, leads to the value $D_o(FO) \cong 44$ kcal/mole, which is in agreement with the value $D(CF_3O - F) = 47$ kcal/mole, calculated on the basis of mean bond energies in the CF_4 and CH_3CH molecules and the heat of formation of CF_3CF [3308].

The quantity $D_o(FO)$, estimated to be equal to $\frac{1}{2} D_o(F_2O)$, is much more reliable than that obtained from data by Dibeler, Reese and Franklin [1329]. We therefore accept in the Handbook

$$D_o(FO) = 44. \pm 10 \text{ kcal/mole}$$

To this value of D_o (FO) corresponds

$$\Delta H°f_o(FO, \text{ gas}) = 33.487 \pm 10 \text{ kcal/mole}$$

<u>F_2O (gas)</u>. Ruff and Menzel [3560, 3561] measured the combustion heat of fluorine, oxygen and F_2O in hydrogen, in the presence of a NaOH solution and obtained $\Delta H°f_{291}(F_2O) = 4.6 \pm 2$ kcal/mole. Brauer [1093] obtained on the basis of the measurements by Ruff and Menzel $\Delta H°f_{298.15}(F_2O) = -7 \pm 2$ kcal/mole.

Wartenberg and Klinkott [4164, 4154] determined the heat of interaction of gaseous F_2O with KOH, KI and HBr solutions. The results of these measurements were recalculated by Bichowsky and Rossini [813] who, taking Ruff's and Menzel's data [3560, 3561] into account, recommended the value $\Delta H°f_{298}(F_2O, \text{ gas}) = 5.5$ kcal/mole.** Evans et al. [1514], on the basis of the data by Wartenberg and Klinkott [4164, 4154], calculted the value $\Delta H°f_{298.15}(F_2O) = 7.6 \pm 2$ k/cal/mole.

The recalculation of the measuring results obtained by Wartenberg and Klinkott [4164, 4154] carried out with more accurate data [3561, 3508]

for the heat of formation of the corresponding solutions led to the following values of $\Delta H^\circ f_{273.15}(F_2O)$: 8.6 kcal/mole (reaction with KOH solution), 7.7 kcal/mole (reaction with KI solution) and 9.7 kcal/mole (reaction with HBr solution).

It is not possible to make a substantiated selection among the values of the heats of formation of F_2O, calculated on the basis of measurements [3560, 3561] and [4164, 4154]. Therefore a mean value was accepted for the Handbook:

$$\Delta H^\circ f_{298.15}(F_2O, \text{газ}) = 8 \pm 3 \text{ kcal/mole}$$

To the accepted value of the heat of formation corresponds

$$D_0(F_2O) = 87.446 \pm 3.2 \text{ kcal/mole}$$

TABLE 55

The Values (in cal/mole) Used for the Thermodynamic Quantities of Fluorine and Its Compounds in the Gaseous State

1 Вещество	D_0	$\Delta H^\circ f_0$	$\Delta H^\circ f_{273.15}$	$\Delta H^\circ f_{298.15}$	$H^\circ_{298.15} - H^\circ_0$	$H^\circ_{298.15} - H^\circ_0$
F	—	18 500	18 995	19 003	1531	1558
F^-	82 100[a]	−63 600	−64 637	−64 656	1456	1481
F_2	37 000	0	0	0	2073	2111
FO	44 000	33 487	33 502	33 502	2071	2106
F_2O	87 446	8 541	8 030	7 997	2552	2604

[a] Reduced value of the energy of detachment of an electron from an F^- ion.

1) Substance.

Chapter 9

CHLORINE AND ITS COMPOUNDS WITH OXYGEN AND FLUORINE

(Cl, Cl^-, Cl_2, ClO, ClO_2, Cl_2O, HOCl, ClF)

The present chapter deals with monatomic and diatomic chlorine, the Cl^- ion, the simplest oxygen compounds of chlorine (ClO, ClO_2, Cl_2O, HOCl) and fluorine (ClF) in the gaseous state.

Apart from the chlorine-oxygen compounds considered in the Handbook there are other multiatomix chlorine oxides which are well-known: Cl_2O_6, Cl_2O_7, Cl_2O_8 . These compounds are unstable at high temperatures and on heating they decompose easily into the elements.

Among the chlorine-fluorine compounds, besides ClF, we also know chlorine trifluoride ClF_3. There are also several unstable compounds of chlorine, fluorine and oxygen (ClO_3F, ClO_2F, ClO_4F, and, possibly, ClOF). These compounds are not considered in the Handbook.

The data given in the present chapter permit a sufficiently accurate calculation of composition and thermodynamic properties of the systems chlorine – oxygen, chlorine – fluorine* and chlorine – oxygen – hydrogen.

Compounds of chlorine with other elements will be dealt with in the chapters 10–12, 15, 16–18, 21–26, 28, 29.

§36. THE MOLECULAR CONSTANTS

Cl. In the electron ground state the chlorine atom has the electron configuration $1s^2\,2s^2\,2p^6\,3s^2\,3p^5$, which corresponds to one ^2P term. The energies of transition to excited electron states of the chlorine atom are hi h (higher than 80,000 cm^{-1}) and therefore these states are not con-

sidered in our Handbook. Table 56 gives the excitation energies and statistical weights of the two components of the ground state ^2P of the chlorine atom, taken from Moore's Handbook [2941].

TABLE 56

Energy Levels of the Cl Atom and the Cl^- Ion.

1 Атом	2 Состояние		Статистический вес 5	Энергия уровня, $см^{-1}$ 6
	3 электронная конфигурация	терм 4		
Cl	$1s^2\,2s^2\,2p^6\,3s^2\,3p^5$	$^2P_{3/2}$	4	0
	$1s^2\,2s^2\,2p^6\,3s^2\,3p^5$	$^2P_{1/2}$	2	881
Cl^-	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6$	^1S	1	0

1) Atom; 2) state; 3) electron configuration; 4) term; 5) statistical weight; 6) level energy, cm^{-1}.

Cl^-. The electron configuration of the negative ion of monatomic chlorine in the ground state is of the type $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$ which corresponds to an ^1S term. By analogy to the argon atom which has the same electron configuration it can be assumed that the energies of the excited states of the Cl^- ion must amount to about 100,000 cm^{-1}, a value that exceeds by far the energy of electron detachment from a Cl^- ion (see p. 502). We therefore assumed in the Handbook that Cl^- has but a single stable state, namely the ground state ^1S.

Cl_2. The emission and absorption spectra of diatomic chlorine has been investigated by many authors in a wide interval of wavelengths, ranging from the visible up to vacuum ultraviolet. The complex character of the chlorine electron spectrum, which consists essentially of continua and diffuse bands, however, renders it very difficult to interpret experimental data and the knowledge of the electron states of the Cl_2 molecule and of its constants is at present very limited. The presence of continua and diffuse bands in the chlorine spectrum is due

to the fact that the Cl_2 molecule has a great number of excited electron states with low energies and common dissociation limits, a considerable part of these states being repulsive states, while the minima of the potential curves of the stable states are shifted with respect to the minimum of the ground state's potential curve to the range of large values of r. In fact, it must be stressed that an interpretation of the chlorine spectrum is rendered much easier by studying the spectra of other halogens (Br_2 and I_2) whose molecules have outer electron shells which are analogous to the electron shell of the Cl_2 molecule.

A theoretical analysis of the electron states of halogen molecules (Cl_2, Br_2 and I_2) and also of diatomic interhalogen compounds, an investigation of their correlations with the states of the corresponding atoms and an interpretation of the results of experimental investigations of halogen spectra were made by Mulliken in a series of papers (see [2987, 2982, 2998]). On the basis of these investigations Mulliken came to the conclusion that the $^1\Sigma_g^+$ state is the electron ground state of halide molecules and the lower electron states, correlated with $^2P + {}^2P$ states of the halogen atoms, must be $^3\Pi_u, {}^1\Pi_u, {}^1\Pi_g$ and $^3\Pi_g$ states [2987]; he showed that the last three states must be of repulsive nature while continua, as observed in the absorption spectra of all halogens in the near ultraviolet or in the visible, correspond to $^1\Pi_u \leftarrow X^1\Sigma_g^+$ transitions. On the basis of theoretical considerations and an analysis of experimental data Mulliken showed (see [2987]) that the spin-orbital coupling in excited electron states of halogen molecules corresponds in its nature to case c according to Hund or is similar to it. Hence follows in particular that the lower excited state of the Cl_2 molecule (as well as of Br_2, I_2 and the molecules of interhalogen compounds) cannot be considered as a single state as it consists essentially of four inde-

pendent states: $^3\Pi_{0_u^+}$, $^3\Pi_{0_u^-}$, $^3\Pi_{1u}$, $^3\Pi_{2u}$. The most intense system of discrete bands in the absorption spectra of Cl_2, Br_2 and I_2 in the visible range (together with the adjacent continuum) was identified by Mulliken with the $^3\Pi_{0_u^+} \leftarrow X^1\Sigma_g^+$ transition and the weak system of bands in the near infrared part of the spectrum of Br_2 and I_2 was identified with a $^3\Pi_{1u} \leftarrow X^1\Sigma_g^{+*}$ transition. A band system of $^3\Pi_{1u} \leftarrow X^1\Sigma_g^+$ has not been observed so far in the chlorine spectrum.

In paper [2998] Mulliken calculates theoretically the splitting of the components of the $^3\Pi_u$ state for the Cl_2, Br_2 and I_2 molecules and came to the conclusion that, with an interatomic distance equal to the equilibrium distance in the $X^1\Sigma_g^+$ state (i.e., above the minimum of the potential curve of this state), the potential curves of the states $^3\Pi_{0_u^-}$, $^3\Pi_{2u}$, $^3\Pi_{1u}$ and $^3\Pi_{0_u^+}$ lie one below the other in this sequence, the state $^3\Pi_{0_u^+}$.** being the highest. In the case of Br_2 and I_2 Mulliken's calculations are in good agreement with the experimental data for the states $^3\Pi_{0_u^+}$ and $^3\Pi_{1u}$ (see Tables 64 and 69). For Cl_2 they permit the assumption that the states $^3\Pi_{1u}$, $^3\Pi_{2u}$ and $^3\Pi_{0_u^-}$, to which transitions are not observed in experiment (see below), must be stable since for Cl_2 in the state $^3\Pi_{0_u^+}$ $D_e \sim 3320$ cm^{-1}, and, therefore, the minimum of the potential curve of this state lies much lower than the dissociation limits of the states $^3\Pi_{1u}$, $^3\Pi_{2u}$, $^3\Pi_{0_u^-}$ and $X^1\Sigma_g^+$.

This point of view is in contradiction with the interpretation of the halogen molecule spectra as suggested by Asundi and Venkateswarlu [584]. According to this intepretation the Cl_2 molecule, besides the $X^1\Sigma_g^+$ state, has only one stable state, correlated with the $^2P + ^2P$ limit (the $^3\Pi_{0_u^+}$, state, for the Br_2 and I_2 molecules there are two such states, ($^3\Pi_{0_u^+}$ and $^3\Pi_{1u}$); the states $^3\Pi_{2u}$ and $^3\Pi_{0_u^-}$ may be possessed by all three molecules and the state $^3\Pi_{1u}$ by Cl_2; just as all residual states, corre-

lated with the dissociation limits $^2P + {}^2P$, they are repulsive states. This conclusion is based on an analysis of halogen emission spectra in the range 1800 – 4800 Å, obtained in a series of papers by Venkateswarlu, which consists of groups of diffuse bands and may be related to transitions from stable electron states with high excitation energies to repulsive states correlated with the $^2P + {}^2P$ dissociation limit. Since the minima of the potential curves of stable states correspond to great internuclear distances and lie above almost horizontal sections of the potential curves of repulsive states, in the spectrum a single diffuse band must correspond to the transition between each pair of states. In the Cl_2 emission spectrum Venkateswarlu [4088] observed three band groups which, in paper [584], were interpreted as transitions from the states $^3\Sigma_u^+, {}^3\Pi_{1g}$ and $^1\Pi_{1g}$ (T_e is equal to 58,000, 67,700 and 75,000cm^{-1}, respectively) to a series of repulsive states. Three bands in the range about 2100 Å were referred to the transitions $^3\Pi_{1g} \rightarrow {}^3\Pi_{1u}, {}^3\Pi_{1g} \rightarrow {}^3\Pi_{2u}$ and $^3\Pi_{1g} \rightarrow {}^3\Pi_{0_u^-}$, and on this basis the conclusion was drawn that the states $^3\Pi_{1u}, {}^3\Pi_{2u}$ and $^3\Pi_{0_u^-}$ are repulsive states.

This conclusion was actually not corroborated in paper [584] by a single theoretical argument. If we take into account that the Cl_2 molecule has a great number of other repulsive states, correlated with the dissociation limit $^2P + {}^2P$, it is obviously impossible to give an unambiguous interprestation of the diffuse bands, so much the more as their relationship to a transition from the state $^3\Pi_{1g}$ with $T_e \sim$ 67,700 cm^{-1} is also problematic. The conclusion of Asundi and Venkateswarlu that, in contrast to Br_2 and I_2, the $^3\Pi_{1u}$ state of Cl_2 is a repulsive state, is also called in question, because the stability of this state increases from I_2 to Br_2 (the dissociation energies of the I_2 and Br_2 molecules in the $^3\Pi_{1u}$ state amount to about 660 and 2240 cm^{-1}) and

it is not justified to expect an inverse dependence for the transition from Br_2 to Cl_2.

It is obvous that for the problem of the stability of the states $^3\Pi_{0_u^-}$, $^3\Pi_{1u}$ and $^3\Pi_{2u}$ of the Cl_2 molecule a final solution can not be found before new experimental data have been obtained which permit an unambiguous interpretation.

The molecular constants of Cl_2 in the states $X^1\Sigma_g^+$ and $B^3\Pi_{0_u}$ – may be determined as a result of analyzing the band system $^3\Pi_{0_u^+} \leftrightarrows {}^1\Sigma^+$. In the emission spectrum of chlorine this band system was obtained by Uchida [4030] and Kitagawa [2423] with the help of low-dispersion devices; the wavelengths of the band edges were not determined with high accuracy and the Cl_2 constants were not determined at all. In the absorption spectrum the band system $^3\Pi_{0_u^+} - {}^1\Sigma_g^+$ was studied by Kuhn [2498], Namakura [3018] and Elliott [1474, 1476]. The authors of [2498, 3018] observed in the spectrum four groups of bands with the short-wave end in the range of 4785 Å and determined the wave numbers of the band edges. These bands are due to transitions from the levels v = 0, 1, 2 and 3 of the state $X^1\Sigma_g^+$ to high vibrational levels of the state $^3\Pi_{0_u^+}^*$. In Elliott's papers [1474, 1476] the Cl_2 absorption spectrum was obtained with a high-dispersion device which made it possible to resolve the rotational structure and to determine the wave numbers of the beginnings of 10 bands, among them seven bands of the Cl_2^{35} molecule and three bands of $Cl^{35}Cl^{37}$ molecules. On the basis of the measured isotope shift in the three Cl_2 molecule bands, Elliott could improve the numeration of the bands observed by him and the authors of the papers [3018, 2498] in the chlorine absorption spectra, and he obtained the following equation for the band edges (see [1476])**:

$$\nu = 17657{,}7 - 255{,}7\ v' + 5{,}42\ v'^2 + 560{,}9\ v'' - 4{,}0\ v''^2. \quad (9.1)$$

The values of the vibrational constants of Cl_2 in the state $X^1\Sigma_g^+$, and corresponding to the above equation, are contained in the present Handbook (see Table 57). They agree with the values recommended in Herzberg's monograph [2020] and in the handbook [649]. Though the accepted values of the vibrational constants of Cl_2 in the state $X^1\Sigma_g^+$ were calculated from data of the four lower vibrational levels (v" = 0, 1, 2 and 3) they are obviously suited well enough to approach the energies of the higher vibrational levels of this state since the calculated levels coincide at 19,950 cm^{-1}, while the dissociation limit of the $X^1\Sigma_g^+$ state lies at 19,969 cm^{-1} (see p. 502) above the level v = 0.

Stamreich et al. [3839] found that in the Raman spectrum of Cl_2 the fundamental frequency is equal to $\Delta G_{1/2} = 557{,}5 \pm 1$ cm^{-1} which is in good agreement with a value calculated from the adopted constant: $\omega_e - 2\omega_e x_e = 556{,}9$ cm^{-1}.

Since in papers [1474, 1476] only bands with v" = 1 and v" = 2 were observed, Elliott could only determine two values of B_v'': B_1 = 0.2412 and B_2 = 0.2395 cm^{-1}. The values of B_e and α_1, corresponding to these quantities are contained in the present Handbook. Since the value of B_c is not established by experiment, the accuracy of the rotational constants of Cl_2 in the state $X^1\Sigma_g^+$, compiled in Table 57, is comparatively low.

The vibrational and rotational constants of Cl_2 in the $B^3\Pi_{0_u^+}$ state, given in Table 57, are also borrowed from Elliott [1476].* In connection with the fact that in papers [3018, 2498, 1474, 1476] in the Cl_2 absorption spectrum only bands with $v' \geq 4$ could be observed, the values accepted for T_e and the vibrational constants of the $^3\Pi_{0_u^+}$ state may contain a small error.** None the less, they are in good agreement with those recently obtained by Venkateswarlu and Khanna [4093] on the

on the basis of an analysis of the band system in the range 2390 – 2600 Å of the Cl_2 emission spectrum (see Table 57) which belongs to a transition from a high electron state of the Cl_2 molecule to the $B^3\Pi_{0_u^+}$ state. In this system bands are observed which correspond to values of v" from 0 to 25.

TABLE 57

Values Accepted for the Molecular Constants of Cl_2, ClO and ClF

1 Молекула	2 Состояние	T_e	ω_e	$\omega_e x_e$	B_e	$\alpha_1 \cdot 10^2$	$D_e \cdot 10^6$	r_e
		3 $см^{-1}$						Å
Cl_2^{35}	$X^1\Sigma_g^+$	0	564,9	4,0	0,2438	0,17	0,18[a]	1,988
	$B^3\Pi_{0_u^+}$	17809,7[b]	261,12[c]	5,42	0,161	0,2[d]	—	2,41
$Cl^{35}O$	$X^2\Pi$	0	868	7,5	0,6425[e]	0,69[f]	2,2	1,546
	$A^2\Pi$[g]	31022,2	563,39	9,31[h]	0,4809	0,53[i]	—	1,79
$Cl^{35}F$	$X^1\Sigma^+$	0	787,5	7	0,516509	0,4359	0,891	1,62813
	$B^3\Pi_{0^+}$	18787,7	380,4	11,2	0,372	1,4	—	1,91

1) Molecule; 2) state; 3) cm^{-1}.

[a] Calculated from Eq. (1.36).

[b] In Herzberg's book [2020] and in the handbook [649] the following values (in cm^{-1}) are given: $T_e = 18310,5$, $\omega = 239,4$, $\omega_e x_e = 5,42$, $B_e = 0,158$, $\alpha_1 = 0,003$.

[c] According to data of Venkateswarlu and Khanna [4093] (in cm^{-1}): $\omega_e = 260,69$, $\omega_e x_e = 5,55$, $\omega_e y_e = 0,0178$, $\omega_e z_e = 1,15 \cdot 10^3$.

[d] $\alpha_2 = -1.10^{-4} cm^{-1}$;

[e] Constant given for v = 0;

[f] Calculated from Eq. (1.38);

[g] $A \sim 200$ cm^{-1};

[h] $\omega_e y_e = -0.07$ cm^{-1};

[i] $\alpha_2 = -4 \cdot 10^{-5} cm^{-1}$.

The accuracy of the values of the rotational constants of Cl_2 in the state $B^3\Pi_{0_u^+}$, compiled in Table 57, is much lower since in papers [1476, 1474] the rotational structure was only studied of the bands with v' = 6, 7, 8 and 11, 12, 13. The corresponding values of B_v as calculated by Elliott in paper [1476], lie on two intersecting straight

lines if plotted in a graph B_v versus v, which does not render it possible to describe their functions $B_v = B_0 - \alpha_1 v$ and to obtain a satisfactory value for B_e or B_0. The values of the constants B_e, α_1 and α_2 given in Table 57 were, when preparing the present Handbook, calculated from B_v values given in paper [1476].

In the past years a series of papers (see 4088, 4093, 2391, 1953, 1955, 2584] were devoted to studies of the chlorine spectra connected with electron states of the Cl_2 molecule. All these electron states have excitation energies exceeding 50,000 cm^{-1} and are not considered in the present Handbook. The interpretation of the observed transitions and the systematism of the high electron states of the Cl_2 molecule may be found in the papers of Asundi and Venkateswarlu [584], Haranath and Rao [1955] and Lee and Walsh [2584].

ClO. The first spectra of ClO were obtained in 1948 by Pannetier and Gaydon [3173] who studied the radiation from a hydrogen flame burning in oxygen with chlorine admixtures. The bands observed in the range 3500–4500 Å did not have sharp edges and were overlapped to a considerable degree by hydroxyl bands which rendered their analysis very difficult. From the spectrograms obtained with a low-dispersion device, the authors [3173] determined the wavelengths of 20 edges with an accuracy of up to 2–5 Å (±10–30 cm^{-1}) and ordered them in the Deslandres scheme, but it was impossible to determine the values of the vibrational quantum number v" and the vibrational constants of ClO.

In 1950 Porter [3301, 3303] obtained the ClO absorption spectrum in pulsed photolysis of chlorine in the presence of oxygen. The band system consisted of two progressions and ranged from 2630 to 3040 Å. From the shape of the bands and also on the basis of theoretical considerations the band system observed was attributed to the transition $^2\Pi - {}^2\Pi$ and each progression to transitions from one of the two com-

ponents of the lower ($v'' = 0$) vibrational levels of the ground state to a series of levels of the excited state. The low dispersion of the apparatus and the complex character of the spectrum did not permit an analysis of the rotational structure of the ClO bands.

On the basis of the results of his measurements and data from [3173] on the emission spectrum of ClO, Porter estimated the wave number of the 0–0 band edge (~30,900 cm^{-1}) and numbered the residual bands.* The vibrational constants of ClO, calculated by Porter, are equal to (in cm^{-1}): $\omega_e'' = 868$; $\omega_e x_e'' = 7{,}5$; $\omega_e' = 557$ and $\omega_e x_e' = 11$. It must be noted that they give a bad description of the wave numbers of band edges. Thus the values calculated from these constants and those found by Pannetier and Gaydon from the emission spectrum differ by 100–150 - cm^{-1}.

In 1958 Durie and Ramsay [1428] again studied the absorption spectrum of ClO in pulsed photolysis of chlorine in the presence of oxygen. The spectrum was obtained in an apparatus with high dispersion and consisted in a progression of bands ($v'' = 0$). In the short-wave range the bands are observed to converge to a limit beyond which the continuum begins. In front of the limit of band convergence the rotational structure of the spectrum is complex since the bands overlap. In the long-wave range the rotational structure was simpler but in many bands the rotational lines were blurred because of a predissociation of the upper state.

Accepting the numeration suggested by Porter [3301] for the bands investigated, Durie and Ramsay determined the values of the vibrational and rotational constants of ClO in the excited state, the vibrational constants being calculated for the beginnings of the bands. This permitted, with the help of an extrapolation of the wave numbers of the beginnings of the bands of the $v+ = 0$** progression, an improvement of

the wave number of the 0–0 band, which was found to be equal to 30,869.7 cm^{-1}. The constants of ClO in the excited $A^2\Pi$ state, found in paper [1428] and given in Table 57 are accepted for the Handbook.

Since in paper [1428] only the progression v" = 0 was observed, it was not possible to determine the vibrational constants and the constant α_1 of the interaction between rotation and vibration in the ground state. The values accepted in the Handbook for B_0 and D_0 in the state $X^2\Pi$ were calculated by Durie and Ramsay from an analysis of the band 12 – 0 which is not overlapped by other bands. On the basis of a theoretical analysis and the data obtained, the authors of paper [1428] came to the conclusion that both ClO states observed are $^2\Pi$ rotational states; they also determined the value of the ClO doublet splitting constant for the two vibrational levels (v' = 5 and v' = 10) of the upper state. The constant of doublet splitting of the ground state could not be determined. For the vibrational constants of ClO in the state $X^2\Pi$ the values suggested by Porter were accepted in the Handbook. The difference between the values of $\Delta G_{v'+1/2}$ calculated with the accepted constants and those obtained on the basis of Pannetier's and Gaydon's experimental data, does not exceed ±20 cm^{-1}, a value that lies within the limits of accuracy of the ClO band edge wave numbers. An extrapolation of the vibrational levels of the $X^2\Pi$ state of ClO according to these constants leads to a dissociation limit which is in satisfactory agreement with the dissociation energy of ClO (see p. 503). The values of ω_e and $\omega_e x_e$ accepted in the Handbook for ClO in the $X^2\Pi$ state amount to ± 15 and ± 2.5 cm^{-1}, respectively.

ClF. The rotational [1742] and the vibration-rotation [3073] spectra of the ClF molecule and also the $^3\Pi_{0^+} - X^1\Sigma$ band system in its electron spectrum [4127, 3660] have been investigated as yet.

The first investigations of the spectrum of this molecule were

made by Wahrhaftig [4127] who determined the constants of ClF in both states, on the basis of an analysis of a series of bands ($v'' \leqslant 1$, $v' < 17$) of the system $^3\Pi_{0^+} \leftarrow {}^1\Sigma$. But the values found for the vibrational constants do not yield a satisfactory description of the wave numbers for the beginnings of the bands, given in paper [4127]; the calculated values and the values obtained by experiment differ by several hundred cm^{-1}. Schumacher, Schmitz and Brodersen [3660] investigated the $^3\Pi_{0^+} - X^1\Sigma^+$ band system anew and observed transitions from the three ground state levels to a series of levels of the higher state, up to $v' = 16$. On the basis of the data obtained the authors of [3660] determined the vibratioal constants of ClF in both states and, with the help of a short extrapolation, they obtained the dissociation limit of the $^3\Pi_{0^+}$ state. The values of the vibrational constants of the ground state (ω_e = = 787.5 cm^{-1} and $\omega_e x_e$ = 7 cm^{-1}) found in this paper cannot be considered as sufficiently exact since they were obtained from transitions from the three low vibrational levels of the ground state.

Nielsen and Jones [3073] investigated the infrared absorption spectrum of ClF and observed the fundamental frequency and the first harmonic of the molecules of $Cl^{35}F$ and $Cl^{37}F$. On the basis of the data obtained the [3073] determined the values of the vibration frequency and the constant of anharmonicity, which amounted to 786.34 and 5.23 – cm^{-1}, respectively, i.e., they were similar to the constants found in an analysis of the ClF electron spectrum in paper [3660]. It must be mentioned that the equation for the band edges in the system $^3\Pi_{0^+} - {}^1\Sigma^+$, in which the ground state constants were taken from Nielsen and Jones [3073] and those of the excited state from Schumacher et al. [3660], describes the frequencies of the band edges for $v \leq 9$, found in the papers [4127, 3660],* with an accuracy of ±3 cm^{-1}.

The values of the vibrational constants of ClF given in the Hand-

were taken from paper [3660]. The values accepted for the ClF ground state constants give, obviously, a sufficiently exact description of the energies of the high vibrational levels of this state.*

The rotational constants of ClF in the $X^1\Sigma^+$ state, given in Table 57, were obtained on the basis of results of a pricision analysis of the micro-wave spectrum of this molecule, carried out by Gilbert, Roberts and Grisword [1742]. Similar values were obtained by Wahrhaftig [4127] for the rotational constants of ClF in the $X^1\Sigma^+$ state, when analyzing the rotational structure of the bands of the $^3\Pi_{0^+} - {}^1\Sigma^+$ system. The rotational constants of the ClF in the $^3\Pi_{0^+}$ state were taken from data of [4127].

It must be mentioned that the ClF molecule, just as the molecules of other diatomic interhalogen compounds and of the halogens themselves, must possess several electron states with low energies, among them also other components of the lower excited state $^3\Pi$. The main part of these states must be of repulsive nature. Corresponding experimental data for ClF do not exist, but ICl and IBr (see Table 69), apart from the state $^3\Pi_{0^+}$, possess the stable states $^3\Pi_1$ and 0^+ with low excitation energies. It may be assumed that with the ClF molecule other components of the low $^3\Pi$ state have also a minimum on the potential energy curves.

$\underline{ClO_2}$. Investigations of the chlorine dioxide absorption spectra [3078, 1166, 1167] and structure studies of the ClO_2 molecule by means of the electron diffraction method [1420, 3203, 953] showed that in the electron ground state the ClO_2 molecule has a symmetrical nonlinear structure (point group C_{2V}). The electron spectrum of chlorine dioxide, positioned in the range 2600–5200 Å and connected with the transition $^2A_2 \leftarrow {}^2B_1$, was investigated in the papers [4040, 2491, 1165, 1166, 1167, 1168, 1169]. A more detailed examination of the ClO_2 electron spectrum was carried out by Coon and Ortiz [1165, 1166, 1168, 1169] who took the

spectra with the help of an apparatus with high dispersion. In a series of bands the fine structure was resolved, individual subbands were discriminated and the isotope effect was observed. The latter fact rendered it essentially easier to analyze the vibrational structure of the spectrum.

Studies of the infrared spectrum of this molecule are useful for a successful analysis of the electron spectrum of chlorine dioxyde. The first infrared spectra of chlorine dioxide were obtained by Bayley and Cassie [611] who observed four bands in the spectrum, two of them (954 and 1105 cm^{-1}) were interpreted as the fundamental frequencies of this molecule. Ku [2491], simultaneously with the electron spectrum of ClO_2, studied its vibration-rotation spectrum in the range of 2500-910 cm^{-1} - (4-11 μ) and found three bands in it which were identical with those observed in paper [611]. In 1951 the infrared spectrum of chlorine dioxide was studied by Hedberg [1980] in the range 10,000 - 666 cm^{-1} (from 1 to 15 μ). Besides the bands observed in [2491, 611]. Hedberg obtained another two bands which he interpreted as $3\nu_3$ and $2\nu_1 + \nu_3$.

It must be mentioned that in the papers of Bailey and Cassie, Ku and Hedberg the ClO_2 bands, connected with deformation vibrations, were not observed.

In order to determine the frequencies of ClO_2 deformation vibrations of the infrared spectrum, Nielsen and Woltz [3078] studied again the spectrum of chlorine dioxide in the range 5000 - 250 cm^{-1} (from 2 to 40 μ). The authors of the latter paper determined the wave numbers of the edges of 10 bands, amoung them those of four new bands, including $\nu_2 = 445$ cm^{-1}, and, thanks to the resolution of the rotational structure, they improved the wave numbers ν_1 and ν_3 of the beginnings of the bands. On the basis of the data they obtained, Nielsen and Woltz found the values of x_{11}, x_{33}, x_{13}, $x_{12} + x_{23}$, ω_1^0, ω_3^0 and, assuming the value x_{22} =

= 0.8 cm^{-1} suggested by Coon and Ortiz in paper [1168], they determined the constants x_{23} and ω_2^0.

The most reliable values of the vibrational constants of ClO_2 were obtained by Coon and Ortiz [1169] who analyzed the electron absorption spectrum of ClO_2, including 114 bands which were attributed to 17 progressions, and determined the vibrational constants of this molecule in the excited electron state as well as the constants ν_1, ν_2, x_{11}, x_{22} and x_{12} of the ground state. On the basis of results of own measurements and data obtained by Nielsen and Woltz [3078 on analyzing the infrared spectrum, Coon and Ortiz calculated the values of the bibrational constants ClO_2 given in Table 58 and accepted in the present Handbook.

The Raman spectrum of ClO_2 in solution was studied in a paper of Kujumzelis [2500] who obtained $\nu_1 = 935 \pm 8$ cm^{-1}, a value that agrees with data obtained in investigations of the infrared and the electron spectra of this molecule.

The structural parameters of the ClO_2 molecule was investigated by the method of electron diffraction in the papers of Brockway [953] ($r_{Cl-O} = 1,53$ Å) , Pauling and Brockway [3203] ($r_{Cl-O} = 1.53 \pm 0.02$ Å, $\angle OClO = 137 \pm 15°$) and Dunitz and Hedberg [1420] ($r_{Cl-O} = 1.491 \pm 0,014$ Å, $\angle OClO = 116.5 \pm 2.5°$). In the latter paper the electron diffraction pictures showed seven diffraction bands; for their interpretation use was made of both the method of successive approximations and the method of radial distribution (after Schomaker).

In investigations of the electron and infrared spectra of ClO_2 in the papers [1166, 3078] the rotational band structure of this molecule was partly resolved. As a result of analyzing the structure of five bands, Coon [1166] determined the quantities B', $(\Delta A - \Delta B)$ and $\Delta B'$ and with $r_{Cl-O} = 1,53$ Å , taken from data of [953], he found for the ground state $\angle OClO = 109 \pm 3°$, and for the excited state $r_{Cl-O} = 1,805 \pm 0,05$ Å and

$\angle OClO = 92 \pm 6°$. After the publication of the paper of Dünitz and Hedberg [1420], Coon [1167] processed again the experimental data obtained in paper [1166] and obtained for the ground state $r_{Cl-O} = 1.484$ Å, $\angle OClO = 115°.3$, and for the excited state $r_{Cl-O} = 1.648$ Å, $\angle OClO = 104°$.

TABLE 58

Values Accepted for the Molecular Constants of ClO_2 ($\sigma = 2$).

Состояние	T_e	ω_1	ω_2	ω_3	x_{11}	x_{22}	x_{33}	x_{12}	x_{23}	x_{13}	$I_A I_B I_C$ 10^{-117} (г·см²)³
1	2				см⁻¹						3
$^2B_1$	0	962,8	455,4	1128,2	−4,4	0	−2,0	−3,0	−14,4	−13	146,47
$^2A_2$	21369,5	711,4	298,0	756,1	−2,44	−1,4	10,2	−4,36	−7,4	− 6,9	304,85

1) State; 2) cm^{-1}; 3) $(g \cdot cm^2)^3$.

On the basis of an analysis of the rotational structure of the Q-branch of the ν_1 -band, Nielsen and Woltz [3078] determined the quantity $(A_{000} - B_{000})$ of the ClO_2 ground state. Using the data obtained by Dünitz and Hedberg and the results of own measurements Nielsen and Woltz obtained the following values for the structural parameters of ClO_2: $r_{Cl-O} = 1,49$ Å and $\angle OClO = 118°,5$. The product of the principal moments of inertia of ClO_2 in the $^2B_1$ -state, given in Table 58, were calculated from these quantities, those for the $^2A_2$ -state with the values of r_{Cl-O} and $\angle OClO$, obtained by Coon [1167].

Cl_2O. The Cl_2O molecule has a nonlinear symmetrical structure (point group of symmetry C_{2v}).

The infrared spectrum of chlorine monoxide was studied for the first time by Bailey and Cassie [615]. In the range from 10,000 to 555 cm^{-1} (from 1 to 18 μ) the authors of [615] observed four bands: 640, 973, 1245 and 1311 cm^{-1}; adjacent to the most longwave band there is still another band of about 680 cm^{-1} which was attributed to the CO_2 molecule. On the basis of investigations of the intensity and the

structure of the observed bands, Bailey and Cassie identified the bands of 973, 1245 and 640 cm^{-1} with the fundamental frequencies ν_1, ν_3 and ν_2 of the Cl_2O molecule; the fourth band, of 1311 cm^{-1}, was identified as pertaining to the frequency $2\nu_2$. The authors of paper [615] noted that the band 640 cm^{-1} could not be identified unambiguously but that it might be the first harmonic of ν_2 vibration.

In a brief note [2058] Hettner, Pohlman and Schumacher focused their attention to the fact that the band in the 680-cm^{-1} range, attributed by Bailey and Cassie to the CO_2 molecule, must in fact belong to the Cl_2O molecule since in the investigated spectrum no other intense band (ν_3) of carbon dioxide could be observed so that it is rather improbable that CO_2 is present as an impurity. This is verified by calculations of Sutherland and Penney [3906] who showed that the frequency relation of Cl_2O accepted in the paper of Bailey and Cassie [615] leads to too high values of the force constants. Assuming that the 680-cm^{-1} band belongs to the Cl_2O molecule, Sutherland and Penney interpreted it as the fundamental frequency of the symmetric valency vibration (ν_2) and the 640-cm^{-1} band as the first harmonic of the frequency ν_2, to which they attributed an amount of about 330 cm^{-1}. The three residual bands, observed by Bailey and Cassie, were interpreted by the authors of [3906] as ν_3 (973 cm^{-1}), $\nu_2 + \nu_3$ (1245 cm^{-1}) and 2 ν_1 (1331 cm^{-1}). The Cl_2O frequency relation suggested by Sutherland and Penney was used in Herzberg's monograph [152]. It must be noted that the Raman spectrum of Cl_2O was not studied and this makes it much more difficult to attribute the frequencies, observed in the infrared spectrum.

Hedberg [1980], studying the HOCl spectrum, found that the ν_2 band of this molecule lies in the range of 1242 cm^{-1}. Analyzing the HOCl spectrum in this range, Hedberg decided that the band of 1245 cm^{-1}, previously observed by Bailey and Cassie, must belong to the HOCl molecule,

produced in an interaction between Cl_2O and water impurities.

On the basis of an investigation of the Cl_2O spectrum in the range 660-10,000 cm^{-1} (from 1 to 15 μ) Hedberg [1980] recommends the values of the fundamental frequencies given in Table 59. Just as in the preceding paper by Bailey and Cassie [615], in Hedberg's paper the frequency ν_2 was not observed and its amount was estimated, assuming 640 cm^{-1} for the harmonic $2\nu_2$.

The frequency values recommended by Hedberg were accepted for the Handbook; the error of the value taken for ν_2 cannot be established at present. If in the papers [3906, 1980] a correct relation is given for the 640 cm^{-1} band, this error does not exceed 10-20 cm^{-1}, if it is not correct, the error may be considerably higher.

The structural parameters of the Cl_2O molecule were determined in [3907, 3203, 1420], by the method of electron diffraction. In the latter paper Dunitz and Hedberg, as a result of analyzing electron diffraction pictures containing 13 diffraction rings by the methods of radial distribution and successive approximations, obtained the values $r_{Cl-O} = 1.701 \pm 0,02$ Å and $\angle ClOCl = 110,8 \pm 1°,0$, which are in good agreement with the preceding less accurate investigations. The product of the principal moments of inertia of Cl_2O, given in Table 59, were calculated for $r_{Cl-O} = 1,701$ Å and $\angle ClOCl = 110°,8$.

After the work on the material of the present chapter had been finished, the authors of the Handbook came to know the paper of Jackson and Millen [2197] who investigated the microwave spectrum of Cl_2O and determined the values of the rotational constants of this molecule: $A_{000} = 1,4025$, $B_{000} = 0,1228$ and $C_{000} = 0.1127$ cm^{-1}. To these rotational constants corresponds a value of $I_A I_B I_C = 1129,8 \cdot 10^{-117}$ $(g \cdot cm^2)^3$, $r_{Cl-O} = 1,70$Å and $\angle ClOCl = 110°$ which is in good agreement with the values accepted in the Handbook.

HOCl. The spectrum of the HOCl molecule was only studied in a single paper, published by Hedberg and Badger [1981]. These authors investigated the infrared absorption spectrum of gaseous HOCl in the range 7143 – 714 cm^{-1} (1.4 – 14 μ) and observed three fundamental frequencies and the harmonic $2\nu_1$, which were also obtained with a high-dispersion apparatus. On the basis of the observed intervals of fine structure of the $2\nu_1$ band, Hedberg and Badger* found $A'' - \frac{1}{2}(B'' + C'') = 19.97\ cm^{-1}$ and $\frac{1}{2}(B'' + C'') = 0.48\ cm^{-1}$. Assuming that in the HOCl molecule the length of the bond O – H is equal to 0.967 Å (as in H_2O) and the length of the Cl – O bond is equal to 1.70 Å (as in Cl_2O) and calculating the experimental values for $A - \frac{1}{2}(B + C)$ and $\frac{1}{2}(B + C)$ for different values of the angle in H – O – Cl, the authors of paper [1981] came to the conclusion that the agreement is best with an angle of 113°.

TABLE 59

Values Accepted for the Molecular Constants of Cl_2O and HOCl

Молекула	ν_1	ν_2	ν_3	$I_A I_B I_C$	σ
1	2 $см^{-1}$			10^{-117} $(г \cdot см^2)^3$	
				3	
Cl_2O	688	320	959	1170	2
HOCl	1242	739	3626	4,4	1

1) Molecule; 2) cm^{-1}; 3) $(g \cdot cm^2)^3$.

A comparison with the valency angle of oxygen in other molecules of the type XY_2 compels us to assume that this value is too high. A recalculation of the quantities $A - \frac{1}{2}(B + C)$ and $\frac{1}{2}(B + C)$, carried out by Gurvich and Novikov [176] for different values of the angle between the bonds and the lengths of the bonds of O – H and Cl – O showed that agreement is best with an angle of 104 ± 3° and the same values of r_{Cl-O} and r_{O-H} as used in paper [1981].

Table 59 gives the values of the fundamental frequencies of HOCl obtained from data of [1981] and the product of the principal moments of inertia calculated for an angle of 104°, r_{Cl-O} = 1.70 and r_{O-H} = 0.967 Å. The error of the accepted structural parameters of the HOCl molecule may reach ±3°, ±0.05 and ±0.01 Å, respectively.

§37. THE THERMODYNAMIC FUNCTIONS OF GASES

The thermodynamic functions of chlorine and its compounds, considered in the present chapter, were calculated for the temperatures from 293.15 to 6000°K, without taking the intermolecular interaction into account, and are given in Tables 47-52, 56 and 57 of Vol. II of the Handbook. In view of the insufficient accuracy of the data on the molecular constants of a series of chlorine compounds, the differences between the constants of the individual isotope modifications were ignored in calculating their thermodynamic functions (with the exception of Cl_2 and ClF). Owing to the absence of data on the constants of the intermolecular potential of chlorine and its compounds, the present Handbook does not give any information on the virial coefficients of the corresponding gases.

Cl. The electron components of the thermodynamic functions of monatomic chlorine was calculated with the help of Eqs. (II.20), (II.21) and the constants compiled in Table 56. The progressive components were calculated from the relations (II.8), (II.9) with the values A_Φ = 3,3532 and A_S = 8.3214 cal/g-atom·deg.

The errors of the calculated values of thermodynamic functions are mainly due to inaccuracies of the physical constants and do not exceed 0.005 cal/g-atom·deg.

The thermodynamic functions of monatomic chlorine, calculated previously in the papers [112, 3314, 1718, 2142, 1514, 3680, 3426, 2462] and in the first edition of the present Handbook, for various temperature

intervals up to 6000°K [2142] and 8000°K [2462], coincide with those given in Table 47 (II), within the limits of 0.001 to 0.002 cal/g-atom·deg. In Zeise's book [4384] thermodynamic functions are given for Cl which were calculated in paper [1718]; in the Handbook by Stull and Sinke [3894] and the 3rd series of the NBS Handbook [3680] data are given which are borrowed from [1514].

$\underline{Cl^-}$. The progressive components of the thermodynamic functions of negatively charged monatomic chlorine are calculated with the same relationships as in the case of monatomic neutral chlorine. The electron components of the thermodynamic functions of Cl^- are equal to zero since the Cl^- ion (see p. 473) has no stable excited electron states, its ground state being a ^1S-state.

The divergence between the values of the thermodynamic functions of Cl^-, given in the first Edition of the Handbook and in the present one (about 0.002 cal/g-atom·deg), is different physical constants used in the calculations. Other calculations of the thermodynamic functions of negatively charged monatomic chlorine are not known in literature.

$\underline{Cl_2}$. The thermodynamic functions of diatomic chlorine, given in Table 49 (II) were calculated from Eqs. (II.161) and (II.162). The values of $\ln\Sigma$ and $T\frac{\partial}{\partial T}\ln\Sigma$ of these equations were calculated according to a method developed by Gordon and Barnes [relations (II.137), (II.138)] for an equilibrium mixture of chlorine isotopes. The calculation was made with averaged values of the molecular constants of Cl_2 found on the basis of the above constants of the Cl_2^{35} molecule, from Eq. (1.43). In Table 60 the values of C_Φ and C_s are compiled for the calculation of the components of progressive motion and rigid rotators, θ and x are used for tables of the anharmonic oscillator and the coefficients in Eqs. (II.137) and (II.138).

The Cl_2 molecule has a comparatively low dissociation energy so

that, when calculating the thermodynamic functions of chlorine at high temperatures, by means of approximation methods, it is necessary to take into account the finite number of discrete rotational states of the gas molecules. The respective corrections were calculated from Eqs. (II.59), (II.60); they become essential at temperatures from 2500 to 3000°K and up to 6000°K they reach values of the order of 0.15 and 0.7 cal/mole·deg for Φ_T^* and S_T^0, respectively.

In §36 it has been mentioned that the chlorine molecule has a great number of excited electron states with low energies; all these states, however, are repulsive and need not be taken into account in calculations of the thermodynamic functions, with the exception of the $^3\Pi_u$ state. A consideration of this state in the values of the thermodynamic functions of chlorine is rendered difficult by the fact that there are no reliable data on the stability of the states $^3\Pi_{1u}$, $^3\Pi_{2u}$ and $^3\Pi_0$ and the low dissociation energy of Cl_2 in the $^3\Pi_{0_u^-}$, which causes considerable errors in the calculations of the components of $^3\Pi_u$ -states by approximation methods. It is not justified to calculate the components of the $^3\Pi_{0_u^-}$ state directly by summation over the energy levels since there are no reliable data available on the rotational constants of Cl_2 in this state.

In the present Handbook the components of the $^3\Pi_u$ -state of the values of Φ_T^* and S_T° were calculated by the simplest method (Eqs. (II.120), (II.121)), the statistical weight was assumed to be equal to 6 under the supposition that the four states $^3\Pi_{0_u^+}$, $^3\Pi_{1u}$, $^3\Pi_{2u}$ and $^3\Pi_{0_u^-}$ are all stable (see p. 476). It is obvious that it is senseless to take into account the differences of the excitation energies of these states, as this was done in paper [3314], if there are no reliable data on the stability of the states $^3\Pi_{0_u^+}$, $^3\Pi_{1u}$ and $^3\Pi_{2u}$.

At low temperatures the error of the calculated values of the thermodynamic functions of diatomic chlorine is determined by the inaccuracy of the values of the physical constants and the rotational constant Cl_2 in the $X^1\Sigma_g^+$ -state used in the calculations; it does not exceed 0.01 cal/mole·deg. At high temperatures (above 2000 – 3000°K) the error due to the approximate accounting for the components of the $^3\Pi_u$ -state become essential. The total errors of the values of Φ^*_{3000} and S°_{3000} were estimated as 0.03 and 0.2 cal/mole·deg, respectively.

The thermodynamic functions of Cl_2 were previously calculated in a series of papers, among which we have to note the paper of Giauque and coworkers [1718, 3706] ($T \leqslant 3000°$ K , the method of Giauque and Overstreet), Huff, Gordon and Morrel [2142] ($T \leq 6000°$K), Butkov [112], Kelley [2363] ($T \leqslant 3000°$ K) , Ribuad [3426] ($T \leq 3000°$K), Evans et al. [1514] ($T \leqslant 3000°$ K) and Potter [3314] ($T \leqslant 5000°$ K) . At temperatures up 3000°K the results of all these calculations are in satisfactory agreement among each other and with the values of the thermodynamic functions given in the present Handbook (with the exception of the data from [112, 2142], calculated in the approximation of the model of rigid rotator -- harmonic oscillator). The divergences observed at higher temperatures are mainly due to differences in the methods of calculation applied. In particular the results of calculations by Potter [3314] differ from those given in the Handbook by 0.038 (0.103) and 0.113 (0.305) cal/mole·deg, for the values of $\Phi^*_{3000}(S^\circ_{3000})$ and $\Phi^*_{5000}(S^\circ_{5000})$, respectively. It must be noted that in paper [3314] a a statistical weight of 5 was attributed to the $^3\Pi_u$ -state (the $^3\Pi_{0_u^-}$ state is assumed to be repulsive state) while for the molecular constants of Cl_2 in this state incorrect values were used as are given in Herzberg's monograph (see first footnote to page 478).

In Zeise's book [4384] results of calculations by Giauque are given for the thermodynamic functions of Cl_2, in the handbooks [3680] and [3894] it is data from paper [1514]. Differences between the values of the thermodynamic functions of Cl_2 given in the first and in the present editions of the Handbook are caused by the fact that in the first edition the calculations were made without corrections for the limited summation over J.

ClF. The thermodynamic functions of chlorine monofluoride, given in Table 57 (II), were calculated from Eqs. (II.161), (II.162). The values of $\ln \Sigma$ and $T\frac{\partial}{\partial T}\ln\Sigma$ were calculated by the Gordon-Barnes method [Eqs. (II.137), (II.138)] for a $Cl^{35}F$ and $Cl^{37}F$ isotope mixture in equilibrium. The calculation was made with averaged values of the molecular constants of ClF, computed from the relations (I.43) on the basis of quantities given in Table 57. In Table 60 the values of the quantities C_Φ and C_s are compiled for the calculation of the progressive motion components, θ and x are given to permit interpolation according to anharmonic oscillator tables and tables of the coefficients of Eqs. (II.137) (II.138), calculated from mean values of the ClF molecular constants. The ClF molecule has a comparatively low dissociation energy so that, when calculating the thermodynamic functions of chlorine monofluoride by an approximation method, it is necessary to introduce corrections for the limited number of rotational energy levels in the $X^1\Sigma^+$-state. The corresponding corrections were calculated from Eqs. (II.59), (II.60).

The components of the excited electron state $^3\Pi$ of the ClF molecule were calculated from Eqs. (II.120), (II.121), i.e., without allowing for the difference of the constats of this molecule in the ground state and in the excited states, assuming that the statistical weight of the state is equal to 6 and the excitation energy is equal to the

TABLE 60

Values of the Constants in the Formulas sed to Calculate the Thermo-Dynamic functions of Cl_2, ClO and ClF

Вещество	θ	$x \cdot 10^3$	$\beta_1 \cdot 10^3$	$\beta_3 \cdot 10^4$	$\frac{q_0}{T}$	$\frac{d_0 \cdot 10^4}{T}$	C_Φ	C_S
1	*град* 2				3 *град*$^{-1}$		4 *кал/моль·град*	
Cl_2	807,14	6,9519	0,7095	0,52	2,90197	4,29	6,1592	13,1147
ClO	1248,9	8,6406	1,0739	1,15	1,08176	7,41	7,3745	14,3300
ClF	1130,3	8,8672	0,8454	0,71	1,35788	4,68	5,2403	12,1958

1) Substance; 2) degree; 3) degree^{-1}; 4) cal/mole·degree

energy of the $^3\Pi_{0^+}$ -state. It is not justified to apply a more accurate method to calculate these components since some substances may be states of the repulsive type and the excitation energy of stable substates may differ considerably from the quantity T_e of the $^3\Pi_{0^+}$ -state.

The main errors of the calculated values of the thermodynamic functions of ClF are due to the fact that it is impossible to accurately take into account the components of the excited states of the ClF molecule, because of the absence of the corresponding experimental data. At temperatures up to 3000°K the total error of the values of Π^*_T, given in Table 57 (II) does not exceed 0.01-0.02 cal/mole·deg, at 6000°K it may reach a value of the order of 0.2 cal/mole·deg for the value of Π^*_T.*

Previously the thermodynamic functions of ClF were calculated in the papers of Cole and Elverum [1148] ($T \leq 2000$°K), Potter [3312] ($T \leq 1500$°K), Ward and Hussey [4149] ($2000° \leqslant T \leqslant 5000$°K), Evans et al. [1514] ($T \leq 1500$°K), Huff et al. [2142] ($T \leq 6000$°K) and Potter [3314] ($T \leq 5000$°K). In all these papers, with the exception of Potter's first [3312], the calculations were made with the vibrational constants of ClF found by Nielsen and Jones [3073]. In the papers [1148, 1514, 3312, 331] the calculations were made according to the method of Mayer and

and Goppert-Mayer, while in papers [4149, 2142] the approximation of the rigid rotator -harmonic oscillator model was used. The most accurate values of the thermodynamic functions of ClF in a wide temperature interval were obtained by Potter [3314]. The differences between the values of the ClF thermodynamic functions obtained by Potter and those given in the Handbook grow with the temperature but do not exceed 0.1 cal/mole·deg for the values of Φ_T^*. These differences are caused by the different values of the vibrational constants of ClF used in the calculations in the statistical weights attributed to the $^3\Pi$ -state* and the fact that different methods of calculation were applied.

In the Handbook of US NBS [3680] the thermodynaric functions given for ClF were calculated in paper [1514]; Zeise's book [4384] gives data from [3312, 1148].

The differences between the values of the thermodynamic functions of ClF given in the first edition of the Handbook and in the present one are explained by the fact that in the first edition the calculation was made with vibrational constants as found in paper [3073] without corrections allowing for the necessity of a limitation of the number of rotational levels of the ground state.

ClO. The thermodynamic functions of ClO, given in Table 50 (II), were calculated from Eqs. (II.161) and (II.162). The values of $\ln \Sigma$ and $T\frac{\partial}{\partial T}\ln\Sigma$ in these equations were calculated with the help of the Gordon-Barnes method on the basis of constants given in §36. Table 60 shows the values of C_Φ, C_S, θ, x and the coefficients of Eqs. (II.137), (II.138) calculated according to these constants. The values of C_Φ and C_S contain the R ln 4 -terms since the ClO molecule has a $^2\Pi$ ground state and the spin-orbital coupling constant is unknown [$\ln\Delta$ and $T\frac{\partial}{\partial T}\ln\Delta$ in Eqs. (II.161) and (II.162) were assumed to be equal to zero]. The components of the excited electron state were calculated without taking

taking into account the differences between the constants of ClO in the states $X^2\Pi$ and $A^2\Pi$ [Eqs. (II.120), (II.121)].

The main error of the calculated values of the thermodynamic functions of ClO at low temperatures is due to the absence of data on the constants of spin-orbital coupling in the $X^2\Pi$ -state. On the basis of a comparison with other gases having molecules with a $^2\Pi$ -type ground state, it can be assumed that the error of the value of $\Phi^*_{298.15}$ is of the order of 0.7 – 0.8 cal/mole•deg. The error due to the inaccuracy of the values taken for the vibrational constants of ClO (see p. 481) amounts to about 0.01, 0.06 and 0.13 cal/mole•deg for the values of $\Phi^*_{298.15}$, and Φ^*_{3000} and Φ^*_{6000}, and those due to the absence of experimental data on the value of the constant α_1 of interaction between rotation and vibration amount to 0.01 and 0.5 cal/mole•deg for Φ^*_{3000} and Φ^*_{6000}, respectively. At high temperatures, when the error caused by the approximate accounting for the multiplet nature of the $X^2\Pi$ state is small, the main inaccuracy of the calculated values of the thermodynamic functions of ClO is caused by the fact that in the calculations it was not allowed for the necessity of limiting the number of rotational levels of the gas molecule and also by the insufficient accuracy of the vibrational constants accepted for the $X^2\Pi$ -state. The total error of the values Φ^*_{3000} and Φ^*_{6000} was estimated to amount to 0.2 and 0.5 cal/mole•deg, respectively.

The differences between the values of the thermodynamic functions of ClO, given in the first and in the present editions of the Handbook are due to differences of the rotational constants used in the calculations and the consideration of rotation-vibration interaction and of the centrifugal distortion of the ClO molecule in the present edition. At 6000° they amount to 0.1 and 0.5 cal/mole•deg for the values of Φ^*_T and S°_T, respectively. Other calculations of thermodynamic functions

of ClO are unknown in literature.

ClO_2. The thermodynamic functions of chlorine dioxide, given in Table 51 (II) were calculated in the approximation of the model of rigid rotator -anharmonic oscillator, with the molecular constants given in the preceding paragraph. The anharmonicity of vibrations of the ClO_2 molecule is taken into account according to Gordon's method (see p. 199). In Table 61 the values of C'_Φ and C'_S are compiled for the calculation of the components of progressive motion and rigid rotator and the values of θ and x are given in order to interpolate according to tables of the anharmonic oscillator. The multiplet nature of the $^2B_1$ ground state of the ClO_2 molecule was allowed for by introducing the term R ln 2 into the constants C'_Φ and C'_S. The components of the excited $^2A_2$ -state were calculated from Eqs. (II.120), (II.121), i.e., without accounting for the difference of the molecular constants of ClO_2 in the states $^2B_1$ and $^2A_2$.

The main errors of the calculated values of the thermodynamic functions of chlorine dioxide at low temperatures are due to the inaccuracy of the values of structural parameters of the ClO_2 molecule used in the calculation and also to the absence of data on the constant of spin-orbital coupling in the $^2B_1$ -state; at high temperatures they are due to the absence of data on the absence of data on the constants of interaction and of centrifugal distortion and to the application of an approximation method of calculation, in particular to the approximate consideration of the excited state. The errors of $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000} have values of the order of 0.1, 0.2 and 0.4 cal/mole·deg.

The thermodynamic functions of ClO_2 were previously calculated in the US NBS [1514, 3680] ($T \leq 1500°K$). Differences between the results of these calculations and the values given in Table 51 (II) amount to

1.37 – 1.45 cal/mole·deg and are obviously due to the fact that in papers [1514, 3680] the multiplet nature of electron ground state of ClO_2 was not taken into account.

Cl_2O. The thermodynamic functions of chlorine monoxide, given in Table 52 (II) were calculated from Eqs. (II.243) and (II.244) in the approximation of the rigid rotator -harmonic oscillator model with the constants given in Table 59. In Table 61 the values of C'_Φ and C'_S are

TABLE 61

Values of the Constants Used for Calculating the Thermodynamic Functions of ClO_2, Cl_2O and of Cl.

1 Вещество	θ_1	θ_2	θ_3	C'_Φ	C'_S
	—	2 град		3 кал/моль·град	
ClO_2[a]	1372,8	643,72	1603,5	7,2105	15,1596
Cl_2O	989,89	460,41	1394,2	8,6531	16,6022
HOCl	1063	1787	5217	2,9784	10,9275

1) Substance; 2) degree; 3) cal/mole·deg.
a) $x_1 = 4.6117 \cdot 10^{-3}$, $x_2 = 0$, $x_3 = 1.7945 \cdot 10^{-3}$.

given for the calculation of the components of the rigid rotator and the progressive motion, as well as the values of θ which were used to obtain the vibrational components.

The main error of the calculated values of the thermodynamic functions of Cl_2O is determined by the inaccuracy of the vibrational constants of the Cl_2O molecule known at present and also by the application of an approximation method of calculation. The total error of the values of $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000} is of the order of 0.1, 1.0 and 1.5 cal/mole·deg, respectively.*

Previously the thermodynamic functions of chlorine monoxide were calculated in Luft's paper [2676] and in the US NBS [1514]. The differences between the results of these calculations and the data given

in Table 52 (II) amount to 0.02 -0.05 cal/mole·deg.

HOCl. The thermodynamic functions of HOCl given in Table 56 (II) were calculated in the approximation of the model of rigid rotator -harmonic oscillator with the constants given in § 36. Table 61 contains the values of C'_Φ and C'_S, entering Eqs. (II.243) (II.244) and the values of θ which are applied in order to calculate the vibrational constants. The main error of the calculated values of the thermodynamic functions is due to the inaccuracy of the vibration frequencies (the known fundamental frequencies) used in the calculations and that of the product of moments of inertia (up to 0.9 cal/mole·deg for Φ^*_T and S°_T) and also to the absence of constants necessary to allow for the anharmonicity of the vibrations, the centrifugal distortion and the interaction between rotation and vibration of the HOCl molecule (up to 0.4 cal/mole·deg with Φ^*_{3000}. The total error of the values of $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000} was estimated as 0.2, 0.5 and 2 cal/mole·deg, respectively.

The thermodynamic functions were previously calculated by Luft [2676] for temperatures up to 1500°K. Since in this paper an incorrect value of the angle in HOCl was used, the results of the calculations differ by a value of about 0.1 cal/mole·deg.

§38. THERMODYNAMIC QUANTITIES

The standard state of chlorine is Cl_2 (gas).

Cl (gas). The heat of formation of monatomic chlorine, in accordance with the accepted value of D_0 (Cl_2) (see below) is equal to

$$\Delta H^\circ_{f_0}(Cl, \text{gas}) = 28{,}55 \pm 0{,}03 \text{ kcal/g-atom}$$

Cl^- (gas). The electron affinity of the chlorine atom, A(Cl), was determined by various scientists, applying different methods (see [2704, 116, 3330]). On the basis of data published before 1953, Pritchard [3330] recommended a value of $A(Cl) = -88.2 \pm 1.5$ kcal/g-atom. In the fol-

In the following years the quantity A(Cl) was determined by Bayley [623] and Bakulina and Ionov [83, 84]. Bailey, studying the surface ionization of potassium chloride, found $A(Cl) = -86{,}6 \pm 2$ kcal/g-atom and, when investigating the ionization of ClF_3 on an incandescent wire, he determined the difference $A(Cl) - A(F) = -5{,}49$ kcal/g-atom. On the basis of results of measurements by the method of surface ionization Bakulina and Ionov determined the values of the analogous differences for a series of halides (see p. 464). Assuming that $A(Br) = -82{,}1$ kcal/g-atom, they found A(Cl) = -87.9 kcal/g-atom [84]. The value of A(Cl) = -86.8 kcal/g-atom corresponds to the value A(Br) = -81 kcal/g-atom, accepted in the present Handbook, and to the experimental results of Bakulin and Ionov, given on p. 464. A similar value (-86 kcal/g-atom) was obtained in Cubicciotti's calculation [1229, 1229a], based on the Born-Haber cycle. In Buchelnikova's review article [116] a value of A(Cl) = -87.8 kcal/g-atom is recommended.

In the present Handbook a value of

$$A(Cl) = -87 \pm 2 \text{ kcal/g-atom}$$

is accepted which was obtained on the basis of results of direct determinations of the quantity A(Cl) in the papers [2704, 623] and on the basis of results of measurements made by Bakulina and Ionov [84].

To the accepted value of A(Cl) corresponds

$$\Delta H^\circ f_0 (Cl^-, \text{gas}) = -58{,}45 \pm 2 \text{ kcal/g-atom}$$

Cl_2(gas). The dissociation energy of Cl_2 molecule may be determined with high accuracy from the limit of convergence of the bands of system $B^3\Pi_{0_u^+} \leftarrow X^1\Sigma_g^+$, and is, according to Kuhn's measurements [2498], equal to 20,850 ± 30 cm^{-1}. The limit of convergence of this system corresponds to the dissociation limit of the $B^3\Pi_{0_u^+}$, state which differs from the value of the dissociation limit of the ground state $X^1\Sigma_g^+$ of the Cl_2 molecule by an amount equal to the excitation energy of the $^2P_{\frac{1}{2}}$

state of the Cl atom (cf. note to p. 475). Taking into account this quantity, given in Table 56, we have: $D_0^\circ(Cl_2) = 20\,850 + 881 = 19\,969 \pm 20$ cm^{-1}, to which corresponds:

$$D_0^\circ(Cl_2) = 57{,}10 \pm 0{,}06 \text{ kcal/mole}$$

This value of $D_0(Cl_2)$ was accepted in the present Handbook.

ClO (gas). The dissociation energy of the ClO melecule was determined by Durie and Ramsay [1428] from the limit of convergence of the band system $A^2\Pi \leftarrow X^2\Pi$, corresponding to the dissociation limit of the $A^2\Pi$ - state of ClO. According to Durie and Ramsay the value of this limit is equal to 38,020 ± 10 cm^{-1}. Since in paper [1428] it was shown that the ClO molecule in the $A^2\Pi$ -state must dissociate into the atoms Cl (^2P) and O (^1D), a value of $D_0^\circ(ClO) = 38\,020 - 15\,868 = 22\,152 \pm 10$ cm^{-1} corresponds to this dissociation limit, i.e.

$$D_0^\circ(ClO) = 63{,}34 \pm 0{,}03 \text{ kcal/mole}$$

A linear extrapolation of the vibrational levels of the $X^2\Pi$ state of ClO results in a less accurate value of the dissociation energy (24,700 cm^{-1} or about 71 kcal/mole).

A value of

$$\Delta H^\circ f_0(ClO, \text{gas}) = 24{,}197 \pm 0{,}05 \text{ kcal/mole}$$

corresponds to the accepted value of $D_0(ClO)$.

ClO_2 (gas). The heat of dissociation of gaseous chlorine dioxide into its elements was measured by Booth and Bowen [865]* and Wallace and Goodeve [4135]** who found that the values of $\Delta H^\circ f_{298}$ (ClO_2, gas) were equal to 23.5 and 26.3 kcal/mole, respectively. It must be noted that the experimental method applied in [4135] and expecially that used in [865] did not permit measurements of sufficient accuracy.

Mayer [2820] discovered a predirsociation in the ClO_2 absorption spectrum, corresponding to the reaction $ClO_2 \rightarrow Cl + O_2$, and determined the thermal effect of this reaction: $\Delta H_0 = 3.6$ kcal/mole.

Calculations based on this quantity yielded the value $\Delta Hf_{298.15}$ (ClO_2, gas) = 24.4 kcal/mole. Finkelnburg and Schumacher [1561] studied in the ClO_2 spectrum the predissociation caused by the process ClO_2 ($^2B_1$) → ClO ($X^2\Pi$) + O (^1D), whose thermal effect was equal to 111 kcal/mole. The authors of paper [1561], however, reckoned that the value they found for the ClO_2 dissociation energy may to too high by about 5–6 kcal/mole; this means that the value of $\Delta H°f_{298.15}$ (ClO_2, gas) = 18.2 kcal/mole based on these data must be too by this amount.

Based on these data, the following value of the heat of formation of ClO_2 has been accepted in the present Handbook:

$$\Delta H°f_{298.15}\ (ClO_2,\ gas) = 25{,}0 \pm 1{,}5 \text{ kcal/mole}$$

which was also recommended by Evans, Munson and Wagman [1514]. The value of $D_0(ClO_2)$ corresponding to it is equal to

$$D_0(ClO_2) = 120{,}932 \pm 1{,}5 \text{ kcal/mole}$$

<u>Cl_2O (gas)</u>. The heat of dissolution of Cl_2O in water was measured by Thomsen [3981] and Neuman and Müller [3055]. Morecver, Thomsen [3981] measured the heat of neutralization of HCl and HOCl by NaOH solution and the heat of Cl_2 dissolution in alkali. These data permitted Evans and coworkers [1514] the calculation of the value $\Delta H°f_{298.15}$ (Cl_2O, gas) = = 18.3 kcal/mole.

The heat of dissolution of Cl_2O in a HI solution was measured by Berthelot and Wallace and Goodeve [4135]; on the basis of the data obtained they calculated the values of the heat of formation of Cl_2O and them equal to 15.9 and 18 kcal/mole, respectively. These values, however, are insufficiently accurate as they were computed as the difference of two high values.

Wallace and Goodeve [4135] and Gunther and Wekua [1892] measured the heat of dissociating of Cl_2O into its elements and obtained values

of the Cl_2O formation heat equal to 21.4 kcal/mole [1892] and 24.7 kcal/mole [1892]. Bichowsky and Rossini [813] showed that the results of these papers may turn out to be incorrect since under the conditions of the experiments ozone is produced which was not taken into consideration in calculating the heat of formation of Cl_2O.

Secoy and Cady [3674] studied the dissolution equilibrium of Cl_2O in water. But they stressed that the equilibrium constants obtained are not reliable which may be explained by a systematic error in the analytic determination of the Cl_2O concentration.

Evans, Manson and Wagman [1514] used the results of a series of investigations of the solubility and the hydrolysis of Cl_2 and Cl_2O to calculate the increment of the isobaric potential in the corresponding reactions and found that for the reaction Cl_2 (gas) + $\frac{1}{2}$ O_2 (gas) → Cl_2O (gas) $\Delta G_{273} = 21{,}95$ kcal/mole, to which a value of $\Delta H°f_{298.15}$ (Cl_2O, gas) = 18,08 kcal/mole corresponds. The authors of paper [1514] considered also the investigations mentioned above and recommended the following value of the heat of formation of Cl_2O:

$$\Delta H°f_{298.15}(Cl_2O,\ gas) = 18{,}1 \pm 0{,}3 \text{ kcal/mole}$$

which was accepted in the present Handbook. To it corresponds

$$D_0(Cl_2O) = 97{,}473 \pm 0{,}31 \text{ kcal/mole}$$

HOCl (gas). On the basis of thermodynamic cycles, including the heats of chlorine hydrolysis in water and in alkaline solutions, Gelles [1677] calculated the value of the dissociation energy of the hydroxyl - chlorine bond: $D_{298}(Cl - OH) = 60$ kcal/mole. To this value corresponds the energy of dissociation of HOCl to atoms which was accepted in the Handbook:

$$D_0(HOCl) = 160 \pm 10 \text{ kcal/mole}$$

and the heat of formation

$$\Delta H°f_0(HOCl,\ gas) = -20{,}831 \pm 10 \text{ kcal/mole}$$

ClF (gas). Schumacher, Schmitz and Brodersen [3660] studied the ClF absorption spectrum and determined the convergence limit of the $B^3\Pi_{0^+} \leftarrow X^1\Sigma^+_g$ band system whose wave number amounts to 21,512 ± 5 cm^{-1}. According to which states* of the Cl and F atoms the dissociation limit of the $B^3\Pi_{0^+}$ state corresponds, the ClF dissociation energy in the ground state and the heat of formation of ClF are equal to:

Dissociation products	D_0 (ClF), kcal/mole	$\Delta H°_f$ (ClF gas), kcal/mole
$F(^2P_{3/2}) + Cl(^2P_{3/2})$	60,35	−13,30
$F(^2P_{3/2}) + Cl(^2P_{1/2})$	59,00	−11,95.

Durie and Gaydon [1426], on the basis of a comparison of the dissociation energies of various interhalogen compounds, came to the conclusion that the lower value of D_0(ClF) is to be preferred. Slutsky and Bauer [3767] did not agree with this conclusion and recommended the higher value of D_0(ClF)** which was also accepted in Gaydon's monograph [1668] and in the review article of Evans, Manson and Wagman [1514]. Later investigations of the dissociation energies of BrF and ICl (see p. 528 and p. 553) showed that it is not justified to select the value of D_0 (ClF) in analogy to other interhalide compounds since it turned out that the dissociation limits of BrF and ICl in the $B^3\Pi_{0^+}$ -state correspond in the one case (BrF) to the excited state of the heavy element and in the other case (ICl) to that of the light element.

The selection between the possible values of D_0 (ClF) may be based on the heat of formation of ClF, measured by thermochemical methods. Ruff and Laass [3557] measured the heat of combustion of hydrogen in fluorine and ClF and found ΔHf (ClF, gas) = −27.4 kcal/mole (see Ruff and Menzel [3561]. Schmitz and Schumacher [3641] measured the reaction heats of ClF and F_2 with NaCl. With the help of the thermal effects of these reactions, the authors of paper [3641] calculated the value of the heat of formation of ClF and obtained −15 kcal/mole. If one uses

the values of the heats of formation of NaF and NaCl and the reaction heat of ClF with NaCl [3641] the calculation yields $\Delta H°f_{298.15}$(ClF, gas) = −13.6 kcal/mole.

The most reliable measurements of the heat of formation of ClF were made by Wicke [4250] and Wicke and Fritz [4255]. In [4250] the thermal effect of the reaction of chlorine – fluorine interaction was measured and $\Delta H°f_{298.15}$ (ClF gas) = − 11.6 ± 0.4 kcal/mole was obtained. In paper [4255] a value of $\Delta H°f_{298.15}$ (ClF gas) = − 11.7 ± 0.5 kcal/mole was obtained by means of the explosion method in a spherical bomb. The results of both papers speak in favor of the lowest value of D_0(ClF). Brodersen and Sicre [973] came to the same conclusion by way of an analogous comparison of the possible values of D_0 (ClF) with the results of calorimetrical measurements.

In the Handbook the following value is accepted:

$$D_0(ClF) = 59{,}0 \pm 0{,}02 \text{ kcal/mole} .$$

The accepted value of error of D_0(ClF) allows only for the extrapolation error in calculating the bands' limit of convergence. The error due to the possibility of incorrect determination of the states arising in the dissociation of the chlorine and fluorine atoms is in this case not taken into account.

The following corresponds to the accepted value of dissociation energy:

$$\Delta H°f_0(ClF, \text{ газ}) = -11{,}95 \pm 0{,}5 \text{ kcal/mole}$$

TABLE 62

Accepted Values (in cal/mole) of the Thermodynamic Quantities of chlorine and its Compounds in Gaseous state

1	D_0	$\Delta H°f_0$	$\Delta H°f_{293,15}$	$\Delta H°f_{298,15}$	$H°_{293,15}-H°_0$	$H°_{298,15}-H°_0$
Cl	—	28 950	28 947	28 952	1473	1499
Cl^-	87 000[a]	−58 450	−59 527	−59 547	1456	1481
Cl_2	57 100	0	0	0	2153	2194
ClO	63 340	24 197	24 179	24 179	2078	2116
ClO_2	120 932	25 592	25 006	25 000	2530	2580
Cl_2O	97 473	18 614	18 105	18 100	2664	2718
HOCl	160 000	−20 831	−21 524	−21 535	2396	2440
ClF^2	59 000	−11 950	−11 972	−11 974	2091	2129

[a]Value of energy of electron detachment from Cl^- - ion. 1) Substance.

Chapter 10

BROMINE AND ITS COMPOUNDS WITH OXYGEN, FLUORINE AND CHLORINE

(Br, Br^-, Br_2, BrO, BrF, BrCl)

The present chapter deals with monatomic and diatomic bromine, the Br^- -ion and the diatomic compounds of bromine with oxygen, fluorine and chlorine in the gaseous state.

Besides BrO we know the following compounds of bromine with oxygen: Br_2O, BrO_2, BrO_3, and Br_3O_8. These compounds, however, are only stable in the solid state at low temperatures.

With fluorine bromine forms three compounds: BrF, BrF_3 and BrF_5. At not too high temperatures BrF_3 and BrF_5* are more stable than BrF. As the temperature rises, however, the lightest of these three molecules, namely BrF, becomes the main component. In literature there are no indications to the existance of any other compounds between bromine and chlorine, apart from BrCl, considered in the Handbook. There are also data on the existence of the compound BrO_2F [3625] which is stable at -50°C.

Since multiatomic compounds of bromine with oxygen, fluorine and chlorine are only stable at comparatively low temperatures, the data given in the Handbook permit the calculation of the composition and the thermodynamic properties of the systems bromine - oxygen, bromine - fluorine, and bromine - chlorine at sufficiently high temperatures. It must be noted that all the bromine compounds dealt with in the present chapter are comparatively unstable at high temperatures, especially in the presence of other elements (hydrogen, metals), they cannot exist

in larger quantities.

Apart from the bromine compounds considered in this chapter, the Handbook contains data on compounds of bromine with iodine (Ch. 11), hydrogen and its isotopes (Ch. 12) and also on bromine derivatives of methane (Ch. 17).

§39. THE MOLECULAR CONSTANTS

Br. In the electon ground state ^2P the bromine atom has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$. The transition energies to excited electron states of the bromine atom exceed 60,000 cm^{-1} so that the excited states of Br are not considered in the present Handbook. Table 63 gives the energies and statistical weights of the two components of the bromine atom's ground state, borrowed from Moor's Handbook [2941].

TABLE 63

Energy Levels of the Br Atom and the Br^- Ion

2 Атом	1 Состояние: 3 Электронная конфигурация	4 терм	5 Статистический вес	6 Энергия, cm^{-1}
Br	$\ldots 4s^2 4p^5$	$^2P_{3/2}$	4	0
	$\ldots 4s^2 4p^5$	$^2P_{1/2}$	2	3685
Br^-	$\ldots 4s^2 4p^6$	^1S	1	0

1) State; 2 atom; 3 electron configuration; 4) term; 5) statistical weight; 6) energy, cm^{-1}.

Br^-. In its ground state the negatively charged ion of monatomic bromine has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$, to which one ^1S-term corresponds. In analogy to the isoelectronic Kr atom the energies of the excited electon states of the Br^- ion must amount to at least 80,000 cm^{-1}. Since the Br^- ionization potential is essentially lower than this quantity (see p. 525) it can be assumed that the Br^-

Br_2. The Br_2 molecule, just as the F_2 and Cl_2 molecules, has a $^1\Sigma_g^+$ ground state and the first excited state is of the type $^3\Pi_u$. The electron spectra of Br_2 were investigated in the visible and ultraviolet ranges by many researchers. A theoretical analysis of the Br_2 spectra caused by transitions between lower electron states of this molecule, among them between the two components of the $^3\Pi_u$ -state and the $^1\Sigma_g^+$ ground state, was carried out by Mulligen (see p. 474).

The Br_2 absorption spectrum in the visible and the near infrared consists of two band systems which correspond to the transitions $A^3\Pi_{1u} - X^1\Sigma_g^+$, $B^3\Pi_{0_u^+} - X^1\Sigma_g^+$ [2498, 991,994, 1262]. The bands of the first system have their limit of convergence at 5107 Å, adjacent to it is the continuous absorption spectrum with two peaks at 4950 and 4150 Å. The emission spectrum of Br_2 was studied in a wide interval of wavelengths. Besides the bands of the system $A^3\Pi_{1u} - X^1\Sigma_g^+$ and $B^3\Pi_{0_u^+} - X^1\Sigma_g^+$, observed in the absorption spectrum, the emission spectrum of Br_2 shows several band systems which are caused by transitions from high electron states of Br_2 [4089, 584, 1951, 4094, 4095, 1955, 4099].

The molecular constants of Br_2 in the states $X^1\Sigma_g^+$, $A^3\Pi_{1u}$ and $B^3\Pi_{0_u^+}$ were determined by Brown [991, 994] and Darbyshire [1262] on the basis of an analysis of the band system $\begin{matrix} B^3\Pi_{0_u^+} \leftarrow X^1\Sigma_g^+, \\ A^3\Pi_{1u} \rightleftharpoons X^1\Sigma_g^+ \end{matrix}$. Brown [991] determined the wave numbers of the band edges, corresponding to the values $v' = 7-21$, $v'' = \leq 5$ of the system $B \leftarrow X$ and $v' = \leq 21$, $v'' = 1-5$ of the system $A \leftarrow X$. The values of the vibrational constants of the ground state of Br_2 found by Brown in this paper, were equal to $\omega_e = 323.86$, $\omega_e x_e = 1.15$ cm^{-1}. Furthermore Brown [994] photographed the Br_2 spectrum in the third order of a 21-foot convave grating with a dispersion of 0.8 Å/mm. In the spectrum 12 bands were observed, with resolved rotational structures, which corresponded to transitions from the levels $v'' = 2 - 4$ of the $X^1\Sigma_g^+$ state to the levels $v' = 7 - 13$ of the $B^3\Pi_{0_u^+}$ state. On the

On the basis of data obtained in papers [991, 994] Brown determined the values of the vibrational and rotational constants of Br_2 in the states $X^1\Sigma_g^+$ and $B^3\Pi_{0_u^+}$. The band systems $B \leftarrow X$ and $A \leftarrow X$ were also studied by Darbyshire, with an apparatus of lower dispersion [1262]. In [1262] about 70 bands of the system $A \leftarrow X$ were studied, which correspond to the values $v' = 1 - 16$, $v'' = 14$ and 23 bands of the system $B \leftarrow X$ with $v' = 0 - 5$, $v'' = 8 - 14$. From the wave numbers of the band edges Darbyshire found the values of the Br_2 constants in the states $X^1\Sigma_g^+$ ($\omega_e = 324.26$, $\omega_e x_e = 1.145$ cm^{-1}), $A^3\Pi_{1u}$ and $B^3\Pi_{0_u^+}$. With the help of measurements of the isotope shift of lines he improved the values of v' of the bands of the system $A \leftarrow X$, altering them by 7 units, and applied the corresponding corrections to the values of the vibrational constants and the excitation energy of the state $A^3\Pi_{1u}$, obtained by Brown [991].

In the present Handbook, as well as in Herzberg's monograph [2040] and in the Handbook [649] one accepted the values of the vibrational and rotational constants of Br_2 in the ground state and in the $B^3\Pi_{0_u^+}$ states found by Brown [994] and the vibrational constants in the $A^3\Pi_{1u}$ state found by Darbyshire [1262].* The accepted values of the molecular constants of Br_2 are compiled in Table 64. Transitions to other components of the states $^3\Pi_u$, ($^3\Pi_{2u}$ and $^3\Pi_{0_u^-}$) were not observed in the Br_2 spectra. It follows from an approximate quantummechanical calculation made by Mulliken [2998] that the $^3\Pi_{2u}$ -state lies below the $^3\Pi_{1u}$ state. Since both states have the same dissociation limit, the potential curve of the $^3\Pi_{2u}$ -state must have a deeper minimum than the potential curve of the $^3\Pi_{1u}$ -state. The question for the stability of the $^3\Pi_{0_u^-}$ state remains open. In the present Handbook, in accordance with paper [2998], we assume that this state is stable with all halogen molecules

(see p. 475).*

Apart from the considered electron states of the Br_2 molecule we know another 9 stable states. Two of them, with excitation energies below 50,000 cm^{-1}, are contained in Table 64. The electron state of Br_2 with an excitation energy of the order of 47,000 cm^{-1} was identified

TABLE 64

Accepted Values of the Molecular Constants of Br_2, BrO, BrF, BrCl

Молекула 1	Состояние 2	T_e	ω_e	$\omega_e x_e$	B_e	$\alpha_1 \cdot 10^3$	$D_0 \cdot 10^8$	r_e
		cm^{-1} 3						Å
Br_2^{79-81}	$X^1\Sigma_g^+$	0	323,2	1,07	0,08091	2,75	2,0	2,284
	$A^3\Pi_{1u}$	13814	170,7	3,69	—	—	—	—
	$B^3\Pi_{0u}^+$	15891,3	169,71	1,913	0,0595	6,25	2,9	2,663
	$C^1\Sigma_u^+$	47000 48516	— 162,0	— 0,29	— —	— —	— —	— —
BrO [a]	$X^2\Pi$	0	777,8	6,8	0,465 [b]	47,0 [c]	67,0 [d]	1,65
	$A^1\Pi$	27871	485,5	5,5	— [b]	— [c]	— [d]	—
BrF	$X^1\Sigma^+$	0	672,8	4,5	0,3563	52,06	40,0 [d]	1,756
	$A^3\Pi_{1u}$	17385	378	16	—	—	— [d]	— [b]
	$B^3\Pi_{0^+}$	18281,2	377,6	4,711	—	—	—	—
BrCl [a]	$X^1\Sigma^+$	0 [e]	443,1	1,8 [e]	0,1505	7,595	6,9 [rd]	2,136
	$A^3\Pi$	(16000) [e]	—	— [e]	—	—	—	—

1) Molecule; 2) state; 3) cm^{-1}.

[a] Mean values of the molecular constants of $Br^{79}X$ and $Br^{81}X$.

[b] Value of B_0.

[c] Calculated from Eq. (1.36).

[d] Calculated from Eq. (1.38).

[e] Estimate.

as a $^1\Sigma_u^+$ state by Venkateswarlu [4089] who observed a group of diffuse bands in the bromine emission spectrum and attributed them to transitions from this state to a series of unstable states. An electron state with an excitation energy of T_e = 48,516 cm^{-1} was found by Venkateswar-

lu when studying the Br_2 emission spectrum in the presence of argon, from a band system connected with transitions from this state to the $B^3\Pi_{0_u^+}$ state. In paper [4089] the type of the state was not established. The values of the constants of Br_2 in the two mentioned states, found by Venkateswarlu, are given in Table 64.

BrO. In the spectrum of the BrO molecule a single band system, $A^2\Pi - X^2\Pi$, was investigated. The BrO emission spectrum in an H_2 + O_2 flame with admixtures of C_2H_5Br and CH_3Br was studied by Waid [4050] and also by Coleman and Gaydon [1153]. Paper [1153] reports on measurements of the wave numbers of the edges of 16 bands corresponding to $v' \leqslant 2, v'' \leqslant 7$, and from the relationships assumed for the bands in this paper, approximate values of the vibrational constants of BrO in the ground state were obtained: $\omega_e = 713$, $\omega_e x_e = 7$ cm^{-1}.

The BrO absorption spectrum was studied by Zeelenberg [4374] and Durie and Ramsay [1428] in the pulsed photolysis of bromine -oxygen mixtures.

Durie and Ramsay [1428] obtained the BrO spectrum in the range 2890 – 3530 Å by means of a spectrograph with a 21-foot grating and also with a Hilger spectrograph. The spectrum consisted of 20 (v' – 0) progression bands with v' -values from 1 to 20; 16 of the 20 bands were diffuse and only in the band 4 – 0 the rotational structure could be resolved. Zeelenberg [4374] observed 15 bands in the BrO absorption spectrum whose wave numbers were in good agreement with those given by Durie and Ramsay. In paper [4374] the BrO spectrum was not analyzed.

Durie and Ramsay [1428] analyzed the vibrational structure of the bands of system $A^2\Pi - X^2\Pi$, taking into account the data obtained by Coleman and Gaydon [1153], when they studied the emission spectrum of BrO; they altered the numeration of the bands suggested by Coleman

and Gaydon by 4 units of the values of v". The vibrational constants of BrO in the states $X^2\Pi$ and $A^2\Pi$ obtained by Durie and Ramsay [1428] are given in Table 63 and are accepted in the present Handbook.

On the basis of an analysis of the rotational structure of the 4 – 0 band Durie and Ramsay [1428] determined the following values of the constant B_0 of the molecules $Br^{79}O$ and $Br^{81}O$ in the states $X^2\Pi$: $B_0(Br^{79}O) = 0{,}455$, $B_0(Br^{81}O) = 0{,}471$ cm^{-1}; the mean value of the constant B_0 of the BrO molecule in the $X^2\Pi$ -state, given in Table 63, corresponds to them. This table contains also the value of the constant α_1 calculated from Eq. (1.36) and the values assumed for the constants ω_e, $\omega_e x_e$ and B_0.

BrF. The electron ground state of the BrF molecule is of the type $X^1\Sigma^+$. Just as with other diatomic interhalogen compounds, the first excited state of the BrF molecule is a state of the type $^3\Pi$. In the BrF spectrum only transitions to two components of this state, $A^3\Pi_1$ and $B^3\Pi_{0^+}$, were investigated. At the same time transitions were observed which are connected with high excited states of the BrF molecule, whose energies exceed 60,000 cm^{-1} [969].

In the BrF spectrum the band system $B^3\Pi_{0^+} - X^1\Sigma^+$, was investigated most frequently; it lies in the range 4360 – 6580 Å and was studied in the absorption spectrum by Brodersen and coworkers [970, 971, 973] and in the emission spectrum by Durie [1423]. The most careful investigation of the BrF constants was made by Brodersen and Sicre [973] who studied the system $A^3\Pi_1 - X^1\Sigma^+$ (range 5200 – 6900 Å) in an apparatus with a dispersion of 2.7 Å/mm. 40 bands of the system $B^3\Pi_{0^+} - X^1\Sigma^+$ ($v' \leq 20$, $v'' \leq 5$), and 10 bands of the system $A^3\Pi_1 - X^1\Sigma^+$ ($v' \leq 8$, $v'' = 0$ and 1) were observed in the spectrum.

The values of the vibrational constants of BrF, found by Brodersen and Sicre [973] from the wave numbers of the band edges are accept-

ed in the present Handbook and given in Table 64.* Previously Durie [1423] obtained similar values (673 and 4 cm^{-1}) for the quantities ω_e and $\omega_e x_e$.

The rotational constants of BrF in the electron ground state given in Table 64, were borrowed from a paper of Smith, Tidwell and Williams [3776] who studied the microwave spectra of $Br^{79}F$ and $Br^{81}F$.

BrCl. The electron ground state of the BrCl molecule is of the type $^1\Sigma^+$.

In the BrCl spectrum two band systems are studied which lie in the range of vacuum ultraviolet, two bands (1 – 0 and 2 – 0) in the infrared range and the 1 – 0 band in the Raman spectrum of the gas and in the microwave spectrum of this molecule.

Both band systems of BrCl in vacuum ultraviolet were obtained in absorption spectra by Cordes and Sponer [1179] who showed that they are caused by transitions to high electron states of this molecule ($T_e \sim 60{,}000$ cm^{-1}) from its ground state. In analogy to molecules of other diatomic interhalogen compounds we assumed in the Handbook that the first stable excited state of BrCl is a $^3\Pi$ state with an energy of about 16,000 cm^{-1}. Transitions connected with this state, however, were not observed in the BrCl spectrum.

As a result of investigating two BrCl band systems, Cordes and Sponer determined the wave number of the edges of 21 bands, but the accuracy of the determination of the edge wave numbers was not high and the band relationships were ambiguous. Cordes and Sponer represented the edge wave numbers they had found in the form of Deslandres tables and obtained $\Delta G_{\frac{1}{2}} = 430$ cm^{-1}.

The BrCl Raman spectrum was studied by Stammreich and Forneris [3836] who found a value of 428 ± 2 cm^{-1} for $\Delta G_{\frac{1}{2}}$. As we mentioned above (see p. 482 and 512), analogous measurements made by Stammreich and

and Gaydon by 4 units of the values of v". The vibrational constants of BrO in the states $X^2\Pi$ and $A^2\Pi$ obtained by Durie and Ramsay [1428] are given in Table 63 and are accepted in the present Handbook.

On the basis of an analysis of the rotational structure of the 4 – 0 band Durie and Ramsay [1428] determined the following values of the constant B_0 of the molecules $Br^{79}O$ and $Br^{81}O$ in the states $X^2\Pi$: $B_0(Br^{79}O) = 0{,}455$, $B_0(Br^{81}O) = 0{,}471$ cm^{-1}; the mean value of the constant B_0 of the BrO molecule in the $X^2\Pi$ -state, given in Table 63, corresponds to them. This table contains also the value of the constant α_1 calculated from Eq. (1.36) and the values assumed for the constants ω_e, $\omega_e x_e$ and B_0.

BrF. The electron ground state of the BrF molecule is of the type $X^1\Sigma^+$. Just as with other diatomic interhalogen compounds, the first excited state of the BrF molecule is a state of the type $^3\Pi$. In the BrF spectrum only transitions to two components of this state, $A^3\Pi_1$ and $B^3\Pi_{0+}$, were investigated. At the same time transitions were observed which are connected with high excited states of the BrF molecule, whose energies exceed 60,000 cm^{-1} [969].

In the BrF spectrum the band system $B^3\Pi_{0+} - X^1\Sigma^+$, was investigated most frequently; it lies in the range 4360 – 6580 Å and was studied in the absorption spectrum by Brodersen and coworkers [970, 971, 973] and in the emission spectrum by Durie [1423]. The most careful investigation of the BrF constants was made by Brodersen and Sicre [973] who studied the system $A^3\Pi_1 - X^1\Sigma^+$ (range 5200 – 6900 Å) in an apparatus with a dispersion of 2.7 Å/mm. 40 bands of the system $B^3\Pi_{0+} - X^1\Sigma^+$ ($v' \leq 20$, $v'' \leq 5$), and 10 bands of the system $A^3\Pi_1 - X^1\Sigma^+$ ($v' \leq 8$, $v'' = 0$ and 1) were observed in the spectrum.

The values of the vibrational constants of BrF, found by Brodersen and Sicre [973] from the wave numbers of the band edges are accept-

ed in the present Handbook and given in Table 64.* Previously Durie [1423] obtained similar values (673 and 4 cm^{-1}) for the quantities ω_e and $\omega_e x_e$.

The rotational constants of BrF in the electron ground state given in Table 64, were borrowed from a paper of Smith, Tidwell and Williams [3776] who studied the microwave spectra of $Br^{79}F$ and $Br^{81}F$.

BrCl. The electron ground state of the BrCl molecule is of the type $^1\Sigma^+$.

In the BrCl spectrum two band systems are studied which lie in the range of vacuum ultraviolet, two bands (1 — 0 and 2 — 0) in the infrared range and the 1 — 0 band in the Raman spectrum of the gas and in the microwave spectrum of this molecule.

Both band systems of BrCl in vacuum ultraviolet were obtained in absorption spectra by Cordes and Sponer [1179] who showed that they are caused by transitions to high electron states of this molecule ($T_e \sim 60{,}000$ cm^{-1}) from its ground state. In analogy to molecules of other diatomic interhalogen compounds we assumed in the Handbook that the first stable excited state of BrCl is a $^3\Pi$ state with an energy of about 16,000 cm^{-1}. Transitions connected with this state, however, were not observed in the BrCl spectrum.

As a result of investigating two BrCl band systems, Cordes and Sponer determined the wave number of the edges of 21 bands, but the accuracy of the determination of the edge wave numbers was not high and the band relationships were ambiguous. Cordes and Sponer represented the edge wave numbers they had found in the form of Deslandres tables and obtained $\Delta G_{\frac{1}{2}} = 430$ cm^{-1}.

The BrCl Raman spectrum was studied by Stammreich and Forneris [3836] who found a value of 428 ± 2 cm^{-1} for $\Delta G_{\frac{1}{2}}$. As we mentioned above (see p. 482 and 512), analogous measurements made by Stammreich and

Forneris with Cl_2 and Br_2 yielded lower values since instead of the Raman spectrum the $\Delta G_{5/2}$ transitions were obtained in the spectrum of resonance fluorescence.

The infrared spectrum of BrCl in the range 400 – 900 cm^{-1} was studied in the papers of Matraw, Pachucki and Hawkins [2812] and Brooks and Crawford [980]. In paper [2812] $\nu(1-0) = 439.5 \pm 0.5$ cm^{-1} was obtained, in paper [980] $\nu(1-0) = 439.5 \pm 0.5$ cm^{-1} and $\nu(2-0) = 876 \pm 1$ cm^{-1} was established. On the basis of their data Brooks and Crawford found $\omega_e = 442.5$, $\omega_e x_e = 1.5$ cm^{-1}; owing to the closeness of the values $2\nu(1-0)$ and $\nu(2-0)$, however, the constant of anharmonicity of BrCl could only be determined in [980] with low accuracy and the error of the value found for $\omega_e x_e$ amounts to about 1 cm^{-1}. The BrCl dissociation energy calculated from Eq. (1.13) and the given values of ω_e and $\omega_e x_e$, is therefore higher by about 12,000 cm^{-1} or 60% than the value accepted in the present Handbook.

In papers [2812, 980] and on preparing the present Handbook the quantity $\omega_e x_e$ of the BrCl molecule in the $X^1\Sigma^+$ state was determined on the basis of approximate estimates. The values found lie within an interval from 1.6 to 1.9 cm^{-1}. The values of the vibrational constants of BrCl in the state $X^1\Sigma^+$ given in Table 64 are borrowed from paper [2812].* The rotational constants of BrCl were chosen on the basis of results of investigating the microwave spectrum of four isotope modifications of this molecule obtained in paper [3777].

§ 40. THE THERMODYNAMIC FUNCTIONS OF THE GASES

The thermodynamic functions of bromine and its diatomic compounds with fluorine, chlorine and oxygen in the gasesous state, calculated without accounting for intermolecular interaction, for the temperatures between 293.15 – 6000°K, are compiled in Tables 58-61, 65, 66 of Vol. II of the Handbook. All calculations were made allowing for

the differences of the constants of isotope modifications of the molecules containing bromine and chlorine atoms.

The constants of the interatomic potential of the gases considered in the present chapter are unknown so that the Handbook does not contain any data on the virial coefficients of these gases.

Br. The electron components of the thermodynamic functions of gaseous monatomic bromine were calculated from the constants given in Table 63, the progressive components were calculated from Eqs. (II.8), (II.9). The constants A_Φ and A_S in the expressions of the progressive components Φ_T^* and S_T° were equal to 5.7757 and 10.7438 cal/g-atom·deg, respectively. The errors of the values of Φ_T^* and S_T° given in Table 58 (II) do not exceed 0.005 cal/g-atom·deg and are virtually entirely due to inaccuracies of the used values of physical constants.

Tables of the thermodynamic functions of monatomic bromine were previously calculated up to 2000°K by Gordon and Barnes [1815] Brewer [1093], Katz and Margrave [2334], up to 3000°K by Butkov [112], Goff et al. [1787], up to 5000°K by Evans et al. [1514], and up to 8000°K by Kolsky et al. [2462].

The differences between the values of the thermodynamic functions of Br, calculated in papers [2334, 1514, 112] and given in Table 58 (II) do not exceed 0.001 cal/g-atom·deg and can be explained by slight differences of the values taken for the physical constants. The thermodynamic functions of Br, calculated in paper [1514], are published in the handbooks [3680, 3894], those calculated by Gordon and Barnes [1815] in Zeise's book [4384].

The differences between the values of the thermodynamic functions calculated in papers [1093, 2462] and compiled in Table 58 (II) amount to 0.01 – 0.02 cal/g-atom·deg and are caused by the fact that in these papers use was made of a value of R in the physical scale of atomic

weights.

The differences between the values of the thermodynamic functions of monatomic bromine, given in the first and in the present editions of the Handbook, amount to 0.005 cal/g-atom·deg and are due to the fact that other values of the physical constants were used.

$\underline{Br^-}$. The progressive components of the thermodynamic functions of the negative ion of monatomic bromine were calculated with the same values of A_Φ and A_S as were used in the case of the neutral monatomic bromine. The electron components are equal to zero since in the Handbook it was assumed that the Br^- ion has no stable excited states and that its ground state is of the type ^1S. The errors of the values of Φ_T^* and S_T° calculated in this way are due to inaccuracies of the physical constants and do not exceed 0.005 cal/g-atom·deg.

The differences between the thermodynamic functions of Br^- given in the first and in the present Editions of the Handbook are caused by the fact that different physical constants were used in the calculations. Other calculations of thermodynamic functions of Br^- are unknown in literature.

$\underline{Br_2}$. The thermodynamic functions of gaseous diatomic bromine given in Table 60 (II) were calculated from Eqs. (II.161) and (II.162). The values of $\ln \Sigma$ and $T\frac{\partial}{\partial T}\ln \Sigma$ in these equations were calculated according to the method of Gordon and Barnes, allowing for the corrections for the limited summation over $\underline{J}$ [Eqs. (II.137), (II.138)] and using the molecular constants given in Table 64. The constants entering the formulas for calculating the thermodynamic functions are compiled in Table 65. In the calculation of the components of the first excited state $^3\Pi_u$ its components $^3\Pi_{0_u^+}$, $^3\Pi_{0_u^-}$, $^3\Pi_{1u}$ and $^3\Pi_{2u}$ were united in a single level with the statistical weight 6 and an excitation energy equal to the arithmetical mean of the excitation energies of the

states $^3\Pi_{0_u^+}$ and $^3\Pi_{1u}$. The calculation was made with Eqs. (II.120), (II.121), i.e., without allowing for the difference of the Br_2 constants in the states $^3\Pi_u$ and $X^1\Sigma_g^+$. Higher electron states of Br_2 with excitation energies exceeding 40,000 cm^{-1} are not taken into account in the calculation.

TABLE 65

Values of the Constants Used in Calculations of the Thermodynamic Functions of Br_2, BrO, BrF, BrCl

1 Вещество	θ	$x \cdot 10^2$	$\beta \cdot 10^2$	$\beta_2 \cdot 10^4$	$\frac{\sigma_0}{T}$	$\frac{d_0 \cdot 10^4}{T}$	C_Φ	C_S
	2 *град*	—	—	—	3 *град*$^{-1}$		4 *кал/моль·град*	
Br_2	465,0	3,3106	0,3405	0,117	8,60511	4,26	10,7416	17,6971
BrO	1119,1	8,7426	1,0181	1,07	1,50114	4,34	9,8818	16,8373
BrF	967,7	6,6905	1,4712	2,266	1,90505	4,44	7,7538	14,7093
BrCl	637,5	4,0623	0,5059	0,260	4,63006	4,26	9,9158	16,8713

1) Substance; 2) degree; 3) deg^{-1}; 4) cal/mole·deg.

The errors of the values of Φ_T^* at T = 298.15, 3000 and 6000°K amount to 0.02, 0.03 and 0.3 cal/mole·deg, respectively. At low temperatures they are mainly due to inaccuracies of the molecular and physical constants and at high temperatures they are caused by the inaccurate consideration of the electron state $^3\Pi_u$ and by the fact that the values chosen for the vibrational constants of Br_2 in the $X^1\Sigma_g^+$ in an unsatisfactory manner.

The thermodynamic functions of diatomic bromine were previously studied by Evans et al. [1514] and Butkov [112] (up to 3000°K) by means of the method of Mayer and Göppert-Mayer, by Gordon and Barnes [1815] (up to 1600°K) by a method of their own, by Zeise [4379] (up to 2000°K) in the rigid rotator-harmonic oscillator approximation, and by Brown [993] ($S^\circ_{298.16}$) with the method of indirect summation.

The results of calculations of [1514, 1815, 993, 112, 4379] and the values given in Table 60 (II) do not differ by more than 0.02 cal/mole·deg,

with the exception of the values of S°_{T}, obtained by Evans et al. [1514] for temperatures above 2000°K, and the values of Φ^{*}_{T} calculated by Zeise [4379] for T > 1000°K. In these two cases the deviation reaches 0.1 cal/mole·deg. These differences are explained by the fact that different methods of calculation were used and different values of the molecular and physical constants were applied in the calculations.

In Zeise's book [4384] and in the Handbook [1093] the thermodynamic functions calculated by Gordon and Barnes [1815] are given; the handbooks [3680, 3894] contain the results of calculations by Evans et al. [1514]. Kelley [2364, 2360] accepts the value of $S^{\circ}_{298.16}$, calculated by Brown [99?] In the summary of [2363] Kelley gives the values of $H^{\circ}_{T} - H^{\circ}_{298.16}$ and $S^{\circ}_{T} - S^{\circ}_{298.16}$ up to 1600°K and an equation for the specific heat of Br_2. With the value of $S^{\circ}_{298.15}$ given in Table 60 (II) -within the limits of accuracy -the value of $S^{\circ}_{298.16}$, agrees which was determined by Hildenbrand et al. [2070] according to results of calorimetric measurements. Differences between the thermodynamic functions of Br_2 given in the first and in the present editions of the Handbook do not exceed 0.01 cal/mole·deg up to 3000°K and grow as the temperature rises, reaching 0.8 cal/mole·deg for S°_{6000} which is due to the fact that in the first edition the limitation of summing over J was not taken into account.

BrO. The thermodynamic functions of gaseous bromine monoxide given in Table 61 (II) were calculated from Eqs. (II.161) and (II.162). The values of $\ln \Sigma$ and $T\frac{\partial}{\partial T}\ln\Sigma$ in these equations were calculated with the help of the Gordon Barnes method, allowing for the corrections for limited summation over J [Eqs. (II.137), (II.138)], and using the molecular constants given in Table 64. Table 65 contains the values of the constants C_{Φ}, C_{S}, θ and x also the coefficients of Eqs. (II.137),

(II.138) calculated according to the molecular constants of BrO. Since the coupling constant of the $X^2\Pi$ state of the BrO molecule is unknown, the quantities $\ln \Delta$ and $T\frac{\partial}{\partial T}\ln \Delta$ in Eqs. (II.137) and (II.138) were assumed to be equal to zero and both C_Φ and C_S comprised a term R ln 4. The components of the excited electron state of the BrO molecule was calculated by means of the simplest method, without taking into account the difference of the BrO constants in the states $X^2\Pi$ and $A^2\Pi$ [Eqs. (II.120) and (II.121)].

The errors of the values of Φ_T^* given in Table 61 (II) amount to 0.7, 0.2 and 0.2 cal/mole·deg at T = 298.15, 3000 and 6000°K, respectively. At low temperatures the errors are mainly caused by inaccurate allowing for the multiplet nature of the electron ground state, while at high temperatures they are due to inaccurate allowing for the excited electron state $A^2\Pi$ and inaccurate constants of BrO in the $X^2\Pi$ state, used in the calculation, in particular to the absence of experimental data on the constant α_1 and the energy of the high vibrational levels of the $X^2\Pi$ state.

Previous calculations of the thermodynamic functions of bromine monoxide are unknown.

BrF. The thermodynamic functions of gaseous bromine monofluoride given in Table 65 (II) were calculated from Eqs. (II.161) and (II.162). The values of $\ln \Sigma$ and $T\frac{\partial}{\partial T}\ln \Sigma$ in these equations were calculated by means of the Gordon-Barnes method, taking into account the limitation of summation over J [Eqs. (II.137) and (II.138)], on the basis of the molecular constants given in Table 64. The constants entering the formulas for calculating the thermodynamic functions of BrF are given in Table 65. The electron components of the thermodynamic functions of BrF were calculated from Eqs. (II.120), (II.121), with a statistical weight of the first excited state $^3\Pi$ equal to 6 and its energy equal to the

mean value of the energies of the states $^3\Pi_{0^+}$ and $^3\Pi_1$.

The errors of the calculated values of Φ_T^* at T = 298.15, 3000 and 6000°K are equal to 0.02, 0.03 and 0.2 cal/mole·deg, respectively and are, at low temperatures, due to inaccuracies of the molecular constants and at high temperatures to inaccurate allowing for the excited electron states and to the fact that the used values of the BrF vibrational constants in the $X^1\Sigma^+$ state do not describe satisfactorily the energies of the high vibrational levels of the electron ground state of the BrF molecule.

The thermodynamic functions of bromine monoflucride were previously calculated according to the method of Mayer and Göppert-Mayer by Evans et al. [1514] (up to 2000°K) and Cole and Elverum [1148] (up to 1500°K). The differences between the results of the calculations of [1514, 1148] and the values given in Table 65 (II) amount to about 0.005 cal/mole·deg at low temperatures and grow as the temperature rises, thus reaching about 0.1 cal/mole·deg with the value of S°_{2000}. These divergences are mainly due to different constants used in the calculations and different methods applied to calculate the thermodynamic functions.

In the Handbook [3680] and in Fialkov's monograph [424] we find the results of calculations made by Evans et al. [1514]. Kelley [2364] accepts an approximate value of $S^\circ_{298.16}$(BrF, gas), which, because of the inaccurate method of calculation, deviates from that given in Table 65 (II) by 0.3 cal/mole·deg.

BrCl. The thermodynamic functions of gaseous bromine monochloride given in Table 66 (II) were calculated from Eqs. (II.161) and (II.162). The values of ln Σ and $T\frac{\partial}{\partial T}\ln\Sigma$ in these equations were calculated according to the Gordon-Barnes method, taking into account the corrections for limited summation over J [Eqs. (II.137), (II.138)] and using the molecular constants of BrCl given in Table 64. The excited electron

states of the BrCl molecule was not taken into consideration owing to the fact that in the spectrum of this molecule transitions connected with low excited states could not be observed (see p. 516). The constants used for calculating the thermodynamic functions of BrCl are compiled in Table 65.

The errors of the calculated values Φ_T^* at T = 298.15, 3000 and 6000°K amount to 0.02, 0.03 and 0.4 cal/mole·deg, respectively. They are due to inaccurate molecular constants and neglection of the excited electron states of BrCl (at high temperatures).

The thermodynamic functions of bromine monochloride were previously calculated according to the method of Mayer and Göppert-Mayer by Evans et al. [1514] (up to 1500°K), Cole and Elverum [1148] (up to 2000°K) and Butkov [113, 112] (up to 3000°K), and by means of the Gordon-Barnes method by Matraw et al. [2812] (up to 1000°K).

The differences between the results of calculations of [1514, 1148, 2812] and the values given in Table 66 (II) do not exceed about 0.01 cal/mole·deg and are due to the fact that different molecular constants were used in these calculations and in the present Handbook. The differences between the results of calculations [112, 113] and the values given in Table 66 (II) are much higher (up to 0.1 cal/mole·deg) and caused by the fact that in these papers an incorrect value was taken for the quantity B_e.

The Handbook [3680] and the book [424] accept the results of calculations by Evans et al. [1514]. In Kelley's resumés [2360, 2364] a value of $S^\circ_{298.16}$ is given that differs from the corresponding value in Table 66 (II) by no more than 0.05 cal/mole·deg, and also the results of calorimetrical determinations of $S^\circ_{298.16}$ made by other authors. In the summary of [2303] Kelley gives the values of $H^\circ_T - H^\circ_{298.16}$ and $S^\circ_T - S^\circ_{298.16}$ up to 2000°K and also an equation for the specific heat of

BrCl.

§41. THE THERMODYNAMIC QUANTITIES

The standard state of bromine is Br_2 (liquid).

Br (gas). The heat of formation of monatomic bromine

$$\Delta H^\circ_{f_0}(Br, \text{gas}) = 28{,}178 \pm 0{,}02 \text{ kcal/g-atom}$$

was calculated from the values of heat of formation and energy of dissociation of Br_2 (gas) accepted in the present Handbook (see below).

Br^- (gas). The results of measuring the electron affinity of the bromine atom, A (Br), obtained until 1944, were considered by Doty and Mayer [1366]. The authors of this paper obtained $A(Br) = -80{,}5 \pm 0{,}4$ kcal/g-atom on the basis of measurements of the ion concentration when bromine vapor was allowed to dissociate on an incandescent tungsten wire. Pritchard [3330], on the basis of an examination of data published until 1953, recommends a somewhat higher value, namely -81.6 ± 1.5 kcal/g-atom.

Bakulina and Ionov [83, 84], by means of the method of surface ionization, determined the differences of the electron affinities of the atoms of all halogens (see p. 464). The absolute value of the quantity A (Br), however, was not determined but was taken from paper [3330]. Bayley [623], on the basis of mass-spectrometrical measurements of the ion concentration during the evaporation of KBr, found $A(Br) = -80{,}9 \pm 1{,}5$ kcal/g-atom.* Cubicciotti [1229] $A(Br) = -79{,}5 \pm 1$ kcal/g-atom as the result of calculations according to the Born-Haber cycle on the basis of published data on the heat of formation of halogen compounds of alkali metals, monatomic halogens and alkali metals in the gaseous state and the lattice energies of the corresponding salts, calculated in theoretical manner in paper [1229].**

On the basis of the above data on the measurements of A (Br) and taking into account the differences between the electron affinities of

F, Cl, Br and I (see p. 464) we accept in the present Handbook the following value:

$$A(Br) = -81 \pm 1{,}5 \text{ kcal/g-atom}$$

To this value of A (Br) corresponds

$$\Delta H^\circ f_0(Br^-, \text{aq}) = -52{,}822 \pm 1{,}5 \text{ kcal/g-atom}$$

Br_2 (liquid). In order to carry out thermodynamic calculations it is necessary to know the enthalpy of liquid bromine at temperatures 293.15 and 298.15°K. In most Handbooks these values are chosen on the basis of measurements [2567, 3899, 3418, 558] . In 1958 Hildenbrand, Kramer, McDonald and Stull [2070] made new more accurate measurements of the specific heat and the melting heat of bromine, according to which

$$H^\circ_{293.15} - H^\circ_0 = 5768 \pm 10 \text{ cal/mole}$$

$$H^\circ_{298.15} - H^\circ_0 = 5859 \pm 10 \text{ cal/mole}$$

These values are accepted in the present Handbook.

The results of measurements of the vapor pressure of bromine were considered and generalized by Lewis and Randall [2604] and later by Kelley [2355]. The values $\Delta Hv_{298.15} = 7{,}588$ kcal/mole [2604] and 7.685 kcal/mole [2355] correspond to the analytical expressions suggested by these authors for the dependence of the heat of evaporation of bromine on the temperature.

Smits and Canneguieter [3800] measured the heat of evaporation of bromine at 283.15° K by means of the method of direct condensation and obtained $\Delta Hv_{283.15} = 7{,}471 \pm 0{,}02$ kcal/mole. A recalculation of this quantity for 298.15°K yielded the values 7.34 kcal/mole [3508] and 7.39 kcal/mole [930].

Hildenbrand and coworkers [2070] measured the heat of evaporation of bromine at 298.15° K by means of the compensation method. The value obtained in paper [2070],

$$\Delta Hv_{298.15}(Br_2, \text{ liq.}) = \Delta H^\circ f_{298.15}(Br_2, \text{ gas}) = 7{,}387 \pm 0{,}027 \text{ kcal/mole}$$

is the most accurate one among the values available in literature and is accepted in the Handbook.*

Br_2(gas). On the basis of an analysis of the results of spectoscopic analyses of bromine [2498, 991, 994] Gaydon [1668] recommends a value of 19,575 cm^{-1} for the limit of convergence of the band system $B^3\Pi_{0_u^+} - X^1\Sigma_g^+$ of the Br_2 molecule. Since the Br_2 molecule in the $B^3\Pi_{0_u}$ and Br state dissociates into the atoms Br $(^2P_{3/2})$ + $(^2P_{\frac{1}{2}})$, the Br_2 dissociation energy in the ground state $X^1\Sigma$ is equal to 19,575 − 685 = = 15,890 cm^{-1}, or

$$D_0(Br_2) = 45{,}434 \pm 0{,}03 \text{ kcal/mole}$$

This value is used in the Handbook. It is in good agreement with the convergence limit of the $A^3\Pi_{1u} - X^1\Sigma_g^+$ band system (15,920 cm^{-1}) which corresponds to a dissociation of Br_2 into the atoms $Br(^2P_{1/2}) + Br(^2P_{3/2})$.

BrO (gas). The dissociation energy of the BrO molecule was determined in 1958 by Durie and Ramsay [1153] as the result of investigating the $A^2\Pi - X^2\Pi$ band system in the absorption spectrum of this molecule. The limit of convergence of the $A^2\Pi - X^2\Pi$ band system was not observed in paper [1153] and therefore Durie and Ramsay estimated it with the help of a short graphical extrapolation and an extrapolation on the basis of own data on the constats of BrO in the $A^2\Pi$ -state. The so obtained energy of the dissociation limit of the $A^2\Pi$ -state with respect to the level v = 0 of the $X^2\Pi$ -state was equal to 35,200 ± 200 cm^{-1}. The BrO molecule in the $A^2\Pi$ -state dissociates into atoms $Br(^2P) + O(^1D)$. The dissociation energy of BrO in the ground state is equal to 35,200 cm^{-1} − 15,868 cm^{-1} = 19,338 cm^{-1} or

$$D_0(BrO) = 55{,}3 \pm 0{,}6 \text{ kcal/mole}^{**}$$

To the accepted value of the BrO dissociation energy corresponds

$$\Delta H^\circ f_0(BrO, \text{ г}) = 31{,}865 \pm 0{,}6 \text{ kcal/mole}$$

BrF (gas). The dissociation energy of the BrF molecule may be de-

termined with high accuracy on the basis of results of investigating the band systems $A^3\Pi_1 - X^1\Sigma^+$ and $B^3\Pi_{0^+} - X^1\Sigma^+$, obtained by Brodersen and Sicre [973]. The authors of [973] determined the limits of convergence of the bands of these systems and found 19,200 ± 30 and 22, 915 ± ± 20 cm^{-1}, respectively.* A dissociation of the BrF molecule into none-excited atoms corresponds to the first value and a dissociation of BrF into either Br ($^2P_{3/2}$) and F ($^2P_{\frac{1}{2}}$) and into Br ($^2P_{\frac{1}{2}}$) and F ($^2P_{\frac{1}{2}}$) and Br ($^2P_{3/2}$) corresponds to the second. Since the difference between the limits of convergence of the band systems $B^3\Pi_{0^+} - X^1\Sigma^+$ and $A^3\Pi_1 - X^1\Sigma^+$ is similar to the excitation energy of the bromine atom, it may be considered as proved that the BrF molecule in the $B^3\Pi_{0^+}$ state dissociates into Br ($^2P_{\frac{1}{2}}$) and F ($^2P_{3/2}$). Then D_0 (BrF) = 22,915 − 3685 = 19,230 ± 20 cm^{-1}, or

$$D_0(BrF) = 54{,}98 \pm 0{,}06 \text{ kcal/mole}$$

This value is used in the Handbook. To it corresponds

$$\Delta H^\circ_f{}_0(BrF, \text{газ}) = -8{,}302 \pm 0{,}5 \text{ kcal/mole}$$

BrCl (gas). Blair and Yost [838], on the basis of results of measuring the heat of reaction of Br_2 with Cl_2 in liquid CCl_4 and of measuring the heat of dissolution of Br_2 and Cl_2 in CCl_4, determined the value of the heat of formation of a BrCl solution in CCl_4 and obtained −1.982 ± 0.030 kcal/mole. The fact that there are no data on the heat of dissolution of BrCl in CCl_4 renders it impossible to use this quantity in calculations of the heat of formation of gaseous BrCl.

The results of measurements of the equilibrium constants of the reaction

$$2\,BrCl(\text{газ}) \rightleftarrows Br_2(\text{газ}) + Cl_2(\text{газ}) \qquad (10.1)$$

are given in Table 66. The last column contains the values of the heat effect of this reaction, calculated on the basis of the thermodynamic functions of the components of the reaction (10.1) accepted in the handbook.

TABLE 66

Values of the Heat Effect of the Reaction (10.1) Calculated on the Basis of Measurements of the Equilibrium Constants.

1 Авторы	2 Метод исследования	T, °K	K_p	3 ΔH_0°, кал/моль
4 Грей и Стайл [1845] . . .	Измерение интенсивности поглощения света парами Br_2, Cl_2 и BrCl	298,15	0,128	377
5 Йост [4366]	13 То же	298,15	0,16	245
6 Диккинсон и Мардок (согласно [3663])	» » »	298,15	0,12	416
7 Веспер и Роллефсон [4103]	» »	301,15	0,107	488
8 Брауэр и Виктор [905] . .	» »	298,15	0,144	349
9 Еллинек и Шютца [2221]	Измерение давления паров Br_2 и Cl_2 над 14 сплавами галоидных солей (KCl, KBr и др.)	1073,15	0,12	1554
10 Шютца [3663]	Измерение давления паров Br_2 и Cl_2 над рас-	773,15	0,1325	693
	15 плавами галоидных солей (AgCl, AgBr и др.)	1073,15	0,140	1224
11 Бисон и Йост [717] . . .	Измерение давления паров в системе	462,15	0,148	461
	16 Cl_2—Br_2— BrCl — NOCl — NOBr — NO			

1) Authors; 2) method of investigation; 3) cal/mole; 4) Gray and Style [1845]; 5) Yost [4366]; 6) Dickinson and Mardok (according to [3663]); 7) Vesper and Rollefson [4103]; 8) Brauer and Viktor [905]; 9) Jellinek and Schütza [2221]; 10) Schütza [3663]; 11) Beeson and Yost [717]; 12) measurement of the intensity of light absorption in Br_2, Cl_2 and BrCl flames; 13) ditto; 14) measurement of the vapor pressure of Br_2 and Cl_2 above melts of halide salts (KCl, KBr, etc.); 15) Measurement of the vapor pressure of Br_2 and Cl_2 above melts of halide salts (AgCl, AgBr, etc.) 16) measurement of the vapor pressure in the system Cl_2 – Br_2 – BrCl – NOCl – NOBr – NO.

The measurements at high temperatures made by Jellinek and Schütza [2221] and Schütza [3663] are less accurate than others since in these measurements neither the bromine and chlorine dissociation, nor the vapor pressure of the halide salts were taken into account. The values calculated on the basis of the other papers are in good agreement, their mean value amounting to $\Delta H_0^\circ = 0{,}39 \pm 0{,}1$ kcal/mole. A similar value was calculated by Butkov [112].

The value of the heat of formation of BrCl used in the Handbook,

$$\Delta H^\circ f_0(\text{BrCl, газ}) = 5{,}297 \pm 0{,}05 \text{ kcal/mole}$$

is based on results of measuring the equilibrium of (10.1); the value

$$D_0(\text{BrCl}) = 51{,}431 \pm 0{,}00 \text{ kcal/mole}$$

TABLE 67

Values (in cal/mole) Used for the Thermodynamic Quantities of Bromine and its Compounds.

1 Вещество	2 Состояние	D_e	$\Delta H°f_0$	$\Delta H°f_{293,15}$	$\Delta H°f_{298,15}$	$H°_{293,15}-H°_0$	$H°_{298,15}-H°_0$
Br	газ	—	28 178	26 750	26 730	1456	1481
Br^-	»	81 000[a]	−52 822	−55 706	−55 752	1456	1481
Br_2	liquid	—	0	0	0	5768	5859
Br_2	газ	45 434	10 921	7 434	7 387	2281	2325
BrO	»	55 300	31 865	30 054	30 029	2093	2131
BrF	»	54 380	−8 302	−10 106	−10 131	2117	2156
BrCl	»	51 431	5 297	3 542	3 518	2205	2247

[a]Value of the energy of electron detatchment from Br^- ion.

1) Substance; 2) state.

Chapter 11

IODINE AND ITS COMPOUNDS WITH OXYGEN, FLUORINE, CHLORINE AND BROMINE

(I, I^-, I_2, IO, IF, ICl, IBr)

The present chapter deals with monatomic and diatomic iodine, the I^- ion and the diatomic compounds of iodine with oxygen, fluorine, chlorine and bromine in gaseous state.

Besides IO we know the following oxygen compounds of iodine: I_2O_3, I_2O_4, I_2O_5, I_2O_8 and I_4O_9. All these compounds exist only in the condensed state and on heating they decay easily into the elements. The most stable iodine oxide, I_2O_5 decays at 275°C.

Among the iodine -fluorine compounds we know IF (gas), IF_5 (solid) and IF_7 (solid). Iodine pentafluoride possesses a comparatively high thermal stability: its decomposition into the elements sets in at temperatures above 400°C. IF_7 displays a still higher thermal stability, it decays at temperatures above 500°C.

Apart from the compound ICl, considered in the Handbook, another extremely unstable compound, ICl_3, was found to exist in the system iodine -chlorine (at 77°C this compound is almost entirely dissociated into ICl and Cl_2).

Among the iodine -bromine compounds only IBr is known.

Since all multiatomic compounds of iodine with oxygen, fluorine, chlorine and bromine are only stable at low temperatures, the data given in the present Handbook describe sufficiently accurate the thermodynamic properties of the systems iodine -oxygen, iodine -fluorine, io-

dine -bromine at temperatures above 500°C.

The compounds of iodine with hydrogen and its isotopes are dealt with in Chapter 12, the iodine-derivatives of methane in Chapter 17.

§42. THE MOLECULAR CONSTANTS

I. In the electron ground state ^2P the iodine atom has the electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^5$. The excited electron states of I are not considered in the present Handbook since their excitation energy exceeds 50,000 cm^{-1}. Table 68 gives the accepted values of energy and statistical weights of the two ground state components of the I atom (according to data given in the Handbook [2941]).

I^-. The negative ion of monatomic iodine has a ground state of the type ^1S with an electron configuration analogous to the electron configuration of the xenon atom. Obviously, the I^- ion has no discrete excited electron states since their energies, judging from the data available of the isoelectronic atom of Xe, must exceed the ionization potential of this ion.

TABLE 68

Energy Levels of the I Atom and the I^- Ion

2 Атом	1 Состояние: 3 электронная конфигурация	4 терм	5 Статистический вес	6 Энергия, $см^{-1}$
J	$...5s^2 5p^5$	$^2P_{3/2}$	4	0
A	$...5s^2 5p^5$	$^2P_{1/2}$	2	7598
J^- A	$...5s^2 5p^6$	^1S	1	0

1) State; 2) atom; 3) electron configuration; 4) term; 5) statistical weight; 6) energy, cm^{-1}. A) J = iodine.

I_2. The I_2 molecule belongs to a small group of molecules whose spectra were thoroughly studied in a wide interval of wavelengths, both in absorption and in emission. Summaries of the results of I_2 spectro-

scopic analyses, published from 1948 to 1950, may be found in Herzberg's book [2020] and in the handbook [649]. Later on, detailed resumes, comprising the results of the subsequent investigations, were compiled by Mathieson and Rees [2808] and Haranath and Rao [1955].

The electron ground state of the I_2 molecule is a $^1\Sigma_g^+$ state and the first excited state is a $^3\Pi_u$ -state. Owing to the fact that, according to Mulliken [2998], the character of the spinorbital coupling in the I_2 molecule corresponds to Gund's case c the excited electron state $^3\Pi_u$ is essentially splitted into four independent states: $^3\Pi_{0_u^+}$, $^3\Pi_{0_u^-}$, $^3\Pi_{1u}$, $^3\Pi_{2u}$.

With the transition to the state $A^3\Pi_{1u}$ the band system A – X (λλ 9300 – 8375 A) is connected. The electron state $B^3\Pi_{0_u^+}$ was studied in the band systems B ← X (λλ 8600 – 4300 A), B → X (λλ 6700 – 5000 A) and D → B (λλ 4420—4000 Å). Indications as to the observation of a $^3\Pi_{2u}$-state may be found in the paper by C. Rao and V. Rao [3388] who interpreted the bands they observed in the ultraviolet fluorescence spectrum as pertaining to an electron transition from the unstable state $^3\Pi_{2g}$ to the stable state $^3\Pi_{2u}$. The vibration frequency of the I_2 molecule in $^3\Pi_{2u}$-state was approximately determined by the authors of paper [3888] as being equal to 380 cm^{-1}. From calculations made by Mulliken [2998] it follows that the $^3\Pi_{2u}$-state must lie below $^3\Pi_{1u}$-state (see p. 512). The $^3\Pi_{0_u^-}$-state of the I_2 molecule, just as those of the molecules of other diatomic halogens, are not investigated by experiment. In the present Handbook this state is assumed to be stable.

The vibrational constants of I_2 in the $X^1\Sigma_g^+$ state were determined for the first time by Loomis [2645] from experimental data of Mecke [2827]. Processing these data, Loomis established the numeration of the bands on the basis of a comparison of the absorption and the fluorescence spectra. The vibrational constants found by Loomis (ω_e'' = 214.36,

$\omega_e''x_e''$ = 0.593 cm^{-1}) were determined according to the edges of 30 bands of the system $B^3\Pi_{0_u^+} - X^1\Sigma_g^+$. The values of the vibrational constants of I_2 in the electron ground state were also determined by Brown [992] according to the edges of 62 bands* of the system $A^3\Pi_{1u} - X^1\Sigma_g^+$ (ω_e'' = = 214.6, $\omega_e''x_e''$ = 0.6 cm^{-1}) and by Rank [3371] as the result of an analysis of the resonance fluorescence spectrum of I_2 (ω_e = 214.57 and $\omega_e x_e$ = = 0.6127 cm^{-1}).** Later on Rank and Baldwin [3372] studied the resonance fluorescence spectrum of I_2 with the help of a Fabry-Perot interferometer, combined with a plane diffraction grating and improved the accuracy of the previous measurements by orders of magnitude. The vibrational constants, calculated by Rank and Baldwin [3372] describe satisfactorily the vibrational levels of I_2 with $v'' \leq 36$.

The values of the vibrational constants of the I_2 molecule in the state $X^1\Sigma_g^+$, obtained by Rank and Baldwin [3372], are used in the present Handbook and are compiled in Table 69. This table contains also the constant of anharmonicity, $\omega_e x_e$, calculated by Mathieson and Rees [2808] according to data of Rank and Baldwin in order to improve the convergence of the vibrational energy levels to the dissociation limit. Studythe I_2 emission spectrum in the range $\lambda\lambda$ 2730 – 2486 Å, Verma [4100] measured the edges of the band system G – X, due to transitions to higher vibrational levels of the ground state (v'' = 41 – 70). The wave numbers of the band edges of this system are satisfactorily described by the vibrational constants given in Table 69.

The rotational constants of the electron ground state of the I_2 molecule were determined by Loomis [2645] (from the absorption spectrum) and by Rank and Baldwin [3372] (from the resonance fluorescence spectrum). The values of the constants B_e, α_e, D_0 obtained in paper [3372] are accepted in the present Handbook and given in Table 69. Loomis [2645]*** obtained values of these constants which agree with them

with them within the limits of error.

The interatomic distance in the electron ground state of I_2 was determined from electron diffraction pictures [2325] (r_0 = 2.662 Å) and agrees with the values calculated from the rotational constant (see Table 69). The rotational constants of I_2 in the excited electron states were not determined.

TABLE 69

Accepted Values of the Molecular Constants of I_2, IO, IF, ICl, and IBr.

1 Молекула	2 Состояние	T_e	ω_e	$\omega_e x_e$	B_e	$\alpha_1 \cdot 10^4$	$D_e \cdot 10^8$	r_e
		3 $см^{-1}$						Å
I_2	$X^1\Sigma_g^+$	0	214,248	0,6074[a]	0,037364	1,206	0,455	2,6667
	$A^3\Pi_{1u}^6$	11888,3	44,0	1,0[b]	—	—	—	—
	$B^3\Pi_{0u}^{6+}$	15641,6	127,35	0,76[c]	—	—	—	—
	$C^3\Sigma_u^-$	39293	110,85	0,644[d]	—	—	—	—
	$D^1\Sigma_g^-$	41411,2	102,2	0,34	—	—	—	—
	$E^3\Sigma_u^-$	45230	93,4	—	—	—	—	—
	$F^1\Sigma_u^+$	46689,3	105,65	0,28	—	—	—	—
	$G^3\Sigma_u^-$	47197,9	96,03	0,298	—	—	—	—
	$H^3\Sigma_u^+$	48072	79	—	—	—	—	—
IO	$X^2\Pi$	0	681,47	4,29[e]	0,34026	26,96[ж]	36	1,8676
	$A^2\Pi$	21557,81	514,57	5,52	0,27635	27,3	33	2,0723
IF	$X^1\Sigma^+$	0	610	3	0,2796[з]	17,5[и]	23,5[к]	1,91[з]
	$B^3\Pi_{0+}$	19054	412,5	3,8	—	—	—	—
ICl^{35}	$X^1\Sigma^+$	0	384,18	1,465	0,114155[л]	5,36[л]	3,95[к]	2,3207
	$A^3\Pi_1$	13744	209,7	1,94741[м]	0,08389	3,828	—	2,7072
	$B^3\Pi_{0+}$	17344	(228)	13	0,090	0,029	—	2,61
	$B'0^+$	18157	(32)	—	—	—	—	—
	$C^1\Sigma^+$	37742	173,2	1,1	—	—	—	—
IBr	$X^1\Sigma^+$	0	267,4[н]	0,77	0,05612[з]	1,91[н]	0,99[к]	2,475[з]
	$A^3\Pi_1$	(12230)	137,8	0,571[о]	—	—	—	—
	$B^3\Pi_{0+}$	(16240)	(150)	4,3	—	—	—	—
	$B'0^+$	16889	65,5	0,24	—	—	—	—
	$C^3\Sigma^-$	35427	43,03	—	—	—	—	—
	$D^1\Delta$	38713	90,1	0,15	—	—	—	—
	$E^1\Sigma^+$	39126	77,0	—	—	—	—	—

1) Molecule; 2) state; 3) cm^{-1}

[a] $\omega_e y_e = -1.30 \cdot 10^{-3}$, $\omega_e z_e = -5.25 \cdot 10^{-6}$, $\omega_e t_e = 1.60 \cdot 10^{-7}$, $\omega_e s_e = +8.26 \cdot 10^{-11}$ cm^{-1}

[b] The excitation energies of the states $^3\Pi_{2u}$ and $^3\Pi_{0u}^-$ are

close to the exitation energies of the states $A^3\Pi_{1u}$ and $B^3\Pi_{0u}^+$.

[c] $\omega_e\beta_e = +0{,}008\ cm^{-1}$;
[d] $\omega_e\beta_e = -0{,}0033\ cm^{-1}$.
[e] $\omega_e\beta_e = +0{,}0078\ cm^{-1}$.
[f] $\omega_e\beta_e = -0{,}013\ cm^{-1}$.
[g] $a_1 = -9{,}7\cdot10^{-6}\ cm^{-1}$.
[h] Estimate;
[i] Calculated from Eq. (1.38);
[k] Calculated from Eq. (1.36).
[l] For ICl^{37} $B_e = 0{,}1093209$, $\alpha_1 = 5.02\cdot10^{-4}\ cm^{-1}$.
[m] $\omega_e y_e = -0.033661\ cm^{-1}$;
[n] Mean value of ω_e. For IBr^{79} $\omega_e = 266.4\ cm^{-1}$ and for IBr^{81} $\omega_e = 268.4\ cm^{-1}$.
[o] $\omega_e y_e = -0.1156$, $\omega_e z_e = 3.09\cdot10^{-3}$, $\omega_e t_e = 2.5\cdot10^{-5}\ cm^{-1}$

The data on the excited electron states of the I_2 molecule with excitation energies $\lesssim 50{,}000\ cm^{-1}$, contained in Table 69, are based on recommendations of Mathieson and Rees [2808] and Haranath and Rao [1955] who analyzed the results of many spectroscopic analyses of I_2. Haranath and Rao studied also a series of band systems, corresponding to transitions to high excited states of I_2. In particular, these researchers were the first who discovered the electron states $E^3\Sigma_u^-$ and $H^3\Sigma_u^+$. In paper [1955a] Haranath and Rao published the results of additional studies of the $D^1\Sigma_g^+ - B^3\Pi_{0u}^+$, band system, lying in the range λλ 4400–3900 A.
The band edges of this system, measured in [1955a], which correspond to v' = 0–20 and v'' = 7–45, are well described by the values of the vibrational constants of I_2 in the states $D^1\Sigma_g^+$ and $B^3\Pi_{0u}^+$ given in Table 69.

IO. The electron ground state of the IO molecule is of the type $X^2\Pi$. IO bands are observed both in the emission spectrum in the case of excitation in flames containing iodomethane admixtures [4049, 837, 1154, 1427, 1428], and in the absorption spectrum in pulsed photolysis

of mixtures of iodine vapor and oxygen [1428].

IO bands were first observed by Vaidya [4049] in the spectrum of flames of methyl alcohol mixed with methyl iodide. Later on the IO band structure was analyzed by Blake and Iredale [837], Coleman, Gaydon and Vaidya [1154] and Durie, Legay and Ramsay [1427]. Blake and Airdale determined the edges of 12 bands and found the following values of the vibrational constants of IO (in cm^{-1}): $\omega_e' = 686$, $\omega_e' x_e' = 6.5$ and $\omega_e'' = 541.8$, $\omega_e'' x_e'' = 16$. Coleman, Gaydon and Vaidya, on the basis of measurements of the wavelengths of 30 band edges recommended somewhat different values (in cm^{-1}): $\omega_e' = 687$, $\omega_e' x_e' = 5$ and $\omega_e'' = 512$, $\omega_e'' x_e'' = 5$.

The most detailed spectrum analysis of IO was carried out by Durie, Legay and Ramsay [1427]. In this work the IO spectrum was excited in the diffuse flame of hydrogen, saturated with iodomethane vapor and recorded in the second order of a 21-foot concave grating. In the IO spectrum the rotational structure of 8 bands (0-2, 0-3, 0-4, 0-6, 2-0, 2-2, 2-9, 3-0) could be resolved and the edges of another 10 bands were measured, bands which did not possess a clear discrete structure."* An analysis of the rotational structure of the eight bands mentioned above showed that the bands pertain to a system connected with the transition $A^2\Pi - X^2\Pi$, where, owing to the intense spin splitting of the excited state $A^2\Pi$, in each band only a single subband, $^2\Pi_{3/2} - {}^2\Pi_{3/2}$, is to be observed. The values of the molecular constants of IO in the states $X^2\Pi$ and $A^2\Pi$, recommended in paper [1427] are accepted in our Handbook and are compiled in Table 69. It must be noted that the vibrational constants of IO calculated by Durie, Legay and Ramsay, yield a very accurate description of the edges of all bands measured in paper [1427] as well as in papers [1154, 1428] published previously.

IF. The IF molecule has the ground state $X^1\Sigma^+$. The IF emission was studied by Durie [1423] who worked with a device whose dispersion

amounted to 6 Å/mm at 4500 Å and 20 Å/mm at 6500 Å. In the spectrum 42 bands of the system $^3\Pi_{0^+} - X^1\Sigma^+$ were observed which corresponded to $v' \leq 11$ and $v'' \leq 9$. The vibrational constants of IF in the states $X^1\Sigma$ and $B^3\Pi_{0^+}$, calculated by Durie according to the band edges, are given in Table 69. The rotational constants of IF in the ground state $X^1\Sigma$, given in Table 69, were calculated from the value r_{IF} = 1.91 ± 0.01 Å, estimated by Schomaker and Stevenson [3648] with the help of the relation $r_{AB} = r_A + r_B - 0{,}09\,(X_A - X_B)$, where r_A, r_B are covalent radii and X_A, X_B the electronegativities of the elements A and B. The applicability of this relation to IF is verified by the coincidence of the measured and calculated values of the interatomic distances of ClF and BrF, within the limits of 0.01 Å.

Other systems have not been observed so far in the IF spectrum though, in analogy to molecules of other diatomic interhalogen compounds, it may be expected that the IF molecule must possess a series of electron states with low excitation energies, particularly a $^3\Pi_1$ - state with an energy lower than that of the $^3\Pi_{0^+}$ state.

ICl. The electron spectra of the ICl molecule were studied in both emission and absorption in wide interval of wavelengths, from the near infrared up to vacuum ultraviolet (cf. [996, 1236, 1178, 1179, 1950, 1952, 2152a, 2153, 1261, 4096]). In these spectra transitions were observed between eight electron states of ICl. Like the molecules of other interhalide compounds, the ICl molecule has a ground state of the type $^1\Sigma^+$ and the first excited state is a $^3\Pi$ -state.

The molecular constants of ICl in the electron ground state were determined as the result of studying the band system $A^3\Pi_1 - X^1\Sigma^+$ in the papers of Darbyshire [1261], Curtis and Patkowski [1236], Hulthen, Johansson and Pilsäter [2153]. In the present Handbook the values of the vibrational constants of ICl in this state were chosen according

to data of Curtis and Patkowski [1236], who studied the $A^3\Pi_1 \leftarrow X^1\Sigma^+$ band system with a high-dispersion device and analyzed the rotational structure of 12 bands of this system (v" = 2, v' = 9–14). The accepted values of the vibrational constants of ICl (cf. Table 69) were calculated by them from the wave numbers of the beginnings of the bands and agree with the values found by Darbyshire from the band edges of seven progressions (v', v"), where $v' = 1$–7 ($\omega_e = 384.6$ and $\omega_e x_e = 1.6$ cm^{-1}) and Hulthen, Johansson and Pilsater from data of the bands $v'' \leq 2$, $v' = 9$–18 ($\omega_e = 384.294$ and $\omega_e x_e = 1.501$ cm^{-1} for ICl^{35}). The value of the rotational constant of ICl found by Curtis and Patkowski ($B_e = 0.11414$ cm^{-1} for ICl^{35}) is in good agreement with the value obtained by Townes et al. [4010], investigating the ICl microwave spectrum and that accepted in the present Handbook (see Table 69).

The molecular constants of ICl in the state $A^3\Pi_1$, given in Table 69, were borrowed from a paper of Curtis and Patkowski [1236]. Owing to the fact that in the system $A^3\Pi_1 - X^1\Sigma^+$ only transition to high vibrational levels of the $A^3\Pi_1$ – state are observed, the accuracy of the used values of the constants and the excitation energy of this state is not high.* The values of the constants ω_e and $\omega_e x_e$ in the state $A^3\Pi_1$, found by Curtis and Patkowski, are in good agreement with the values obtained by Haranath and Rao [1950] in studying the $C^1\Sigma - A^3\Pi_1$ band system.

The molecular constants of ICl in the state $B^3\Pi_{0^+}$, given in Table 69, were obtained by Brown and Gibson [996], investigating the $B^3\Pi_{0^+} \leftarrow X^1\Sigma^+$ band system.

The state $B^3\Pi_{0^+}$ is in strong interaction with the repulsive state 0^+. Owing to this interaction the ICl molecule in the $B^3\Pi_{0^+}$ state has only three vibrational levels and may exist in the stable state $\underline{B}'0^+$, whose potential curve has a minimum in the zone of intersection of the

of the potential curves of the states $B^3\Pi_{0^+}$ and 0^+.

Besides the four stable electron states mentioned, we know that the ICl molecule may also possess another state ($C^1\Sigma^+$) with an excitation energy below 50,000 cm^{-1}. The molecular constants of ICl in the in the $C^1\Sigma^+$ state are given in Table 69, on the basis of data obtained by Haranath and Rao [1950].

IBr. The electron spectrum of the IBr molecule was studied in the papers [995, 1179, 583, 1178, 1950, 1954, 4096], dealing with the band system connected with transitions between nine stable electron states of IBr. Just as with other diatomic interhalogen molecules, the electron ground state of IBr is a $^1\Sigma^+$ -state and the first excited state is a $^3\Pi$ -state. Two components of the latter state, $A^3\Pi_1$ and $B^3\Pi_{0^+}$, were found by experiment. The band system $A^3\Pi_1 \leftarrow X^1\Sigma^+$ and $B^3\Pi_{0^+} \leftarrow X^1\Sigma^+$ of the IBr molecule were investigated by Brown [995] who observed 67 bands of the system $A^3\Pi_1 \leftarrow X^1\Sigma$ with the values $v'' = 0$–4, $v' = 9$–44 and 14 bands of the system $B^3\Pi_{0^+} - X^1\Sigma^+$ with $v'' = 3$–7, $v' = 2$–5. Moreover, Brown discovered that, owing to the intersection of the potential curve of the state $B^3\Pi_{0^+}$ with the potential curve of the repulsive state 0^+, a stable electron state of the type $B'0^+$ forms. In the band system $B'0^+ - X^1\Sigma$ Brown observed 75 bands corresponding to $v'' = 0$–4, $v'' = 8$–37. In order to determine the vibrational constants of the ground state, Brown used the data for all three band systems, selecting the bands for which the isotope shift of frequencies has been measured. The vibrational constants of IBr in the ground state, found by Brown, were accepted in our Handbook and are compiled in Table 69.

The vibrational constants of the IBr molecule in the states $A^3\Pi_1$, $B^3\Pi_{0^+}$ and $B'0^+$, just as the constants of another three states ($C^3\Sigma^-$, $D^1\Delta$ and $E^1\Sigma^+$), whose excitation energy does not exceed 50,000 cm^{-1} (cf.

Table 69), are given in our Handbook according to data of Venkateswarlu and Verma [4096].

The rotational structure of the IBr bands was not resolved in works published before 1960. The interatomic distance $r_e(IBr) = 2.475$ Å, given in Table 69 was estimated by the authors of the Handbook as the halfsum of $r_e(I_2)$ and $r_e(Br_2)$ (see Tables 69 and 64). The error of the estimated value of $r_e(IBr)$ was assumed as equal to ± 0.01 A since the value of $r_e(BrCl)$, calculated analogously, coincides with that found by experiment with an accuracy of up to 0.001 A and the value of $r_e(ICl)$ with an accuracy of up to 0.005 A. The value of the constants B_e of the IBr molecule in the state $X^1\Sigma^+$ given in Table 69 was calculated with the help of the estimated value of $r_e(IBr)$ and thereafter, according to Eqs. (I.38) and (I.36), the constants α_1 and D_0^* were calculated.

§43. THE THERMODYNAMIC FUNCTIONS OF THE GASES

The thermodynamic functions of gaseous iodine and its diatomic compounds with fluorine, chlorine, bromine and oxygen, calculated without taking into account the intermolecular interactions, are given for the temperatures from 293.15 to 6000°K in Tables 67, 68, 69, 70, 74, 75, 76 of Vol. II of the Handbook. Because of the absence of data on the constants of the intermolecular potential, our Handbook does not contain any data on the quantities necessary to allow for the intermolecular interactions in the thermodynamic functions of iodine and its compounds in the gaseous state.

I. The thermodynamic functions of gaseous monatomic iodine, given in Table 67 (II), were calculated by means of Eqs. (II.22) and (II.23) in which the following values were assumed: $A_\Phi = 7.1544$ and $A_\zeta = 12.1225$ cal/g-atom·deg. The electron components were calculated according to Eqs. (II.20), (II.21) on the basis of data of Table 68 on the energy levels of the iodine atom.

The errors of the values of the thermodynamic functions of I, given in Table 67 (II), do not exceed 0.005 cal/g-atom·deg and are due to inaccuracies of the values of physical constants used.

The thermodynamic functions of monatomic iodine were previously calculated by Murphy [3007] (up to 1500°K), Zeise [4377], Brewer [1093] (up to 2000°K), Goff et al. [1787] (up to 2778°K), Evans et al. [1514] (up to 5000°K, and Kelley [2363, 2360]. Differences between the values of the thermodynamic functions calculated in paper [1514] and those given in Table 67 (II) are due to the fact that different values were used for the physical constants and amount to 0.001 cal/g-atom.deg. The divergences between the results of papers [3007, 5466, 1093] are much greater (up to 0.03 cal/g-atom.deg] and are also due to the usage of different values of the physical constants. Zeise [4384] uses the results of calculations by Murphy [3007]. In the Handbooks [3680, 3894] the thermodynamic functions of monatomic iodine given were borrowed from [1514]. Goff et al. [1787] calculated the specific heat of monatomic iodine up to 2777.78°K (5000°R). The differences between the thermodynamic functions of monatomic iodine, calculated in the first and in the present Editions of the Handbook (about 0.005 cal/g-atom.deg) are caused by the usage of different values of the physical constants in the calculations.

$\underline{I}^-$. The progressive components of the thermodynamic functions of negatively charged monatomic iodine were calculated according to the values of A_Φ and A_S given above for monatomic iodine. The electron components are equal to zero.

The errors of the calculated values of Φ_T^* are due to inaccuracies of the physical constants used in the calculations and don not exceed 0.005 cal/g-atom·deg. Differences between the results calculated in the first and in the present Editions of the Handbook are, just as in the case of I, due to the fact that other physical constants were

used. Other calculations of the thermodynamic functions of I^- are unknown in literature.

TABLE 70

Values of the Constants used in Calculations of the Thermodynamic Functions of Gaseous I_2, IO, IF, ICl, IBr.

1 Вещество	θ	$x \cdot 10^2$	$\beta_1 \cdot 10^2$	$\beta_2 \cdot 10^4$	$\frac{\varphi_0}{T}$	$\frac{d_0 \cdot 10^3}{T}$	C_Φ	C_S
	2 *град*	–	–	–	3 *град*$^{-1}$		4 *кал/моль-град*	
I_2	308,2	2,8350	0,3233	0,106	18,63537	4,556	13,3546	20,6101
IF	877,7	4,9180	0,6278	0,402	2,49329	4,204	9,3858	16,3413
IO	990,49	6,2952	0,7954	0,649	2,05078	4,357	11,6904	18,6459
ICl	549,85	3,7942	0,4679	0,222	6,16694	4,323	11,5030	18,4594
IBr	384,7	2,8796	0,3411	0,117	12,40541	4,384	13,6144	20,5699

1) Substance; 2) degree; 3) deg^{-1}; 4) cal/mole·deg.

$\underline{I}_2$. The thermodynamic functions of gaseous diatomic iodine, given in Table 69 (II) were calculated from Eqs. (2.161) and (2.162). The quantities $\ln \Sigma$ and $T\frac{\partial}{\partial T} \ln \Sigma$ in these equations were calculated by means of the Gordon-Barnes method, allowing for corrections for the limitation of summation over $\underline{I}$ [Eqs. (2.137) and (2.138)] on the basis of the molecular constants of I_2 given in Table 69. The values of the constants C_Φ, C_S, θ and x, as well as the coefficients of Eqs. (2.137), (2.138), were calculated from the accepted molecular constants of I_2 given in Table 70. The components of the excited electron states of the I_2 molecule were calculated from Eqs. (2.120), (2.121), i.e., without allowing for the differences of the constants of the gas molecules in the ground state and in the excited state. The individual components of the $^3\Pi_u$ -state were considered as a single state with the statistical weight 6 and an excitation energy equal to the halfsum of the excitation energies of the states $^3\Pi_{0^+_u}$ and $^3\Pi_{1u}$. Other excited states of I_2 (see Table 69) are not taken into account in the calculations.

The errors of the calculated values of the thermodynamic functions

of diatomic iodine at low temperatures are due to inaccuracies of the used values of the molecular and physical constants and do not exceed 0.01 cal/mole·deg. At high temperatures they grow rapidly, mainly owing to the fact that it is impossible to allow sufficiently well for the components of the excited electron states of the I_2 molecule, since the necessary data are not available. The errors of the values of $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000} given in Table 69 (II) are estimated to amount to 0.01, 0.02 and 0.2 cal/mole·deg, respectively.

The thermodynamic functions of diatomic iodine were previously calculated by Murphy [3007] (Φ^*_T up to 1500°K) according to Kassel's method, by Zeise [4377] (Φ^*_T up to 2000°K) in the harmonic oscillator - rigid rotator approximation, Brewer [1093] (S°_T and $H^\circ_T - H^\circ_0$ up to 2000°K), Evans et al. [1514] (up to 3000°K) according to the method of Mayer and Göppert-Mayer. Differences of the results of calculations made in [4377, 3007, 1093] and the values given in Table 69 (II) do not exceed 0.02 cal/mole·deg at low temperatures and may be explained by differences in the values used for the molecular and physical constants; at high temperatures they reach 0.06 cal/mole·deg and are mainly due to different methods of calculation applied in the papers mentioned and in the Handbook. Zeise, in the book [4384], gives the results of calculations he made earlier [4377]. Brewer [1093] uses values of Φ^*_T calculated by Murphy [3007] and Zeise [4377]. In the Handbooks [3680, 3894] and in the paper of Shirley and Giauque [3709] the data obtained by Evans at al. [1514] are used. Kelley [2363] gives the values of $H^\circ_T - H^\circ_{298.16}$ and $S^\circ_T - S^\circ_{298.16}$ up to 1500° and an equation for the specific heat of I_2.

Differences in the results of calculations of the thermodynamic functions in the first and the present Editions of the Handbook do not exceed 0.01 cal/mole·deg at low temperatures. At high temperatures these

reach 0.2 and 0.8 cal/mole·deg with the values of Φ_T^* and S_T, respectively, since in the First Edition of the Handbook the necessity of limiting the summation over I was ignored.

IO. The thermodynamic functions of gaseous iodine monoxide, IO, given in Table 70 (II), were calculated from Eqs. (2.161), (2.162) on the basis of the values of molecular constants contained in Table 69. The quantities $\ln \Sigma$ and $T\frac{\partial}{\partial T}\ln \Sigma$ were calculated according to the Gordon-Barnes method [Eqs. (2.137), (2.138)] without introducing corrections for the limitation of summation over I. The values of the quantities $C_\Phi, C_S, 0$ and x as well as the coefficients of Eqs. (2.137), (2.138), were calculated according to the accepted molecular constants of IO given in Table 70. Since the IO molecule has an electron ground state of the type $^2\Pi$, the terms R ln 4 are included in the values of C_Φ and C_S. A more accurate consideration of the multiplet nature of the $X^2\Pi$ state of IO was impossible since the coupling constant of this state had not been determined. $\ln\Delta_M$ and $T\frac{\partial}{\partial T}\ln\Delta_M$ in Eqs. (2.161) and (2.162) were therefore assumed to be equal to zero. The components of the excited state $A^2\Pi$ in the values of Φ_T^* and S_T° were calculated according to Eqs. (2.120), (2.121) i.e., without allowing for the differences between the constants of IO in the ground state and in the excited electron state.

The errors of the calculated thermodynamic functions of IO are of the orders of 0.7, 0.2 and 0.2 cal/mole·deg for the values of Φ_T^* at 298.15, 3000 and 6000°K, respectively. At low temperatures these errors are due to the approximate consideration of the multiplet nature of the electron ground state of IO, while at temperatures above 2000-3000°K they are caused by the insufficient accuracy of the known constants of IO and the absence of data on the other excited states of this molecule.

The thermodynamic functions of IO were the first that were publis-

ed.

IF. The thermodynamic functions of gaseous iodine monofluoride given in Table 74 (II) were calculated from Eqs. (2.161), (2.162) on the basis of the molecular constants of IF compiled in Table 69. The quantities $\ln \Sigma$ and $T\frac{\partial}{\partial T}\ln \Sigma$ were calculated by the Gordon-Barnes method, taking into account the corrections for the limitation of summation over the rotational quantum number [Eqs. (2.137) and (2.138)]. The components of the excited electron states of the IF molecule were calculated with the help of Eqs. (2.120) and (2.121) with a statistical weight of the $^3\Pi$ electron state chosen equal to 6 and with an energy of this state taken equal to the excitation energy of the state $^3\Pi_{0^+}$.

The values of C_Φ, C_S, θ and x, as well as the coefficients of Eqs. (2.137) and (2.138), calculated according to the accepted constants of IF, are contained in Table 70.

The errors of the calculated values of Φ_T^* at 298.15, 3000 and 6000°K amount to 0.05, 0.1 and 0.2 cal/mole·deg, respectively. These errors are at low temperatures due to inaccurate values used for the molecular constants of IF, particularly to those of the vibrational constants and the constants B_0 and α_1, and at high temperatures they are caused by the approximate consideration of the excited electron states.

Previously the thermodynamic functions of iodine monofluoride were calculated by Evans et al. [1514] (up to 1500°K) according to the method by Mayer and Göppert-Mayer, and Cole and Elverum [1140] (up to 2000°K). Differences between the results of calculations of [1514] and the values given in Table 74 (II), do not exceed 0.02 cal/mole·deg and are caused by different physical and molecular constants used. The differences between the values of Φ_T^* calculated in paper [1148] and the data of Table 74 (II) are much greater; they reach 0.3 cal/mole·deg, owing to the fact that in paper [1148] errors were admitted in the calcu-

lations. In the Handbook [3680] and in the book [424] we find the results of calculations by Evans et al. [514].

ICl. The thermodynamic functions of gaseous iodine monochloride given in Table 75 (II) were calculated from Eqs (2.161) and (2.162). The quantities $\ln \Sigma$ and $T\frac{\partial}{\partial T}\ln \Sigma$ were calculated according to the Gordon-Barnes method, allowing for corrections for the limitation of summation over I and using the molecular constants of ICl, given in Table 69. The quantities C_Φ, C_S, θ, x and the coefficients of Eqs. (2.137), (2.138), calculated with the accepted values of the molecular constants of ICl, are given in Table 70. The components of the excited electron states were calculated according to Eqs. (2.120), (2.121) with a statistical weight of the $^3\Pi$ electron state equal to 6 and with an excitation energy of this state, assumed as equal to the halfsum of the energies of the states $^3\Pi_{0^+}$ and $^3\Pi_1$. The electron states $B'0^+$ and $^1\Sigma^+$ of the ICl molecule were not taken into consideration in calculating the thermodynamic functions of iodine monofluoride. The main errors of the calculated thermodynamic functions of ICl are at low temperatures due to inaccuracies of the physical constants, at high temperatures to inaccurate values of the vibrational constants of ICl in the state $X^1\Sigma^+$ and approximate consideration of the excited electron states of this molecule. They amount to 0.01, 0.03 and 0.2 cal/mole·deg with the values of Φ_T^* at 298.15, 3000 and 6000°K, respectively.

The thermodynamic functions of iodine monochloride were previously calculated by Evans et al. [1514] (up to 1500°K) and Cole and Elverum [1148] (up to 2000°K) according to the method of Mayer and Göppert Mayer. Divergences between the results of calculations in [1514, 1148] and the values contained in Table 75 (II) amount to about 0.04 and about 0.01 cal/mole·deg, respectively, and are explained by the fact that different values of the molecular constants were used. In the

Handbook [3680] and in the book [424] we find the thermodynamic functions of ICl borrowed from paper [1514]. In paper [2364] Kelley gives the results of calorimetrical determinations of $S^\circ_{298.16}(ICl)$ which are in satisfactory agreement with the values contained in Table 75 (II). In the summary of [2363] Kelley gives the values of $H^\circ_T - H^\circ_{298.16}$ and $S^\circ_T - H^\circ_{298.16}$ (up to 2000°K) and also an equation for the specific heat of ICl.

IBr. The thermodynamic functions of gaseous iodine monobromide given in Table 76 (II) were calculated from Eqs. (2.161) and (2.162). The values of $\ln \Sigma$ and $T\frac{\partial}{\partial T}\ln\Sigma$ were calculated with the help of the Gordon-Barnes method, taking into account corrections for the limitation of summation over I [Eqs. (2.137) and (2.138)] and making use of the molecular constants given in Table 69. The quantities C_Φ, C_S, θ and x_i, as well as the values of the coefficients in Eqs. (2.137), (2.138), were calculated with the values accepted for the molecular constants of IBr, given in Table 70. The components of the excited electron state $^3\Pi$ were calculated from Eqs. (2.120), (2.121) with a statistical weight taken equal to 6 and with an excitation energy assumed to be equal to the halfsum of the energies of the states $^3\Pi_{0^+}$ and $^3\Pi_1$.

The states $B'0^+$ and $^1\Sigma^+$, just as other states with energies higher than 35,000 cm^{-1} (see Table 69) are not considered in the calculation. The errors of the calculated values of Φ^*_T at 298.15, 3000 and 6000°K are of the order 0.02, 0.04 and 0.2 cal/mole·deg, respectively.

The thermodynamic functions of iodine monobromide were previously calculated by Evans et al. [1514] (up to 1500°K). Cole and Eiverum [1148] (up to 2000°K) according to the method of Mayer and Göppert-Mayer, and Zeise [4379] (up to 2000°K) in the approximation of the model of rigid rotator -harmonic oscillator. The differences between the results of calculations in [1514] and the values given in Table 76 (II)

do not exceed 0.02 cal/mole·deg and are due to the fact that different molecular constants of IBr were used in paper [1514] and in the present Handbook. The differences between the results of calculations in [1148, 4379] and the corresponding values contained in Table 76 (II) are much greater (up to 0.1 cal/mole·deg) owing to the fact that in paper [1148] an incorrect value was used for the rotational constant of IBr which differs strongly from that given in Table 69, while in paper [4379] an incorrect method of calculation was applied. Zeise [4384] borrows the results of calculations from [4379]; in the Handbook [3680] and in the book [424] we find the results from paper [1514], in Kelley's resumes [2364, 2360] the results of calorimetrical determinations of $S^\circ_{298.16}$ obtained by other authors; in the summary of [2363] Kelley gives the values $H^\circ_T - H^\circ_{298.16}$ and $S^\circ_T - S^\circ_{298.16}$ up to 2000°K and an equation for the equation of the specific heat of IBr.

§44. THE THERMODYNAMIC QUANTITIES

The standard state of iodine I_2 (cryst.).

I (gas). The heat of formation of monatomic gaseous iodine

$$\Delta H^\circ f_0(I, \text{gas}) = 25{,}587 \pm 0{,}030 \text{ kcal/g-atom}$$

is calculated on the basis of the dissociation energy and the heat of formation of I_2 (gas) accepted in the present Handbook (see below).

I^-(gas). In Pritchard's paper [3330] a review is given of all papers published until 1953 and dealing with the determination of the electron affinity of the iodine atom. Pritchard recommends a value of A (I) = −74.6 ± 1.5 kcal/g-atom. The very same value is recommended in Buchel'nikova's review article [116]. Bakulina and Ionov [83, 84] measured the difference between the values of the electron affinities of the atoms of all halogens (see p. 464). With the help of the data from [83, 84] and the value of A (Br) accepted in the Handbook, we may find A (I) = −74.8 kcal/g-atom which agrees with the value recommended by

Pritchard. A similar value, A (I) = −73.3 ± 1.7 kcal/g-atom, was calculated from Bayley's data [623] who measured the quantity A (Br) − A (I), in the ionization of IBr on an incandescent tungsten wire.*

In the present Handbook the value

$$A(I) = -74{,}6 \pm 1{,}5 \text{ kcal/g-atom}$$

has been accepted, to which corresponds

$$\Delta H^\circ f_0(I^-, \text{ газ}) = -49{,}013 \pm 1{,}5 \text{ kcal/g-atom}$$

I_2 (cryst.). The specific heat of crystalline iodine was measured at temperatures from 10 to 300°K by Nernst, Koref and Lindeman [3044], Nernst [3041, 3042], Günther [1889] and Lange [2558]. Frederick and Hildebrand [1602] measured the specific heat of crystalline iodine in the interval 325–386.8°K. A paper of Brounshteyn, Yudin and Lukovskiy [108] contains a table on the thermodynamic functions of crystalline iodine, obtained on the basis of analyzing and processing the results of a great many investigations, according to which**

$$H^\circ_{298.15} - H^\circ_0 = 3105 \text{ cal/mole},$$

$$H^\circ_{298.15} - H^\circ_0 = 3171 \text{ cal/mole}.$$

The errors of these data, used in our Handbook, amounts to ± 20 cal/mole.

I_2 (gas). Brounshteyn, Yudin and Lukovskiy [108] considered the results of iodine vapor pressure measurements obtained in the papers [3365, 694, 695, 911, 1912, 1746]. It was shown that the most accurate data were obtained by Gillespie and Fraser [1746] at low temperatures. The measurements of the other authors were made at higher temperatures and are therefore less reliable.*** In the Handbook we accept the following value of the heat of sublimation of iodine:

$$\Delta Hs_0(I_2, \text{ крист.}) = \Delta H^\circ f_0(I_2, \text{ газ}) = 15{,}608 \pm 0{,}050 \text{ kcal/mole}$$

a value, recommended in paper [108] on the basis of experimental data obtained by Gillespie and Fraser [1746].****

The most accurate value of the dissociation energy of the I_2 molecule was obtained by determining the limits of the band range and the

continuous range of the absorption spectrum corresponding to the transition $B^3\Pi_{0_u^+} - X^1\Sigma$. Herzberg [2020] and Gaydon [141], on the basis of data obtained by Kuhn [2498], accept a value of 20,037 cm^{-1} for the energy of the dissociation limit of the $B^3\Pi_{0_u^+}$ state (correlated with the states $I(^2P_{3/2}) + I(^2P_{3/2})$ of the iodine atoms), from which the following value of the dissociation energy of I_2 in the state $X^1\Sigma$ is obtained: 20,037 cm^{-1} – 7598 cm^{-1} = 12,439 cm^{-1}. This value is in good agreement with the value 12,445 cm^{-1} found by Brown [992] from the limit of convergence of the $A^3\Pi_{1u} - X^1\Sigma$ band system. In the present Handbook, just as in Herzberg's and Gaydon's monograph, a value of the dissociation energy of the I_2 molecule is accepted that was calculated from Kuhn's data:

$$D_e(I_2) = 35{,}566 \pm 0{,}030 \quad \text{kcal/mole}$$

IO (gas). The IO dissociation energy was determined by Coleman, Gaydon and Vaidya [1154] on the basis of a linear extrapolation of the energies of 12 lower vibrational levels of the ground state: $D_0(IO)$ = = 44 ± 5 kcal/mole.

Durie and Ramsay [1428], from a linear extrapolation of the first four vibrational levels of the $A^2\Pi$ excited state, found that $D_0' = 10{,}200$ cm^{-1}. Since the dissociation energies of ClO and BrO in the $A^2\Pi$ states are lower by about 10% than the values obtained by a linear extrapolation of several lower levels, Durie and Ramsay used the value $D_C'(IO)$ = = 9200 cm^{-1}. Taking into account the excitation energy of this state, equal to 21,476 cm^{-1}, and assuming that the IO molecule in the $A^2\Pi$ state dissociate into the atoms $I(^2P_{3/2}) + O(^1D)$, Durie and Ramsay obtained a value of $D_e = 14\,800 \pm 1800$ cm^{-1} or 42 ± 5 kcal/mole* for the IO dissociation energy. Preferring the values obtained by extrapolating the vibrational levels of the ground state, we accept the following value** in the present Handbook:

$$D_0(IO) = 44 \pm 5 \text{ kcal/mole}$$

to which corresponds:

$$\Delta H^\circ_f(IO, \infty) = 40{,}574 \pm 5 \text{ kcal/mole}$$

IF (gas). Durie and Gaydon [1426], by means of a short graphical extrapolation of 11 lower levels of the excited state $B^3\Pi_{0^+}$, determined the dissociation energy of If in this state: $D'_0 = 4615 \pm 300 cm^{-1}$. The dissociation limit of the $B^3\Pi_{0^+}$ state, which is by 23,570 ± 300 cm^{-1} higher than the lower level of the $X^1\Sigma$ state of IF, corresponds to the dissociation into one excited and one nonexcited atom, just as with the molecules of other diatomic interhalide compounds. According to the states of the I and F atoms, to which the $B^3\Pi_{0^+}$ -state of IF corresponds, the dissociation energy of this molecule in the ground state is equal to 23,166 ± 300 cm^{-1} ($IF(B^3\Pi_{0^+}) \rightarrow F(^2P_{1/2}) + I(^2P_{3/2})$) or 15,978 ± 300 cm^{-1} ($IF(B^3\Pi_{0^+}) \rightarrow F(^2P_{3/2}) + I(^2P_{1/2})$). Durie and Gaydon [1426], on the basis of the mean values of the I – F bond energies in the IF_5 and IF_7 molecules, accepted the lower value. The conclusions drawn by Durie and Gaydon were subject to a critical analysis by Slutsky and Bauer [3767] and Evans, Manson and Wagman [1514]. The arguments of these authors are, however, not indisputable. A substantiated selection of one of the two possible values of D_0 (IF) seems to be impossible at present. A comparison with other interhalogen compounds, as in the case of ClF (see p. 506), cannot serve as a basis of such a selection.

In the Handbook we accept a value of the dissociation energy equal to 23,166 ± 300 cm^{-1}, or

$$D_0(IF) = 66{,}2 \pm 1.2 \text{ kcal/mole}$$

The error of the accepted value of D_0 (IF) includes the error of determining the energy of the dissociation limit of IF in the state $B^3\Pi_{0^+}$, caused by the extrapolation of the vibrational levels but does not allow for the error arising owing to the indeterminacy of the elec-

tron states of the IF dissociation products.

A value of

$$\Delta H^{\circ}f_{0}(IF, \infty) = -22{,}113 \pm 1{,}3 \text{ kcal/mole}$$

corresponds to the accepted value of the dissociation energy.

ICl (gas). In the papers by Gibson and coworkers [1726, 996] the limits of convergence of the ICl band were determined for the systems $A^3\Pi_1 - X^1\Sigma$, $B^3\Pi_{0^+} - X^1\Sigma$ and $B'0^+ - X^1\Sigma$. In paper [1726] it was found that the dissociation limit of the ICl molecule in the $A^3\Pi_1$ -state is equal to 17,410 ± 30 cm^{-1} to which the nonexcited dissociation products $I\,(^2P_{3/2}) + Cl\,(^2P_{3/2})$ correspond. In accordance with these results, it was found in paper [996] that the dissociation limit of ICl in the states $B^3\Pi_{0^+}$ and $B'0^+$ is equal to 18,260 ± 30 cm^{-1}, to which $I\,(^2P_{3/2}) + Cl\,(^2P_{1/2})$ corresponds. These data were used by Gaydon [1668] in order to calculate the ICl dissociation energy; a value of $D_0(ICl) = 49{,}78 \pm 0.1$ kcal/mole corresponds to it. This value agrees with the results of measuring the equilibrium constants of the reaction

$$2ICl(\infty) \rightleftarrows I_2(\infty) + Cl_2(\infty), \qquad (11.1)$$

obtained by Mc Morris and Yost [2723].

Later on the dissociation limit of the ICl molecule in the $A^3\Pi_1$ - state was determined by precision measurements, described in papers [1443a] and [2152a]. Ebelhard, Cheng and Renner [1443a] studied the magnetic rotation in the ICl^{35} spectrum, corresponding to the $A^3\Pi_1 \leftarrow X^1\Sigma$ transition. They detected the levels of vibrational energy of the ICl^{35} molecule in the $A^3\Pi_1$ -state, up to $v' = 28$ and observed the disappearance of the spectrum of magnetic rotation at 17,357 ± 3 cm^{-1}, which they identified with the limit of convergence of the bands in the system $A^3\Pi_1 - X^1\Sigma$. Hulthén, Järlsäter and Koffman [2152a] studied the $A^3\Pi_1 \leftarrow X^1\Sigma$ band system in high resolution up to $v' = 35$, where the system of vibrational energy levels of ICl in the $A^3\Pi_1$ -state

breaks off, and discovered a new system of vibrational energy levels of ICl near the dissociation limit of the $A^3\Pi_1$ -state, which lies above the previously known level system that ends at v' = 35. They designated this new system of vibrational energy levels by X_1, X_2, X_3, ... Paper [2152a] reports on the observation of the levels X_1, X_2, X_3, X_4, X_5; it was found in it that the disappearance of the spectrum of magnetic rotation at 17,357 cm^{-1}, observed in [1443a], corresponds to the X_3 -level. From the limit of convergence of the progression of X-levels, Hulthén, Järlsäter and Koffman determined the dissociation limit of the ICl^{35} molecule in the $A^3\Pi_1$ -state as equal to 17,366.0 ± 0.5 cm^{-1}, to which a value* of

$$D_0(ICl) = 49{,}654 \pm 0{,}001 \text{ kcal/mole}$$

corresponds. This value of D_0 (ICl) is accepted in the present Handbook. To it corresponds

$$\Delta H^\circ_f{}_0(ICl, \text{ газ}) = 4{,}483 \pm 0{,}030 \text{ kcal/mole}$$

IBr (gas). Müller [2969], Bodenstein and Schmidt [856], McMorris and Yost [2723] studied the equilibrium of the reaction

$$2IBr(\text{газ}) \rightleftarrows I_2(\text{газ}) + Br_2(\text{газ}). \qquad (11.2)$$

The values of the equilibrium constants and the values of the thermal effects of the reaction (11.2) and the heat of formation of IBr, obtained by different authors on the basis of these equilibrium constants, are contained in Table 71.

Blair and Yost [838] determined the reaction heats of I_2 and Br_2 with liquid CCl_4 and the heat of dissolution of the reaction components in CCl_4. A calculation according to the data of Blair and Yost shows that the heat of formation of IBr (gas) at 0°K is equal to 11,986 cal/mole.

Yost, Anderson and Skoog [4360], on the basis of data obtained by Blair and Yost [838] and results of own measurements of the partial

vapor pressures of the reaction components of (11.2) above a solution in CCl_4, determined the value of the free energy of formation of IBr from gaseous I_2 and Br_2 ($\Delta G^\circ_{298.15} = -1790$ cal/mole), to which a value of $\Delta H^\circ f_0 = 11{,}85$ kcal/mole corresponds.

TABLE 71

Thermal Effects of the Reaction (11.2) and Heats of Formation of IBr, Calculated From the Results of Measuring the Equilibrium Constants

Авторы 1	T,°K	K_p	ΔH°_0, 2 кал/моль	$\Delta H^\circ f_0$ (IBr), кал/моль
Миллер [2969] . . 3	578	0,0130	3393	11 568
4 Боденштейн и Шмидт [856]	1495	0,093	2039	11 795
Мак-Моррис и Йост [2723] 5	388,2	0,0016	3894	11 318
» »	424,4	0,0021	4028	11 252
» »	449,2	0,0025	4108	11 211

1) Authors; 2) cal/mole; 3) Müller; 4) Bodenstein and Schmidt; 5) Mc Morris and Yost

TABLE 72

Accepted Values (in cal/mole) of the Thermodynamic Quantities of Iodine and Its Compounds

Вещество 1	Состояние 2	D_0	$\Delta H^\circ f_0$	$\Delta H^\circ f_{293.15}$	$\Delta H^\circ f_{298.15}$	$H^\circ_{293.15} - H^\circ_0$	$H^\circ_{298.15} - H^\circ_0$
I	3 Газ	—	25 587	25 491	25 483	1 456	1481
I^-	»	74 600[a]	—49 013	—50 566	—50 599	1 456	1481
I_2	4 Крист.	—	0	0	0	3 105	3171
I_2	Газ	35 566	15 608	14 877	14 855	2 374	2418
IO	»	44 000	40 574	40 116	40 104	2 114	2153
IF	»	63 200	—22 113	—22 568	—22 580	2 134	2174
ICl	»	49 654	4 453	4 095	4 085	2 241	2284
IBr	»	47 917	11 858	9 738	9 702	2 326	2369

1) Substance; 2) state; 3) gas; 4) cryst.

[a]Value of the energy of electron detachment from an I^- -ion.

Brown [995], as a result of studying the IBr absorption spectrum, determined the limit of convergence of the $A^3\Pi - X^1\Sigma$ band system with high accuracy, obtaining $14{,}660 \pm 5$ cm^{-1}. The value of the IBr disso-

ciation energy corresponding to it is equal to

$$D_0(IBr) = 41{,}917 \pm 0{,}015 \text{ kcal/mole}$$

and is accepted in the present Handbook.* A value of

$$\Delta H^\circ f_0(\text{IBr}, \text{газ}) = 11{,}848 \pm 0{,}040 \text{ kcal/mole}$$

corresponds to it. The results of thermodynamic measurements and measurements of the equilibrium constants of the reaction (11.2) yields similar values.

Chapter 12

THE COMPOUNDS OF HYDROGEN AND ITS ISOTOPES WITH HALOGENS (HF, DF, TF, HCl, DCl, TCl, HBr, DBr, TBr, HI, DI, TI)

The present chapter deals with the compounds of fluorine, chlorine, bromine and iodine with hydrogen, deuterium and tritium. Since the differences in the thermodynamic properties of the compounds of protium and the natural isotope mixture of hydrogen are insignificant, the halogen compounds of protium are not considered in the Handbook.

Apart from the simplest molecule HF, in hydrogen fluoride vapor there exist associated molecules $(HF)_2$, $(HF)_3$, $(HF)_4$, etc., which are stable at high pressures and comparatively low temperatures (cf. [356]). In thermodynamic calculations of processes occurring at temperatures above 100°C, such molecule associations may be ignored (with the exception of the cases where the HF vapor pressure is much higher than 1 atm). In the vapors of hydrogen compounds of chlorine, bromine and iodine associated molecules do not exist.

The stability of the halogen-hydrogen compounds drops sharply from fluorine to iodine. As HF is one of the most stable fluorine compounds and does not dissociate even at very high temperatures, HI dissociates considerably earlier at temperatures of 200 – 300°C.

In the first edition of the Handbook only HF, DF, TF, HCl, HBr, HI was considered. In this edition the thermodynamic functions of these compounds were not recalculated since the improvements of the molecular constants of these gases achieved in the time after the issue of the first edition, have only an insignificant influence on their thermody-

namic functions.

The data given in the present Handbook permit a sufficiently accurate calculation of the composition and the thermodynamic properties of the system formed by hydrogen (and its isotopes) with fluorine, chlorine, bromine and iodine.

§45. THE MOLECULAR CONSTANTS

Data on the molecular constants of diatomic compounds of hydrogen and its isotopes with halogens is mainly based upon studies of the infrared absorption spectra in which the bands are observed that correspond to transitions between the first four vibrational states. Pure rotational spectra (infrared and microwave) of molecules of several hydrogen halides were also studied. The electron spectra of hydrogen halides are investigated insufficiently.

The electron ground state of the hydrogen halide molecules is a $^1\Sigma$ state. It follows from the correlation rule by Wigner – Witmer that the first excited electron states of the hydrogen halides must be of the type $^1\Pi$ and $^3\Pi$ (cf. [151], p. 250). In spectroscopic studies transitions connected with $^3\Pi$ -states were not observed; such states are obviously unstable.* The stable excited electron states of hydrogen halide molecules [3322] found by experiment have excitation energies higher than 55,000 cm^{-1} and are therefore not considered in the present Handbook.

In the determination of the molecular constants of the isotope variants of hydrogen halides, the authors of the original papers and of the present Handbook often made use of the relations of (1.43) which link the constants of different isotope modifications of diatomic molecules.

It must be noted that the values of the molecular constants of hydrogen halides, among them those obtained from Eqs. (1.43), give a

good description of the energies of the lower vibrational and rotational states of these molecules. But the accuracy of approximation of high vibrational and rotational levels of the electron ground states of hydrogen halide molecules by these constants, with the exception of HF, is obviously not high.

HF. The infrared spectrum of gaseous HF in the range 364–1500 cm^{-1} and the ultraviolet spectrum, corresponding to transitions from the levels of the excited electron state $V^1\Sigma^+$ to the levels of the ground state $X^1\Sigma^+$, are investigated.

The molecular constants of HF in the electron ground state were determined as the result of studying the vibration-rotation spectrum, by Kirkpatrik and Salant [2409], Talley, Kaylor and Nielsen [3919], Naudé and Verleger [3033], Benedict, Bullock, Silverman and Grosse [723], Kuipers, Smith and Nielsen [2499], and on the basis of studying the vibration-oscillation spectrum and the electron spectrum, by Johns and Barrow [2258]. The rotational constants of HF were also determined on the basis of studying the purely rotational infrared spectrum of this molecule by Smith and Nielsen [3775].

Kirkpatrik and Salant [2409] calculated the vibrational and rotational constants of HF on the basis of an own analysis of the bands 3-0 and 4-0 and of results of measuring the 1-0 band, from a paper by Imes [2169] (see Table 73). The vibrational constants of HF, calculated by Kirkpatrik and Salant [2409] were used in the first edition of Herzberg's monograph [151] and in the handbook [649]. The values of the rotational constants given in the book [151] were recalculated by Herzberg according to data from paper [2409] (see Table 73), whereas in the handbook [649] values are used that were obtained in earlier studies of the vibration-rotation spectrum [3919].

In 1950 new results were published of investigations of the HF

Table 73

Values (in cm^{-1}) of the Molecular Constants of HF in the State $X^1\Sigma$, According to Data of Various Authors

1 Постоянная	2 Киркпатрик и Салант [2409], 1935 г.	3 Наде и Верлегер [3033], 1950 г.	4 Талли, Кейлор, Нильсен [3919], 1950 г.	5 Бенедикт, Буллок, Силверман, Гросс [723], 1953 г.	6 Кейперс, Смит и Нильсен [2400], 1956 г.	7 Джонс и Барроу [2258], 1959 г.
ω_e	4141,305	4143,01	4138,522	—	4137,253	4139,031
$\omega_e x_e$	90,866	91,60	90,060	—	88,726	90,43924
$\omega_e y_e$	0,921	1,03	0,980	—	0,5334	1,177722
$\omega_e z_e$	—	—	0,025	—	—0,0211	0,0722748[a]
B_e	20,920[b]	20,9003	20,939	20,945	20,9456	20,9486
α_1	0,7523[b]	0,7432	0,7705	0,751	0,7888	0,797107
α_2	—	—	0,005	—	0,00873	0,0140235[a]
D_e	0,00215	0,00108	0,0022[d]	0,00242[d]	0,00213	0,002151
β_1	0,000256	0,0002	—	—	0,000038	0,0000587[e]
H_0	—	—	—	—	$1{,}76 \cdot 10^{-9}$	—

a $\omega_e t_e = 4{,}32161 \cdot 10^{-6}$, $\omega_e s_e = 1{,}41709 \cdot 10^{-6}$ cm^{-1}

b According to calculations made by Herzberg [151] with data from [2409], taking into account that α_0: $B_e = 20{,}967$, $\alpha_1 = 0{,}879$ cm^{-1} (the value of the constant α_2 is not given in the monograph [151]).

c $\alpha_0 = 1{,}181565 \cdot 10^{-3}$, $\alpha_1 = 1{,}0003 \cdot 10^{-4}$, $\alpha_2 = 4{,}14067 \cdot 10^{-6}$ cm^{-1}

d Value of D_0 given;

e $\beta_0 = -1{,}4427 \cdot 10^{-4}$, $\beta_0 = -3{,}2655 \cdot 10^{-6}$ cm^{-1}.

1) Constant; 2) Kirkpatrik and Salant; 3) Naudé and Verleger; 4) Talley, Kaylor, Nielsen; 5) Benedict, Bullok, Silverman, Gross; 6) Kuipers, Smith and Nielsen; 7) Johns and Barrow.

vibration-rotation spectrum [3033, 3919], carried out in order to improve the vibrational and rotational constants. Naudé and Verleger [3033] obtained the bands 2-0, 3-0 and 4-0 with resolved structure in first and second orders of a diffraction grating with a dispersion of 2.6 and 1.3 Å/mm, respectively. The results of these measurements, together with the results of Imes' measurements [2169] of the 1-0 band, were used of the authors of paper [3033] in order to calculate the molecular constants of HF (see Table 73). Talley Kaylor and Nielsen

[3919], by means of an instrument with high dispersion, resolved the rotational structure of the bands 1-0 and 2-0. The results of analyzing the rotational structure of these bands, obtained in paper [3919], together with the results of analyzing the bands 3-0 and 4-0, obtained by Kirkpatrik and Salant [2409], were used by Talley, Keylor and Nielson in order to calculate the vibrational and rotational constants of HF. The latter are given in Table 73 and were accepted in the second edition of Herzberg's monograph [2020] and in the first edition of the present Handbook. The values of the molecular constants of HF, found by Talley, Kaylor and Nielson [3919] are much more accurate than those obtained earlier by Naudé and Verleger [3033] and Kirkpatrik and Salant [2409] as this may be seen from a comparison of the values of molecular constants of HF, obtained in papers [3319, 3033, 2409] and in the paper by Johns and Barrow [2258] where theresults of previous investigations were improved, with new data on the HF spectrum, obtained by Johns and Barrow (cf. Table 73).

Furthermore, in order to obtain more accurate values of the molecular constants of HF in the state $X^1\Sigma$, the HF emission spectrum in a $H_2 + F_2$ flame [723, 2755], the HF absorption spectrum in the far and near infrared [3775, 2499] and the ultraviolet spectrum of HF were studied [2258].

The emission spectrum of HF in a $H_2 + F_2$ flame was studied by Benedict, Bullock, Silverman and Grosse [723] in the range 363-1180 cm^{-1} and Mann, Boll and More [2755] in the range 960-1820 cm^{-1}. In paper [723] HF bands were observed which correspond to $v \leq 7$ and $\Delta v = 1, 2, 3$, ($I \geq 18$). The data obtained in paper [723], however, only permit an improvement of the values of the rotational constants (cf. Table 73). Mann, Boll and Moore report in a short note [2755] on own measurements of HF bands, corresponding to $v \leq 9$ and $v = 3, 4, 5$ ($I \leq 20$), made with

a high-dispersion instrument.

Kuipers, Smith and Nielsen [2499] studied the rotational structure of the bands 1-0 and 2-0 in the absorption spectrum of HF in the range 400-770 cm^{-1} and the purely rotational spectrum ($10 \leq I \leq 15$) in the range 41-67 cm^{-1}, in both absorption and emission. In the paper [2499], on the basis of data obtained by these authors and Kirkpatrik and Salant [2409] for the bands 3-0 and 4-0, the vibrational and rotational constants were calculated (see Table 73). The most accurate results were obtained in paper [2409] for the rotational constants. In particular, in paper [2409] the values of the constants H_0 and H_1 were determined as amounting to $1.76 \cdot 10^{-7}$ and $2.1 \cdot 10^{-7}$ cm^{-1}, respectively.

In the ultraviolet spectrum of HF Johns and Barrow [2258] recorded about 1600 lines of the band system $V^1\Sigma^+ - X^1\Sigma^+$. The bands observed in paper [2258] correspond to transitions to high vibrational levels of the electron ground state ($9 \leq v'' \leq 19$). On the basis of an analysis of the bands of this system and the results of earlier studies, reported in papers [2499, 2409, 2755],* of the vibration-rotation spectrum of HF, corresponding to transitions between lower vibrational levels ($v'' \leq 9$), Johns and Barrow derived an equation of sixth order in v, describing the vibrational levels of the HF molecule in the $X^1\Sigma^+$ state, up to the dissociation limit. Johns and Barrow also analyzed the rotational structure of bands in the ultraviolet spectrum of HF and determined the values of the rotational constants.

The values of the molecular constants of HF in the $X^1\Sigma^+$ state, obtained by Johns and Barrow [2258], are the most accurate ones, they are given in Table 74.**

DF. The infrared absorption spectrum of gaseous DF was studied by Talley, Kaylor and Nielsen [3919] in the range 2850-5900 cm^{-1}. The authors of paper [3919] analyzed the rotational structure of the bands

1-0 and 2-0, determined the beginning of the bands and the rotational constants of DF. In paper [3919] the vibrational constants of DF were calculated on the basis of Eqs. (1.43) according to the vibrational constants of HF. Herzberg [2020] calculated the vibrational constants of DF according to the beginnings of the 1-0 and 2-0 bands; for the rotational constants the values determined in paper [3919] were used. The values of the molecular constants of DF(ω_e = 2998.25, $\omega_e x_e$ = 45.71, B_e = 11.007, α_1 = 0.2935, $D_e = 6.5 \cdot 10^{-4}$ cm^{-1}) were accepted in the first edition of the Handbook.

Later on Johns and Barrow [2258] studied the ultraviolet spectrum of DF in which they recorded about 1900 lines of 34 bands of the $V^1\Sigma^+ - X^1\Sigma^+$ system. The bands observed in paper [2258] correspond to transitions to high vibrational levels of the electron ground state ($15 \leqslant v'' \leqslant 24$) . With the help of the results of an analysis of the rotational structure of these bands and the results of studying the infrared spectrum of DF [3919], Johns and Barrow derived equations which give a very accurate description of the vibrational and rotational energy levels of DF up to the dissociation limit of the $X^1\Sigma^+$ -state. The values of the vibrational and rotational constants of DF, obtained in paper [2258], are in excellent agreement with the data calculated from Eqs. (1.43) on the basis of the corresponding constants of HF, determined in the same paper

The values of the molecular constants of DF in the $X^1\Sigma^+$ state obtained by Johns and Barrow [2258] are contained in Table 74.

TF. The TF spectrum was studied by Johns and Goldblatt [2300]. They obtained the TF absorption spectrum in the range 2400-4800 cm^{-1}, analyzed the rotational structure of the bands 1-0 and 2-0 and determined the following values of the molecular constants of TF: ω_e = 2508.5, $\omega_e x_e$ = 32.54, B_e = 7.692, α_1 = 0.176, $D_0 = 2.5 \cdot 10^{-4}$ cm^{-1}.

In the present edition of the Handbook we accepted for TF the same values of the molecular constants as were calculated for the first edition from Eqs. (1.43), on the basis of the molecular constants of DF, recommended in Herzberg's book [2020] (see Table 79). These values of the TF constants differ slightly from those found in paper [2300].

HCl. The results of investigating the spectra of HCl, published until 1950, are summarized in Herzberg's monograph [2020] and in the handbook [649]. In the following years the vibration-rotation spectrum of HCl was investigated by Naudé and Verleger [3033], Mills, Thompson and Williams [2920] and Haeusler and Barchewitz [1926], and the purely rotational spectrum of HCl was studied by Mc Cubbin [2696] and Hansler and Oetjen [1945]. The electron spectrum of HCl was studied in the papers [3322, 4113, 3475, 1796, 2201].

For the electron ground state $X^1\Sigma$ of the HCl^{35} molecule Herzberg, in the second edition of his book [2020] recommends the values of the vibrational constants given by Lindholm in 1939 [2618] and the values of the rotational constants found by Herzberg and Spinks [2047]. Virtually the same values of the molecular constants of HCl^{35}, based on the results of studying the HCl spectrum, obtained by Lindholm in 1943 [2619], are given in the handbook [649].

In the paper by Herzberg and Spinks [2047] the values of the vibrational and rotational constants of HCl^{35} and HCl^{37} were determined on the basis of a structural analysis of the 3-0 band and the data obtained in paper [2865] in studies of the 1-0 and 2-0 bands. The values of the molecular constants of HCl^{35} found in paper [2047] were given in the first edition of Herzberg's monograph [151].

Lindholm reports in his papers [2618, 2619] on investigations of the bands 4-0 and 5-0, carried out with a device of a dispersion of 1.8 Å/mm. On the basis of the data obtained and the results of analyzing

Table 74

Accepted Values of the Molecular Constants of HF, HCl, HBr, HI, Their Deutero -and Tritium -derivatives in the Electron Ground States.

Molecule	ω_e	$\omega_e x_e$	B_e	$\alpha_1 \cdot 10^2$	$D_e \cdot 10^4$	$\beta_1 \cdot 10^6$	r_e
	cm^{-1}						Å
HF	4139,031	90,43924[a]	20,9486	79,7107[b]	21,51	58,7[c]	0,916834
DF	3001,008	47,9689[d]	11,00375	30,362[e]	5,941	11,75[f]	0,917078
TF	2507,87	31,98	7,701	17,18	3,2[g]	—	0,917
HCl^{35}	2989,74	52,05[h]	10,5909	30,19	5,30[g]	—	1,2747
DCl^{35}	2144,77	26,92[g]	5,44826	11,20	1,37	0,6	1,2744
TCl^{35}	1775,86	18,36[g]	3,7470	6,38	0,77	—8,4	1,2746
HBr^{79}	2649,00	45,11	8,4690	23,13	3,905	8	1,414
DBr^{79}	1885,33	22,73[i]	4,2902	8,39	0,964	2,2	1,4144
TBr^{79}	1550,17	15,368[g]	2,9004	4,66	0,441	0,83	1,4144
HI	2309,53	39,73	6,512	17,2	2[g]	—	1,6090
DI	1640,16	20,16	3,2840	6,142	0,53[g]	—	1,6092
TI	1345,50	13,57	2,2065	3,391	0,24[g]	—	1,609

[a] $\omega_e y_e = 1{,}177722$, $\omega_e z_e = 7{,}22748 \cdot 10^{-3}$, $\omega_e t_e = 4{,}32161 \cdot 10^{-3}$, $\omega_e s_e = 1{,}41709 \cdot 10^{-4}$ cm^{-1}.

[b] $\alpha_2 = 1{,}402335 \cdot 10^{-6}$, $\alpha_3 = 1{,}181565 \cdot 10^{-8}$, $\alpha_4 = 1{,}0093 \cdot 10^{-4}$, $\alpha_5 = 4{,}36087 \cdot 10^{-6}$ cm^{-1}.

[c] $\beta_2 = -1{,}4427 \cdot 10^{-6}$, $\beta_3 = -3{,}2655 \cdot 10^{-7}$ cm^{-1}.

[d] $\omega_e y_e = 0{,}585039$, $\omega_e z_e = 2{,}81024 \cdot 10^{-3}$, $\omega_e t_e = 9{,}03504 \cdot 10^{-4}$, $\omega_e s_e = 2{,}02898 \cdot 10^{-6}$ cm^{-1}.

[e] $\alpha_2 = 3{,}8495 \cdot 10^{-6}$, $\alpha_3 = 1{,}7593 \cdot 10^{-6}$, $\alpha_4 = 9{,}1687 \cdot 10^{-6}$, $\alpha_5 = 3{,}1044 \cdot 10^{-7}$ cm^{-1}.

[f] $\beta_2 = -2{,}094 \cdot 10^{-7}$, $\beta_3 = -3{,}436 \cdot 10^{-8}$ cm^{-1}.

[g] Value of D_0 given

[h] $\omega_e y_e = 0{,}056$ cm^{-1}.

[i] $\omega_e y_e = 0{,}036$ cm^{-1}.

[k] $\omega_e y_e = 0{,}012$ cm^{-1}.

[l] $\omega_e y_e = -0{,}0106$ cm^{-1}.

[m] $\omega_e y_e = -0{,}0059$ cm^{-1}.

the bands 1-0, 2-0 [2865] and 3-0 [2047] Lindholm achieved a slight improvement of the values of vibrational constants of HCl^{35}. Later on the structure of the bands 4-0 and 5-0 were again calculated by Naudé and Verleger [3033] who obtained values of the molecular constants of HCl^{35} which were very similar to those found by Lindholm [2619].*

The fundamental band of HCl was studied by Mills, Thompson and Williams [2920] with a device of high dispersion which permitted them to improve the wave number of the beginning of this bands and also the values of the rotational constants.** In the past years the 2-0 band was measured by Haeusler and Barchewitz [1926] and the purely rotation-

al spectrum of HCl was considered in the papers [2696] (in the range 100-700 μ or 100-1.43cm^{-1}) and [1945] (in the range 40-120 μ or 250-83.3 cm^{-1}). But these papers did not achieve an improvement of the molecular constants of HCl.*

In the present Handbook we accepted for the electron ground state of HCl the data of the molecular constants recommended by Herzberg [2020], given in Table 74. These values of the molecular constants of HCl were also accepted in the first edition of the Handbook.

According to data given by Herzberg [2020] and in the Handbook [649], the energies of the stable excited electron states of HCl exceed 70,000 cm^{-1}. These states are not considered in the present Handbook. Jacques and Barrow [2201] investigated the electron spectrum of HCl in the range 1980-2375 Å and photographed the bands connected with transitions to high vibrational levels of the electron ground state (v" = 10-16). They showed that the wave numbers of the edges of these bands are well described by the constants found as a result of analyzing the vibration-rotation infrared spectrum of HCl.

DCl. The main band in the infrared spectrum of DCl was obtained for the first time by Hardy, Barker and Dennison [1956] who used a device with low dispersion. Later on it was studied with a high-dispersion device by Pickworth and Thompson [3239] who carried out a detailed analysis of the rotational structure of this band.**

The first and the second harmonics of DCl were obtained by Van Horne and Hause [4057] with the help of an instrument of high dispersion. On the basis of the results of analyzing the rotational structure of these bands in paper [4057] the rotational constants were determined; they are in good agreement with the values found by Pickworth and Thompson. From the beginnings of the bands 1-0, 2-0, 3-0, Van Horne and Hause calculated the vibrational constants of DCl^{35} and DCl^{37}.

The purely rotational spectrum of DCl in the infrared range was studied by Hansler and Oetjen [1945] and that in the microwave range by Cowan and Gordy [1206, 1207, 1204a]. In paper [1204a] the frequencies of purely rotational transitions of DCl were measured in the range 40-140 μ (250-71.4 cm^{-1}) corresponding to $\underline{I}$ = 6-20; the values obtained for the rotational constants agree with those found by Pickworth and Thompson [3239]. In the microwave range the frequency of the rotational transition $\underline{I} = 0 \rightarrow 1$ and the value of the constant B_0 were determined with high accuracy.

The values of the molecular constants of DCl accepted in the present Handbook are given in Table 74. The values of the vibrational constants were taken from paper [4057], those of the rotational constants from papers [1206, 1207, 3239].* In Herzberg's monograph [2020] and in the handbook [649] values were given for the molecular constants of DCl that were calculated in paper [1956] from the isotope ratios (1.43) on the basis of obsolete values of the molecular constants of HCl.

TCl. The TCl spectrum was studied in the infrared range (1600-1850 cm^{-1}) by Jones and Robinson [2303] and in the microwave range (about 7.35 cm^{-1}) by Barrus and coworkers [1034]. Jones and Robinson [2303] analyzed the rotational structure of the bands 1-0 of the molecules TCl^{35} and TCl^{37} and determined the wave numbers of the beginnings of the bands of both molecules and the rotational constants B_e, α_1, D_e and β_1. In paper [2303] the values of the vibrational constants of the TCl^{35} and TCl^{37} molecules were calculated on the basis of the wave numbers of the beginnings of the 1-0 bands and calculations according to Eqs. (1.43), using the vibrational constants of HCl and DCl. In the microwave spectrum [1034] the frequency of the rotational transition $\underline{I} = 1 \rightarrow 0$ of the molecules TCl^{35} and TCl^{37} was measured and the values of the rotational constant B_0 were determined which were in good agree-

ment with the values of this quantity obtained in investigating the infrared spectrum in paper [2303].

The values of the molecular constants of TCl in the electron ground state, obtained by Jones and Robinson [2303] were accepted in the present Handbook and are given in Table 74.

HBr. The infrared spectrum of hydrogen bromide was studied in the papers by Plyler and Barker [3276], Naudé and Verleger [3033], and Thompson, Williams and Callomon [3977] with high-disper ion devices. In paper [3276] the rotational structure of the bands 1-0 and 2-0 was analyzed, in paper [3033] the rotational structure of the band 4-0. In Herzberg's monograph [2020] and in the handbook [649], on the basis of results of investigating the HBr infrared spectrum, published until 1950, the values of the vibrational constants are accepted that were determined in the paper by Plyler and Barker and the values of the rotational constants found in paper [3033].

Later on Thompson, Williams and Callomon [3977] studied the rotational structure of the 1-0 band of the HBr^{79} and HBr^{81} molecules by means of a spectrometer of high resolving power. On the basis of an analysis of the structure of these bands the authors of paper [3977] achieved an improvement on the values of the wave numbers of the beginnings of the bands and the values of the rotational constants of HBr. The values of the rotational constants of HBr^{79} and HBr^{81} were calculated by Thompson and coworkers on the basis of the obtained wave numbers of the beginnings of the 1-0 bands and the wave numbers of the bands 2-0 and 4-0 obtained in papers [3276, 3033].

The values of the molecular constants of HBr in the electron ground state found by Thompson, Williams and Callomon [3977] are accepted in the present Handbook and given in Table 74.*

The frequencies of the transitions $\underline{I}$ = 5-14 were measured in the

infrared rotation spectrum of HBr (40-120 μ or 250-83.3 cm^{-1}) by Hansler and Oetjen [1945]; but in this paper the rotational constants of HBr were not calculated.

The electron spectrum of HBr was investigated in the papers [3322, 1796, 679, 3476]. As the result of these investigations it was established that HBr has two stable excited electron states whose energies amount to 68,409 and 71,867 cm^{-1}.

DBr. The infrared absorption spectrum of DBr was investigated by Keller and Nielsen [2348] with an apparatus of high dispersion in the range 1700-5400 cm^{-1} which contains the fundamental frequency and the two first harmonics of the molecules DBr^{79} and DBr^{81}. Keller and Nielsen analyzed the rotational structure of these bands and determined the rotational and vibrational constants* of the molecules DBr^{79} and DBr^{81}.

The pure rotation spectrum of DBr in the infrared range from 220 to 60 cm^{-1} (45-170 μ) was studied by Palik [3166] and in the microwave range (about 1 mm) by Gordy and Burrus [1824], Cowan and Gordy [1207] and Cowan [1204a]. Palik measured the frequencies of 15 transitions, corresponding to $\underline{I}$ = 7-21 and determined the values of the constants $\underline{B}_0$ = 4.2467 cm^{-1} and $\underline{D}_0 = 8.8 \cdot 10^{-5}$ cm^{-1}. In the papers [1824, 1207, 1204a] the frequency of the rotational transition 1-0 was measured and the values of the rotational constants $\underline{B}_0$ of the molecules DBr^{79} and DBr^{81} were determined with a higher accuracy than in papers [2348, 3166].

In the present Handbook the values of the molecular constants of DBr are accepted that were obtained in paper [2348], taking the value of B_0 into account which was found in studying the microwave spectrum in papers [1824, 1207, 1204a]. The accepted values of the molecular constants are given in Table 74.

TBr. In the TBr spectrum single band was studied which lies in the infrared range and the purely rotational transition $\underline{I} = 1 \rightarrow 0$ [3486, 1034] in the microwave range. The rotational structure of the 1-0 band was studied by Jones and Robinson for a mixture of TBr^{79} and TBr^{81} molecules [2303] who, on the basis of the results of this analysis, determined the values of the following constants (in cm^{-1}): $\nu_0(1-0) = 2519.26$, $B_e = 2.8993$, $\alpha_1 = 0.0459$, $D_e = 4.5 \cdot 10^{-5}$, $\beta_1 = -1.9 \cdot 10^{-6}$. The values obtained for the molecular constants are in good agreement with the constants calculated for TBr^{79} and TBr^{81} with the help of Eqs. (1.43) on the basis of the molecular constants of HBr^{79}, HBr^{81} and DBr^{79}, DBr^{81}.

The results of measuring the frequency of the rotational transition $\underline{I} = 1 \rightarrow 0$ in the microwave range [3486, 1034] permitted a determination of the values of the constants B_0 of the molecules TBr^{79} and TBr^{81} which were found to be equal to 2.877060 and 2.87446 cm^{-1}.

In the present Handbook we accepted values of the vibrational and rotational constants (with the exception of B_0) of TBr^{79} in the electron ground state that were calculated by Jones and Robinson [2303] by means of Eqs. (1.43) on the basis of the molecular constants of DBr^{79} and DBr^{81}. For the rotational constant $\underline{B}_0$ a value was used which was obtained in paper [1034] in an investigation of the TBr^{79} microwave spectrum. The accepted values of the molecular constants of TBr^{79} and given in Table 74.

HI. The results of studies of the HI spectra, published until 1950, were considered in Herzberg's monograph [2020] and in the handbook [649] where values of the constants of the HI molecule in the electron ground state are recommended which were found by Naudé and Verleger [3033]. In the following years the HI infrared spectrum was studied and reported in papers [879, 3166] and its microwave spectrum in

papers [1205, 1204a].

Naudé and Verleger [3033] studied the rotational structure of the 4-0 band of HI. On the basis of results of this investigation in [3033] the beginnings of the 4-0 band was determined and the following rotational constants were obtained (in cm^{-1}): $B_e = 6.551$ and $\alpha_1 = 0.183$, $D_e = 2.13 \cdot 10^{-4}$ and $\beta_1 = 3 \cdot 10^{-6}$.

Tje vibrational constants of HI were calculated by Naudé and Verleger and the basis of the wave numbers of the beginnings of the bands 1-0 and 2-0, found by A. Nielsen and G. Nielsen [3075] and the value of ν_0 (4-0), found in paper [3033]. The molecular constants of HI, accepted in the present Handbook, are compiled in Table 74. The values of the vibrational constants were chosen according to Naudé and Verleger. The rotational constants of HI were taken according to data of Boyd and Thompson [879] who studied again the rotational structure of the 1-0 band with a spectrometer of high resolution.

The rotation spectrum of HI was studied in the infrared range from 220 to 60 cm^{-1} (45-170 μ) by Palik [3166] and in the microwave range by Cowan and Gordy [1205] and Cowan [1204a]. Palik measured the frequency of 14 rotational transitions of HI with $\underline{I} = 5$-18 and calculated the values of the constants: $\underline{B}_0 = 6.4275$ cm^{-1} and $\underline{D}_0 = 2.05 \cdot 10^{-4}$ cm^{-1}. In papers [1205, 1204a] a more accurate value was obtained for the constant $\underline{B}_0 = 6.426387$ cm^{-1} on the basis of measuring the frequency of the rotational transition $\underline{I} = 1 \rightarrow 0$ in the microwave spectrum.*

The electron spectrum of HI was studied in the papers [3322, 3476]. In these investigations transitions were observed which are connected with two stable excited electron states of the HI molecule, whose energies are equal to 57,905 and 63,475 cm^{-1}.

DI. In the infrared spectrum of DI two bands are observed: the fundamental frequency and the first harmonic; they were studied by

Jones [2299]. On the basis of an analysis of the rotational structure of these bands, Jones determined the values of the vibrational and rotational constants. Virtually identical values of the constants $\underline{B}_0$ and $\underline{D}_0$ were found by Palik [3166] as the result of studying the pure rotation spectrum of DI in the infrared range from 222 to 60-cm^{-1} (45-170 μ). A somewhat higher value of the rotational constant $\underline{B}_0$ = 3.25548 cm^{-1} was found in investigations of the rotational transition J = 1→0 in the microwave spectrum of DI [1031, 1207, 1204a].

The values of the molecular constants of DI (in the electron ground state) accepted in the present Handbook, are given in Table 74. The values of the constants ω_e, $\omega_e x_e$, α_1 and $\underline{D}_0$ contained in Table 74 were determined by Jones [2299] on the basis of results of analyzing the rotational structure of the bands 1-0 and 2-0; the value of the constant $\underline{B}_e$ was calculated from the constant $\underline{B}_0$, obtained in studies of the microwave spectrum of DI [1031, 1207, 1204a] and the constant α_1 obtained by Jones.

TI. The TI spectrum was only studied in the microwave range by Rosenblum and Nethercot [3486] who determined the frequency of the rotational transition J = 1-0 with high accuracy.

The values of the molecular constants of TI given in Table 74 were calculated with the help of Eqs. (1.43) on the basis of the values of the molecular constants of DI, given in this table.

The value of the constant $\underline{B}_0$ = 2.193257 cm^{-1}, calculated according to the data of Rosenblum and Nethercot [3486], is in good agreement with the value corresponding to the values of $\underline{B}_e$ and α_1, given in Table 74.

§46. THERMODYNAMIC FUNCTIONS OF GASES

The thermodynamic functions of gaseous compounds of hydrogen and its isotopes with halogens were calculated in the temperature interval

293.15-6000°K without taking the intermolecular interaction into account and are given in the Tables 44-46, 53-55, 62-64 and 71-73 of Volume II of the Handbook. The calculations were carried out by means of the Gordon-Barnes method on the basis of the molecular constants compiled in Table 74.* The thermodynamic functions were calculated for the natural isotope mixtures of chlorine and bromine with mean values of the molecular constants. The excited electron states of the gas molecules were not taken into account in the calculations since at temperatures below 6000°K the contribution of the corresponding components is infinitesimal.

The errors of the calculated thermodynamic functions of gaseous hydrogen halides and their deuterium and tritium derivatives are at low temperatures (below 2000°K) caused chiefly by the application of inaccurate values of the physical constants, while at high temperatures (above 2000°K) they are due to inaccuracies of the energies of high vibrational and rotational levels when they are calculated from constants, describing the experimental values of low levels, and to the fact that the necessity of limiting the summation over J was not taken into account in the calculations. The errors of the values of Φ_T^* of the compounds considered are at 298.15°K not higher than 0.01 cal/mole·deg, while at 3000 and 6000°K they amount to 0.02 and 0.05 cal/mole·deg, respectively.

Owing to the absence of data on the constants of the intermolecular potential of the compounds of hydrogen and its isotopes with halogens, the present Handbook does not contain any data on the virial coefficients of the corresponding gases.

HF. The thermodynamic functions of gaseous hydrogen fluoride given in Table 44 (II) were calculated for the first edition of the Handbook according to the Gordon-Barnes method on the basis of the

molecular constants of HF recommended by Herzberg [2020] and given in Table 73. The values of the constants C_Φ, C_S, θ, x and the coefficients of Eqs. (2.137), (2.138), calculated from the accepted molecular constants of HF, are given in Table 75.

TABLE 75

Values of the Constants Used in Calculating the Thermodynaimic Functions of Compounds of Hydrogen and Its Isotopes With Fluorine, Chlorine, Bromine and Iodine.

1 Вещество	θ	$x \cdot 10^2$	$\beta_1 \cdot 10^3$	$\beta_2 \cdot 10^4$	$\frac{q_0}{T}$	$\frac{q_1}{T} \cdot 10^4$	C_Φ	C_S
	град 2	—	—	—	3	*град*$^{-1}$	4 *кал/моль·град*	
HF	5953,26	21,764	3,737	15,80	0,033822	7,24	—5,0809	1,8741
DF	4312,98	15,246	2,698	7,94	0,06401	7,66	—3,6673	3,2877
TF	3807,57	12,752	2,254	5,46	0,091289	7,67	—2,8231	4,1319
HCl	4300,74	17,410	2,884	9,12	0,066612	6,75	—1,9453	5,0097
DCl	3084,82	12,565	2,073	4,59	0,12899	6,75	—0,5521	6,4034
TCl	2553,77	10,333	1,720	3,12	0,18778	7,0	0,2729	7,2234
HBr	3811,07	17,028	2,765	8,35	0,083215	7,86	0,8720	7,8275
DBr	2712,18	12,055	1,973	4,14	0,16365	7,33	2,2529	9,2084
TBr	2229,87	9,911	1,620	2,76	0,24168	7,33	3,0640	10,0195
HI	3322,26	17,203	2,672	7,80	0,10818	6,73	2,7594	9,7144
DI	2359,92	12,292	1,886	3,78	0,21363	6,96	4,1338	11,0893
TI	1935,89	10,086	1,548	2,51	0,31743	6,96	4,9439	11,8994

1) Substance; 2) degree; 3) deg^{-1}; 4) cal/mole·deg.

The values of the thermodynamic functions of HF, calculated from more accurate values of the molecular constants of HF (see Table 74) deviate only insignificantly from those given in the Handbook. Thus the difference between the value of Φ^*_{6000}, given in Table 44 (II) and that calculated from the molecular constant of HF from Table 74, amounts to 0.005 cal/mole·deg. In paper [110] the thermodynamic functions of HF were calculated by means of different methods on the basis of the same values of the molecular constants. These calculations showed that with hydrogen fluoride up to temperatures not higher than 6000°K the Gordon-Barnes method yields virtually the same results as the method of direct summation over the levels of vibrational and rotational energies.

The thermodynamic functions of gaseous HF were previously calculat-

ed by Murphy and Vance [3010] (up to 2000°K) according to the Gordon-Barnes method, by Huff, Gordon and Morrell [2142] (up to 6000°K) by the method of direct summation, by Cole, Farber and Elverum [1149] and Potter [3313] (up to 5000°K) according to the method by Mayer and Göppert-Mayer. The differences between the values of the thermodynamic functions of HF, given in papers [3010, 1149] (up to 3000°K) and in Table 44 (II) amounts to about 0.02 cal/mole·deg and is due to the fact that different values were taken for the molecular and physical constants. The results of calculating the thermodynamic functions of HF in the papers [2142] (up to 5000°K) and [3313] (up to 2000°K) virtually coincide with the values of the corresponding quantities of Table 44 (II).* The differences between the values of the thermodynamic functions of HF, given in the papers [3313, 1149] and in Table 44 (II) are at high temperatures considerable; they reach for S°_{5000} about 0.07 cal/mole·deg. This deviation is explained by the approximate character of the method by Mayer and Göppert-Mayer whose effect is greatest at high temperatures.

The results of the calculations of the thermodynamic functions of HF, obtained by Murphy and Vance [3010] were reproduced in the papers by Brewer [1093] and Kelley [2364, 2363]. In Zeise's book [4384] values are given for the thermodynamic functions of HF that were calculated by Cole et al. [1149].

DF, TF. The thermodynamic functions of gaseous fluorodeuterium and fluorotritium, given in Tables 45 (II) and 46 (II), were calculated according to the Gordon-Barnes method for the first edition of the present Handbook. The thermodynamic functions of fluordeuterium was calculated according to the molecular constants of DF, recommended by Herzberg [2020] and given on p. 563, the thermodynamic functions of fluorotritium accordirg to the molecular constants of TF, given in Ta-

ble 74. Table 75 contains the constants C_Φ, C_S, θ and $\underline{x}$ as well as the values of the coefficients in Eqs. (2.137), (2.138), calculated with the accepted constants of DF and TF. It must be noted that the thermodynamic functions of DF, calculated according to the molecular constants given in Table 74 are virtually the same as those given in Table 45 (II). The difference between the values of Φ^*_{6000} amounts to 0.004 cal/mole·deg.

The thermodynamic functions of gaseous fluorodeuterium had been calculated previously by Potter [3313] (up to 5000°K) according to the method by Mayer and Göppert-Mayer. Up to 2000°K the values of the thermodynamic functions of DF, given in paper [3313] and in Table 45 (II) do not differ by more than 0.01 cal/mole·deg. At higher temperatures these differences increase, reaching 0.03 and 0.08 cal/mole·deg with the values of Φ^*_{5000} and S°_{5000}, owing to the inaccuracy of the method by Mayer and Göppert-Mayer.

The thermodynamic functions of gaseous fluorotritium was calculated for the first time when the first edition of the present Handbook was prepared. Other calculations of the thermodynamic functions of TF and unknown.

HCl. The thermodynamic functions of gaseous hydrogen chloride given in Table 53 (II) were calculated from Eqs. (2.161) and (2.162). The values of $\ln \Sigma$ and $T\frac{\partial}{\partial T}\ln\Sigma$ in these equations were calculated by means of the method by Gordon and Barnes (Eqs. (2.137) and (2.138)). The calculation was made with mean values of the molecular constants, obtained on the basis of values of the molecular constants of HCl^{35}, given in Table 74. The values of the constants C_Φ, C_S, θ, x and the coefficients of Eqs. (2.137), (2.138), calculated from the averaged molecular constants, are compiled in Table 75. It must be noted that a calculation of the thermodynamic functions of HCl, carried out with the molecular

constants obtained in paper [3033] (see note to p. 565) yields virtually the same values of the thermodynamic functions of HCl as were given in Table 53 (II).*

The thermodynamic functions of gaseous hydrogen chloride were previously calculated by the method of direct summation by Giauque and Overstreet [1718] (up to 3000°K), Gordon and Barnes [1812, 1813] (up to 1000°K) and Urey and Rittenberg [4041] (up to 700°K). Potter [3314] used the method by Mayer and Göppert-Mayer to calculate the thermodynamic functions of HCl (up to 5000°K) and Linnett [2621] worked with the approximation of the harmonic oscillator and rigid rotator (up to 573°K). The thermodynamic functions of HCl, calculated up to 6000°K are also given in the abstract by Huff, Gordon and Morrell [2142].**

The differences between the values of the thermodynamic functions of HCl given in the papers [1718, 1812, 1813, 4041, 2621] and those of Table 53 (II) amount to 0.02 to 0.05 cal/mole·deg (up to 3000°K) and are mainly due to differences of the used values of physical constants. Sherman and Giauque [3706] calculated the corrections to the values of Φ_T^* given in paper [1718] which take into account the new values of the physical constants. With these corrections the thermodynamic functions of HCl, calculated by Giauque and Overstreet [1718], deviate from the values of the corresponding quantities in Table 53 (II) within the limits of 0.002 cal/mole·deg. The differences between the values of the thermodynamic functions of HCl, given in paper [3314] and in Table 53 (II) are essential at high temperatures which is explained by the fact that in paper [3314] the approximate method by Mayer and Göppert-Mayer was used.

Giauque and Wiebe [1721] calculated $S^\circ_{298.16}$ (HCl, gas) = 34.45 ± 0.15 cal/mole·deg on the basis of results of calorimetrical measurements; the value they obtained is in good agreement with the value giv-

en in Table 53 (II).

In Brewer's paper [1093] and in Zeise's handbook [4384] the values of the thermodynamic functions of HCl were borrowed from [1718, 1812]. In the handbook of the US NBS [3680] apparently new values of the physical constants were used. In Kelley's abstract [2363] we find an equation for the specific heat of HCl and the values of $H_T^\circ - H_{298.16}^\circ$ and $S_T^\circ - S_T^\circ - S_{298.16}^\circ$ are calculated up to 2000°K, on the basis of results of calculations from [1718, 1812].

DCl, TCl. The thermodynamic functions of gaseous deuterium chloride and tritium chloride given in the Tables 54 (II) and 55 (II) were calculated from Eqs. (2.161) and (2.162). The values of $\ln \Sigma$ and $T\frac{\partial}{\partial T}\ln \Sigma$. were calculated according to the Gordon-Barnes method [Eqs. (2.137) and (2.138)]. The calculations were made with mean values of the molecular constants of DCl^{35}, DCl^{37} and TCl^{35}, TCl^{37}, obtained from the molecular constants of DCl^{35} and TCl^{35}, given in Table 74. Table 75 contains the values of C_Φ, C_S, θ, x and the coefficients of Eqs. (2.137), (2.138) obtained from the averaged constants of the molecules DCl and TCl.

The thermodynamic functions of gaseous DCl^{35} were previously calculated by Urey and Rittenberg [4041] by means of the method of direct summation for $T \leq 700$°K. The values of the thermodynamic functions of tritium chloride were published for the first time.

HBr. The thermodynamic functions of gaseous hydrogen bromide given in Table 62 (II) were calculated from Eqs. (2.161) and (2.162). The values of $\ln \Sigma$ and $T\frac{\partial}{\partial T}\ln \Sigma$ were calculated with the help of the Gordon-Barnes method [Eqs. (2.137), (2.138)]. The calculations were made with mean values of the molecular constants of HBr^{79} and HBr^{81}, obtained with the molecular constants of HBr^{79} given in Table 74. The values of C_Φ, C_S, θ, x, and the coefficients of Eqs. (2.137), (2.138) are cal-

culated from the averaged molecular constants of HBr given in Table 75.

The thermodynamic functions of gaseous hydrogen bromide were previously calculated by Gordon and Barnes [1815] (up to 1600°K) by means of the method they had developed. Differences between the values of the thermodynamic functions of HBr, given in paper [1815], and those of table 62 (II) are equal to about 0.02 cal/mole·deg which is chiefly due to different values used for the physical constants.

The values of the thermodynamic functions of HBr calculated by Gordon and Barnes are used in the handbooks [3680, 4384] and in paper [1093].

Giauque and Wiebe [1722] found the value of $S^\circ_{298.16}$(HBr, gas) = 47.6 ± 0.1 cal/mole·deg on the basis of results of calorimetric measurements; this value is in satisfactory agreement with the values given in Table 62 (II). Kelley [2364] uses the values of $S^\circ_{298.16}$(HBr, gas) obtained in papers [1815, 1722]. In paper [2363] Kelley gives an equation for the specific heat of HBr derived by him on the basis of calculations of Gordon and Barnes [1815]. This equation was used in paper [2363] in order to calculate $H^\circ_T - H^\circ_{298}$ and $S^\circ_T - S^\circ_{298}$ up to 1600°K.

DBr, TBr. The thermodynamic functions of gaseous deuterium chloride given in Tables 63 (II) and 64 (II) were calculated by means of Eqs. (2.161) and (2.162). The values of $\ln \Sigma$ and $T\frac{\partial}{\partial T}\ln \Sigma$ in these equations were calculated with the help of the Gordon-Barnes method, using mean values of the molecular constants of DBr^{79}, DBr^{81} and TBr^{79}, TBr^{81}. The averaged constants of these molecules were calculated from Eqs. (1.43) and the molecular constants of DBr^{79} and TBr^{79} given in Table 74. In Table 75 we find the values of C_Φ, C_S, θ, x and the coefficients of Eqs. (2.137), (2.138), calculated with the averaged constants of DBr and TBr.

The tables of the thermodynamic functions of deuterium bromide and tritium bromide are the first published in literature.

HI. The thermodynamic functions of gaseous hydrogen iodide, given in Table 71 (II) were calculated from Eqs (2.161) and (2.162). The values of $\ln \Sigma$ and $T\frac{\partial}{\partial T}\ln \Sigma$ in these equations were calculated by means of the Gordon-Barnes method on the basis of the molecular constants of HI given in Table 74. The values of C_Φ, C_S, θ, x, and the coefficients of Eqs. (2.137) and (2.138) calculated from the accepted constants of HI, are given in Table 75. It must be noted that the improvement of the constant B_0 of the HI molecule, obtained by Cowan and Gordy [1205] when studying the microwave spectrum (see page 571), does virtually not influence the values of the thermodynamic functions of HI since the corresponding correction amounts to only 0.001 cal/mole·deg. The thermodynamic functions of hydrogen iodide were previously calculated by Murphy [3007] (up to 1500°K) by means of the Gordon-Barnes method and by Urey and Rittenberg [4041] (up to 700°K) by the method of direct summation. The differences between the values of the thermodynamic functions of HI given in papers [3007, 4041] and in Table 71 (II) amount to 0.01-0.05 cal/mole·deg and are due to the application of different values of the molecular and physical constants. The thermodynamic functions of HI, calculated by Murphy [3007] and extrapolated up to 2000°K, are used in Brewer's paper [1093] and in Zeise's handbook [4381].

Giauque and Wiebe [1723] obtained $S^\circ_{298.16}$(HI, gas) = 49.5 ± 0.1 cal/mole·deg on the basis of calorimetric measurements. In Kelley's abstract [2364] use is made of a value of $S^\circ_{298.16}$ of gaseous HI obtained in the papers [3007, 1723]. Kelley [2363], on the basis of results calculated by Murphy [3007], derived an equation for the specific heat of gaseous HI and used it to calculate $H^\circ_T - H^\circ_{298}$ and $S^\circ_T - S^\circ_{298}$ to 2000°K.

DI, TI. The thermodynamic functions of gaseous deuterium iodide and tritium iodide, given in Tables 72 (II) and 73 (II), were calculated from Eqs. (2.161) and (2.162). The values of $\ln \Sigma$ and $T \frac{\partial}{\partial T} \ln \Sigma$ were calculated by means of the Gordon-Barnes method on the basis of the molecular constants of DI and TI, given in Table 74. In Table 75 we find the values of C_Φ, C_S, θ, x and the coefficients of Eqs. (2.137), (2.138) calculated from the accepted constants of these gas molecules.

The calculation of the thermodynamic functions of TI, allowing for the more accurate value of B_0 of the TI molecule found in paper [3486] (see page 572) alters the values of Φ_T^* and S_T° by 0.005 cal/mole·deg, compared with the corresponding values contained in Table 73 (II).

The thermodynamic functions of gaseous deuterium iodide were previously calculated by Blagg and Murphy [835] (up to 1500°K) according to Kassel's method, and also by Urey and Rittenberg [4041] (up to 700°K) by means of the method of direct summation. The difference between the values of the thermodynamic functions of DI given in the papers [835, 4041] and those of Table 72 (II) does not exceed 0.05 cal/mole·deg and is due to the use of different values of the molecular and physical constants. The thermodynamic functions of tritium iodide were calculated for the first time.

§47. THERMOCHEMICAL QUANTITIES

HF (gas). Berthelot and Moissan [797] measured the thermal effect of the reaction of elementary fluorine with a potassium sulfide solution. The value calculated on the basis of these measurements, ΔH_f° (HF, gas) = − 39 kcal/mole, is of mere historical significance.

The heat of combustion of fluorine in hydrogen was measured by Wartenberg and Fitzner [4162] and Ruff and Laass [3557]. The hydrogen fluoride produced in the combustion under the experimental conditions of [4162, 3557] contains a great number of associated molecules so that,

in calculations of ΔHf(HF, gas) as the result of calorimetrical measurements, it is necessary to introduce appropriate corrections. Previously, when these corrections were calculated in [4162, 3557] an error was admitted. Later on it was corrected by Ruff and Menzel [3561] who calculated for ΔHf(HF, gas) a value of −63.8 kcal/mole [4162] and −64.2 kcal/mole [3557]. But even these corrected values may only be used as approximations since the authors of [4162, 3557, 3561] calculating the correction for the association, started from a simplified scheme of the association equilibrium, assuming that in the vapor, besides the monomeric molecules only cyclic molecules $(HF)_6$ may be present. Electron diffraction studies made subsequently showed that the associated molecules appearing in the fluorohydrogen vapor consist of zig-zag-shaped chains of various lengths and that there are no cyclic molecules in the vapor (as to details of this question, see [356]).

In the note of Armstrong and Jessup [567] it was indicated that they determined the heat of combustion of ammonia in fluorine (−181.56 kcal/mole). To this value corresponds the heat of formation of hydrogen fluoride, equal to −64.2 kcal/mole. But the authors of [567] indicate that the agreement between the value of ΔHf (HF) found by them and the values of earlier papers cannot be taken as a proof of the accuracy of the measurements, since in all these papers like errors could have been made in allowing for the association of HF in the vapor (in paper [567] the method of calculating this correction is not described).

Wartenberg and Schütza [4172] measured the heat of combustion of fluorine in hydrogen at a temperature of 100°C, where the association of HF molecules in the vapor is inessential and obtained: $\Delta H°f_{373}$ (HF, gas) = −64.45 ± 0.1 kcal/mole ($\Delta H°f_{298.15}$ = −64.41 kcal/mole). In modern handbooks and individual papers a value of −64.2 kcal/mole is accepted for the heat of formation of hydrogen fluoride at 298.15°K,

which is an average of the values obtained in the papers [4162, 3557, 3561, 4172]. For the error of the heat of formation of HF values of ±0.2 or ±0.5 kcal/mole are suggested in literature. The latter value is more correct.

Johns and Barrow [2258], when studying the electron spectrum of HF, observed bands connected with transitions to high vibrational levels of the ground state ($9 \leq v \leq 19$). A short extrapolation with respect to the vibrational levels of the ground state yielded a value of D_0 (HF) = 135.1 ± 0.3 kcal/mole for the dissociation energy. This value is more accurate than the value calculated on the basis of the heat of formation of HF and the dissociation energy of fluorine. But the value of $\Delta Hf_{298.15}$ (HF, gas) = −64.97 ± 0.6 kcal/mole corresponding to it has a considerable error as it depends on a comparatively inaccurate value of $D_0(F_2)$.

Since the value of the heat of formation of HF is used in the calculation of the heat of formation of most fluorides, it is necessary, in the first place, to base our considerations on the heat of formation instead of on the dissociation energy. Therefore we accepted the following value in the Handbook:

$$\Delta H^\circ_{f_{298.15}}(\text{HF, газ}) = -64{,}2 \pm 0{,}5 \text{ kcal/mole}$$

The results of investigations by Johns and Barrow [2258] also speak in favor of the imperative necessity of improving the data on the heat of formation of HF.*

To the value accepted for the heat of formation corresponds

$$D_0(\text{HF}) = 134{,}322 \pm 0{,}7 \text{ kcal/mole}$$

DF (gas), TF (gas). The values of the dissociation energy

$$D_0(\text{DF}) = 135{,}923 \pm 0{,}7 \text{ kcal/mole}$$

$$D_0(\text{TF}) = 136{,}616 \pm 0{,}7 \text{ kcal/mole}$$

accepted in the Handbook were calculated from Eq. (4.17) with the help

of the accepted value of $D_0(HF)$ and the molecular constants of HF, DF and TF given in Table 74. The following value of the heat of formation of DF and TF corresponds to this value of the dissociation energy:

$$\Delta H^\circ_f(DF, \text{gas}) = -64{,}886 \pm 0{,}9 \text{ kcal/mole}$$

$$\Delta H^\circ_f(TF, \text{gas}) = -65{,}178 \pm 0{,}9 \text{ kcal/mole}$$

HCl (gas). The numerous measurements of the heat of formation of hydrogen chloride were reviewed by Bichowski and Rossini in their handbook [813] and in Roth's survey [3514].

Rossini [3497] measured the heat of combustion of chlorine in hydrogen and obtained the following value of the heat of formation of HCl: $\Delta H^\circ f_{298.15} = -22063 \pm 12$ kcal/mole. Roth [3515, 3514], on the basis of the papers [4163, 3530] recommended −21,830 ± 20 cal/mole as the better value.

Lacher and coworkers [2510] measured the reaction heat of hydrogen plus chlorine and found $\Delta H^\circ f_{298.15}$ (HCl, gas) = −22030 ± 50 cal/mole. This value is in good agreement with the results of measurements by Rossini [3497]. The most accurate measurement of the heat of formation of hydrogen chloride was carried out by Rossini [3497]. The value of

$$\Delta H^\circ f_{298.15}(HCl, \text{gas}) = -22{,}063 \pm 0{,}012 \text{ kcal/mole}$$

he obtained was commonly acknowledged and accepted in the present Handbook. The value of

$$D_0(HCl) = 102{,}204 \pm 0{,}035 \text{ kcal/mole}$$

corresponds to it.

DCl (gas), TCl (gas). The values of the dissociation energies

$$D_0(DCl) = 103{,}396 \pm 0{,}035 \text{ kcal/mole}$$

$$D_0(TCl) = 103{,}919 \pm 0{,}035 \text{ kcal/mole}$$

accepted in the Handbook were calculated from Eq. (4.17) with the help of the accepted value of D_0 (HCl) and the molecular constants of DCl and TCl, given in Table 74. To these values corresponds

$$\Delta H^\circ_f(DCl, \text{gas}) = -22{,}309 \pm 0{,}050 \text{ kcal/mole}$$

$$\Delta H^\circ f_0\,(\mathrm{TCl},\ \text{gas}) = -22{,}431 \pm 0{,}050 \text{ kcal/mole}$$

HBr (gas). Bichowsky and Rossini [813], on the basis of measurements by Thomsen [3981] and Berthelot [791, 777] of the thermal effects of a series of reactions, calculated the value of the heat of formation of hydrogen bromide: $\Delta H^\circ f_{298.15} = -8.66$ kcal/mole.

Roth and Borger [3522, 3523] measured the heat of dissolution of silver in hydrobromic acid and found the much lower value of -3.5 ± 0.3 kcal/mole for ΔHf (HBr, gas). But later it was established by Roth [3515] that this value was incorrect. Roth [3515] measured the heat of reaction of $AgNO_3$ solutions with hydrochloric and hydrobromic acids and obtained a value of -7.59 ± 0.11 kcal/mole for ΔHf(HBr). In the very same paper Roth determined the heat of reaction of chlorine and bromine with a hydrazine chloride solution and calculated ΔHf (HBr, gas) $= -7.90 \pm 0.15$ kcal/mole.

The heat of reaction of hydrogen and bromine in the gaseous state was measured by Lacher, Casali and Park [2507]. A value of

$$\Delta H^\circ f_{298.15}\,(\mathrm{HBr},\ \text{gas}) = -8{,}74 \pm 0{,}13 \text{ kcal/mole}$$

corresponds to the value of $\Delta Hf_{376.15} = -12.473$ kcal/mole he obtained. The former value which was obtained by means of a direct method was accepted in the Handbook. The values based on the results of measurements in [791, 777, 3515] are less accurate since they include a series of additional quantities among them such that are insufficiently verified.

To the value of $\Delta H^\circ f_{298.15}$ accepted the following value corresponds:

$$D_0\,(\mathrm{HBr}) = 86{,}678 \pm 0{,}13 \text{ kcal/mole}$$

DBr (gas), TBr (gas). The values of the dissociation energies

$$D_0\,(\mathrm{DBr}) = 87{,}758 \pm 0{,}13 \text{ kcal/mole}$$

$$D_0\,(\mathrm{TBr}) = 88{,}231 \pm 0{,}13 \text{ kcal/mole}$$

accepted in the Handbook were calculated from Eq. (4.17) by means of

the above value of D_0 (HBr) and the molecular constants given in Table 74. The following values correspond to them:

$$\Delta H°f_0(DBr, \text{gas}) = -7{,}043 \pm 0{,}13 \text{ kcal/mole}$$
$$\Delta H°f_0(TBr, \text{gas}) = -7{,}115 \pm 0{,}13 \text{ kcal/mole}$$

HI (gas). Bichowsky and Rossini [813], on the basis of Thomsen's measurements [3981] of thermal effects of a series of reactions, calculated $\Delta H°f_{291}$(HI, gas) = 5.91 kcal/mole. Later on Thomsen's data were recalculated once again by Roth [3515] who calculated the values of 6.02, 5.13 and 5.85 kcal/mole for the heat of formation of HI (gas).

Günther and Vekua [1892] determined the thermal effect of the reaction

$$\tfrac{1}{2}Cl_2 \text{ (gas)} + HI \text{ (gas)} \rightarrow HCl \text{ (gas)} + \tfrac{1}{2}I_2 \text{ (solid)}. \qquad (12.1)$$

A value of $\Delta H°f_{298.15}$ (HI, gas) = 6.2 kcal/kcal/mole corresponds to the value of −28.26 kcal/mole (reduced to p = const) found by these authors.

Stegmüller [3843] measured the emf of an element in which the reaction

$$\tfrac{1}{2}H_2 \text{ (gas)} + \tfrac{1}{2}I_2 \text{ (gas)} \rightarrow HI \text{ (gas)}, \qquad (12.2)$$

took place and obtained a value of −1.7 kcal/mole for the thermal effect of this reaction, to which a value of $\Delta H°f_{298.15}$ (HI, gas) = 5.73 kcal/mole corresponds.

The equilibrium constants of the reaction (12.2) were determined in the papers [4042, 847, 947, 3947, 3007, 814]. On the basis of the values of the thermodynamic properties of iodine and its compounds accepted in the Handbook (cf. also [100]) and the results of measuring the equilibrium constants, a value of

$$\Delta H°f_{298.15}(HI, \text{gas}) = 6{,}286 \pm 0{,}1 \text{ kcal/mole}$$

was calculated which is in good agreement with the results of measurements by Gunther and Vekua [1892]. This value was accepted in the Hand-

b . To it corresponds

$$D_0(HI) = 70{,}407 \pm 0{,}1 \text{ kcal/mole}$$

DI (gas), TI (gas). The values of the dissociation energies

$$D_0(DI) = 71{,}352 \pm 0{,}1 \text{ kcal/mole}$$
$$D_0(TI) = 71{,}768 \pm 0{,}1 \text{ kcal/mole}$$

accepted in the Handbook, were calculated from Eq. (4.17) with the helps of the accepted value of $D_0(HI)$ and the molecular constants of HI, DI and TI, given in Table 74. The values of

$$\Delta H^\circ f_0(DI, \text{ газ}) = 6{,}772 \pm 0{,}1 \text{ kcal/mole}$$
$$\Delta H^\circ f_0(TI, \text{ газ}) = 6{,}757 \pm 0{,}1 \text{ kcal/mole}$$

correspond to these values of the dissociation energies of DI and TI, respectively.

TABLE 76

Accepted Values (in cal/mole) of the Thermochemical Quantities of the Halogen Compounds of Hydrogen and Its Isotopes

1 Вещество	D_0	ΔHf_0	$\Delta H^\circ f_{293.15}$	$\Delta H^\circ f_{298.15}$	$H^\circ_{293.15} - H^\circ_0$	$H^\circ_{298.15} - H^\circ_0$
HF	134 322	—64 190	—64 199	—64 200	2020	2055
DF	135 923	—64 886	—64 899	—64 905	2030	2065
TF	136 610	—65 178	—65 193	—65 195	2033	2068
HCl	107 204	—22 022	—22 061	—22 063	2030	2065
DCl	108 396	—22 309	—22 357	—22 365	2035	2070
TCl	108 919	—22 431	—22 481	—22 485	2038	2072
HBr	86 678	—6 868	—8 712	—8 740	2032	2067
DBr	87 758	—7 043	—8 897	—8 929	2037	2072
TBr	88 231	—7 115	—8 971	—8 999	2040	2075
HI	70 407	6 812	6 302	6 286	2034	2069
DI	71 352	6 772	6 252	6 232	2039	2074
TI	71 768	6 757	6 237	6 222	2044	2079

1) Substance.

Chapter 13

SULFUR AND ITS COMPOUNDS

(S, S_2 SO, SO_2, SO_3, S_2O, SH, H_2S, SF, SF_2, SF_4, SF_6, SOF_2, SO_2F_2)

Under normal conditions elementary sulfur occurs in the form of a solid crystalline substance, the rhombic sulfur. At 368.5°K rhombic sulfur transforms into another crystalline modification of sulfur which is monoclinic. X-ray diffraction studies of the crystalline structure of rhombic sulfur [4150] showed that it consists of S_8 ring molecules. Under special conditions also other allotropic modifications of crystalline sulfur may be obtained.

Thus, Rice [3428, 3427], when suddenly cooling sulfur vapor down to the temperature of liquid nitrogen, obtained purple and green sulfur.* David and Hamann [1270] found that in a shock wave, at a pressure of 230,000 atm, rhombic sulfur transforms into a new allotropic modification, possessing a high electrical conductivity, which is therefore denoted as metallic sulfur. The allotropy of sulfur was studied in detail by Erämetsä [1487–1489].

Monoclinic sulfur melts at 388.4°K. Up to 432°K sulfur is a yellow mobile liquid, consisting of S_8 ring molecules. Above 432°K sulfur grows brown, its viscosity increases sharply, which is explained by the rupture of the S_8 ring molecules and the formation of chain molecules of the same composition (cf. [1675, 2481, 3521]). From about 460°K on the viscosity of sulfur decreases gradually as the temperature increases and at about 670°K the liquid, maintaining its brown color, again becomes mobile up to the boiling point (717.8°K). The decrease in vis-

cosity of liquid sulfur beginning at 460°K is explained by a rupture of the S_8 chain molecules and the appearance of chain molecules of fewer sulfur atoms. When liquid sulfur is rapidly cooled down, various modifications of amorphous sulfur appear [3621]. They are thermodynamically unstable and under normal conditions they transform to the rhombic modification of crystalline sulfur.

The most careful calorimetrical investigations of the thermodynamic properties of elementary sulfur in condensed states were carried out by Eastman and McGavock [1441] (from 13 to 376°K) and West [4213] (from 298 to 678°K). The specific heat of liquid sulfur (up to 693°K) was measured by the authors of [908, 1544, 3110]. It must be noted that data on the thermodynamic properties of rhombic sulfur may be found in West's review [4217] and in the articles of Bradley [887], Gee [1675], Evans and Wagman [1516] and on monoclinic sulfur in Bradley's paper [887].

The composition of sulfur vapor at not too high temperatures is very complex. It has been established by experiment that it contains S_8, S_6, S_4 ring molecules, S_2 molecules and S atoms. The results of measurements of sulfur vapor densities, obtained by Neumann [3057], showed that sulfur vapor over condensed phases, and also in absence of condensed phases up to 1000°K, consists mainly of S_8 molecules. Studies of the vapor density of sulfur at higher temperatures [3318, 2438, 909] results in the conclusion that these vapors also contain S_6, S_4 and S_2 molecules.* At a total vapor pressure of 1 atm and a temperature of 1300°K the sulfur vapor consists mainly of S_2 molecules, at 2500°K and above it consists of S atoms.

The molecular and thermodynamic properties of octatomic sulfur in gaseous state were considered by Guthrie, Scott and Waddington [1902] and Luft [2678]. In Luft's paper [2678] the molecular and thermodynamic

properties of S_4 and S_6 were considered and the values of the molecular and thermodynamic constants were estimated for the nonobserved ring molecules S_3, S_5 and S_7 and the biradicals S_3, S_4, S_6 and S_8 (open chains). Luft's calculations of the composition of sulfur vapor, allowing for sulfur molecules of different atomicity, showed that besides the molecules S_2, S_4, S_6, S_8, we must expect that in sulfur vapor a noticeable quantity of S_3, S_5 and S_7 ring molecules may be present. According to these calculations the content of biradicals in sulfur vapor is insignificant. Luft could also show that a further polymerization of sulfur with the formation of molecules of a more complex structure than S_8 is energetically disadvantageous and need not take place.

In the present Hand book we consider only monatomic and diatomic sulfur (S and S_2), the fundamental components of vapor at high temperatures.

We know seven oxides of sulfur: SO, S_2O, S_2O_3, SO_2, SO_3, S_2O_7 and SO_4. Under normal conditions the main sulfur oxides are sulfur dioxide and trioxide, SO_2 and SO_3, at high temperatures it is dioxide and monoxide, SO_2 and SO. Under certain conditions the semioxide S_2O may be formed. In the present Handbook, among all sulfur oxides, we consider only SO, SO_2, SO_3 and S_2O. The other sulfur oxides S_2O_3, S_2O_7, SO_4 are rather unstable and rarely investigated compounds which form under special conditions and are unknown in the gaseious state.

In the papers [3017, 3103] it was suggested to assume the existence of the isomeric form SOO, besides the usual form of the SO_2 molecule, which, in its type, resembles the ozone molecule. On the basis of this assumption it was possible to explain the appearance of a series of bands in the explosion spectra of the mixture $CS_2 + O_2$ [3017] and in the spectrum of pulsed photolysis of SO_2 and SO_3 [3103]. In this connection it were interesting to make further experimental studies in or-

der to verify or refute this assumption.

In the present Handbook we consider only the simplest sulfur hydrides, hydrogen sulfide H_2S and hydrosulfite HS. Higher hydrides of sulfur, such as H_2S_2, H_2S_3, H_2S_2, are also known. These compounds are, however, unstable and decay easily at high temperatures.

Among the simplest compounds of sulfur with oxygen and hydrogen it is sulfuric acid, H_2SO_4, which has been studied most thoroughly. In the gaseous state, however, this compound is rather unstable and decays easily into SO_3 and H_2O. The equilibrium constant of the corresponding reaction was measured by Bodenstein and Katayama [852] in the temperature interval of from 598 to 756°K.

The other acids of sulfur, in the gaseous state, are still less stable than H_2SO_4 and were not investigated.

The existence of four compounds of sulfur and fluorine was established by experiment: S_2F_2, SF_4, SF_6 and S_2F_{10}. The most stable of them is sulfur hexadluoride, SF_6. In the present Handbook we deal with SF_4, SF_6, SF and SF_2. The latter compounds must, obviously, be formed in the dissociation of SF_4 and SF_6.

Besides the numerous compounds mentioned above, in the Handbook we also consider two oxyfluorides of sulfur, namely SOF_2 and SO_2F_2. Other sulfur-fluorine compounds are not considered in the Handbook, just as the compounds of sulfur with chlorine, bromine and iodine.

Compounds of sulfur with other elements are considered in Chapters 14 (NS), 15 (PS) and 21 (CS, COS, CS_2).

In all cases where we do not assert the contrary, when discussing the molecular constants of sulfur and its compounds, we consider the isotopic modification of molecules, containing the most-spread sulfur isotope S^{32}.

§48. THE MOLECULAR CONSTANTS

S. The sulfur atom in its ground state $^3P_2$ has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^4$. In Table 77 we find the energy levels of the sulfur atom [2941] which correspond to the given electron configuration.

The excitation energies of states of the sulfur atom, corresponding to other electron configurations, exceed, according to [2941], 50,000 cm^{-1}. In the present Handbook we do not consider these electron states of the sulfur atom.

TABLE 77

Energy levels of the sulfur atom

1 Номер уровня	2 Состояние: 3 электронная конфигурация	2 Состояние: 4 терм	Статистический вес 5	Энергия, $см^{-1}$ 6
0	$1s^2 2s^2 2p^6 3s^2 3p^4$	$^3P_2$	5	0,0
1	$1s^2 2s^2 2p^6 3s^2 3p^4$	$^3P_1$	3	396,8
2	$1s^2 2s^2 2p^6 3s^2 3p^4$	$^3P_0$	1	573,6
3	$1s^2 2s^2 2p^6 3s^2 3p^4$	$^1D_2$	5	9239,0
4	$1s^2 2s^2 2p^6 3s^2 3p^4$	$^1S_0$	1	22181,4

1) Number of level; 2) state; 3) electron configuration; 4) term; 5) statistical weight; 6) energy, cm^{-1}.

S$_2$. The spectrum of the S_2 molecule was studied by many scientists in both the visible and the ultraviolet ranges. The band system $C^3\Sigma_u^- \rightleftarrows X^3\Sigma_g^-$, which lies in the range 14,000-41,000 cm^{-1} (7110-2400 Å) has been studied most completely. In literature we also find indications as to the existence of other band systems of S_2 [1318a, 3484a, 3484b, 2037, 2730, 2731, 3936a]. But among these it was only two band systems lying in the range of vacuum ultraviolet [2730, 2731] that were analyzed and attributed to transitions of the type $^3\Pi_u \rightarrow X^3\Sigma_g^-$.

The vibrational structure of the system $C^3\Sigma_u^- - X^3\Sigma_g^-$ was analyzed for the first time by Rosen [3480] according to the band edges in the

fluores ence spectra of sulfur vapor. The results of this analysis were improved by Fowler and Vaidya [1586] who, in the S_2 emission spectrum, measured the positions of the band edges corresponding to ($v' \leq 18$ and $v'' \leq 30$. Owing to the weak dispersion of the spectrographs used in [3480, 1586], the rotational structure of the S_2 bands was not studied. It was studied later on by Naudé and Christy [1105, 3024-3027, 3034], Ol'ssonom [3136-3140] and Ikenoue [2164], working with specrographs of high dispersion. In early investigations [3027, 1105] Naudé and Chris , otained incorrect values of B_e'' and B_e' ($B_e'' = 0.409$, $B_e' = 0.319$ cm^{-1}), a fact that was found out by Olsson [3136-3138]. The values of the constants B_e, α_1, D_e of S_2 of the S_2 molecule in the states $X^3\Sigma_g^-$ and $C^3\Sigma_u^-$ (see Table 78) were determined by Naudé [3024, 3026] on the basis of an analysis of the rotational structure of a great number of bands ($v' \leq 7$, $v'' = 2, 3, 4, 7, 8, 14...27$) which were studied in the papers of Naudé and Christy [1105, 3025-3027], Olsson [3136-3140] and Wilson (not Published). The very values of the rotational constants of S_2 in the states in the states $X^3\Sigma_g^-$ and $C^3\Sigma_u^-$ are recommended in Herzberg's book [2020] and in the handbook [649]. The equilibrium values of the rotational constants of S_2 in the states $X^3\Sigma_g^-$ and $C^3\Sigma_u^-$ were also calculated in [3140, 2164] but the values obtained are less accurate than those of paper [3024] because the data were applied to a smaller number of bands.

The constants of multiplet splitting of the $X^3\Sigma_g^-$ and $C^3\Sigma_u^-$ states of S_2 were determined by Olsson [3140] and Naudé and Verleger [3034] who analyzed the multiplet structure of the bands of the system $C^3\Sigma_u^- - X^3\Sigma_g^-$, on the basis of Kramers' relations (cf. Eqs. (1.24a)). The most complete studies of the multiplet splitting of the $^3\Sigma$ state of S_2 were carried out by Naudé and Verleger [3034]. The values of the constants of multiplet splitting obtained by these authors are given in Table 78. The multiplet structure of the S_2 band in the system $C^3\Sigma_u^- - X^3\Sigma_g^-$ wer not

analyzed on the basis of the more accurate equations (1.24) given by Schlapp.

The values of the vibrational constants of S_2 in the state $C^3\Sigma_u^-$, given in Table 78, were determined by Olsson [3140] from the edges of a great many bands ($v' \leq 5$, $v'' \leq 37$) of the system $C^3\Sigma_u^- - X^3\Sigma_g^-$. In this case the following values of the vibrational constants of S_2 in the electron ground state were obtained: $\omega_e'' = 725.8$, $\omega_e''x_e'' = 2.85$ cm^{-1}. In Naudé's paper [3026] similar values are given for the vibrational constants of S_2 in the electron ground state $S_2(\omega_e'' = 725.68 \pm 0.01$, $\omega_e''x_e'' = 2.852$ cm$^{-1})$, which were calculated by Wilson. The latter values were accepted by Herzberg [2020] and in the handbook [649], and also in the present Handbook (see Table 78).

The accepted values of the vibrational constants of the electron ground state of S_2 give a good description of 30 lower levels of vibrational energy of this molecule (cf. [1668], p. 469). An extrapolation of the vibrational levels with respect to these constants, however, yields too high a value to the dissociation limit ($D_0 = 45830$ cm^{-1})*. Therefore, in order to obtain a satisfactory description of the high vibrational energy levels of the $X^3\Sigma_u^-$ state of S_2, it is necessary to introduce in the expression of $G_0(v)$ terms proportional to the third or a higher power of v.

The band system $C^3\Sigma_u^- - X^3\Sigma_g^-$ of the S_2 molecule is very similar to the Schumann-Runge band system of the O_2 molecule (see page 300). It must be noted that among the O_2 band systems studied the Schumann-Runge system is the only one which is not forbidden; the other band systems of O_2 are forbidden by the corresponding selection rules and are observed in absorption only if thick layers of absorbing substance are used, and in emission only under special conditions of excitation. The creation of similar conditions in the case of sulfur vapors, however,

TABLE 78

Accepted Values of the Molecular Constants of S_2, SO, SH and SF

Molecule	state	T_e	ω_e	$\omega_e x_e$	B_e	α_1	D_0	r_e
		cm^{-1}						Å
S_2	$X^3\Sigma_g^-$	0[a]	725,63	2,85	0,2955	0,0016	$1,96 \cdot 10^{-12}$	1,889
	$a^1\Delta_g$	5000[b]	—	—	—	—	—	—
	$b^1\Sigma_g^+$	8000[b]	—	—	—	—	—	—
	$A^3\Delta_u$	22000[b]	—	—	—	—	—	—
	$B^3\Sigma_u^+$	23000[b]	—	—	—	—	—	—
	$c^1\Sigma_u^-$	23500[b]	—	—	—	—	—	—
	$C^3\Sigma_u^-$	31835[a]	434,0	2,75	0,2919	0,0018	—	2,180
SO	$X^3\Sigma^-$	0	1148,19	6,116	0,72018	0,00562	$1,133 \cdot 10^{-6}$	1,482
	$a^1\Delta$	6500[b]	—	—	—	—	—	—
	$b^1\Sigma^+$	11000[b]	—	—	—	—	—	—
	$A^3\Delta$	28000[b]	—	—	—	—	—	—
	$B^3\Sigma^+$	29000[b]	—	—	—	—	—	—
	$c^1\Sigma^-$	30000[b]	—	—	—	—	—	—
	$C^3\Sigma^-$	41628,7	630,4	4,79	0,5020	0,0062	$1,280 \cdot 10^{-6}$	1,775
SH	$X^2\Pi_i$	0[f]	2692	47,6	9,607	0,292	$4,80 \cdot 10^{-4}$	1,3407
	$A^3\Sigma^+$	31033,03[g]	1979,8	97,65	8,521	0,464[e]	$6,66 \cdot 10^{-4}$[g]	1,4230
SF	$X^2\Pi_i$	0	810[b]	—	0,55[b]	—	—	1,61[b]

[a] $\varepsilon = -23,7\ cm^{-1}$, $\gamma = +0,06\ cm^{-1}$.

[b] Estimate.

[c] $\varepsilon = -26,4\ cm^{-1}$, $\gamma = +0,12\ cm^{-1}$.

[d] $A_0 = -376,96\ cm^{-1}$.

[e] $\gamma_0 = 0,313\ cm^{-1}$.

[f] $\alpha_2 = -0,022\ cm^{-1}$.

[g] After [2259a]. $D_e = 6,36 \cdot 10^{-6}\ cm^{-1}$ and $\beta_1 = 0,60 \cdot 10^{-6}\ cm^{-1}$.

is connected with great experimental difficulties.

Herzberg and Mundie [2037] tried to obtain in the S_2 absorption spectrum band systems which correspond to forbidden transitions. With an optical path length in sulfur vapor of up to 6 m, Herzberg and Mundie discovered previously unknown absorption bands extending up to 8700 Å. But since the dispersion of the apparatus was low these bands could not be analyzed. Desirant and Duchesne [1318a] discovered a weak system of bands in the infrared range of the S_2 emission spectrum. Rosen and Bouffioux [3484a] obtained this band system with a device of

of high dispersion which enabled them to measure the edges of seven bands. Later on, Rosen and Bouffioux made use of Legendre's table and found: $\nu_{00} = 13\,327$, $\omega_e' = 990$, $\omega_e'' = 487$ cm^{-1}. But in paper [3484a] no assumptions were made on the electron states of S_2, to transitions between which this band system could correspond. The band system of S_2, observed in papers [1318a, 3484a] were not studied afterwards.

In view of the structural similarity of the valence electron shells of the O_2 and S_2 molecules, we may assume that the electron states of the molecules (at least the lower ones) must be similiar. In the case of O_2 the electron states $X^3\Sigma_g^-$ and $C^3\Sigma_u^-$ are separated by another five electron states: $a^1\Delta_g^-$, $b^1\Sigma_g^+$, $A^3\Delta_u$, $B^3\Sigma_u^+$ and $c^1\Sigma_u$ (cf. Table 19). It is very probable that the S_2 molecule too possesses similar electron states.*

The problem of the correspondence of the excitation energy values of equivalent electron states of isoelectronic diatomic molecules was considered by Shifrin [463] (cf. page 84). In Table 78 the values of excitation energies of the electron states $a^1\Delta_g^-$, $b^1\Sigma_g^+$, $A^3\Delta_u$, $B^3\Sigma_u^+$ and and $c^1\Sigma_u$ of the S_2 molecule are given as calculated on the basis of Eq (1.31), suggested by Shifrin, and also the values of the excitation energies of the O_2 molecule and the values of $r_e(O_2, X^3\Sigma_g^-)$ and $r_e(S_2, X^3\Sigma_g^-)$. The errors of the so determined values of the excitation energies of S_2 electron states not observed in the spectra may be estimated as amounting to $\pm$ 1000 cm^{-1}. It must be noted that the value of $T_e(S_2, C^3\Sigma_u^-)$ calculated from Eq. (1.31), differs from the experimental value (given in Table 78) by no more than 15 cm^{-1}.

Previously it had been assumed in literature [1176] that the S_2 molecule might possess an excited electron state of the type $^1\Sigma_g^+$, whose energy was estimated as amounting to 2500 cm^{-1}. Zeise's calculations [4383] of the equilibrium of $2SO \rightleftarrows \frac{1}{2}S_2(^3\Sigma_g^+) + SO_2$, showed that

the first excited state of S_2 must lie higher than this was assumed in paper [4383], in accordance with the energy values of the lower electron states of S_2, accepted in the present Handbook.

In both the absorption spectrum [2730, 2731] and the emission spectrum [3936a] of S_2 band systems were discovered in the far ultraviolet. In the wavelength range 1600-1900 Å two band systems in the S_2 absorption spectrum were investigated by Maeder [2730, 2731] who designated them as the systems C and D. These band systems correspond to transitions from excited electron states with excitation energies (T_e), equal to 55,598 and 58,707.2 cm^{-1}, to the electron ground state $X^2\Sigma_g^-$. In Herzberg's book [2020] and in the Handbook [649] this state is assumed to be a $^3\Pi_u$ state. In paper [2730] Maeder analyzed the vibrational structure of the systems C and D and determined the values of the vibrational constants for the corresponding excited states of S_2. Tanaka and Ogawa [3936a] observed two band systems in almost the same range of the S_2 emission spectrum as Maeder (1700-2000 Å). An analysis they made showed that in these systems the upper states lie closely together, the transitions occurring to a common lower state which, in all probability, is the $X^3\Sigma_g^-$ ground state of the S_2 molecule. The upper electron states in the systems discovered in paper [3936a], are close to the excited electron state $^3\Pi_u$, found by Maeder. The types of these states could not be identified by Tanaka and Ogawa.

SO. In the SO spectrum a single band system, $C^3\Sigma^- - X^3\Sigma^-$, was studied in detail; it lies in the wavelength range from 2200 to 4000 Å. Other band systems were not observed in the SO spectrum.

Lowater [2665] and Johnson and Cameron [2264] were the first who observed the $C^3\Sigma^- - X^3\Sigma^-$ band system in the spectrum of an electric discharge in SO_2. Afterwards it was studied in detail by Henri and Wolff [1991] and Marvin [2787]. The nature of the bands of the SO mole-

cule, observed in the papers [2264, 2665] was identified by Henri and Wolff [1991]. Working with prism spectrographs of medium dispersion, these researchers observed 39 bands of the system $C^3\Sigma^- - X^3\Sigma^-$ and from the band edges they analyzed the vibrational structure. The rotational structure of the SO bands in paper [1991] was insufficiently resolved so that it could not be analyzed. Martin [2787] obtained an SO spectrum with completely resolved rotational structure of seven bands in second order of a concave diffraction grating and showed that it belongs to transitions between two states of the type $^3\Sigma$ of the SO molecule. In paper [2787] the nature of the SO bands, suggested by Henri and Wolff, was accepted, according to which the bands studied by Martin correspond to the values $v' = 0$, $v'' = 4, 5, \ldots, 9$ and $v' = 1$, $v'' = 4$. Martin measured also the position of the edges of seven bands corresponding to $v' \leq 3$ and $v'' = 3, 4$ (according to the numeration of Henri and Wolff). The results of these measurements were thoroughly analyzed by Martin who, in this way, determined the values of the vibrational and rotational constants of SO in the states $X^3\Sigma^-$ and $C^3\Sigma^-$, which, until 1959, were considered as quite reliable and were recommended in Herzberg's book [2020] and in the Handbook [649].

In paper [2787] the triplet splitting of lines of the bands 0-6, 0-7, 0-8, 0-9, 0-10, 0-11, 1-6, corresponding to $K > 30$ and $K < 13$, could be resolved. But the splitting was analyzed only for the lines of the bands 0-10, carresponding to $K < 13$, since in the residual cases we have a mixed superposition of lines of different branches. Martin found that a subsequent application of Kramers' relations (1.24a) (cf. page 79) does not yield a satisfactory description of triplet splitting of individual lines of SO in the system $C^3\Sigma^- - X^3\Sigma^-$. It seems that in the given case an application of Schlapp's equations (1.24) might have been more successful.

In the past it was tried several times to obtain the absorption spectum of SO. At that time the SO absorption spectrum was assumed to be observed in the vapor of the substance which forms when the products of SO_2 decomposition in an electrical discharge are condensed. But later on it was shown that the spectrum observed pertains to sulfur semioxide S_2O (cf. p. 611). Hicks [2067] tried to obtain the SO absorption spectrum when heating a mixture of sulfur and oxygen up to 1100° but he did not succeed.

The absorption spectrum of SO was observed for the first time by Myerson, Taylor and Hanst [3017] who subjected explosions of CS_2 + O_2 mixtures to spectroscopic investigations. The authors of paper [3017] measured the edges of 12 bands of SO which corresponded to $v' \leq 3$ and $v'' = 1, 2, 3, 4, 5^*$ and determined the position of nine rotation lines of the 1-4 band. The results of these measurements proved to be in full agreement with the results of analogous measurements in the emission spectrum [1991, 2787]. A comparison of the results of studying the absorption and emission spectra of SO enabled Myers, Taylor and Hanst to show that the lower electron state $^3\Sigma^-$ of the system $^3\Sigma^- - {}^3\sigma_g^-$ is the ground state of the SO molecule.

Afterwards the SO absorption spectrum was studied by Norrish and Oldershaw [3103] when studying the pulsed photolysis of SO_2 and SO_3. In the spectrum, taken with a device of medium dispersion, he oberved 23 bands of SO in the wavelength range 2220-2830 Å, 15 of which, lying in the range 2220-2510 Å, were observed for the first time. Norrish and Oldershaw found that the positions of the edges of these bands could not be described by the vibrational constants found in paper [2787] and could not be reconciled with the numeration of bands used in the papers of Henri and Wolff and Martin. A new analysis of the vibrational structure of the $C^3\Sigma^- - X^3\Sigma^-$ band system, taking into account

the results of measuring the absorption spectrum and the data obtained in studying the SO emission spectrum [1991, 2787] enabled Norrish and Oldershaw to show that the numeration of the $C^3\Sigma - X^3\Sigma$, band system, used in papers [1991, 2787], is incorrect. The actual values of v'' proved to be higher by two units than suggested in papers [1991, 2787]. It must be noted that progressions, corresponding to transitions to the levels v'' = 0 and 1, are virtually not observed in emission spectra of SO as they are very weak in intensity. In connection with the renumeration of the vibrational energy levels of SO for the state $X^3\Sigma_g$, Norrish and Oldershaw [3103] recalculated the vibrational and rotational constants of the $X^3\Sigma$ and $C^3\Sigma$ states of SO on the basis of results of all investigations of the $C^3\Sigma - X^3\Sigma$ band system. The values of the molecular constants of SO in the states $X^3\Sigma$ and $C^3\Sigma$ calculated by Norrish and Oldershaw [3103] were accepted in the present Handbook and are given in Table 78.

The molecules of SO, S_2 and O_2 are isosteric. Owing to this it must be expected that their lower electron states are of the same type. In fact, the electron ground states of all these molecules are of the type $X^3\Sigma^-$. The excited electron state $C^3\Sigma^-$ of these molecules has also been carefully studied; the values of the excitation energies of this state, for the SO, S_2 and O_2 molecules, satisfy the empirical relation (1.31) suggested by Shifrin [463]. As to O_2, apart from the electron states $X^3\Sigma^-$ and $C^3\Sigma^-$, we know three singlet and two triplet electron states whose excitation energies are lower than the excitation energy of the $C^3\Sigma^-$ (see Table 19). In the present Handbook we assume that the SO molecule, besides the two electron states $X^3\Sigma^-$ and $C^3\Sigma^-$, studied spectroscopically, will also possess states which are of the same type as the electron states of O_2 mentioned above, with excitation energies smaller than the excitation energy of the state $C^3\Sigma^-$. The values of the

excitation energies of these compounds, calculated by (1.31), and the corresponding O_2 (Table 19) and SO data (for the $X^3\Sigma^-$ state) are given in Table 78. The errors of the excitation energy values, estimated in this way, of the nonobserved electron states of SO, may be assumed to amount to ± 1000 cm^{-1}.

SH. In the spectrum of the radical SH a single band system, $A^2\Sigma - X^2\Pi_i$ is investigated, which lies in the wavelength range 3200-3700 A

The absorption spectrum of the radical SH was obtained for the first time by Lewis and White [2606] in an r-f pulsed discharge in H_2S. These authors observed two 0-0 subbands which correspond to the transitions $^2\Sigma \leftarrow {}^2\Pi_{3/2}$ and $^2\Sigma - {}^2\Pi_{\frac{1}{2}}$. Analyzing the rotational structure of the subband $^2\Sigma \leftarrow {}^2\Pi_{3/2}$ they could show that the $^2\Pi$ state of SH is a reversed state. Later on the subbands 0-0 of the $^2\Sigma - {}^2\Pi$ system of the radical SH were observed in the emission spectrum by Gaydon and Whittingham [1671], Dyne and Style [1438] and Leach [2573]. Leach [2573] analyzed the rotational structure of the 0-0 bands and determined the values of the rotational constants for the $^2\Pi$ and $^2\Sigma$ states which were found to be similar to the values of the corresponding constants obtained by Lewis and White [2606].

In paper [2574] Leach reports on spectral analyses he made with H_2S and D_2S discharges, where he could observe the 0-0 and 0-1 bands of the SH radical and the bands 0-0, 0-1 and 0-2 of the radical SD. From the edges of the SD bands Leach [2574] determined the values of the vibrational constants of the electron ground state of SD ($\omega''_e = 1933$, $\omega''_e x''_e = 24.5$ cm^{-1}), on the basis of which the vibrational constants of the electron ground state of SH were calculated with the help of Eqs. (1.43). The latter are accepted in the present Handbook and given in Table 78. The vibrational constants of SH, determined by Leach in paper [2574] are in good agreement with the values of these quantities, obtained with the help of the empirical relations given in [2474, 441].

The bands 0-0, 1-0 and 2-0 of the radicals SH and SD were studied with absorption spectra obtained in pulsed photolysis of H_2S and D_2S

[3301, 3356, 2259b]. Porter [3301] was the first who obtained the bands 0-0 and 1-0 of the radicals SH and SD by means of this method with a prism spectrograph, bands whose rotational structure was partially resolved. From these data Porter calculated roughly approximate values of the vibrational constants of SH in the states $A^2\Sigma$ and $X^2\Pi$. Afterwards the bands 0-0 and 1-0 of the radicals SH and SD were obtained by Ramsay [3356] by means of the method of pulsed photolysis, with well resolved rotational structure in second order of a spectrograph with a 21-foot grating. Johns and Ramsay [2259b] obtained the 2-0 bands of these radicals with the help of the same method, in fourth order of an analogous spectrograph.

Ramsay [3356] analyzed the rotational structure of the bands 0-0 and 1-0 in detail and determined exact values of the rotational constants (B_0 and D_0) and the constants of spin-orbital coupling (A_0 and γ_0) for the states $X^2\Pi_1$ and $A^2\Sigma^+$ of the radicals SH and SD and also the excitation energies of the $A^2\Sigma^+$ states of these radicals and the values of the constants $\Delta G_{\frac{1}{2}}$ and α_1 of these states. On the basis of these data Ramsay calculated approximate values of the constants ν_e, ω_e', $\omega_e'X_e'$, ω_e'', $\omega_e''X_e''$, B_e'' and α_1'' of the radicals SH and SD, making use of the relations (I.43), the approximate relation (1.38) and of the assumption that ν_e (SH) = = ν_e (SD). An analysis of the rotational structure of the 2-0 bands of the radicals SH and SD, carried out by Johns and Ramsay [2259b], permitted an essential completion of the data obtained previously by Ramsay [3356] so that these authors could determine the values of the molecular constatns of SH and SD in the $A^2\Sigma^+$ state, without applying Eqs. (1.43).

The values of the molecular constants of SH in the $X^2\Pi_1$ state and in the $A^2\Sigma^+$ state, accepted in the present Handbook, are given in Table 78. The vibrational constants of SH in the $X^2\Pi_1$ state given in Table

78 are, as already mentioned, taken from Leach's data [2574], the rotational constants B_e and α_1 were calculated by Khachkuruzov [441] from data of [3356] and [2574], allowing for the correlation of the values of molecular constants of diatomic hydrides and deuterides of the elements of the second and third periods of Mendeleyev's table. The value of the constant D_0 of the $X^2\Pi_1$ state of SH given in Table 78 was determined by Ramsay [3356]. The molecular constants of SH in the $A^2\Sigma^+$ state given in Table 78 were determined by Johns and Ramsay [2259a] on the basis of results of analyzing the rotational structure of the bands 0-0, 1-0 [3356] and 2-0 [2259b]. The values of the excitation energy of the $A^2\Sigma^+$ state of SH, given in Table 78, are based on the quantity ν_{00} = = 30662.42 cm^{-1}, determined in Ramsay's work [3356], and the values of the vibrational constants of SH in the states $X^2\Pi_1$ and $A^2\Sigma^+$.

SF. The spectrum of the diatomic radical SF has not been observed. None the less, an investigation of the laws governing the values of the constants of diatomic molecules makes it possible to predict approximate values of the molecular constants of SF.

The electron ground state of the radical SF must be the same as with the isosteric radicals ClO, OF, OH, SH, i.e., a $^2\Pi_1$ state. A comparison of the molecular constants of diatomic fluorides of the elements of the second and third periods as well as the application of data of the corresponding compounds in multiatomic fluorides of the same elements makes it possible to estimate the values of the interatomic distance and the force constant of the radical SF: $r_e = 1.60 \pm 0.05$ Å, $k_e = (4.6 \pm 0.2) \cdot 10^5$ dyne·cm^{-1}. To these values of the constants r_e and k_e correspond the values of the constants B_e and ω_e given in Table 78 and accepted in the present Handbook. The error of the accepted value of the vibration frequency of SF was estimated to amount to ± 30 cm^{-1}, that of the constant B_e to ±0.05 cm^{-1}.

SO_2. The sulfur dioxide molecule is nonlinear, symmetrical (point

group of symmetry C_{2v}, and has three fundamental frequencies in both the infrared spectrum and the Raman spectrum.

The results of studying the infrared spectrum and the Raman spectrum of SO_2, obtained until 1944, were considered by Herzberg [152]. In these investigations only a narrow section of the SO_2 spectrum was comprised, ranging from 500 to 2500 cm^{-1}. The rotational structure of the bands was only resolved by Barker [637]; according to his measurements the fundamental frequencies SO_2 are the following: $\nu_1 = 1151.38$, $\nu_2 = 517.84$, $\nu_3 = 1361.50$ cm^{-1}.

Later on Shelton, Nielsen and Fletcher [3699, 3700, 3077] studied the infrared absorption spectrum of sulfur dioxide in the range 450-5500 cm^{-1} in which they observed 17 bands of SO_2. But only with seven bands* they succeeded in resolving and analyzing the rotational structure. In order to determine the vibrational constants of SO_2, Shelton, Nielsen and Fletcher approximated the wave numbers of the centers of the bands investigated by polynomials, quadratic in the vibrational quantum numbers. The values of the vibrational constants of SO_2 obtained by Shelton, Nielsen and Fletcher [3699, 3700] are accepted in the present Handbook and given in Table 79.

The fundamental frequencies of SO_2**are, according to data of these authors, equal to $\nu_1 = 1151.38$, $\nu_2 = 517.69$, $\nu_3 = 1361.76$ cm^{-1}.

The accuracy of the SO_2 vibrational constants in Table 79 is not high since in papers [3699, 3700] they have been determined from the band centers and not from the zero lines and in their determination the possibility of resonance interactions between the vibrational states of SO_2 was not taken into account. Judging from the differences between the experimental and the calculated values of the centers of the bands, the errors of the frequencies of the normal vibrations of the SO_2 molecule, given in Table 79, may amount to ±2 cm^{-1} and those of the con-

TABLE 79

Accepted Values (in cm^{-1}) of the Molecular Constants of SO_2 ($\sigma = 2$)

Постоянная 1	Значение 2	Постоянная	Значение	Постоянная	Значение
ω_1	1167,00	x_{33}	−3,00	x_{13}	−13,71
ω_2	526,27	x_{23}	−5,17	A_{000}	2,02740
ω_3	1380,91	x_{12}	−2,05	B_{000}	0,344179
x_{11}	−3,99	x_{22}	−3,90	C_{000}	0,293534

1) Constant; 2) value.

stants of anharmonicity to from 0.5 to 1 cm^{-1}. For seven bands of SO_2 with resolved rotational structure (see note to page 604) Shelton, Nielsen and Fletcher [3699] made an approximate analysis of the rotational structure, taking into account that the SO_2 molecule resembles a symmetrical top. This fact enabled the authors of paper [3699] to find approximate values of the differences $A_{v_1v_1v_1} - B_{v_1v_2v_3}$ for the vibrational constants of (100), (010), (200) and the values of the constant $Bv_1v_2v_3$ for the states in (001), (101) and (011).*

The pure rotation spectrum of SO_2 lies in the microwave range. The microwave spectrum of SO_2 was investigated for the first time by Dailey, Golden and Wilson [1244] who determined the frequency of 11 transitions between high rotational energy levels. On the basis of the corresponding quantum-mechanical formulas for the rigid rotator and approximate allowance of the effect of centrifugal elongation, these authors determined the values of the structural parameters of the SO_2 molecule; they were in agreement with the results of electron diffraction studies [517]. The values of the frequencies of rotational transitions of SO_2, calculated in paper [1244] are, however, rather different from the values obtained by observation. This stimulated Sirvetz [3752] again to study the microwave range of the SO_2 spectrum and to take the centrifugal distortion better into account when analyzing the

measuring results. On the basis of these data he determined the values of the principal moments of inertia of the SO_2 molecule for the vibrational ground state.

Crable and Smith [1208] measured the frequencies of six rotational transitions, corresponding to $\Delta J = 0$ and +1 between lower rotational energy levels ($J = 0$–7). For these levels the influence of the centrifugal distortion of the molecules is insignificant so that the authors of paper [1208] calculated the rotational constants of SO_2 without introducing corrections for the centrifugal distortion. The values of the rotational constants of SO_2 obtained by Crable and Smith are accepted in the present Handbook and given in Table 79. The values of the corresponding quantities calculated according to Sirvetz' data [3752] are, within the limits of error of determination, in agreement with those given in Table 79.

Kivelson [2424] used the results of measuring the microwave spectrum of SO_2 obtained by Crable and Smith [1208] and Sirvetz [3752] and the equation for the rotational energy levels of nonrigid asymmetric rotators (almost symmetrical) he had derived together with Wilson [2425], in order to calculate the rotational and centrifugal constants of the SO_2 molecule. The values of the rotational constants of SO_2, calculated by Kivelson, also agree, within the limits of error of determination, with the values obtained by Crable and Smith [1208].*

The values of the rotational constants given in Table 79 correspond to the following values of structural parameters of the SO_2 molecule: $r_{S-O} = 1.4321$ Å, $\angle O-S-O = 119°21'$.

The pure rotation spectrum of SO_2 in the infrared was obtained by Danti and Lord [1260] in the range 100–200 μ. The results of measuring the infrared spectrum of SO_2 in this range and the values of the rotational constants of SO_2, determined from the microwave spectra [2424],

enabled the authors of paper [1260] to determine the value of the constant of centrifugal distortion, $D_k = 7.61 \cdot 10^{-5}$ cm^{-1}, in agreement with the value calculated from the force constants of SO_2. In paper [1260] the values of two other constants of centrifugal distortion of the SO_2 molecule were also calculated.

We know a great many investigations of the electron spectra of SO_2. The corresponding papers were treated in the reviews of Sponer [3825, 3827], Walsh [4140] and Mulliken [3002]. According to Walsh [4140], the states $^1B_1$ and $^1B_2$ with excitation energies of 25,775 and 29,622 cm^{-1}, respectively, [2864, 2863], are nearest to the electron ground state ($^1A_1$) of SO_2.

$\underline{SO_3}$. Raman spectrum analyses [1685], measurements of the dipole moments [3804] and analyses of the results of electron diffraction measurements [3170] agreed in the result that the SO_3 molecule is of plane symmetry with the structure of a regular equilateral triangle with the sulfur atom in its center and the oxygen atoms at the vertices (point group of symmetry D_{3h}). From the fact that it belongs to the D_{3h} point group of symmetry it follows that the SO_3 molecule must have four fundamental frequencies: one frequency of plane symmetrical vibration, ν_1, one frequency ν_2 of nonplane vibration, and two doubly degenerate frequencies ν_3 and ν_4. The frequencies ν_3 and ν_4 correspond to plane vibrations of the molecule, ν_3 to an antisymmetric valency vibration and ν_4 to a deformation vibration. The frequencies ν_1, ν_3 and ν_4 must be active in the Raman spectrum and the frequencies ν_2, ν_3 and ν_4 in the infrared spectrum.

The Raman spectrum of liquid sulfur trioxide was investigated in a series of papers [808, 4083, 631, 1685]; the Raman spectrum of the gas, however, was studied in a single paper [1685]. The infrared spectrum was obtained for both the liquid and the gas [1684]. The spectra

of liquid and gaseous sulfur trioxide differ essentially from one another. This is due to the fact that the sulfur trioxide vapor consists of SO_3 molecules [2578], whereas in the liquid, owing to the strong polymerization, complex molecules $(SO_3)_n$ exist besides the SO_3 molecules [1685].

The Raman spectrum of gaseous sulfur trioxide was obtained by Gerding, Nijveld and Muller [1685] who discovered in it a single line at 1069 cm^{-1}, corresponding to the intense line at 1068 cm^{-1} in the Raman spectrum of liquid sulfur trioxide [808, 4083]. The identity of this line of the SO_3 molecule is not suoject to doubt; it follows from polarization measurements [808, 4083] that it corresponds to the frequency of the fully symmetrical vibration ν_1.

Unlike the gas spectrum, in the Raman spectrum of liquid sulfur trioxide a great number of lines were discovered in the interval from 120 to 1500 cm^{-1} by Gerding, Nijveld and Muller [1685]. In order to find out which of these lines belongs to the SO_3 molecule, the authors of paper [1685] studied the Raman spectra of liquid sulfur trioxide at various temperatures and the Raman spectra of liquid mixtures of SO_3 and SO_2 with varying content of sulfur trioxide. It was observed that in the Raman spectra of liquid sulfur trioxide the intensity of three lines, corresponding to the frequencies 532, 1068 and 1389 cm^{-1}, increases as the temperature rises. The intensities of the same lines in the Raman spectra of the mixtures increased as the quantity of sulfur dioxide dropped. From this observation Gerding, Nijveld and Muller drew the conclusion that these three lines belong to the SO_3 molecule. Measurements of the degree of polarization of the lines at 1389 and 532 cm^{-1} [4083, 631] showed that they are depolarized. Owing to this they were attributed the frequencies ν_3 and ν_4 by the authors of [1685]. The similarity of the values of these frequencies and the frequencies

ν_3 and ν_2 of the SO_2 molecule was considered in paper [1685] as an additional argument (see page 604).

Gerding and Lecomte [1684] obtained the infrared absorption spectrum of gaseous and liquid sulfur trioxide in the range of 500 to 1430 cm^{-1} with a low-dispersion prism spectrometer. In the spectrum of gaseous sulfur trioxide these researchers oberved two bands of medium intensity at 652 and 1123 cm^{-1} and a very intense band at 1333 cm^{-1}. Gerding and Lecomte interpreted the frequency of 652 cm^{-1} as the frequency of the nonplane vibration of ν_2, the 1123 cm^{-1} frequency was attributed to the SO_2 admixture to the sulfur trioxide sample under investigation, and the frequency of 1333 cm^{-1} was interpreted as the frequency of the plane antisymmetrical vibration of ν_3. Taking into account the results of Raman spectrum investigations [1685], Gerding and Lecomte [1684] recommended the following values for the fundamental frequencies of the SO_3 molecule: $\nu_1 = 1069$, $\nu_2 = 652$, $\nu_3 = 1333$, $\nu_4 = 532$ cm^{-1}; they were accepted in Herzberg's monograph [152]. But in the handbook by Yost and Russel [4365] and in the paper of Stockmayer, Kavanagh and Mickley [3871] quite other values were used for the fundamental frequencies of SO_3, namely $\nu_1 = 1069$, $\nu_2 = 532$, $\nu_3 = 1333$, $\nu_4 = 560$ cm^{-1}, as suggested by Stevenson. The fact that Stevenson revised the interpretation of the vibrational spectra of SO_3 was caused by the disagreement between the thermodynamic functions of SO_3, calculated on the basis of the frequencies recommended by Gerding and Lecomte [1684] and the structural parameters found by Palmer [3170] on the one hand and the experimental values of the equilibrium constants of the reaction

$$SO_3(\text{г}) = SO_2(\text{г}) + \tfrac{1}{2}O_2(\text{г}), \qquad (23.1)$$

determined in the papers [854, 3948, 213] etc., on the other. It is, however, easy to show [442, 443] that the changes in the frequency values ν_2 and ν_4, suggested by Stevenson, are voluntary and are in con-

tradiction with the absence of absorption in the infrared spectrum of SO_3 in the range of from 500 to 650 cm^{-1}, established by Gerdin and Lecomte. Moreover, the values of the thermodynamic functions of gaseous sulfur trioxide, calculated on the basis of Stevenson's values of the SO_3 frequencies, do not correspond to the experimental values of the equilibrium constants of reaction (13.1) either.

The discrepancy between the thermodynamic functions of gaseous sulfur tricxide, calculated from the frequencies of SO_3, recommended by Gerding and Lecomte [1684] and the experimental values of the equilibrium constants of reaction (13.1) are, apparently, due to the fact that the frequencies ν_1, ν_2, ν_3 as used by Gerding and Lecomte were determined from the spectra of gaseous sulfur trioxide, whereas the frequency ν_4 was chosen on the basis of studies of the Raman spectrum of liquid sulfur trioxide [1685]. By way of the example of the frequency ν_3 we may see how strongly the quantities of one and the same frequency of the SO_3 molecule may differ if we compare gas and liquid. In an investigation of the Raman spectrum of liquid sulfur trioxide a value of 1389 cm^{-1} was obtained in [1685] for ν_3, while the infrared spectrum of the gas yielded a value of 1333 cm^{-1} [1684]. We must therefore expect that the frequency ν_4 of the free SO_3 molecule has a lower value than that of the nonfree SO_3 molecule in the liquid, which, according to [1685, 1684] is equal to 532 cm^{-1}. Calculations carried out by Khachkuruzov [442, 443], based on an application of the most reliable experimental values of the equilibrium constants of reaction (13.1) and data from [3528, 3508] for the thermal effect of this reaction, showed that for the free SO_3 molecule in the gas $\nu_4 = 440 \pm 30$ cm^{-1}.

In Table 80 we find the values of the fundamental frequencies of SO_3 and the value of the product of the principal moments of inertia of this molecule accepted in the present Handbook. The latter quantity

was calculated on the basis of the following values of the structural parameters of the SO_3 molecule $r_{S-O} = 1.43 \pm 0.02$ Å, $< O-S-O = 120°$; they were obtained by Palmer [3170] when analyzing the results of electron diffraction measurements.

TABLE 80

Accepted values of the molecular constants of SO_3 and S_2O

1 Молекула	ν_1	ν_2	ν_3	ν_4	$I_A I_B I_C$	σ
	2. $см^{-1}$				$10^{-...}$ $г^3 \cdot см^6$	3
SO_3	1069	652	1333(2)	440(2)	1082	6
S_2O	679	370	1165	—	618,15	1

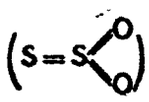
1) Molecule; 2) cm^{-1}; 3) $g^3 \cdot cm^4$.

S_2O. The existence of sulfur semioxide molecules was proved by Meschi and Myers in 1956 [2854, 2855]. Paper [2854] gives the results of mass-spectrometrical, stoichiometrical and gasometrical investigations of the so-called "sulfur monoxide Schenk"* and showed that this substance is an equimolecular mixture of sulfur dioxide and semioxide. This conclusion was verified by studies of the microwave spectrum of "sulfur monoxide Schenk" [2855, 2856]. The conclusion as to the content of a compound of the type $(S_2O)_x$ in "sulfur monoxide Schenk" was drawn already earlier in investigation by [3386] and Murthy [3012].

The studies of the microwave spectrum of sulfur semioxide made by Meschi and Myers [2855, 2856] showed that the S_2O molecule is nonlinear with the sulfur atom at the vertex of the angle. The value of the rotational constants of S_2O, obtained in the papers [2855, 2856], $A_{000} = 1.39811$, $B_{000} = 0.16675$, $C_{000} = 0.15034$ cm^{-1}, were used as basis for a calculation of the product of the principal moments of inertia of the S_2O molecule given in Table 80. According to calculations of Meschi and Myers, [2856], the structural-parameter values of S_2O corresponding to

it, are equal to $r_{S-O} = 1.465 \pm 0.010$, $r_{S-S} = 1.884 \pm 0.010$ Å < S-S-O = 118° ± 30'.

In studies of the absorption spectra of vapor of "sulfur monoxide Schenk" [1177, 246, 247, 2289] bands were observed in the ultraviolet and infrared ranges which belong to S_2O, but previously they were falsely attributed to other molecules. The most complete study of the S_2O absorption spectrum was carried out by Jones [2289]. Jones [2289] obtained the infrared absorption spectrum of S_2O in the range 400-2000 cm^{-1} with the help of a prism spectrometer, and the ultraviolet spectrum in the range from 2500 to 3500 Å in second order of a concave diffraction grating with a dispersion of 1.2 Å/mm. In the infrared spectrum Jones discovered two bands of the types A and B whose centers were at 679 and 1165 cm^{-1}, respectively. In the ultraviolet spectrum he observed a system of diffuse bands in the range from 3100 to 3400 Å. These bands were previously observed with a device of lower dispersion by Cordes and Schenk [1177] and Kondratyev [246, 247]. Jones [2289] could partially analyze the vibrational structure of one subsystem of bands in the ultraviolet spectrum of S_2O. The vibration frequencies of the S_2O molecule corresponding to them proved to be equal to 679 cm^{-1} and about 400 cm^{-1} in the ground state and in the excited electron state, respectively.

Jones tried to interpret the spectrum described in paper [2289] on the basis of the assumption that it pertains to the S_2O_2 molecule. Among all possible structural types of the S_2O_2 molecule, the trigonal model  is the only one that is in approximate agreement with the band contours observed in the infrared. Meschi and Myers [2854-2856] showed that the bands with the centers at 679 and 1165 cm^{-1}, observed

by Jones, must in fact be interpreted as the frequencies ν_1 and ν_3 of the symmetric and antisymmetric vibrations of the S_2O molecule. The calculations of the fundamental frequencies of the S_2O molecule, carried out in paper [2856], which were based on the assumption that the tensile force constants of the bonds S-S and S-O are quite the same as with the molecules of S_2 and SO_2 and that the deformation constant of S_2O is the same as in the case of SO_2, yielded the following results: $\nu_1 = 660$, $\nu_2 = 360$, $\nu_3 = 1150$ cm^{-1}. Analogous calculations made by the authors of the Handbook before paper [2856] was published resulted in the following: $\nu_1 = 728$, $\nu_2 = 412$, $\nu_3 = 1274$ cm^{-1}. The results of these calculations are in good agreement with Jones' spectroscopic data.* In the present Handbook we therefore used the values determined by Jones [2289] from the infrared spectrum as the fundamental frequencies of the valency vibrations of S_2O and estimated the deformation frequency ν_2 as amounting to 370 ± 30 cm^{-1} (see Table 80). Meschi and Myers [2856] estimated a value of $\nu_2 = 370 \pm 30$ cm^{-1} from the side lines in the microwave spectrum of S_2O, noting that Blukis, in an unpublished paper, found a value of $\nu_2 = 387$ cm^{-1}, studying the infrared spectrum of S_2O.

$\underline{H_2S}$. The hydrogen sulfide molecule is nonlinear, symmetrical (point group of symmetry C_{2v}) and has three fundamental frequencies which are active in both the infrared spectrum and the Raman spectrum.** The results of spectroscopic studies of hydrogen sulfide obtained until 1944 are considered in Herzberg's book [152]. Later on these data were considerably improved and completed owing to the development of the technique of recording infrared spectra.

Individual sections of the infrared absorption spectrum of hydrogen sulfied were obtained with high resolution and analyzed in the papers [1225, 1212, 1931, 1838, 3099, 502, 503, 505-508, 2809, 3098, 2177, 3146, 499, 3597]. On the basis of the results of these studies Table

81 was compiled which contains the values of the vibrational energy levels and effective values of the rotational constants of 20 vibrational states of the H_2S molecule.

Bailey, Thompson and Hale [622] were the first who succeeded in determining the vibrational constants of H_2S. But these authors had only very limited and inaccurate data on the spectrum of the H_2S molecule at their disposal so that the values of the vibrational constants they calculated are of mere historical interest. On the basis of much more accurate experimental values of the vibrational energy levels, Allen, Cross and King [504] calculated the vibrational constants of H_2S, taking into account the Darling-Dennison resonance between the vibrational states $(v_1 \geq 2,\ v_2,\ v_3)$ and $(v_1 - 2,\ v_2,\ v_3 + 2)$. The values of the vibrational constants of H_2S, obtained by Allen, Cross and King differ essentially from those obtained previously in paper [622]. A value of 47 cm^{-1} was obtained in paper [504] for the constant W of Darling-Dennison resonance.

In connection with new studies of the infrared spectrum of hydrogen sulfide, the vibrational constants of H_2S were recalculated by Allen and Plyler in paper [508]. The calculations were based on an approximation of the vibrational energy levels by a square expression, allowing for the Darling-Dennison resonance between the vibrational states $(v_1 \geq 2,\ v_2,\ v_3)$ $(v_1 - 2,\ v_2,\ v_3 + 2)$. The values of the vibrational constants of H_2S obtained in paper [508] are accepted in the present Handbook and given in Table 82.

The values of the vibrational constants of H_2S obtained by Allen and Plyler [508] resemble the values found by Allen, Cross and King [504].* The values of the vibrational constants given in Table 82 give a satisfactory description of the vibrational energy levels of H_2S, corresponding to $v_1,\ v_3 \leq 3$ and $v_2 \leq 2$. It may be expected, however,

TABLE 81

Experimental Values (in cm^{-1}) of the Vibrational Energy Levels and the Rotational Constants of H_2S

$v_1v_2v_3$	$G_0(v_1v_2v_3)$	$A_{v_1v_2v_3}$	$B_{v_1v_2v_3}$	$C_{v_1v_2v_3}$	1 Работа
000	0	10,373[a]	8,991[a]	4,732[a]	[1225, 1838]
010	1182,68[6]	10,724[a]	9,211[a]	4,670[a]	[506]
020	2353,93[6]	11,099[a]	9,443[a]	4,610[a]	[499]
100	2614,56[6]	10,249[a]	8,831[a]	4,663[a]	[499]
001	2625[a]	9,90[r]	9,04[r]	4,65[r]	[1931]
110	3779,23	10,595[a]	8,985[a]	4,603[a]	[3597]
011	3789,07[6]	10,517[a]	9,124[a]	4,619[a]	[3597]
021	4939,23[6]	10,871[a]	9,332[a]	4,582[a]	[506]
200	5145,12	10,059	8,719	4,612	[506]
101	5147,36[6]	10,078[a]	8,709[a]	4,608[a]	[506]
210	6288,28	10,394	8,918	4,547	[507]
111	6289,26[6]	19,398[a]	8,935[a]	4,548[a]	[507]
201	7576,3[6]	9,97	8,54	4,55	[1838]
300	7751,9	10,08	8,52	4,54	[1838]
003	7779,2[6]	9,80	8,68	4,57	[1838]
211	8697,3	10,29	8,75	4,48	[2177]
301	9911,05[6]	9,883	8,340	4,474	[1225, 1838]
004	10188,25	9,605	8,560	4,477	[1838]
103	10194,48[6]	9,698	8,466	4,490	[1838]
311	11008,78	10,197	8,559	4,411	[2177]

[a]Used in paper [205] to calculate the constants of vibration rotation interaction, given in Table 82.

[b]Used in paper [508] to calculate the vibrational constants given in Table 82.

[c]Allen and Plyler [508], by way of calculations, obtained a value of 2627.48 cm^{-1} for the center of the ν_3 -band.

[d]The values of the rotational constants of the state of (001) obtained in paper [1931] requires verification.

1) Paper.

that these constants only permit a rather approximate description of the higher vibrational energy levels of H_2S, corresponding to high values of the vibrational quantum numbers.

The rotational constants of the vibrational ground state of H_2S were determined for the first time by Cross [1225] as the result of analyzing the rotational structure of the band $3\nu_1 + \nu_3$, obtained by means of a device with high dispersion (2.5 Å/mm). Taking the classical correction for the rigidity of the molecule into account, Cross obtained the following: $A_{000} = 10.373$, $B_{000} = 8.991$, $C_{000} = 4.732$ cm^{-1}. Later on Crawford and Cross [1212] again analyzed the

TABLE 82

Accepted Values (in cm^{-1}) of the Molecular Constants of H_2S ($\sigma = 2$).

Постоянная 1	Значение 2	Постоянная 1	Значение 2	Постоянная 1	Значение 2
ω_1	2721,92	x_{23}	−21,09	α_1^B	0,190
ω_2	1214,51	x_{12}	−94,68	α_2^B	−0,222
ω_3	2733,36	A_e	10,360	α_3^B	0,092
x_{11}	−25,09	α_1^A	0,124	C_e	4,8225
x_{22}	−5,72	α_2^A	−0,351	α_1^C	0,069
x_{33}	−24,00	α_3^A	0,201	α_2^C	0,060
x_{13}	−19,69	B_e	9,021	α_3^C	0,052

1) Constant; 2) state.

rotational structure of the band $3\nu_1 + \nu_3$ (from data of paper [1225]), applying the quantum-mechanical theory of centrifugal distortion of multiatomic molecules [4288]. They obtained the following values of the rotational constants of H_2S: $A_{000} = 10.393$, $B_{000} = 9.040$, $C_{000} = 4.723$ cm^{-1}, recommended in Gertsberg's monograph [152].

Grady, Cross and King [1838], using a device of high dispersion, could resolve the rotational structure of the bands $4\nu_3$ and $\nu_1 + 3\nu_3$. A structural analysis of these bands yielded the same values of the rotational constants of the vibrational ground state as were obtained previously in paper [1225].

The values of the rotational constants of H_2S in the vibrational

ground state were also determined from the pure rotation spectrum in the infrared.* With the help of a vacuum spectrometer with a set of diffraction gratings, Genzel [1679] measured the frequency of 89 rotational transitions of H_2S in the range 10-85 cm^{-1} and calculated the following values of the rotational constants (without a correction for the centrifugal distortion): $A_{000} = 10.340$, $B_{000} = 9.034$, $C_{000} = 4.725$ cm^{-1}. Burrus and Gordy [1030] measured the frequencies of the rotational transitions $1_{-1}-1_{+1}$ (for H_2S^{32}, H_2S^{33}, H_2S^{34}) and 2_0-2_{+2} (for H_2S^{32}) in the microwave range and, ignoring the effect of zero vibrations,** they obtained: $A_{000} = 10.551$, $B_{000} = 9.223$, $C_{000} = 4.921$ cm^{-1}.

In the present Handbook we chose the values obtained by Cross et al. in [1225, 1838] for the rotational constants of the vibrational ground state of H_2S, since in the papers [1212, 1679, 1030] the values of these constants were determined less accurately. The errors of the accepted values of the constants A_{000} and B_{000} are not lower than ± 0.05 cm^{-1} and the value accepted for the constant C_{000} has an error of at least ± 0.01 cm^{-1}.

Table 81 gives the effective values of the rotational constants of H_2S for 20 vibrational constants, obtained by a series of researchers on the basis of analyses of the corresponding bands of the vibration-rotation spectrum. The effective values of the rotational constants for the nine nonperturbed vibrational states of H_2S, given in Table 81, were used by Kane [205] in order to calculate the vibration-rotation constants and the equilibrium values of the rotational constants** which were accepted in the present Handbook and are given in Table 82.

The following values of the structural parameters correspond to the equilibrium values of the rotational constants of the H_2S molecule given in Table 82: r_e (S-H) = 1.3360 Å, $\angle$H-S-H = 92°13'.

The electron spectrum of the H_2S molecule was studied in the pa-

pers [3321, 2010, 843, 3325].* In the range 2000-3000 Å Price, Teegan and Walsh [3325] observed a continuous spectrum. Discrete bands were observed in the range 1190-1600 Å. It was shown in the papers [3321, 3325] that the edges of the Q-branches of the discrete bands form a Rydberg series, a fact that makes it possible to determine the ionization potential of H_2S. The excitation energies of the lower electron states of H_2S have not been determined.

SF_2. The structure and the spectrum of the SF_2 molecule has not been studied by experiment. The spectra of the SCl_2 molecule [641, 3152, 2009] and its structure [517] were studied by a series of authors. The spectra and structures of the molecules of S_2Cl_2 and S_2Br_2 were studied more than once. Results of preliminary studies of the spectrum of S_2F_2 are also at our disposal [633]. A comparison of the results of these studies as well as investigations of the spectra and structures of these molecules, such as SF_6, SOF_2, SO_2F_2, $SOCl_2$, SO_2Cl_2 etc., permits definite conclusions as to the structure and the values of the vibration frequencies of the SF_2 molecule.

In the present Handbook it has been assumed that, like the SCl_2 and F_2O molecules, the SF_2 molecule belongs to the point group of symmetry C_{2v}, i.e., it is a symmetrical nonlinear triatomic molecule. The length of the S-F bond in the SF_2 molecule is assumed to equal that of the radical SF: $r_{S-F}'(SF_2) = 1.60 \pm 0.05$ Å. The angle between the S-F bonds in the SF_2 molecule must be close to 90° and in any case not smaller than 90°. A comparison of the valency angles between the bonds in such molecules as H_2O, H_2S, Cl_2O, Cl_2S, SO_2Cl_2 and SO_2F_2, makes it possible assume that $\angle$F-S-F in the SF_2 molecule must be smaller than 100°. In connection with these estimations of the possible limiting values of the valency angle between the S-F bonds in the SF_2 molecule, a value of $\angle$F-S-F $(SF_2) = 95 \pm 5°$ was accepted in the Hand-

book. The accepted values of the structural parameters used to calculate the products of the principal moments of inertia of the SF_2 molecule are given in Table 83.

TABLE 83

Accepted Values of the Molecular Constants of SF_2, SF_4, SF_6, SOF_2, SO_2F_2

Молекула	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9	$I_A I_B I_C$	σ
1	2 $см^{-1}$									3 10^{-114} $(г \cdot см^2)^3$	—
SF_2	850	400	800	—	—	—	—	—	—	360	2
SF_4	889	715	557	235	401	867	532	728	463	8775,5	2
SF_6	769,4	639,5(2)	932(3)	613(3)	522(3)	345(3)	—	—	—	28900	24
SOF_2	1333	808	530	410	748	390	—	—	—	1656,8	1
SO_2F_2	1269	848	553	274	360	1502	539	885	386	4485,5	2

1) Molecule; 2) $см^{-1}$; 3) $(г \cdot см^2)^3$.

The nonlinear triatomic SF_2 molecule must have three fundamental frequencies: ν_1, the frequency of the fully symmetrical vibration, ν_2, the frequency of the deformation vibration and ν_3, the frequency of the antisymmetric valence vibration. A comparison of the experimental values of the corresponding frequencies in the molecules of S_2F_2, SOF_2, SO_2F_2 and SCl_2, S_2Cl_2, $SOCl_2$ and SO_2Cl_2 shows that the frequencies ν_1 and ν_3 of the SF_2 molecule must be close to 800 $см^{-1}$ and the frequency ν_2 must then be close to 400 $см^{-1}$. The data available on the frequencies of triatomic molecules indicate that the frequencies ν_1 and ν_3 of the SF_2 molecule must differ by about 50 $см^{-1}$. But these data do not permit an unambiguous solution of the problem which of these two frequencies is the higher one. In the present Handbook we assumed ν_1 is the greater than ν_3, just as in the case of the F_2O molecule.

The values of the fundamental frequencies of SF_2, chosen on the the basis of these considerations, are given in Table 83. The errors assumed for the used values of ν_1 and ν_3 do not exceed 80 $см^{-1}$, where-

as the error of the value accepted for ν_2 was estimated to amount to $\pm$ 50 cm^{-1}.

SF_4. Basic information on the structure and the vibration frequencies of the molecule of sulfur tetrafluoride may be obtained from the paper of Dodd, Woodward and Roberts [1360] who studied the infrared spectrum and the Raman spectrum of SF_4.*

Dodd, Woodward and Roberts [1360] obtained the Raman spectrum of liquid sulfur tetrafluoride in the range 100-1000 cm^{-1} and the infrared spectrum of the gas in the range 400-5000 cm^{-1} using prism spectrometers of medium dispersion. Measurements of the degree of depolarization of the Raman spectrum lines, of the relative band intensities in the infrared spectrum and considerations on the form of the band contours (in connection with the different assumptions as to the structure of the SF_4 molecule and the selection rules corresponding to them) led the authors of paper [1360] to the conclusion that the SF_4 molecule pertains to the point group of symmetry C_{2v}. This conclusion agrees with the results of electron diffraction studies of the molecular structure of SeF_4 [876] and $TeCl_4$ [3862], the magnitude of the dipole moment of the SF_4 molecule [1359a] and with results of analyses of the nuclear magnetic resonance spectrum [1190, 2965] and of the microwave spectrum [1907a] of sulfur tetrafluoride.

Considering the problem of the structure of the SF_4 molecule, Dodd, Woodward and Roberts started from the assumption [1747] that the electron configuration of the valence shell of SF_4 corresponds to an sp^3d hybridization of the sulfur atom and is similar to the electron configuration of the PF_5 molecule which also possesses ten valence electrons.** In contrast to the PF_5 molecule has an undivided pair of electrons, not participating in the formation of chemical bonds and occupying one of the three equatorial positions, owing to whic

the SF_4 molecule must have the structure of a deformed tetrahedron. In this case the S-F bonds in SF_4 must be heterodynamic, in the same way as with PF_5.*

On the basis of these ideas on the structure of the SF_4 molecule, Dodd, Woodward and Roberts analyzed the band contours in the infrared spectrum of sulfur tetrafluoride with the help of the method of Badger and Zumwalt [604], assuming that all S-F bonds were equally long, amounting to 1.58 Å. This analysis permitted, on the other hand, the determination of the probable values of the valency angles of F-S-F and their limiting values, compatible with the molecule symmetry and the band contours and, on the other hand, a verification of the correctness of the values assumed for the S-F bond length. This analysis shows that the SF_4 molecule has differently large valency angles of F-S-F lying opposite to the symmetry axis of the molecule. Dodd, Woodward and Roberts showed that these angles (designated by 2φ and 2θ) must satisfy the inequalities $55° < \varphi < \theta < 125°$, $\varphi < 70°$, $\theta < 90°$ and obtained a series of possible values of the angles φ and θ, compatible with the shape of the band contours. A comparison of these results makes it possible to chose the following values of the angles of F-S-F in the SF_4 molecule:** $2\varphi = 120 \pm 20°$, $2\theta = 140 \pm 40°$. Comparing the experimental and calculated values of the distances between the peaks of the P and R branches of a series of bands, Dodd, Woodward and Roberts convinced themselves that the value of r_{S-F} $(SF_4) = 1.58$ Å they used must be close to the true value. We therefore accept in the present Handbook the value r_{S-F} $(SF_4) = 1.58 \pm 0.06$ Å.

The products of the principal moments of inertia, calculated on the basis of the values of structural parameters of the SF_4 molecule, are given in Table 83.***

Owing to the fact that the SF_4 molecule pertains to the C_{2v} point group of symmetry, it must have nine fundamental frequencies: four frequencies of fully symmetrical vibrations of type A_1 (ν_1, ν_2, ν_3, ν_4), one vibration frequency of type A_2 (ν_5) and two frequencies of each of the types B_1(ν_6, ν_7) and B_2(ν_8, ν_9). All nine frequencies are active in the Raman spectrum. In the infrared spectrum all frequencies are active, except for ν_5.

The values of the fundamental frequencies of SF_4 accepted in the present Handbook are based on the interpretation of the spectra of sulfur tetrafluoride, suggested by Dodd, Woodward and Roberts [1360] (cf. Table 83). This interpretation might obtain a further improvement since even the authors of paper [1360] did not give a fully unambiguous identification of a series of frequencies. Thus, for the frequency ν_5 paper [1360] suggests two possible values: 401 and 645 cm^{-1}. In the present Handbook the lower value was selected for the frequency ν_5 which is immediately observed in the Raman spectrum.

SF_6. On the basis of electron diffraction studies [907, 961] and spectroscopic analyses [1886, 1498, 1451] it was established that the SF_6 molecule has the structure of a regular octahedron so that it belongs to the point group of symmetry O_h. The SF_6 molecule has six fundamental frequencies: one frequency of the completely symmetrical vibration of the type A_{1g} (ν_1), four frequencies of triply degenerate vibrations of the type F (ν_3, ν_4, ν_5, ν_6) and one frequency of the doubly degenerate vibration of the type E_g(ν_2). The frequencies ν_1, ν_2 and ν_5 are only active in the Raman spectrum, the frequencies ν_3 and ν_4 are only active in the infrared spectrum while the frequency ν_6 does not appear in these spectra.

The results of spectroscopic studies of SF_6, published until 1944, are considered in Herzberg's monograph [152].

In 1957 Gullikson, Nielsen and Stair [1886] obtained the Raman spectrum of gaseous sulfur hexafluoride by means of a three prism spectrograph with a dispersion of 15 Å/mm. The values of the frequencies ν_1, ν_2, ν_5 and ν_6* of the SF_6 molecule obtained in paper [1886] are accepted in the present Handbook (cf. Table 83).

The infrared spectrum of SF_6 was investigated by Eucken and Aherens [1498], Lagueman and Jones [2514], Edelson and Mc Afee [1451] and Gaunt [1659].

Eucken and Aherens [1498] obtained the infrared spectrum of SF_6 in the range from 400 to 2000 cm^{-1} with a prism spectrometer of low dispersion. For the frequencies ν_3 and ν_4, active in the infrared spectrum, they found values amounting to 965 and 617 cm^{-1}. The frequency ν_6, nonactive in the SF_6 spectrum, was assumed by Eucken and Aherens to amount to 363 cm^{-1}, on the basis of data on the specific heat of gaseous sulfur hexafluoride.

In 1951 Lagueman and Jones [2514] again studied the infrared spectrum of SF_6 in the range from 400 to 5000 cm^{-1}. The values they found for the frequencies ν_3 and ν_4 are equal to 940 and 615 cm^{-1}, for the frequency ν_6 the same value was assumed as in paper [1498]. At the same time the infrared spectrum of SF_6 was studied by Edelson and Mc Afee [1451] who found that a series of frequencies, attributed by Lagueman and Jones to the SF_6 molecule, actually pertain to S_2F_{10} and they showed that the value of the frequency ν_6 used in paper [2514] is too high by 10-20 cm^{-1}.

In 1953 the infrared spectrum of SF_6 was reexamined by Gaunt [1659] in the range 400-5000 cm^{-1}. In paper [1659] the difficulties the researchers previously encountered in investigating the infrared spectrum of SF_6 were considered and a more satisfactory and complete interprestation of the spectrum was given. The values of the frequen-

cies ν_3 and ν_4 determined by Gaunt are accepted in the present Handbook (cf. Table 83). On the basis of an analysis of the composite frequencies, Gaunt chose the value of 344 cm^{-1} for the frequency ν_6, which is virtually the same as that calculated in paper [1886] on the basis of the harmonic frequency $2\nu_6$, observed in the Raman spectrum.

The length of the S-F bond in the SF_6 molecule was determined by Braune and Knoke [907] by means of electron diffraction analyses, who obtained $r_{S-F}=1,56 \pm 0,02$ Å, and Brockway and Pauling [961] who obtained $r_{S-F}=1,58 \pm 0,03$ Å . In the present Handbook we accept the value of r_{S-F} (SF_6) obtained by Braune and Knoke since the very same value of the S-F bond length was obtained in electron diffraction studies of the molecules of S_2F_{10} [1971] and $S_2F_{10}O_2$ [1972]. The products of the principal moments of inertia of the SF_6 molecule, given in Table 83, were calculated in agreement with the values accepted for the bond length S-F.

$\underline{SOF_2}$. On the basis of electron diffraction studies and spectroscopic analyses it was established that the SOF_2 molecule, like the $SOCl_2$ and $SOBr_2$ molecules, has a pyramidal structure and belongs to the point group of symmetry C_S. The SOF_2 molecule has six fundamental frequencies: four frequencies of the completely symmetrical vibrations (ν_1, ν_2, ν_3, ν_4) and two frequencies of antisymmetrical vibrations (ν_5, ν_6), which appear in both the infrared spectrum and the Raman spectrum.

The Raman spectrum of liquid sulfur oxydifluoride [720, 4358] the infrared spectrum [3134] and the microwave spectrum of gaseous SOF_2 [1552] were investigated.

The infrared spectrum of gaseous SOF_2 was obtained by O'Loane and Wilson [3134] in the range 240-5000 cm^{-1} by means of a prism spectrometer. In paper [3134] the frequencies in the infrared spectrum are

interpreted on the basis of results of earlier studies of the Raman spectrum of liquid SOF_2 [720, 4358] and results of studying the spectra of SO_2, SO_2F_2, $SOCl_2$, SO_2Cl_2, SF_6 and PF_3. The values of the fundamental frequencies of SOF_2 found by O'Loane and Wilson are accepted in the present Handbook and given in Table 83.

The pure rotation spectrum in the microwave range of $S^{32}O^{16}F_2^{19}$ and $S^{32}O^{18}F_2^{19}$ was studied by Ferguson [1552] who determined the values of the rotational constants of these molecules as wellll as the dipole moment and the structural parameters of the SOF_2 molecule. The values of the rotational constants of the molecule $S^{32}O^{16}F_2^{19}$ (A_{000} = 0.287357, B_{000} = 0.278758, C_{000} = 0.165213 cm^{-1}) obtained in paper [1552] are used in the Handbook in order to calculate the product of the principal moments of inertia of SOF_2 whose values are given in Table 83. The corresponding values of the structural parameters of SOF_2 are, according to Ferguson, the following: r_{S-O} = 1.412 ± 0.001, r_{S-F} = 1.585 ± 0.001 Å, < F-S-F = 92°49′ ± 5′, < O-S-F = 106°49′ ± 5′.

$\underline{SO_2F_2}$. The SO_2F_2 molecule pertains to the point group of symmetry C_{2v} and has nine fundamental frequencies: four frequencies of vibrations of the type A_1 (ν_1, ν_2, ν_3, ν_4), one frequency of torsion oscillations of the type A_2 (ν_5) and the frequencies ν_6, ν_7 and ν_8, ν_9 of vibrations of the types B_1 and B_2. All fundamental frequencies of SO_2F_2 are active in the Raman spectrum. In the infrared spectrum all frequencies appear with the exception of ν_5.

The infrared spectrum of gaseous SO_2F_2 was investigated by Perkins and Wilson [3222] in the range 539-3000 cm^{-1} and Hunt and Wilson [2158a] in the range 250-4000 cm^{-1}. The Raman spectra of liquid and gaseous SO_2F_2 were studied by Bender and Wood [720] The microwave spectrum of SO_2F_2 was studied in papers [1619, 2611].

Perkins and Wilson [3222] were the first who interpreted the in-

frared vibration spectrum of SO_2F_2; they determined the values of all the fundamental frequencies except ν_4 which was estimated in paper [3222] to amount to about 300 cm^{-1}. The frequency of torsion oscillations, ν_5, was estimated as equal to 385 cm^{-1} on the basis of the relationships between the band at 767 cm^{-1} and the harmonic $2\nu_5$.

In the Raman spectrum of SO_2F_2 gas Bender and Wood [720] observed six bands with the centers at 388, 543, 847, 883, 1270 and 1502 cm^{-1} which were attributed to the frequencies ν_5 and ν_9, ν_3 and ν_7 (the broad band with the center at 543 cm^{-1}), ν_2, ν_8, ν_1, ν_6, respectively. In paper [2611] it was tried to determine the frequency ν_4 by way of analyzing the rotational transitions in excited vibrational states of SO_2F_2, observed in the microwave spectrum. In this paper a value of 388 ± 15 cm^{-1} was suggested for the frequency ν_4.

The correctness of the frequency relations of the vibrational spectrum of SO_2F_2 suggested by Perkins and Wilson [3222] was doubted by Stammreich, Kowai and Tavares [3838] in connection with their investigations of the Raman spectrum of CrO_2Cl_2. This induced Hunt and Wilson [2158a] again to study the infrared spectrum of SO_2F_2 in a wider temperature range. In the long-wave part of the infrared spectrum they discovered bands at 274, 386 and 539 cm^{-1} not observed previously, which were attributed to the frequencies ν_4, ν_9 and ν_7, respectively. In paper [3222] the frequencies ν_9 and ν_7 were falsely attributed to the bands at 539 and 553 cm^{-1}. According to the reinterpretation of the infrared spectrum of SO_2F_2 in paper [2158a] the band at 553 cm^{-1} corresponds to the frequency ν_3. The frequency of the torsion oscillation, ν_5, was determined by Hunt and Wilson as 360 cm^{-1} by way of attributing the band at 720 cm^{-1} to the harmonic frequency $2\nu_5$. The band at 388 cm^{-1} observed previously in the Raman spectrum [720] was falsely attributed to the frequency ν_5, whereas actually it corresponds to the

frequency ν_9. With only four fundamental frequencies (ν_1, ν_2, ν_6, ν_8) the interpretations agreed with those given in papers [3222, 2158a].

In the present Handbook the data recommended by Hunt and Wilson [2158a] on the basis of their studies (cf. Table 83) are used for the the fundamental frequencies of the SO_2F_2 molecule.

The structure of the SO_2F_2 molecule was first determined by Stevenson and Russel [3861] on the basis of own electron-diffraction studies. In paper [3861] the following values were obtained for the structural parameters of SO_2F_2: $r_{S-O} = 1.43 \pm 0.02$ Å, $< O-S-O = 130 \pm 10°$, $< F-S-F = 100 \pm 8°$. Later on the structural parameters of the SO_2F_2 molecule were determined from the microwave spectra in the papers [1619, 2611]. In paper [1619] for the S-O bond length a value was obtained which deviates considerably from that found in electron diffraction studies [3861] which is attributed to the subsequent, more accurate and careful investigation of the microwave spectrum of SO_2F_2 in paper [2611].*

Lide, Mann and Fristrom [2611] measured very accurately the frequencies of the rotational transitions in the vibrational ground states of the molecules of $S^{32}O_2F_2$ and $S^{34}O_2F_2$ and $S^{32}O_2F_2$ and the frequencies of the rotational transitions in excited vibrational states of the molecule $S^{32}O_2F_2$. On the basis of these data in paper [2611] the following values were obtained for the rotational constants of the vibrational ground state: $S^{32}O_2F_2$: $A_{000} = 0.171260$, $B_{000} = 0.169218$, $C_{000} = 0.168684$ cm^{-1}.

The values of the products of the principal moments of inertia of SO_2F_2 given in Table 83 were calculated from the values of the rotational constants determined in paper [2611], taking into account the occurrence in nature of the stable isotopes of sulfur.

The values of the rotational constants of $S^{32}O_2F_2$ and $S^{34}O_2F_2$ obtained in paper [2611] correspond to the following values of the

structural parameters: $r_{S-O} = 1.405 + 0.003$ Å, $r_{S-F} = 1.530 \pm 0.003$ Å, $< O-S-O = 123°58' \pm 12'$, $< F-S-F = 96°7' \pm 10'$.

§49. THE THERMODYNAMIC FUNCTIONS OF THE GASES

The thermodynamic functions of gaseous S, S_2, SO, SH, SF, SO_2, SO_3, S_2O, H_2S, SF_2, SF_4, SF_6, SOF_2 and SO_2F_2 were calculated in the temperature interval fo 293.15-6000°K without allowing for the intermolecular interaction and are given in Tables 77-90 of Vol. II of the Handbook. All calculations were based upon the values of the molecular constants accepted in the foregoing section. In the calculations sulfur was assumed to be in its natural isotope composition, but the differences in the values of the molecular constants of the isotope modifications of the molecules were not taken into account since the errors they cause in the values of the thermodynamic functions are smaller than the errors due to other causes.

For sulfur dioxide and sulfur hexafluoride Tables 399 and 400 of Vol. II of the Handbook give the values of the virial coefficients and their derivatives which make it possible to take into account the influence of intermolecular interaction on the influence of intermolecular interaction on the values of the thermodynamic functions of these gases.

S. The thermodynamic functions of monatomic sulfur, calculated from Eqs. (2.22) and (2.23) in the temperature interval 293.15-6000°K, are given in Table 77 (II). The values of the constants A_Φ and A_S were assumed to amount to 3.0544 and 8.0223 cal/g-atom·deg, respectively. The electron components were calculated by direct summation over the energy levels of the S atom which are given in Table 77. The errors of the calculated values of Φ_T^* do not exceed 0.003 cal/g-atom·deg and are mainly due to inaccuracies of the values of physical constants used. The error of the value of Φ_{6000}^*, which is due to the fact that levels

with energies higher than 50,000 cm^{-1} were neglected, is equal to 10^{-4} cal/g-atom·deg.

The thermodynamic functions of monatomic sulfur were calculated for the first time by Montgomery and Kassel [2940] (Φ_T^* up to 5000°K) and Kelly [2357, 2364] (C_p° up to 5000°K and $S^\circ_{298.15}$). According to the values of C_p° of monatomic sulfur, calculated by Kelley [2357], interpolation equations were then derived and used to calculate the values of the other thermodynamic functions of S. In this way tables of the thermodynamic functions of monatomic sulfur were compiled in the papers of Kelley [2363] and Wunderlich [4345], which are used in Zeise's handbook [4384]. In Brewer's resumé [1093] the results of calculations of Montgomery and Kassel [2940] and Kelley [2357] are given.

In the calculations of the thermodynamic functions of monatomic sulfur Montgomery and Kassel [2940] and Kelley [2357] took into account only the electron ground state ^3P of the sulfur atom. The neglection of the higher energy levels of the sulfur atom caused a deviation in the values of the thermodynamic functions given in the papers [2940, 2357, 2363, 4345, 4384, 1093] and in Table 77 (II) which amounts to 0.01 and 0.1 cal/g-atom·deg in the values of Φ^*_{3000} and Φ^*_{5000}, respectively.

The thermodynamic functions of monatomic sulfur were also calculated by Goff and Gratch [1787] (S_T° for S^{32} up to 2778°K), Evans and Wagman [1516] (Φ_T^* and S_T° up to 5000°K), Katz and Margrave [2334] (Φ_T^* up to 2000°K) and Kolsky, Gilmer and Gilles [2462] (Φ_T^* up to 8000°K). In the handbook of the US NBS [3680] values are given for the thermodynamic functions of S which are very close to the values published in paper [1516].

In the papers [1787, 1516, 2334, 2462] the thermodynamic functions of monatomic sulfur were calculated taking account of the excited electron states of the S atom. The slight deviations from the corresponding

values given in Table 77 (II) are due to differences in the values of the physical constants.*

The differences between the values of the thermodynamic functions of monatomic sulfur, given in Table 77 (II) and those in the corresponding table of the first edition of the Handbook are also caused by differences in the used values of the physical constants.

S_2. The thermodynamic functions of diatomic sulfur, given in Table 78 (II), were calculated from Eqs. (2.161) and (2.162). The values of $\ln \Sigma$ and $T\frac{\partial}{\partial T}\ln\Sigma$ in these equations were calculated by means of the Gordon-Barnes method (Eqs. (2.137), (2.138)) without allowing for the limitation of summation over the rotational energy levels. The S_2 molecule has an electron ground state of the type $^3\Sigma_g^-$. The splitting of the rotational levels of S_2 in this state were taken into account according to Eqs. (2.147) and (2.148). All calculations were made with the molecular constants given in Table 78.**

The excited electron states $a^1\Delta_g$, $b^1\Sigma_g^+$, $A^3\Delta_u$, $B^3\Sigma_u^+$, $c^1\Sigma_u^-$ and $C^3\Sigma_u^-$ of the S_2 molecule were taken into account by means of Eqs. (2.120) (2.121), i.e., under the supposition that the statistical sum with respect to the vibration-rotation levels of all electron states has the same value as with the electron ground state.

The quantities entering the formula used to calculate the thermodynamic functions of S_2 are given in Table 84.

The errors of the calculated values of Φ_T^* are equal to 0.1, 0.1 and 0.3 cal/mole·deg at T = 300, 3000 and 6000°K, respectively. At low temperatures the errors are mainly due to inaccurate allowing for the $^3\Sigma$ -type ground state. At high temperatures they are due to inaccuracies of the used values of excitation energies of the electron states and to the fact that the accepted values of the vibrational constants give a bad description of the energies of the high vibrational levels

of the states $X^3\Sigma$ [the dissociation energy of S_2 found by experiment differs from that obtained by linear extrapolation (cf. page 650)].

The thermodynamic functions of a diatomic medium was previously calculated by Montgomery and Kassel [2940], Godnev and Sverdlin [158] and Evans and Wagman [1516].

Montgomery and Kassel [2940] calculated the vales of Φ_T^* from 250 to 5000°K by means of Kassel's method [2333], using the molecular constants of S_2 found by Naudé and Christy [3027, 1105]. The multiplet structure of the $X^3\Sigma$ state of S_2 is taken into account by the term R ln 3, the excited electron states of S_2 are neglected. The vibrational states of S_2, used in the calculations of Montgomery and Kassel, are close to the values accepted in the present Handbook, but for the rotational constant an incorrect value was chosen. The error in determining the value B_e of the S_2 molecule, obtained by Naudé and Christy [3027, 1105] was discovered by Badger [598] who found $r_e(S_2) = 1.84$ Å.* In connection with this Cross [1226] calculated the corrections to the values of Φ_T^*, calculated by Montgomery and Kassel [2940]. Later on the values of Φ_T^* of diatomic sulfur, based on the calculations of Montgomery and Kassel and allowing for the corrections to them found by Cross, were given in the Handbooks by Kelley [2357], Ribaud [3426], Zeise [4384] and in Brewer's paper [1093].

Godnev and Sevrdlin [158] calculated the thermodynamic functions of S_2 in the temperature interval 100-5000°K using the same molecular constants as Montgomery and Kassel [2940]. Unlike the latter authors, Godnev and Sverdlin, in order to calculate the thermodynamic functions of S_2, used the method of immediate summation over the vibrational and rotational energy levels applying the recurrence formulas of Johnston and Chapman [2273]. They took into account the multiplet splitting of the rotational levels of the $X^3\Sigma_g^-$ state. But the authors of paper [158]

knew only the value of the constant $\gamma = -0.1$ cm^{-1} [3027]. They assumed that the value of the constant ε was equal to zero. As mentioned in paper [158], there is virtually no difference between the values of the thermodynamic functions of S_2, compared with the simpler consideration of the multiplet nature of the $X^3\Sigma_g^-$ state with the help of the term R ln 3. Just as Montgomery and Kassel [2940], Godnev and Sverdlin did not take the excited electron states of S_2 into account. The values of C_p° of diatomic sulfur, calculated by Godnev and Sverdlin [158] are used in Kelley's handbook [2357]. Starting from the results of these calculations, Kelley [2357] derived an interpolation equation for C_p° which was then used by Brewer [1093] and Wunderlich [4345] to calculate the entropy of S_2. The values of S_T°, calculated by Wunderlich are given in Zeise's handbook [4384]. Similar values of S_T° for S_2 may be found in Ribaud's handbook [3426].

Evans and Wagman [1516] calculated the thermodynamic functions of S_2 up to 1500°K from the molecular constants given in Herzberg's book [2020]. The calculations were carried out by means of the method of Mayer and Goeppert-Mayer (see p. 159) without taking into account the multiplet splitting of the rotational energy levels of the electron ground state and without considering the excited electron states of S_2. The values of the thermodynamic functions of S_2, calculated by Evans and Wagman [1516] are given in the handbooks [3680, 119a, 3894].*

The thermodynamic functions of S_2 contained in the first edition of the Handbook were calculated with the same molecular constants of the electron ground state $X^3\Sigma_g^-$, as are used in the present edition. The Gordon-Barnes method was applied in the calculations, the multiplet nature of the $^3\Sigma_g^-$ state was taken into account approximately through the term R ln 3. In the calculations the excited electron state $C^3\Sigma_\mu^-$ was also taken into account, whereas the electron states with lower

excitation energies, not observed in the spectrum of S_2, were ignored.

The deviation of the values of the thermodynamic functions of S_2, given in the papers [2940, 158, 1516] and in the handbooks [2357, 4384, 3426, 3680, 3894, 420], from the corresponding values of Table 78 (II) is mainly due to the fact that in the present Handbook we took into account the splitting of the electron ground state $X^3\Sigma_g^-$ into substates and also considered the excited electron states of S_2. Moreover, the differences in the values of the thermodynamic functions are attributed to the fact that in earlier calculations other values of the molecular constants of S_2 and of the universal physical constants were used. The values given in Table 78 (II) agree best with the values of the thermodynamic functions of S_2 given in the first edition of the Handbook, in paper [1516] and in the handbooks [3680, 3894]. The greatest differences are to be observed between the values of the thermodynamic functions of S_2 calculated by Montgomery and Kassel [2940] and those obtained by Godnev and Sverdlin [158]; this is attributed to the fact that these authors used incorrect values of the rotational constants of the S_2 molecule in their calculations.

The differences between the values of the thermodynamic functions of S_2, given in the first edition of the Handbook and those of Table 78 (II) are due to the fact that we took into account the splitting of the $X^3\Sigma$ states into substates and the states $a^1\Delta_g$, $b^1\Sigma_g^+$, $A^3\Delta_u$, $B^3\Sigma_u^+$ and $c^1\Sigma_u^-$; in the values of Φ_T^* 0.91, 0.22, and 0.56 cal/mole·deg at T = 298.15, 3000 and 6000°K, respectively. The values of the thermodynamic functions of S_2 given in the present Handbook and in papers [1516, 3680, 3894] differ by about the same values.

SO. The thermodynamic functions of sulfur monoxide, given in Table 79 (II) were calculated from Eqs. (2.161), (2.162). The values of ln Σ and $T\frac{\partial}{\partial T}\ln\Sigma$ in these equations were calculated by means of

the Gordon-Barnes method [cf. Eqs. (2.137), (2.138)] without allowing for the limitation of summation over the rotational energy levels. In calculating the thermodynamic functions of SO the multiplet nature of the electron ground state $X^3\Sigma^-$ was taken into account by means of the term R ln 3 in the values of C_Φ and C_S, the excited electron states were taken into account under the assumption that the statistical sum over the vibration-rotation levels is for all electron states equal to that of the ground state [cf. Eqs. (2.120), (2.121)]. All calculations were based on the molecular constants of SO given in Table 78)

The constants entering the formula for calculating the thermodynamic functions of SO are given in Table 84.

TABLE 84

Values of the Constants Used in Calculations of the Thermodynamic Functions of Gaseous S_2, SO, SH and SF

1 Вещество	θ	$x \cdot 10^6$	$\beta_1 \cdot 10^6$	$\beta_2 \cdot 10^6$	$\frac{q_0}{T}$	$\frac{d_0}{T} \cdot 10^6$	C_Φ	C_S
	2 *град*				3 *град*$^{-1}$		4 *кал/моль·град*	
S_2	1044,10	3,927	0,5429	0,30	2,3584	3,153	7,3030	12,2711
SO	1652,00	5,327	0,7833	0,63	0,96886	3,06	6,3804	13,3359
SH	3873	17,682	3,0864	9,53	0,073462	7,45	5,9007	10,8689
SF	1165	—	—	—	—	—	7,6781	14,6336

1) Substance; 2) degree; 3) deg^{-1}; 4) cal/mole·deg.

The errors in the values of Φ_T^* contained in Table 79 (II) are estimated to amount to 0.4, 0.05 and 0.15 cal/mole·deg at T = 300, 3000 and 6000°K, respectively. At low temperatures (T < 1000°K) the errors in the thermodynamic functions of SO are mainly due to the fact that the splitting of the rotational levels of the $^3\Sigma^-$. At high temperatures the errors are chiefly caused by inaccuracies of the values chosen for the excitation energies of the electron states and the fact that the used values of the vibrational constants give a bad description of the energies of the vibrational levels which are close to the dissociation limit. This fact is proved by the considerable divergence

between the value of the dissociation limit of the SO molecule corresponding to the values accepted for the vibrational constants, and the value of the dissociation energy of SO (cf. page 651).

The thermodynamic functions of gaseous sulfur monoxide were previously calculated by Montgomery and Kassel [2940] (Φ_T^* up to 5000°K), Kelley [2357, 2363], (C_p°, $H_T^\circ - H_{298.16}^\circ$ and $S_T^\circ - S_{298.16}^\circ$ up to 5000°K), Zeise [4384] (S_T° up to 3000°K), Evans and Wagman [1516, 3680] (up to 1500°K) and the authors of the first edition of the present Handbook. All these papers used values of the molecular constants of SO found by Martin [2787] which differ from those used in the present Handbook. A characteristic feature of the thermodynamic functions of SO, given in the present Handbook, consists in the fact that it was the first time that they were calculated with the excited electron states of SO with comparatively low excitation energies taken into account, states which have not been observed as yet in the spectra. The approximate consideration of the multiplet nature of the electron ground state through the term R ln 3 is a common feature of all calculations of thermodynamic functions of SO.

It must be noted that in the papers [2940, 2357, 4345, 1516, 420] different methods were used to calculate the thermodynamic functions of SO and different values of the physical constants were applied. The thermodynamic functions of SO, given in the first edition of the Handbook, are most similar as to the method of calculation and the used values of the physical constants to those in the present Handbook. The differences in the values of Φ_T^* in the first and in the present editions of the Handbook amount to 0.032, 0.003 and 0.258 cal/mole·deg at T = 298.15, 3000 and 6000°K, respectively. At low temperatures this deviation is mainly due to the differences in the used values of the molecular constants, at high temperatures it is due to the fact that a

series of excited electron states of SO with comparatively low excitation energies have been taken into account in the present edition of the Handbook.

SH. The thermodynamic functions of hydrosulfite, given in Table 83 (II) were calculated from Eqs. (2.161) and (2.162) The values of $\ln \Sigma$ and $T\frac{\partial}{\partial T}\ln\Sigma$ in these equations were calculated by means of the Gordon-Barnes method [cf. Eqs. (2. 137), (2.138), the values of $\ln \Delta_M$ and $T\frac{\partial}{\partial T}\ln\Delta_M$ were calculated from Eqs. (2.149) and (2.150). In the calculations the excited electron state $A^2\Sigma^+$ is also taken into account. The calculations were based on the values of the molecular constants of SH, given in Table 78. The values of the constants in the formulas used to calculate the thermodynamic functions of SH are given in Table 84.

The errors in the values of the thermodynamic functions of SH are due to inaccuracies of the molecular constants, mainly to that of the value of the constant $\omega_e x_e$ given in Table 78, which was estimated as $\pm$ 5 cm^{-1}. The errors of the calculated values of Φ_T^* at $T \leq 3000°K$ do not exceed 0.02 cal/mole·deg as the error of the value of Φ_{6000}^* was estimated as 0.06 cal/mole·deg.

The thermodynamic functions of SH were previously calculated by Haar and Friedman [1910] with the help of an electronic computer. The authors of paper [1910] derived formulas in order to calculate the thermodynamic functions of diatomic perfect gases in cases where the electron ground states of the molecules are of the type $^2\Pi$. The equation given by Hill and Van-Vleek, (1.25), for the rotational energy levels, was used in the derivation. The formulas used in paper [1910] are equivalent to the formulas derived by Khachkuruzov and Brounshteyn [445] (cf. page 171). Unlike the latter authors, Haar and Friedman took into account a series of terms in the expressions for the statistical

sum over the rotational states which are additional terms to the Euler-Macloren formula and are significant only at low temperatures. For SH and T = 298.15°K these terms are negligibly small so that they were not allowed for in calculating Table 83 (II). The centrifugal distortion, the anharmonicity of vibrations and the vibration-rotation interaction in SH were taken into account in paper [1910] according to the method by Mayer and Goeppert-Mayer [285] (cf. page 159), using the molecular constants obtained by Ramsay [3356]. The values of the thermodynamic functions of SH up to 3000°K obtained by Haar and Friedman [1910] differ from the corresponding values of table 83 (II) by at most 0.004 cal/mole·deg for Φ_T^* and 0.008 cal/mole·deg for S_T°. With T > 3000°K the thermodynamic functions of SH have, according to Haar and Friedman, lower values than assumed in the present Handbook which is explained by the minor accuracy of the method of calculation used in paper [1910].

The differences in the values of the thermodynamic functions of SH between the present and the first editions of the Handbook are due to the fact that different values have been used for the molecular constants; with T = 298.15, 3000 and 6000°K they amount to 0.005, 0.04 and 0.06 cal/mole·deg with Φ_T^* and 0.006, 0.07 and 0.09 cal/mole·deg, respectively, with S_T°.

SF. The thermodynamic functions of sulfur monofluoride, given in Table 85 (II), are calculated from Eqs. (2.161) and (2.162) in the approximation of the harmonic oscillator-rigid rotator model. The molecular constants used in the calculations are given in Table 78. The values of the constants in the equations used to calculate the thermodynamic functions of SF are given in Table 84.

The errors of the calculated values of Φ_T^* amount to 0.07, 0.5 and 0.6 cal/mole·deg at T = 298.15, 3000 and 6000°K, respectively, and are due to inaccuracies in the values chosen for the molecular constants and disregard of the vibration anharmonicity of SF. The disagreement between the thermodynamic functions of SF calculated in the First and Second Editions of the Handbook (from 0.01 to 0.15 cal/mole·deg) are due to the fact that different values of the molecular

constants (particularly of ω_e) were used in the calculations.

In literature there are no data on other calculations of the thermodynamic functions of SF.

SO_2. The thermodynamic functions of gaseous sulfur dioxide given in Table 80 (II) were calculated according to Eqs. (2.243) and (2.244) in the approximation of the anharmonic oscillator-rigid rotator model, with molecular constants given in Table 79. In the calculations of the thermodynamic functions the anharmonicity of the SO_2 molecule's vibrations were taken into account by means of Gordon's method [cf. Eqs. (2.185), (2.186)]. The values of the constants used in calculating the thermodynamic functions of SO_2 are given in Table 85.

TABLE 85

Values of the Constants Used to Calculate the Thermodynamic Functions of SO_2.

1 Постоянная	2 Значение	1 Постоянная	2 Значение	1 Постоянная	2 Значение
θ_1, град 3	1668,26	$y_{12} \cdot T$, град 3	2,949	$\sigma_C T$, град 3	0,42224
θ_2, град 3	752,760	$y_{13} \cdot T$, град 3	19,722	$\frac{1}{3}\sigma_{BC} T$, град 3	0,15241
θ_3, град 3	1973,773	$y_{23} \cdot T$, град 3	5,610	$\frac{\sigma_B^2 \sigma_C}{12\,\sigma_A} T$, град 3	0,005974
x_1	0,003440	$q_0 T^{-1/2}$, град$^{-1/2}$ 3	2,27002	A_Φ, кал/моль·град 4	5,1174
x_2	0,005733	$\sigma_A T$, град 3	2,91637	A_S, кал/моль·град 4	10,0853
x_3	0,003768	$\sigma_B T$, град 3	0,49509		

1) Constant; 2) value; 3) deg. 4) cal/mole·deg.

The errors in the calculated values of the thermodynamic functions of SO_2 are at 298.15°K mainly due to inaccuracies in the values of the molecular constants used, to the neglection of the differences in the molecular constants of the isotope modifications of the SO_2 molecule* and to the inaccuracy of the values used for the physical constants. The errors in the values of the thermodynamic functions of SO_2 at 3000°K are chiefly caused by the fac that the interaction between vibration and rotation was not taken into account and at 6000°K

they are due to the latter cause and to the neglection of the limitation of summation over the rotational energy levels. The total errors in the value of Φ_T^* at T = 298.15, 3000 and 6000°K amount to 0.01, 0.15 and 0.5 cal/mole.deg, respectively.

The thermodynamic functions of gaseous sulfur dioxide were first found from Gordon's molecular constants [1804] (Φ_T^* from 298.16-2800°K) and with those given by Cross [1227] (from 298.1 to 1800°K) in the approximation of the harmonic oscillator-rigid rotator model. Gordon's calculations [1804] were based upon incorrect values of the moments of inertia of SO_2, taken from paper [2183]. This explains the deviation of the values of Φ_T^*, obtained in papers [1804, 1227] amounting to 0.4 cal/mole·deg. Cross' calculations of the thermodynamic functions of SO_2 [1227] were based on values of the moments of inertia from [1228] and the fundamental frequencies from [602] which were similar to those used in the present Handbook. The thermodynamic functions of SO_2 calculated by Cross [1227] are used in the Handbooks [2357, 4384, 3426, 4365, 2312] and in the review article [1093]. Kelley [2357] extended Cross' calculations [1227] of the specific heat of SO_2 up to 3000°K and derived an empirical equation which he used later in order to calculate $H_T^\circ - H_{298}^\circ$ and $S_T^\circ - S_{298}^\circ$ [2363]. The values of the thermodynamic functions of SO_2, given in the Handbook [137], are close to the corresponding values in Cross' paper [1227]. The differences between the values of Φ_T^* and S_T° of sulfur dioxide obtained by Cross [1227] and used in the present Handbook (up to 1800°K) amount of 0.1 cal/mole·deg and are chiefly caused by the application of different values of the molecular and physical constants.

The thermodynamic functions of SO_2 were calculated with the anharmonicity of vibrations taken into account, by Evans and Wagman [1516] (up to 1500°K), using molecular and physical constants close to those

accepted in the present Handbook. These authors, however, did not know the experimental values of the constant of anharmonicity of SO_2 determined in 1953 by Shelton, Nielsen and Fletcher [3699]. In paper [1516] the constants of anharmonicity of SO_2 were estimated approximately from the equation $x_{ij} = 0.003\ (\nu_i + \nu_j)$ where ν_i, ν_j denote the fundamental frequencies of SO_2 while the proportionality factor was calculated on the basis of the corresponding data for SO. Evans and Wagman took the anharmonicity of vibrations of SO_2 into account by means of the method of Mayer and Goeppert-Mayer which was extended by Stockmayer, Kavanagh and Mickley [3871] to multiatomic molecules. The Handbook of the US NBS [3680] gives for SO_2 the results of calculations by Evans and Wagman [1516] reduced by 0.02 cal/mole·deg (with Φ_T^* and S_T^c). The values of Φ_T^* and S_T° obtained for SO_2 by Evans and Wagman [1516] and those given in the present Handbook differ by at most 0.01 cal/mole.deg.*

The thermodynamic functions of SO_2 given in the present Handbook and those of its first edition are identical.

Giauque and Stevenson [1719] measured the specific heat of sulfur dioxide from 15 to 264°K and on the basis of these data the entropy of gaseous sulfur dioxide was calculated, $S^\circ_{298.15} = 59.24 \pm 0.10$ cal/ /mole.deg, a value that was accepted in Kelley's handbook [2363]. The value of $S^\circ_{298.15}$, found by Giauque and Stevenson agrees within the limits of error of determination with the value calculated in the present Handbook from molecules constants of SO_2.

S_2O. The thermodynamic functions of sulfur semioxide, given in Table 82 (II), were calculated from Eqs. (2.243) and (2.244) in the approximation of the harmonic oscillator-rigid rotator model, using the molecular constants given in Table 80. The values of the constants used in calculating the thermodynamic functions of S_2O are given in

Table 87.

The errors in the values of the thermodynamic functions of S_2O are chiefly due to neglecting the anharmonicity of the vibrations of the S_2O molecule and inaccurate values of the frequency ν_2 of deformation oscillation given in Table 80. The total error in the values of Φ_T^* at 298.15, 3000 and 6000°K was estimated as amounting to 0.4, 1.5 and 2.0 cal/mole·deg, respectively.

The thermodynamic functions of S_2O have not been calculated previously.

$\underline{SO_3}$. The thermodynamic functions of gaseous sulfur trioxide given in Table 81 (II), were calculated in the approximation of the harmonic oscillator-rigid rotator model from Eqs (2.243) and (2.244) with the molecular constants given in Table 80. The values of the constants used to calculate the thermodynamic functions of SO_3 are given in Table 87.

The errors in the values of the thermodynamic functions of SO_3 are chiefly due to inaccurate values of the molecular constants and neglection of the anharmonicity of molecular vibrations. The errors due to these causes were estimated for Φ_T^* at 298.15, 3000 and 6000°K as 0.3, 0.8 and 1.0 cal/mole·deg, respectively.

Earlier determinations of the thermodynamic functions of gaseous sulfur trioxide [854, 454] were based on experimental data of the equilibrium constants of the oxidation reaction of SO_2 to SO_3. Calculations of the thermodynamic functions of gaseous sulfur trioxide were carried out by Stevenson,* Fontana** (up to 1500°K) and Stockmayer, Kavanagh and Mickley [3871] (up to 1200°K), using the molecular constants of SO_3. Stevensen and Fontana calculated the thermodynamic functions of SO_3 in the approximation of the harmonic oscillator-rigid rotator model, wheras Stockmayer, Kavanagh and Mickley tried in

in their calculations to consider approximately the anharmonicity of molecular vibrations. All these calculations were based upon identical values of the structural parameters of the SO_3 molecule, determined by the electron diffraction method by Palmer [3170], which are also accepted in the present Handbook. Khachkuruzov [443] showed that incorrect values were used for the fundamental frequencies of the SO_3 molecule in the calculations of Stevenson, Fontana and the authors of paper [3871].

The choice of incorrect values of the fundamental frequencies of SO_3 by the authors of paper [3871] is partly compensated by the consideration of the vibrational anharmonicity. Using the values suggested by Stevenson (cf. page 609) for the fundamental frequencies of the SO_3 molecule, the authors of paper [3871] determined the constants of anharmonicity of SO_3 on the basis of experimental values of the equilibrium constants of the reaction (13.1). The "constants of anharmonicity" of the SO_3 molecule found in this way and the values of the fundamental frequencies accepted in paper [3871] were used by Stockmayer, Kavanagh and Mickley in order to calculate the thermodynamic functions of gaseous sulfur trioxide according to the method by Mayer and Goeppert-Mayer.

Evans and Wagman [1516] extended the calculations of the authors of paper [3871] to 1500°K and introduced corrections for the changed values of the physical constants. At T = 298.15, 1000 and 1500°K the differences in the corresponding values of Φ_T^* given in paper [1516] and in Table 81 (II) amount to 0.160, 0.086 and 0.180 cal/mole·deg, respectively, and the values of S_T° differ at the same temperatures by 0.337, 0.379 and 1.175 cal/mole·deg. The differences in the values of Φ_T^* at T = 298.15, 1000 and 1500°K, given in the handbooks [4384, 3426] (based on Fontana's calculations), and those of Table 81 (II), amount

to 0.21, 0.58 and 0.67 cal/mole·deg, respectively.

The thermodynamic functions of gaseous sulfur trioxide, calculated in papers [3871, 1516] are given in many review articles and in the handbooks [3508, 3680, 2364, 149, 119a]. In the first edition of the present Handbook sulfur trioxide has not been considered.

H_2S. The thermodynamic functions of hydrogen sulfide, given in Table 84 (II) were calculated, taking into account the anharmonicity of vibrations, the interaction between vibrations and rotations and the centrifugal distortion of the H_2S molecule. The calculations were carried out according to Gordon's method* [cf. Eqs. (2.185), (2.186)] on the basis of molecular constants given in Table 82. The centrifugal distortion of the H_2S molecule was taken into account according to Eqs. (2.222), (2.223). The values of the constants in Eqs (2.185), (2.186) used in the calculations of the thermodynamic functions of H_2S are given in Table 86.

TABLE 86

Values of the Constants Used in the Calculations of the Thermodynamic Functions of H_2S

1 Постоянная	2 Значение	1 Постоянная	2 Значение	1 Постоянная	2 Значение
θ_1, *град* 3	3834,00	$y_{22}T$, *град* 3	30,344	b_{11}	0,000184
θ_2, *град*	1718,09	C'_{999} *град*	2,269	b_{22}	0,000742
θ_3, *град*	3849,45	p_1, *град*$^{-1}$	$1,90 \cdot 10^{-5}$	b_{33}	0,000356
x_1	0,009416	p_3, *град*$^{-2}$	$0,22 \cdot 10^{-4}$	c_{113}	—0,001195
x_2	0,004790	$q_0 T^{-3/2}$, 3 *град*$^{-3/2}$	0,048888	c_{133}	0,000484
x_3	0,003970	a_1	0,023832	c_{333}	—0,000348
$y_{12}T$, *град* 3	28,330	a_2	—0,022924	$A\Phi$, *кал/моль·град* 4	3,2354
$y_{13}T$, *град*	136,22	a_3	0,020298	AS, *кал/моль·град* 4	8,2035

1) Constant; 2) value; 3) degree; 4) cal/mole.deg.

The errors in the values of the thermodynamic functions of H_2S, given in Table 84 (II) for temperatures below 2000°K are chiefly caused by inaccuracies of the values used for the molecular constants, while at temperatures, exceeding 2000°K, they are due to the fact that the

number of levels of rotational energy was not limited. The total errors of the values of Φ_T^* at 298.15, 3000 and 6000°K were estimated as 0.02, 0.15 and 0.4 cal/mole·deg.

The thermodynamic functions of hydrogene sulfide were calculated by means of the molecular constants of H_2S obtained by Cross [1226] (from 212.77 to 1800°K), Evans and Wagman [1516] (to 1500°K) and Haar, Bradley, and Friedman [1909] (from 50 to 5000°K).

Cross [1226] calculated the thermodynamic functions of H_2S in the approximation of the harmonic oscillator - rigid rotator model on the basis of values of the moments of inertia he found on analyzing the fine structure of bands in the vibrat on-oscillation spectrum [1224, 1225]* and approximate values of the fundamental frequencies ($\nu_1 = \nu_3 = 2620$, $\nu_2 = 1260$ cm^{-1}). The values of the thermodynamic functions of H_2S, calculated by Cross, are given in the handbooks [2364, 2363, 4384, 3426, 2312].** Brewer [1093] corrected the results of Cross' calculations [1226] for the centrifugal distortion of the H_2S molecule. Owing to the approximate method of calculation and the inaccuracy of the used values of molecular constats, the values of Φ_T^* and S_T° obtained by Cross for T = 298.15 – 1800°K are smaller than the corresponding quantities of Table 84 (II) by 0.01–0.3 cal/mole·deg.

Evans and Wagman [1516] calculated the thermodynamic functions of H_2S on the basis of the vibrational constats obtained by Allen, Cross and King [504]. In the calculation the vibrational anharmonicity was taken into account according to the method of Mayer and Goeppert-Mayer. The rotational components of the thermodynamic functions were calculated in the approximation of the rigid rotator but allowing for centrifugal distortion of the molecule according to Eq. (2.220). The differences in the values of Φ_T^* and S_T° from 1000 to 1500°K, obtained in paper [1516] and in the present Handbook amount to 0.02 cal/mole·deg and

are chiefly due to differences in the values of molecular constants used. The thermodynamic functions of H_2S, calculated by Evans and Wagman [1516] are given in the handbook of the US NBS [3680] and in Vvedenskiy's book [119a].

Haar, Bradley and Friedman [1909] calculated the thermodynamic function of H_2S, HDS, HTS, D_2S, DTS and T_2S in the temperature interval of from 50 to 5000°K by a method, analogous to the method of Mayer and Goeppert-Mayer, taking into account the centrifugal distortion of the molecules according to Eq. (2.220) and the expression (2.176a) for the statistical sum over the rotational energy levels. The values of the molecular constatns of H_2S, used in the calculations of Haar, Bradley and Friedman, are close to the values, accepted in the present Handbook. Owing the fact that in paper [1909] a less accurate method was used in order to take into account the vibrational anharmonicity, the vibration-rotation interaction and the centrifugal distortions of the molecules, however, the values of the thermodynamic functions of H_2S obtained in paper [1909] and in the present Handbook, diverge considerably at high temperatures. Thus, for example, the difference between the values of Φ^*_{5000} and S°_{5000} amounts to 0.2 and 0.6 cal/mole·deg, respectively.

The thermodynamic functions of hydrogen sulfide were not calculated in the first edition of the Handbook.

$\underline{SF_2}$, $\underline{SF_4}$. The thermodynamic functions of sulfur difluoride and sulfur tetrafluoride, given in Tables 86 (II) and 87 (II), were calculated in the approximation of the harmonic oscillator - rigid rotator model, according to Eqs. (2.243), (2.244), with the molecular constants of SF_2 and SF_4 given in Table 83. The values of the constants C'_Φ and C'_S as well as the value of θ_n, used to calculate the thermodynamic functions of SF_2 and SF_4, are given in Table 87.

The errors in the calculated values of the thermodynamic functions of SF_2 and SF_4 are caused by inaccuracies in the used values of the constants of these molecules and the fact that the vibrational anharmonicity had not been taken into account. With SF_2 the total errors in the values of Φ_T^* at 298.15, 3000 and 6000°K were estimated as 0.3, 1.5 and 2 cal/mole.deg, with SF_4 they amount to 1, 4 and 5 cal/mole·deg.

Previously the thermodynamic functions of SF_2 and SF_4 were calculated when the first edition of the present Handbook was compiled. The values of the thermodynamic functions of SF_2 given in the present edition of the Handbook differ from those given in the first edition by 0.1 to 0.4 cal/mole.deg which is due to the fact that other values have been used for the fundamental vibrational frequencies. The differrences in the values of Φ_T^* and S_T° of sulfur tetrafluoride, given in the first and in the present editions of the Handbook, amount to 1 to 3 cal/mole.deg. These great differences are mainly due to changes in the structural data of the SF_4 moleule as well as in the molecular constants.

$\underline{SF_6}$. The thermodynamic functions of gaseous sulfur hexafluoride given in Table 88 of Vol. II of the Handbook, were calculated in the approximation of the harmonic oscillator - rigid rotator model from Eqs. (2.243), (2.244) and the molecular constants of SF_6 given in Table 83. The values of the constants used in calculating the thermodynamic functions of SF_6 are given in Table 87.

The errors in the values of the thermodynamic functions of SF_6 are chiefly caused by inaccuracies of the used values of molecular constants and the neglection of vibrational anharmonicity. The total errors in the values of Φ_T^* at 298.15, 3000 and 6000°K were estimated as 0.4, 5 and 6 cal/mole.deg, respectively.

TABLE 87

Values of the Constants Used to Calculate the Thermodynamic Functions of SO_3, S_2O, SF_2, SF_4, SF_6, SOF_2, SO_2F_2

Постоянная 1	SO_3	S_2O	SF_2	SF_4	SF_6	SOF_2	SO_2F_2
θ_1, град 2	1538	977	1223	1279	1107	1918	1826
θ_2, град 2	938	532	576	1029	920,1(2)	1163	1220
θ_3, град 2	1918(2)	1676	1151	801	1341(3)	763	796
θ_4, град 2	633(2)	—	—	338	882(3)	590	394
θ_5, град 2	—	—	—	577	751(3)	1076	518
θ_6, град 2	—	—	—	1247	496(3)	561	2161
θ_7, град 2	—	—	—	765	—	—	776
θ_8, град 2	—	—	—	1047	—	—	1273
θ_9, град 2	—	—	—	666	—	—	555
C'_Φ, 3 кал/моль·град	6,1475	9,1545	6,8396	11,3046	8,4489	10,3470	10,4674
C'_S, 3 кал/моль·град	14,0966	17,1036	14,7887	19,2537	16,3980	18,2961	18,4165

1) Constant; 2) degree; 3) cal/mole·deg.

The thermodynamic functions of sulfur hexafluoride were previously calculated by Eucken and Bertram [1499] (C_v° from 273.15 to 573.15°K), Kelley [2363, 2364] ($H_T^\circ - H_{298.16}^\circ$, $S_T^\circ - S_{298.16}^\circ$ from 298.16 to 2000°K and $S^\circ_{298.15}$), Meyer and Buell [2866] (C_p° from 298 to 5000°K) and Gaunt [1659] Φ_T^* and S_T° fro 100 to 500°K). The values of the specific heat of SF_6, calculated by Eucken and Bertram [1499] are given in the Handbook [2312], those calculated by Meyer and Buell [2866] in Zeise's handbook [4384]. In the paper by Eucken and Bertram [1499] a value of $S^\circ_{298.15}(SF_6, \text{gas}) = 69.43$ cal/mole.deg was obtained on the basis of calorimetrical measurements, which approaches the value of $S^\circ_{298.15}$, given in the present Handbook much better than those given in other papers.

The differences between the values of the thermodynamic functions of SF_6, given in the present Handbook and in the papers mentioned above, are mainly due to differences in the used values of the molecular constants, especially in the values taken for the S–F bond length of the SF_6 molecule. The slight differences between the values of the thermo-

dynamic functions of sulfur hexafluoride, given in the first and the present editions of the Handbook are due to the fact that other values were used for the fundamental frequencies of the SF_6 molecule and the physical constants.

$\underline{SOF_2}$, $\underline{SO_2F_2}$. The thermodynamic functions of gaseous SOF_2 and SO_2F_2, given in Tables 89 (II) and 90 (II), were calculated in the approximation of the harmonic oscillator-rigid rotator model with molecular constants, given in Table 83. The values of the constants C'_Φ, C'_S, and the quantity θ_n used in calculating the thermodynamic functions of SOF_2 and SO_2F_2 are given in Table 87.

The errors in the calculated values of the thermodynamic functions of SOF_2 and SO_2F_2 are mainly due to the application of inaccurate values of the molecular constants and the neglection of vibrational anharmonicity. For SOF_2 the total errors in the values of Φ^*_T at 298.15, 3000 and 6000°K were estimated as 0.1, 2.0 and 3.0 cal/mole.deg. and for SO_2F_2 they were 0.2, 3.0 and 4.0 cal/mole.deg, respectively.

The thermodynamic functions of SOF_2 were previously calculated in the approximation of the harmonic oscillator-rigid rotator model by O'Loan and Wilson [3134] (from 273.15 to 1500°K) on the basis of the same values of the thermodynamic constants as are given in the present Handbook. None the less the values of Φ^*_T and S°_T, obtained in paper [3134] differ from those given in the present Handbook by about 6.83 cal/mole.deg which is attributed to an error admitted by O'Loan and Wilson in calculating the thermodynamic functions of SOF_2.

Bockhoff, Petrella and Pace [845a] calculated $S^\circ_{217.78}$ (SO_2F_2, gas) = = 62.63 cal/mole.deg on the basis of results of calorimetrical measurements, and on the basis of calculations according to the molecular constants they obtained a value of 63.24 cal/mole.deg for this quantity. The difference of 0.61 cal/mole.deg observed was attributed by the au-

thors of [845a] to the disordered structure of solid SO_2F_2 at 0°K. It must be noted that Bockhoff, Petrella and Pace used in their calculations incorrect values of the molecular constants of SO_2F_2 so that a value of $S^\circ_{217.78}$ (SO_2F_2, gas) = 64.14 cal/mole·deg was accepted in the present Handbook for the molecular constants. It seems that in the calculations of [845a] incorrect data were used for the structural parameters of the SO_2F_2 which had been obtained in paper [1619] (cf. note to page 627).

In the first edition of the present Handbook SOF_2 and SO_2F_2 were not considered.

§50. THE THERMODYNAMIC QUANTITIES

The standard state of sulfur is S (cryst. rhombic).

In the Handbook the following values are accepted for the enthalpy of rhombic sulfur: $H^\circ_{293.15} - H^\circ_0 = 1025 \pm 5$ cal/g-atom; $H^\circ_{293.15} - H^\circ_0 = 1053 \pm 5$ cal/g-atom; they are based on results of calorimetrical measurements by Eastman and Mc Gavock [1441].

S (gas). The value of the heat of formation of monatomic sulfur, used in the Handbook,

$$\Delta H^\circ f_0(S, \text{gas}) = 64{,}687 \pm 0{,}3 \text{ kcal/g-atom}$$

was calculated on the basis of values of the heat of formation and the energy of dissociation of SO (cf. below).

S_2 (gas). Braune, Peter and Neveling [909] studied in great detail the equilibrium in sulfur vapor at temperatures not higher than 1000°K and obtained $\Delta H^\circ f_0$ (S_2, gas) = 27.3 kcal/mole. But this value is inaccurate because of the absence of reliable data on the composition of the sulfur vapor.

A more reliable value of the heat of formation of diatomic sulfur may be calculated on the basis of results of investigating the dissociation reaction of hydrogen sulfide:

A more reliable value of the heat of formation of diatomic sulfur may be calculated on the basis of results of investigating the dissociation reaction of hydrogen sulfide:

$$2H_2S(\text{gas}) \rightleftarrows 2H_2(\text{gas}) + S_2(\text{gas}), \qquad (13.2)$$

since this equilibrium was studied at temperatures above 1000°K where S_2 is the chief component of sulfur vapor. Evans and Wagman [1516], on the basis of values of the equilibrium constants of the reaction (13.2) obtained by Preuner [3316], Preuner and Schupp [3319] and Randall and Bichowsky [3368], calculated $\Delta H°f_0(S_2\ \text{gas}) = 30.806 \pm 0.15$ kcal/mole. A recalculation of the data from [3316, 3319, 3368], using the values of the thermodynamic properties of the components of reaction (13.2) accepted in the Handbook, yields a value of

$$\Delta H°f_0(S_2, \text{gas}) = 30{,}87 \pm 0{,}15 \text{ kcal/mole}$$

which is accepted in the present Handbook. The value of the dissociation energy corresponding to it amounts to

$$D_0(S_2) = 98{,}504 \pm 0{,}6 \text{ kcal/mole}$$

The quantity $D_0\ (S_2)$ cannot be determined unambiguously from spectroscopic data owing to the difficulties connected with the interpretation of the S_2 spectrum. This problem was carefully studied by Gaydon [1668] who recommended a value of $D_0\ (S_2) = 101 \pm 3$ kcal/mole (4.4 ev). Later data of SO and S_2 verified the correctness of this choice (Cf. [918] and [1156a]). The value of $D_0\ (S_2)$ recommended by Gaydon agrees with the value accepted in the present Handbook within the limits of error of determination but is less accurate.

SO (gas). Dewing and Richardson [1327] measured the equilibrium constants of the reactions

$$SO_2(\text{gas}) \rightleftarrows SO(\text{gas}) + \tfrac{1}{2}O_2(\text{gas}), \qquad (13.3)$$

$$S_2(\text{gas}) + 2SO_2(\text{gas}) \rightleftarrows 4SO(\text{gas}) \qquad (13.4)$$

and used the data obtained to calculate the heats of formation of SO

from S_2 and O_2 at 0°K; they obtained -15.4 ± 0.3 kcal/mole and -15.2 kcal/mole. Previously Pierre and Chipman [3245] calculated a rather different value (-18.7 kcal/mole) on the basis of measurements of the constant of equilibrium of the reaction (13.4). But owing to a series of causes (see [3246, 2783]), the value of the heat of formation of SO, obtained by Pierre and Chipman, is less accurate than that found by Dewing and Richardson.

Calculations of the heat of formation of SO from S_2 and O_2, based on the values of the equilibrium constants of reactions (13.3) and (13.4), determined in paper [1327], and values of the thermodynamic properties of the components of these reactions, accepted in the present Handbook, virtually yield the same results as were obtained in paper [1327]. The value of the standard heat of formation,

$$\Delta H^\circ f_0(SO, \text{газ}) = 0{,}1 \pm 0{,}3 \text{ kcal/mole}$$

accepted in the present Handbook, corresponds to the heats of formation of SO from O_2 and S_2 found by Dewing and Richardson.

The dissociation energy of SO was determined by Martin [2787] who obtained 119.5 kcal/mole (5.053 ev) on the basis of own data on the predissociation in the $C^3\Sigma - X^3\Sigma^-$ band system in the spectrum of the SO molecule. But these values, given in Herzberg's [2020] and Gaydon's [1668] monographs,* are incorrect because of errors in the band numeration carried out in paper [2787]. Norrish and Oldershaw [3103] corrected this error and recalculated the molecular constants and the SO dissociation energy, using data from Martin [2787]. The value obtained by these researchers,

$$D_0(SO) = 123{,}574 \pm 0{,}030 \text{ kcal/mole}$$

is used in the present Handbook.

The accepted value of D_0 (SO) agrees with that of the long-wave limit of photochemical decay of SO_2 into SO and O, determined by Korn-

feld and Weegman [2464].

SO_2 (gas). The results of measuring the heat of combustion were considered by Bichowsky and Rossini [813]. The main drawback of most of these papers is the side reaction of SO_3 formation.

Eckman and Rossini [1449], unlike the previous researchers, measured the heat of combustion of gaseous sulfur in oxygen. This enabled him to carry out the reaction under the conditions of surplus sulfur, where SO_2 is the only product of combustion. Eckman and Rossini obtained a value of the heat of formation of SO_2 (gas) equal to -70.958 ± 0.05 kcal/mole. Taking into account the improved value of the atomic weight of sulfur (32.066 instead of 32.06), we accepted in the Handbook the following value:

$$\Delta H^\circ f_{298.15}(SO_2, \text{gas}) = -70{,}96 \pm 0{,}05 \text{ kcal/mole}$$

To this value of the heat of formation corresponds

$$D_0(SO_2) = 253{,}014 \pm 0{,}3 \text{ kcal/mole}$$

SO_3 (gas). Evans and Wagman [1516], on the basis of measurements of the equilibrium constants of SO_3 dissociation (13.1) carried out by many authors, calculated the value of the heat of formation of SO_3 (gas) and obtained -94.7 ± 0.5 kcal/mole. In the present Handbook we used the measuring values of the equilibrium constants of SO_3 dissociation to calculate the thermodynamic functions of SO_3 (gas) (cf. pages 609-611, and 641) and not to determine the heat of formation of SO_3.

The value of the heat of formation of SO_3 may be calculated on the basis of the thermal effect $\Delta H_{293.15} = -33.66 \pm 0.06$ kcal/mole of the reaction

$$SO_2(\text{gas}) + \tfrac{1}{2}O_2(\text{gas}) \rightarrow SO_3(\text{liq.}). \qquad (13\ 5)$$

measured by Roth, Grau and Meichsner [3527].

On the basis of the value of the heat of evaporation, $\Delta Hv_{298.15}$ (SO_3, liqu.) = 10.22 kcal/mole [3508] and the used value of the heat of

formation of SO_2, a value of

$$\Delta H^\circ f_{298.15}(SO_2, \text{ газ}) = -94{,}4 \pm 0{,}1 \text{ kcal/mole}$$

was obtained which is accepted in the present Handbook. To it corresponds

$$D_0(SO_2) = 334{,}709 \pm 0{,}3 \text{ kcal/mole}$$

S_2O (gas). The heat of formation and the dissociation energy of S_2O may be calculated in an approximate way from the limit of predissociation, discovered by Jones [2289], in the ultraviolet absorption spectrum of vapor of this compound. This limit was found to be at 31,-702 cm^{-1} and corresponds to the dissociation of the bond S-SO. From data given in paper [2289] it follows that the limit of predissociation in the S_2O spectrum found in it must correspond, within the limits of ± 300 cm^{-1}, to the dissociation energy of the S-SO bond.* Starting from these data and the values of the other thermodynamic quantities used in the present Handbook, the dissociation energy of S_2O was calculated:

$$D_0(S_2O) = 214 \pm 1 \text{ kcal/mole}$$

this value is accepted in the present Handbook. The following value of the heat of formation corresponds to it:

$$\Delta H^\circ f_0(S_2O, \text{ газ}) = -25{,}639 \pm 1{,}2 \text{ kcal/mole}$$

SH (gas). The dissociation energy of the radical SH was determined in the papers [3301, 3356, 2259b] on the basis of investigations of the $A^2\Sigma^+ - X^2\Pi_1$ band system. The upper limit of the possible values of D_0 (SH) was determined by Porter [3301] and Ramsay [3356] from the predissociation to be observed in the 1-0 band; they obtained 92.7 kcal/mole. The lower limit of the possible values of D_0 (SH) was dedetermined by Jones and Ramsay [2259b] on the basis of investigating the 2-0 band; they obtained 70.9 kcal/mole. In the papers [3301, 3356, 2259b] the dissociation energy of SH was also determined from the value

of $D_0(SH)$ in the state $A^2\Sigma^+$ (D_0' (SH) and the excitation energy of the $A^2\Sigma^+$ state of SH (see Table 78) under the assumption that SH dissociates from the $A^2\Sigma^+$ state to the $H(^2S) + S(^1D)$ state. In all these papers the quantity $D_0'(SH)$ was determined by linear extrapolation of the vibrational energy levels of the $A^2\Sigma^+$ state. The most accurate value of D_0 (SH) was obtained in this way be Jones and Ramsay [2259b]. The value of $D_0(SH) = 28480 \pm 1000$ cm^{-1} or

$$D_0(SH) = 81{,}4 \pm 2{,}9 \text{ kcal/mole}$$

obtained in paper [2259b] is accepted in the present Handbook. Similar values of $D_0(SH)$ but with a greater error were obtained by Porter [3301] (84.9 kcal/mole) and Ramsay [3356] (82.8 kcal/mole).

The heat of formation of SH, corresponding to the accepted value of D_0,

$$\Delta H^\circ f_0(SH, \text{ газ}) = 34{,}919 \pm 3 \text{ kcal/mole}$$

agrees with the values obtained from the results of mass-spectrometrical investigations of the dissociative ionization of alkyl mercaptan molecules under the influence of electron impact [1599, 3859, 3860] ($\Delta H^\circ f_{298.15} = 38.4 \pm 5$ kcal/mole) and a value obtained from results of studying the thermal dissociation of benzyl, methyl, and ethyl mercaptan in a toluene stream [3675] ($\Delta H^\circ f_0 = 32 \pm 5$ kcal/mole).

<u>H_2S (gas)</u>. The heat of combustion of hydrogen sulfide to SO_2 (gas) and H_2O (liqu.) was first measured by Thomsen [3981]. The value of $\Delta Hc_{291.15} = -136.71$ kcal/mole he found was recalculated by Bichowsky and Rossini [813], taking into account that sulfuric acid forms in the combustion products. A value of $\Delta H^\circ f_{298.15}$ (H_2S, gas) = −5.2 kcal/mole corresponds to the corrected value of $\Delta Hc_{291.15} = -134.1$ kcal/mole. Thomsen [3981] measured also the thermal effect of the reaction between hydrogen sulfide and elementary iodine. Bichowsky and Rossini [813], on the basis of results of these measurements, calculated

$\Delta H°f_{291.15}$ (H_2S, gas) = -5.5 kcal/mole. A repetition of these calculations, taking the value of $\Delta H°f_{298.15}$ (HI), gas), accepted in the Handbook, into account, yielded a considerably smaller value of $\Delta H°f_{298.15}$ (H_2S, gas) = -4.7 kcal/mole.

A repeated measurement of the heat of combustion of hydrogen sulfide was made by Zeumer and Roth [4386] who considered thoroughly the formation of sulfuric acid. A value of $\Delta H°f_{298.15}$ (H_2S, gas) = = -4.82 ± 0.15 kcal/mole corresponds to the value of $\Delta Hc_{298.15}$ (H_2S, gas) = -134.49 kcal/mole they obtained. Kapustinskiy and Kan'kovskiy [210] measured the heat of combustion of hydrogen sulfide under conditions of lack of oxygen so to avoid side reactions of SO_3 and sulfuric acid formation. Under these conditions the products of combustion of H_2S were SO_2 (gas), H_2O (liqu.) and sulfur.* A value of $\Delta H°f_{298.15}$(H_2S, gas) = -4.92 ± 0.1 kcal/mole corresponds to the values of the heat of combustion, obtained in paper [210].

The heat of formation of H_2S may also be determined on the basis of results of measuring the equilibrium in reactions in which this gas is involved. Pollitzer's [3289] measurements of the value of the equilibrium of a reaction between iodine and hydrogen sulfide yielded a value of $\Delta H°f_{298.15}$ (H_2S, gas) = -4.81 ± 0.20 kcal/mole [1516]. The data on the reaction equilibrium of the formation of H_2S from the elements, given in the book by Lewis and Randall [283] enabled Bichowsky and Rossini [813] to calculate $\Delta H°f_{291.15}$ (H_2S, gas) = -5.0 kcal/mole.

Thus, the results of determining the heat of formation of hydrogen sulfiede are in good agreement with one another. More accurate are the values, based on calorimetrical measurements by Zeuner and Roth [4386] and Kapustinskiy and Kan'kovskiy [210]. In the Handbook we accept the mean value

$$\Delta H^\circ_{298,15}(H_2S,\ gas) = -4,87 \pm 0,10 \text{ kcal/mole}$$

to which the following value corresponds:

$$D_0(H_2S) = 172,129 \pm 0,32 \text{ kcal/mole}$$

SF (gas). The dissociation energy of the SF molecule has not been determined experimentally but it can be estimated on the basis of a comparison with the mean rupture energies of S–F bonds in the molecules of SF_4 and SF_6 and comparison with the dissociation energies of such molecules as ClF and ClO. The mean rupture energy of the S–F bonds in SF_4 and SF_6 is equal to 78 kcal/mole. This quantity may be considered as the upper limit of $D_0(SF)$ on the basis of a comparison of the mean bond energies of the molecules CH_4, CF_4, CCl_4 and SiF_4 with the dissociation energies of the corresponding diatomic molecules CH, CF, CCl and SiF. On the other hand, a comparison of the dissociation energies of the molecules of oxides and fluorides of the elements according to the periods of Mendeleyev's table permits the assumption that $D_0(SF)$ must at least be equal to D_0 (ClF) = 59 kcal/mole.

It is thus justified to assume that 78 kcal/mole > D_0 (SF) > > 59 kcal/mole. The ClO molecule, for which $D_0(ClO)$ = 63.34 kcal/mole, is most similar to the SF molecule. It is therefore very probable that the dissociation energies of the isoelectronic molecules SF and ClO have similar values.

On the basis of the above considerations, we accept a value of

$$D_0(SF) = 65 \pm 5 \text{ kcal/mole}$$

in the Handbook; the following value corresponds to it:

$$\Delta H^\circ_f{}_0(SF,\ gas) = 18,187 \pm 5 \text{ kcal/mole}$$

SF_2 (gas). The dissociation energy of the SF_2 molecule may approximately be estimated as $2D_0(SF)$ = 130 kcal/mole. A more satisfactory estimate is based on considering the fact that the mean bond energy of

X-Y in triatomic molecules of the type XY_2 is, as a rule, a little higher than the dissociation energy of the corresponding diatomic molecules XY. The ratio $\frac{E_0(S-X)}{D_0(SX)}$ for H_2S and SH and for SO_2 and SO is equal to 1.03. If we assume that this ratio amounts to 1.03 ± 0.02 for the molecules of SF_2 and SF, we have $E_0(S-F)_{SF}$ = 67 ± 7 kcal/mole; hence we find

$$D_0(SF_2) = 134 \pm 14 \text{ kcal/mole.}$$

A value of

$$\Delta H^\circ f_0(SF_2, \text{ gas}) = -32{,}313 \pm 14 \text{ kcal/mole}$$

corresponds to the value of $D_0(SF_2)$ accepted.

<u>SF_4 (gas)</u>. The heat of formation of gaseous sulfur tetrafluoride were determined by Vaughan and Muetterties [4074a] on the basis of results of calorimetrical measurements of the reaction heat of SF_4 hydrogenation:

$$\Delta H^\circ f_{298.15}(SF_4, \text{ gas}) = -171{,}7 \pm 2{,}5 \text{ kcal/mole}$$

The value of $\Delta H^\circ f_{298.15}(SF_4, \text{ gas})$ determined in paper [4074a] is accepted in the Handbook. The value of the dissociation energy corresponding to it is equal to

$$D_0(SF_4) = 308{,}601 \pm 3 \text{ kcal/mole}$$

<u>SF_6 (gas)</u>. The heat of formation of sulfur hexafluoride was determined on the basis of calorimetrical measurements of the heat of combustion in fluorine. Such measurements were made for the first time by Yost and Claussen [4362] who obtained $\Delta H^\circ f_{298.15}$ (SF_6, gas) = −262 kcal/mole. This value is inaccurate since the authors of paper [4362] did not have sufficiently pure fluorine at their disposal and did not take into consideration that other sulfur fluorides may also form.

Analogous investigations, recently carried out by Gross [1862a], yielded the value

$$\Delta H^\circ f_{298.15}(SF_6, \text{ gas}) = -268{,}5 \pm 0{,}7 \text{ kcal/mole}$$

accepted in the present Handbook. Although no details are given in the communication [1862a] on Gross' experimental studies, there is no doubt that he used sufficiently pure fluorine in his experiments. A comparison of the mean bond energies in SF_4 and SF_6 also shows that many reasons speak in favor of the value obtained by Gross [1862a].

The following value corresponds to the value accepted for the heat of formation of SF_6:

$$D_0(SF_6) = 460{,}862 \pm 4 \text{ kcal/mole}$$

<u>SOF_2 (gas)</u>. The heat of formation of SOF_2 may be calculated from the heats of formation of $SOCl_2$, SO_2Cl_2 [3508] and SO_2F_2 (see below), if we assume that the energies of detachment of an oxygen molecule from molecules of SO_2Cl_2 and SO_2F_2 are equal. A corresponding calculation yields the value

$$-\Delta H^\circ_{f_{298,15}}(SOF_2, \text{ gas}) = -162 \pm 20 \text{ kcal/mole}$$

which is accepted in the present Handbook.

The following value corresponds to the value accepted for the heat of formation of SOF_2:

$$D_0(SOF_2) = 321{,}472 \pm 20 \text{ kcal/mole}$$

<u>SO_2F_2 (gas)</u>. The heat of formation of gaseous SO_2F_2 was calculated by Reese, Dibeler and Franklin [3416] on the basis of own measurements of the SO_2 ionization potential and the potential connected with the appearance of SO_2^+ ions in the dissociative ionization of SO_2F_2 under electron impact. In accordance with the data given in paper [3416] we accept in the present Handbook

$$-\Delta H^\circ_{f_{298,15}}(SO_2F_2, \text{ gas}) = -235 \pm 5 \text{ kcal/mole}$$

To the value of the heat of formation accepted corresponds:

$$D_0(SO_2F_2) = 422{,}629 \pm 10 \text{ kcal/mole}$$

TABLE 88

Accepted Values (in cal/mole) of the Thermodynamic Quantities of Various Sulfur Compounds

Вещество 1	Состояние 2	D_0	$\Delta H^\circ_f{}_{0}$	$\Delta H^\circ_f{}_{298,15}$	$\Delta G^\circ_f{}_{298,15}$	$H^\circ_{298,15} - H^\circ_0$	$H^\circ_{298,15} - H^\circ_0$
S	3 Крист. 4 ромб.	—	0	0	0	1025	1053
S	5 Газ	—	64 667	65 225	65 225	1563	1591
S_2	»	100 802	30 670	30 649	30 632	1829	1857
SO	»	123 072	100	106	97	2051	2057
SO_2	»	253 014	—70 353	—70 944	—71 000	2474	2521
SO_3	»	334 709	—93 061	—94 381	—94 400	2765	2826
SCO	»	214 000	—25 639	—26 000	—26 111	2659	2672
CS	»	81 000	34 919	35 035	35 029	2133	2172
H_2S	»	272 129	—4 178	—4 848	—4 [illegible]	2339	2380
SF	»	95 000	18 187	18 209	18 200	2093	2121
SF_2	»	194 000	—32 313	—32 810	—32 823	2600	2654
SF_4	»	308 601	—169 914	—171 683	—171 700	3402	3489
SF_6	»	460 852	—285 175	—288 473	—288 500	3946	4061
SOF_2	»	321 472	—160 798	—161 984	—162 000	2932	2999
SO_2F_2	»	422 829	—203 168	—204 981	—205 000	3325	3407

1) Substance; 2)state; 3) crystalline; 4) rhombic; 5) gas.

Chapter 14

NITROGEN AND ITS COMPOUNDS

(N, N^+, N_2, N_2^+, N_3, NO, NO^+, NO_2, N_2O, NH, NH_2, NH_3, N_2H_4, HNO, NF, NF_2, NF_3, FNO, NS)

In the present chapter we consider the thermodynamic properties of nitrogen and its most important compounds with oxygen, hydrogen, fluorine and sulfur. Compounds of nitrogen with other elements are dealt with in Chapters 15 and 21-26.

In the present handbook one may find the most complete description of elementary nitrogen. The tables of the thermodynamic properties of N, N^+, N_2, N_2^+ and N_3 contain all essential components which may be formed by nitrogen at temperatures up to 20,000°K. Mass-spectrometry data are available [2311, 3582, 3583, 4070a] which prove the existence of an N_4^+ ion, but there is no reason to assume that tetratomic nitrogen is stable at not too high temperatures.

Nitrogen and oxygen, apart from the compounds NO, NO^+, NO_2 and N_2O considered in the present handbook, also form other compounds (e.g., N_2O_3, N_2O_4 and N_2O_5) which are thermodynamically unstable even at temperatures on the order of 300-500°K (cf. [475]). The same is true for the oxygen compounds of nitrogen of the peroxide type, NO_3 [3651] and N_2O_6 [75]. The compound N_2O_2 also exists which is only stable at temperatures close to the boiling point of NO [1362].

Of the nitrogen-hydrogen compounds, NH, NH_2 NH_3 and N_2H_4 are considered in the present handbook. These compounds are of low stability even at low temperatures; another compound of nitrogen with hydrogen,

HN_3, is also known which explodes even at common temperatures, forming N_2 and H_2. The molecules of N_2H, N_2H_2, N_2H_3, N_3H_3, etc., must also be unstable; they were identified in mass-spectrometric investigations of the disintegration of HN_3 and N_2H_4 (cf., e.g., [1577, 1578]).

The system of H + N + O is represented in the present handbook by its simplest compound HNO. Other components of this system, such as HNO_2, HNO_3, NH_2OH, NH_4OH, etc., in the gaseous state, are rather unstable (cf., e.g., [1478, 475]) and are not dealt with in the present handbook.

Among the compounds of nitrogen with fluorine, NF, NF_2 and NF_3 are treated in our handbook.

In the past year the existence of such compounds as N_2F_2 [3626, 3577] and N_2F_4 [1146, 2610a] has become known. These compounds are not considered in the present handbook (see [475]).

The compounds of nitrogen with fluorine and oxygen are represented in the handbook by the simplest compound FNO. The other members of this system, just as in the case of the system of H + N + O, are unstable in the gaseous state (cf. e.g., [3753]).

Of the sulfur compounds of nitrogen known in literature the NS molecule has been dealt with in the present handbook.

The data given in the present handbook are thus sufficient to permit sufficiently accurate calculations of the thermodynamic properties of the systems nitrogen-hydrogen, nitrogen-oxygen, nitrogen-hydrogen-oxygen. As regards the systems nitrogen-fluorine and nitrogen-hydrogen-fluorine, the data contained in the present handbook seem to be insufficiently complete.

The extremely high value of the dissociation energy of the nitrogen molecule, $D_0(N_2) \approx 225$ kcal/mole, results in a low stability of most of the nitrogen compounds, particularly at high temperatures. The

most important components of the systems containing nitrogen are therefore N_2 at very high temperatures, N, N^+ and N_2^+. The thermodynamic properties of these substances were calculated up to temperatures of 20,000°K. The thermodynamic properties of NC and NO^+ were also calculated up to 20,000°K since these compounds are of particular interest in calculations of the electron and ion concentrations in gases at high temperatures.

§51. THE MOLECULAR CONSTANTS

N. In the ^4S ground state the nitrogen atom has the electron configuration $1s^2 2s^2 2p^3$ which is the same for another two states, ^2P and ^2D. If one 2p-electron is excited, three groups of states appear (cf. page 52) whose ionization limits lie by 117,345, 132,660 and 150,000 cm^{-1} higher than the lower $^4S_{3/2}$-level of the nitrogen atom. The first group consists of doublet and quartet terms with $L = 1$ (if $\ell = 0$) and $L = |\ell|, |\ell \pm 1|$ (if $\ell > 0$) the second one of doublet terms with $L = 2$ (if $\ell' = 0$); $L = 1, 2, 3$ (if $\ell' = 1$) and $L = \ell, \ell \pm 1, \ell \pm 2$ (if $\ell' > 2$) and the third group consists of doublet terms with $L = \ell''$.

Besides the states considered, the nitrogen atom has a great number of terms, connected with the excitation of a 2s-electron or the simultaneous excitation of two or more electrons. However, the excitation energies of all these states, with the exception of the groups of terms $1s^2 2s2p^3(^5S)n\ell^{III}$ and $1s^2 2s2p^3(^3D)n\ell^{IV}$, are high (higher than 200,000 cm^{-1}) and not considered in the present handbook.

In Table 89, we find the energy levels of the nitrogen atom, corresponding to the above six electron configurations, which were determined on the basis of values recommended by Moore [2941]. Levels with similar values of the excitation energies were united to a single level with a total statistical weight and a mean value of the excitation energy.

In Moore's tables [2941], we find data on the excitation energies

of individual levels, pertaining to the two groups of terms, $2s^2 2p^2(^3P)n\ell$ and $2s^2 2p^2(^1D)n\ell'$, mainly with $L \leq 3$. Owing to the fact that for the residual levels there are no experimental data on their excitation energies, the latter were estimated in accordance with the general rules stated in Chapter 1, and on the basis of certain laws observed to govern the arrangement of the nitrogen levels (cf. page 55).*

TABLE 89

Energy Levels of the Nitrogen Atom N

1 Номер уровня	2 Состояние: электронная конфигурация 3	4 терм	5 Статистический вес	6 Энергия, см$^{-1}$
0	$1s^2 2s^2 2p^3$	^4S	4	0
1	$1s^2 2s^2 2p^3$	$^2D_{5/2}$	6	19223
2	$1s^2 2s^2 2p^3$	$^2D_{3/2}$	4	19231
3	$1s^2 2s^2 2p^3$	^2P	6	28840
4	$1s^2 2s^2 2p^2(^3P)3s$	^4P	12	83340
5	$1s^2 2s^2 2p^2(^3P)3s$	^2P	6	86190
6	$1s^2 2s^2 2p^4$	$^4P, ^2S, ^2D$	24	88140
7	$1s^2 2s^2 2p^2(^3P)3p$	^4S	2	93582
8	$1s^2 2s^2 2p^2(^3P)3p$	^4D	20	94840
9	$1s^2 2s^2 2p^2(^3P)3p$	^4P	12	95510
10	$1s^2 2s^2 2p^2(^3P)3p$	$^4S, ^2D$	14	95810
11	$1s^2 2s^2 2p^2(^3P)3p$	^2P	6	97790
12	$1s^2 2s^2 2p^2(^1D)3s$	^2D	10	99650
13	$1s^2 2s^2 2p^2(^3P)4s$	P	18	103860
14	$1s^2 2s^2 2p^2(^3P)3d$	P, D, F	90	104900
15	$1s^2 2s^2 2p^2(^3P)4p$	$S, ^2P, ^4P^\circ, D$	54	106900
16	$1s^2 2s^2 2p^2(^3P)5s$ $\ldots 2p^2(^3P)4d$ $\ldots 2p^2(^1D)3p$	P P, D, F ^2D	118	110200
17	$\ldots 2p^2(^1D)3p$ $\ldots 2p^2(^3P)\ldots$ $\ldots 2p^2(^3P)5d$ $\ldots 2p^2(^3P)6s$	^2P $S^\circ, P^\circ, D^\circ$ P, D, F P	168	112700

1 Номер уровня	2 Состояние: электронная конфигурация 3	4 терм	Статистический вес 5	Энергия, $см^{-1}$ 6
18	. . . $2p^2(^3P)6p$ . . . $2p^2(^3P)6d$ . . . $2p^2(^3P)7s$	S^o, P^o, D^o P, D, F P	162	114140
	. . . $2p^2(^3P)7p$ . . . $2p^2(^3P)5s$ . . . $2p^2(^3P)$	S^o, P^o, D^o P $P, D, {}^2F, {}^4F^o$	162	114880
20	. . . $2p^2(^3P)5p$ . . . $2p^2(^3P)3s$ . . .	S^o, P^o, D^o P $P, D, {}^2F, {}^4F^o$	162	115500
21	. . . $2p^4(^3P)9p$ . . . $2p^4(^3P)9d$ . . . $2p^4(^3P)10s$	S^o, P^o, D^o $P, D, {}^2F, {}^4F^o$ P	162	115800
22	. . . $2p^4(^3P)10p$, $11p$ . . . $2p^4(^3P)10d$, $11d$ . . . $2p^4(^3P)11s$, $12s$	S^o, P^o, D^o $P, D, {}^2F, {}^4F^o$ P	324	116200
23	. . . $2p^4(^3P)12p$ . . . $2p^4(^3P)12d$ . . . $2p^4(^3P)13s$	S^o, P^o, D^o $P, D, {}^2F, {}^4F^o$ P	162[a]	116550
24	. . . $2p^4(^3P)4<n<12$, $3<l<11$ . . . $2p^4(^3P)13l$, $1<l<12$	$L=\|l\|, \|l\pm1\|$	7560[b]	117345
25	. . . $2p^4(^1D)3p$ . . . $2p^4(^1D)3d$ . . . $2p^4(^1D)4<n<13$, $0<l<12$	$^2F^o$ S^o, P^o, D^o, F^o, G^o $L=\|l\|, \|l\pm1\|, \|l\pm2\|$	4864[c]	132000
26	. . . $2p^4(^1S)3<n<13$, $0<l<12$	$L=\|l\|$	1002[d]	150000
27	. . . $2s^2p^4(^3S)3<n<13$, $0<l<12$	$L=\|l\|$	5010[e]	164500
28	. . . $2s^2p^4(^3D)3<n<13$, $0<l<12$	$L=\|l\|$	15030[f]	209000

1) Number of level
2) State
3) Electron configuration
4) Term
5) Statistical weight
6) Energy, cm^{-1}

[a] Value of p_{23} given for $n \leq 12$; with $n \leq 13$ $p_{23} = 180$.

[b] Value of p_{24} given for $n \leq 11$; with $n \leq 12$ $p_{24} = 9990$; with $n \leq 13$, $p_{24} = 13{,}014$.

[c] Value of p_{25} given for $n \leq 11$; with $n \leq 12$ $p_{25} = 6424$; with $n \leq 13$, $p_{25} = 8114$.

[d] Value of p_{26} given for $n \leq 11$; with $n \leq 12$ $p_{26} = 1290$; with $n \leq 13$, $p_{26} = 1628$.

[e] Value of p_{27} given for $n \leq 11$; with $n \leq 12$ $p_{27} = 6450$; with $n \leq 13$, $p_{27} = 8140$.

[f]Value of p_{28} given for $n \leq 11$; with $n \leq 12$ p_{28} = = 19,350; with $n \leq 13$, p_{28} = 24,420.

*Levels not observed experimentally are marked by an asterisk.

N^+. In the ^3P ground state, the positive nitrogen ion has the electron configuration $1s^2 2s^2 2p^2$ which is the same for another two states: ^1D and ^1S. The excitation of one 2p-electron is accompanied by the appearance of one group of states with the electron configuration $1s^2 2s^2 2p(^2P)nl$, whose ionization lies 238,846.7 cm^{-1} above the lower level of the group, the substate $^3P_0$. The electron states of this group has high excitation energies and is not considered in the present handbook.

In Table 90 the energy levels of the positive nitrogen ion are given; the values are used in the subsequent calculations and were chosen on the basis of quantities recommended by Moore [2941].*

TABLE 90

Energy Levels of the N^+ Ion

1 Номер уровня	2 Состояние: электронная конфигурация 3	2 Состояние: терм 4	Статистический вес 5	Энергия, $см^{-1}$ 6
0	$1s^2 2s^2 2p^2$	$^3P_0$	1	0,00
1	$1s^2 2s^2 2p^2$	$^3P_1$	3	49,1
2	$1s^2 2s^2 2p^2$	$^3P_2$	5	131,3
3	$1s^2 2s^2 2p^2$	^1D	5	15315,7
4	$1s^2 2s^2 2p^2$	^1S	1	32687
5	$1s^2 2s 2p^3$	^5S	5	47108
6	$1s^2 2s 2p^3$	^3D	15	82250

1) Number of level
2) State
3) Electron configuration
4) Term
5) Statistical weight
6) Energy, cm^{-1}

N_2. The spectrum of molecular nitrogen belongs to the most carefully investigated spectra of diatomic molecules. At present, we know about 50 stable electron states of N_2 [3001]. The scheme of these states is given in Fig. 10 and the transitions observed between chem are indicated.

In the present handbook we consider only such electron states of N_2 whose excitation energies do not exceed 90,000 cm^{-1}.

The electron ground state of N_2 is a state of the type $^1\Sigma_g^+$. In the N_2 electron spectrum the bands connected with the ground state are referred to the well-studied Lyman-Birge-Hopfield system ($a^1\Pi_g - X^1\Sigma_g^+$), the Birge-Hopfield system ($b'^1\Sigma_u^+ - X^1\Sigma_g^+$) and the Vegard-Kaplan system ($A^3\Sigma_u^+ - X^1\Sigma_g^+$) (cf. Fig. 10).* The rotational structure of the bands of the $a^1\Pi_g - X^1\Sigma_g^+$ system in the emission spectrum was analyzed by Watson and Koontz [4184, 4185] (v" = 0.1), Spinks [3824] (v" = 10-14), Appleyard [563] (v" = 13 and 14), Wilkinson and Houk [4277] (v" = 2-5) and Lofthus [2637] (v" = 10-15). The data obtained by Wilkinson and Houk with an apparatus of 1.33 A/mm dispersion in the range of 900-1700 A and Lofthus, with a device of 0 43 A/mm dispersion, in the range of 1940-2050 A, were the most accurate ones. The band edges in this system, corresponding to values of V" = 13-27, were measured by Herman [2000, 2007] also in the emission spectrum.**. In the absorption spectrum the bands of the $a^1\Pi_g - X^1\Sigma_g^+$ system were only observed with v" = 0 Tanaka [3934], Wilkinson [4273]).

The system $b'^1\Sigma_u^+ - X^1\Sigma_g^+$ was studied by Wilkinson [457] who measured the rotational structure of the bands of this system with a device of the dispersion 8.4 A/mm in the Schuman range, these bands corresponding to the values v" = 13-21, and by Wilkinson and Houk [4277] who found the bands with v" = 6-12.

The rotational structure of the bands of the system $A^3\Sigma_u^+ - X^1\Sigma_g^+$

in the N_2 emission spectrum was investigated by Janin [2211, 2212, 2213] ($v'' = 3$-10) and Wulf and Melvin [4344] ($v'' = 4$-6), and in the absorption spectrum by Wilkinson [4276]. R. Herman and L. Herman [1999, 2001, 2003] measured the band edges in this system in the emission spectrum ($v'' = 2$-15).

The Raman spectrum of N_2 was one of the first that was investigated (Rasetti [3399, 3400]). Later on this spectrum was observed by Miller [2913], Oxholm and Williams [3159] and Stoicheff [3873]. The data obtained in the latter paper are the most accurate ones.

The vibrational constants of the electron ground state of N_2, calculated by Herman [2007] according to the band edges of the system $a^1\Pi_g - X^1\Sigma_g^+$ (see above), are recommended in the handbook [649] and in Herzberg's monograph [2020]. The limit of convergence of the vibrational levels, corresponding to these constants, however, amount to 84,286 cm^{-1} with $v_{max} = 64$, a value that does not agree with the dissociation energy of N_2 which is equal to 78,717 cm^{-1} (cf. page 758). The constants obtained in later papers [4277, 2637, 3873] describe better the experimental data available but lead also to an incorrect value of the dissociation limit. Considering this, new values of the vibrational constants were calculated when compiling the present handbook, using a four-term equation and a method, described on page 66 (cf. [477]). As initial data, we chose the values of $\Delta G_{v+1/2}$ for $v'' = 0$-25, measured in the papers of Stoicheff [3873] ($v'' = 0$), Wilkinson and Houk [4277] ($v'' = 2$-3 from the system $a^1\Pi_g - X^1\Sigma_g^+$ and $v'' = 5$-9 from the system $b'^1\Sigma_g^+ - X^1\Sigma_g^+$), Wulf and Melvin [4344] ($v'' = 4$), Lofthus [2637] ($v'' =$ = 10-14), Chulanovskiy [457] ($v'' = 15$-20) and Herman [2007] ($v'' = 21$--25 from the b nd edges). In the calculation it was also taken into account that $\Delta G_{v_{max}+1/2} = 0$. Applying the method of successive approximations we found values of the vibrational constants of the N_2 ground state

that yielded a limit of convergence of 78,810 cm^{-1} with $v_{max} = 58$. These constants are used in the present handbook and given in Table 92.

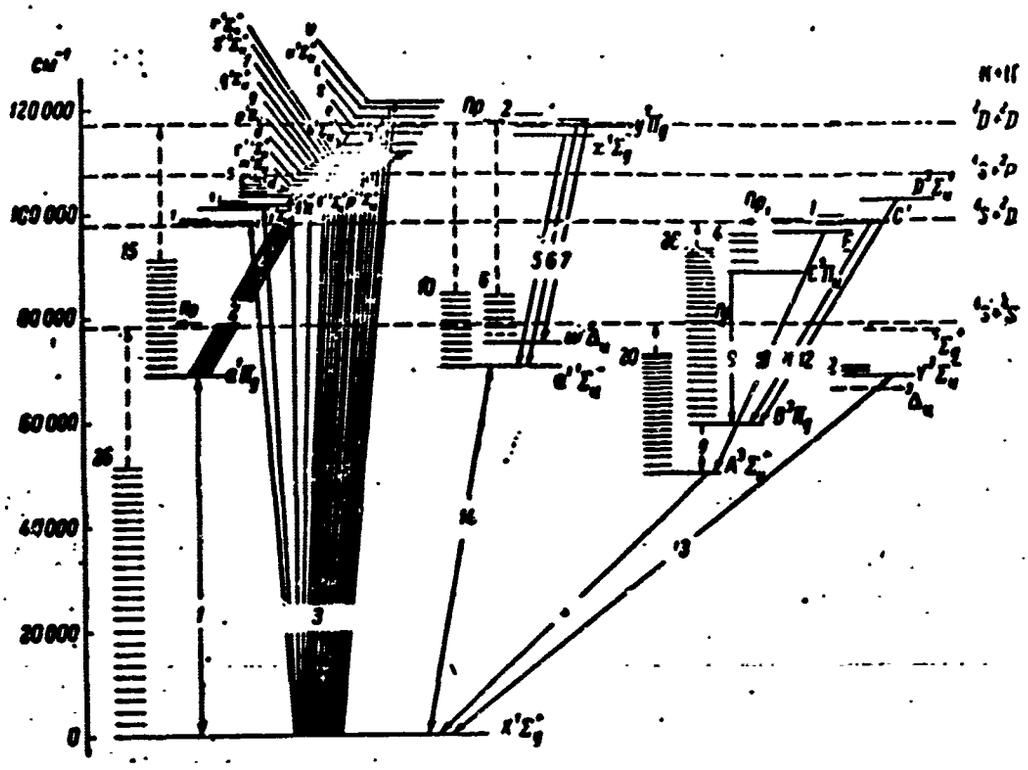


Fig. 10. Energy level scheme of the N_2 molecule. The heavy horizontal lines represent the electron states. The finer lines correspond to the vibrational levels. The digits on the left indicate the numbers of levels observed with the given state. The dashed arrows indicate the dissociation limits of the electron states. These limits are marked by dashed horizontal lines. The horizontal arrows (Pr) indicate the predissociation. The electron transitions, observed in the N_2 spectrum, are described by full arrows where 1)corresponds to the $a^1\Pi_g - X^1\Sigma_g^+$ band system (Lyman-Birge-Hopfield bands) 2) to the Gaydon band system with the low $a^1\Pi_g$-state, 3) to the Birge-Hopfield band system with the low $X^1\Sigma_g^+$ state, 4) to the $A^3\Sigma_u^+ - X^1\Sigma_g^+$ band system (Vegard-Kaplan bands), 5) to the $x^1\Sigma_g^- - a'^1\Sigma_u^-$ band system (fifth positive system) 6 and 7) to the band systems $y^1\Pi_g - a'^1\Sigma_u^-$ and $y^1\Pi_g - w^1\Delta_u$ (Kaplan bands), 8) to the $B^3\Pi_g - A^3\Sigma_u^+$ band system (first positive system), 9) to the $C^3\Pi_u - B^3\Pi_g$ band system (second positive system), 10) to the $E - A^3\Sigma_u^+$ band system, 11) to the $C' - B^3\Pi_g$ band system (Goldstein-Kaplan bands), 12) to the $D^3\Sigma_u^+ - B^3\Pi_g$ band system (fourth positive system), 13) to he $Y^3\Sigma_u^- - X^1\Sigma_g^+$ band system and 14) to the $a'^1\Sigma_u^- - X^1\Sigma_g^+$ band system.

Table 91 contains the values of $\Delta G_{v+1/2}$, measured in experiments and calculated from the vibrational constants proposed by various authors which are also adopted in the present handbook and compiled in Table 92. Comparing the data given in Table 91, we find that the values of $\Delta G_{v+1/2}$, calculated from the constants used in the present handbook, are in satisfactory agreement with the experimental data for $v \leq 25$ (the mean deviation amounts to about 2 cm^{-1}) and converge to a correct dissociation limit.

TABLE 91

Values of $\Delta G_{v+1/2}$ (in cm^{-1}) of the N_2 Molecule in the $X^1\Sigma_g^+$ State

v	Экспериментальные данные 1	2 Расчет по постоянным		
		[2007][a]	[2637][b] b	табл. 92
0	2329,66 [3873]	2330,72	2329,66	2329,70
5	2187,7 [4277]	2186,51	2186,47	2184,33
10	2041,4 [2637]	2041,60	2041,43	2041,38
15	1892,5 [457]	1894,45	1894,53	1896,43
20	1745,7 [457]	1743,54	1745,77	1745,10
25	1590 [2007]	1587,35	1595,15	1583,02
v_{max}	78717	84286	89472	78810[c]

1) Experimental data; 2) calculated from the constants.

a $\Delta G_{v+1/2} = 2359,61 - 28,912(v+1) + 0,0225,3(v+1)^2 - 0,002036(v+1)^3$; $v_{max} = 64$.

b $\Delta G_{v+1/2} = 2358,07 - 28,376(v+1) - 0,0372(v+1)^2$; $v_{max} = 74$.

c $v_{max} = 58$.

The values of the rotational constants of N_2 in the ground state which are accepted in the present handbook and given in Table 92 were calculated by Lofthus [2637] on the basis of results of own measurements of the rotational structure of the bands of the $a^1\Pi_g - X^1\Sigma_g^+$ system (see above) and using the value of $B_0 = 1.9897 \pm 0.0003$ cm^{-1}, ob-

tained by Stoicheff [3873] from the Raman spectrum. These values of the rotational constants agree satisfactorily with all experimental data on the rotational structure of the N_2 bands, except the data of Watson and Koontz [4184, 4185] which, according to Wilkinson and Houk [4277], are inaccurate.

The first excited state $A^3\Sigma_u^+$ of the N_2 molecule is the highest state of the Vegard-Kaplan band system, observed only if $v' \leq 5$ [1999, 2001] and the lowest state of the first positive system of bands ($B^3\Pi_g - A^3\Sigma_u^+$ investigated more completely [3287, 3023, 1062, 3598, 1066, 2007, 1994, 2006a, 4203a](cf. Fig. 10). The most careful investigation of the first positive system was carried out by Carroll [1062] and Carroll and Sayers [3598, 1066]. In paper [1062] the rotational structure of the bands 1-0, 2-1 and 3-2 of this system was investigated with a device of high dispersion and the rotational constants of N_2 were calculated for both states. The vibrational constants were found as a result of studying a great number of other bands of the system, obtained with a device whose dispersion was much lower [3598, 1066]. In Table 92, we find the values of the molecular constants of N_2 in the $A^3\Sigma_u^+$ state, calculated in papers [1062, 3598, 1066]. An extrapolation of the vibrational levels of the $A^3\Sigma_u^+$ state, calculated from these constants, leads to a limit of 80,500 cm^{-1} with $v_{max} = 37$, whereas the $A^3\Sigma_u^+$ state has a dissociation limit of 78,717 cm^{-1}, in common with the ground state. In order to eliminate this disagreement, in paper [477] the term $-0{,}855 \cdot 10^{-8} c^8$, calculated by a method described on page 69, was added to the four-term equation, obtained by Carroll and Sayers [1066].

The molecular constants of N_2 in the $B^3\Pi_g$ state may also be found in studying the bands of the second ($C^3\Pi_u - B^3\Pi_g$) [1005, 1006, 1037, 2213, 1066] and the fourth ($D^3\Sigma_u^+ - B^3\Pi_g$) [1699] positive systems (cf. Fig. 10). The constants calculated by Carroll [1062] and Carroll and

TABLE 92

Accepted Values of the Molecular Constants of N_2

State	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	$\omega_e z_e$	B_e	α_1	$D_e \cdot 10^6$	r_e
	cm^{-1}								A
$X^1\Sigma_g^+$	0	2359,434	14,946	0,05111	0,00146	1,9983	0,01709[a]	6	1,0975
$A^3\Sigma_u^+$	50205,5[b]	1460,11	13,863	0,003486	0,0022667[c]	1,4550	0,0183	5,80[d]	1,2862
$B^3\Pi_g$	59583,4[a,e]	1735,30	14,989	0,052839	0,0022079[f]	1,6386	0,0185	5,93	1,2120
$^3\Delta_u$	60500[m,g]	1490[m,g]	—	—	—	1,45[m,g]	—	—	1,287
$Y^3\Sigma_u^-$	66270,9	1517,69	12,22	—	—	1,472	0,0161	5,5	1,2787
$a'^1\Sigma_u^-$	68152,17	1530	12	0,333	—	1,480	0,0164	6	1,275
$a^1\Pi_g$	69285,6	1593,70	13,825	—	—	1,6181	0,0183	6	1,2196
$w^1\Delta_u$	72101,67	1548	8	—	—	1,496	0,0166	10	1,268
$^1\Sigma_g^+$	79000[m,g]	—	—	—	—	—	—	—	—
$C^3\Pi_u$	89105	2065,1	17,08	−2,15	—	1,8259	0,0195	6,0[h]	1,1481

a [a] $\alpha_e = -4{,}6 \cdot 10^{-3}$ cm^{-1}.
b [b] $a = -0{,}444$, $\gamma = -0{,}002$ cm^{-1}.
c [a] $-0{,}855 \cdot 10^{-6}$ [e] see page 670
d [c] $\beta_1 = 0{,}08 \cdot 10^{-4}$ cm^{-1}.
c [a] $A = 42{,}3$ cm^{-1}.
f [e] $-6{,}917 \cdot 10^{-13}$ [e] see page 671
g [m] Estimate
h [a] $\beta_1 = -0{,}813 \cdot 10^{-4}$ cm^{-1}.

Sayers [3598, 1066] for this state, on the basis of an analysis of the bands of the first positive system, are, however, most reliable and are among the accepted values given in Table 92. The vibrational levels of the $B^3\Pi_g$ state, calculated from these constants, converge to the limit 101,975 cm^{-1} with $v_{max} = 43$, whereas, according to the correlations adopted in our handbook, the dissociation limit of the $B^3\Pi_g$ state must be equal to 98,070 cm^{-1}. In view of this, in paper [477], the term $B^3\Pi_g$, calculated by means of a method described on page 69, was added to the four-term equation of Carroll and Sayers [1066] for the energy of the vibrational levels of the $6.917 \cdot 10^{-13} \cdot v^{10}$ state.

The state $^3\Sigma_u^-$ was identified in the N_2 spectrum by Ogawa and Tanaka [3116] (in the emission spectrum) and by Wilkinson [4276a] (in the absorption spectrum) who observed for the first time the bands of

the forbidden system $Y^3\Sigma_u^- - X^1\Sigma_g^+$ in the ultraviolet range. Moreover, Carroll and Rubalkava [1065] attributed the band at 8265.5 A in the N_2 spectrum to the system $Y^3\Sigma_u^- - B^3\Pi_g$ instead of to the system $^3\Delta_u - B^3\Pi_g$ as this was suggested by Le Blanc, Tanaka and Jursa [2577] (cf. also [1340a]). On the basis of an analysis of the rotational structure of four bands of the system $Y^3\Sigma_u^- - X^1\Sigma_g^+$, Wilkinson [4276a] calculated the molecular constants of N_2 in the $Y^3\Sigma_u^-$ state, which are accepted in the present handbook and given in Table 92. Less accurate values of the constants (T_{00} = 65850.4, ω_e = 1515.7 and $\omega_e x_e$ = 11.0 cm^{-1}) were obtained by Ogawa and Tanaka [3116] from the band edges.

A few years ago, only transitions connected with the states $x^1\Sigma_u^-$ (fifth positive system) and $y^1\Pi_g$ (Kaplan bands) [2638, 2639] (cf. Fig. 10) were known for the states $a'^1\Sigma_u^-$ and $w^1\Delta_u$ of the N_2 molecule. Since transitions from these states to the ground state were unknown, it was impossible to accurately determine their excitation energies. In 1959, Wilkinson [4276, 4275] and Ogawa and Tanaka [3115] discovered a new band system of N_2 in the vacuum ultraviolet which was attributed to the forbidden transition $a'^1\Sigma_u^- - X^1\Sigma_g^+$. As a result of studying the fine structure of the bands of this system which was photographed in high resolution, Wilkinson and Mulliken [4280] (cf. also Ogawa and Tanaka [3116]) obtained $T_{00}(a'^1\Sigma_u^-)$ = 67738.18 cm^{-1} which resulted in $T_{00}(w^1\Delta_u)$= 71697.68 cm^{-1}. These values of the excitation energies are accepted in the present handbook and are given in Table 92, together with the vibrational and rotational constants determined by Lofthus [2638] for the $a'^1\Sigma_u^-$ state and Lofthus and Mulliken [2639] for the $w^1\Delta_u$ state.

The state $a^1\Pi_g$ of the N_2 molecule is well investigated as a result of investigating the bands of the Lyman-Birge-Hopfield system (cf. page 666). In the present handbook the molecular constants of N_2 in this state were chosen from data obtained by Lofthus [2637].

The existence of a state of the type $^5\Sigma_g^+$, correlated with the ground state of the nitrogen atom, ($^4S + {}^4S$), was predicted by Gaydon [141] in order to explain the predissociation of the N_2 molecule into the states $a^1\Pi_g$ and $B^3\Pi_g$. Herzfeld and Broida [2054], in the visible range of the absorption spectrum of solid nitrogen, observed bands (without fine structure) which they related to the transition $^5\Sigma_g^+ - A^3\Sigma_u^+$ of the N_2 molecule. Oldenberg [3126], who obtained analogous bands in the emission spectrum of a gas discharge, came to the conclusion that these bands were identical with the bands of the Goldstein-Kaplan system [1936, 1661, 1662] which had previously been attributed [1936] to the $C' - B^3\Pi_g$ system of the N_2 molecule. But later on, on the basis of investigations of the isotope effect in emission spectra, obtained in Ar or N_2 matrices containing traces of O_2, Broida and Peron [976a] showed that the bands in the visible range which previously [2054, 3126] had been attributed to the system $^5\Sigma_g^+ - A^3\Sigma_u^+$ of the N_2 molecule, in truth belong to the transition $A^3\Sigma_u^+ - X^3\Sigma_g^-$ of the O_2 molecule. As regards the $^5\Sigma_g^+$ state of the N_2 molecule, we therefore have a single reliable quantity at our disposal, namely the dissociation energy of this state, $D_e \approx 850$ cm^{-1}, determined by Bayes and Kristiakowsky [696a] on the basis of results of measuring the relative population of the states $B^3\Pi_g$ and $Y^3\Sigma_u^-$ in the afterglow spectrum of active nitrogen. A value of $T_e(^5\Sigma_g^+) \approx 79{,}000$ cm^{-1} corresponds to this value of D_e; it has been accepted in the present handbook.

The values of the molecular constants of N_2 in the $C^3\Pi_u$ state were taken according to the recommendation of Hertzberg [2020]. The handbook [649] gives the same values of the constants of this state.

In addition to the states considered above, according to Mulliken [3001], the N_2 molecule must possess another stable state with an excitation energy below 90,000 cm^{-1} which is attributed to the type $^3\Delta_u$.

In spite of many attempts (cf., e.g., [242 , 696, 1994], etc.), bands connected with this state have as yet not been observed in the N_2 spectrum. In Table 92 we find the values of the molecular constants of N_2 in the $^3\Delta_u$ state as recommended by Mulliken [3001] on the basis of own estimates.

N_2^+. The ground state of the N_2^+ molecule is a $^2\Sigma_g^+$-type state with which the following three well-studied band systems are connected: $A^2\Pi_u - X^2\Sigma_g^+$, $B^2\Sigma_u^+ - X^2\Sigma_g^+$ and $C^2\Sigma_u^+ - X^2\Sigma_g^+$. Moreover, the band system $^2\Pi - A^2\Pi_u$ was observed in the N_2^+ spectrum [2214, 2215].

The system of the bands $B^2\Sigma_u^+ - X^2\Sigma_g^+$ (the first negative system of nitrogen) was investigated by Herzberg [2013], Coster and Brons [1187], Childs [1097], Parker [3185, 3186], Crawford and Tsai [1218] and Douglas [1369]. The latter author photographed the bands corresponding to transitions between high vibrational levels of both states (up to the bands 29-21) in high resolution and, on the basis of a common analysis of the data obtained and the results of studies of other authors [1187, 3185, 3186, 1218], he suggested the following equation for the energy of the vibrational levels of the molecules in the ground state:

$$G_0(v) = 2191{,}00v - 16{,}190v^2 - 0{,}0303v^3 - 0{,}00092v^4. \qquad \text{(XIV.1)}$$

Equation (XIV.1) describes with high accuracy the energy of the vibrational levels with $v'' \leq 21$, obtained as a result of analyzing the band system $B^2\Sigma_u^+ - X^2\Sigma_g^+$, as well as the systems $A^2\Pi_u - X^2\Sigma_g^+$ and $C^2\Sigma_u^+ - X^2\Sigma_g^+$. In the case of high values of v, however, this equation obviously yields a bad approximation of the energy of the vibrational levels of N_2^+ since according to it, the levels converge to 59,630 cm^{-1}, whereas the N_2^+ dissociation energy is equal to 70,396 $\pm$ 30 cm^{-1} (cf. page 758). Owing to the fact that it proved impossible to choose a single equation that could satisfactorily approximate the energy of all vibrational levels of the ground state of the N_2^+ molecule up to the

dissociation limit, the authors of the handbook (cf. [478]) derived the equation

$$G_0(v) = 2234{,}022v - 20{,}01851v^2 + 0{,}035137v^3, \qquad \text{(XIV.2)}$$

for the energies of levels with v" > 21, which converges to the limit of 70,396 cm^{-1} with v_{max} = 68. The coefficients of Eq. (XIV.2) were obtained (cf. page 69) on the basis of the values of $G_0(20)$ = 36,954.4 and $G_0(21)$ = 38,411.7 found in paper [1369] and the condition of convergence of the vibrational levels to the dissociation limit (Eqs. (1.14a) and (1.14b)).

In the present handbook, the energy of the vibrational levels of the ground state of N_2^+ with v" $\leq$ 21 was calculated from the values of the vibrational constants, suggested by Douglas [1369] (cf. Table 94) and the energy of the vibrational levels with v" > 21 were calculated with the help of Eq. (XIV.2).

The values of the rotational constants (B_e, α_1 and α_2) of the ground state of the N_2^+ molecule given in Table 94 were obtained by Wilkinson [4271] as the result of an analysis of the fine structure of the bands 3-6, 3-8, 3-9, 3-10, 4-10 and 4-11 of the system $C^2\Sigma_u^+ - X^2\Sigma_g^+$. With these constants the equation yields the values of B_v with an accuracy of up to $\pm$0.002 cm^{-1}, for v $\leq$ 21, obtained by various authors. The values of the constants of centrifugal distortion in the state $X^2\Sigma_g^+$, given in Table 94, were found by Childs [1097] when studying the bands 0-0 and 0-1 of the system $B^2\Sigma_u^+ - X^2\Sigma_g^+$. These constants are in good agreement with the results of the subsequent papers by Parker [3185] and Wilkinson [4271].

The existence of an $A^2\Pi_u$ state of the N_2^+ ion had been predicted by Brons [977] on the basis of studying the perturbations in the $C^2\Sigma_u^+$ state. The bands related to the system $A^2\Pi_u - X^2\Sigma_g^+$ were first observed by Meinel [2843, 2842] in the dawn spectrum, then by Dalby and Douglas

[1254] under laboratory conditions. Douglas [1370] analyzed the rotational structure of the bands 2-0, 3-1,4-2 (and partly 1-0) of the system $A^2\Pi_u - X^2\Sigma_g^+$ photographed in first order with a 6-meter concave grating, with a dispersion of 2.5 A/mm in the range of 6890-9500 A, and calculated the values of the rotational and vibrational constants and also the constant of doublet splitting of the $A^2\Pi_u$ state. Janin and d'Incan [2214, 2215] investigated the bands of the system $^2\Pi - A^2\Pi_u$, connected with the vibrational levels of $v'' = 2$-8 of the $A^2\Pi_u$ state and achieved some improvement of the values of the vibrational constants.* The dissociation energy of the $A^2\Pi_u$ state, calculated on the basis of these constants, is equal to 59,430 cm^{-1}. The true value of this quantity, under the assumption that the states $A^2\Pi_u$ and $X^2\Sigma_g^+$ of the N_2^+ molecule have a common dissociation limit, amounts to 61,370 $\pm$ $\pm$ 40 cm^{-1}. To improve the description of the vibrational energy levels of the $A^2\Pi_u$ state which are close to the dissociation limit, a value of $\omega_e z_e = -0.00011$ cm^{-1} [478] was added, when preparing the present handbook, to the vibrational constants found in paper [2214], using a method described on page 69. The convergence of the vibrational levels to the true value of $D_0(N_2^+, A^2\Pi_u)$ was then achieved with $v_{max} = 67$.

Table 94 contains the values of the vibrational constants of N_2^+ in the $A^2\Pi_u$ state, obtained by Janin and d'Incan [2214] and improved in paper [478], and the values of the rotational constants, found by Douglas [1370].

The molecular constants of N_2^+ in the state $B^2\Sigma_u^+$ were determined in a series of papers (Herzberg [2013], Coster and Brons [1107], Childs [1097]) on the basis of results of investigating the bands of the system $B^2\Sigma_u^+ - X^2\Sigma_g^+$, corresponding to $v' \leq 13$. Douglas [1369], investigating the same system, obtained bands corresponding to transitions to higher vibrational levels of the $B^2\Sigma_u^+$ state, up to $v' = 29$. The data

obtained by Douglas prove the anomaly of the v-dependence of the vibrational levels of the $B^2\Sigma_u^+$ state (as this was suggested by Gaydon [1668]). Douglas explained this effect by the strong interaction between the states $B^2\Sigma_u^+$ and $C^2\Sigma_u^+$, which results in a mutual repulsion of the potential curves of both states and a distortion of the shape of

TABLE 93

The Values (in cm^{-1}) of $G_0(v)$ and B_v of the N_2^+ Molecule in the $B^2\Sigma_u^+$ State

v	$G_0(v)$	B_v	v	$G_0(v)$	B_v
0	0	2,073	26	36308,9	1,063
1	2371,5	2,049	27	36870,7	1,036
2	4690,3	2,025	28	37408,3	1,003
3	6950,7	2,002	29	38215,7	0,977
4	9147,1	1,980	30	38797,7	0,948
5	11280,9	1,926	31	39352,7	0,920
6	13310,9	1,896	32	39879,7	0,891
7	15[illegible]	1,852	33	40379,7	0,863
8	[illegible]2	1,810	34	40853,7	0,834
9	[illegible],1	1,763	35	41299,7	0,804
10	20423,8	1,710	36	41719,7	0,772
11	21903,7	1,653	37	42112,7	0,738
12	23275,1	1,595	38	42478,7	0,702
13	24551,4	1,545	39	42817,7	0,668
14	25747,7	1,494	40	43129,7	0,634
15	26874,3	1,452	41	43414,7	0,597
16	27941,4	1,404	42	43672,7	0,561
17	28956,9	1,367	43	43903,7	0,522
18	29922,9	1,328	44	44108,7	0,482
19	30844,9	1,293	45	44285,7	0,440
20	31726,9	1,256	46	44435,7	0,394
21	32571,9	1,220	47	44550,7	0,348
22	33381,9	1,188	48	44657,7	0,292
23	34156,9	1,152	49	44730,7	0,230
24	34900,9	1,[illegible]	50	44778,7	0,150
25	35618,6	1,088	51	44802,7	0,030

these curves (see also [1840]). This anomaly is so strong that it proved impossible to set up the usual exponential equation for the $B^2\Sigma_u^+$ state in terms of $G_0(v)$ and B_v. Therefore, instead of recommending arbitrary values of the molecular constants of N_2^+ in the $B^2\Sigma_u^+$ state, the present handbook gives in Table 93 the values of $G_0(v)$ and B_v for

this state. For values of $v \leq 29$ the corresponding quantities were obtained experimentally by Douglas [1369], for $v > 29$ they were obtained by the authors of the handbook with the help of a graphical extrapolation; it has been assumed in this case that the state $B^2\Sigma_u^+$, just as the state $A^2\Pi_u$, has a dissociation limit in common with the ground state, i.e., $D_0(N_2^+, B^2\Sigma_u^+) = 44{,}830\ cm^{-1}$. This holds with the exception of the constant of centrifugal distortion D_0 in the $B^2\Sigma_u^+$ state which, in the present handbook, was chosen according to Childs' recommendation [1097] and is given in Table 94.

TABLE 94

Accepted Values of the Molecular Constants of N_2^+

State	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	$\omega_e z_e$	B_e	α_1	$D_0 \cdot 10^6$	r_e
	cm^{-1}								Å
$X^2\Sigma_g^+$	0	2207,19[a]	16,146[a]	−0,0285[a]	0,00082[a]	1,9258	0,01743[b]	5,90[c]	1,118
$A^2\Pi_u$	9166,4[d]	1903,42	15,00	—	−0,00011	1,722	0,018	4,0	1,165
$B^2\Sigma_u^+$	25586,0[e,f]	—	—	—	—	—[g]	—	6,85	—[h]
$C^2\Sigma_u^+$	64819,5	2064,5	7,7	−0,56	—	1,82[g]	—	—	1,22[h]

a) These constants describe the vibrational energy levels with $v = 0 - 21$. With $v = 22 - 68$ the equation $G_0(v) = 2234.022\ v - 20.01851\ v^2 + 0.035137\ v^3$ holds.

b) $\alpha_2 = -0.000164\ cm^{-1}$; c) $\beta_1 = 0.29 \cdot 10^{-6}\ cm^{-1}$; d) $A = 81.5\ cm^{-1}$.

e) The values of $G_0(v)$ and B_v are given in Table 93 for all vibrational levels of the $B^2\Sigma_u^+$ state.

f) Value of ν_{00} given.

g) Value of B_0 given according to Setlow [3689].

h) Value of r_0 given.

Experimental data on the levels of vibrational and rotational energy of the N_2^+ molecule in the $C^2\Sigma_u^+$ state are rather scanty (experimental data are only available for $v \leq 8$) but we know that anomalies in the level energy values of this state arise even with small v.

Watson and Koontz [4183] and Baer and Miescher [607] have tried

to determine the values of the vibrational constants. The constants obtained by Watson and Koontz were incorrect, as this was shown by Setlow [3689], because of an incorrect numeration of the vibrational levels used in paper [4183]. The constants found by Baer and Miescher do not yield a quite satisfactory description of the experimental data obtained in other papers [3933, 4271]. There is, in particular, a divergence between the calculated and the experimental values of $G_0(v)$ that exceeds 20 cm^{-1} for v = 8. In the presence of strong perturbations of the energy levels of the $C^2\Sigma_u^+$ state it is, however, inopportune to calculate more accurate values of the vibrational constants. The vibrational constants of this state, recommended by Baer and Miescher [607] are therefore accepted in the present handbook and given in Table 94. The same table also contains the rotational constant B_0 of the $C^2\Sigma_u^+$ state found by Setlow [3689]. The value of this constant exhibits a great error since the anomaly in the B_v values is particularly strong with small v.*

NO. The electron ground state of the NO molecule is of the type $^2\Pi_r$. In the present handbook we also consider the following six excited electron states of NO: $A^2\Sigma^+$, $B^2\Pi$, $C^2\Pi$, $D^2\Sigma^+$, $B'^2\Delta$ and $E^2\Sigma^+$ (cf. Fig. 11) with excitation energies of from 43,964.5 to 60,629 cm^{-1}. The presence of such a great number of electron states in a comparatively narrow range was for many years a source of difficulties and confusion in analyzing and interpreting the electron spectra of NO. But at present, as a result of the papers of Sutcliffe and Walsh [3902], Herzberg, Lagerquist and Miescher [2036], Barrow and Miescher [658] and Lagerquist and Miescher [2528], the problem of the interpretation of these states may be considered as solved.**

The ground state $X^2\Pi_r$ of the NO molecule is connected with seven excited states, forming the system of bands $\gamma(A^2\Sigma^+ - X^2\Pi_r)$, $\beta(B^2\Pi_r -$

$- X^2\Pi_r$), $\delta(C^2\Pi_r - X^2\Pi_r)$, $\varepsilon(D^2\Sigma^+ - X^2\Pi_r)$, $\beta'(B'^2\Delta - X^2\Pi_r)$ and $E^2\Sigma^+ - X^2\Pi_r$. The data obtained in investigating the γ bands ([1881, 3628, 1663, 3627], etc.) and, in particular, the δ-bands [2036], etc.), the ε-bands ([658], etc.) and the β'-bands [606a, 2906, 2908], etc.), do not permit a calculation of sufficiently accurate values of the molecular constants of the ground state, since in these systems bands were observed which correspond to transitions or only a single vibrational level of this state ($v'' = 0$) (δ, ε and β' systems) or, in the case of a γ-band, to a level with $v'' \leq 8$ (Gaydon [1663]). From this point of view it was investigations of the β system of NO which yielded the most valuable results. Jenkins, Barton and Mulliken [2232], in 1927, analyzed

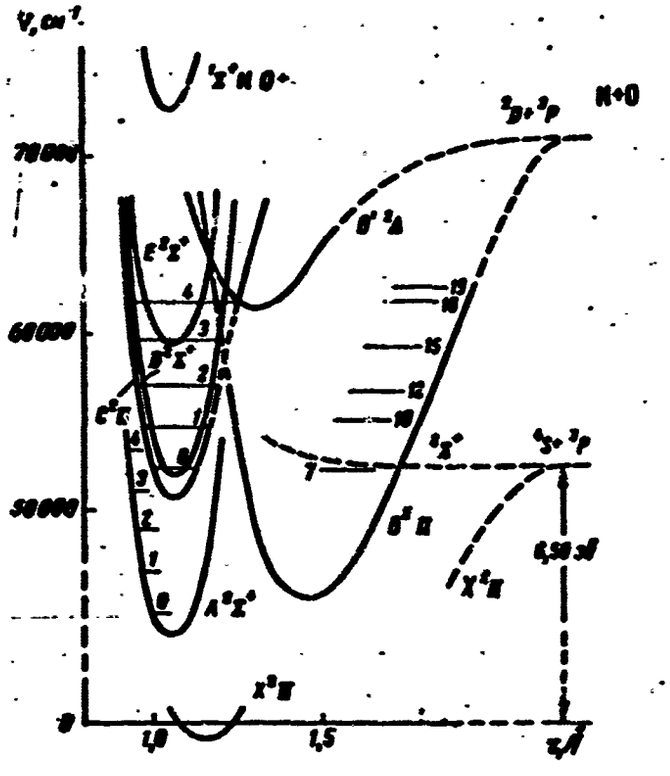


Fig. 11. Schematic representation of the potential curves of the NO molecule (after Herzberg, Lagerquist and Miescher [2036]).

thoroughly a great number of bands of the β system, corresponding to v'' values from 4 to 16, with the help of a grating spectrograph (dis-

persion about 0.97 A/mm in second order), and calculated the values of the vibrational constants. In 1954, with the help of a low-dispersion device (about 58 A/mm), Brook and Kaplan [978] measured the band edges in the ß system up to values of v" = 23. The bands of the ß system, corresponding to small values of v", were observed by Schmid [3628] and Gaydon [1664]; the measuring accuracy, however, was not high in these papers. In the absorption spectrum (Herzberg, Lagerquist and Miescher [2036]) the ß bands were only measured with v" = 0.

The most accurate energy values of low vibrational levels of the ground state were obtained in investigations of the vibration-rotation spectrum of NO in the infrared range [1748, 3067, 3694, 3972]. In the paper of Gillette and Eyster [1748], by way of processing the measuring results of the bands 1 – 0, 2 – 0 and 3 – 0 in the infrared spectrum and the ß bands in the electron spectrum [2232], the vibrational constants were calculated for which, in subsequent measurements of the infrared bands in the papers of Nichols, Hause and Noble [3067] (bands 2 – 0 and 3 – 0) and also in those of Shaw [3694] and Thompson and Green [3972] (band 1 – 0), virtually the same results were obtained.

The vibrational constants, calculated by Gillette and Eyster [1748], yield an exact description only of the lower vibrational levels while the constants, suggested by Jenkins, Barton and Mulliken [2232] describe more accurately the high vibrational levels (cf. Table 95).

Considering the fact that an extrapolation of the vibrational levels with respect to the values of the constants, recommended in the papers [1748, 2232] does not converge at the dissociation limit of NO which amounts to 52,476 cm^{-1} (cf. page 762), the values of the vibrational constants of the electron ground state of NO were again calculated when preparing the present handbook, using a fourth-order equation and applying the method described on page 66. In the calcula-

TABLE 95

Energies of the Vibrational Levels $G_0(v)$ of the NO Molecule in the State $X^2\Pi_r$ (in cm^{-1})

v	Experimental Data	Calculation from constants		
		[2232][a]	[1748][b]	табл. 97
1	1876,10 [3972]	1877,73	1876,00	1876,52
2	3724,16 [3067]	3726,84	3724,23	3724,33
3	5544,28 [3067]	5547,51	5544,42	5543,75
11	19088,2 [2232] [c]	19101,7	19088,7	19097,6
12	20866,4 [2232] [c]	20868,8	20867,0	20866,9
13	22206,1 [2232] [c]	22209,6	22207,2	22206,0
21	33483 [978] [c]	33483	33519	33475
22	34752 [978] [c]	34757	34807	34742
23	35982 [978] [c]	35990	36067	35976
v_{max}	52450	55175	63562	52480[d]

a [a] $G_0(v) = 1882{,}119\,v - 14{,}4243\,v^2 + 0{,}04021\,v^3 - 0{,}001351\,v^4$; $v_{max} = 51$.

b [b] $G_0(v) = 1880{,}08\,v - 13{,}97\,v^2 + 0{,}0012\,v^3$; $v_{max} = 67$

c. [c] Calculated from values of $\Delta G_{v+1/2}$ determined experimentally.

d [d] $v_{max} = 47$.

tions we used values of $G_0(v)$ which, in the case of v = 1, were taken from Thompson and Green [3972], with v = 2 and 3 from Nichols, Hause and Noble [3067], with v = 4-13 from Jenkins, Barton and Mulliken [2232], with v = 16-23 from Brook and Kaplan [978], and also a rounded value of the NO disscciation energy (52,500 cm^{-1}). By way of successive approximations, with v_{max} = 47, we calculated the values of the constants, given in Table 97; moreover, we find in Table 95 a comparison of several values of $G_0(v)$, calculated from new constants and determined in experiments.

It should be noted that, since the ground state of NO is of the type $^2\Pi_r$, there exist two sets of vibrational levels for each of the substates $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ which are shifted with respect to one another by about 124 cm^{-1}. The values of $\Delta G_{v+1/2}$ of these substates differ

by about 0.2 cm^{-1} with v = 0 and 10 cm^{-1} with v = 23. Gillette and Eyster [1748] and Jenkins, Barton and Mulliken [2232] set up the vibrational energy equations separately for either substate. The values of the vibrational constants used in the present handbook are the averages of the two substates. The corresponding error of the quantity ω_0 amounts to $\pm$0.1 cm^{-1}; with the other substates the error is virtually vanishing.

The values of the rotational constants of the NO molecule in the state $X^2\Pi_r$ were calculated repeatedly on the basis of results of investigations of the electron ([2232], etc.) and the vibration-rotation spectra [1748, 3067, 3694, 3972, 2454], and the rotation spectra in the infrered [3167] and the microwave range [1031, 1643, 1645, 1644, 1534, 1535]. In the paper of Thompson and Green [3972], devoted to investigating the fundamental bands of the infrared spectrum of NO, the results of basic outstanding papers on the determination of the rotational constants are summarized. A calculation with constants obtained by Gillette and Eyster [1748] as a result of a simultaneous treatment of own measurements of the infrared bands 3 – 0, 2 – 0 and 1 – 0 and data of Jenkins, Barton and Mulliken [2232] yields the best agreement with the values of B_v found in experiments (up to v = 13). In particular, the value of B_0 = 1.6957 cm^{-1}, calculated with these constants, coincides virtually with the value of B_0 = 1.6958 cm^{-1} found by Gallagher and Johnson [1644] as the result of microwave measurements and the value of $B_e = 1.6956\ cm^{-1}$ determined by Palik and Rao [3167] from the infrared rotation spectrum of NO. In like manner, we have a good agreement between the calculated and experimentally determined effective values of the rotational constants of each of the substates. The values of B_e and α_1 of the NO molecule in the ground state, obtained by Gillette and Eyster [1748], are accepted in the present handbook and are given in Table 97.

The constant of centrifugal distortion was determined through experiments in a series of papers devoted to the investigation of the NO molecule spectra in the infrared [1748, 3694, 3972] and in the microwave range [1644]. The measurements by Thompson and Green [3972], where the quantity $D_0 = D_1 = 5.1 \cdot 10^{-6}$ cm^{-1} was obtained as the result of analyzing the rotational structure of the 1 – 0 band with a maximum value of J equal to 33.5, may be viewed as most reliable. The values found by other authors are close to this value ($5.0 \cdot 10^{-6}$ by Gillette and Eyster [1748], $6 \cdot 10^{-6}$ by Shaw [3694], $5.9 \cdot 10^{-6}$ by Gallagher and Johnson [1644]). The table of the accepted values of the molecular constants of NO also contains the values of D_0 for the $X^2\Pi_r$-state found by Thompson and Green [3972].

The constant of spin-orbital coupling, A, of the NO molecule in the ground state has been determined in a series of papers devoted to the investigation of the electron and infrared spectra of NO. In the present handbook we ignore the dependence of A on the vibrational quantum number $\underline{v}$ and assume that $A = A_0 = 123.3$ cm^{-1}, according to data, obtained by Shaw [3694].

Since the ratio $A/B \approx 73$, the type of bond of the NO molecule in the ground state $^2\Pi_r$ resembles case $\underline{a}$ according to Gund.

The investigation of the microwave spectrum of NO [1643, 1644, 1534, 1535] permitted the determination of the hyperfine structure of the rotational bands, i.e., the splitting of the components of Λ doublets. This splitting is, however, insignificant (about 0.01 cm^{-1}) with the state $^2\Pi_{1/2}$ and negligibly small with the state $^2\Pi_{3/2}$.

Apart from the bands of the γ-system, another two systems are connected with the first excited state $A^2\Sigma^+$ of the NO molecule, namely $D^2\Sigma^+ - A^2\Sigma^+$ and $E^2\Sigma^+ - A^2\Sigma^+$, which were studied by Feast [1539]. The γ-system was observed in both the emission and the absorption spectrum;

in the emission spectrum, in spite of a great many papers [3627, 3628, 1663, 1700, 1287, 1288, 1289], bands with v' > 3 could not be obtained. On the basis of this fact it was proposed to assume that predissociation occurs at v' = 4 which is accompanied by a breakoff of the vibrational structure. But as a result of investigations of the NO absorption spectrum in the ultraviolet range, with a vacuum spectrograph of a dispersion of 0.63 A/mm, the bands 4 – 0 and 5 – 0 of the γ system were discovered [2036, 658] which are strongly overlapped by the bands of the ε system. An analysis of own data with v' = 4 and 5 and data obtained by Gerö and Schmid [1700] with v' = 0 – 3, Barrow and Miescher [658] calculated the vibrational and rotational constants of the state $A^2\Sigma^+$ which are accepted in the present handbook and given in Table 97. The constant of centrifugal distortion D_0, contained in this table, was found by Gerö and Schmid [1700]. The values of constants recommended by other authors (among them by Feast [1539] whose data are accepted in the handbook [649] and partly in Herzberg's monograph [2020]) agree with those given in Table 97, are, however, obviously less accurate since they were calculated on the basis of results of measuring bands corresponding to values with v' $\leq$ 3.

According to Sutcliffe and Walsh [3902] and also Barrow and Miescher [658], the dissociation limit of the $A^2\Sigma^+$ state must be related with the atomic states of $N(^4S) + O(^5S)$ or $N(^4S) + O(^3S)$, i.e., it must lie 126,220 or 129,240 cm^{-1} above the ground state. According to the constants accepted in the present handbook, the vibrational levels of the $A^2\Sigma^+$ state converge to the limit of 128,670 cm^{-1} with $v_{max} = 71$.

The bands of the δ-system $B'^2\Delta - B^2\Pi_r$ are connected with the next excited electron state of the NO molecule ($B^2\Pi_r$). The bands of the system $B'^2\Delta - B^2\Pi_r$ were observed by Duffieux and Grillet [1413], Tanaka and Ogawa [3936] and Ogawa [3112, 3113]. Baer and Miescher [607] iden-

tified 10 bands ($v'' \leq 4$) of this system according to data of Tanaka and Ogawa [3936]. Since the rotational structure of the bands was not resolved, the values obtained for the vibrational constants of both states are of low accuracy.

The investigations of the β system have already been mentioned (cf. page 680). It is an interesting particularity of this system that in the emission spectrum [2232, 3628, 1664, 1288] only bands connected with values of $v' \leq 6$ are observed whereas in the absorption spectrum Herzberg, Lagerquist and Miescher [2036] obtained the β-bands up to $v' = 19$ and Barrow and Miescher [658] supposedly discovered also the bands 22-0 and 24-0.* Herzberg, Lagerquist and Miescher (for details see Lagerquist and Miescher [2528]) assumed that the potential curve of the $B^2\Pi_r$ state in the range $v' = 7$ intersects the curve of the repulsive state $^2\Sigma^+$, dissociating into normal atoms which may explain the fact that the levels of the $B^2\Pi_r$ with $v' > 7$ are not observed in the emission spectrum.**

Barrow and Miescher [658] summarized the experimental values (chiefly obtained by Herzberg, Lagerquist and Miescher [2036]) of the energies of the vibrational levels and of the rotational constants B_v for the $B^2\Pi_r$ state up to $v = 19$. Barrow and Miescher, however, did not give the values of the vibrational and rotational constants.

On the basis of data contained in the paper of Barrow and Miescher [658], the authors of the present handbook (cf. [477]) calculated the values of the vibrational constants of the $B^2\Pi_r$ state with the help of a fourth-order equation, following Herzberg, Lagerquist and Miescher [2036] in assuming that the NO molecule in this state has a dissociation limit of $N(^2D) + O(^3P)$. These constants were accepted in the present handbook and are given in Table 97. It should be noted that the accepted values of the vibrational constants were calculated on the basis

of experimental data of the substate $^2\Pi_{1/2}$, but when these constants are used with the substate $^2\Pi_{3/2}$ a small error arises which may be neglected. In Table 96 for several values of v of the $B^2\Pi_r$-state values of $G_0(v)$ are given which were determined by experiment and calculated from constants, recommended by a series of authors or such as are given in the present handbook. The values of the rotational constants of the $B^2\Pi_r$ state were also calculated from data of [658] and are given in Table 97.

TABLE 96

Energies of the Vibrational Levels $G_0(v)$ of the NO Molecule in the $B^2\Pi_r$ State (in cm^{-1})

v	Experimental data [658]	Calculated from constants		
		[2222][a]	[2628][b]	табл. 97
1	1022,0	1022,1	1021,9	1022,3
4	3998,3	4004,9	3998,2	4001,0
10	9604,8	9550,0	9548	9607,4
14	13103,1	13229	12949	13093,9
19	17103,1	17564	16986	17125,5
v_{max}	26200	—	35500	26332[c]

a $G_0(v) = 1029{,}429\,v - 7{,}460\,v^2 + 0{,}1017\,v^3$.
b $G_0(v) = 1029{,}4\,v - 7{,}480\,v^2$; $v_{max} = 70$.
c $v_{max} = 30$.

The $B^2\Pi$-state is a normal state, the type of bond in it resembles Case a according to Hund. According to data given in the paper of Barrow and Miescher [658], the values of the spin-orbital coupling constant A grows considerably as v increases; in the handbook, however, we assume that $A = A_0 = 31.3\ cm^{-1}$.

The C-state of the NO molecule was previously considered as a state of the type $^2\Sigma^+$ and the vibrational levels of this state, corresponding to $v > 0$ were assumed not to exist since in the emission spec-

tra [3629, 1664] transitions connected with levels with v' > 0 were not observed. As in the cases of the $A^2\Sigma^+$ and $B^2\Pi_r$ states, this effect was explained by predissociation. In 1952, however, Herzberg, Lagerquist and Mlescher [2036] discovered in the NO absorption spectrum bands 0-0, 1-0, 2-0, 3-0 and 4-0 of the δ system and showed that this system pertains definitely to the $^2\Pi - {}^2\Pi$ transition, while the type of bond in the upper state $C^2\Pi$ resembles Case b according to Gund. As in the case of the $B^2\Pi_r$ state, the emission spectrum does not contain transitions from levels

TABLE 97

Accepted Values of the Molecular Constants of NO

State	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	$\omega_e z_e$	B_e	α_1	$D_e \cdot 10^6$	r_e
	cm^{-1}								Å
$X^2\Pi_r$	0[a]	1905,585	14,648	0,0724	0,002316	1,7046	0,00178	5,1	1,1508
$A^2\Sigma^+$	43884,6[b]	2374,8	16,46	—	—	1,9972	0,01928	6,0	1,0631
$B^2\Pi_r$	45918[c]	1038,20	8,224	0,1608	0,00462	1,124	0,012	2,7	1,417
$C^2\Pi_r$	52073	2455,7	18,9	—	—	2,008	0,054	5,4[e]	1,060
$D^2\Sigma^+$	53085	2323,90	22,885	0,75	0,22	2,0025	0,02175	6,1	1,0617
$B'^2\Delta_i$	60364,5	1216,8	15,86	—	—	1,330	0,019	—	1,303
$E^2\Sigma^+$	60629	2373,06	15,87	—	—	1,9863	0,0182	5,6[f]	1,0660

a $A = 123{,}3$ cm^{-1}. c Calculated from Eq. (1.36)
b $A = 31{,}3$ cm^{-1}. d $\beta_1 = 2 \cdot 10^{-6}$ cm^{-1}.

with v > 0 which was explained by Herzberg et al. [2036] (cf. also [2528]) as the consequence of an intersection of the potential curve of the $C^2\Pi$ state with the curve of the repulsive state $^2\Sigma^+$. The mutual perturbation of the states $C^2\Pi$ and $B^2\Pi$, investigated by these authors, makes it difficult to calculate the vibrational and rotational constants of NO in the $C^2\Pi$ state. Based on the results of paper [2036]* the authors of the present handbook calculated the molecular constants of NO in the state $C^2\Pi$ and the values obtained are compiled in Table 97.

The molecular constants of NO in the next excited state $D^2\Sigma^+$ may be calculated from an analysis of the ε system of bands.** In the emis-

sion spectrum this system was studied by Gaydon [1664], Gero, Schmid and Szily [1701] and Ogawa [3114]; transitions were only observed to occur from the two vibrational levels v' = 0 and v' = 1 of the state $D^2\Sigma^+$.* Investigating the ε system in the absorption spectrum, Barrow and Miescher [658] obtained bands corresponding to $v' \leq 4$ and calculated the molecular constants of NO in the $D^2\Sigma^+$ state which are also adopted in our handbook and contained in Table 97. Barrow and Miescher noted that the intersection of the potential curves of the states $B^2\Pi$ and $D^2\Sigma^+$ gives rise to some weak interactions whose most important consequence is a change of the value of $B_3(D^2\Sigma^+)$ by 0.0056 cm^{-1} compared with the nonperturbed value.

Fron an analysis of the 0-0 band of the $D^2\Sigma^+ - E^2\Sigma^+$ system, Feast [1539] calculated $B_0' = 1.9912$ and $D_0' = 5.8 \cdot 10^{-6}$ cm^{-1}.

The $B'^2\Delta$ state of the NO molecule is connected with the $B'^2\Delta -$ $- B^2\Pi$ band system mentioned above (see page 685). Moreover, this state is an upper state of the β' system of bands with whose investigation Miescher [2906, 2908, 606] and Tanaka [3931] were concerned in several papers. The state B' was first identified as a state of the type $B'^2\Sigma^+$, but Miescher [2906, 2908], as a result of analyzing several bands of the β' system with values of $v' \leq 5$, could show that the B' state is an inverted $^2\Delta$ state whose type of bond resembles Case b according to Gund and he calculated the molecular constants of NO in this state. These constants are accepted in the present handbook and given in Table 97.

The molecular constants of NO in the $E^2\Sigma^+$ state were obtained by Feast [1539] (cf. also [1228a]) when analyzing the rotational structure of the bands 0-1, 1-1 and 2-2 of the system $E^2\Sigma^+ - A^2\Sigma^+$. These values of the constants are accepted in the present handbook and given in Table 97. After Feast's paper had been published, a communication came out

dealing with investigations of new absorption bands of NO in the far ultraviolet carried out by Tanaka, Seya and Mori [3937]. The authors of [3937] referred these bands to the transition $E^2\Sigma^+ - X^2\Pi$. An analysis of the band edges yielded the values of the vibrational constants of the $E^2\Sigma^+$ state which agreed with those found by Feast [1539].

It must be noted that a determination of the vibrational constants of NO in the excited electron states is difficult owing to the fact that the dissociation limits of these states, with the exception of the $B^2\Pi_r$ state and, to a certain degree, of the $A^2\Sigma^+$ state, are unknown. We may only assume that this limit is high and has an energy of 100,000 cm^{-1} or more.

NO^+. The NO^+ bands were first observed by Baer and Miescher [606] in the Schuman range of the emission spectrum of a discharge in helium, containing NO. But the bands obtained by Baer and Miescher could not be accurately identified. Tanaka [3931], who tried to reproduce these bands, assumed that they were belonging to the system $A^1\Pi - X^1\Sigma^+$ of the NO^+ molecule and calculated the vibrational constants for both states. Somewhat later, Baer and Miescher [607] demonstrated beyond a doubt that these bands belong to the indicated system. In 1955, Miescher [2906, 2907] again measured the system $A^1\Pi - X^1\Sigma^+$ of the NO^+ molecule with an apparatus of higher dispersion (2.5 and 0.62 A/mm, respectively, in first and fourth orders of grating) and by way of analyzing the bands 1-1, 1-2, 0-1, 0-2, 0-3, 0-4 and 0-5, he calculated the vibrational and rotational constants of the states $A^1\Pi$ and $X^1\Sigma^+$. These values of the constants are used in the present handbook and given in Table 98.

A linear extrapolation of the vibrational levels of the ground state of NO^+ leads to a value of $D_0 = 85{,}216$ cm^{-1} with $v_{max} = 72$ which is somewhat smaller than the value of $D_0(NO^+) = 87{,}683$ cm^{-1}, calculated under the supposition that in the $X^1\Sigma^+$ state the NO^+ molecule dissociates into the atoms $N(^4S) + O^+(^4S)$ (see page 763). In order to elim-

inate this inconsistency, another term, proportional to v^4 [478] was added to the equation of energy of the vibrational levels. The coefficient $\omega_0 z_0$, calculated in accordance with the relations (1.14a) and (1.14b), is equal to 0.0000815 cm^{-1}; in this case, the vibrational levels of the ground state of NO^+ converge to the dissociation limit 87,700 cm^{-1}.

In analogy with the isoelectronic molecules (e.g., CO or N_2) we may expect that the NO^+ molecule has a series of triplet electron states, among them such with excitation energies below the $A^1\Pi$ state. This has been verified in a paper of Tanaka [3927] who observed in the absorption spectrum of NO several Rydberg series with three different limits of convergence. In the present handbook these limits were identified with the excited electron states $a^3\Pi$, $a'^3\Sigma^+$ and $d^3\Pi$ of the NO^+

TABLE 98

Accepted Values of the Molecular Constants of NO^+

State	T_e	ω_e	$\omega_e z_e$	B_e	α_1	$D_0 \cdot 10^6$	r_e
	cm^{-1}						Å
$X^1\Sigma^+$	0	2377,1	16,35[a]	2,002	0,0202	6,0	1,0618
$a^3\Pi$	40000	—	—	—	—	—	—
$a'^3\Sigma^+$	58000	1338[b]	—	—	—	—	—
$d^3\Pi$	73000	1277	—	—	—	—	—
$A^1\Pi$	73489,6	1608,9[b]	23,3	1,587[d]	0,024	8,0	1,1826[e]
$e^3\Sigma^-$	75000[c]	1150[b]	—	1,251[f]	—	—	1,3574[g]

[a] $\omega_e z_e = 0{,}0000815\ cm^{-1}$.
[b] Value given of ω_0
[c] Estimate
[d] Value given of B_0
[e] Value given of r_0

molecule. The excitation energies of these states, given in Table 98, were calculated on the basis of data obtained by Tanaka [3927]. For the two states $a'^3\Sigma^+$ and $d^3\Pi$ the values of ω_0 are also given which were obtained by Tanaka. The values of ω_0 = 1150 and B_0 = 1.251 cm^{-1} of the

$e^3\Sigma^-$ state, given in Table 98, were calculated by Miescher [2907] on the basis of an analysis of the perturbations in the $A^1\Pi$ state. It must be noted that the excitation energies of the triplet states of NO^+ exhibit an error reaching ± 2000 cm^{-1}.

NH. In the spectrum of NH molecules four band systems were investigated, one of them connected with the transition between the triplet states ($A^3\Pi_i - X^3\Sigma^-$) and three with transitions between the singlet states ($c^1\Pi - a^1\Delta$, $c^1\Pi - b^1\Sigma^+$, $d^1\Sigma^+ - c^1\Pi$).* On the basis of an analysis of the papers published up to 1950, Herzberg [2020] and the authors of the handbook [649] compiled the tables of molecular constants of NH for all six electron states of the molecule; for the ground state $X^3\Sigma^-$ a value of ω_e was recommended that was calculated from Eq. (1.36).

After 1950, the system $A^3\Pi_i - X^3\Sigma^-$ in the emission spectra of NH and ND was subject to additional investigations in the papers of Pannetier, Gaydon and Guenebaut [3174, 3175, 3172, 3176, 3178, 3179, 3180, 1872, 3177, 1872a, 1872b]. The spectra were excited in an explosion of hydrazoic acid and also in the "atomic" flame of HN_3 + H. Based on measurements of the band edges of (0-0, 0-1, 1-0, 1-1, 1-2, 2-1 and 2-2) of the system $A^3\Pi_i - X^3\Sigma^-$, the values of the vibrational constants of the NH molecule in the states $A^3\Pi_i$ and $X^3\Sigma^-$ were calculated. These values are accepted in the present handbook and given in Table 99. An analysis of the rotational structure of the bands 0-1 and 1-0, carried through by the above authors, led to results which virtually agreed with the values of the rotational constants of the states $X^3\Sigma$ and $A^3\Pi_i$ previously found by Funke [1628] by way of analyzing the fine structure of the bands 0-0 and 1-1 and recommended in Herzberg's monograph [2020] and in the handbook [649]. These values of the rotational constants are also accepted in the present handbook** (cf. Table 99).

It must be noted that the system $A^3\Pi_i - X^3\Sigma^-$ of the molecules of

NH and ND were also studied in the absorption spectra of these radicals in matrices of argon, krypton and xenon at 4.2°K by MacCarty and Robinson [2688] (cf. also [3458, 3459]). In these investigations, however, the molecular constants of NH were not determined.

The molecular constants of NH in the states $a^1\Delta$ and $c^1\Pi$ given in Table 99, were obtained by Florent and Leach [1569] in 1952, when investigating the bands 1-0, 0-0 and 0-1 of the $c^1\Pi - a^1\Delta$ system in the emission spectrum of NH and ND. The vibrational constants were calculated by the authors of paper [1569] from the isotope shift of the bands observed.

Since bands corresponding to mutually combined transitions are not observed in the NH spectrum, the values of the excitation energies of singlet states of the NH molecule could not be determined by experiment. Florent and Leach [1569] estimated the quantity $T_e(a^1\Delta)$ under the assumption that in the $a^1\Delta$ state the NH molecule dissociates into the atoms $N(^2D) + H(^2S)$. Since in the $X^3\Sigma^-$ ground state the NH molecule dissociates nnto atoms in the ground states, $N(^4S) + H(^2S)$, the relation

$$T_e(a^1\Delta) = D_e(X^3\Sigma^-) - D_e'(a^1\Delta) + E[N(^2D)],$$

must hold true, where $E[N(^2D)]$ is the excitation energy of the N atom in the ^2D-state. Calculating the dissociation energy of NH in the state $a^1\Delta$(D_e^{Δ}= 43580 cm^{-1}) by means of a linear extrapolation and assuming a value of the dissociation energy of NH in the ground state that was also calculated with the help of a linear extrapolation by Pannetier and Gaydon [3174] (D_e = 33970 cm^{-1}), Florent and Leach obtained $T_e(a^1\Delta)$ = 9600 cm^{-1} (1.2 ev).

The main error in the value of $T_e(a^1\Delta)$ is due to the inaccurate determination of the dissociation energy, though Florent and Leach meant that this inaccuracy might amount to the same order of magnitude for both constants so that it would not exert an essential influence

on the final result. It must be noted that Mulliken [2984] and the authors of the handbook [649] recommend $T_e(a^1\Delta) \approx 1.1$ ev. Taking the approximate nature of the estimates of this quantity into account, a value of $T_e(a^1\Delta) = 9000$ cm^{-1} (about 1.1 ev) was accepted in the present handbook, with a possible error of ± 1000 cm^{-1}.

The values of the constants of the NH molecule in the $b^1\Sigma^+$ state, given in Table 99, were borrowed from Herzberg's monograph [2020] and the handbook [649]. In Table 99, we find all known electron states of NH, except the $d^1\Sigma^+$ state which lies about 80,000 cm^{-1} higher than the ground state.

TABLE 99

Accepted Values of the Molecular Constants of NH, NF and NS

Molecule	State	T_e	ω_e	$\omega_e x_e$	B_e	α_1	$D_0 \cdot 10^3$	r_e
		cm^{-1}						Å
NH	$X^3\Sigma^-$	0	3266	76,5	16,65	0,64	1,67[a]	1,038
	$a^1\Delta$	9000[c] [b]	3314	63	16,78	0,67	1,68[a,c]	1,034 [e]
	$b^1\Sigma$	17500[c] [b]	3480[c] [b]	—	16,40[d]	—	1,46	1,046[A] [e]
	$A^3\Pi_i$	29773 [b]	3186	87,5	16,67	0,78	1,72[e,f]	1,037
	$c^3\Pi$	40300[c] [b]	2502	180	14,81	1,38	2,11[a,c]	1,100
NF	$X^3\Sigma$	0	1000[c] [b]	—	1,067[c] [b]	—	—	1,40
NS	$X^2\Pi_r$	0[=g]	1219,1	7,5	0,77364	0,00612	0,00125[a,c]	1,4950
	$^2\Delta_{3/2}$	40000,21	970,65	8,65				
	A				0,80804	0,00695	0,00147[a]	1,5762
	$^2\Delta_{5/2}$	40049,76	340,4	4,60				
	$^2\Pi_{1/2}$	43300,4						
	B		780	—	0,66[c,r] [d]	—	—	1,62[A] [e]
	$^2\Pi_{3/2}$	43399,1						
	$C^2\Sigma$	43296,2	1403,5	8,75	0,8267[c,r] [d]	—	—	1,446[A] [e]

a [a] $H_0 = 9 \cdot 10^{-6}$ cm^{-1}.
b [b] Estimate
c [c] Calculated from Eq. (1.36) [=] $A = 223{,}03$ cm^{-1}. [g]
d [r] Value given of B_0
e [A] Value given of r_0
f [e] $H_0 = 5 \cdot 10^{-6}$ cm^{-1}.

NF. There does not exist any literature on investigationsof the NF spectrum. Considering this, the molecular constants of NF given in the present handbook were chosen on the basis of approximate estimations.

The value of the interatomic distance in the NF molecule was estimated as being equal to 1.40 ± 0.05 A, on the basis of the values of the bond lengths r_{N-H} in the molecules of NH and NH_3 (1.038 and 1.017 A, respectively) and r_{N-F} in the molecules of NF_3 (1.371 A).

The vibrational frequency of the NF molecule was calculated from Eq. (1.42), assuming that the force constant k_e is equal to the force constant f_d of the NF_3 molecule ($4.36 \cdot 10^5$ dyne·cm^{-1} [3608]). A comparison of the known values of k_e of diatomic molecules XY with the corresponding force constants f_d of molecules of the type XY_3 shows that this approximation is fully justified. Basing upon this estimate a value of ω_e = 1000 ± 100 cm^{-1} was used in the present handbook.

In the first edition of the handbook [420], on the basis of a graphical estimation for NF, the following values were accepted: B_0 = = 1.257 cm^{-1} (r_{N-F} = 1.29 A) and ω_e = 1200 cm^{-1}. We see that in the given case a graphical estimation yields inaccurate results. In addition to this, we must note that a calculation according to the semiempirical relation (1.41), suggested by Guggenheimer [1880] (with r_{N-F} = 1.40 A), speaks in favor of a value of ω_e = 1200 cm^{-1}. But an estimation with the help of Guggenheimer's rule may yield a very great error.

In analogy with the isoelectronic molecule O_2, the electron ground state of the NF molecule is of the type $^3\Sigma$.

The adopted values of the molecular constants of NF are given in Table 99.

NS. In 1932, Fowler and Bekker [1585] discovered two band systems

in the spectrum of a discharge in sulfur vapor with an admixture of nitrogen, which, as to their structure and positions, reminded them of the γ and β systems of NO. The new systems were attributed to the transitions $^2\Sigma - ^2\Pi$ and $^2\Pi - ^2\Pi$ in the NS molecule and the lower state of the two systems was identified with the molecule's ground state for which the following vibrational constants were determined: $\omega_e = 1220$ and $\omega_e x_e = 7.5$ cm^{-1}. An analysis of the rotational structure of the bands is not contained in the paper of Fowler and Bekker.

In 1951, Zeeman [4375] investigated the fine structure of the bands 0-0 and 0-1 of the system $^2\Sigma - ^2\Pi$ in the NS emission spectrum with the help of an apparatus of high dispersion, and he determined the rotational constants of both states and the coupling constant A of the lower state $^2\Pi_r$. Zeeman, just as Fowler and Bekker, assumed that this state is the electron ground state of NS. This assumption was finally verified by Barrow, Downie and Laird [653] who investigated the system $^2\Sigma - ^2\Pi$ in the absorption spectrum. The rotational constants of the states $X^2\Pi$ and $^2\Sigma$ obtained in paper [653] are in good agreement with the data obtained by Zeeman [4375]. In addition to this, as a result of a partial analysis of the bands 2-0, 1-0, 0-0 and 0-1 of the β system of NS, Barrow, Downie and Laird [653] showed that this system belongs to the transition $^2\Delta - ^2\Pi$ and not to $^2\Pi - ^2\Pi$ as this had been proposed by Fowler and Bekker [1585] and Zeeman [4375]. This relationship was later verified by Barrow, Drummond and Zeeman [655] who analyzed the entire rotational structure of the bands of the β system of NS from spectrograms previously obtained by Zeeman [4375]. Barrow, Drummond and Zeeman [655] discovered another band system, pertaining to NS, and attributed it to the transition $^2\Pi - ^2\Pi$. Taking the results of previous papers [1585, 4375, 653] into account, Barrow, Drummond and Zeeman [655] compiled a table of the molecular constants

for all electron states of NS known at present. These constants are accepted in our handbook and are given in Table 99.

N_3. The assumption of the existence of an N_3 molecule is rather old (cf.[2917]) but a more or less unambiguous identification of the infrared spectrum of this molecule was achieved only in 1956 [2917, 711]. According to Walsh [4140], the N_3 molecule must be linear and symmetrical. In this case, in the infrared spectrum only two frequencies ν_2 and ν_3, are active while the frequency ν_1 appears only in the Raman spectrum.

With the help of the method of separating the products of a discharge in N_2 and the products of an HN_3 photolysis in an inert gas matrix at low temperatures, Milligan, Brown and Pimentel [2917] and also Bekker, Pimentel and Thiel [711] obtained a series of absorption bands, among which the 2150-cm^{-1} band was attributed to the antisymmetric vibration ν_3 of the N_3 molecule.

The residual frequencies of N_3 could not be identified unambiguously, though the band observed in the range of 737 cm^{-1} was suggested to be attributed to the doubly degenerated deformation vibration ν_2 [2917]. As there are no other more reliable data on this value, it was adopted in the present handbook.

The frequency ν_1 of the symmetric valence vibration of N_3, which does not appear in the infrared spectrum, was evaluated by the authors of the handbook on the basis of the well-known value of the frequency ν_3, assuming that $f_{dd} = 0.12\ f_d$ which holds true for all azides investigated [1849]. Thus, from Eq. (P4.31), we calculated $\nu_1 = 1400$ cm^{-1}.

The values chosen for the fundamental frequencies of N_3 are given in Table 100; the possible errors amount to $\pm 10\%$ with ν_1 and ν_2 and $\pm 5\%$ with ν_3. In the same table, we find the value of the moment of inertia of N_3, calculated with $r_{N-N} = 1.15$ A (mean of all azides studied

[1849, 1507]). The possible eeror of the chosen value of r_{N-N} lies within the limits of ±0.05 A.

TABLE 100

Accepted Values of the Molecular Constants of N_3 in the Electron Ground State

ν_1	$\nu_2(2)$	ν_3	I	•
cm^{-1}			10^{-40} g·cm^2	
1400	737	2150	6,151	2

In the photolysis of hydrazoic acid, Thrush [3988] observed a series of diffuse bands in the range of 2670-2730 A which he attributed to a transition in the N_3 molecule and, in analogy with the isoelectronic molecule CO_2^+, he assumed that the N_3 molecule must have a $^2\Pi_g$ electron ground state.

NO_2. In the electron ground state the NO_2 molecule is a nonlinear symmetrical molecule (point group C_{2v}) and belongs to the type of asymmetrical rotators.* All three nondegenerate fundamental frequencies of NO_2 appear in the Raman spectrum and in the infrared spectrum. But owing to the strong absorption in the visible and ultraviolet ranges the Raman spectrum of NO_2 cannot be observed. Investigations of the infrared and ultraviolet spectra of NO_2 carried out until 1940 are reviewed in Herzberg's monograph [152] where the following values are recommended for the values of the fundamental frequencies: ν_1 = 1320, ν_2 = 648 and ν_3 = 1621 cm^{-1}. In the first investigations of the NO_2 spectrum devices with low dispersion were used with which it was impossible to resolve the rotational structure and determine the zero lines of the infrared bands. Moreover, the ν_1 band was not observed because of its weak intensity in the infrared spectrum, and the value of 1320

cm^{-1} was chosen by Herzberg on the basis of results of investigating the ultraviolet spectrum [1958]. In 1949, Wilson and Badger [4296], investigating the NO_2 spectrum in the range 400-6700 cm^{-1} (1.5-25 μ) with a prism spectrograph, recorded for the first time a weak band in the range of 1306 cm^{-1}, which was related to the ν_1 vibration, and also found the center of the ν_2 band lying in the range of 755 cm^{-1}. Later on, Brown and Wilson [988] who also used a prism apparatus, could determine a more precise position of the ν_2 band center with the value of 750.6 $\pm$ 0.3 cm^{-1}. In 1953, Moore [2943] investigated nine composite bands of NO_2 in the range 2900-7150 cm^{-1} (1.4-3.4 μ), with the help of a spectrograph with a grating, permitting a resolution of the order of 15,000. Using the results obtained by Brown and Wilson [988] for the ν_2 band, Moore calculated all vibrational frequencies and the constants of anharmonicity of the molecule $N^{14}O_2$. In 1957, Weston [4222], studying the $N^{15}O_2$ spectrum with a prism instrument, calculated the vibrational constants of $N^{15}O_2$ and also improved the values of ω_2 and x_{22} for the $N^{14}O_2$ molecule compared to those suggested by Moore [2943], taking into consideration the new and more accurate data of the ν_2 band obtained by Keller and Nielsen [2349, 2350] with a grating spectrograph. The constants recommended by Weston for $N^{14}O_2$ have the following values (in cm^{-1}): $\omega_1 = 1361.4$, $\omega_2 = 776.8$, $\omega_3 = 1668.6$, $x_{11} = -7.1$, $x_{22} = -7.5$, $x_{33} = -15.9$, $x_{12} = -16.0$, $x_{13} = -33.4$, $x_{23} = -8.2$. These constants correspond to the following values of the fundamental frequencies: $\nu_1 = 1322.5$, $\nu_2 = 749.9$ and $\nu_3 = 1616.0$ cm^{-1}. Finally, Nielsen and coworkers [2353, 3885] again measured the fine structure of the ν_2 band and in precisely the same range they could identify new lines, related with the band $2\nu_2 - \nu_2$. Based on the data obtained, a value of $x_{22} = -0.6$ cm^{-1} was found which differs essentially from the value recommended by Moore [2943] and Weston [4222].

It is a serious lack of the papers discussed above that the fine structure of the ν_1 and ν_3 bands was not measured accurately. This fact stimulated Nielsen and coworkers to undertake comprehensive studies of the spectra of $N^{14}O_2$ and $N^{15}O_2$ which they obtained with high dispersion in the range of 670-5900 cm^{-1} (1.7-15 μ) with the help of a grating apparatus. In 1958, the results of these investigations were published in a paper of Arakawa and Nielsen [564]. With $N^{14}O_2$ six bands of the type A(ν_3, $\nu_1 + \nu_3$, $2\nu_1 + \nu_3$, $3\nu_1 + \nu_3$, $3\nu_3$ and $\nu_1 + 3\nu_3$) and four bands of the type B(ν_1, ν_2, $2\nu_2 - \nu_2$ and $2\nu_3$ were obtained. By way of analyzing the rotational structure the beginnings of the bands were determined and the vibrational frequencies and the constants of anharmonicity were calculated; these values are accepted in the present handbook and compiled in Table 101. The following values of the fundamental frequencies correspond to these values of the vibrational constants: $\nu_1 = 1319.7$, $\nu_2 = 749.8$, $\nu_3 = 1617.75$ cm^{-1}. The quantity ν_1 has the greatest error (0.5 cm^{-1}) which is due to the strong overlapping of the corresponding bands of NO_2 by the intense band of H_2O. It must also be noted that the quantity x_{12} was calculated in paper [564], using the results of measuring the ultraviolet spectrum of NO_2.

Just as in the case of any other molecule of the type of an asymmetric rotator, it is a very cumbersome task to calculate the rotational constants of NO_2. But, owing to the fact that the NO_2 molecule approaches to a symmetrical rotator, the fine structure of the bands of NO_2 may be analyzed under the assumption that it is indeed a symmetrical rotator. Using the data obtained by Brown and Wilson [988], Moore [2943] found for $N^{14}O_2$ $\tilde{B}_0 = 0.429$ and $A_0 - \bar{B}_0 = 7.26$ cm^{-1}. To these values correspond those of $r_{N-O} = 1.188$ A and $\angle O - N - O =$ $= 134°4'$. As a result of a more complete analysis of the rotational structure of the infrared bands of $N^{14}O_2$, Arakawa and Nielsen [564]

obtained $\tilde{B}_0 = 0.423$ and $A_0 - \tilde{B}_0 = 7.58$ cm^{-1}. These values agree better with $\tilde{B}_0 = 12648.6 \pm 2.5$ Mc (0.4219 ± 0.0001 cm^{-1}) and $A_0 - \tilde{B}_0 = 227{,}020 \pm 40$ Mc (7.5726 ± 0.0013 cm^{-1}) found by Bird [817, 818] from the microwave spectrum of $N^{14}O_2$.* On the basis of measurements of the pure rotation spectrum of $N^{14}O_2$ [819] a value of $A_0 - \tilde{B}_0 = 7.573$ cm^{-1} was obtained which is also in very good agreement with the results of microwave measurements.

The values of the rotational constants of the ground state of $N^{14}O_2$, accepted in the present handbook and given in Table 101, were calculated from data of Bird's paper [818]. These constants correspond to $r_{N-O} = 1.197$ A and $\angle O - N - = 134°15'$ which agrees satisfactorily with the results of electron diffraction measurements ($r_{N-O} = 1.20 \pm \pm 0.02$ A, $\angle O - N - = 132 \pm 1°$ [1119], $r_{N-O} = 1.20$ A, $\angle O - N - O = = 132°.5$ [3472]).

As a result of fine-structure measurements with several bands of NO_2, the constants of centrifugal distortion were obtained in a series of papers [988, 2349, 2350, 2943, 819]. In the present handbook these constants are chosen according to a paper of Danti and Lord [1260] (cf. Table 101) in which the quantities D_J, D_{JK} and D_K are calculated

TABLE 101

Accepted Values (in cm^{-1}) of the Molecular Constants of $N^{14}O_2$ ($\sigma = 2$) in the Electron Ground State

Constant	Value	Constant	Value	Constant	Value
ω_1	1357,8	x_{23}	−16,4	B_0	0,4330
ω_2	756,8	x_{13}	− 9,7	C_0	0,4108
ω_3	1665,5	x_{12}	−28,7	D_J	$2{,}83 \cdot 10^{-6}$ [a]
x_{11}	−9,0	x_{33}	− 2,7	D_{JK}	$-1{,}89 \cdot 10^{-6}$
x_{22}	−0,5	A_0	7,9945	D_K	$2{,}41 \cdot 10^{-6}$

a) In paper [1260] a value of $D_J = 2.83 \cdot 10^{-7}$ cm^{-1} is given, which seems to be incorrect (cf. [564]).

on the basis of data obtained by Bird [818] and Arakawa and Nielsen [564].

It must be noted that Arakawa and Nielsen [564] succeeded in determining the values of three (of nine) constants of vibration-rotation interaction: $\alpha_1^B = -0.0028$, $\alpha_3^B = -0.0024$ and $\alpha_2^A = 0.36$ cm^{-1} (with $N^{14}O_2$).

The electron states of the NO_2 molecule are analyzed in Walsh's review article [4140] which also contains a compilation of references as to investigations of the ultraviolet spectrum of NO_2. According to Walsh, the electron ground state of NO_2 belongs to the type $^2A_1$, i.e., it is a doublet. The first excited state of NO_2 has a low excitation energy and the bands corresponding to transitions between the ground state and the first excited state must lie in the near infrared. As the result of investigating the electron spectrum of NO_2 at liquid-helium temperatures, Robinson, McCarty and Keetly [3461] came to the conclusion that the beginning of the most long-wave electron transition in the NO_2 spectrum corresponds to the band of 8900 A. Based upon these data the energy of the first excited electron state of NO_2 was chosen in our handbook as equal to 11,000 cm^{-1}. The authors of paper [3461] also came to the conclusion that in the wavelength range below 6200 A there must still exist at least two band systems which are connected with other excited electron states of NO_2. One and the same value, namely 16,000 cm^{-1}, is taken as the excitation energy of these states and used in the present handbook. According to Walsh [4140], the three excited states of NO_2 are all doublets.* Electron transitions in the ultraviolet range are connected with electron states with high excitation energies and these states are therefore not considered in the present handbook.

N_2O. The N_2O molecule has a linear nonsymmetrical structure in

the form of NNO and belongs to the point group of symmetry $C_{\infty v}$. The three fundamental vibrational frequencies of this molecule are active in both the infrared spectrum and the Raman spectrum, the deformation vibration ν_2 is doubly degenerate.

The vibration-rotation spectrum of N_2O is one of the most carefully studied spectra of multiatomic molecules, its analysis, however, is difficult because of the presence of a Fermi resonance in the Σ-states $(p, 0^0, \nu_3)$, $(p - 1.2^0, \nu_3)$, ..., $(0, 2p^0, \nu_3)$ and in the Π-states $(p, 1^1, \nu_3)$, $(p - 1, 3^1 \nu_3)$, ..., $(0, 2p + 1^1, \nu_3)$.

On the baris of results of papers published up to 1944, the vibrational frequencies and the constants of anharmonicity of N_2O were calculated in Herzberg's monograph [152]. Some years later, in 1950, G. Herzberg and L. Herzberg [2029], on the basis of results of fine-structure analyses of more than 20 new bands of N_2O in the range 8000-14,000 cm^{-1}, obtained in high resolution, calculated new values of the vibrational constants which describe a little better both the older data and the new experimental data.

In the period of 1950-1960, the infrared spectrum of N_2O was studied by many authors. A detailed review on the results of investigations carried out until 1955 was given by Grenier-Besson [1856] who tabulated the results of measurements of 66 bands of N_2O on the basis of own papers published together with her co-authors [534, 535, 634] and papers of other authors (G. Herzberg and L. Herzberg [2029], Plyler and Barker [3275] Thompson and Williams [3976], Douglas and Moller [1377], Taylor [3950]). These data which were, as a rule, obtained with an accuracy of 0.1-0.2 cm^{-1} with devices of high resolution, and comprise a great number of vibrational levels with quantum numbers of $v_1 \leq 5$, $v_2 \leq 6$, $l \leq 3$ and $v_3 \leq 6$. Among the measured bands we find the components of several doublets and triplets of Fermi resonance. Based

on this great experimental material, the values of zero frequencies, the constants of anharmonicity and also the constants of Fermi resonance were calculated [1856, 1857, 537, 1858]. These constants are accepted in the present handbook and given in Table 102. The constant of Fermi resonance was also determined by Nielsen and coworkers [2544, 3087, 3394]; the value he obtained, $k = 42.3 \pm 3$ cm^{-1} ($W = 29.9 \pm 2$ cm^{-1}) agrees with the value of $k = 40$ cm^{-1} ($W = 28.3$ cm^{-1}), recommended by Grenier-Besson [1856] and given in Table 102. A comparison of the frequencies of more than 40 bands, calculated from the accepted constants, with those measured experimentally [1856] shows that the nonperturbed vibrational levels and a great part of the perturbed levels of N_2O are described by these constants with an error of ± 1 cm^{-1} at most. Only with certain doublet or triplet components of Fermi resonance the difference between the calculated and the measured quantities exceeds this value. This may be explained by the approximate character of considering the Fermi resonance and also by a possibly incorrect determination of the frequencies of a series of bands. For example, a calculation of ν_0 of the 11^10 band yields a value of 1880.04 cm^{-1} which differs essentially from the value of $\nu_0 = 1867.5$ cm^{-1} obtained in an old paper by Plyler and Barker [3275]. But later, Plyler, Tidwell and Allen [3286], investigating a series of N_2O bands in high resolution, improved the values of ν_0 for several bands as compared to the values obtained in preceding papers. For the band 11^10, a value of $\nu_0 = 1880.37 \pm 0.04$ cm^{-1} was found which is in excellent agreement with the value calculated from the accepted constants. Thus, the vibrational constants accepted for the N_2O molecule, may now be considered as most reliable, although it must be pointed out that these constants give a less good description of the vibrational levels of N_2O with high values of v_i than of those with small v_i. This is caused by the fact that the

constants of anharmonicity, y_{ijk}, are not available and that the perturbations of higher order than the Fermi resonance have been neglected.

After the review article of Grenier-Besson [1856], besides the paper of Plyler, Tidwell and Allen [3286] mentioned above, several other papers were published, devoted to investigations of the infrared spectrum of N_2O [2544, 3394, 3698, 1130]. In these papers individual values were improved, particularly those of ν_1, ν_2 and a series of constants of anharmonicity but the changes are either insignificant or, as in the case of the new values of x_{22} and x_{12}, obtained in the paper of Shearer, Wiggins, Guenther and Rank [3698], cannot be considered as quite reliable.

The rotational structure of the N_2O bands was studied by Thompson and Williams [3976], Christensen and Thompson [1102], Douglas and Møller [1377], Rao and Nielsen [3394], G. Herzberg and L. Herzberg [2029].

The calculation of the rotational constants of N_2O is complicated by the presence of Fermi resonance and l-doubling. More precisely, these difficulties are mainly connected with the calculation of α_2. Different authors recommend different values of α_2: −0.00022 [2029], −0.000258 and 0.000424 [3976], −0.00042 [1102, 1377], − 0.00056 [3394]. The last of these values may be taken as the most accurate one; it was calculated by Rao and Nielsen [3394] on the basis of results of measuring the 01^10 band, obtained by Lakshmi, Rao and Nielsen [2544] and the constant of l-doubling in this band, $q_{010} = 0.000792\ cm^{-1}$, found by Burrus and Gordy [1032] from the microwave spectrum. Measuring the bands 10^00 and 02^00, Rao and Nielsen [3394] also calculated the value of $\alpha_1 = 0.00199\ cm^{-1}$ which is in good agreement with the data of other authors (0.00170 [2029, 1102], 0.00172 [1377], 0.00168 [3976]). The value of $\alpha_3 = 0.00345\ cm^{-1}$ is chosen in our handbook from data obtained in a paper of Douglas and Møller [1377]. Within the limits of 0.00001

cm^{-1} this value agrees with the values obtained in the papers of other authors. The values of $B_{000} = 0.41898$ and $D_0 = 0.18 \cdot 10^{-6}$ cm^{-1}, borrowed from the paper of Douglas and Møller, are verified by the results of investigating the infrared vibration-rotation spectrum [2029, 2544, 3976, 3286, 3425], the pure rotation spectrum in the infrared [3167] and in the microwave range [2260, 1032] of N_2O. The values accepted for the rotational constants of N_2O are given in Table 102. The values of the geometrical parameters of N_2O, corresponding to the constants used, are equal to $r_{N-N} = 1.1257$ and $r_{N=O} = 1.1863$ A.

TABLE 102

Accepted Values (in cm^{-1}) of the Molecular Constants of N_2O ($\sigma = 1$) in the Electron Ground State

Constant	Value	Constant	Value	Constant	Value	Constant	Value
ω_1	1300,43	x_{22}	— 0,17	x_{33}	—14,22	α_1	0,00199
$\omega_2(2)$	585,62	x_{23}	—15,10	W	28,3	α_2	—0,00056
ω_3	2281,80	x_{13}	0,52	S_{33}	0,52	α_3	0,00345
x_{11}	—5,21	x_{12}	—27,26	B_e	0,42114	D_e	$0,18 \cdot 10^{-6}$

The electron spectra of N_2O in the ultraviolet range were studied repeatedly (cf. reviews of Sponer and Teller [3827] and Walsh [4140] and the original investigations [4385, 1841, 574], etc.). According to the results of these investigations, the ground state of N_2O is of the type $^1\Sigma$, the first stable excited electron state has the energy $T_0 = 59,529$ cm^{-1}.*

$\underline{NH_2}$. Among the great many experimental and theoretical investigations of the NH_2 spectrum (see the review articles of Ramsay [3363] and Proisy [3333]) we find in the first place papers of exclusively astrophysical interest, not concerned with the problems of determining molecular constants. Particularly, the complex band system in the range

4000-8300 A, observed in the emission spectrum of a discharge tube filled with ammonia gas (the so-called α-bands of ammonia) and attributed to the electron spectrum of NH_2 have as yet not been identified. The same bands appearing in the absorption spectrum have a less complex structure and are connected with the lower vibrational level (0, 0, 0) of the NH_2 ground state so that they may only be used to determine the structural parameters of the molecule.

Herzberg and Ramsay [2040, 2041, 3358, 3359, 3360, 3362, 3363], using multichannel bulbs to study the absorption spectrum in pulsed photolysis of ammonia and hydrazine in the visible range, obtained a spectrum which was attributed to an electron transition in NH_2 in which the lower state ^2B is the ground state of the molecule. In accordance with the results of a theoretical analysis (Walsh [4139]) it was found that the NH_2 molecule in the electron ground state is nonlinear and asymmetrical. For this state, the rotational constants of NH_2, calculated by Ramsay [3360, 3359, 3358, 3362] from the combinatory differences according to the sum rule of Mecke [2831] are accepted in the present handbook and given in Table 103. According to these constants, we have $r_{N-H} = 1.024$ A and $\angle H - N - H = 103°$.

In the last time, in order to determine the fundamental frequencies of NH_2, it was tried to obtain the infrared spectrum of this molecule. For this purpose Tanner and King [3944] investigated the absorption spectrum of the products of pulsed photolysis of hydrazine in the 3 μ range. Referring the 3200-cm^{-1} band to the frequency ν_1 and assuming $\nu_3 \approx 3280$ cm^{-1}, the authors of paper [3944] calculated $\nu_2 = 1060$ cm^{-1}, using the values of the force constants $f_d = 5.74 \cdot 10^5$ dyne·cm^{-1} and $f_\alpha = 0.31 \cdot 10^5$ dyne·cm^{-1}. With this identification of the frequencies, Tanner and King took into account the evaluation of the fundamental frequencies of the NH_2 molecule carried out by Herzberg and Ramsay

[2041] in the approximation of the field of valence forces, using Eq. (P4.30) for the angles 180, 150, 120 and 90° and the values of f_d = = $6.0 \cdot 10^5$ and $f_\alpha = 0.6 \cdot 10^5$ dyne·cm^{-1}. But when the calculations of Herzberg and Ramsay were checked in the preparation work of the present

TABLE 103

Accepted Values (in cm^{-1}) of the Molecular Constants of NH_2 (σ = = 2), HNO (σ = 1) and FNO (σ = 1)

Molecule	State	T_{000}	ν_1	ν_2	ν_3	A_{000}	B_{000}	C_{000}
NH_2	X^2B_1 A^2A_1	0 10250	3380 —	1400 —	3440 —	23,62 —	12,94 —	8,19 —
HNO	X^1A'' A^1A'	0 13154,4	3450 —	1570 —	1110 —	18,47923 —	1,41152 —	1,30714 —
FNO	X^1A''	0	1844,03	765,85	521	3,17549	0,395070	0,350524

handbook (cf. [476]), it was shown that these authors have obviously admitted an error in the calculations, thus obtaining values of ν_2 that were too low for all angles (from 1038 for 90° to 1075 cm^{-1} for 180°).

Moreover, in the paper of Bekker, Pimentel and Thiel [711] (cf. also [3962a]), devoted to an investigation of the infrared absorption spectrum of the intermediate products of pulsed photolysis of hydrazoic acid HN_3, with the help of the method of separation in the matrix, it was suggested to relate the 1290-cm^{-1} band to the deformation frequency ν_2 of the NH_2 molecule. It is likewise of interest to note that the deformation frequency of the group of NH_2 in the molecules of different amines has a value of the order of 1300-1500 cm^{-1} and is never smaller than 1300 cm^{-1} [4024a].

In the present handbook, the values of the fundamental frequencies

of NH_2 were calculated from Eqs. (P4.28) on the basis of the force constants (in 10^{-5} dyne·cm^{-1}) $f_d = 6.45$, $f_{dd} = 0.0045$, $f_\alpha = 0.539$ and $f_{d\alpha} = 0.133$, assumed to equal the force constants of NH_3. These constants were in their turn calculated from Eqs. (P4.37) on the basis of the fundamental frequencies of NH_3, given in Table 106. When calculating the force constants of NH_3, the quantity $f_{d\alpha}$ was borrowed from paper [4087]. The values of the fundamental frequencies of NH_2 obtained in this way vary within the limits of ± 40 cm^{-1} if all force constants of NH_3 were given the values recommended in paper [4087].

Taking the fact into account that the values of the fundamental frequencies of vibration of NH_2, obtained experimentally in papers [711, 3944], cannot be viewed as unambiguous, the frequency values accepted in the present handbook (cf. Table 103) were calculated by means of Eqs. (P4.28). The possible error of the frequencies accepted amounts to 5-7%.

The first excited electron state $^2A_1\Pi_u$ of the NH_2 molecule with an excitation energy of 10,250 cm^{-1} (cf. Dressler and Ramsay [1404]) is the upper state of the electron transition in NH_2 investigated in the papers of Herzberg and Ramsay mentioned above, and in the paper of Robinson and McCarty [3460] who used the method of separation in the matrix. In this state, which has the statistical weight 2, the NH_2 molecule is linear.

As already mentioned above, the electron ground state of NH_2 is of the type $^2B_1$ and is therefore a doublet state.

$\underline{NF_2}$. In literature there are no data on investigations of the NF_2 spectrum. The constants of NF_2 were estimated under the assumption that this molecule is nonlinear and symmetrical (see Walsh [4139]), analogous to the NH_2 molecule. The interatomic distance $r_{N-F} = 1.37$ A and the angle between the bonds, $\angle F - N - F = 100°$, was estimated with the help

of relevant data of the NF_3 molecule, taking into account the changes of the analogous data of the molecules of NH_2 and NH_3. The possible errors of the estimated values do not exceed ± 0.03 A with r_{N-F} and $\pm 3°$ for $\angle F - N - F$.

The fundamental frequencies of the NF_2 molecule were calculated from Eqs. (P4.28), when preparing the present handbook, using the force constants of NF_3 given in the paper of Wilson and Polo [4297]. Since the NF_3 molecule has four fundamental frequencies, Wilson and Polo, in order to obtain the potential function with five force constants, gave different values of the constant $f_{d\alpha}$ and proposed four sets of force constants satisfying the values of the fundamental frequencies of NF_3 they had found. In the calculation the two extreme sets of force constants were used (in 10^{-5} dyne·cm^{-1}): f_d(4.28 and 5.27), f_{dd}(4.48 and 0.96), f_α(1.06 and 0.97) and $f_{d\alpha}$ (0.28 and 0.46).

In the present Handbook we used the mean values of the two sets of constants. The possible errors of the accepted values of the frequencies do not exceed 10%.*

In Table 104 we find the fundamental frequencies of NF_2 and the products of the principal moments of inertia, calculated on the basis

TABLE 104

Accepted Values of the Molecular Constants of NF_2 in the Electron Ground State

ν_1	ν_2	ν_3	$I_A I_B I_C$	σ
1 cm^{-1}			2	
1060	530	970	75,00	2

1) cm^{-1}; 2) (g·cm^2)^3.

of the geometrical parameters of the NF_2 molecule** estimated above.

Since the NF_2 molecule possesses an unpared electron, its ground

state, as in the case of NH_2, must be a doublet.

HNO. The HNO molecule was first discovered spectroscopically in 1957 by Dalby [1252, 1253] in the products of pulsed photolysis of nitromethane, nitroethane, isoamyl nitrate and a mixture of ammonia and nitric acid. The absorption spectrum was photographed in the range of 6500-7700 A with a grating spectrograph of high resolution (about 0.1 cm^{-1}). Three bands were observed with a rotational structure that was characteristic of an asymmetrical rotator. These bands (0,0,0-0,0,0; 0,0,1-0,0,0 and 0,1,0-0,0,0) were attributed to the electron transition $^1A''-^1A'$ of the HNO molecule. On the basis of an analysis of the bands the rotational constants were calculated for the upper and lower states, and also the frequencies ν_2 and ν_3 of the upper state and the quantity ν_{00}. This interpretation was verified by an analysis of the spectrum of the isotope molecule DNO. It was also assumed that the lower state is the ground state of HNO.

Later on Brown and Pimentel [986] worked with the method of separation of the products of photolysis of nitromethane and methyl nitrite in an argon matrix at 20°K and discovered two frequencies (1570 and 1110 cm^{-1}) in the infrared spectrum, which they interpreted as the frequencies ν_2 and ν_3 of the HNO ground state. In paper [986] the assumption that hee molecule has a curved structure with a double bond between the N and O atoms was verified.

Finally, Cashion and Polanyi [1070] studied the emission spectrum in the ranges 7150-16,700 cm^{-1} (0.6-1.4 μ) and 2560-3700 cm^{-1} (2.7-3.9 μ) which appeared as a result of the reaction H + NO; they obtained for the ground state $\nu_1 = 3450 \pm 30$ cm^{-1}, thus verifying the data obtained previously by Brown and Pimentel [986] for the ground state and Dalby [1253] for the excited state.

As a result of an investigation of the electrom spectrum of HNO

[1253] the excited singlet state of HNO (ν_{00} = 13,154 cm^{-1}) was discovered, in which the molecule, just as in the ground state, is nonlinear.

The fundamental frequencies of vibration of the HNO molecule, given in Table 103, were chosen in the present Handbook according to data of Brown and Pimentel [986] (ν_2 and ν_3) and Cashion and Polanyi [1070] (ν_1) for the ground state and according to data of Dalby [1253] (ν_2 and ν_3) and Cashion and Polanyi [1070] (ν_1) for the excited state. We may assume that the error in the determination of these quantities does not exceed ±30 cm^{-1}.

The rotational constants of HNO in both states are borrowed from Dalby's paper [1253] where they have been determined with high accuracy (of the order of ±0.001 cm^{-1}). These constants correspond to the following values of the geometrical parameters of the HNO molecule in the electron ground state [1253]: r_{N-O} = 1.2116, r_{N-H} = 1.0628 A and ∠H–N–O = 108°.58.

FNO. The FNO molecule, analogous to the HNO molecule (and also ClNO and BrNO [1028]), has a nonlinear structure with the N atom at the vertex of the triangle.

The infrared spectrum of this molecule was first investigated in 1950 by Jones and Woltz [2296] in the range of 260-7000 cm^{-1}; these authors observed all three fundamental frequencies and several harmonics and composite frequencies. Later Woltz, Jones and Nielsen [4314] again measured the positions of a series of bands and Magnuson [2737], using a device with high resolution, improved the values of the frequencies ν_1 and ν_3. In Table 103 we find the values of the fundamental frequencies of vibration of the FNO molecule, chosen in the present Handbook according to data from [4314, 2737].

The rotational structure of the bands ν_1 and ν_3 was investigated by Magnuson [2737] and interpreted with the help of the equation for a

nonrigid symmetric rotator. In paper [2737] the values of the rotational constant B, of the constant of centrifugal distortion, $D \approx 10^{-6}$ cm^{-1}, and the constants of anharmonicity, $x_{33} = -1.06$ and $x_{12} = 1.02$ cm^{-1}, were obtained. Moreover, in preceding commun cations of the same author [2735, 2736] the values of the three rotational constants, A_{000}, B_{000} and C_{000} were determined which were obtained as a result of investigating the microwave spectrum of FNO. These values are accepted in the present Handbook and given in Table 103. The following structural parameters of the FNO molecule correspond to them: $r_{N-F} = 1.52$, $r_{N=O} = 1.13$ A and $\angle F-N-O = 110°.2$.

NH_3. The ammonia molecule has the form of a regular pyramid with the N atom at the vertex. In accordance with this structure the NH_3 molecule belongs to the point group C_{3v} and has four fundamental frequencies: two (ν_1 and ν_2) fully symmetrical and two (ν_3 and ν_4) doubly degenerate ones. The four fundamental frequencies of NH_3 are all active in both the infrared spectrum and the Raman spectrum. But ammonia has a very complex spectrum which is difficult to interpret. This is mainly due to the inversion of line doubling which is caused by the presence of two equilibrium positions of the N atom with respect to the plane of the hydrogen atoms, and also by the resonance perturbation caused by the similar values of ν_1 and $2\nu_4$ and also ν_1 and ν_3.

The basic papers on investigations of the NH_3 spectrum, published until 1956, are analyzed in Herzberg's monograph [152]. The values of the fundamental frequencies of NH_3 ($\nu_1 = 3335.9$ and 3337.5, $\nu_2 = 931.58$ and 968.08, $\nu_3 = 3414$ and $\nu_4 = 1627.5$ cm^{-1}), recommended by Herzberg, were chosen on the basis of data obtained by Dennison and Hardy [1315], Sheng, Barker and Dennison [3701], Barker [636], etc. In paper [152] we also find a table of the frequency values of a series of composite bands and harmonics of ammonia, determined by various authors. In par-

ticular, this table contains the frequency values of harmonics of vibration ν_1 up to $6\nu_1$.

After 1945 the ammonia spectrum was studied more than once. In a series of papers [2711, 2951, 3265] the devices used had a low resolving power so that the results obtained are not very accurate. The results of some other investigations are only published in the form of preliminary communications [4318, 4319, 2337, 1924, 1925]. The papers of Cumming and Welsh [1232, 1233], in which a value of ν_3 = 3442.9 cm^{-1} was obtained, are of great importance.

The most complete and systematic investigation of the vibration-rotation spectrum of NH_3 (and also ND_3) was carried through in the past years by Benedict, Plyler and Tidwell [734, 739, 740, 740a] (cf. also [732, 733, 735]). These authors, working with a grating instrument, with a resolution of 0.1-0.2 cm^{-1} and analyzed the fine structure of a great number of bands lying in the range investigated. In the present Handbook the values of the fundamental frequencies of NH_3 are chosen according to data recommended by Benedict and Plyler [734]. The values of ν_1 given in Table 106 are mean

edict and Plyler [734]. The values of ν_i given in Table 106 are mean

TABLE 105

Values (in cm^{-1}) of G_0 (0, v_2, 0,0) for the Electron Ground State of the NH_3 Molecule

$v_2 = 0^s$	0^a	1^s	1^a	2^s	2^a	3^s	3^a
0,00	0,793	932,51	968,32	1597,6	1662,16	2383,46	2895,48

values of the two components of inverted doubling. In paper [734] some constants of anharmonicity of ammonia were also calculated (x_{33}, x_{13}, x_{14}, x_{34}, x_{12}, x_{23} and x_{24}). But when preparing the present Handbook

the constants of anharmonicity were recalculated [476] where, apart from data of [734], the table of the frequency values of composite bands and harmonics of NH_3, contained in Herzberg's monograph [152] (see above). As a result of this calculation the constants x_{11} and x_{44} were obtained and the value of the constant x_{13} was considerably improved; the other quantities were obtained in virtual agreement with the data found by Benedict and Plyler [734]. In Table 106 the values of the constants of anharmonicity are given according to results of paper [476].

The main difficulty in the determination of the vibrational constants from experimental data is connected with the description of vibrational levels related with the fully symmetrical vibration v_2. The inverse doubling of this vibration is considerable and increases rapidly as the quantum number v_2 grows. In Table 105 we find the energy values of the vibrational levels G_0 (0, v_2, 0,0), found by Benedict, Plyler [734] and Garing, Nielsen and Rao [1653] (for G_0 (0, 2^a, 0,0). The lower component of splitting is marked with an s, the upper component with an a.

An analysis of the quantities given in Table 105 shows that it is impossible to calculate the constant of anharmonicity x_{22} on the basis of the experimental data available. It is obvious that the usual quadratic expression is in the given case not suitable to describe the energies of the vibrational levels. This problem is connected with the exact solution of the wave equation for a potential function with a second minimum. Manning [2763], with the help of an expression that he found for this potential, achieved a numerical solution to the wave equation on the basis of the data on the inverse splitting with $v_2 \leq$ $\leq 3^s$, known at this time, which essentially agree with those given in Table 105. On the basis of Manning's paper the quantity G_0 (0, v_2, 0,0)

could be extrapolated to higher values of v_2 but the value of G_0 (0, 3^a, 0,0) = 2840 cm^{-1}, calculated in paper [2763] differs considerably from the experimental value (cf. Table 105).

The calculation of the constants in Manning's equation for a potential with a second minimum is extremely complex and cumbersome and the limitedness of experimental data renders it unsuitable to recalculate these constants, taking the changes of these data into account. In the present Handbook it was assumed according to Godnev's paper [156] that the components of inverse doubling of the harmonics of the second fully symmetrical vibration of NH_3, beginning with $v_2 = 4$, have equal intervals between each other which amount to $v_2/2$, i.e., 475 cm^{-1}. Thus G_0 (0, 4^3, 0,0) = 3370, G_0 (0, 4^a, 0,0) = 3845 cm^{-1}, etc.

Following these papers of Benedict, Plyler and Tidwell, results of investigations of the vibration-rotation spectrum of NH_3 were published in literature by Garing, Nielsen, Rao [1651, 1652, 1653], Tsuboi, Shimanouchi and Mizushima [4025] and Mould, Price and Wilkinson [2960]. In these papers it was mainly the range of 700-1300 cm^{-1} of the NH_3 spectrum that was investigated; it contains the v_2 band. The molecular constants of NH_3 obtained by these authors from an analysis of this band is in good agreement with those given in our Handbook. In the paper of Garing, Nielsen and Rao [1653] the bands $2v_2$ and v_4 were also analyzed. The value of v_0 for $2v^a_2$, obtained by these authors and accepted in the present Handbook (cf. Table 105) is more accurate than that given in literature (1910 cm^{-1}).

The rotational constants, the constants of interaction of rotation and vibration and the constants of centrifugal distortion of NH_3 are chosen in the present Handbook according to data of Benedict and Plyler [734] and are given in Table 106. The structural parameters of NH_3, corresponding to the accepted values of B_{0000} and A_{0000}, are equal to

r_{N-H} = 1.0173 A and ∠H–N–H = 107°.78, which is in good agreement with the data obtained by the method of electron diffraction (r_{N-H} = 1.015 A, ∠H–N–H = 106.6 ± 106.6 ± 4°.0 [518]). The rotational constants of NH_3, obtained by other authors from examinations of the pure rotation spectrum in the infrared [2696] and in the microwave range (cf., e.g., [4011]), the Raman spectrum [1233] and the vibration-rotation spectrum in the infrared [1653, 2960, 4025] are in good agreement with those given in the present Handbook.

TABLE 106

Accepted Values (in cm^{-1}) of the Molecular Constants of NH_3 in the Electron Ground State (σ = 3)

1 Постоянная	2 Значение	Постоянная	Значение	Постоянная	Значение
ν_1	3336,68	x_{14}	—7,1	α_1^B	—0,230
ν_2	950,42	x_{23}	32,0	α_1^A	0,078
$\nu_3(2)$	3463,77	x_{24}	—10,7	α_2^A	0,048
$\nu_4(2)$	1626,75	x_{34}	—17,6	α_3^A	—0,009
x_{11}	—51,3	B_{0000}	9,9443	α_4^A	0,066
x_{12}	—18,5	A_{0000}	6,196	D_J	$8,00 \cdot 10^{-4}$
x_{13}	—18,0	α_1^B	0,135	D_{JK}	$-14,18 \cdot 10^{-4}$
x_{22}	20,2	α_2^B	0,015	D_K	$7,36 \cdot 10^{-4}$
x_{33}	—171,8	α_3^B	0,176		

1) Constant; 2) value.

It must be noted that a great number of papers is devoted to investigations of the rotational structure of the inverse spectrum of NH_3 in the infrared and microwave ranges, but the effect of inverse doubling of the rotational lines is unessential for the present Handbook. Many references as to investigations of the inverse spectrum of NH_3 in the microwave range may be found in the books by Gordy, Smith and Trambarulo [164] and Townes and Schawlow [416, 4011].

The electron ground state of the NH_3 molecule is a singlet. It is

known from investigations of the ultraviolet spectrum of ammonia (cf. review of Walsh [4143]) that the first excited electron state of NH_3 has an excitation energy of 46,157 ± 30 cm^{-1}. This value has been verified by Wash and Warshop [4146a] in a paper published recently.

$\underline{NF_3}$. The NF_3 molecule belongs to the point group of symmetry C_{3v} and has the structure of a regular pyramid with the N atom at the vertex. All four fundamental frequencies of NF_3, two of them (ν_3 and ν_4) being doubly degenerate, appear in both the infrared spectrum and the Raman spectrum.

The infrared spectrum of NF_3 in the gaseous state was first investigated by Bailey, Hale and Thompson [618]. Thereafter Wilson and Polo [4297] again studied the NF_3 spectrum and arrived at results quite different from the data obtained by Bailey, Hale and Thompson [618]. The interpretation of the frequencies of NF_3, given in the paper of Wilson and Polo [4297] was verified by Pace and Pierce [3161] who measured anew the infrared spectrum of gaseous NF_3 and also obtained the first Raman spectrum of liquid NF_3. The satisfactory agreement of the Raman spectrum with the infrared spectrum speaks in favor of the correctness of the frequency interpretation in the paper [4297, 3161]. The fundamental frequencies according to data of Pace and Pierce [3161] differ but slightly (by 1-5 cm^{-1}) from those found by Wilson and Polo [4297]. It must be noted that in the paper of Pace and Pierce the sample of NF_3 used had a higher degree of purity. In Table 107 we therefore chose the values of fundamental frequencies of the NF_3 molecule according to Pace and Pierce [3161].

The rotational constants of the NF_3 molecule were determined by Sheridan and Gordy [3703] on the basis of an analysis of the microwave spectrum. These values are accepted in the present Handbook and given in Table 107. The corresponding values of the geometrical parameters

TABLE 107

Accepted values (in cm^{-1}) of the Molecular Constants of NF_3 (σ = 3) in the Electron Ground State

ν_1	ν_2	$\nu_3(2)$	$\nu_4(2)$	A_{0000}	B_{0000}
1031	642	907	497	0,194934	0,356278

are equal to r_{N-F} = 1.371 A and $\angle F-N-F$ = 102°.9, which, within the limits of experimental accuracy agree with the values of r_{N-F} = 1.37 ± ± 0.02 A and $\angle F-N-F$ = 102.5 ± 1°5', determined by Schomaker and Lu [3647] using the electron diffraction method. The values of B_0 of NF_3, determined on the basis of microwave measurements in paper [2260], differ insignificantly from those given in the present Handbook.

N_2H_4. In the hydrazine molecule which consists of two NH_2 groups linked by an N–N bond, a damped internal rotation occurs around this bond. Penney and Sutherland [3218], on the basis of quantum mechanical calculations, showed that the stable configuration of N_2H_4 is such a configuration in which the NH_2 groups are turned by 90° with respect to one another (gauche configuration). The authors of paper [3218] could also show that the cis and trans configurations of the N_2H_4 molecule, just as in the case of hydrogen peroxide H_2O_2 (cf. p. 207), must be unstable. This was also verified by the results of measurements of the dipole moment [341, 589], investigations of the rotational structure of one of the bands of the infrared spectrum [4351] and a comparison of the frequencies observed in the infrared spectrum and in the Raman spectrum.*

The N_2H_4 molecule, having a gauche configuration, pertains to the point group C_2 and must have 12 nondegenerated vibrational frequencies

TABLE 108

Accepted Values of the Molecular Constants of Hydrazine N_2H_4 in the Electron Ground State (σ = 2)[a]

1 Постоянная	2 Значение	Постоянная	Значение	Постоянная	Значение
ν_1, $см^{-1}$	3280	ν_6, $см^{-1}$	780	ν_{11}, $см^{-1}$	1275
ν_2, $см^{-1}$	3325	ν_7, $см^{-1}$	376,?	ν_{12}, $см^{-1}$	950
ν_3, $см^{-1}$	1587	ν_8, $см^{-1}$	3314	$I_A I_B I_C \cdot 10^{117}$, $г^3 \cdot см^6$	6,995
ν_4, $см^{-1}$	1275	ν_9, $см^{-1}$	3350		
ν_5, $см^{-1}$	1098	ν_{10}, $см^{-1}$	1628	$I_{пр} \cdot 10^{40}$, $г \cdot см^2$	1,4597

[a]Potential barrier of internal rotation V_0 = 4850 cal/ /mole. 1) Constant; 2) value.

appearing in both the infrared spectrum and the Raman spectrum. We know a great number of papers devoted to investigations of the Raman spectrum in solid and liquid states [2166, 2167, 2317, 1829, 4123, 3903] and in the infrared spectrum in solid, liquid and gaseous states [2254, 1609, 1607, 263, 264, 4123, 1735, 4351]. The interpretation of the fundamental frequencies of hydrazine, given by the various authors (cf., e.g., [1607, 1735, 3667, 4350]), are, however, unambiguous in many respects. In the present Handbook we use the interpretation of Yamaguti [4350] which he achieved on the basis of his own analysis of the normal vibrations of the hydrazine molecule. The values of the fundamental frequencies recommended by Yamaguchi and given in Table 108 were chiefly obtained by Giguere and Liu [1735] as the result of investigating the infrared spectrum of N_2H_4 in the gaseous, solid and liquid states in the range of 750-6500 cm^{-1}.

The structural parameters of the N_2H_4 molecule were determined on the basis of electron diffraction measurements [1739, 2952a] and in investigations of the rotational structure of the infrared spectrum [4351].* In paper [2952a], as a result of an application of the sector

method and the analysis of the diffraction picture with a microphotometer, the following values were obtained: $r_{N-N} = 1.449 \pm 0.004$, $r_{N-H} = 1.022 \pm 0.006$ A and $\angle N-N-H = 112.0 \pm 1°.5$. Previously Giguere and Schomaker [1739] had obtained $r_{N-N} = 1.47 \pm 0.02$, $r_{N-H} = 1.04 \pm 0.06$ A, $\angle H-N-H = 102-114°$ and $\angle N-N-H = 108 \pm 8°$. On the basis of investigations of the rotational structure of the fundamental transition of the torsional vibration ν_7, Yamaguchi, Ichishima, Shimanouchi and Mizushima [4351] obtained $A'' - B'' = 3.981 \pm 0.004$ and $\bar{B}'' = 0.809 \pm 0.002$ cm^{-1}; hence a value of $r_{N-N} = 1.453 \pm 0.005$ A was calculated and the values of $r_{N-H} = 1.020-1.025$ A and $\angle N-N-H = 112-112°5'$ were estimated. The same authors found that the parameter of asymmetry in the vibrational ground state of N_2H_4 must be smaller than 10^{-3} and, based on this they suggested a value of 90-95° for the angle φ made by the two NH_2 groups being turned with respect to one another.

On the basis of the values of the rotational constants $A'' - \bar{B}''$ and $\bar{B}''$, obtained in paper [4351] and considering the results of electron diffraction studies of Morino et al. [2952a], Yungman and Gurvich [476], when preparing the present Handbook, calculated the following values of the structural parameters of the N_2H_4 molecule: $r_{N-N} = 1.4365$, $r_{N-H} = 1.016$ A, $\angle N-N-H = \angle H-N-H = 109°28'16''$ (tetrahedral angle) and $\Phi = 91°30'$. The following values of the principal moments of inertia correspond to these values of the structural parameters of N_2H_4: $I_A = 3.470 \cdot 10^{-39}$, $I_B = 3.450 \cdot 10^{-39}$ and $I_C = 0.5843 \cdot 10^{-39}$ $g \cdot cm^2$ which are similar to the values of $I_A = (3.469 \pm 0.016) \cdot 10^{-39}$ $I_B = (3.451 \pm 0.017) \cdot 10^{-39}$ and $I_C = (0.5843 \pm 0.0007) \cdot 10^{-39}$ $g \cdot cm^2$, calculated on the basis of results of measuring the rotational structure of the ν_7 band [4351]. The value of the reduced moment of inertia was found in [476] as being equal to $I_{pr} = 1.4597 \cdot 10^{-40}$ $g \cdot cm^2$. In the present Handbook we chose the values of the structural parameters and the moments of inertia of N_2H_4, calculated in paper [476] (cf. Table 108).*

Since in the N_2H_4 molecule a damped internal rotation takes place, it is necessary also to know the magnitude of the damping potential. The exact form of the potential curve of the internal rotation of hydrazine is unknown. On the basis of theoretical considerations, Penney and Sutherland [3218] assumed that this curve, as in the case of H_2O_2, has two identical minima (cf. curve 1 in Fig. 8), corresponding to the two isomeric gauch configurations, and two maxima, one of which (V_1 = ~ 6100 cal/mole) corresponding to the cis configuration, the other (V_2 = 4600 cal/mole) to the transconfiguration.

Owing to the fact that there are no reliable data on the form of the potential barrier of N_2H_4, it can be assumed, as this has been done in the case of H_2O_2 (cf. p. 387), that the potential curve of internal rotation has a simple cosinusoidal shape with two minima (n_m = 2) (cf. curve 3 of Fig. 8). The main characteristic feature of this curve is the effective height of the potential barrier, V_0. On the basis of their own estimations of the torsional vibration frequency ν_7 = 360 cm^{-1}, Scott et al. [3667] obtained V_0 = 2800 cal/mole. This value was verified by a theoretical calculation based on an electrostatic model [2793, 2563]. Luft [2672], however , assumes that the potential barrier of internal rotation in the hydrazine molecule must be much higher than 2800 cal/mole. Because of the absence of the data necessary to determine V_0, Luft does not give a reliable value of this quantity and assumes that $6 < V_0 < 18$ (V_0 in kcal/mole).

When preparing the material of the present Handbook the value of V_0 of hydrazine was estimated on the basis of a comparison of the values of standard entropy of a perfect gas ($S°_{298.15}$), obtained experimentally by Scott et al. [3667] from calorimetrical measurements (56.97 ± 0.30 cal/mole·deg), and calculated in the approximation of the rigid-rotator – harmonic oscillator model on the basis of the accepted

values of the vibrational frequencies and the moments of inertia (cf. Table 108) using the Tables of Pitzer and Gwinn [3259] for the components of internal rotation. A value of V_0 = 4850 cal/mole was found as the results of this estimation; it has been accepted in the present Handbook and is given in Table 108. The possible error in the accepted value of V_0 amounts to 1500 cal/mole and is chiefly due to the inaccuracy of the calorimetrical determination of the standard entropy of hydrazine. It must be mentioned that the error in determining V_0 which is caused by the fact that we do not know the shape of the potential curve of internal rotation, may have a higher value.

The N_2H_4 molecule, according to the configuration assumed (point group C_2), has the symmetry number $\sigma = 2$. The electron ground state of N_2H_4 is a singlet. In literature there are no data on the excited electron states of N_2H_4.

§52. THE THERMODYNAMIC FUNCTIONS OF THE GASES

The thermodynamic functions of nitrogen and its compounds in the gaseous state, considered in the present Handbook, were calculated with the constants accepted in the preceding section and given in Tables 91-109 of Vol. II of the Handbook, without taking intermolecular interaction into account. For the six gases N, N^+, N_2, N_2^+, NO and NO^+) the thermodynamic functions were calculated up to 20,000°K and for the thirteen gases (N_3, NO_2, N_2O, NH, NH_2, NH_3, N_2H_4, HNO, NF, NF_2, NF_3, FNO and NS) up to 6000°K. The differences of the molecular constants of the individual isotope modifications were neglected in the calculations since the content of N^{15}, compared to N^{14}, is negligibly small in natural isotope mixtures (cf. Appendix 1). In Table 402-405 of Vol. II of the Handbook the values of the virial coefficients and their derivatives with respect to temperature are given for N_2, NO, N_2O and NH_3, which permits calculations of the thermodynamic functions of these gas-

es in which molecular interaction is taken into account.

N. The thermodynamic functions of monatomic nitrogen N, given in Table 91 (II), were calculated from Eqs. (II.22)-(II.23) in the temperature interval of 293.15-20,000°K. The values of Φ^*_{el} and S_{el} in these equations were calculated with the help of a high-speed electronic computer by way of direct summation over the energy levels of the nitrogen atom, accepted in the present Handbook and given in Table 89. In the calculation of the statistical sum of the electron states their finite number was taken into account, in accordance with a method described in §6, the highest value of the principal quantum number, n_{max}, being determined from Eq. (II.18). In the calculation of the progressive components Φ^*_{post} and S°_{post} from Eqs. (II.8)-(II.9) it was assumed that $A_\Phi = 0.58490$ and $A_S = 5.55310$ cal/g-atom·deg. Details of the calculation of the thermodynamic functions of monatomic nitrogen at 5000 and 15,000°K are given in §6.

The errors of the values of the thermodynamic functions of monatomic nitrogen calculated in this way are at temperatures below 10,000° K mainly due to inaccuracies of the fundamental physical constants and do not exceed 0.002-0.003 cal/g-atom·deg, as regards the values of Φ^*_T and S°_T. At higher temperatures those errors become essential which are connected with the application of an approximation method in order to determine n_{max}. An error in this quantity of ±1 (with $n_{max} = 13$) causes errors in the values of Φ^*_T, equal to ±0.02 and ±0.15 cal/g-atom·deg at 15,000 and 20,000°K, respectively.*

It must be noted that the error in the values of the thermodynamic functions caused by inaccurate estimations of the energies of the individual levels is smaller than these values by orders of magnitude.

The thermodynamic functions of monatomic nitrogen were previously calculated in a series of papers among which we must mention the recent

calculations of Huff, Gordon and Morrell [2142] up to 6000°K, of the US NBS [3680] up to 5000°K, Kolsky et al. [2462] up to 8000°K, Predvoditelev, Stupochenko, Samuylov et al. [336] up to 20,000°K and Martinek [2792] up to 40,000°K. The results of all these calculations from 8000 to 10,000°K agree as a rule with the data given in Table 91 (II), with errors determined by the differences of the fundamental physical constants.* Above 10,000°K the energy levels of the N atom with high excitation energies, taken into account in the present Handbook but not observed in experiments, contribute essentially to the values of the thermodynamic functions. This explains the fact that the values of the functions of N given in Table 91 (II) are, beginning with these temperatures, higher than the values calculated by Predvoditelev, Stupochenko, Samuylov et al. [336] and Martinek [2792] (in paper [336] the calculation was carried through with the help of Fermi's method, without taking the nonobserved electron states into account, while in paper [2792] only the first excited states ^2P and ^2D of the nitrogen atom were considered in the calculations). The corresponding differences in the entropies at 20,000°K reach 5.2 and 6.4 cal/g-atom·deg.

$\underline{N^+}$. The thermodynamic functions of the positive ion of monatomic nitrogen N^+, given in Table 90 (II) were calculated from Eqs. (II.22)-(II.23) in the temperature interval of 293.15-20,000°K. The quantities Φ^*_{el} and S_{el} in these equations were determined by direct summation over the energy levels of the nitrogen ion, accepted in the present Handbook and given in Table 90. In the calculation of the progressive components Φ°_{post} and S°_{post} from Eqs. (II.8)-(II.9) it was assumed that, as in the case of N, $A_\Phi = 0.58490$ and $A_S = 5.55310$ cal/g-atom·deg.

The errors of the values of the thermodynamic functions of the positive nitrogen ion calculated in this way are determined by the in-

accuracy of the fundamental physical constants, the neglection of the high energy levels of the N^+ ion and the approximate character of the calculating method used. With $T \leq 10{,}000°K$ the errors in the values of $\Phi°_T$ and $S°_T$ do not exceed ±0.003-0.005 cal/g-atom·deg.

The thermodynamic functions of N^+ were calculated by Predvoditelev, Stupochenko, Samuylov et al. [336] up to 20,000°K, by Martinek [2792] up to 40,000°K and Green, Poland and Margrave [1851a] up to 50,000°K. The results of the calculations in [336, 1851a] agree satisfactorily in the entire temperature integral with the values calculated in the present Handbook. The values of the entropy of N^+, given in Martinek's paper [2792] differ from the values given in Table 92 (II) by 0.15-0.30 cal/g-atom·deg in the interval of 10,000-20,000°K. These divergences may be explained by an error in the calculations of [2792] since a checking calculation of the thermodynamic functions, using the level energies of N^+ accepted by Martinek [2792], yielded a better agreement with the data obtained in the present Handbook.

N_2. The thermodynamic functions of diatomic nitrogen N_2, given in Table 93 (II) were calculated from Eqs. (II.34)-(II.35) in the temperature interval of from 293.15-20,000°K. The values of Q_{vn} and $T\frac{\partial \ln Q_{vn}}{\partial T}$ in these equations were obtained from Eqs. (II.131)-(II.132) in which the values of $\ln \Sigma'$ and $T\partial \ln \Sigma'/\partial T$ were calculated with the help of a high-speed electronic computer by direct summation over the vibrational and rotational levels of the states $X^1\Sigma^+_g$, $A^3\Sigma^+_u$ and $B^3\Pi_g$. The level energy values were obtained from the corresponding equations with the values of the molecular constants of N_2 in these states given in Table 92. The v-dependence of J_{max} in each state is shown in Fig. 12. The multiplet nature of the states $A^3\Sigma^+_u$ and $B^3\Pi_g$ is taken into account by means of the statistical weights 3 and 6, respectively, in the expressions of the statistical sum, though the data given in Table 92 permit

a more accurate calculation on the basis of the corresponding constants of multiplet splitting. The error due to this simplification is negligibly small since the states $A^3\Sigma^+_u$ and $B^3\Pi_g$ have high excitation energies.

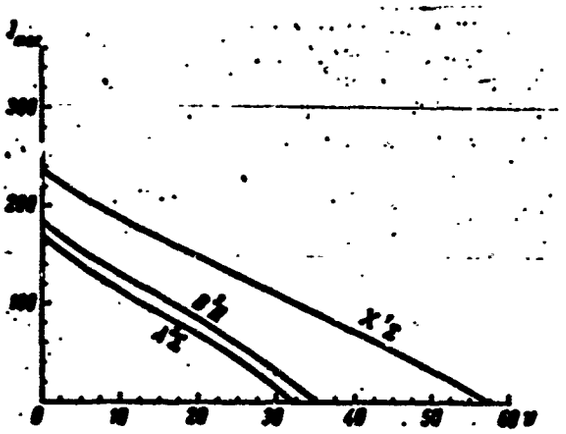


Fig. 12. J_{max} as a function of $\underline{v}$ for the electron states $X^1\Sigma^+_g$, $A^3\Sigma^+_u$ and $B^3\Pi_g$ of the N_2 molecule.

The contribution of the residual excited states of N_2 ($^3\Delta_u$, $Y^3\Sigma^-_u$, $a'^1\Sigma^-_u$, $a^1\Pi_g$, $w^1\Delta_u$ and $C^3\Pi_u$) is taken into account in the calculation of the thermodynamic functions by means of second terms in the equations (II.131)-(II.132), where δ and $T\partial\delta/\partial T$ were calculated from Eqs. (II.125) and (II.134) on the basis of the molecular constants given in Table 92. Since the vibrational and rotational constants of N_2 in the $^3\Delta_u$ state are unknown, the quantity $[(1 - z_X)/(1 - z_i)]\cdot B^X_0/B^i_0$ of this state was assumed to be equal to one. An analogous approximation was admitted for the state $C^3\Pi_u$, since the excitation energy of this state is high and the corresponding contribution to the value of δ is sc small that the difference of the molecular constants of N_2 in the ground state and in the excited states is insignificant. In the calculation of the thermodynamic functions the $^5\Sigma^+_g$ state is not taken into

consideration since it is well known (cf. p. 673) that this state has a veryflat potential curve and its contribution to the statistical sum over the states is therefore negligibly small. The electron states of N_2 whose excitation energies do not exceed 90,000 cm^{-1} are taken into account in the calculation. Up to temperatures of the order of 15,000°K this limitation does not give rise to considerable errors; at higher temperatures the error becomes noticeable and amounts to 0.2 cal/mole·deg with the values of $S^\circ_{20,000}$. It has been found to be not expedient to include electron states with excitation energies higher than 90,000 cm^{-1} in the calculations because of the indeterminacy of the values of the statistical weight of these states.

In the calculation of the progressive components Φ°_{post} and S°_{post} from Eqs. (II.8) and (II.9) it was assumed that $A_\Phi = 1.2736$ and $A_S = 6.2418$ cal/mole·deg.

Owing to the accuracy of the initial molecular constants of N_2 it can be assumed that the total error of the thermodynamic functions with $T \leq 10,000$-12,000°K is mainly due to the inaccuracy of the basic physical constants and does not exceed ±0.005-0.01 cal/mole·deg. At higher temperatures the errors in determining the number and energies of the vibrational and rotational levels of the various states, the neglection of the electron states with high excitation energies and also the error in estimating the amount of the excitation energy of the $^3\Delta_u$ state (cf. p. 673) increase the errors of the values of Φ^*_T up to about ±0.1 cal/mole·deg at 20,000°K.

The thermodynamic functions of N_2 were previously calculated several times. In almost all handbooks [3680, 2142, 3426, 3507] the tables compiled by Wagman et al. [4122] for temperatures up to 5000°K are used as bases. These tables were obtained as the result of a recalculation of the thermodynamic functions of N_2, calculated by Johnston and Davis

[2274] and Giauque and Clayton [1713] with the method of direct summation, a recalculation in which the new values of the physical constants were used. The differences between the data given in Table 93 (II) and those of the handbooks mentioned above are insignificant, except for the values of the entropy at temperatures of the order of 4000°K and more. This is the region where, obviously, the consideration of the limitation of the levels and the introduction of second and third constants of anharmonicity in the equation of $G_0(v)$ of the state $X^1\Sigma_g^+$, accepted in the present Handbook, becomes effective. In spite of this the divergence remains small and does not exceed 0.009 cal/mole·deg. The calculation of the thermodynamic functions of N_2 according to Kassel's method (cf. p.156) was carried out by Goff and Gratch [1786] up to 2800°K and continued up to 5000°K by Hilsenrath et al. [2076]. The data of Table 93 (II) differ at all temperatures from the results of the calculations of Goff and Gratch [1786] and Hilsenrath et al. [2076] by about 0.008 cal/mole·deg which is mainly due to differences in the values of the rotational constants used.

In the book of Vukalovich et al. [137] we find a table of the thermodynamic functions of N_2 in the interval 0-3000°C, calculated with the help of a method developed by the authors themselves [137]. These data differ from the date of our Handbook (in the case of the entropy) by an amount of the order of 1 cal/mole·deg in the entire temperature interval which, obviously, indicates the presence of errors in the calculations of [137].

In the past years several calculations of the thermodynamic functions of N_2 for temperatures higher than 6000°K have been published in the literature. Döring [1363] calculated the functions of N_2 up to 20,000°K using a method analogous to Kassel's method and taking four excited electron states into account. The molecular constants used by

Döring [1363] are already obsolete and the differences between the data of Table 93 (II) and the values calculated by Doring with $T \leq 15{,}000°K$ amount to about 0.03-0.04 cal/mole·deg. At higher temperatures the differences increase rapidly, reaching 1.45 cal/mole·deg with the values of $S°_{20{,}000}$. These great divergences may be explained chiefly by the fact that in Döring's paper [1363] the summation over v and J was not limited.

Fickett and Cowan [1556] calculated the thermodynamic functions of N_2 up to 12,000°K by means of an approximation method (see p. 320). The greatest difference between the results of calculation of [1556] and the calculation by means of the method of direct summation amounts to 0.025 cal/mole·deg with the values of $S°_T$ at 12,000°K.

Predvoditelev, Stupochenko, Samuylov et al. [336] calculated the thermodynamic functions of N_2 up to 20,000°K (see p. 321). A comparison of the values of the entropy, calculated in paper [336] with the data given in Table 93 (II) shows that at 20,000°K there are virtually no differences; at lower temperatures the divergence increases (for example, at 12,000°K it amounts to 0.3 cal/mole·deg).

Beckett and Haar [714] calculated the thermodynamic functions of N_2 up to 25,000°K. At temperatures above 10,000° the divergence of the results of calculations in our Handbook and the calculations of Beckett and Haar increases rapidly, reaching values of the order of 1 cal/mole·deg with the values of $S°_{20{,}000}$, which is caused by the insufficient accuracy of the method applied by Beckett and Haar (see p. 321).

Using Fast's data [1532] in order to calcudate the statistical sum with respect to the intramolecular states of N_2, Martinek [2792] calculated the thermodynamic functions of nitrogen in the interval 1000-12,000°K. The differences between the results of calculation in [2792] and those in the present Handbook do not exceed 0.5 cal/mole·deg in

this temperature interval. These differences are caused by the approximate nature of Fast's calculation [1532] in which the method of Mayer and Goeppert-Mayer has been applied (see p. 159).

In the first edition of the Handbook [420] the thermodynamic functions of N_2 were calculated up to 6000°K according to the method of Gordon and Barnes on the basis of constants somewhat different from those used in the present edition, a fact that gives rise to differences which, on the average, amount to 0.01 cal/mole·deg.

$\underline{N^+_2}$. The thermodynamic functions of the positive ion of diatomic nitrogen, N^+_2, given in Table 94 (II), were calculated from Eqs. (II.34)-(II.35) in the temperature interval 298.15-20,000°K. The quantities $\ln Q_{vn}$ and $T\partial \ln Q_{vn}/\partial T$ in these equations were determined from the relations (II.131), (II.132), in which the values of $\ln \Sigma'$ and $T\partial \ln \Sigma'/\partial T$ were calculated with a high-speed electronic computer, by means of direct summation over the vibrational and rotational energy levels of the states $X^2\Sigma^+_g$, $A^2\Pi_u$ and $B^2\Sigma^+_u$. The energy values of the vibrational levels of the state $X^2\Sigma^+_g$ (see p. 676) were determined by means of two equations for the values of v = 0-21 and v = 22-68. The energy values of the rotational levels of this state and also the vibrational and rotational levels of the state $A^2\Pi_u$ were obtained from the corresponding equations with the constants given in Table 94. When calculating $Q_{kol.vr}$ and $T - \partial Q_{kol.vr}/\partial T$ for the $B^2\Sigma^+_u$ state, the values of $G_0(v)$ and B_v, given in Table 93, were substituted immediately into the equations. The v-dependence of J_{max} in the case of the states $X^2\Sigma^+_g$, $A^2\Pi_u$ and $B^2\Sigma^+_u$ is shown in Fig. 13. The multiplet nature of all three states was taken into account by the introduction of the statistical weights 2, 4 and 2, respectively, into the expression of the statistical sum over the states. Owing to the absence of data on the values of the corresponding constants, it is not possible to take the mul-

tiplet splitting of the $X^2\Sigma^+_g$ and $B^2\Sigma^+_u$ states better into account, but this does not affect the accuracy of the calculation. In the case of the $A^2\Pi_u$ state it is not suitable tc use Eqs. (1.25) for the energy of the rotational levels since the corresponding correction to the values of the N^+_2 functions is negligibly small. The state $C^2\Sigma^+_u$, having an excitation energy higher than 64,000 cm^{-1}, is taken into account, neglecting the differences between the vibrational and rotational constants of the states $X^2\Sigma^+_g$ and $C^2\Sigma^+_u$.*

In the calculation of the progressive components Φ^*_{post} and S^o_{post} from Eqs. (II.8) and (II.9) it was assumed that, just as in the case of N_2, A_Φ = 1.2736 and A_S = 6.2418 cal/mole·deg.

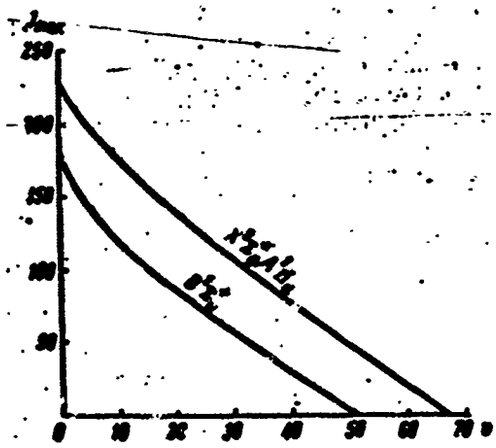


Fig. 13. J_{max} as a function of v for the electron states $X^2\Sigma^+_g$, $A^2\Pi_u$ and $B^2\Sigma^+_u$ of the N^+_2 molecule.

The calculation of the thermodynamic functions of N^+_2 carried out in this way for temperatures below 10,000-12,000°K implies an error not exceeding ±0.01 cal/mole·deg, which is mainly due to an inaccuracy of the basic physical constants. At higher temperatures the errors of the functions is higher and amounts to about ±0.1-0.2 cal/mole·deg at 20,000°K. This is mainly due to the fact that the N^+_2 molecule (analogous to the isoelectronic molecule CN) may have a series of excited electron states with excitation energies of about 60,000 cm^{-1}. These states are not taken into account in the calculation of the thermodynamic functions because of the absence of the corresponding molecular constants.

The thermodynamic functions of N^+_2 were calculated by Beckett and

Haar [714] (see p. 321), up to 25,000°K. The results of the calculation of [714] agree satisfactorily with the data of the present Handbook, up to 10,000°K; at higher temperatures the divergence increases and reaches 0.7 cal/mole·deg with the values of $S°_{20,000}$.

A comparison of the results of calculations of the thermodynamic functions of N^+_2, given in Table 94 (II), with the data obtained by Predvoditelev, Stupochenko, Samuylov et al. [336], shows that only above 10,000°K the divergence becomes noticeable, reaching 0.25 cal/mole·deg with the value of $S°_{20,000}$.

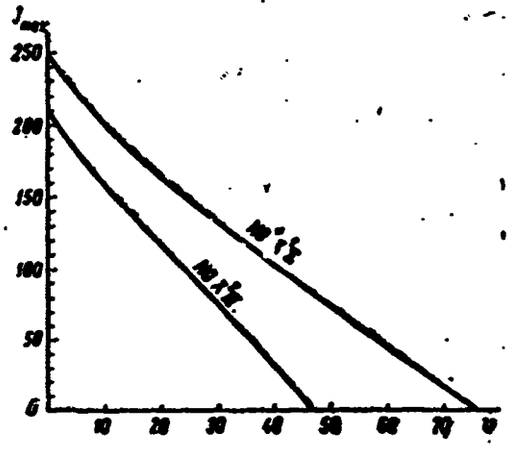


Fig. 14. J_{max} as a function of v for the electron states $X^2\Pi_r$ of the NO molecule and $X^1\Sigma^+$ of the NO^+ molecule.

NO. The thermodynamic functions of nitrogen oxide NO, given in Table 96 (II), were calculated from Eqs. (II.120)-(II.121) in the temperature interval of 293.15-20,000°K on the basis of the molecular constants given in Table 97. Ln $Q_{kol.vr}$ and $T\partial Q_{kol.vr}/\partial T$ for the ground state $X^2\Pi_r$ were calculated with a high-speed electronic computer, by means of a direct summation over the levels of vibrational and rotational energies up to $v_{max} = 47$ and the values of J_{max} were calculated for each vibrational state according to the method described on p. 73. Fig. 14 shows J_{max} as a function of v. The energy values of the rotational levels were calculated from Eq. (1.25). The values of $\Delta\Phi^*_{el}$ and ΔS_{el} for all six excited electron states of NO ($A^2\Sigma^+$, $B^2\Pi_r$, $C^2\Pi_r$, $D^2\Sigma^+$, $B'^2\Delta_1$ and $E^2\Sigma^+$), having excitation energies of from 40,000 to 60,000 cm^{-1}, were calculated from Eqs. (II.126)-(II.127). The quantities $\Delta\Phi^*_{el}$ and ΔS_{el} contribute essentially

to the values of the thermodynamic functions at temperatures higher than 6000°K. The progressive components Φ^*_{post} and S°_{post} were calculated from Eqs. (II.8)-(II.9) using the values A_Φ = 2.8559 and A_S = = 7.8241 cal/mole·deg.

The errors of the thermodynamic functions of NO calculated in this way amount to about 0.005-0.01 cal/mole·deg at temperatures not exceeding 6000-8000°K and are mainly due to inaccuracies of the basic physical constants. At higher temperatures the error increases and may reach ±0.1-0.2 cal/mole·deg for the value of Φ^*_T at 20,000°K. This is explained by the approximate character of considering the excited electron states and also by the fact that at high temperatures the inaccuracy of extrapolating the upper vibrational and rotational levels of the ground state becomes more noticeable.

The first tables of the thermodynamic functions of NO were compiled for a wide temperature interval (up to 5000°K) by Johnston and Chapman [2272] in 1933 by the method of direct summation over the vibrational and rotational energy levels. This table was accepted without any change by Zeise [4384]. Moreover, in a series of handbooks [2142, 3426, 3680, 3507] it was virtually one and the same table of the thermodynamic functions of NO that was published until present times, for temperatures up to 5000°K (up to 6000°K in [2142]), with reference to unpublished calculations of the US National Bureau of Standards.

At low temperatures the differences between the results of these calculations and the data of Table 96 (II) are small (a few thousandths of one cal/mole·deg at 298.15°K). These differences grow as the temperature rises, reaching values of the order of 0.1 cal/mole·deg with the values of the entropy at 5000-6000°K.

Since in the paper of Johnston and Chapman [2272] detailed information is given on the initial constants and the method of calculation,

it is possible to find out the causes of these differences. The main source of them is the difference in the values of the fundamental physical constants and molecular constants used in the calculations. The correction for the difference of the physical constants was calculated by means of a method applied in paper [4122] of Wagman et al. The corrections for the differences of the molecular constants are first of all due to inaccuracies of the rotational constants of the ground state of NO, determined by Jenkins, Barton and Mulliken [2232] and used by Johnston and Chapman in their calculations. This causes a change by 0.02 cal/mole·deg in the values of Φ^*_T and S_T which is independent of the temperature. Moreover, the value of $F_{3/2}$ (0, 3/2) − $F_{1/2}$ (0, 1/2) = = 129.55 cm^{-1} used by Johnston and Chapman, could be improved in later measurements; in the present Handbook it was assumed as amounting to 125.07 cm^{-1}. The correction for this difference, which must be made in the calculation, is essential mainly at low temperatures (about 0.015 cal/mole·deg at 298.15°K). The results of a recalculation of the data

TABLE 109

Values (in cal/mole·deg) of Φ^*_T of Nitrogen Oxide NO

T°, K	1 По Джонстону и Чапману [2272]	По Джонстону и Чапману [2272] (пересчет) 2	По табл. 96(II) 3
298,15	42,985	42,973	42,977
1000	51,878	51,854	51,857
3000	60,567	60,540	60,528
5000	64,888	64,861	64,836

1) After Johnston and Chapman [2272]; 2) after Johnston and Chapman [2272] (recalculated); 3) from Table 96 (II).

of Johnston and Chapman and a comparison with the data of the present Handbook may be found in Table 109. From the data given in this table

we see that a recalculation at temperatures below 3000°K yields a satisfactory agreement of the results of calculations. At higher temperatures the differences again begin to grow which, obviously, can be explained by the inaccuracy of the rotational constants used in the paper of Johnston and Chapman. The limits of summation over J seem to have a weak influence on the calculating results in the range of temperatures considered, but it is possible that this is another source oferror in paper [2272].

The values of the thermodynamic functions of NO in the interval 0-3000°C, given in the book by Vukalovich et al. [137], are in satisfactory agreement (within the limits of 0.03 cal/mole·deg, in the case of the entropy) with the data given in Table 96 (II).

In the first edition of the Handbook the thermodynamic functions of NO were calculated by means of the tabular method of Gordon and Barnes. The differences between the calculating results of the first and the present editions of the Handbook increase systematically with the temperature and reach 0.044 cal/mole·deg with the values of Φ^*_T and 0.076 cal/mole·deg with the values of $S°_T$ at 6000°K. This divergence is mainly explained by differences in the initial molecular constants and also by the limitation with respect to J, applied in the calculations of the present edition.

Several calculations of the thermodynamic functions of NO also exist for high temperatures. Fickett and Cowan [1556] calculated the thermodynamic functions of NO up to 12,000°K with the help of an approximation method (see p. 320). The greatest difference, compared with the results given in Table 96 (II), amount to 0.28 cal/mole·deg with the value of $S°_{12,000}$. In the calculation of Predvoditelev, Stupochenko, Samuylov et al. [336], for NO up to 20,000°K, the values obtained for the functions differ by at most 0.4 cal/mole·deg at 20,000°K from

the data of the present Handbook. The thermodynamic functions of NO, calculated by Beckett and Haar [714] are in bad agreement with the values given in Table 96 (II). At temperatures higher than 1000°K the divergence increases rapidly, reaching a value of the order of 1.4 cal/ /mole·deg with the values of $S^\circ_{20,000}$.

NO^+. The thermodynamic functions of NO^+, the positive ion of nitrogen oxide, given in Table 97 (II), were calculated with the help of Eqs. (II.120)-(II.121) in the temperature interval 298.15-20,000°K on the basis of the molecular constants given in Table 98. The values of $\ln Q_{kol.vr}$ and $T\partial \ln Q_{kol.vr}/\partial T$ for the ground state $X^1\Sigma^+$ were calculated with a high-speed electronic computer, by means of direct summation over the vibrational and rotational energy levels, given by the appropriate equations up to $v_{max} = 77$ and the values of J_{max}, calculated for each vibrational state by means of the method described on p. 73. The v-dependence of J_{max} is shown in Fig. 14. The values of $\Delta\Phi^*_{el}$ and ΔS_{el} for the excited electron states of NO^+ ($a^3\Pi$, $a'^3\Sigma^+$, $d^3\Pi$, $A^1\Pi$ and $e^3\Sigma^-$) were calculated by means of the simplest method (Eqs. II.120) and (II.121)) since the molecular constants of all these states, with the exception of the $A^1\Pi$ state, were determined with the help of estimations and have considerable errors. In the calculation of the progressive components from Eqs. (II.8)-(II.9) it has been assumed that $A_\Phi = 2.8559$ and $A_S = 7.8241$ cal/mole·deg, as in the case of NO.

At temperatures below 6000-8000°K the errors of the thermodynamic functions calculated in this way are caused by the inaccuracies of the constants of NO^+ in the ground state and of the basic physical constants; they amount to about ±0.01 cal/mole·deg. At higher temperatures the main source of errors is the error in the values of the excitation energies of the states $a^3\Pi$, $a'^3\Sigma^+$, $d^3\Pi$ and $e^3\Sigma^-$. The total error of the value of $\Phi^*_{20,000}$ is of the order of ±0.2 cal/mole·deg.

The thermodynamic functions of NO^3 were calculated by Beckett and Haar [714] up to 25,000°K. The calculating results of [714] agree well with the data of the present Handbook up to 10,000°K. At higher temperatures the divergence increases rapidly and amounts to about 2 cal/ /mole·deg with the values of $S°_{20,000}$ which is mainly explained by the neglection of the triplet excited states of NO^+ in the calculations of [714].

The results of the calculations of the thermodynamic functions of NO^+, carried out by Predvoditelev, Stupochenko, Samuylov et al. [336] also differ considerably from the data of the present Handbook (maximum difference 2 cal/mole·deg with the values of $S°_{20,000}$). This may be explained by the strongly inaccurate estimates of the molecular constants of NO^+ in paper [336].

NH. The thermodynamic functions of the imyl NH, given in Table 100 (II), were calculated from Eqs. (II.161)-(II.162) in the temperature interval 293.15-6000°K on the basis of the values of the molecular constants of NH accepted in the present Handbook (see Table 99). The values of $\ln \Sigma$ and $T\,\partial \ln \Sigma/\partial T$ in these equations were calculated with the help of the tabular method of Gordon and Barnes (Eqs. (II.137)-(II.138)), without any correlation for the limitation of summation over J; the values of $\ln \Delta_M$ and $T\,\partial \ln \Delta_M/\partial T$ were assumed as equal to zero and the multiplet nature of the ground state $X^3\Sigma^-$ of the NH molecule was taken into account by means of an additional term, R ln 3, in the values of C_ϕ and C_S. It must be expected that the error caused by this approximation is insignificant. In Table 110 we find the values of C_ϕ and C_S, calculated from Eqs. (II.163)-(II.164), θ and $\underline{x}$, necessary for the calculation of the components of the harmonic and anharmonic oscillators, and also the coefficients of Eqs. (II.137)-(II.138).

The values of $\Delta\Phi^*_{el}$ and ΔS_{el} for the excited states $a^1\Delta$, $b^1\Sigma$ and

$A^3\Pi$ of the NH molecule were calculated with the help of the same approximation method (Eqs. (II.120)-(II.121)), in spite of the fact that the excitation energies of these states, particularly of $a^1\Delta$, are comparatively low. It is, however, not suitable to take the excited electron states into account more accurately since the value accepted for T_e in the $a^1\Delta$ state is very inexact (the same is true for the state $b^1\Pi$). This inaccuracy may occasion an error of up to 0.01 cal/mole·deg in the values of Φ^*_{3000}, which amounts to about half the contribution of all electron states at this temperature. The state $c^1\Pi$ is not taken into account since up to 6000°K its contribution to the thermodynamic functions of NH is negligibly small.

It may be expected that the vibrational constants, given in Table 99, yield an inaccurate description of the energy levels of the ground state of the NH molecule near the dissociation limit since the value accepted for the dissociation energy of NH is lower by about 250 cm^{-1} than the value obtained by linear extrapolation. The corresponding error in the values of Φ^*_{6000} amounts to 0.04 cal/mole·deg. Corrections for the limitation of an upper limit of summation over J yield values which do not exceed 0.005 cal/mole·deg for the quantity Φ^*_{6000}.

TABLE 110

Values of the Constants Used to Calculate the Thermodynamic Functions of NH, NS and NF

1 Вещество	θ	$x\cdot10^2$	$\beta_1\cdot10^2$	$\beta_2\cdot10^4$	$\frac{a_0}{I}$	$\frac{d_0\cdot10^4}{I}$	$\frac{I_0\cdot10^{12}}{I^2}$	C_Φ	C_S
	2 град				3 $град^{-1}$		3 $град^{-2}$	4 кал/моль·град	
NH	4600,088	24,036	3,9055	17,35	0,04257	8,707	—0,8256	—3,2966	3,6589
NS	1754,029	6,1521	0,7941	0,65	0,902136	2,927	—	5,3073	12,2626
NF	1438,79	—	—	—	—	—	—	4,4712	11,4267

1) Substance; 2) deg; 3) deg^{-1}; 4) cal/mole·deg.

Taking into account the approximation mentioned above and the inaccuracy of the values of the initial constants, the values of Φ^*_T have errors of ±0.02; ±0.05 and ±0.01 cal/mole·deg at 298.15, 3000 and 6000°K, respectively.

The thermodynamic functions of NH were previously calculated by Ward and Hussey [4149] in the temperature interval 2000-5000°K, in the approximation of the harmonic oscillator – rigid rotator model. The di differences between the results of the calculation in [4149] and the data given in Table 10 (II) reach 0.85 cal/mole·deg with the values of S°_{5000} which is explained by the approximate character of the calculation in [4149].

The table of the thermodynamic functions of NH given in the present Handbook is the same as that given in the first edition of the Handbook.

NS. The thermodynamic functions of sulfur mononitride NS, given in Table 109 (II) were calculated from Eqs. (II.161)-(II.162) in the temperature interval 293.15-6000°K on the basis of the values of the molecular constants of NS accepted in the present Handbook (see Table 99). The values of $\ln \Sigma$ and $T\,\partial \ln \Sigma / T$ in these equations were calculated by means of the tabular method of Gordon and Barnes (Eqs. (II.137)-(II.138)), without correction for the limitation of summation over J, the values of $\ln \Delta_M$ and $T\,\partial \ln \Delta M/\partial T$ were determined from Eqs. (II.151)-(II.152), since the NS molecule has a $^2\Pi_r$ ground state, the type of bond in it pertaining to case a according to Hund (A/B ≈ 290). In Table 110 we find the values of C_Φ and C_S, calculated from Eqs. (II.163)-(II.164), θ and x, necessary to calculate the components of harmonic and anharmonic oscillators, and also the coefficients of Eqs. (II.137)-(II.138).

The excited electron states of NS are not taken into account,

i.e., the quantities $\Delta\Phi^*_{el}$ and ΔS_{el} were considered as being equal to zero. The corresponding error is negligibly small and does not exceed 0.002 cal/mole·deg with the value of S°_{6000}.

The errors of the thermodynamic functions of NS calculated in this way are mainly determined by the accuracy with which the upper vibrational and rotational energy levels are described by the molecular constants accepted. In particular, the dissociation energy of NS, calculated by a linear extrapolation of the vibrational levels of the ground state, is higher by 8700 cm^{-1} than the value of D_0(NS) accepted in the present Handbook. But owing to the fact that the dissociation energy of NS is comparatively high (higher than 40,000 cm^{-1}), the corresponding errors do not exceed 0.02 cal/mole·deg with the value of Φ^*_{6000}. The total error of the values of Φ^*_T at 298.15, 3000 and 6000°K amounts to ±0.005, ±0.01 and ±0.03 cal/mole·deg, respectively.

The table of the thermodynamic functions of NS given in the present Handbook agrees entirely with the table punished in the first edition. Other calculations of the thermodynamic functions of NS are unknown in literature.

NF. The thermodynamic functions of nitrogen monofluoride, given in Table 105 (II), were calculated from Eqs. (II.161)-(II.162) in the temperature interval 293.15-6000°K on the basis of the values of ω_e and B_0, given in Table 99. The calculation was made in the approximation of the rigid rotator – harmonic oscillator model and the values of ln Σ and ln Δ_M in these equations were therefore assumed as vanishing. In order to take the multiplet nature of the ground state $X^3\Sigma^-$ into account in calculating C_Φ and C_S from Eqs. (II.163)-(II.164), it was assumed that $p_M = 3$. The values of C_Φ and C_S, and also the values of θ of NF are given in Table 110.

Owing to the fact that the thermodynamic functions of NF were cal-

culated with the help of estimated values of the molecular constants, the accuracy of the calculated functions is not high, and only because of the possible errors in the initial constants the error of the quantity Φ^*_{3000} amounts to about ±0.3 cal/mole·deg. Since the anharmonicity of the vibrations, the centrifugal distortion in the rotations and other effects were not taken into account in these calculations, the total error in the values of Φ^*_T amounts to approximately ±1.0, ±0.5 and ±1.0 cal/mole·deg at 298.15, 3000 and 6000°K, respectively.

Previously the thermodynamic functions of NF were calculated in the first edition of the Handbook. The difference of about 0.35 cal/mole·deg in the values of Φ^*_T and S°_T between the data of the present and the first editions is due to the differences of the values of B_0 used. Other calculations of the thermodynamic functions of NS are not known in literature.

N_3. The thermodynamic functions of triatomic nitrogen, N_3, given in Table 95 (II), were calculated from Eqs. (II.241)-(II.242) in the temperature interval 293.15-6000°K on the basis of the values of the molecular constants of N_3 accepted in the present Handbook (see Table 100). The calculation was made in the approximation of the rigid rotator – harmonic oscillator model, ignoring the excited electron states so that part of the terms in Eqs. (II.241) and (II.242) was taken as equal to zero. Table 111 gives for N_3 the values of θ_n, corresponding to the values accepted for the fundamental frequencies of this molecule, and also the values of C_Φ and C_S, calculated from Eqs. (II.245)-(II.246). Since the electron ground state of the N_3 molecule pertains to the type $^2\Pi$, $p_M = 4$ was substituted in the calculations of C_Φ and C_S.

The error of the value of Φ^*_{3000}, due to the inaccuracies of the initial constants, amounts to about 0.7 cal/mole·deg. The total error

of the values of Φ^*_T at 298.15, 3000 and 6000°K reaches ±0.1, ±1.5 and ±2.0 cal/mole·deg, respectively.

The thermodynamic functions of N_3 have been published for the first time.

NH_2, HNO. The thermodynamic functions of the amine NH_2 and the oxide-imyl HNO, given in Tables 101 (II) and 104 (II), respectively, were calculated from Eqs. (II.243)-(II.244) in the temperature interval 293.15-6000°K on the basis of the values of the molecular constants of NH_2 and HNO, accepted in the present Handbook (see Table 103). The calculations were carried out in the approximation of the rigid rotator - harmonic oscillator model so that part of the terms in Eqs. (II.243)-(II.244) were taken as equal to zero. For NH_2 and HNO Table 111 gives the values of θ_n, corresponding to the values accepted for the fundamental frequencies of the molecules considered, and also the values of C'_Φ and C'_S, calculated from Eqs. (II.247)-(II.248). When calculating C'_Φ and C'_S for NH_2 it was assumed that $p_M = 2$ since the electron ground state of this molecule is a doublet. For HNO $p_M = 1$. The values of $\Delta\Phi^*_{el}$ and ΔS_{el} for both gases were calculated on the basis of Eqs. (II.120)-(II.121), i.e., the differences between the values of the vibrational and rotational constants of the ground state and the excited state were neglected. Taking the approximate character of the calculation of thermodynamic functions into consideration, this neglection may be viewed as justified.

The total error of the values of Φ^*_T calculated in this way for the temperatures of 298.15, 3000 and 6000°K amounts for NH_2 to ±0.05, ±0.8 and ±1.5 cal/mole·deg and for HNO to ±0.01, ±0.5 and ±1.2 cal/mole·deg, respectively. These errors are mainly due to the approximate character of the calculations and moreover, in the case of NH_2, to the inaccurate values of the fundamental frequencies.

Other calculations of the thermodynamic functions of NH_2 and HNO are unknown in literature.

TABLE 111

Values of the Consonants Used to Calculate the Thermodynamic Functions of N_3, NO_2, N_2O, NH_2, HNO, NF_2, NF_3 and FNO

Вещество	θ_1	θ_2	θ_3	θ_4	C'_Φ	C'_S
	град				кал/моль·град	
N_3	2014,31	1000,30	3003,40	—	6,0790[a]	13,0345[a,b]
NO_2[c]	1925,96	1079,96	2373,72	—	3,8328	11,7819
N_2O[d]	1852,18	846,872	3242,96	—	5,9036[a]	11,9591[a,b]
NH_2	4963,11	2014,31	4963,44	—	−6,7368	1,2123
HNO	4963,83	2258,90	1587,06	—	−0,4994	7,4497
NF_2	1481,95	782,550	1385,63	—	5,7792	13,7283
NF_3	1483,30	923,703	1304,96	715,078	6,9687	14,9178
FNO	2053,17	1101,90	749,610	—	5,1874	13,1365

a) Value given of C_f. b) Value given of C_S. c) $X_1 = 5.3116 \cdot 10^{-3}$, $X_2 = 9.8078 \cdot 10^{-3}$, $X_3 = 9.6492 \cdot 10^{-3}$. d) $X_1 = 4.0472 \cdot 10^{-3}$, $X_2 = 0.28882 \cdot 10^{-3}$, $X_3 = 6.6994 \cdot 10^{-3}$.

<u>NF_2 and FNO.</u> The thermodynamic functions of nitrogen difluoride NF_2 and nitrogen oxifluoride FNO, given in Tables 106 (II) and 108 (II), respectively, were calculated from Eqs. (II.243)-(II.244) in the temperature interval 293.15-6000°K, based on the values of the molecular constants of NF_2 and FNO, accepted in the present Handbook (see Tables 103 and 104). The calculations were made in the approximation of the rigid rotator – harmonic oscillator model, without taking excited electron states into account so that part of the terms in Eqs. (II.243)-(II.244) were put equal to zero. In Table 111, for NF_2 and FNO, the values are given of θ_n, corresponding to the values taken for the fundamental frequencies of the molecules considered, of C'_Φ and C'_S, calculated from Eqs. (II.251)-(II.252). In the calculation of C'_Φ and C'_S for NF_2 it was assumed that $p_M = 2$, since the electron ground state of this molecule is a doublet.

The total error of the calculated values of Φ^*_T at 298.15, 3000 and 6000°K amounts to ±0.2, ±1.4 and ±2.0 cal/mole·deg with NF_2 and ±0.01, ±0.7 and ±1.2 cal/mole·deg for FNO. These errors are caused by the approximate character of the calculations; moreover, in the case of NF_2, by the inaccuracy of the values of the molecular constants, and in the case of FNO, the accuracy is influenced by the neglection of an electron state which is not observed in experiments but, analogous to HNO, must have a low excitation energy.

The thermodynamic functions of FNO were previously calculated by Stephenson and Jones [3846] up to 1500°K, with the same molecular constants as used in the present Handbook. The insignificant deviations of the results of calculations (about 0.03 cal/mole·deg) which are independent of the temperature, may be explained by the fact that the authors of [3846] used somewhat obsolete values of the fundamental physical constants.

The thermodynamic functions of NF_2 have been published for the first time.

$\underline{NF_3}$. The thermodynamic functions of nitrogen trifluoride, NF_3, given in Table 107 (II), were calculated from Eqs. (II.243)-(II.244) in the temperature interval 293.15-6000°K, based on the values of the molecular constants of NF_3, accepted in the present Handbook (see Table 107). The calculation was carried through in the approximation of the rigid rotator – harmonic oscillator model, without taking excited electron states into account so that part of the terms of Eqs. (II.243)-(II.244) were taken as equal to zero. Table 111 gives for NF_3 the values of θ_n, corresponding to the accepted values of the fundamental frequencies of this molecule, and the values of C'_Φ and C'_S, calculated from Eqs. (II.247)-(II.248).

The total error of the values of the thermodynamic functions of

NF_3, calculated in this way, is mainly due to the approximate character of the calculation. The errors of the values of Φ^*_T at the temperatures of 298.15, 3000 and6000°K amount to ±0.05, ±0.5 and ±1.5 cal/mole·deg, respectively.

The thermodynamic functions of NF_3 up to 1500°K were previously calculated by Wilson and Polo [4297]; the results of this calculation virtually agree with the data given in Table 107 (II).

$\underline{NO_2}$. The thermodynamic functions of nitric oxide, NO_2, given in Table 98 (II), were calculated from Eqs. (II.243)-(II.244) in the temperature interval 293.15-6000°K, based on the values of the molecular constants of NO_2, accepted in the present Handbook (see Table 101). The values of R ln Σ and R [ln Σ + (T∂/∂T) ln Σ] in these equations were calculated by means of the tabular method of Gordon (Eqs. (II.185)-(II.186)) but all constants of interaction of rotation and vibration were considered as vanishing in the calculation, in spite of the fact that part of these constants have been determined experimentally. This approximation is due to the indeterminacy of the values of the residual constants of interaction which renders the error greater than the contribution of the known constants. The quantities R ln $(1 + \rho_1 T + \rho_2 T^2)$ and R $(\rho_1 T + 2\rho_2 T^2)/(1 + \rho_1 T + \rho_2 T^2)$ in Eqs. (II.243)-(II.244) were cal calculated from the values of $\rho_1 = 4.026 \cdot 10^{-5}$ deg^{-1} and $\rho_2 = 3.903 \cdot 10^{-9}$ deg^{-2}, obtained from Eqs. (II.228)-(II.229) with $B_0 = (B_0 + C_0)/2$. This approximation is fully justified since the NO_2 molecule is similar to the type of symmetrical rotators. The quantities $\Delta\Phi^*_{el}$ and ΔS_{el} were calculated from Eqs. (II.120)-(II.121) assuming that, according to the data given on pp. 701-704, $\nu^A = 11{,}000$ cm^{-1}, $p_A = 2$, $\nu^B = \nu^C = 16{,}000$ cm^{-1} and $p_B + p_C = 4$.

Table 111 contains the values of θ_n and X_n, corresponding to the accepted values of the vibrational frequencies and the constants of an-

harmonicity of NO_2, and also the values C'_Φ and C'_S, calculated from Eqs. (II.247)-(II.248) with $p_M = 2$ (since the electron ground state of the NO_2 molecule is a doublet).

The total error of the values of Φ^*_T of NO_2 calculated in this way for 298.15, 3000 and 6000°K amounts to ±0.05, ±0.15 and ±0.3 cal/mole·deg, respectively.

The tables of the thermodynamic functions of nitric oxide up to 2000°K, given in the Handbooks of Kelley [2363], Ribaud [3426] and Zeise [4380], based on the calculation of Giauque and Kemp [1716], who used values of the fundamental frequencies of NO_2 ($\nu_1 = 1373$, $\nu_2 = 641$ and $\nu_3 = 1615$ cm^{-1}) and of the product of the moments of inertia ($14.4 \cdot 10^{-117}$ g^3cm^6) which are obsolete at present, so that the results given in Table 98 (II) cannot be compared with the data contained in these handbooks. This is particularly true for Zeise's calculation [4380] up to 3000°K, where the wrong assumption was made that $p_M = 4$. The calculations of Morozov [303] ($T \leq 1000$°K) and Al'tshuller [530] ($T \leq 1500$°K) were made in the approximation of the rigid rotator – harmonic oscillator model with virtually the same values of the fundamental frequencies as were used in the present Handbook. The differences between the values, given in Table 98 (II) and the data of Al'tshuller, reach 0.4 cal/mole·deg with the values of S°_{1500} and are mainly due to the fact that the anharmonicity of vibrations and the centrifugal distortion of NO_2 have been taken into account in the present Handbook. The deviations from Morozov's data are small and do not exceed several hundredths of cal/mole·deg; this is explained by the fact that the difference in the calculating methods is compensated by the difference of the products of the moments of inertia* used in the calculations.

N_2O. The thermodynamic functions of nitroux oxide, N_2O, given in Table 99 (II), were calculated from Eqs. (II.241)-(II.242) in the tem-

perature interval 293.15-6000°K, based on the values of the molecular constants of N_2O, accepted in the present Handbook (cf. Table 102). The values of R ln Σ and R [ln Σ + (T∂/∂T) ln Σ] in these equations were determined by means of Gordon's tabular method (cf. Eqs. (II.195)-(II.196). The constants $\rho_1 = 1.42534 \cdot 10^{-6}$ deg^{-1} and $\rho_2 = 6.09478 \cdot 10^{-12}$ deg^{-2} were calculated from Eqs. (II.224)-(II.225). The excited electron states were not taken into account in calculating the thermodynamic functions of N_2O. The components of Fermi resonance, calculated from the equations

$$\Delta\Phi^* = \frac{R}{2}\left(\frac{hc}{kT}W_0\right)^2 \frac{e^{-\theta_n/T}}{(1-e^{-\theta_n/T})(1-e^{-\theta_s/T})^2}, \qquad \text{(XIV.3)}$$

$$\Delta S = \Delta\Phi^*\left[2\frac{\theta_n}{T}\left(1+\frac{e^{-\theta_n/T}}{1-e^{-\theta_n/T}}+\frac{e^{-2\theta_n/T}}{1-e^{-2\theta_n/T}}\right)-1\right], \qquad \text{(XIV.4)}$$

(cf. [4323, 4326]), were added to the quantities calculated from Eqs. (II.241)-(II.242). Table 111 contains the values of θ_n and X_n, corresponding to the accepted values of the vibrational frequencies and the constants of anharmonicity of N_2O, and also the values of C_Φ and C_S, calculated from Eqs. (II.245)-(II.246).

The error of the thermodynamic functions of N_2O calculated in this way are small and seem not to exceed ±0.05, ±0.1 and ±0.3 cal/mole·deg with the values of Φ^*_T at 298.15, 3000 and 6000°K, respectively.

The Fermi resonance in N_2O was taken into account for the first time in the Handbook. The tables of the thermodynamic functions (up to T = 1500-2000°K) in Ribaud's [3426] and Zeise's [4384] handbooks were mainly based on the results of Kassel's paper [2332] in which the molecular constants of N_2O, found by Plyler and Barker [3275] were used in the calculations. These constants deviate essentially from those used in the present Handbook. In the book by Vukalovich et al. [137] the tables of the molecular functions were calculated with the help of the molecular constants given in Herzberg's monograph [152]. The main

cause of the deviation of the results of calculations of the thermodynamic functions in [3426, 4384, 137] from the data of the present Handbook is the use of different constants of anharmonicity, x_{22} (−2.28 cm^{-1} in Herzberg's book [152] compared to −0.17 in the present Handbook). This results in a difference of up to 0.2 cal/mole·deg in the entropy values at 2000°. In Kelley's book [2363] we find a table of the values of $S°_T$ for N_2O up to T = 2000°K; the deviations from the data of Table 99 (II) increase as the temperature rises, up to 0.15 cal/mole·deg at 2000°K. Since the values of $S°_T$ in Table 99 (II) are higher than those in Kelley's paper, it may be assumed that the calculation (in [2363] in Kelley's work there are no indications as to the method of calculation and the initial constants) was made in the approximation of the rigid rotator – harmonic oscillator model.

The values of the thermodynamic functions of N_2O up to 1500°K given in the paper of Pennington and Kobe [3221] agree best with the data of the present Handbook (maximum deviation 0.02 cal/mole·deg with the entropy at 1500°K). The molecular constants used in the calculations of [3221] were determined by G. Herzberg and L. Herzberg [2029] (see p. 704). These constants deviate a little from those used in the present Handbook in the calculations of the thermodynamic functions at temperatures below 1500°K. The method of taking into account the anharmonicity of vibrations and the vibration-rotation interaction, developed by the authors of [3221] (see p. 205), compared with Gordon's method at these temperatures, does not cause essential differences either.

<u>NH_3.</u> The thermodynamic functions of ammonia, NH_3, given in Table 102 (II), were calculated from Eqs. (II.243)-(II.244) in the temperature interval 293.15-6000°K, using the values of the molecular constants of NH_3, accepted in the present Handbook (see Tables 105 and 106). The values of R ln f and R [ln Σ + (T∂/∂T) ln Σ] in these equa-

tions were determined by means of Gordon's tabular method (cf. Eqs. (II.185)-(II.186)). The constants $\rho_1 = 1.385 \cdot 10^{-5}$ deg^{-1} and $\rho_2 = 4.584 \cdot 10^{-10}$ deg^{-2} were calculated with the help of Eqs. (II.228)-(II.229).

Excited electron states were not considered in calculating the thermodynamic functions of NH_3; since the ammonia molecule has no internal rotation the values of $\Phi^*_{vn.vr}$ and $S_{vn.vr}$ were also assumed as equal to zero. In Table 112 we find the values of θ_n and X_n, corresponding to the accepted values of the fundamental vibrational frequencies and the constants of anharmonicity of NH_3, the coefficients a_i, b_{ii} and c_{ik} of Eqs. (II.185)-(II.186) and also the values of C'_Φ and C'_S, calculated from Eqs. (II.251)-(II.252).

Owing to the absence of data on the value of the constant of anharmonicity, x_{22} (see p. 716), all terms in Eqs. (II.185)-(II.186), containing $n = 2$, could not be calculated. The components in Φ^*_T and S°_T, due to fully symmetrical deformation vibrations v_2, were therefore calculated by direct summation over the values of the vibrational level energies, given in Table 105. It has been assumed that with $v_2 \geq 4$ these levels are harmonic oscillator levels with an oscillation frequency of 475 cm^{-1} (see p. 717). The terms $R \ln Q_{v_2}$ and $R [\ln Q_{v_2} + (T\partial/\partial T) \ln Q_{v_2}]$ were thus added to Eqs. (II.243)-(II.244), where

$$Q_{v_2} = 1 + \exp\left(-\frac{1,141}{T}\right) + \exp\left(-\frac{1341,69}{T}\right) + \exp\left(-\frac{1393,21}{T}\right) + \exp\left(-\frac{2298,6}{T}\right) + \\ + \exp\left(-\frac{2748,09}{T}\right) + \exp\left(-\frac{3429,79}{T}\right) + \frac{\exp\left(-\frac{4165,99}{T}\right)}{1-\exp\left(-\frac{653,43}{T}\right)}. \quad \text{(XIV.5)}$$

In the present Handbook the thermodynamic functions of ammonia were calculated with averaged values of the rotational constants, i.e., without taking inverse doubling of the rotational levels of NH_3 into account. In accordance with this, the quantity σ was chosen equal to 6 instead of 3 when calculating C'_Φ and C'_S. It follows from a paper of

TABLE 112

Values of the Constants Used to Calculate the Thermodynamic Functions of NH_3

Постоянная 1	Значение 2	Постоянная 1	Значение 2	Постоянная 1	Значение 2
θ_1, град	4948,40	$a_1 \cdot 10^3$	1,9870	$c_{12} \cdot 10^4$	5,6836
θ_2, град	5008,10	$a_2 \cdot 10^3$	1,6973	$c_{14} \cdot 10^4$	—6,0069
θ_4, град	2392,35	$a_4 \cdot 10^3$	—1,7803	$c_{24} \cdot 10^4$	—7,1923
X_1	0,014916	$b_{11} \cdot 10^4$	3,2929	C'_Φ, кал/моль·град	—8,7172
X_2	0,0053149	$b_{22} \cdot 10^4$	3,0119	C'_S, кал/моль·град	—0,7681
X_4	0,0106254	$b_{44} \cdot 10^4$	4,5431		

1) Constant; 2) Value; 3) cal/mole·deg.

Godnev [156] that it is fully justified to neglect the inverse doubling of the rotational levels for a temperature interval as considered in the present Handbook.

The main source of errors in the values of the thermodynamic functions of NH_3 is the neglection of the anharmonicity of the vibration ν_2 and also the inaccuracy of the constants of anharmonicity. The error of the value of Φ^*_{3000} due to these causes may reach ±0.075 cal/mole·deg. The total error in the values of Φ^*_T at 298.15, 3000 and 6000°K amounts to ±0.05, ±0.1 and ±0.5 cal/mole·deg, respectively.

The thermodynamic functions of NH_3 were previously calculated either in the approximation of the rigid rotator – harmonic oscillator model (Thompson [3971], Khlebnikov and Morozov [451] and Sundaram, Suczek and Cleveland [3900a] up to 1000°K and a series of calculations carried out up to 1938, mentioned in Wilson's review [4291]), or in the approximation of the rigid rotator-harmonic oscillator model (Thompson [3971], Khlebnikov and Morozov [451] and Sundaram, Suczek and Cleveland [3900a] up to 1000°K and a series of calculations carried out up to 1938, mentioned in Wilson's review [4291]), or in the approximation of the rigid rotator-anharmonic oscillator model (Stephenson and McMahon

[3848] up to 2000°K, Din et al. [1350] up to 1000°K) or in the approximation of the nonrigid rotator-harmonic oscillator model, with the anharmonicity of the vibrations ν_2 taken into account by means of direct summation over the energy levels of this vibration (Harrison and Kobe [1960] up to 1500°K). The rotation-vibration interaction was only taken into account in calculating the specific heat of ammonia for temperatures between 0 and 150°C (Haupt, Teller [1974]). The molecular constants of NH_3 used in these calculations and accepted in the present Handbook, differ as a rule only slightly from one another; the main sources of divergence of the calculating results are therefore the different methods used to calculate the thermodynamic functions and the differences of the basic physical constants applied. Thus, the results of the calculations by Thompson [3971] and Khlebnikova and Morozov [451] agree virtually with one another and differ from those calculated in the present Handbook by 0.03 cal/mole·deg at 298.15°K and by 0.15 cal/mole·deg at 1000°K in the values of the entropy. The deviations are at low temperatures caused by the correction according to Stripp and Kirkwood (Eq. (II.176a)), not taken into account in the papers [3971, 1960]; at higher temperatures the fact that the centrifugal distortion and the vibrational anharmonicity has been taken into account becomes effective.

The calculation of Stephenson and McMahon [3848] was made up to 2000°K without taking into account the vibrational anharmonicity and the vibration-rotation interaction; this explains the deviation of the results of calculations in [3848] from the data of the present Handbook, which reaches 0.209 cal/mole·deg with the values of $S°_{2000}$. The deviation from the results obtained by Din et al. [1350], reaching 0.1 cal/mole·deg with $S°_{1000}$, is explained by the same causes. The results obtained by Harrison and Kobe [1960] are the best available in litera-

ture. The maximum differences between the values given in Table 102 (II) and in paper [1960] appear with the values of Φ^*_T at low temperatures. This is explained by the fact that the authors of paper [1960] did not take into consideration the correction according to Stripp and Kirkwood (see above). At higher temperatures the deviations first decrease and then rise again but do not exceed 0.028 cal/mole·deg with the values of S°_{1500}. This effect is explained by the fact that in the beginning the deviations due to the small differences in the values used for the level energy values with inverse doubling predominate (in the paper of Harrison and Kobe [1960] the contribution of these levels is greater), and then the values of the vibrational anharmonicity and of the interaction between vibrations and rotations begin to grow, which is taken into account in the present Handbook.

N_2H_4. The thermodynamic functions of the hydrazine N_2H_4, given in Table 103 (II), were calculated from Eqs. (II.243)-(II.244) in the temperature interval 293.15-6000°K, using the values of the molecular constants of N_2H_4, accepted in the present Handbook (see Table 108). The calculation was carried out in the approximation of the rigid rotator-harmonic oscillator model; the components R ln Σ, R ($\rho_1 T + 2.5\rho_2 T^2$), $\Delta\Phi^*_{el}$, R [ln Σ + (T∂/∂T) ln Σ], R ($2\rho_1 T + 7.5\rho_2 T^2$) and ΔS_{el} were put equal to zero. The components of internal rotation, $\Phi^*_{vn.vr}$ and $S_{vn.vr}$ were calculated from Eqs. (II.236)-(II.237) in which the values of ($\Phi^*_{sv.vr} - \Phi^*_{vn.vr}$) and ($S_{sv.vr} - S_{vn.vr}$) were determined from the tables of Pitzer and Gwinn [3259], on the basis of the arguments $1/Q_{sv.vr} = 1/0.168727\sqrt{T}$ and $V_0/RT = 4850/RT$. Calculating $Q_{sv.vr}$ from Eq. (II.231) it was assumed that $n_m = 2$ and in Eqs. (II.236)-(II.237) it was assumed that $\sigma_i = 1$. Table 113 contains the values of θ_n, corresponding to the accepted values of the fundamental frequencies of N_2H_4, and the values of C'_Φ and C'_S, calculated from Eqs. (II.251)-(II.252).

The main source of errors in the values of thermodynamic functions of N_2H_4, calculated in th is way, is the absence of exact data on the shape of the potential curve of internal rotation and the indeterminacy of the magnitude of V_0 of the potential barrier, connected with this. It can be assumed that at temperatures of 500-1000°K the total error of the functions does not exceed the value of the error in $S°_{298.15}$, determined experimentally by Scott et al. [3667] (cf. p. 723). At higher temperatures the error increases because of the neglection of the vibrational anharmonicity, the interaction between vibrations and rotations, the centrifugal distortion of the molecule on rotation, and other effects. At the temperatures 3000 and 6000°K the total error of the values of Φ^*_T amounts to ±0.7 and ±1.2 cal/mole·deg, respectively.

There is a single calculation of the thermodynamic functions of N_2H_4 (up to 1500°K) published in literature by Scott et al. [3667] who also applied the approximation of the rigid-rotator-harmonic oscillator model. In paper [3667] the contribution of internal rotation was calculated under the assumption that the gauche configuration with damped rotation is in equilibrium with the transconfiguration with free rotation, the difference between the energies of these configurations

TABLE 113

Values of the Constants Used to Calculate the Thermodynamic Functions of N_2H_4

1 Постоянная	2 Значение	Постоянная	Значение	Постоянная	Значение
θ_1, *град* 3	4719,23	θ_6, *град*	1579,79	θ_{10}, *град*	2342,35
θ_2, *град*	4783,98	θ_8, *град*	1122,26	4 θ_{11}, *град*	1366,85
θ_3, *град*	2283,36	θ_9, *град*	4768,15	C'_{Φ}, *кал/моль·град*	1,9697
$\theta_4=\theta_{12}$, *град*	1834,46	θ_{10}, *град*	4819,85	C'_S, *кал/моль·град*	9,9188

1) Constant; 2) Value; 3) degree; 4) cal/mole·deg.

amounting to 2800 cal/mole. The sums of the rotational and vibrational degrees of freedom of both configurations were assumed to be equal to one another, since, according to Pitzer [3255], a change in the vibration frequencies occurring in a transition from one configuration to another, is compensated in the state sum by a change of the moments of inertia. The value of 2800 cal/mole of the potential barrier of internal rotation was determined by Scott et al. [3667] on the basis of the value of $\nu_7 = 360\ cm^{-1}$ suggested by them for the frequency of torsion oscillation. The value of $S°_{298.15} = 57.41$ cal/mole·deg calculated by Scott et al., differs by 0.44 cal/mole·deg from that obtained with the help of calorimetrical measurements, which goes beyond the limits of experimental errors. The authors of [3667] explained this deviation by assuming a residual entropy. Collins and Lipscomb [1157], however, a result of X-ray diffraction studies of the structure of crystalline hydrazine, showed that in the case of hydrazine the residual entropy must be equal to zero. It is thus more likely that the deviations of the results of the calculations of Scott et al. from the experimental data may be caused by the method of taking into account the internal rotation and also by the value of the potential barrier. The differences between the results of the calculations in [3667] and the data given in Table 103 (II) grow in the case of $S°_T$ from 0.42 cal/mole·deg at 298.15°K to 1.57 cal/mole·deg at 1500°K. In the case of Φ^*_T the corresponding differences amount to 0.19 and 1.10 cal/mole·deg.

§53. THE THERMODYNAMIC QUANTITIES

The standard state of Nitrogen is N_2 (gas).

N (gas). The value of the heat of formation of monatomic nitrogen

$$\Delta H°_f{}_0(N, \text{gas}) = 112{,}536 \pm 0{,}055 \text{ kcal/g-atom}$$

accepted in the present Handbook, was calculated on the basis of the accepted value of the dissociation energy of N_2 (see below).

N^+ (gas). The ionization potential of monatomic nitrogen was chosen according to Moore's recommendation [2941] as equal to 117.345 ± ± 10 cm^{-1} or

$$I(N) = 336{,}62 \pm 0{,}03 \text{ kcal/g-atom.}$$

The following value corresponds to it:

$$\Delta H°f_0 (N^+, \text{gas}) = 448{,}056 \pm 0.07 \text{ kcal/g-atom.}$$

N_2 (gas). For a long time the value of the dissociation energy of diatomic nitrogen was the object of an extended discussion and the topic of a series of review articles (cf., e.g., Gaydon [141, 1668], Kottrell [255], Brewer and Search [932], Sehon and Szwarc [3677]). The chief interest of the discussion was focused to the two possible values of $D_0(N_2)$, equal to 9.759 and 7.375 ev; most of the authors preferred the value of 9.759 ev, though there were no sound arguments speaking in favor of this choice.

The value of the dissociation energy of nitrogen may be determined by way of analyzing the predissociation in the N_2 spectrum. In particular, Büttenbender and Herzberg [1037] who observed discontinuities in the rotational structures at the vibrational levels of v = 2, 3 and 4 of the $C^3\Pi_u$ state, used the data obtained to determine the dissociation limit of N_2, for which a value of 97,944 ± 40 cm^{-1} (12.143 ev) was found. If this limit is assumed to be correlated with the states $N(^4S) + N(^2D)$, the dissociation energy of N_2 in the electron ground state must be equal to 78,717 cm^{-1} (9.759 ev); the value of $D_0(N_2)$ = = 59,490 cm^{-1} (7.375 ev) corresponds to a correlation of this limit with the states $^2D + ^2D$. A criterion, important for the choice of one of these two values of $D_0(N_2)$, is the interpretation of the predissociation in the states $a^1\Pi_g$ and $B^3\Pi_g$, corresponding to the dissociation limit of N_2 equal to about 9.8 ev. Gaydon [1668] proposed to assume these predissociations as caused by the low-stability state $^5\Sigma^+_g$, dis-

sociating into nitrogen atoms in the normal states ($^4S + {}^4S$). If this is true, $D_0(N_2) = 9.759$ ev. There exist, however, almost only indirect experimental proofs of the existence of a low-stability ($D_e \approx 850$ cm^{-1}) electron state $^5\Sigma^+_g$, dissociating into nitrogen atoms with $^4S + {}^4S$ (see p. 673). Based on the data obtained from investigating the N_2 spectrum alone, it is therefore impossible to choose unambiguously between the two possible values of the dissociation energy, though the value of 9.759 ev is more likely [1376a].

A choice of the value of the dissociation energy of N_2 may also be based on a determination of the dissociation energies of NO, N^+_2 and CN. The dissociation energies of N_2 and NO are linked with one another by a thermodynamic equation and two values of $D_0(NO)$ (6.506 and 5.314 ev) correspond to the two possible values of $D_0(N_2)$; the accuracy of the former is determined by the accuracy of the heat of formation of NO. According to the discussions of the values of dissociation energy of NO in the present Handbook (see p. 762), the value of $D_0(NO) = 6.506$ ev is more likely; it corresponds to a value of $D_0(N_2) = 9.759$ ev. On the basis of the results of investigating the band system $B^2\Sigma^+_u - X^2\Sigma^+_g$ of the N^+_2 molecule, Douglas [1369] came to the conclusion that an extrapolation of the vibrational levels of both electron states to the value of $D_0(N^+_2) = 70{,}396$ cm^{-1}, to which a value of $D_0(N_2) = 78{,}717$ cm^{-1} (9.759 ev) corresponds, is better justified than an extrapolation to the lower value of $D_0(N^+_2)$.

The value of the dissociation energy of N_2 may also be determined in investigations of various high-temperature processes.

Zel'dovich [195] showed that under certain conditions the dissociation energy may be calculated on the basis of data on measurements of the speed of detonation waves. Kristiakowsky, Knight and Malin [2415, 2417] used this method to determine the dissociation energy of nitro-

gen. A comparison of the detonation velocities measured in a mixture of dicyan and oxygen with those calculated with the help of various possible values of the dissociation energy of nitrogen, showed that the value of $D_0(N_2)$ cannot be lower than 9.759 ev. Toennies and Green [3995, 3996], Christian, Duff and Jarger [1103], Semenov [371] and Hornig [2129], studying the shock wave velocity in nitrogen, arrived at the same result.

Thomas, Gaydon and Brewer [3964] investigated the violet band system of CN in the spectrum of a dicyan-oxygen flame and determined the "vibrational temperature" of this flame. A comparison of the flame temperature measured with the temperatures calculated with the various possible values of $D_0(N_2)$ showed that the value of 9.759 ev was the correct one. A more accurate measurement of the temperature of this flame was carried out by Conway, Wilson and Gross [1163] by means of the method of spectrum line inversion. The authors of paper [1163] also arrived at the result that the value of $D_0(N_2)$ = 9.759 ev must be the true one.

The most serious objection (see, e.g., [255]) against the higher value of the dissociation energy of nitrogen was previously based on the results of investigations by means of the method of electron impact. But the last papers of Hagstrum [1930], Kandel [2320], Burns [1027], Clarke [1124], Frost and McDowell [1621] and Thorburn and Craggs [3984], showed that the earlier investigations displayed errors and arrived at results that verified the value of $D_0(N_2)$ = 9.759 ev.

Hendrie [1989] investigated the dissociation of nitrogen up to 3450°K. In this work a directed magnetic field separated the particles with high magnetic moments from a molecular beam. Even at 3450°K the beam was found to be free from nitrogen atoms which permitted an establishment of the lower limit of the dissociation energy of nitrogen at

8.80 ev. This limit speaks in favor of the value of $D_0(N_2)$ = 9.759 ev. Farber and Darnell [1528] came to the same conclusion when studying the dissociation of nitrogen on a tungsten wire.

It must be noted that quantum-mechanical calculations [997, 2160] also verify the higher value of $D_0(N_2)$.

Based on the results of investigations considered above, we accept in the present Handbook the following value of the dissociation energy of nitrogen:

$$D_0(N_2) = 9{,}759 \pm 0{,}005 \text{ ev} = 225{,}072 \pm 0{,}110 \text{ kcal/mole}$$

N^+_2 (gas). The first ionization potential of diatomic nitrogen was determined repeatedly with the help of the method of electron impact (see Hagstrum's review [1929]). The accuracy of this method is not high, it amounts to about ±0.2 ev. Moreover, in the method of electron impact it is the potential at which the N^+_2 ion appears that is measured directly, a quantity which can be taken as the ionization potential only under certain suppositions (see [1929]). An accurate value of $I(N_2)$ was obtained as the result of investigating the Rydberg series in the N_2 molecular spectrum; this was done by Worley and Jenkins [4331] and Worley [4330] (see also Tanaka, Takamine [3938, 3940]). This value, 125,665.8 ± 10 cm^{-1}, or

$$I(N_2) = 359{,}311 \pm 0{,}03 \text{ kcal/mole}$$

was accepted in the present Handbook. To it correspond

$$\Delta H^\circ f_0(N^+_2, \text{gas}) = 359{,}311 \pm 0{,}03 \text{ kcal/mole}$$

and the value of the energy of dissociation of N^+_2 in N and N^+, equal to

$$D_0(N^+_2) = 201{,}281 \pm 0{,}09 \text{ kcal/mole}$$

N_3 (gas). Gray and Waddington [1847] measured the heat of dissolution of a series of azides and subsequently [1848], based on the data obtained in paper [1847], they calculated the energies of the crystal

lattices of these azides and obtained the following value of the heat of formation of N_3:

$$\Delta H^\circ f_{298.15}(N_3, g) = 116 \pm 5 \text{ kcal/mole}$$

which is accepted in the present Handbook.* The corresponding value of the dissociation energy of N_3 into atoms is equal to

$$D_0(N_3) = 220{,}702 \pm 5 \text{ kcal/mole}$$

Thrush's estimate of the dissociation energy of N_3 [3988] (D_0 > > 229 ± 4 kcal/mole) agrees within the limits of error with the value accepted in the present Handbook.

NO (gas). The results of investigating the NO spectrum do not permit an exact determination of the dissociation energy of this molecule which, as mentioned above (see p. 758), may be calculated with the help of the dissocition energies of N_2 and O_2 and the heat of formation of NO.

Berthelot [773, 781] measured the heat of combustion of dicyan and ethylene in oxygen and in NO. Based on the data obtained, a value of 21.6 kcal/mole was obtained for the value of the heat of formation of NO. The same value was obtained by Thomsen [3981]. The literature data on the equilibrium of the reaction

$$\tfrac{1}{2}N_2 + \tfrac{1}{2}O_2 \rightleftarrows NO$$

were collected by Lewis and Randall [2604, 3367] and Giauque and Clayton [1713]. The authors of the present Handbook used these data to calculate the value oi the heat of formation of NO and obtained $\Delta H^\circ f_0$(NO, gas) = 22.6 ± 0.4 kcal/mole (which corresponds to $\Delta H^\circ f_{298.15}$(NO, gas) = = 22.7 kcal/mole). It sh ould be mentioned that the calculated value of $\Delta H^\circ f_0$ varies systematically with the temperature of experiment which indicates a violation of equilibrium or the presence of side reactions.

Koerner and Daniels [2455] measured the heat of combustion of ex-

cessive red phosphorus in a mixture of O_2 with N_2 and in NO. The difference of the heats of these reactions, in the case where the reaction products forming are the same, is equal to the heat of formation of NO from the elements. As established by Koerner and Daniels, in the combustion a considerable amount of P_4O_6 is formed beside P_4O_{10}. The introduction of corresponding corrections is rendered difficult by the lack of sufficiently reliable values of the heat of formation of P_4O_6. The authors of paper [2455] had to carry through an unreliable (for more than 4 kcal) extrapolation of the results of individual measurements toward zero content of P_4O_6 and obtained for the heat of formation of NO a value of 21.8 kcal/mole. In the present Handbook we accept the following value of the heat of formation:

$$-\Delta H^\circ f_{298.16}(NO, \text{gas}) = 21{,}6 \pm 1 \text{ kcal/mole}$$

The following value corresponds to this heat of formation of NO:

$$D_0(NO) = 150.043 \pm 1 \text{ kcal/mole} = 6.506 \text{ ev.}$$

It must be noted that the results of investigating the NO spectrum, though, as mentioned above, they do not render it possible to obtain an exact value of $D_0(NO)$, definitely speak in favor of a value of ~6.5 ev. Thus, for example, Brook and Kaplan [978], investigating the β-system in the NO spectrum, observed bands, corresponding to transitions to vibrational levels of the electron ground state with $v'' \leq 23$. The energy of the latter observable vibrational level (about 4.5 ev) is such that an extrapolation of levels leading to a value of the dissociation energy <6.5 ev, may be achieved only if there exist some rare anomalies in the energies of the vibrational levels of the NO ground state with large values of v. Moreover, an application of the method of electron impact to investigating the dissociation energy of NO, also yields unambiguously a value of $D_0(NO) \approx 6.5$ ev [1131, 1623]. Thus we see that independent determinations of the dissociation energy of NO

yield a value that speaks in favor of the value of $D_0(N_2)$, accepted in the present Handbook.*

NO^+ (gas). The value of the ionization potential of NO was measured by the method of electron impact (see review of Hagstrum [1929]) and photoionization (cf. the paper of Watanabe and coworkers [4175, 4176, 4178] and also Walker and Wassler [4132a]). Based on a series of papers on the method of electron impact, Hagstrum [1929] recommends a value of I(NO) = 9.4 ± 0.2 ev. Photoionization measurements make it possible to determine the longwave limit of the ionization continuum with an accuracy of ±0.02 ev, which exceeds the accuracy of measurements with the electron impact method by orders of magnitude. With the help of the photoionization method Watanabe [4175] obtained a value of 9.25 ± 0.02 ev or

$$I(NO) = 213{,}387 \pm 0{,}5 \text{ kcal/mole}$$

This value has been accepted in our Handbook. To it correspond the heat of formation

$$\Delta H^\circ f_0 (NO^+, g) = 234{,}867 \pm 1{,}1 \text{ kcal mole}$$

and an energy of dissociation of NO^+ into N and O^+, equal to

$$D_0 (NO^+) = 250{,}708 \pm 1{,}1 \text{ kcal/mole}$$

NO_2 (gas). The results of a great many investigations of the equilibrium of

$$NO + \tfrac{1}{2} O_2 \rightleftarrows NO_2$$

were collected and recalculated by Randall [3367] and Giauque and Kemp [1716]. These authors obtained virtually the same values ($\Delta H^\circ_{298.15}$ = = −13.587 and −13.562 kcal/mole). In the present Handbook we give a value of the heat of formation calculated with these data:

$$\Delta H^\circ f_{298.15} (NO_2, g) = 8{,}2 \pm 1{,}2 \text{ kcal/mole.}$$

The error of this value is first of all due to the insufficient accura-

cy of the value of the heat of formation of NO. The following value corresponds to the accepted one:

$$D_0(NO) = 221{,}843 \pm 1{,}2 \text{ kcal/mole.}$$

N_2O (gas). In order to determine the heat of formation of nitrous oxide N_2O the heat of its combustion in hydrogen [3981, 1060, 1550] and carbon monoxide [781, 3981, 1550, 591, 1061] were measured. The most accurate of these papers are the papers of Fenning and Cotton [1550] and Awbery and Griffiths [591], in which values of 19.74 ± 0.07 and 19.5 ± 0.22 kcal/mole, respectively, were obtained for the heat formation of N_2O.

In the paper of Carlton-Sutton, Ambler and Williams [1061] the heat of formation of N_2O was determined with the help of the method of measuring the heat of its decomposition into nitrogen and oxygen. These authors showed that this method yields a more accurate value of the heat of formation of N_2O, compared to the method of combustion. In the further calculations in the present Handbook we use the value of the heat of formation

$$\Delta H^\circ_{f_{298,15}}(N_2O, \text{gas}) = 19{,}52 \pm 0{,}1 \text{ kcal/mole.}$$

found by Carlton-Sutton, Ambler and Williams. The following value corresponds to it:

$$D_0(N_2O) = 263{,}725 \pm 0{,}15 \text{ kcal/mole.}$$

NH (gas). A linear extrapolation of the vibrational levels (v" = = 0, 1, 2) of the $X^3\Sigma^-$ ground state of the NH molecule yields a value of D_e = 33,970 cm^{-1} or about 4.0 ev (Pannetier and Gaydon [3174]). Since values obtained by means of a linear extrapolation are usually too high, Gaydon [1668] recommends the value 3.7 ± 0.5 ev (about 85.3 kcal/mole) and indicates that Glockler [1761], by means of a comparison of the force constants and the dissociation energies of a series of hydrides, obtained a value of 3.74 ev for the dissociation energy of NH.

With the help of the method of electron impact, Franklin, Dibeler and Reese [1598] measured the potential at which N^+_2 appears (16.0 ± ± 0.1 ev) in the reaction $HN_3 = N^+_2 + NH$. Using a value of 71.66 kcal/ /mole for the heat of formation of HN_3 [1848] and 15.576 ev for the ionization potential of N_2 (see above), the dissociation energy $D_0(NH) = 82.7$ kcal/mole was calculated which is in good agreement with the value obtained by linear extrapolation.

Reed and Snedden [3412a] used the method of electron impact to measure the potential at which N^+ and NH^+ ions appear in NH_3. The potential of appearance of these ions enabled the authors of [3412a] to find the dissociation energy $D_0(HN - H) = 4.0 \pm 0.15$ ev (a value of $D_0(NH) = 81.7 \pm 4$ kcal/mole).

The results of measurements of $D_0(NH)$ by the method of electron impact [1598, 3412a] and the estimate obtained by the method of linear extrapolation [1668] are in good agreement. In the present Handbook a value of*

$$D_0(NH) = 83 \pm 3 \text{ kcal/mole,}$$

is used for the dissociation energy of NH, to which a value of

$$\Delta H^\circ f_0(NH, \text{gas}) = 81{,}168 \pm 3 \text{ kcal/mole}$$

corresponds.

<u>NH_2 (gas).</u> Szwarc [3911] investigated the kinetics of the thermodynamic dissociation of hydrazine in a toluene current and obtained $D_0(H_2N - NH_2) = 60 \pm 3$ kcal/mole. This value was verified by Foner and Hudson [1578], who measured the potential at which the NH^+_2 ion appears in N_2H_4 and the ionization potential of NH_2 and obtained $D_0(H_2N - - NH_2) = 58 \pm 9$ kcal/mole. A value of

$$\Delta H^\circ f_0(NH_2, \text{gas}) = 43 \pm 2 \text{ kcal/mole,}$$

corresponds to the value of $D_0(H_2N - NH_2)$ found by Szwarc [3911]; the former has been accepted in the present Handbook. A similar value was

calculated by Al'tshuller [528]. The value

$$D_0(NH_2) = 172{,}8 \pm 2 \text{ kcal/mole.}$$

corresponds to the accepted value of the heat of formation of NH_2.

NH_3 (gas). Berthelot [795] and Thomsen [3981], who measured the heat of combustion of ammonia gas obtained values of −11.2 and −11.7 kcal/mole for the heat of its formation. Haber, Tamaru and Oeholm [1913] established that the accuracy of these quantities were low and the possible error amounted to 1 kcal/mole. The same authors [1913] measured the heat of decomposition of ammonia and obtained $\Delta H^\circ f_{298.15}$ (NH_3, gas) = −11.09 kcal/mole.

Becker and Roth [713] (see also [255]) measured the heat of formation of ammonia most accurately. These authors measured the heat of neutralization of ammonium oxalate, the heat of combustion of ammonium oxalate and a series of other heats and found a value of

$$\Delta H^\circ f_{298.15}(NH_3, \text{ gas}) = -11{,}01 \pm 0{,}07 \text{ kcal/mole}$$

This value, which is in good agreement with the results of measurements by Haber et al. [1913], has been accepted in the present Handbook. The following value corresponds to it:

$$D_0(NH_3) = 276{,}806 \pm 0{,}1 \text{ kcal/mole.}$$

N_2H_4 (gas). Hughes, Corruccini and Gilbert [2144] measured the heat of combustion of hydrazine and obtained $\Delta H^\circ C_{298.15} = -148.635 \pm \pm 0.03$ kcal/mole. Later on this value was recalculated by Cole and Gilbert [1150] who used a more accurate value of the heat of combustion of benzoic acid, used as standard, and obtained $\Delta H^\circ C_{298.15} = -148.68$ kcal/ /mole. A very similar value, $\Delta H^\circ C_{298.15} = -148.619$ kcal/mole, was found by Aston, Rock and Isserow [576]. A correction for the improved value of the heat of combustion of benzoic acid leads, according to data of [576], to a value of the heat of combustion of hydrazine of $\Delta H^\circ c_{298.15} = -148.664$ kcal/mole. Based on the results of papers [1150, 576], a

value of $\Delta H^\circ f_{298.15} = 12.04 \pm 0.02$ kcal/mole was calculated for the heat of formation of hydrazine in liquid state.

The heat of evaporation of hydrazine, $\Delta H^\circ v_{298.15} = 10.7 \pm 0.75$ kcal/mole, was measured by Scott, Oliver, Gross, Hubbard and Huffman [3667]. Combining these values for the heat of formation of hydrazine in the gaseous state, we may find

$$\Delta H^\circ f_{298.15}(N_2H_4, \text{gas}) = 22{,}74 \pm 0{,}08 \text{ kcal/mole.}$$

To this value, which has been accepted in the present Handbook, a value of

$$D_0(N_2H_4) = 405{,}486 \pm 0{,}14 \text{ kcal/mole}$$

corresponds.

HNO (gas). Cashion and Polanyi [1070] studied the infrared chemoluminescence which appears when hydrogen atoms react with NO. The authors assume that the band at 16,000 cm^{-1} corresponds to the energy necessary for the association of hydrogen atoms with NO. Assuming that the activation energy of this process is equal to zero, the authors of paper [1070] recommend a value of 46 kcal/mole as the lower limit of D_0(H–NO); a value of 27 kcal/mole for the upper limit of $\Delta H^\circ f_0$(HNO), gas) corresponds to it.

Recently Clement and Ramsay [1128a], who investigated the predissociation in the HNO spectrum, found an upper limit of 48.6 kcal/mole for D_0(H–NO), to which a lower limit of $\Delta H^\circ f_0$(HNO, gas) = 25.5 kcal/ /mole corresponds.

Luft [2674] estimated the value of the heat of formation of HNO with the help of three different methods: he used the results of the decomposition of NH_2OH in solutions, the values of the bond energies in nitrogen compounds, and the graph of D(X–NO) versus the ionization potential of X. The value of

$$\Delta H^\circ f_0(\text{HNO, gas}) = 25 \pm 5 \text{ kcal/mole}$$

obtained is in good agreement with those recommended by Cashion and Polanyi [1070] and Clement and Ramsay [1128a] and has been accepted in the present Handbook. The following value corresponds to it:

$$D_0(HNO) = 198{,}155 \pm 5 \text{ kcal/mole.}$$

NF (gas). The dissociation energy of the NF molecule was estimated from the mean bond energies of N–F in NF_3 and N–H in NH_3 and the dissociation energy of NH. It has been assumed that the dissociation energies of NH and NF are proportional to the mean bond energies in NH_3 and NF_3.

A value of

$$D_0(NF) = 60 \pm 6 \text{ kcal/mole}$$

corresponds to the value obtained in this way; it has been accepted in the present Handbook. The following value corresponds to it:

$$\Delta H^\circ f_0(NF, \text{gas}) = 71{,}036 \pm 10 \text{ kcal/mole.}$$

Reese and Dibeler [3415] determined the potentials at which the NF^+ and NF^+_2 ions appear in NF_3. But the absence of data on the ionization energies of NF and NF_2 do not permit the use of these results in calculations of the heat of formation of these radicals.

NF_2. The heat of formation of NF_2 may be calculated from the energy of rupture of the N–N bonds in the N_2F_4 molecules. A calculation of the quantity $D(F_2N–NF_2)$ on the basis of measurements of the potentials at which the NF^+ and NF^+_2 ions appear in the mass spectrum of N_2F_4 [2661a, 2011b] yields contradictory and unreliable results (30 and 53 kcal, respectively) which is caused by the ambiguous interpretation of the mechanism of dissociative ionization of N_2F_4 in the mass spectrometer [1146a]. Colburn and Johnson [1146a, 2260a] measured the value of $D(F_2N–NF_2)$ by means of two methods: from the temperature dependence of the ultraviolet absorption of N_2F_4 in the 260μ band (where the NF_2 absorption is assumed to take place) and from the temperature dependence

of the pressure on N_2F_4 at constant volume. Both methods yielded virtually equal results, on the basis of which the authors of paper [2260a] recommend for $D(F_2N-NF_2)$ at 100°C a value of 20.8 ± 1 kcal/mole. Using a value of −2 ± 2.5 kcal/mole for $\Delta H°f_{298.15}(N_2F_4, gas)$ (according to unpublished data of Armstrong, Marantz and Coyle), Colburn and Johnson obtained a value of $\Delta H°f_{298.15}(NF_2, gas)$ = 9.4 kcal/mole. Finally Herron and Dibeler [2011c], in mass-spectrometrical investigations of the equilibrium of thermal dissociation of N_2F_4, obtained a value of 21.5 ± ± 1.6 kcal/mole for $D(F_2N-NF_2)$ in the interval of 30-400°C, which leads to a value of $\Delta H°f_{298.15}(NF_2, gas)$ = 9.8 ± 2.1 kcal. Based on the results of the papers [1146a, 2011c, 2260a] we chose the following value for the present Handbook:

$$\Delta H°f_{298.15}(NF_2, gas) = 9{,}5 \pm 2{,}5 \text{ kcal/mole}$$

A value of

$$D_0(NF_2) = 139{,}433 \pm 3{,}0 \text{ kcal/mole}$$

corresponds to this value of $\Delta H°f_{298.15}(NF_2, gas)$.

<u>NF_3 (gas).</u> Ruff and Wallauer [3566] measured the heat of explosion of a mixture of NF_3 with surplus hydrogen in a calorimetrical bomb and found −166 ± 1.7 kcal/mole. A value of $\Delta H°f_{298.15}(NF_3, gas)$ = −26.6 ± 2 kcal/mole corresponds to this value.

Armstrong, Margantz and Coyle [567a] burnt a mixture of NF_3 with hydrogen in the presence of water and obtained for the heat of this reaction $\Delta H°_{298.15}$ = −205.3 ± 3.2 kcal/mole which corresponds to $\Delta H°f_{298.15}(N_3, gas)$ = −30.7 ± 3.4 kcal/mole. The same authors [567a] measured the heat of combustion of NF_3 in a surplus of ammonia and found $\Delta H°_{298.15}$ = −259.15 ± 1.0 kcal/mole, which corresponds to $\Delta H°f_{298.15}(NF_3, gas)$ = −29.4 ± 2.1 kcal/mole. Based on these measurements, Armstrong et al. [567a] recommend a value of

$$\Delta H^\circ_{f_{298.15}}(NF_3, gas) = -29{,}7 \pm 1{,}8 \text{ kcal/mole},$$

which has been accepted in the present Handbook. The following value corresponds to it:

$$D_0(NF_3) = 196{,}361 \pm 2{,}5 \text{ kcal/mole}.$$

FNO (gas). Johnston and Bertin [2287, 800] measured the heat of the reaction $2NO + F_2 = 2FNO$ in a calorimeter and obtained a value of $\Delta H_{298.15} = -74.8 \pm 0.8$ kcal/mole. To this value corresponds a heat of formation of FNO, equal to -15.8 kcal/mole. In the same paper [800] the absorption spectrum of the FNO molecule was obtained in the near ultraviolet and the dissociation energy of FNO in the excited state, with the formation of $NO(^2\Sigma^+)$ and $F(^2P)$, was found to be equal to 33,200 cm^{-1}. But since the energy of transition of FNO to the excited state is unknown, this value of the dissociation energy cannot be used to calculate the heat of formation of FNO.

An estimation of the heat of formation of FNO, based on the assumption that the dissociation energies of the bonds F–N and N=O in the FNO molecule are equal to the dissociation energies of the molecules of NF and NO, leads to a value of the heat of formation of FNO, equal to -20 kcal/mole.

In the present Handbook we chose a rounded value of the heat of formation,

$$\Delta H^\circ_{f_{298.15}}(FNO, gas) = -16 \pm 1 \text{ kcal/mole},$$

calculated from Bertin's data [2287]. A value of

$$D_0(FNO) = 205{,}452 \pm 1{,}1 \text{ kcal/mole}$$

corresponds to the accepted value of the heat of formation.

NS (gas). There exists no literature on experimental investigations of the dissociation energy of the NS molecule. A linear extrapolation of the vibrational levels of NS in the ground state, from constants, given in Table 99, yields a value of ~6.0 ev (about 138 kcal/

/mole). Since in the case of NO a linear extrapolation yields a value higher by about 20% than the true dissociation energy, we chose in our Handbook a value of

$$D_0(NS) = 115 \pm 20 \text{ kcal /mole.}$$

The following corresponds to the value accepted:

$$\Delta H^\circ f_0(NS, \text{gas}) = 55{,}761 \pm 20 \text{ kcal/mole.}$$

TABLE 114

Accepted Values (in cal/mole) of the Thermodynamic Quantities of Nitrogen and Its Compounds in the Gaseous State

Вещество [1]	D_0 или I [2]	$\Delta H^\circ f_0$	$\Delta H^\circ f_{298.15}$	$\Delta H^\circ f_{298.15}$	$H^\circ_{293.15} - H^\circ_0$	$H^\circ_{298.15} - H^\circ_0$
N	—	112 536	112 974	112 981	1456	1481
N^+	336 830[a]	448 056	450 170	450 203	1676	1702
N_2	228 072	0	0	0	2037	2072
N_2^+	359 311[a]	359 311	360 768	360 792	2038	2072
N_3	220 702	116 906	116 011	116 000	2160	2202
NO	150 043	21 480	21 600	21 600	2158	2194
NO^+	213 267[a]	234 867	236 323	236 347	2038	2072
NO_2	221 843	8 667	8 009	8 000	2400	2444
N_2O	263 725	20 334	19 830	19 514	2243	2289
NH	83 000	81 168	81 183	81 183	2025	2060
NH_2	172 800	43 000	42 333	42 320	2335	2375
NH_3	276 806	—9 374	—11 010	—11 030	2358	2400
N_2H_4	405 486	26 114	22 787	22 740	2678	2736
HNO	198 155	25 000	24 316	24 305	2346	2388
NF	80 000	71 036	71 041	71 042	2080	2097
NF_2	130 433	10 103	9 507	9 500	2495	2544
NF_3	196 361	—28 325	—29 080	—29 700	2764	2827
FNO	205 452	—15 420	—15 996	—16 000	2508	2558
NS	115 000	55 76[illegible]	55 924	55 915	2206	2243

a) Values given for the ionization potentials of the corresponding neutral molecules or atoms of nitrogen.

1) Substance; 2) or.

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[Footnotes]

663 When the thermodynamic functions of monatomic nitrogen had been calculated, a paper of Eriksson [1491] was published (see also [1491a]) in which, apart from improved values of the well-known energy levels of the N atom, also a series of levels is listed which have as yet not been observed experimentally:

TABLE

1 Состояние		Статистический вес	5 Энергия, $см^{-1}$
2 электронная конфигурация	3 терм	4	
$...2s^22p^2(^1D)3p'$	$^2F^o_{5/2}$	8	110715,35
$...2s^22p^2(^1D)3p'$	$^2F^o_{7/2}$	6	110710,95
$...2s^22p^2(^3P)5p$	$^2D_{5/2}$	6	111905,80
$...2s^22p^2(^3P)5p$	$^2D_{3/2}$	4	110853,26
$...2s^22p^2(^1S)3s'$	$^2S_{1/2}$	2	116278,83
$...2s^22p^2(^1D)3d'$	$^2G^o_{9/2}$	10	120149,44
$...2s^22p^2(^1D)3d'$	$^2G^o_{7/2}$	8	120[illegible]

1) State; 2) electron configuration; 3) term; 4) statistical weight; 5) energy, cm^{-1}.

In the present Handbook the energy of the state $2s^22p^2(^3P)5p\cdot{}^2D$ was assumed to be equal to that of the state $2s^22p^2P^3P)\cdot 6s^4P$, i.e., about 112,600 cm^{-1}, and the remaining states, listed above, were referred to the corresponding ionization limits. The improvement of the energy values of the terms of N known previously that was achieved in paper [1491] does not go beyond the limits of 2-6 cm^{-1}. An exception is made by the terms $2s^22p^2(^3P)4p\,^4P_{5/2}$, $^4P_{3/2}$ and $^4P_{1/2}$, for which the maximum deviation in the energy values, compared to those given in Moore's handbook [2941], amounts to 132 cm^{-1}.

665 After the calculations of the thermodynamic functions of N^+ had been finished with the values of the energy levels given in Table 90, Eriksson published his results of investigating the spectrum of N^+ [1490]. The table of level energies given in paper [1490] is more complete than that in Moore's handbook [2941], the excitation energies of the levels $^3P_0$, $^3P_1$, $^3P_2$, ^1D and ^1S with the electron configuration $1s^22s^22p^2\ ^3D$ differ from those given in [2941] by 0.4-1.8 cm^{-1}, those of the levels $1s^22s2p^3\ ^5S$ by 383 cm^{-1} and of the levels $1s^22s\cdot 2p^3\ ^3D$ by 6 cm^{-1}.

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660 In the past two years two new band systems were discovered in the N_2 spectrum, corresponding to the forbidden transitions $a'\ ^1\Sigma^-_u - X^1\Sigma^+_g$ and $Y^3\Sigma^-_u - X^1\Sigma^+_g$ (see pp. 672-673).

In 1934 Kaplan and Levans [2322] communicated on investigations of the band systems $a^1\Pi_g - X^1\Sigma^+_g$, corresponding to v" = = 15-22. Results of these investigations have, as far as we know, not been published.

676 For a long time the numeration of the vibrational levels of the $A^2\Pi_u$ state of the N^+_2 molecule was the subject of discussions. Considering the fact that the 0-0 band of the system $A^2\Pi_u - X^2\Sigma^+_g$ was not observed in the spectrum, Bagaryatskiy and Fedorova [78] assumed that the numeration must be reduced by one as compared to the numeration suggested by Meinel [2843] and used by Douglas [1370] and Janin and d'Incan [2214, 2215]. Nicholls [3066] assumes that the absence of an 0-0 band in the system $A^2\Pi_u - X^2\Sigma^+_g$ of the N^+_2 molecule in the 1.1μ range can be explained by the strong absorption of H_2O in this range. Finally, Lin [2615], comparing the calculated and the observed isotope mixture in the bands $A^2\Sigma_u - X^2\Sigma^+_g$, showed that the numeration of the vibrational levels of the $A^2\Pi_u$ state, suggested by Meinel [2843] and used in the present Handbook is correct.

679* After the choice of the molecular constants of N^+_2 and the calculation of the thermodynamic functions, Carroll published a paper [1064], devoted to investigating the $C^2\Sigma^+_u - X^2\Sigma^+_g$ system, obtained in high resolution. Based on the analysis of 15 bands, Carroll determined the values of $\Delta G_{v+1/2}$ and B_v for v' = 0-6. The values of $\Delta G_{v+1/2}$, obtained in paper [1064] are in satisfactory agreement with those calculated from the constants accepted in the present Handbook (the maximum deviation does not exceed 4 cm^{-1}), whereas the value of B_0 = = 1.5098 differs essentially from that given in Table 94.

679** There also exist higher states of NO [3927, [illegible], 3902, 3932] which form a Rydberg series; but their excitation energies exceed 100,000 cm^{-1} so that these states are not considered in the present Handbook.

According to Mulliken [2982] (see also [950]) the NO molecule

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must have another stable state ($^4\Pi$) with an excitation energy of about 4.5 ev (about 36,000 cm^{-1}). Berstein and Herzberg [761a], however, did not discover in the NO spectrum a band system connected with this state. Based on investigations of the NOCl absorption spectrum in the ultraviolet range, Goodeve and Katz [1795a] suggested an excitation energy of about 8000 cm^{-1} for the $^4\Pi$ state of the NO molecule. Finally, in 1960, Broida and Peyron [976a] assumed that the bands, observed in an Ar matrix, containing N_2 and O_2 impurities, at a temperature of 4.2°K, may be referred to the transition $^4\Pi - X^2\Pi$ of the NO molecule, and estimated the excitation energy of the $^4\Pi$ state as equal to 4.7 ev. Obviously, it is at present impossible to recommend any reliable values of the molecular constants of NO in this state, so that it is not taken into consideration in the following calculations.

686* The β-system was previously also investigated in the absorption spectrum in a series of papers [2587, 2911, 3929, 3902]. But in these papers the interpretation of the bands was either wrong [2587, 2911] or not quite unambiguous [3902, 3929].

686** In 1960 Deézsi [1287a] observed bands in the emission spectrum of active nitrogen which he interpreted as the bands 7-16, 7-18 and 7-19 of the β-system of NO. Based on an analysis of the breakoff of the rotational structure of the gamma bands, Deézsi obtained the limiting curve of dissociation and found $D_0(NO) = 53,226 \pm 300$ cm^{-1}. With this value of the dissociation energy, the potential curves of the states $B^2\Pi_r$ and $^2\Sigma^+$ must intersect at $v' > 7$, i.e., it becomes possible to observe bands of the β-system which correspond to $v' = 7$ (see, however, the footnote to p. 763).

688* In paper [2036] the wavelengths of the edges of observed bands of the δ-system were measured and the values of B_v were calculated for $v' = 0-4$.

688** It had been suggested [2037] to consider the ε-bands as a continuation of the γ-system for which, as indicated above, bands with $v'' > 3$ were not observed in the emission spectrum. But later on it was shown that $D^2\Sigma^+$ is an independent state.

688 Recently Deézsi and Matrai [1288] observed the bands 2-9 and 2-8 of the ε-system in the emission spectrum and showed that these bands can be described satisfactorily by the molecular constants, calculated by Ogawa [3114] ($\omega_e' = 2327$, $\omega_e x_e' = 23$, $B_e' = 1.998$, $\alpha' = 0.018$ cm^{-1}).

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693* The potential curves of the stable electron states of NH, observed in the spectra, are shown in Fig. 2 (see p. 62).

693** After we had chosen the molecular constants of NH for the present Handbook, Dixon published a paper [1353] devoted to the analysis of the rotational structure of the bands 0-0 and 1-0 of the system $A^3\Pi_i - X^3\Sigma^-$ of the NH molecule, photographed in high resolution. Using the data obtained by Funke [1628] for the 1-1 band of this system, Dixon calculated the following values of the constants (in cm^{-1}): $B''_0 = 16.3454$, $B'_0 = 16.3221$, $\alpha''_1 = 0.646$, $\alpha'_1 = 0.744$, $D''_0 = 1.685 \cdot 10^{-3}$, $D'_0 = 1.758 \cdot 10^{-3}$, $\Delta G''_{1/2} = 3125.6$ and $\Delta G'_{1/2} = 3034.00$. The constants given in Table 99, are of low accuracy but are in satisfactory agreement with these values. In Dixon's paper the constants of multiplet splitting of the state $X^3\Sigma^-$ ($\lambda = 0.928$; $\mu = -0.053\ cm^{-1}$) and the constant of spin-orbital coupling in the state $A^3\Pi_i$ ($A = -35.02\ cm^{-1}$) were also determined.

699 It had once been assumed [612, 613] that the NO_2 molecule were linear; this assumption was refuted in, e.g., Herzberg's monograph [152].

702 Besides the data obtained as a result of his own investigations Bird used data, previously obtained by MacAfee [2685, 2686] and reinterpreted by himself, in order to calculate the constants.

703 Recent [1851b, 2703a] quantum mechanical calculations of the NO_3 molecule yielded values of excitation energies of lower electron states which agree essentially with those accepted in the present Handbook.

706 After the choice of the molecular constants and the calculation of the thermodynamic functions of N_2O for the present Handbook, a paper of Tidwell, Plyler and Benedict [3989b] was published in which the vibrational and rotational constants of N_2O were considerably improved and, in particular, the constants of anharmonicity, y_{ijk}, and the constants γ_{ik} of interaction between vibration and rotation were determined.

711* A calculation of the fundamental frequencies of NF_2, recommended by Schatz [3608] ($f_d = 4.36 \cdot 10^5$; $f_{dd} = 0.67 \cdot 10^5$, $f_\alpha = 1.02 \cdot 10^5$; $f_\alpha = 1.02 \cdot 10^{-5}$; $f_{d\alpha} = 0.34 \cdot 10^5$ dyne/cm), leads to

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values which, within the above limits of error, agree with those given in the present Handbook.

711** When the present chapter had been finished, Harmoni et al. [1956a] published a paper devoted to the investigation of the infrared spectrum and structure of NF_2. The following values were obtained in paper [1956a]: $\nu_1 = 1074$, $\nu_3 = 935$ cm^{-1} and $\angle F-N-F = 104°.2$.

719 Schatz and Levin [3610], investigating the absolute intensities, also obtained values of the fundamental frequencies of NF_3 which are similar to those found in papers [4297, 3161].

720 Wagner and Bulgozdy [4123], based on investigations of the temperature dependence of the N_2H_4 spectra (with both the infrared spectrum and the Raman spectrum), came to the conclusion that the transconfiguration is more stable and that the transconfiguration must be in equilibrium with the two isomeric gauche configurations of hydrazine. In a recent paper of Giguere and Liu [1735] a temperature dependence of the spectrum could not be observed and the authors suggested to explain the results obtained by Wagner and Bulgozdy [4123] by the appearance of hydrogen bonds in condensed phases.

721 The microwave spectrum of N_2H_4 was obtained in paper [2460] but a spectrum analysis was not carried through.

722 Based on the structural parameters of N_2H_4 recommended in paper [1739], Scott, Oliver, Gross and Hubbard [3667] calculated the following values of the moments of inertia: $I_A = 3{,}698 \cdot 10^{-40}$, $I_B = 3{,}533 \cdot 10^{-40}$, $I_C = 0{,}618 \cdot 10^{-40}$ and $I_{pr} = 1.53 \cdot 10^{-40}$ $g \cdot cm^2$.

725 The application of newer data, obtained by Eriksson [1491] (see p. 663) in the calculation of the thermodynamic functions of N does not cause changes in the values of Φ^*_T, exceeding 10% of the errors given.

726 An exception is made by the thermodynamic functions of N, given in the book by Vukalovich et al. [137] up to 3000°C and differing from those calculated in the present Handbook by 0.02-0.03 cal/g-atom·deg in the entropy values.

733 Owing to this the improvement of the molecular constants in the state $C^2\Sigma^+_u$, achieved by Carroll [1064] (see footnote to p. 679), is inessential in the calculation of the thermodynamic functions of N^+_2.

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748 When the calculation of the thermodynamic functions of NO_2 for the present Handbook had been finished, Gordon published a paper [1817a] in which the thermodynamic functions of NO_2 were calculated for the temperatures between 298.15 and 6000° K. The calculation in Gordon's paper was made according to the Pennington-Kobe method (see p. 205), using molecular constants of NO_2 which are in essential agreement with those accepted in the present Handbook (see Table 101). In the calculation of [1817a] a correction for the interaction between rotations and vibrations was taken into account, not so the centrifugal distortion. Moreover, in Gordon's calculation the excited electron states of NO_2 were not taken into account which chiefly causes an increase with temperature of the deviations of the quantities given in Table 98 (II) from Gordon's values, up to 2.1 cal/mole·deg at 6000°K in the case of the values of $S°_T$.

749 Following Kassel [2332], Ribaud [3426] gives the thermodynamic functions of N_2O up to 1500°K, taking the nuclear spin into account, which contributes R ln 9 = 4.366 cal/mole·deg to the values of Φ^*_T and $S°_T$, while the table of Φ^*_T was borrowed from Kassel [2332] and the table of $S°_T$ was obviously calculated in the approximation of the harmonic oscillator-rigid rotator model.

753 In view of the nonuniform changes of the first differences in the values of $S°_T$ in the interval 400-900°K in paper [1350] it can be assumed that an error was admitted in the calculation of these values, which may reach 0.05-0.06 cal/mole·deg.

761 Based on theoretical considerations, Singh [3744] obtained a value of 113 kcal/mole for the heat of formation of N_3.

763 As mentioned on p. 685, Deézsi [1287a], analyzing the break-off of the rotational structure of the γ-bands in the NO spectrum, obtained a value of $D_0(NO) = 53{,}266 \pm 300$ cm^{-1} (6.60 ± 0.04 ev). Using this value, one obtains $\Delta H°f_{298.15}$ (NO, gas) = 19.3 ± 0.9 kcal/mole, which does not agree with the value of 21.6 ± 1 kcal/mole, accepted in the present Handbook. The data available at present do not yet permit us to draw final conclusions as to the reliability of the values of $D_0(NO)$, obtained in paper [1287a].

765 Recently, by means of a semiempirical method, Companion and

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Ellison [1159a] estimated a value of $D_0(NH) = 3.61$ ev (83.3 kcal/mole) which is in good agreement with the value accepted in the present Handbook.

Chapter 15

Phosphorus And Its Compounds

(P, P_2, P_4, PO, P_4O_6, P_4O_8, P_4O_{10}, PH, PF, PF_2, PF_3, PF_5, POF_3, PCl, PCl_3, PCl_5, $POCl_3$, PS, PN)

Three main allotopic modifications of solid phosphorus are known: white, red and black phosphorus.* The transformations of solid phosphorus modifications into others and the properties of the individual modifications have been investigated in numerous works (see the handbooks [4365, 3717, 4070]). Jacobs [2199] measured the heat of reaction of different modifications of solid phosphorus with bromine in a solution of carbon disulfide.** The results of these measurements showed that under normal conditions, the crystalline black phosphorus is the thermodynamically most stable, red phosphorus is less stable and white phosphorus the least stable. Nevertheless, the α-modification of white phosphorus, which is formed by condensation of phosphorus vapor, has been used as the standard state of phosphorus in the literature and the present handbook. The thermodynamic properties of phosphorus in the solid and liquid states are not discussed in the handbook because the boiling point of phosphorus is relatively low (554°K, according to [3894]).

The main components of phosphorus vapor, P, P_2 and P_4, are discussed in this handbook. According to the mass-spectrometric study [2376], small quantities of the molecule P_3 and P_8 are also present in phosphorus vapor.

The main oxides of phosphorus, the pentoxide, dioxide and trioxide exist in the solid state under normal conditions and their chemical com-

position is described by the formulae P_2O_5, PO_2 and P_2O_3; the molecular composition of these compounds is described by the formulae P_4O_{10}, P_4O_8 and P_4O_6. The most stable phosphorus oxide is the pentoxide. Three polymorphous forms of solid phosphorus pentoxide are known [2075]. An experimental investigation of the thermodynamic properties of phosphorus pentoxide in the solid and gaseous states has been carried out by Frandsen [1595].

Only the gaseous pentoxide, dioxide and trioxide, of phosphorus (P_4O_{10}, P_4O_8, P_4O_6) are discussed in the present Handbook and also the most important product of their dissociation at high temperatures, the radical PO.

The literature contains indications concerning the existence of other compounds of phosphorus with oxygen: the intermediate products of the oxidation of phosphorus, P_4O, P_4O_2 and others [266, 2851 369, 1246-1248] and the peroxide compounds PO_3 and P_2O_3 [4365, 3717]. These compounds are not very stable, however, and the data presented in the Handbook are sufficient for calculating the composition and thermodynamic properties of the system phosphorus-oxygen at high temperatures.

Of the compounds of phosphorus with hydrogen only the radical PH is discussed in the Handbook. The hydrides of phosphorus known under normal conditions, phosphine PH_3 and diphosphine P_2H_4, are highly unstable compounds (the thermodynamic properties of PH_3 and PD_3 are presented in the works [451, 4365, 3900a and 3314a]). The not very stable compound PH_2 can exist under certain conditions [3361, 3363, 2689a], whose properties have not yet been investigated.

The phosphoric acids (H_3PO_4, HPO_3, etc.) are not discussed in the Handbook, because these compounds are known only in the condensed states and are completely decomposed upon evaporation into water vapor and the corresponding phosphorus oxide.

The following compounds of phosphorus with fluorine are discussed in the Handbook: PF, PF_2, PF_3, PF_5, POF_3 and the compounds of phosphorus with chlorine: PCl, PCl_3, PCl_5 and $POCl_3$. The mixed compounds of phosphorus with fluorine and chlorine are not very stable and have been much less investigated. The data presented in the Handbook are sufficient for calculating the compositions and thermodynamic properties of the phosphorus-fluorine (or chlorine)-oxygen system.

The simplest compounds of phosphorus with nitrogen, PN, sulfur, PS, and carbon, CP (see Chapter 21) are also discussed in the Handbook.

§ 54. MOLECULAR CONSTANTS

P. In the basic electronic state $^4S_{3/2}$ the phosphorus atom has the following electronic configuration: $1s^2 2s^2 2p^6 3s^2 3p^3$.

Table 115 presents the energy levels of the phosphorus atoms corresponding to the indicated electronic configuration, in accordance with the handbook of Moore [2941].* The following electronic state of the phosphorus atom, $^4P_{\frac{1}{2}}$, corresponding to the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^2 4s$ has the energy of 55939.23 cm^{-1}. This and the higher energy levels of the phosphorus atom are not discussed in the present Handbook.

TABLE 115

Energy Levels of the Phosphorus Atom

Номер уровня A	B Состояние: электронная конфигурация C	B Состояние: терм D	Статистический вес E	Энергия, $см^{-1}$ F
0	$1s^2 2s^2 2p^6 3s^2 3p^3$	$^4S_{3/2}$	4	0
1	$1s^2 2s^2 2p^6 3s^2 3p^3$	$^2D_{3/2}$	4	11361,7
2	$1s^2 2s^2 2p^6 3s^2 3p^3$	$^2D_{5/2}$	6	11376,5
3	$1s^2 2s^2 2p^6 3s^2 3p^3$	$^2P_{1/2}$	2	18722,4
4	$1s^2 2s^2 2p^6 3s^2 3p^3$	$^2P_{3/2}$	4	18748,1

A) Number of level; B) state; C) electronic configuration; D) term; E) statistical weight; F) energy, cm^{-1}.

$\underline{P_2}$. In studies of the spectra of diatomic phosphorus it has been found that the molecule P_2 has five stable electronic states: $X^1\Sigma_g^+$, $A^1\Pi_g$, $B^1\Sigma_u^+$, C and D (see Table 116).

The system of bands $B^1\Sigma_u^+-X^1\Sigma_g^+$ situated in the wavelength region 2000-3300 Å is the most easily studied. It has been first detected by Geuter [1704] in the emission spectrum of P_2. An analysis of the vibrational structure of this system has been carried out first by Yakovleva [481] who studied the fluorescence and absorption spectra of phosphorus vapor on a medium-dispersion spectrograph. Later on the band system $B^2\Sigma_u^+-X^1\Sigma_g^+$ was investigated on the basis of the emission spectra of P_2 in the works [2015, 2231, 573, 2031, 2765, 2764, 2766, 3829a, 3389].*

A detailed investigation of the band system $B^1\Sigma_u^+-X^1\Sigma_g^+$ was carried out by Herzberg [2015] on the basis of data obtained by him on a quartz spectrograph and a two-meter vacuum spectrograph with diffraction grating and also on the basis of spectra, obtained by Yakovleva [481] and Jenkins and Ashley [2231]. The vibration constants of P_2 in the states $B^1\Sigma_u^+$ and $X^1\Sigma_g^+$ which are presented in the book of Herzberg [2020] and in the handbook [649] were determined in the work [2015] on the basis of the band edges, corresponding to $v' = 0, 1, \ldots, 11$, and $v'' = 4, 5, \ldots, 32$. The bands corresponding to $v' = 10$ and 11, in the work [2015] were obtained with a resolved rotational structure for the study of predissociation in the system $B^1\Sigma_u^+-X^1\Sigma_g^+$ and the determination of the dissociation energy of the molecule P_2 (see §56).

The rotational structure of the band system $B^1\Sigma_u^+-X^1\Sigma_g^+$ has been studied later by Ashley [573], G. Herzberg, L. Herzberg and Milne [2031], Rao [3389], Marais [2764, 2765] and Marais and Verleger [2766], in the work of Marais [2764, 2765] and Marais and Verleger [2766]. The best resolution of the rotational structure of the bands was achieved, which made it possible to investigate the perturbations of the rotational lev-

els in the state $B^1\Sigma_u^+$ and to determine with greater accuracy the values of the rotational constants of P_2 in the states $X^1\Sigma_g^+$ and $B^1\Sigma_u^+$.

TABLE 116

Accepted Values of the Molecular Constants of P_2 and PO

Молекула A	Состояние B	T_e	ω_e	$\omega_e x_e$	B_e	α_1	$D_e \cdot 10^6$	r_1
		C $см^{-1}$						A
P_2	$X^1\Sigma_g^+$	0	780,4278	2,8038[a]	0,30624	0,00167	0,18854[б]	1,885
	$A^1\Pi_g$	34515,34	618,88	2,97[в]	0,27520	0,00169	—	1,9083
	$B^1\Sigma_u^+$	46030,83	475,2217	2,6035[г]	0,24166	0,00165	—	2,122
	$C^д$	50480	628[к]	—	—	—	—	—
	$D^е$	66330	600	3,5	—	—	—	—
PO	$X^3\Pi_r$	0[ж]	1233,42	6,57	0,7331	0,0055	1,03[б]	1,4730
	$A^3\Sigma^+$	19500[з, и]	1400[к]	—	—	—	—	—
	$B^3\Sigma^+$	30841,61	1166,2	14,10	0,7476	0,0088	—	1,462
	$C^3\Sigma^+$	40406,77	1291,16	8,98	0,7801	0,0054	—	1,4313
	$D^3\Sigma^+$	47235	750	5	—	—	—	—
	$E\ (^3\Delta)^к$	48718[з] 48745[з]	<1160	—	—	—	—	—
	$E'\ (^3\Delta)^к$	48757,5[з] 48854,7[з]	1301	—	—	—	—	—
	$F^ж$	53323,1[з]	1457,6[к]	—	0,792	0,008	—	1,420

a — а $\omega_e y_e = -0.00533$ cm^{-1}.

b — б Calculated by means of Formula (1.36a).

c — в Calculated by means of Formula (1.38) in which it was assumed $\omega_e \cong \Delta G_{1/2}$.

d — г $\omega_e y_e = 0.0235$ cm^{-1}.

e — д The value $\Delta G_{\frac{1}{2}}$ is given.

f — е The type of state is unknown.

g — ж $A_0 = 224.03$, $p = 0.0073$ cm^{-1}.

h — з The value of T_0 is given.

i — и Estimate.

k — к The type of state has not been determined uniquely.

A) Molecule; B) state; C) cm^{-1}.

Marais [2764, 2765] and Marais and Verleger [2766] obtained the system of the bands $B^1\Sigma_u^+ - X^1\Sigma_g^+$ in the third and fourth order of a curved

diffraction grating with a dispersion of 0.85 and 0.65 Å/mm, respectively. The 13 bands (5-20, 5-21, 6-21, 6-23, 7-23, 7-24, 8-27, 8-28, 9-29, 10-29, 10-31, 11-31) were analyzed in the work [2766] and the 12 bands (3-16, 4-17, 4-18, 6-22, 7-27, 8-25, 8-26, 8-29, 9-27, 9-30, 10-30, 11-32) in the work [2764]. L. Herzberg and Milne [2031] determined the zero lines of the bands 0-5, 0-6, 0-7, 2-15 and 3-16 in the work [2766] on the basis of the measurement results of G. Herzberg. On the basis of all these results Marais and Verleger [2766] calculated the excitation energy of the electronic state $B^1\Sigma_u^+$ and the values of the vibrational constants of P_2 in the states $X^1\Sigma_g^+$ and $B^1\Sigma_u^+$. The latter differ slightly from the values of the corresponding magnitudes, found by Herzberg [2015] on the basis of the band edges. The values of the vibrational and rotational constants of P_2 in the states $X^1\Sigma_g^+$ and $B^1\Sigma_u^+$, determined by Marais and Verleger [2766], have been used in the present Handbook and are presented in Table 116.

Douglas and Rao [1379] in 1958 detected the existence of the stable electronic state $A^1\Pi_g$ in the P_2 molecule, which has a smaller excitation energy than the state $B^1\Sigma_u^+$. These researchers obtained the emission spectrum of phosphorus vapor (being present in helium in small quantity) on an apparatus with a dispersion of 0.32 Å/mm. Among a large number of bands of the system $B^1\Sigma_u^+-X^1\Sigma_g^+$, five previously not observed intense bands 1-0, 0-0, 0-1, 0-2 and 0-3 belonging to the system $A^1\Pi_g-X^1\Sigma_g^+$, were detected. The rotational structure of these five bands was analyzed in detail and the positions of the individual lines determined up to $J = 65$, in the work [1379]. On the basis of this analysis, Douglas and Rao calculated the molecular constants of P_2 in the states $X^1\Sigma_g^+$ and $A^1\Pi_g$. The values of the molecular constants of P_2 in the state $X^1\Sigma_g^+$, found in the work [1379] are close to the values of the corresponding constants, presented in Table 116 ($\omega_e = 780.89$; $\omega_e x_e = 2.820$; $\omega_e y_e = -0.00511$;

$B_e = 0.30359$; $\alpha_1 = 0.001477$; $\alpha_2 = -3.2 \cdot 10^{-6} cm^{-1}$, $r_e = 1.8931$ Å).

The constants of P_2 in the state $A^1\Pi_g$, determined by Douglas and Rao, were used in the present Handbook and are presented in Table 116.

In contrast to the earlier investigations of the spectrum of P_2, Douglas and Rao [1379] analyzed the bands corresponding to the transitions to the lower levels of the vibrational energy of the state $X^1\Sigma_g^+$ ($v'' = 0, 1, 2, 3$).* Hence the value of the vibrational constants of P_2 for the state $X^1\Sigma_g^+$ found in the work [1379] approximate the experimental values of the lower levels of the vibrational energies of this state more closely than the constants, determined by Herzberg [2015] and Marais and Verleger [2766]. The values of G(v) for the high levels of the vibrational energy of P_2 ($v > 10$) in the ground electronic state approximate equally satisfactorily the vibrational constants, proposed in the works [2015, 2766, 1379]. Extrapolation of the levels of the vibrational energy of P_2 to the dissociation limit on the basis of the vibrational constants, recommended by Herzberg [2015] leads to values of $v_{max} = 106$ and $G_0(106) = 44,487$ cm^{-1}, while $v_{max} = 107$ and $G_0(107) = 44,343$ cm^{-1} correspond to the vibrational constants, found by Douglas and Rao [1379]. The experimental value of the dissociation energy of P_2, based on investigations of predissociation, has been found by Herzberg [2015], as being $40,590 \pm 30$ cm^{-1} (see §56).

For molecules which are isosteric with P_2 (N_2, PN, SiS, AlCl) electronic states $^1\Pi$, analogous to the electronic state $A^1\Pi_g$ of the P_2 molecule, discovered by Douglas and Rao, are also known [1379]. For some of them, however, (N_2, SiS, AlCl), electronic states with a lower excitation energy are known. Hence, the possibility of the existence of stable electronic states of P_2 with a lower excitation energy than $A^1\Pi_g$, which have not yet been detected in the spectrum of this molecule, cannot be excluded.

The emission spectrum of P_2 in the Schumann region has been studied by Dressler [1402, 1403]. This author found two new systems, situated within the wavelength range of 1680-1760 and 1500-1530 Å. By means of the edges of the R-branches of the bands in this system Dressler established that they correspond to transitions with previously unknown electronic states of P_2 with high excitation energies (states C and D) into the basic electronic state $X^1\Sigma_g^+$. The data obtained by Dressler for these electronic states of P_2 are presented in Table 116.

PO. The basic electronic state of the PO molecule is the state $^2\Pi_r$. The existence of seven stable excited electronic states (see Table 116) of which only two states, $B^2\Sigma^+$ and $C^2\Sigma^+$, have been studied in as much detail as the basic state is known. Band systems of PO have been observed in the visible region of the spectrum ($A^2\Sigma^+-X^2\Pi_r$, $E-B^2\Sigma^+$, $E'-B^2\Sigma^+$), in the ultraviolet region ($B^2\Sigma-X^2\Pi_r$ or the β-system, $C^2\Sigma^+-X^2\Pi_r$ or γ-system) and in the Schumann region ($D^2\Sigma^+-X^2\Pi_r$, $E-X^2\Pi_r$, $F-X^2\Pi_r$).

The molecular constants of PO in the basic electronic state were determined in the investigations on the β and γ band systems. These band systems were first observed by Geuter [1704] and Petrikaln [3230, 3231], who drew attention to their great similarity with the β- and γ-systems of the NO bands, for which reason they were given the same designations in the literature. Later on the β-system of the PO bands was investigated by Curry, L. Herzberg and G. Herzberg [1235], Ramanadham, Rao and Sastry [3351], Dressler [1402], and Singh [3747]; the γ-system by Ghosh and Ball [1705], Sen-Gupta [3684] and Rao [3397]. The β and γ systems of the PO bands were obtained with maximum resolution in the works [3747, 3397] on apparatuses with a dispersion of 0.35 A/mm. In the β-system [3747], the rotational structure could be analyzed only for three bands (0-0, 0-1, and 1-1) while in the γ-system

[3397] an analysis of the rotational structure was carried out for seven bands (0-0, 0-1, 1-0, 1-2, 2-1, 2-3, 2-4). The values found by Rao [3397] for the molecular constants of PO in the $X^2\Pi_r$ state, are used in the present Handbook and are presented in Table 116. They are in good agreement with the values of the corresponding values, found by Singh [3747] as a result of the analysis of the rotational structure of the three bands of the β-system.* Similar values of the vibrational constants ($\omega_e'' = 1232.5$, $\omega_e''x_e'' = 6.5$ cm^{-1}) were found by Dressler [1402] on the basis of measurement of the edges and an analysis of the contours of 24 bands in the β-system. Less accurate values of the vibrational constants of PO in the $X^2\Pi_r$ state were determined earlier in the works [1235, 3351, 1705] on the basis of the edges of the bands in the β- and γ-systems. Prior to publication of the works [3397, 3747], the rotational constants of PO in the $X^2\Pi_r$ state were known only on the basis of an analysis of the rotational structure of the bands in the γ-system, carried out by Sen-Gupta [3684]. The values of the rotational constant B_e, found by Sen-Gupta ($B_e(^2\Pi_{\frac{1}{2}}) = 0.7613$, $B_e(^2\Pi_{3/2}) = 0.7645$ cm^{-1}) differ by far from the values obtained by Rao [3397] and Singh [3747]. Rao showed that this difference is due to the systematic errors committed in the work [3684] during the determination of individual line positions in the bands of the γ- system and during the analysis of their rotational structure.

Rumpf [3567] observed in the spectrum of the green luminescence, which accompanies the cold oxidation of phosphorus, a system of bands, situated in the region 3260-6500 A. He measured the positions of the edges on 14 bands of this system and arranged them formally in two Deslandres schemes, which can be reunited by a shift of approximately 530 cm^{-1}. Hence Rumpf suggested that the PO bands observed by him are due to transitions from two close electronic states ($\nu_{00} = 19,024$ and

19,571 cm^{-1}) to the ground state. This suggestion made by Rumpf with regard to the possibility of the existence of two closely adjoining electronic states of PO with an excitation energy of about 19,000 cm^{-1} is not reliable because the PO spectrum in the work [3567] had been obtained on an apparatus with low dispersion and its analysis was carried out in a formal manner without taking into account that owing to a splitting of the $X^2\Pi_r$ state bands with differently graduated edges are present in the PO spectrum.

Analogous defects in the investigation of the β-system of PO in the work [3351] led its authors to the conclusion that the upper states of this system are two close electronic states $^2\Sigma$ and $^2\Pi$ with excitation energies T_e = 30260.8 and 30606.5 cm^{-1}. In reality, the upper state of the β-system in the PO bands is the $B^2\Sigma^+$ state with an excitation energy of T_e = 30841.61 cm^{-1} as has been shown by Dressler [1402] and Singh [3747]. Comparison with other diatomic molecules, whose electron shells are similar in structure to the electron shell of PO, does not provide any basis for assuming that the PO molecule has two close electronic states with excitation energies of the order of 19,000 cm^{-1}. The molecule SiF is the most similar to the PO molecule in the structure of the electron shell. According to the data in Table 201, the first excited electronic state of the SiF molecule is the $A^2\Sigma^+$ state with T_e = 22858.4 cm^{-1}, to which apparently, corresponds the electronic state of PO with an excitation energy of about 19,000 cm^{-1}, discovered by Rumpf.

In the present Handbook it has been assumed that the first excited electronic state of the PO molecule is the $A^2\Sigma^+$ state in analogy with the $A^2\Sigma^+$ state of SiF with an excitation energy T_0 = 19,500 ± 500 cm^{-1}. The last value has been estimated on the basis of a comparison between the values of ν_{00}, found for this state by Rumpf [3567] (see above) with

the values of T_e, ascribed to the $B^2\Sigma^+$ state in the work [3351] and the values of T_e for the $B^2\Sigma^+$ state, found in the works [1402, 3747].* The value of $\Delta G_{\frac{1}{2}}$ of the PO molecule in the $A^2\Sigma^+$ state, presented in Table 116, has been determined by Rumpf [3567] on the basis of analysis of the vibrational structure of the band system $A^2\Sigma^+ - X^2\Pi_r$, carried out by him.

The molecular constants of PO in the electronic state $B^2\Sigma^+$, presented in Table 116, are based on the results of an analysis of the rotational structure of the bands 0-0, 0-1, 1-1 of the β-system, obtained by Singh [3747], and on the results of an analysis of the vibrational structure of this system, carried out by Dressler [1402].**

The values of the vibrational constants of PO in the state $B^2\Sigma^+$ presented in Table 116 were calculated by Dressler on the basis of the approximate values of the lines of 24 bands in the β system in excellent agreement with the values $\Delta G_{\frac{1}{2}} = 1137.41$ cm^{-1}, obtained by Singh. The values of the remaining constants of PO in the $B^2\Sigma^+$ state, presented in Table 116, are based on the results of the analysis by Singh.

The values of the molecular constants of PO in the $C^2\Sigma^+$ state presented in Table 116 were determined by Rao [3397] on the basis of an analysis of the rotational structure of the bands in the gamma system. The vibrational constants of PO in the $C^2\Sigma^+$ state ($\omega_e' = 1391.0$, $\omega_e'x_e' = 7.65$ cm^{-1}) had been determined previously by Ghosh and Ball [1705] on the basis of the band edges in the γ-system and the rotational constants ($B_e = 0.8121$, $\alpha_1 = 0.0056$ cm^{-1}) by Sen-Gupta [3684]. The great difference in the values of the rotational constant B_e, found for PO in the state $C^2\Sigma^+$ in the works [3684, 3397] is due to errors in the measurements and analysis of the rotational structure of the γ-system of the PO bands committed in the work [3684].

The electronic states of the molecule PO with higher excitation

energies (states $D^2\Sigma^+$, E, E' and F) were detected by Dressler [1402] and Durga and Rao [1422] during a study of the PO spectrum in the Schumann and visible regions of the spectrum. Within the wavelength intervals of 1970-2140, 2050-2170 and 1820-1930 A, Dressler found three doublet systems of PO bands, corresponding to transitions from the previously not investigated excited states of PO in the ground state $X^2\Pi_r$. Dressler could not determine the type of these electronic states in consequence of the low dispersion of the apparatus. He designated them by the letters C, D and E. In Table 116, the corresponding states are designated by the letters, D, E and F. The data on the states D and F presented in Table 116 were obtained by Dressler on the basis of an analysis of the band systems $D \rightarrow X^2\Pi_r$ and $F \rightarrow X^2\Pi_r$. The problem of the type of electronic states D, E and F was not discussed in the work [1402]. It is assumed in Table 116 that the D-state of the PO molecule is a $^2\Sigma^+$ state on the basis of the analogy with the corresponding state of SiF (see Table 201). The molecular constants of PO in the two close doublet excited states E and E' presented in Table 116 were obtained were obtained by Durga and Rao [1422] as a result of an analysis of the band systems $E \rightarrow B^2\Sigma^+$ and $E' \rightarrow B^2\Sigma^+$, situated in the visible region of the spectrum. In the opinion of the author of the work [1422], the states E and E' are $^2\Delta$-states.

PH. The spectrum of the molecule PH is very similar to the spectrum of NH but has been studied in considerably less detail. As in the case of NH, the ground electronic state of PH is the state $X^3\Sigma^-$. On the basis of a study of the spectrum, the existence of two excited electronic states of PH has been established: $b^1\Sigma$ and $A^3\Pi_i$. It is assumed in the present Handbook, in analogy with NH, that the molecule PH can also exist in the excited electronic states $a^1\Delta$ and $c^1\Pi$.

The spectrum of the molecule PH has been investigated in detail

in the wavelength range of 3200–3500 A, in which the bands 1 ← 0 [2586a] and 0 → 0 [1704, 3210, 2191, 2192] of the system $A^3\Pi_1$–$X^3\Sigma^-$ are situated. The spectrum of PH has been investigated in less detail in the visible region (5000–5700 A) where the band system $b^1\Sigma^-$–$X^3\Sigma^-$ is situated [2670]. For the molecule PD, only the band 0–0 of the system $A^3\Pi_1$–$X^3\Sigma^-$ has been investigated [2191, 2192].

TABLE 117

Accepted Values of the Molecular Constants of PH, PF, PCl, PS and PN

Молекула A	Состояние B	T_e	ω_e	$\omega_e x_e$	B_e	α_1	$D_e \cdot 10^6$	r_e
		cm^{-1} C						A
PH	$X^3\Sigma^-$	0[a]	2390[b]	42[b]	8,554	0,284	430	1,4208
	$a(^1\Delta)$[a] c	9010[b]	—	—	—[d]	—	—	—
	b,Σ^-	17860	—	—	8,0[d]	—	—	—
	$A^3\Pi_i$	29321,9[e]	1833,78[f]	—	8,2819	0,4728	570[g]	1,447
	$c(^1\Pi)$[a] c	40000[b]	—	—	—	—	—	—
PF	$X(^2\Sigma)$[a] c	0	930[b]	—	0,56[b]	—	—	1,60[b]
PCl	$X(^2\Sigma)$[a] c	0	540[b]	—	0,24[b]	—	—	2,05[b]
PS	$X^2\Pi_r$	0[h]	730,5	3,0	0,29[d]	—	0,178[i]	1,92[k]
	$A(^2\Delta)$[a] c	22170	510	—	—	—	—	—
	$B(^2\Pi)$[a] c	22270 34667	535,5	3,5	0,28[d]	—	—	2,03[k]
PN	$X^1\Sigma^+$	0	1337,24	6,983	0,78621	$5,57 \cdot 10^{-6}$	1,09[i]	1,4869
	$A^1\Pi$	39686,52	1103,09	7,222	0,73071	$6,63 \cdot 10^{-6}$	1,29[i]	1,5424

a — $\varepsilon = +0.733$; $\gamma = -0.078$ cm^{-1}.
b — Estimate.
c — The type of state has not been determined unequivocally.
d — The value of the constant B_0 is given.
e — $A_0 = -115.67$ cm^{-1}.
f — The value of $\Delta G_{\frac{1}{2}}$ is given.
g — $D_e = 5.23 \cdot 10^{-4}$; $\beta_1 = 0.85 \cdot 10^{-4}$ cm^{-1}.
h — $A_0 \approx 321.4$ cm^{-1}.
i — Calculated by means of the formula (1.36a).
k — The value of r_0.

A) Molecule; B) state; C) cm^{-1}.

The values adopted in the Handbook for the vibrational constants of PH in the $X^3\Sigma^-$ state (see Table 117) were estimated by Khachkuruzov [441] on the basis of diagrams showing the corresponding constants of the molecules of the diatomic hydrides as a function of the number of electrons in the external electron shell. The summary of Herzberg [2020] and the Handbook [649] give only the value $\omega_0 \approx 2380$ cm^{-1}, estimated by Pearse [3210] by means of the approximate relation (1.36a). The values of the rotational constants of PH in the state of $X^3\Sigma^-$ presented in Table 117 have been calculated in the work [441] by means of the relations [1.43] on thebasis of the values of the constant B_0 of the molecules PH and PD, obtained by Ishaq and Pearse [2191, 2192] as a result of an analysis of the rotational structure of the band 0-0 of the system $A^3\Pi_1 - X^3\Sigma^-$. The values of the constants D_0, ε and γ, presented in Table 117 for the $X^3\Sigma^-$ state of PH, were also determined in these investigations.

On the basis of the analogy with the NH molecule it has been assumed in the present Handbook that the first excited electronic state of PH is the $^1\Delta$ state with an excitation energy of about 9000 cm^{-1} (see Table 99 and 117). The uncertainty in the adopted value of the excitation energy of the $a^1\Delta$ state of PH is estimated to be $\pm$ 1000 cm^{-1}.

The results of the investigation of the emission spectra of PH in the visible region [2670] and the comparison with the system of electronic states of the NH molecule (see Table 99) attest to the fact that the second excited electronic state of the PH molecule is the $^1\Sigma^-$ state with an excitation energy of 17,860 cm^{-1} (see Table 117). The emission spectrum of PH in the visible region has been detected by Ludlam [2670] during investigation of the flame spectra of a mixture of the vapor of white phosphorus and hydrogen. In the wavelength range 5000-5700 A he observed three diffuse bands with centers at 19,615,

19,044 and 17,860 cm^{-1}. On the basis of the partial analysis of the rotational structure, carried out in the work [2670], it was found that these bands are due to transitions of PH from the $^1\Sigma^-$ state to the $X^3\Sigma^-$ state. However, it was not possible to analyze the vibrational structure of the $b^1\Sigma^- - X^3\Sigma^-$ system in [2670]. The value of the constant B_0 in the molecule PH in the state $b^1\Sigma^-$ presented in Table 117 is based on the results of the analysis of the rotational structure of the bands in this system [2670]. The error in it is ± 0.08 cm^{-1}. The uncertainty in the values for the excitation energy of the $b^1\Sigma^-$ state of PH used in Table 117 has been estimated as ± 1000 cm^{-1}.

The molecular constants of PH in the $A^3\Pi_1$ state were determined in the works [3210, 1741, 1006, 2191, 2192] on the basis of an analysis of the rotational structure of the band 0-0 in the system $A^3\Pi_i - X^3\Sigma^-$ and in the work [2586a] on the basis of an analysis of the rotational structure of the bands 1-0 and 0-0 of the same system. Pearse [3210] analyzed 27 branches of the band 0-0, corresponding to the transitions between the states $A^3\Pi_1$ and $X^3\Sigma^-$ and found that the $A^3\Pi_1$ state of PH is intermediate between the Hund cases a and b with regard to the type of spinorbital coupling. The ex tation energy of the state $A^3\Pi_1$ given in Table 117 is the ν_{00} of the $Q_2(1)$ line of the 0-0 band, found for th system $A^3\Pi_1 - X^3\Sigma^-$ in the work [3210]. The magnitude of the constant of the spin-orbital coupling of PH in the $A^3\Pi_1$ state has been determined with the greatest accuracy by Legay [2586a] on the basis of an analysis of the rotational structure of the bands 1-0 and 0-0 in the system $A^3\Pi_1 - X^3\Sigma^-$ and calculation of the perturbations in the position of the energy levels of PH in the state $A^3\Pi_1$, caused by the influence of the other electronic states. The values of the molecular constants of PH in the state $A^3\Pi_1$, given in Table 117, were selected on the basis of data recommended in the work [2586a].

The existence of an excited elec. onic state $c^1\Pi$ with an excitation energy of the order of 40,000 cm^{-1} is indicated in Table 117.

The existence of this electronic state of PH is assumed in the present Handbook on the basis of the analogy with NH (see Table 99). The error in the values of the excitation energies of the $c^1\Pi$ state of PH given in Table 117 can be assumed to be about $\pm$ 1000 cm^{-1}.

PF, PCl. The spectra of the PF and PCl molecules have not been observed.* Nonetheless, a comparison of the analysis results obtained on the spectra of other diatomic molecules makes it possible to predict the type of ground electronic state of PF and PCl and the probable values of the molecular constants.

The ground electronic state of the PF and PCl molecules should be of the same type as in the isosteric molecules O_2, SO, S_2, NH, NF and PH, i.e., it should be the $^3\Sigma$ state.

Comparison of the molecular constants of the diatomic fluorides and chlorides of the elements of the Periodic Groups II and III and consideration of the experimental data for the corresponding bonds in the monoatomic fluorides and chlorides of the same elements allow of the conclusion that the vibration frequencies and interatomic distances of the molecules PF and PCl are close to the values for these magnitudes in the molecules SiF and SiCl, respectively (see Table 210) and that, in any case, they should be intermediate between the values of the corresponding constants for SiF and SF in the case of PF and for SiCl and SCl in the case of PCl. the values of the constants ω_e and r_e for the molecules PF and PCl determined by this method has been used in the present Handbook and are given in Table 117.

The uncertainty in the values of ω_e for the molecules PF and PCl presented in Table 117 is estimated to be $\pm$ 30 cm^{-1}, and in the values of r_e as $\pm$ 0.02 and $\pm$ 0.5 , respectively.

PS. The bands of the PS molecule were first observed by Dressler and Miescher [1403] in the discharge spectrum of helium containing

small additions of P_4S_3 vapor. An investigation of the spectrum of PS has been carried out by Dressler [1402] on an apparatus with medium dispersion. Two systems of doublet bands of PS, situated in the wavelength region 2720-3090 and 4240-5940 A* have been described in the work [1402]. Dressler measured the edges of the bands in these systems (corresponding to $v' \leq 5$ and $v'' \leq 7$) and the distances between the edges. On the basis of these data he analyzed the vibrational structure of both systems and found that the lower state of PS in both systems is the same. Dressler pointed out that this state should be the ground electronic state $X^2\Pi$ of the PS molecule. He determined the approximate magnitude of the constant of the spin-orbital interactions of PS in the state $X^2\Pi$, and also carried out a partial analysis of the rotational structure of the bands of one of the systems. The values of the molecular constants found by Dressler in the work [1402] are given in Table 117.

The electronic ground state of the molecule PS should be the state $^2\Pi_r$, because this is the ground state of all isosteric molecules (PO, NO, NS, SiF, CCl, SiH, etc.). The types of excited electronic states of PS, whose transitions to the state $X^2\Pi_r$ were observed in the work [1402], but have not been determined in this work. In the present Handbook these states are regarded as $A^2\Delta$ and $B^2\Pi$ states on the basis of the analogy with the NS molecule (see Table 99).

PN. The electronic ground state of the molecule PN is the state $X^1\Sigma$. Only one band system $A^1\Pi - X^1\Sigma$ situated in the wavelength region 2400-3000 A has been investigated in the PN spectrum. The emission of this band system has been investigated by Curry, L. Herzberg, and G. Herzberg [1235], and Ghosh and Datta [1706], and the absorption by Moureu, Rosen and Wetroff [2964].

The most detailed investigation of the band system $A^1\Pi - X^1\Sigma$

of the molecule PN has been carried out by Curry, L. Herzberg and G. Herzberg [1235] on the basis of spectrograms obtained in the first and second order of a diffraction grating with a mean dispersion of 5.7 and 2.8 A/mm. The authors of the work [1235] observed 32 bands in the system $A^1\Pi - X^1\Sigma$, corresponding to $v' \leq 9$ and $v'' \leq 10$. The rational structure has been completely resolved and analyzed only for six bands (0-0, 0-1, 0-2, 1-0, 1-2 and 1-3), only the position of the edges having been measured for the other 26 bands in the work [1235]. These results enabled the authors of the work [1235] to calculate the rotational constants of PN in the states $X^1\Sigma$ and $A^1\Pi$ and to determine the zero lines of the bands with unresolved rotational structure.*

The results of the investigations on the band system $A^1\Pi - X^1\Sigma$ of the molecule PN, obtained by Curray, L. Herzberg and G. Herzberg were confirmed in the works [1706, 2964] in which this band system had been obtained with considerably less resolution than in the work [1235]. Ghosh and Datta [1706] measured the edges of 23 bands in the system $A^1\Pi - X^1\Sigma$ of the PN molecule in emission and carried out an analysis of its vibrational structure. Moureu, Rosen and Wetroff [2964] investigated the absorption spectrum of phosphorus paranitride (P_nN_n, solid) vapor in the wavelength region 2000-8000 A, in which they found the bands 0-0, 0-1, 1-0 and 2-1 of the system $A^1\Pi - X^1\Sigma$ of the PN molecule. The correctness of the assumptions made by the authors of the works [1235, 1706] concerning the fact that the state $X^1\Sigma$ is the electronic ground state of the PN molecule, has been proved in the work [2964].

The values of the molecular constants, found by Curry, L. Herzberg and G. Herzberg [1235], which are presented in Table 117, have been adopted in the present Handbook for the states $X^1\Sigma$ and $A^1\Pi$ of the PN molecule. Identical values for the molecular constants were

recommended in the monographs of Herzberg [2020] and in the Handbook [649].

$\underline{P_4}$. The P_x molecule has the structure of a regular tetrahedron, in the corners of which the four phosphorus atoms are situated (point symmetry group T_d). The structure of the molecule P_4 has been determined as a result of the analysis of the spectra of phosphorus (white phosphorus [1903], a solution of white phosphorus in CS_2 [1903, 764], liquid phosphorus [4078] and its vapor [1903]) and electrondiffraction investigation [2817].

The molecule P_4 has three basic frequencies ν_1, ν_2, ν_3 of the symmetry types A, E and F_2. All three frequencies(ν_1 is polarized, ν_2 and ν_3 are depolarized) are active in the Raman spectrum. In the infrared spectrum only the ν_3 frequency is active.

The Raman spectrum of liquid phosphorus has been investigated by Venkateswaran [4078] who determined the values of all three fundamental frequencies of the P_4 molecule, presented in Table 118. The Raman spectrum of phosphorus vapor has not been studied.

The infrared spectrum of phosphorus vapor was obtained by Gutowsky and Hoffman [1903] on the prism spectrometer in the region 400–1200 cm^{-1}, in which they observed five absorption bands with maxima at 464.5, 910, 1075, 1150 and 1173 cm^{-1}, identified by them as the following fundamental frequencies of the P_4 molecule: ν_3, $2\nu_3$, $\nu_1 + \nu_3$, and $2\nu_2 + \nu_3$.* The infrared spectrum of white phosphorus and of solutions of white phosphorus in CS_2 were investigated in the works [1903, 764]. The results of these studies confirmed the values of the fundamental frequencies of the P_4 molecule, determined in the work [4078] and adopted in the present Handbook. Pistorius [3250b] calculated the approximate values of $\omega_1 + 2x_{11} + x_{12} = 604$ cm^{-1}, $\omega_2 + 1/2x_{12} = 381$ cm^{-1} and $\omega_3 = 506$ cm^{-1}, on the basis of data in the

works [4078] and [1903] on the fundamental frequencies, overtones and composite frequencies of the P_4 molecule.

The basic structural parameter of the tetrahedral P_4 molecule is the length of the P-P bond. An electron diffraction study on phosphorus vapor, carried out by Maxwell, Hendricks and Mosley [2817], led to the value $r_{P-P} = 2.21 \pm 0.02$ A, which has subsequently not been improved. It has been used in the calculation of the products of the principal inertia moments of the P_4 molecule, quoted in Table 118.

TABLE 118

Adopted Values of the Molecular Constants of P_4, P_4O_6, P_4O_8 and P_4O_{10}

Постоянная A	P_4	P_4O_6	P_4O_8	P_4O_{10}
ν_1, $см^{-1}$	606(1)	613(1)	—	424(1)
ν_2, $см^{-1}$	363(2)	613(1)	—	721(1)
ν_3, $см^{-1}$	465(3)	465(2)	—	1417(1)
ν_4, $см^{-1}$	—	1029(2)	—	278(2)
ν_5, $см^{-1}$	—	370(3)	—	650(2)
ν_6, $см^{-1}$	—	568(3)	—	952(2)
ν_7, $см^{-1}$	—	302(3)	—	300(3)
ν_8, $см^{-1}$	—	407(3)	—	450(3)
ν_9, $см^{-1}$	—	643(3)	—	600(3)
ν_{10}, $см^{-1}$	—	919(3)	—	257(3)
ν_{11}, $см^{-1}$	—	—	—	329(3)
ν_{12}, $см^{-1}$	—	—	—	559(3)
ν_{13}, $см^{-1}$	—	—	—	764(3)
ν_{14}, $см^{-1}$	—	—	—	1033(3)
ν_{15}, $см^{-1}$	—	—	—	1386(3)
$I_A I_B I_C$, 10^{-117} $г^3 \cdot см^6$	15 803	478 500	$1.23 \cdot 10^6$	$3.00 \cdot 10^6$
σ B	12	12	2	12

A) Constant; B) $g^3 \cdot cm^6$.

P_4O_6. X-ray, electron diffraction and spectroscopic investigations have shown that phosphorus trioxide in all states of aggregation consists of P_4O_6 molecules belonging to the point symmetry group T_d. The molecule P_4O_6 has 10 basic frequencies: the frequencies ν_1 and ν_2 of the fully symmetrical vibrations of type A_1, the frequencies ν_3 and ν_4 of the doubly degenerate vibrations of type E, the frequencies ν_5 and ν_6 of the triply degenerate vibrations of type F_1 and the

frequencies ν_7, ν_8, ν_9 and ν_{10} of the triply degenerate vibrations of type F_2. All the fundamental frequencies of P_4O_6, with the exception of ν_5 and ν_6 are active in the Raman spectrum, while only the frequencies ν_7, ν_8, ν_9 and ν_{10} are active in theinfrared spectrum.

The Raman spectra of liquid and solid phosphorus trioxide have been studied by Gerding, Brederode and Decker [1682]. In the Raman spectrum of liquid phosphorus trioxide they observed eight lines which, in correspondence with the measurement results on their intensity and polarizability, were identified with the nine basic frequencies of the P_4O_6 molecule. The most intense and practically fully polarized line at 613 cm^{-1} in the work [1682] is identical with the frequencies ν_1 and ν_2, whose values are believed to le very similar. The weakest line at 370 cm^{-1} is identical with the frequency ν_5. The observation of this line in the Raman spectrum was possible because of the presence of fairly strong molecular interactions in liquid phosphorus trioxide. The other six lines in the Raman spectrum of liquid phosphorus trioxide were identified by Gerding, Brederode and Decker with the frequencies ν_3, ν_4, ν_7, ν_8, ν_9 and ν_{10} of the P_4O_6 molecule. Comparison of the basic frequencies of the molecules P_4O_6 and SF_6 led the authors of the work [1682] to the conclusion that the values of the frequencies ν_5 and ν_6 of the molecule P_4O_6 are closely similar to the values of the fundamental frequencies of the same type of the SF_6 molecule, equal to 363 and 525 cm^{-1}.

The infrared spectrum of liquid phosphorus trioxide has been studied by Sidorov and Sobolev [373] in the region of 430 to 4000 cm^{-1} by means of a prism spectrometer. 11 weak bands were recorded in the work [373]. Two of these were identified with the fundamental frequencies ν_7 and ν_8 of the P_4O_6 molecule and the other bands with the composite frequencies and the overtones of P_4O_6. Quite unconvincing is

the identification of the very weak band at 568 cm^{-1} with the frequency $2\nu_{10}$ in the interpretation of the infrared spectrum of phosphorus trioxide proposed in the work [373]. Most satisfactory is the identification of this band with the frequency ν_6, which can be observed in the infrared spectrum of liquid phosphorus trioxide by virtue of the strong molecular interactions. This identification agrees with the fact pointed out by Gerding, Brederode and Decker [1682] that the frequency ν_6 should have a value close to 525 cm^{-1} and allows of a more satisfactory identification of the bands in the infrared spectrum of P_4O_6 with centers at 1188 and 1471 cm^{-1} with the frequencies $\nu_6 + \nu_9$ and $\nu_6 + \nu_{10}$.*

The vibrational spectra of phosphorus trioxide vapor have not been studied.

The values of the fundamental frequencies of the P_4O_6 molecule adopted in the present Handbook are presented in Table 118. For the frequency ν_6 the above indicated value, based on the data of the work [373] for theinfrared spectrum of liquid phosphorus trioxide have been used. For the other fundamental frequencies of the P_4O_6 molecule, the values determined in the work [1682] as a result of an investigation of the Raman spectrum of liquid phosphorus trioxide, were used.

The phosphorus atoms in the P_4O_6 molecule are arranged at the corners of a regular tetrahedron and are bound to each other not directly but via oxygen atoms which are arranged symmetrically in the interspace between two neighboring phosphorus atoms (see Appendix 3, Fig. 55). Maxwell, Hendricks and Deming [2816] and Hampson and Stosick [1944] investigated the structure of the molecule P_4O_6 on the basis of electron diffraction measurements. The most reliable results were obtained by Hampson and Stosick, according to whom the basic struc-

tural parameters of the P_4O_6 molecule have the following values: $r_{P-O} = 1.65 \pm 0.02$, $r_{P=P} = 2.95 \pm 0.03$ A, $\angle P - O - P = 127.5 \pm 3°$, $\angle O - P - O = 99 \pm 3°$.

The value adopted in Table 118 for theproduct of the principal inertia moments of P_4O_6 were calculated on the basis of the above presented values of the structural parameters for this molecule.

P_4O_8. The composition of the molecule of phosphorus dioxide has been determined on the basis of measurements of the vapor density of PO_2, obtained by West [4211] and Emmet and Schultz [1481]. The data of West have been interpreted in the works [4365, 917] as attesting to the existence of a P_8O_{16} molecule while the data of Emmet and Schultz are interpreted by these researchers and in the works [4365, 3717] as indicating the existence of the P_4O_8 molecule. The composition of phosporus dioxide vapor is evidently complex and can vary, depending on investigation conditions, within wide limits.

In the works [3717, 917] and in the present Handbook, the gaseous phosphorus dioxide is regarded as a product of the thermal decomposition of gaseous phosphorus pentoxide intermediate between P_4O_{10} and P_4O_6. In correspondence with this it is assumed that gaseous phosphorus dioxide consists of P_4O_8 molecules, formed by combination of two oxygen atoms with the tetrahedral skeleton P_4O_6 (see Appendix 3, Fig. 56). At the same time, as in the case of the molecule P_4O_{10}, the P – O bonds, entering into the composition of the P_4O_6 structure, are regarded as ordinary and these formed by the combination of oxygen atoms with P_4O_6, as double bonds. Such a molecule should belong to the point symmetry group C_2.

The spectra of phosphorus dioxide have not been studied. The P_4O_8 molecule has 30 vibrational degrees of freedom. The frequencies corresponding to these have not been estimated because the vibrational

components of the thermodynamic functions of gaseous P_4O_8 can be more satisfactorily accounted for on the basis of the vibrational components of the thermodynamic functions of P_4O_{10} and P_4O_6 (see Page 828).

The product of the principal moments of inertia of the P_4O_8 molecule, presented in Table 118, were calculated by means of the formulae (P3.59) on the basis of the above-indicated model and the values of the structural parameters, adopted in the present Handbook for the P_4O_{10} molecule.

P_4O_{10}. By means of x-ray, electron diffraction and spectroscopic studies it has been established that the molecule P_4O_{10} belongs to the point symmetry group T_d. This molecule has 15 fundamental frequencies: the frequencies ν_1, ν_2, ν_3 of fully symmetrical vibrations of type A_1, the frequencies ν_4, ν_5, ν_6 of the doubly degenerate vibrations of type E, the frequencies ν_7, ν_8, ν_9 of the triply degenerate vibrations of type F_1 and the frequencies ν_{10}, ν_{11}, ν_{12}, ν_{13}, ν_{14}, ν_{15} of the triply degenerate vibrations of type F_2. All the fundamental frequencies of the P_4O_{10} molecule, with the exception of ν_7, ν_8 and ν_9, are active in the Raman spectrum. In the infrared spectrum, only the frequencies ν_{10}, ν_{11}, ν_{12}, ν_{13}, ν_{14}, ν_{15} of the fundamental frequencies of the P_4O_{10} molecule are active. The values of the fundamental frequencies of phosphorus pentoxide are known on the basis of the results of studies of the Raman spectrum [1683] and the infrared spectrum [1238, 374] of its low-temperature crystalline modification, which is built up of P_4O_{10} molecules. The vibrational spectra of phosphorus pentoxide vapor have not been studied.

Gerding and Decker [1683] detected in the Raman spectrum of the low-temperature modification of solid phosphorus pentoxide 12 intense lines which they identified with the fundamental frequencies of the P_4O_{10} molecule, corresponding to vibrations of the types A_1, E and F_2.

Daasch and Smith [1238] obtained the infrared spectrum of phosphorus pentoxide in the region 514–2500 cm^{-1} but left it without interpretation. Sidorov and Sobolev [374] investigated the infrared spectrum of phosphorus pentoxide in the region 416–4000 cm^{-1} and showed that the vibrational spectra of this compound agree in an optimum manner with the model of the P_4O_{10} molecule, belonging to the point symmetry group T_d.

The results of the studies on the infrared spectrum of phosphorus pentoxide, obtained by Sidorov and Sobolev, are in statisfactory agreement with the results of the investigations on the Raman spectrum [1683] and also with the data presented in the work [1238] for the infrared spectrum.

The values of the fundamental frequencies of the P_4O_{10} molecule of the types A_1, E and F_2 found as a result of the spectroscopic investigations [1683, 374] are presented in Table 118.

The frequencies ν_7, ν_8 and ν_9 of the P_4O_{10} molecule, corresponding to the vibrations of the type F_1, can be approximately estimated by comparison of the corresponding frequencies of the molecules P_4O_6 and P_4O_{10}. If the values of the fundamental vibration frequencies of the type A_1, E and F_2 of the molecules P_4O_6 and P_4O_{10}, based on the results of investigations of the vibratic spectra of phosphorus trioxide and pentoxide, presented in Table 118, are compared a·i the values of the frequencies of type F_1 of the P_4O_6 molecule ν_5 and ν_6 are taken into account, the fundamental frequencies ν_7, ν_8 and ν_9 can be estimated as 300, 450 and 600 cm^{-1}, respectively. These values have been adopted in the present Handbook, because the specific heat of phosphorus pentoxide vapor, calculated on the basis of the vibrational frequencies of the P_4O_{10} molecule ($C_{p\,1000}$ = 73.5 cal/mole degree), given in Table 118, coincides with the mean specific heat of

phosphorus pentoxide vapor within the temperature range 650-1350°K (73.6 ± 2 cal/mole·degree) determined by Frandsen [1595] as a result of calorimetric measurements. The uncertainty in the values of the basic frequencies ν_7, ν_8, and ν_9 of the P_4O_{10} molecule adopted in the Handbook must be assumed to be no less than ± 50 cm^{-1}.

The geometrical structure of the P_4O_{10} molecule has been fairly accurately determined by electron diffraction studies [2817, 1944, 67]. Its basis is the P_4O_6 structure (analogous in structure to the molecule of phosphorus trioxide) to each of the four phosphorus atoms of which is joined an additional oxygen atom (see Appendix 3, Fig. 57). The P-O bonds, which form the structure of P_4O_6, are ordinary, while the P-O bonds, formed by combination of oxygen atoms with the P_4O_6 structure, can be characterized as double bonds.

The structural parameters of the molecule P_4O_{10}, determined by Hampson and Stosick [1944] as a result of electron diffraction studies on phosphorus pentoxide vapor, are equal to:

$$r_{P-O} = 1{,}62 \pm 0{,}02 \text{ Å}, \quad \angle O-P-O = 101{,}5 \pm 1°,$$
$$r_{P=O} = 1{,}39 \pm 0{,}02 \text{ Å}, \quad \angle O-P=O = 116{,}5 \pm 1°,$$
$$r_{P-P} = 2{,}84 \pm 0{,}03 \text{ Å}, \quad \angle P-O-P = 123{,}5 \pm 1°.$$

Similar values of the structural parameters of the P_4O_{10} molecule were obtained by Akishin, Rambidi and Zasorin [67] (r_{P-O} = 1.60 ± ± 0.01, $r_{P=O}$ = 1.40 ± 0.03 A, ∠P − O − P = 124.5 ± 1°).

The product of the principal moments of inertia of the P_4O_{10} molecule presented in Table 118, has been calculated on the basis of its structural parameters, found by Hampson and Stosick [1944].

$\underline{PF_2}$. The spectru and structure of the PF_2 molecule have not been studied experimentally. It is assumed in the present Handbook that the PF_2 molecule has a nonlinear symmetry and belongs to the point group symmetry C_2. The values of the structural parameters and fundamental

frequencies of the PF_2 molecule have been approximately estimated on the basis of the corresponding magnitudes for the PF_3 molecule.

For the structural parameters of the PF_2 molecule, the same values were adopted as for the PF_3 molecule (see page 807) under the assumption that the error of the adopted value of r_{P-F} is not less than ± 0.02 A and that of the angle between the P-F bonds not less than $\pm 10°$. On the basis of the adopted values of the structural parameters, the product of the principal moments of inertia of the PF_2 molecule, which is given in Table 119, has been calculated.

TABLE 119

Adopted Values of the Molecular Constants for PF_2, PF_3, PCl_3, POF_3 and $POCl_3$

Молекула 1	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	$I_A I_B I_C$	σ
	2 $см^{-1}$						10^{-117} $(г \cdot см^2)^3$ 3	
PF_2	802	443	866	—	—	—	276,2	2
PF_3	892	487	860(2)	344(2)	—	—	1898	3
PCl_3	507,4	260,1	485,5(2)	189,0(2)	—	—	60921	3
POF_3	1415	573	470	990(2)	485(2)	345(2)	5905,2	3
$POCl_3$	1289,9	486,24	267,39	581,2(2)	337,44(2)	192,85(2)	101810	3

1) Molecule; 2) cm^{-1}; 3) $(g \cdot cm^2)^3$.

According to the hypothesis concerning the structure of the PF_2 molecule which has been adopted in the Handbook, it should have three fundamental frequencies. The values of the latter have been calculated by means of the equations (P4.29) and the values of the force constants of the PF_3 molecule.* The values for the fundamental frequencies of the PF_2 molecule thus obtained are given in Table 119. The error of these values is estimated to be 10 - 15%.

Because there is one unpaired electron in the electron shell of the PF_2 molecule, it is assumed in the present Handbook that the electronic ground state of this molecule is a doublet.

$\underline{PF_3}$, $\underline{PCl_3}$. The molecules PF_3 and PCl_3 belong to the point group

symmetry C_3 and have a pyramidal structure with the phosphorus atom at the top (See Appendix 3, Fig. 38). Such molecules have four fundamental frequencies, which are active in the Raman spectrum and in the infrared spectrum. The following values have been adopted in the present Handbook for the frequencies of PF_3 and PCl_3: ν_1, the frequency of the fully symmetrical valency vibration of type A_1, ν_2, the frequency of the fully deformation vibration of type A_1, ν_3, the frequency of the doubly degenerate antisymmetrical valency vibration of type E, and ν_4, the frequency of the degenerate deformation vibration of type E.

The Raman spectra of liquid and gaseous phosphorus trifluoride were obtained by Yost and Anderson [4359], the infrared spectrum of gaseous PF_3 by Gutowsky and Liehr [1904] and Wilson and Polo [4297]. Wilson and Polo investigated the infrared spectrum of PF_3 in the region from 250 to 1850 cm^{-1} and showed that the assignment of the frequencies, adopted in the works [4359, 1904] is erroneous. The values of the fundamental frequencies of PF_3, found by Wilson and Polo [4297] were adopted in the present Handbook and are presented in Table 119.

Electron diffraction studies on the geometrical structure of the PF_3 molecule were carried out by Brockway and coworkers [965, 3203, 954] who obtained the following results: $r_{P-F} = 1.52 \pm 0.04$, A, $\angle F - P - F = 104 \pm 4°$.

The microwave spectrum of PF_3 has been investigated in the works of Gordy and his coworkers [1820, 1821, 1749]. The data obtained in these works enabled Gilliam, Edwards and Gordy [1749] to determine the values of the rotational constant $B_0 = 7819.900$ Mcps = 0.260843 cm^{-1}. This result has been used in the works [1749, 4283] for calculating the length of the P-F bond in the molecule PF_3. In the work [1749]

$\angle F - P - F = 104 \pm 3°$ was taken on the basis of the electron diffraction data of Brockway [954] and r_{P-F} was calculated as 1.546 ± 0.008 A. A comparison was carried out in the work [4283] between the structural parameters of the molecules FOF_3, PSF_3, $POCl_3$, $PSCl_3$, PF_3, PCl_3, and NF_3, determined as a result of an analysis of the microwave spectra and electron diffraction investigations and it was found that the angle between the P-F bonds in the molecule PF_3 should be close to 100°. Thus adopting $\angle F - P - F = 100°$, the authors of the work [4283] calculated $r_{P-F} = 1.535$ A. The authors of the work [4283] believe that $\angle F - P - F$ in the molecule PF_3 cannot be greater than $\angle F - N - F$ in the molecule NF_3, equal to 102°9', according to [3703]. Hence the uncertainty of the value of $\angle F - P - F$ proposed in the work [4283] can be estimated to be $\pm 2°$ and the value of r_{P-F} as ± 0.005 A.

On the basis of the data, presented in the work [4283] the following values of the structural parameters of the molecule PF_3 have been adopted in the present Handbook: $r_{P-F} = 1.535 \pm 0.005$ A, $\angle F - P - F = 100 \pm 2°$, which were used in the calculation of the product of the principal moments of inertia of PF_3, which is given in Table 119.

The fundamental frequencies of the molecule PCl_3 were determined on the basis of the Raman spectra of liquid and gaseous phosphorus trichloride [806, 807, 4080, 1041, 1757, 3093, 906] and on the basis of studies of the infrared spectrum of gaseous phosphorus trichloride [3132, 1275, 2657]. The values of the fundamental frequencies of the PCl_3 molecule found in these works agree with each other within the limits of 10 cm^{-1}. The most accurate values of these magnitudes were determined by Davis and Oetjen [1275] on the basis of the results of investigations carried out on the infrared spectrum of gaseous phosphorus trichloride. The values of the fundamental vibration frequencies of the PCl_3 molecule obtained in the work [1275]

were adopted in the present Handbook and are given in Table 119. The error of the values of the fundamental frequencies of PCl_3 found in the work [1275] are estimated as ± 0.2 to ± 0.5 cm^{-1}.

The infrared spectrum of gaseous phosphorus trichloride has been investigated by Davis and Oetjen [1275] in the range 85–550 cm^{-1}, and on apparatuses with smaller dispersion by Lorenzelli and Moller [2657] in the range 222–500 cm^{-1} and by O'Loane [3132] in the range 190 cm^{-1} (ν_4). The most detailed investigation of the Raman spectra of liquid and gaseous phosphorus trichloride has been carried out by Nielsen and Ward [3093].

The structural parameters of the PCl_3 molecule were determined in electron diffraction studies of the molecular structure of phosphorus trichloride by Wierl [4263, 4264] and Brockway [965, 954] and also in investigations of the microwave spectra of the isotopic PCl_3 molecules, $PCl_2{}^{35}$, $PCl_2{}^{35}Cl^{37}$ and $PCl_3{}^{37}$ by Kisliuk and Townes [2411, 2412]. The results obtained in all these investigations agree with each other. The most accurate values of the structural parameters of PCl_3 were calculated by Kisliuk and Townes on the basis of the values of the rotational constant B_0 of the $PCl_3{}^{35}$ molecule found by them (2617.1 Mcps = 0.087297 cm^{-1}) and of $PCl_3{}^{37}$ (2487.5 Mcps = 0.082974 cm^{-1}). On the basis of the data, obtained in the works [2411, 2412] the following values of the structural parameters of the PCl_3 molecule have been adopted in the present Handbook: $r_{P-Cl} = 2.043 \pm 0.04$ A, $\angle Cl - P - Cl = 100°6' \pm 30'$. The adopted values of the structural parameters were used for the calculation of the product of the principal moments of inertia of the molecule PCl_3, whose value is given in Table 119.

$\underline{POF_3}$, $\underline{POCl_3}$. The molecules POF_3 and $POCl_3$ have a pyramidal structure (see Appendix 3, Fig. 41) and belong to the point group ym-

metry C_{3v}. They have six fundamental frequencies: the frequencies ν_1, ν_2, ν_3 of the fully symmetrical vibrations of type A_1, and the frequencies ν_4, ν_5, ν_6 of the doubly degenerate vibrations of type E, which are active in the Raman spectra as well as in the infrared spectra.*

The vibrational spectra of the POF_3 molecule have been investigated by Delwaulle and Francois [1306] (Raman spectrum of liquid POF_3) and Gutowsky and Liehr [1904] (infrared spectra of gaseous POF_3). The frequency ν_3 of the fundamental frequencies of the POF_3 molecule has not been observed in the Raman spectrum [1306] and the frequency ν_6 could not be detected in the infrared spectrum [1904].

The infrared spectrum of gaseous POF_3 has been obtained by Gutowsky and Liehr [1904] in the range of 470-2820 cm^{-1} and has been interpreted on the basis of the utilization of the results obtained in studies of the Raman spectrum [1306], an analysis of the band contours and the results of calculations. The frequency of the doubly degenerate composite vibration ν_6 was taken as being equal to 345 cm^{-1}, because the overtone $2\nu_6 = 690$ cm^{-1} has been observed in the infrared spectrum of POF_3 [1904]. The frequency ν_6 was observed in the Raman spectrum of liquid POF_3 [1306], where it was found to be equal to 337 cm^{-1}. The values of the fundamental frequencies ν_4 and ν_5, determined on the basis of the infrared spectrum of gaseous POF_3 [1904] is approximately 8 cm^{-1} higher than that found on the basis of the Raman spectrum of liquid POF_3 [1306]. It is natural to assume that the same difference should also exist for the frequency ν_6. This assumption leads to the value 345 cm^{-1}, found by Gutowsky and Liehr on the basis of the overtone $2\nu_6$.

The values obtained in the work [1904] which are given in Table 119 have been adopted in the present Handbook for the fundamental fre-

quencies of the POF_3 molecule. The error of these values can be estimated as ± 3 cm^{-1}.

The microwave spectra of the isotope species of the molecule POF_3 have been studied in the works [3682, 1821, 4283, 1978, 1033] and the values of the constants B_0, D_J and D_{JK} of the molecules $PO^{16}F_3$ and $PO^{18}F_3$ were determined with great accuracy. The most accurate values of these constants fot the molecule $PO^{16}F_3$ were obtained by Burrus and Gordy [1033]: B_0 = 4594.262 Mcps (0.1532478 cm^{-1}), D_J = = 1.020 kcps ($3.402 \cdot 10^{-7}$ cm^{-1}), D_{JK} = 1.284 kcps ($4.283 \cdot 10^{-7}$ cm^{-1}).

The structural parameters of the POF_3 molecule were determined first by Brockway and Beach [958] on the basis of analysis of electron diffraction data: $r_{P-O} = 1.56 \pm 0.03$, $r_{P-F} = 1.52 \pm 0.02$ A, $\angle F - P - F = 107 \pm 2°$, which were later determined with greater accuracy in studies of the microwave spectra of isotopic species of POF_3 in the works [4283, 1978]. It was found in these works that the values of the structural parameters of POF_3, obtained by Brockway and Beach, are inconsistent with the values of the constant B_0 of the molecules $PO^{16}F_3$ and $PO^{18}F_3$, determined with great accuracy on the basis of the microwave spectrum. Williams, Sheridan and Gordy [4283] found that the following values of the structural parameters of POF_3 give the best agreement with the microwave data: $r_{P-O} = 1.45 \pm 0.03$, $r_{P-F} = 1.52 \pm 0.02$ A, $\angle F - P - F = 102.5 \pm 2°.0$. It was also found in the work [4283] that these values of the structural parameters of POF_3 agree much better with the results of the electron diffraction study, carried out by Brockway and Beach, than the values, proposed in the work [958]. The values of the structural parameters of the molecule POF_3 recommended by Williams, Sheridan and Gordy [4283] were adopted in the present Handbook. In particular, they were used in the calculation of the product of the principal moments of inertia of POF_3,

...ion is given in Table 119.

The values of the basic frequencies of the $POCl_3$ molecule were determined on the basis of studies of the Raman spectrum of liquid phosphorus oxytrichloride [4080, 2560, 1040, 3733]. Later on, six lines were detected, three of which are polarized and three depolarized, which served as a basis for assigning them to the frequencies ν_1, ν_2, ν_3 and ν_4, ν_5, ν_6, respectively. Langseth [2560] obtained the Raman spectrum of liquid phosphorus oxytrichloride with the highest dispersion. The Handbook values of the basic frequencies of the $POCl_3$ molecule given in Table 119, correspond to maxima of the bands in the Raman spectrum of the liquid, measured by Langseth [2560]. On the basis of investigations on the vibrational spectra of liquid and gaseous POF_3 in the works [1306, 1904], the values of the basic frequencies of the $POCl_3$ molecule given in Table 119 must be considered to be 5 cm^{-1} too low.

The infrared spectrum of liquid phosphorus oxytrichloride has been obtained by Daasch and Smith [1238] in the region 475-5000 cm^{-1}, but has not been analyzed. The photometric curve, presented in the work [1238] shows five sharp absorption maxima, related by the authors to the frequencies ν_2, ν_4, $\nu_2 + \nu_3$, ν_1 and $\nu_1 + \nu_2$.

The assignment of the fundamental frequencies of the $POCl_3$ molecule adopted in the present Handbook has also been used by Zionek, Piotrowski and Walsh [4389a] on the basis of the calculations of the basic frequencies and force constants of the molecules $POCl_3$, POF_3, $PSCl_3$ and PSF_3 carried out by them (see also [4389b]). The correctness of this assignment has been disputed by Ott and Giauque [3152a] in connection with the fact that the value of $S°_{298.15}(POCl_3, gas)$ determined by them on the basis of the results of calorimetric measurements differed by 0.37 cal/mole·degree from the value calculated on

the basis of the molecular constants of $POCl_3$ which is identical with that adopted in the Handbook. The authors of the work [3152a] found that if the assignments of the frequencies ν_3 and ν_5 change places, this difference will be of the order of error of the value of $S°_{298.15}$ ($POCl_3$, gas) based on the data of the calorimetric measurements. However, they did not determined the magnitude of error in the value of $S°_{298.15}$($POCl_3$, gas), calculated from the molecular constants of $POCl_3$. This was due mainly to the inaccuracy of the known values of the molecular constants of $POCl_3$ and amounts to approximately ± 1 cal/mole·degree. Hence the modification in the assignment of the basic frequencies of the molecule $POCl_3$, proposed by Ott and Giauque is untenable.

The structural parameters of the molecule $POCl_3$ were first determined by Brockway and Beach [958] on the basis of the results of electron diffraction investigations ($r_{P-O} = 1.58$, $r_{P-Cl} = 2.02$A, $\angle Cl - P - Cl = 106°$). Later on, Williams, Sheridan and Gordy [4283] determined, as a result of investigations of the microwave spectra of $POCl_3^{35}$ and $POCl_3^{37}$ with great accuracy the values of the constant B_0 of these molecules, which do not agree with the above-presented values of the structural parameters of $POCl_3$. The values of the constant B_0 of the molecules $POCl_3^{35}$ and $POCl_3^{37}$, found in the work [4283] satisfy the following values of the structural parameters best: $r_{P-O} = 1.45 \pm 0.03$, $r_{P-Cl} = 1.99 \pm 0.02$A, $\angle Cl - P - Cl = 103.6 \pm 2.0°$. In order to eliminate this contradiction in the values of the structural parameters of $POCl_3$, obtained in the works [958, 4283], Badgley and Livingston [605] again carried out an electron diffraction study of the structure of $POCl_3$, using a better method than in the work [958]. The values of the structural parameters of $POCl_3$ obtained by Badley and Livingston ($r_{P-O} = 1.45 \pm 0.05$, $r_{P-Cl} = 1.995 \pm 0.02$ A, $\angle Cl - P - Cl = 103.5 \pm 1°$) practically coincide with the values found

by Williams, Sheridan and Gordy [4283].

The values of the structural parameters of the $POCl_3$ molecule, obtained in the work [4283] and subjected to electron diffraction investigation [605] were adopted in the present Handbook. These values were used in the calculation of the product of the principal moments of inertia of $POCl_3$, whose value is given in Table 119.

PF_5; PCl_5. The molecules PF_5 and PCl_5 belong to the point group symmetry D_{3h} and have the structure of a regular three-cornered bipyramid with the phosphorus atoms in the symmetry center (see Appendix 3, Fig. 46). The vibrations of these molecules are determined by eight fundamental frequencies: the frequencies ν_1, ν_2 of the valency vibrations of type A_1' (fully symmetrical and antisymmetrical) the frequencies ν_3, ν_4 of the deformation vibrations of type A_2'' (fully symmetrical and antisymmetrical) and four frequencies of the doubly degenerate vibrations of type E' (frequencies ν_5, ν_6, ν_7) and of type E" (frequency ν_8). In the infrared spectra of PF_5 and PCl_5 are active the frequencies ν_3, ν_4, ν_5, ν_6, ν_7* and inactive the frequencies ν_1, ν_2, ν_8. In the Raman spectra are active all the fundamental frequencies, with the exception of ν_3, ν_4, the lines, corresponding to the frequencies ν_1 and ν_2 being polarized and those corresponding to the frequencies ν_5, ν_6, ν_7, ν_8 being depolarized.

The infrared spectrum of gaseous PF_5 has been investigated by Gutowsky and Liehr [1904] and Pemsler and Plante [3215].** The Raman spectrum of phosphorus pentafluoride was not studied.

Gutowsky and Liehr [1904] obtained the spectrum of PF_5 on a prism spectrometer with low dispersion in the region from 500 to 1800 cm^{-1} where they detected four strong absorption bands with centers at 534, 576, 948 and 1025 cm^{-1}, which they assigned to the frequencies ν_6, ν_4, ν_3 and ν_5. Pemsler and Planet [3215] obtained the PF_5 spectrum on a

prism spectrometer with medium dispersion in the region from 480 to 2050 cm^{-1}. These authors determined the positions of several additional weak absorption bands, which had not been recorded by Gutowsky and Liehr. The centers of the strong absorption bands were measured by Pemsler and Planet [3215] in agreement with the meausrements of Gutowsky and Liehr [1904]. The infrared spectrum of PF_5 has not been interpreted by Pemsler and Planet.

On the basis of the equations (P4.43) for the oscillation frequencies of the bipyramidal molecules XY_5, the values of the fundamental oscillation frequencies ν_3, ν_4, ν_5 and ν_6 of the molecule PF_5, found by Gutowsky and Liehr [1904], and the data on the fundamental frequencies of the molecules PCl_5, AsF_5, $AsCl_5$ etc., calculations were carried out in the work [416b] of the values of the fundamental frequencies of the PF_5 molecule under different assumptions with respect to the values of the force constants. Of a number of variants of the values of the fundamental frequencies of PF_5 thus obtained, one variant was selected in which the calculated values of the frequencies ν_3, ν_4, ν_5 and ν_6 were closest to the experimental values. The frequency values corresponding to this variant for ν_1, ν_2, ν_7 and ν_8 were adopted in the present Handbook and are given in Table 120. For the frequencies ν_3, ν_4, ν_5 and ν_6, values are given in Table 120, found by Gutowsky and Liehr [1904] on the basis of the infrared spectrum of PF_5. The uncertainty in the values of the frequencies ν_3, ν_4, ν_5 and ν_6 given in Table 120 for PF_5 is estimated to be ± 3 cm^{-1}, for the frequencies ν_1, ν_2 and ν_8 it is ± 50 cm^{-1} and for the frequency it is ν_7, $\pm$ 25 cm^{-1}.

The structure of the molecule PF_5 was determined by Braune and Pinnow [910] and Brockway and Beach [958] on the basis of electron diffraction studies carried out by them on gaseous phosphorus penta-

fluoride. In theworks [910, 958] it was found that the PF_5 molecule has the structure of a three-cornered bipyramid with the phosphorus atom in the symmetry center and at equal distances from it five fluorine atoms, situated in the corners of the bipyramid. The length of the P – F bond in the PF_5 molecule was determined by Braune and Pinnow as being 1.54 ± 0.02 A, while Brockway and Beach determined this bond length as 1.57 ± 0.02 A.

TABLE 120

Adopted Values of the Molecular Constants of PF_5 and PCl_5

Molecule[1]	ν_1	ν_2	ν_3	ν_4	ν_5 (2)	ν_6 (2)	ν_7 (2)	ν_8 (2)	$I_A I_B I_C$	σ
	2 cm^{-1}								[3] $(g \cdot cm^2)^3$	
PF_5	835[a]	508[a]	948	576	1025	534	412[a]	559[a]	17 258	6
PCl_5	394	394	465	176[a]	502	335	100	280	638 600	6

a) Estimate; 1) molecule; 2) cm^{-1}; 3) $(g \cdot cm^2)^3$.

The conclusion made by the authors of the works [910, 958] that all the P – F bond lengths in the molecule PF_5 are the same, is evidently not quite correct, because other indices (the force constants and bond energies) readily show the non-equivalence of the axial and radial P – F bonds in the PF_5 molecule. It is also known that the lengths of the axial and radial X – Y bonds in other bipyramidal molecules of the type XY_5 differ considerably from each other. These circumstances suggest that the length of the axial P – F bond in the PF_5 molecule is slightly greater than the length of the radial bond, in analogy to the case of the PCl_5 molecule (see further on). It is not possible, however, to carry out a satisfactory estimate of this magnitude. The value of $r_{P-F}(PF_5)$, found by Braune and Pinnow [910] evidently corresponds to the length of the radial P – F bond in the PF_5 molecule.* The value of $r_{P-F}(PF_5)$ found by Brockway and Beach [958] is some average value of the bond length P – F in the molecule

PF_5. Hence, the model of the PF_5 molecule with equal P – F bonds, whose length is $r_{P-F} = 1.57 \pm 0.04$ A, proposed in the works [910, 958] has been adopted in the present Handbook. On the basis of these conceptions, the product of the principal inertia moments of the PF_5 molecule, whose value is given in Table 120, has been calculated by means of the formulae (P3.44).

The Raman spectra of phosphorus pentachloride were investigated by Krishnamurti [2486] and Moureu, Magat and Wetroff [2961-2963]. The Raman spectra of liquid, solid and gaseous PCl_5 and also solutions of PCl_5 in CCl_4 and PCl_3 were studied in the works [2961-2963]. The authors of these works observed in the Raman spectrum of liquid PCl_5 six frequencies (100, 190, 271, 392, 449, 495 cm^{-1}), which they took as the fundamental frequencies of the PCl_5 molecule in their early attempts at interpretation of the vibrational spectra of phosphorus pentachloride [3864, 3719]. Moureau, Magat and Wetroff [2961-2963] observed only three diffuse lines, corresponding to frequencies of 90, 226 and 400 cm^{-1}, in the Raman spectrum of gaseous PCl_5.

In 1957, Wilmshurst and Bernstein [4284] obtained the infrared spectra of gaseous PCl_5 in the region 333-1250 cm^{-1} and of a solution of PCl_5 in CS_2 in the region 416-2000 cm^{-1} and also the Raman spectrum of a saturated solution of PCl_5 in gasoline. The results of the analysis of these spectra and the data on the vibrational spectra of PCl_5, obtained earlier in the works [2691-2693], made it possible to determine with much greater reliability as in the works of Stevenson and Yost [3684] and Siebert [3719] and the values of the fundamental frequencies of the PCl_5 molecule. The values of these magnitudes recommended by Wilmshurst and Bernstein [4284] are given in Table 120. The frequencies ν_1, ν_2, ν_7 and ν_8 were determined on the basis of the Raman spectrum of PCl_5 in gasoline and frequencies ν_3, ν_5, ν_6 on the

basis of the infrared spectrum of gaseous PCl_5. The frequency ν_4 is beyond the limits of the infrared spectrum of PCl_5 investigated in the work [4284]. The calculations of the force constants of the molecule PCl_5 presented by Wilmshurst and Bernstein enabled them to compute the value $\nu_4 = 176\ cm^{-1}$, which has been confirmed by the interpretation of the composite frequencies and overtones in the vibrational spectra.

It was found in electron diffraction studies on the molecular structure of PCl_5, carried out by Ronault [3536, 3537] and Siebert and Schomaker,* that the molecule PCl_5 has a regular bipyramidal structure in which the P – Cl bond lengths corresponding to three radial and two axial chlorine atoms, are unequal. It was found that the axial P – Cl bonds in the PCl_5 molecule are longer than the radial bonds by about 0.15 A. The most reliable values of these magnitudes, obtained by Ronault in the work [3537] are r_{P-Cl} (axial) = 2.19 ± ± 0.08, r_{P-Cl} (radial) = 2.04 ± 0.06 A, were adopted in the present Handbook and used in the computation of the products of the principal inertia moments of PCl_5 (see Table 120) by the formulae (P3.45).

The non-equivalence of the axial and radial P – Cl bonds in the PCl_5 molecule is also confirmed by the values of the force constants, found by Wilmshurst and Bernstein [4284] and the investigation of the reactivity of different chlorine atoms in the PCl_5 molecule, carried out by Downs and Johnson [1400] on the basis of the method of radioactive tracers.

§55. THERMODYNAMIC FUNCTIONS OF GASES

The thermodynamic functions of gaseous P, P_2, PO, PH, PF, PCl, PS, PN, P_4, P_4O_6, P_4O_8, P_4O_{10}, PF_2, PF_3, PCl_3, PF_5, PCl_5, POF_3, $POCl_3$, calculated for the temperature range of 293.15-6000°K without taking into account the intermolecular interaction, are given in Tables 110-

-128 of volume II of the Handbook.

P. The thermodynamic functions of monatomic phosphorus, calculated on the basis of Eqs. (II.22) and (II.23), are presented in Table 110 (II). The values of the constants A_Φ and A_S in these equations were taken as equal to 2.9504 and 7.9185 cal/g-atom·degree, respectively. The electronic components were calculated by means of Eqs. (II.20) and (II.21) on the basis of the energy levels of the phosphorus atom given in Table 115.

The uncertainties of the values of Φ^*_T and S°_T, given in Table 110 (II) do not exceed 0.005 cal/g-atom·degree. They are due mainly to the inaccuracy of the values of the physical constants, adopted in the Handbook.

The thermodynamic functions of monatomic phosphorus have been calculated earlier by Stevenson and Yost [3864] (Φ^*_T up to 1500°K, $S^\circ_{298.16}$); Brewer [1093] (to 2000°K), Kelley [2363, 2364] ($S^\circ_T - S^\circ_{298.16}$ up to 1600°K, $S^\circ_{298.16}$), Katz and Margrave [2334] (Φ^*_T to 2000°K), Stull and Sinke [3984] (to 3000°K), Kolsky et al [2462] (Φ^*_T to 8000°K), Potter and Distefano [3314a] (Φ^*_T, S°_T, C°_P to 5000°K).

The calculations of the thermodynamic functions of P in the works [3864, 1093, 2363, 2364] were evidently carried out without taking into account the electronic component in consequence of its smallness at $T < 2000$°K. The results of these calculations, with the exception of the values of Φ^*_T in the work [3864], agree within the limits of 0.02 cal/g-atom·degree with the values of the corresponding values in Table 110 (II). The differences are due to differences in the adopted values of the physical constants and the atomic weight of phosphorus. The values of Φ^*_T, calculated by Stevenson and Yost [3864], are smaller than the corresponding values in Table 110 (II) by about 3.4 cal/g-atom·degree in consequence of errors in the calculations of these

authors. The erroneous results of the calculations of Stevenson and Yost are presented in the summaries of Zeise [4381, 4384] and Vvedenskiy [119a]. In the book of Zeise [4384] they are supplemented by the S°_T values, which contain an analogous error.

The values of the thermodynamic functions of P, given in the works [2334, 3894, 2462, 3314a] and in the first edition of t e present Handbook, agree with the values of the corresponding magnitudes in Table 110 (II) within the limits of the above-indicated uncertainty of the data in this Table. The slight differences are due to differences in the adopted values of the physical constants.

P_2. The thermodynamic functions of diatomic phosphorus, given in Table 111 (II) were calculated by means of Eqs. (II.161) and (II.162). The values of $\ln \Sigma$ and $T \frac{\partial}{\partial T} \ln \Sigma$ in these equations were calculated by the method of Gordon andBarnes [see Eqs. (II.137) and (II.138)] without taking into account the number of rotational levels, on the basis of the molecular constants, presented in Table 116. The two excited electronic states of the molecule P_2: $A^1\Pi_g$ and $B^1\Sigma^+_u$ were taken into account in the calculation of the thermodynamic functions of diatomic phosphorus. The components of these states were calculated by means of Eqs. (II.120) and (II.121), i.e., without taking into account the difference between the constants of P_2 in the excited and ground electronic states. Table 121 gives the values of θ and x, the coefficients in the equations (II.137), (II.138) and the constants C_Φ and C_S in the equations (II.161), (II.162).

The uncertainty in the values of Φ^*_T of diatomic phosphorus, given in Table 111 (II), do not exceed 0.01 cal/mole·degree over the entire temperature interval.

The thermpdynamic functions of diatomic phosphorus had been calculated previously by Godnev and Sverdin [159] to (2000°K), Stevenson

and Yost [3864] (Φ^*_T to 15000°K, $S°_{298.16}$), Kelly [2363, 2364], ($S°_T - S°_{298.16}$ to 2000°K, $S°_{289.16}$), Stull and Sinke [3894] (to 3000°K) and Potter and Distefano [3314a] (to 5000°K). Godnev and Sverdin [159] carried out the calculation by the method of Gordon and Barnes taking into account the nuclear spin. Stevenson and Yost [3864] used the method of direct summation and the molecular constants of P_2 from the work of Ashley [573]. The differences in the values of Φ^*_T, presented in the works [159],* [3864] and in Table 111 (II) amount to approximately 0.05 cal/mole·degree owing to the use of less accurate values of the molecular and physical constants in these works as compared with the present Handbook. Brewer [1093], Zeise [4381, 4384] and Vvedenskiy [119a] presented the values of the thermodynamic functions of P_2, calculated by Stevenson and Yost. Kelley [2363], on the basis of the specific heat of P_2 as a function of temperature, adopted by him, calculated the values $H°_T - H°_{298.16}$ and $S°_T - S°_{298.16}$ to 2000°K. The differences between the values of $S°_T$, calculated on the basis of the data of Kelley [2363, 2364] and those given in Table 111 (II) are 0.01 to 0.08 cal/mole·degree. The thermodynamic functions of P_2, as calculated by Stull and Sinke [3894] and Potter and Distefano [3314a], are very close to the values, given in Table 111 (II). The slight differences (which do not exceed 0.02 cal/mole·degree in the values of Φ^*_T) are mainly due to the differences in the adopted values of the molecular constants.

The values of the thermodynamic functions of P_2, given in the first and in the present edition of the Handbook, practically coincide. At high temperatures the differences are due to the fact that in the first edition the components of the electronic excitation have not been taken into account which leads to a difference of 0.004 and 0.01 cal/mole·degree in the values of Φ^*_{6000} and $S°_{6000}$, respectively.

TABLE 121

Values of the Constants for the Calculation of the Thermodynamic Functions of Gaseous P_2, PO, PH, PF, PCl, PS and PN

Вещество A	θ, град B	$x \cdot 10^2$	$\beta_1 \cdot 10^4$	$\beta_2 \cdot 10^4$	$\frac{q_0}{T}$	$\frac{d_0 \cdot 10^4}{T}$	C_Φ	C_S
					B град$^{-1}$		кал/моль·град C	
P_2	1122,64	3,59	0,5467	0,31	2,2763	2,8105	5,2732	12,2287
PO	1774,63	5,327	0,7530	0,58	0,95175	2,685	6,8483	13,8038
PH	3430	17,6	3,367	12,7	0,082624	8,45	0,2739	7,2294
PF	1194	—	—	—	—	—	6,9934	13,9489
PCl	777	—	—	—	—	—	9,4933	16,4488
PS	1064,0	4,06	—	—	2,3966	2,942	9,5606	16,5160
PN	1923,6	5,222	0,7110	0,51	0,88735	2,486	3,8262	10,7812

A) Substance; B) degree; C) cal/mole·degree.

PO. The thermodynamic functions of gaseous phosphorus monoxide, given in Table 113 (II), were calculated on the basis of Eqs. (II.161) and (II.162). The values $\ln\Sigma$ and $T\frac{\partial}{\partial T}\ln\Sigma$ in these equations were calculated by the method of Gordon and Barnes [see relations (II.137), (II.138)] without introducing corrections for the limited number of rotational states; the values $\ln\Delta_M$ and $T\frac{\partial}{\partial T}\ln\Delta_M$ were calculated by means of Eqs. (II.149) and (II.150). The calculations was carried out on the basis of the molecular constants of PO, given in Table 116. The components of the excited electronic states $A^2\Sigma$, $B^2\Sigma$, $C^2\Sigma$, $D^2\Sigma$ were calculated without taking into account the difference in the constants of PO in these states and the ground state $X^2\Pi$ on the basis of Eqs. (II.120) and (II.121). Table 121 gives the values of θ, x, the coefficients in the equations (II.137), (II.138) and the constants C_Φ and C_S in the equations (II.161), (II.162). The values of C_Φ and C_S include the terms R ln 4, corresponding to the state $X^2\Pi$.

The uncertainty in the values of the thermodynamic functions of PO, given in Table 113 (II), at $T < 1000°K$ are mainly due to the inaccuracy of the adopted values of the molecular and physical constants. At higher temperatures they are due mainly to the failure to take into

account the finite number of energy levels of the molecule PO, the difference between the calculated and experimental values of $D_0(PO)$ and the inaccuracy in the estimate of the excited electronic states. The total uncertainty in the calculated values of Φ^*_T of phosphorus monoxide, due to the above-mentioned causes, is estimated to be 0.005; 0.01 and 0.02 cal/mole·degree at T = 298.15; 3000 and 6000°K, respectively.

The thermodynamic functions of PO had been calculated earlier by Kelley [2364] ($S°_{298.16}$) and Potter and Distefano [3314a] (Φ^*_T, $S°_T$ and $C°_p$ from 273.15 to 5000°K). On the basis of older data, Kelley [2364] calculated $S°_{298.16} = 53.15 \pm 0.10$ cal/mole·degree. The calculations of Potter and Distefano were based on the same values of the molecular constants of PO in the states $X^2\Pi_r$, $B^2\Sigma^+$ and $C^2\Sigma^+$, as in the present Handbook, but the state $A^2\Sigma^+$ with an excitation energy of about 19,500 cm^{-1} was disregarded. In consequence of this the difference in the values of Φ^*_T, given in the work [3314a] and that in Table 113 (II) at $T \leq 3000°K$, does not exceed 0.005 cal/mole·degree, but at $T > 3000°K$ it increases systematically and attains 0.018 cal/mole·degree at 5000°K.

The differences between the values of the thermodynamic functions of PO, calculated in the first and present editions of the Handbook, do not exceed 0.1 cal/mole·degree. They are due to the difference in the adopted values of the molecular constants and also the fact that new, earlier unknown excited electronic states of PO have been taken into account in the present Handbook.

PH. The thermodynamic functions of gaseous phosphorus monohydride, given in Table 117 (II) were calculated in accordance with Eqs. (II.161) and (II.162) on the basis of the molecular constants of PH in Table 117. The values of $\ln\Sigma$ and $T \frac{\partial}{\partial T} \ln\Sigma$ in the equations (II.161) and

(II.162) were calculated by the method of Gordon and Barnes [see Eqs. (II.137 and (II.138)] without taking into account thecorrections for the limited number of rotational levels of the state $X^3\Sigma$. The values of $\ln \Delta_M$ and $T \frac{\partial}{\partial T} \ln \Delta_M$ were calculated on the basis of Eqs. (II.147) and (II.148) taking into account the splitting of the rotational energy levels of PH in the state $X^3\Sigma$. Four excited electronic states of PH were taken into account in the calculation ($a^1\Delta$, $b^1\Sigma$, $A^3\Pi$, $c^1\Pi$). The components of these states were calculated by means of Eqs. (II.120) and (II.121), i.e., without taking into account the differences between the molecular states of PH in the excited and ground states. Table 121 gives the values of θ, x, the coefficients in Eqs. (II.137) and (II.138) and also the constants C_Φ and C_S, which were calculated by means of the adopted values of the molecular constants of PH. The addends R ln 3, corresponding to the state $X^3\Sigma$, are included in the value of S_Φ and C_S.

The uncertainty in the calculated values of Φ^*_T of gaseous PH at $T < 1000°K$ does not exceed 0.01 cal/mole·degree. At higher temperatures the uncertainty is greater on account of the inaccurate excitation energy of the electronic states, the fact that a limited number of rotational states was ignored and because of the differences between the experimental and calculated values of the dissociation energy of PH. They amount to 0.03 and 0.1 cal/mole·degree in the values of Φ^*_T at T equal to 3000 and 6000°K, respectively.

The thermodynamic functions of PH had been calculated previously by Kelley [2364] ($S°_{298.16}$) and in the preparation of the first edition of the present Handbook.

The differences between the values of the thermodynamic functions of PH, calculated in the first and present editions of the Handbook, are due to the difference in the adopted values of the molecular con-

stants and the calculation methods. At temperatures up to 1000°K they amount to 0.2 and 0.1 cal/mole·degree for Φ^*_T and S°_T, respectively. The greater difference for Φ^*_T is due to the fact that the more accurate calculation of the multiplicity of the $X^3\Sigma$ states by the method, adopted in the present Handbook, affects mainly the Φ^*_T values. At higher temperatures the differences in the values of Φ^*_T and S°_T increase and amount to approximately 0.5 and 1.5 cal/mole·degree for Φ^*_{6000} and S°_{6000}, respectively, because the excited electronic states of PH were taken into account in the present edition of the Handbook.

PF, PCl. The thermodynamic functions of gaseous phosphorus monofluoride and monochloride, given in Table 118 (II) and 123 (II), were calculated by means of Eqs. (II.161) and (II.162), using the approximate model of the rigid rotator–harmonic oscillator. The calculation was carried out on the basis of the molecular constant, adopted in Table 117. Table 121 gives the values of θ, C_Φ and C_S, using in the calculation the thermodynamic functions of the two gases. Because the electronic ground state of the molecules PF and PCl is the state $^3\Sigma$, the addends Rln 3 are included in the value of C_Φ and C_S.

The uncertainty in the calculated values of the thermodynamic functions of phosphorus monofluoride and monochloride is predominantly due to the absence of experimental data on the molecular constants of PF and PCl and the use of the most approximate calculation method. For Φ^*_T it is estimated to be 0.05; 0.15 and 0.3 cal/mole·degree at 298.15; 3000 and 6000°K, respectively.

The thermodynamic functions of PF had been calculated earlier for the first edition of the present Handbook. The differences between the results of this calculation and the values, presented in Table 118 (II), are explained by a certain difference in the molecular constants

used in the calculations and do not exceed 0.2 cal/mole·degree.

Other calculations of the thermodynamic functions of PF and PCl are not known in the literature.

PS. The thermodynamic functions of gaseous phosphorus monosulfide, given in Table 127 (II), were calculated on the basis of the equations (II.161) and (II.162) and the molecular constants of PS, given in Table 117. The values of $\ln\Sigma$ and $T\frac{\partial}{\partial T}\ln\Sigma$ in these equations were calculated by the method of Gordon and Barnes [see the relations (II.137) and (II.138)] without applying corrections for the limited number of rotational levels of the state $X^2\Pi$. The values of $\ln\Delta_M$ and $T\frac{\partial}{\partial T}\ln\Delta_M$ were calculated by means of Eqs. (II.149) and (II.150). The components of the excited electronic states $A^2\Delta$ and $B^2\Pi$ of the PS molecule were calculated by means of Eqs. (II.120) and (II.121), i.e., without taking into account the differences between the constants of PS in the ground and excited electronic states. Table 121 gives the values of the magnitudes θ and x, the coefficients in the equations (II.137) and (II.138) and the constants C_Φ and C_S in Eqs. (II.161) and (II.162). The values of C_Φ and C_S include the addends R ln 4, corresponding to the state $X^2\Pi$.

The uncertainty in the calculated values of the thermodynamic functions of PS at $T < 1000°K$ are mainly due to the inaccuracy of the constant of the multiplet splitting and the constant B_e (the uncertainty in the value of $\Phi^*_{298.15}$ is 0.8 cal/mole·degree). At higher temperatures the errors are due mainly to the inaccuracy of the constant B_e and amount to approximately 0.3 cal/mole·degree in the values Φ^*_T at T, equal to 3000 and 600°K. Other calculations of the thermodynamic functions of PS are not known in the literature.

PN. The thermodynamic functions of gaseous phosphorus mononitride are presented in Table 128 (II). The calculation was carried out on the

basis of Eqs. (II.161) and (II.162) using the molecular constants of PN in Table 117. The values of $\ln\Sigma$ and $T\frac{\partial}{\partial T}\ln\Sigma$ in these equations were calculated by the method of Gordon and Barnes [see relations (II.137) and (II.138)] without applying corrections for the limited number of rotational levels $X^1\Sigma$. The components of the excited state $A^1\Pi$ were calculated on the basis of Eqs. (II.120) and (II.121), i.e., without taking into account the differences between the constants of PN in the states $X^1\Sigma$ and $A^1\Pi$.

Table 121 gives the values of θ, x, the coefficients in Eqs. (II.137) and (II.138) and also the constants C_Φ and C_S in Eqs. (II.161) and (II.162).

The uncertainties in the calculated values of the thermodynamic functions of PN does not exceed 0.01 cal/mole·degree in the values Φ^*_T over the entire temperature range.

The thermodynamic functions of PN were calculated previously by Kelley [2364] ($S°_{298.16}$), McCallum and Leifer [2687] (up to 1000°K) and Potter and Distefano [3314a] (to 5000°K). Only the electronic ground state of the PN molecule was taken into account in these calculations, for which the same values of the constants were adopted as in the present Handbook. McCallum and Leifer [2687] carried out the calculations by the method of Mayer and Goeppert-Mayer and used several values of the physical constants different from those in the present Handbook. Potter and Distefano [3314a] carried out the calculation by a more accurate method and on the basis of using the same values of the physical constants as in the present Handbook. The values of the thermodynamic functions of PN, given in the works [2364, 2687, 3314a] coincide with the values of the corresponding magnitudes in Table 128 (II) within the limits of the above-indicated uncertainty of the latter.

The thermodynamic functions of PN, calculated in the work [2687] are presented in the Handbook of Zeise [4381, 4384]. The values of the thermodynamic functions of PN, given in the first and present editions of the Handbook are identical.

P_4. The thermodynamic functions of gaseous tetratomic phosphorus, given in Table 112 (II), were calculated on the basis of Eqs. (II.243) and (II.244) using the approximate model of the harmonic oscillator - rigid rotator on the basis of the molecular constants, given in Table 118. Table 122 gives the values of θ and the constants C'_Φ, C'_S, which enter into Eq. (II.243) and (II.244).

The uncertainty in the calculated values of the thermodynamic functions are due to the failure to take into account the anharmonic vibrations of the molecule P_4 and the inaccuracy of the adopted values of the molecular constants. They amount approximately to 0.3; 2.0 and 3.0 cal/mole·degree in the values $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000}, respectively.

The thermodynamic functions of P_4 had been calculated earlier using the approximate model of the harmonic oscillator-rigid rotator by Stevenson and Yost [3864] (Φ^*_T, $H^\circ_T - H^\circ_0$ to 1500°K and $S^\circ_{298.16}$), Kelley [2363, 2364] (to 1500°K), Stull and Sinke [3894] (to 3000°K), Thyagarajan and Cleveland [3989a] (to 1000°K) and Potter and Distefano [3314a] (to 5000°K). In all these calculations it was assumed that the P_4 molecule is tetrahedral and that $r_{P-P} = 2.21$ A, as in the present Handbook. Hence the difference between the results of these calculations and the values of the corresponding magnitudes in Table 112 (II) could be due only to the difference in the adopted values of the fundamental frequencies of the P_4 molecule and the values of the physical constants. The marked difference between the values of the thermodynamic functions, presented in the work [3989a] and Table 112 (II)

is due to a gross error in the calculations of the authors of this work: the translational and rotational components were added to the vibrational components, divided by R. For the calculation of these vibrational components, the authors of the work [3989a] used the values of the magnitudes of $\omega_1 + 2x_{11} + x_{12}$, $\omega_2 + {}^1/_2 x_{12}$ and ω_3, calculated by Pistorius [3250b] (see p. 797).

TABLE 122

Values of the Constants for the Calculation of the Thermodynamic Functions of Gaseous P_4, P_4O_6, P_4O_8, P_4O_{10}, PF_2, PF_3, PF_5, POF_3, PCl_3, PCl_5 and $POCl_3$

Вещество A	θ_n (θ_n) град B	C'_Φ	C'_S
		кал/моль·град C	
P_4	872 (1); 522 (2); 669(3)	8,7373	16,6861
P_4O_6	882 (1); 882 (1); 1480 (2); 669 (2) 532 (3); 817 (3); 1322 (3); 925 (3) 885 (3); 434 (3)	13,8348	21,7839
P_4O_8	—	18,7386	26,6877
P_4O_{10}	2039 (1); 1037 (1); 610 (1); 1370 (2) 935 (2); 400 (2); 1991 (3); 1486 (3) 1099 (3); 804 (3); 473 (3); 370 (3) 863 (3); 647 (3); 432 (3)	16,4202	24,3693
PF_2	1154 (1); 637 (1); 1246 (1)	6,5311	14,4799
PF_3	1263 (1); 701 (1); 1237 (2); 495 (2)	8,3658	16,3145
PF_5	1201 (1); 880 (1); 1364 (1); 829(1) 1574 (2); 768 (2); 593 (2); 804 (2)	10,2519	18,2006
POF_3	2036 (1); 1256 (1); 681 (1); 1424 (2) 998 (2); 496 (2)	9,9886	17,9389
PCl_3	730,0 (1); 374,2 (1); 710,0 (2) 271,9 (2)	13,1389	21,0880
PCl_5	567 (1); 567 (1); 969 (1); 253 (1) 852 (2); 482 (2); 144 (2); 403 (2)	15,3370	23,2861
$POCl_3$	1365,90 (1); 699,60 (1); 384,72 (1) 839,22 (2); 485,51 (2); 277,47 (2)	13,9780	21,9270

A) Substance; B) degree; C) cal/mole·degree.

Obsolete values of the fundamental oscillation frequencies of the

molecule P_4 were used in the calculations of Stevenson and Yost [3864] owing to which the difference between the values of Φ^*_T, given in the work [3864] and in Table 112 (II) is about 0.1 cal/ mole·degree. The thermodynamic functions of P_4, calculated by Stevenson and Yost and several additional calculations, carried out by other authors, are presented in the summaries of Brewer [1093], Ziese [4381, 4384] and Vvedenskiy [119a]. The values of the fundamental frequencies of the P_4 molecule, used in the calculations of Kelley [2363, 2364] and Stull and Sinke [3894], are unknown. It can merely be stated that the differences between the values of Φ^*_T and S°_T, presented in these works and those in Table 112 (II) do not exceed 0.05 cal/mole·degree. In the calculations of Potter and Distefano [3314a] it was assumed that ν_3 = = 461 cm^{-1} on the basis of the infrared spectrum of a solution of white phosphorus in CS_2 [764] in contrast to ν_3 = 465 cm^{-1}, adopted in the present Handbook on the basis of a study of the Raman spectrum of liquid phosphorus [4078] and the infrared spectrum of phosphorus vapor [1903]. In consequence of this, the calculations of Potter and Distefano led to slightly larger values of the thermodynamic functions of P_4 than those given in Table 112 (II). The values of the thermodynamic functions of P_4, given in the first and second editions of the Handbook, are identical.

$\underline{P_4O_6}$. The thermodynamic functions of gaseous phosphorus trioxide, given in Table 114 (II) were calculated by means of Eqs. (II.243) and (II.244) using the approximate model of the harmonic oscillator-rigid rotator with the molecular constants, adopted in Table 118. The values of the constants θ_n and C'_Φ and C'_S, which enter into the formula for calculating the thermodynamic functions of P_4O_6, are given in Table 122.

The uncertainty in the calculated values of the thermodynamic

functions are mainly due to the failure to take into account the anharmonic vibrations and the inaccuracy of the molecular constants and amount approximately to 1, 7 and 10 cal/mole·degree in the values of Φ^*_T at 298.15; 3000 and 6000°K.

The differences in the thermodynamic functions of P_4O_6, given in the first and present editions of the Handbook, amount to 0.1 cal/mole·degree for 298.15°K and 0.5 cal/mole·degree for medium and high temperatures. The divergence is due to a certain difference in the molecular constants of P_4O_6, used in the calculations. Other calculations of the thermodynamic functions of P_4O_6 are not known in the literature.

P_4O_8. The thermodynamic functions of gaseous phosphorus dioxide given in Table 115 (II) were calculated on the basis of the Eqs. (II.243) and (II.244). The vibrational components of the thermodynamic functions of P_4O_8 were calculated as the arithmetic mean of the corresponding components of phosphorus trioxide and pentoxide, because an estimate of the fundamental frequencies of the $P4_08$ molecule is impossible at the present time. The rotational components of the functions of P_4O_8 were calculated, using an approximate model of the rigid rotator. The values of the constants C'_Φ and C'_S in the formula (II.243) and (II.244) are given in Table 122.

The uncertainty in the calculated values of the thermodynamic functions of P_4O_8 is due to the use of a coarse method of estimating vibrational components and the absence of experimental data on the structural parameters of P_4O_8. These amount to approximately 2, 9 and 13 cal/mole·degree in the values of Φ^*_T at T = 298.15; 3000 and 6000°K respectively. The difference between the values of the thermodynamic functions of P_4O_8, given in the first and present edition of the Handbook, amount to about 5 cal/mole·degree on account of the

changes in the vibrational components of P_4O_6 and P_4O_{10}, which led to a change in the vibrational components of P_4O_8. Other calculations of the thermodynamic functions of P_4O_8 are not known in the literature.

P_4O_{10}. The thermodynamic functions of phosphorus pentoxide, given in Table 116 (II), were calculated by means of Eqs. (II.243) and (II.244) using the approximate model of the harmonic oscillator - rigid rotator with the molecular constants, adopted in Table 118. Table 122 gives the values of θ_n and the constants C'_Φ and C'_S in the formulae (II.243) and (II.244).

The uncertainty in the calculated values of the thermodynamic functions of phosphorus pentoxide are due to neglecting the anharmonic vibrations and to the inaccuracy of the molecular constants of this molecule. They amount to approximately 2, 10, and 15 cal/mole·degree in the values of Φ^*_T at T = 298.15; 3000 and 6000°K.

On the basis of the results of the calorimetric measurements, obtained by Frandsen [1595], Kelley [2363] developed an equation for the dependence of $H^\circ_T - H^\circ_{298.15}$ on the temperature and calculated the values of $H^\circ_T - H^\circ_{298.15}$ and $S^\circ_T - S^\circ_{298.15}$ for solid phosphorus pentoxide and its vapor up to 1400°K. On the basis of the molecular constants of P_4O_{10}, the thermodynamic functions of gaseous phosphorus pentoxide were calculated for the first time during the preparation of the first edition of the present Handbook. In consequence of the fact that the values of several frequencies of the doubly and triply degenerate vibrations of the P_4O_{10} molecule in the first edition of the Handbook were much too low, the differences between the corresponding values of Φ^*_T and S°_T, presented in the first and present edition of the Handbook, amount to approximately 10 cal/mole·degree. The thermodynamic functions of gaseous P_4O_{10} were also calculated on the basis of the molecular constants by Topley [4000] for the temperature inter-

val 298.16-1400°K. The values of the thermodynamic functions of P_4O_{10} given in the work [4000] agree with the values, given in Table 116 (II) within the limits of the above-indicated uncertainty of the latter.

PF_2. The thermodynamic functions of gaseous phosphorus difluoride given in Table 119 (II), were calculated by means of Eqs. (II.243) and (II.244) using the approximate model of the harmonic oscillator - rigid rotator with the molecular constants of PF_2, given in Table 119. Table 122 gives the values of θ_n and also the values of the constants C'_Φ and C'_S in the eqs. (II.243) and (II.244) used in the calculations. Because the molecule PF_2 has a doublet electronic ground state, the addends R ln 2 are included in the values of C'_Φ and C'_S.

The uncertainty in the calculated values of the thermodynamic functions of phosphorus difluoride are due to the disregard of the anharmonic nature of the vibrations of the molecule PF_2 and the inaccuracy of the adopted values of the molecular constants. These are approximately 0.3; 1.5 and 2.0 cal/mole·degree in the values of Φ^*_T at T = 298.15; 3000 and 6000°K, respectively. The thermodynamic functions of phosphorus difluoride, given in the first and present editions of the Handbook, are identical. Other calculations of the thermodynamic functions of PF_2 are not known.

PF_3. The thermodynamic functions of phosphorus trifluoride, given in Table 120 (II), were calculated on the basis of Eqs. (II.243) and (II.244) in accordance with the approximate model of the harmonic oscillator - rigid rotator with the molecular constants, adopted in Table 119. Table 122 gives the values of θ_n and also the constants C'_Φ and C'_S in the equations (II.243) and (II.244), used in the calculations.

The uncertainties in the calculated values of the thermodynamic

functions of PF_3 are due mainly to neglecting the anharmonic vibrations of the molecules and the inaccuracy of the values of the molecular constants used in the calculations. These have a magnitude of the order of 0.5; 2.0 and 3.0 cal/mole·degree in the values of Φ^*_T at T = = 298.15; 3000 and 6000°K, respectively.

The thermodynamic functions of PF_3 have been calculated earlier by Stevenson and Yost [3864] (to 1000°K), Kelley [2363, 2364] (to 2000°K), Wilson and Polo [4297] (to 1500°K) and Potter and Distefano [3314a] (to 5000°K). The calculations of Stevenson and Yost [3864], based on obsolete starting data, were later supplemented by Kelley [2363, 2364] and Zeise [4384]. The results of these calculations are given in the summaries of Zeise [4381, 4384] and Vvedenskiy [119a]. The differences between the values of Φ^*_T and S°_T of phosphorus trifluoride, given in the works [3864, 2363, 2364, 4384] and in Table 120 (II) amount to 0.5-1.5 cal/mole·degree in consequence of the fact that inaccurate values of the molecular constants were used in these works. The calculations of Wilson and Polo [4297] and Potter and Distefano [3314a] were based on the same values of the molecular constants of PF_3 as in the present Handbook. The same values of the physical constants and atomic weights of the elements were used in the work [3314a] as in the Present Handbook. The differences between the values of Φ^*_T and S°_T of phosphorus trifluoride, given in the work [4297] and in Table 120 (II) amount to approximately 0.04 cal/mole·degree; the corresponding differences between [3314a] and Table 120 (II) are about 0.003 cal/mole·degree. The former are due to a certain difference in the adopted values of the molecular weight of PF_3 and the physical constants, the latter are due to rounding off in the calculations.

The thermodynamic functions of PF_3, presented in the first and present editions of the Handbook, are identical.

$\underline{PF_5}$. The thermodynamic functions of phosphorus pentafluoride,

given in Table 121 (II), were calculated by means of Eqs. (II.243) and (II.244) using the approximate model of the harmonic oscillator - rigid rotator with the molecular constants, given in Table 120. Table 122 gives the values of θ_n abd also the values of the constants C'_Φ and C'_S in the formulae for the ca culation of the thermodynamic functions of PF_5.

The uncertainties in the calculated values of the thermodynamic functions are mainly due to neglecting the anharmonic vibrations of this molecule and the inaccuracy of the molecular constants of PF_5 used in the calculations. They are of a magnitude of the order of 1, 6 and 8 cal/mole·degree in the values of Φ^*_T at T = 298.15; 3000 and 6000°K. The thermodynamic functions of PF_5, given in the first and present editions of the Handbook, are identical. Other calculations of the thermodynamic functions of PF_5 are not known in the literature.

$\underline{POF_3}$. The thermodynamic functions of phosphorus oxytrifluoride, given in Table 122 (II), were calculated on the basis of Eqs. (II.243) and (II.244) by means of the approximate model of the harmonic oscillator - rigid rotator with the molecular constants of POF_3, given in Table 119. Table 122 gives the values of θ_n and also the values of the constants C'_Φ and C'_S which enter into the formulae (II.243) and (II.244).

The uncertainties in the calculated values of the thermodynamic functions of POF_3 are mainly due to the fact that the anharmonic vibrations of the molecule POF_3 were neglected and to the inaccuracy of the molecular constants. These amount to 0.5; 3 and 4 cal/mole·degree in the values of Φ^*_T at T = 298.15; 3000 and 6000°K.

The thermodynamic functions of POF_3 in the approximate model of the harmonic oscillator - rigid rotator, were calculated by Ziomek

and Piotrowski [4389b] within the temperature range of 200-1000°K. The values of Φ^*_T and S°_T given in the work [4389b] exceed the corresponding values of these magnitudes in Table 122 (II) by about 0.2 cal/mole·degree in consequence of a slight difference in the adopted values of the molecular constants. In particular, the authors of the work [4389b] used the values of the basic frequencies of the molecule POF_3, found by Delwaulle and Francois [1306] during their investigations of the Raman spectrum of liquid phosphorus oxytrifluoride for calculating the thermodynamic functions of gaseous POF_3.

PCl_3. The thermodynamic functions of gaseous phosphorus trichloride, given in Table 124 (II), were calculated by means of Eqs. (II.243) and (II.244) on the basis of the approximate model of the harmonic oscillator - rigid rotator with the molecular constants of PCl_3, given in Table 119. Table 122 gives the values of θ_n and also the values of the constants C'_Φ and C'_S, which enter into the formulae (II.243) and (II.244).

The uncertainties in the calculated values of the thermodynamic functions of PCl_3 are mainly due to the disregard for the anharmonic vibrations of the molecule PCl_3 and the inaccuracy of the molecular constants. These amount to about 0.4; 2.5 and 3 cal/mole·degree in the values for Φ^*_T at T = 298.15; 3000 and 6000°K.

The thermodynamic functions of PCl_3 have been calculated previously by Stevenson and Yost [3864] (Φ^*_T to 1000°K and $S^\circ_{298.16}$) and Kelley [2363, 2364] ($S^\circ_T - S^\circ_{298.16}$ to 1000°K and $S^\circ_{298.16}$). The values of Φ^*_T for PCl_3, calculated in the work [3864], are given in the summaries of Zeise [4381, 4384]. The values of S°_T to 1000°K, calculated on the basis of the data in the work [3864] are also presented in the book [4384] for PCl_3. Kelley [2363] established the interpolation equations for $H^\circ_T - H^\circ_{298.15}$ on the basis of the equations for the

specific heat of PCl_3 and calculated the values of $H^\circ_T - H^\circ_{298.16}$ and $S^\circ_T - S^\circ_{298.16}$ to 1000°K. The thermodynamic functions of PCl_3, calculated in the works [3864, 2363, 2364, 4384] differ from those given in Table 124 (II) by about 0.2 cal/mole·degree, mainly because of the differences in the adopted values of the molecular constants of PCl_3.

The thermodynamic functions of PCl_3 were not given in the first edition of the Handbook.

PCl_5. The thermodynamic functions of gaseous phosphorus pentachloride given in Table 125 (II), were calculated by means of Eqs. (II.243) and (II.244) in accordance with the approximate model of the harmonic oscillator - rigid rotator with the molecular constants of PCl_5, given in Table 120. Table 122 shows the values of θ_n and also the values of the constants C'_Φ and C'_S which enter into formulae (II.243) and (II.244).

The uncertainties in the calculated values of the thermodynamic functions of PCl_5 are caused by the disregard for the anharmonic vibrations of the molecule PCl_5 and the inaccuracy of the molecular constants. These amount to 2, 6 and 8 cal/mole·degree in the values of Φ^*_T at T = 298.15; 3000 and 6000°K, respectively.

The thermodynamic functions of PCl_5 had been calculated earlier by Stevenson and Yost [3864] (Φ^*_T to 1000°K, $S_{298.16}$), Kelley [2363] ($S^\circ_T - S^\circ_{298.16}$ to 500°K) and Wilmshurst and Bernstein [4284] (to 1500°K). The thermodynamic functions of PCl_5, calculated in the work [3864] are given in the summaries of Zeise [4381, 4384]. The values of S°_T for PCl_5 to 500°K, calculated by Zeise on the basis of the data in the work [3864] were also given in the book [4384]. Kelley [2363] established the interpolation equation for $H^\circ_T - H^\circ_{298.15}$ on the basis of the equations for the specific heat of PCl_5 and calculated the val-

ues of $H^\circ_T - H^\circ_{298.16}$ and $S^\circ_T - S^\circ_{298.16}$ to 500°K. The differences between the thermodynamic functions of PCl_5, calculated in the works [3864, 2363, 2364, 4284] and those given in Table 125 (II), are 0.7 to 5 cal/mole·degree. These differences can be explained by the difference in the adopted values of the molecular constants of PCl_5. Wilmshurst and Bernstein [4284] calculated the thermodynamic functions of PCl_5 on the basis of the vibrational constants, obtained by the authors of the work [4284]. The interatomic distances, also calculated by the authors of the work [4284], on the basis of Badger's rule [596] from the force constants, coincided with the data from the work of Ronault [3537] which were adopted in the present Handbook. However, an error was committed in the calculation of the inertia moments of PCl_5 by the authors of the work [4284], owing to which the values of the thermodynamic functions of PCl_5, calculated by them are approximately by 0.3 cal/mole·degree lower than those given in Table 125 (II).

The thermodynamic functions of PCl_5 have not been given in the first edition of the Handbook.

$POCl_3$. The thermodynamic functions of gaseous phosphorus oxytrichloride, given in Table 126 (II), were calculated by means of Eqs. (II.243) and (II.244) on the basis of the approximate model of the harmonic oscillator - rigid rotator with the molecular constants, adopted in Table 119. The values of the constants C'_Φ and C'_S which enter into formula (II.243) and (II.244) and also the values of C_n, used in the calculations, are given in Table 122.

The uncertainty in the calculated values of the thermodynamic functions of $POCl_3$ are mainly due to the fact that the anharmonic vibrations of the molecule $POCl_3$ were disregarded and to the inaccuracy of the molecular constants. These are 0.7, 4 and 5 cal/mole·degree in

the values of Φ^*_T at T = 298.15; 3000 and 6000°K.

The thermodynamic functions of gaseous $POCl_3$ had been calculated earlier by Stevenson and Yost [3864] (Φ^*_T to 1000°K and $S^\circ_{298.16}$), Ziomek, Piotrowski and Walsh [4389a] ($S^\circ_{298.16}$), Ott and Giauque [3152a] (to 500°K) and Ziomek and Piotrowski [4389b] (to 1000°K). Zeise [4381, 4384] supplemented the calculations of Stevenson and Yost on the basis of the molecular constants of $POCl_3$, adopted in the work [3864]. The Tables of the thermodynamic functions, established by Zeise in the work [4381], are presented in the book by Vvedenskiy [119a]. The calculations of Stevenson and Yost [3864] and Ziese [4381, 4384] were based on the erroneous values of the structural parameters of the molecule $POCl_3$, found by Brockway and Beach [958] (see page 810). Owing to this, the values of Φ^*_T and S°_T, given in the works [3864, 4381, 4384, 119a] exceed the values of the corresponding magnitudes in Table 126 (II) by about 0.2 cal/mole·degree.

Ziomek, Piotrowski and Walsh [4389a], using the same values of the molecular constants of $POCl_3$ as in the present Handbook, calculated $S^\circ_{298.15}$ = 77.37 cal/mole·degree in agreement with the values, given in Table 126 (II). The correctness of this value was disputed by Ott and Giauque [3152a], who calculated $S^\circ_{298.15}$ = 77.75 cal/mole·degree on the basis of the results of their calorimetric measurements. However, the value of $S^\circ_{298.15}$, calculated in the work [4389a] on the basis of the molecular constants of $POCl_3$ and in the work [3152a] on the basis of calorimetric measurements, do not contradict each other, if one takes into account that the uncertainty of the value $S^\circ_{298.15}$, calculated on the basis of the molecular constants of $POCl_3$, is about 1 cal/mole·degree. Besides, the possibility cannot be excluded, that the structure of solid $POCl_3$ at 0°K is not completely ordered, in consequence of which Ott and Giauque could have obtained

a slightly higher value of $S°_{298.15}$.* These circumstances were not taken into account by Ott and Giauque, who interpreted the above- mentioned difference in the values of $S°_{298.15}$ ($POCl_3$, gas) as an error with regard to the fundamental frequencies of the $POCl_3$ molecule, although the results of the analysis of the spectra of $POCl_3$ did not provide any grounds for this (see page 811). Altering the assignment of the fundamental frequencies of $POCl_3$ in such a manner that the value of $S°_{298.15}$, calculated on their basis, should be close to that found by them on the basis of the calorimetric measurements, Ott and Giauque calculated the values of the thermodynamic functions of gaseous $POCl_3$ for the temperature interval 15-500°K in the work [3152a]. The values of Φ^*_T and $S°_T$, given in the work [3152a] exceed the values of the corresponding magnitudes, given in Table 126 (II) by 0.2--0.4 cal/mole·degree.

In 1961, Ziomek and Piotrowski [4389b] published a Table of the thermodynamic functions of $POCl_3$, calculated by means of the same molecular constants, as in the present Handbook for T = 200-1000°K. The corresponding values of the thermodynamic functions of $POCl_3$, given in the work [4389b] and in Table 126 (II), agree. The objections of Ott and Giauque [3152a] in the work [4389b] were not examined.

The thermodynamic functions of $POCl_3$ were not given in the first edition of the Handbook.

§56. THERMOCHEMICAL MAGNITUDES

The standard modification of Phosphorus is the α modification of crystalline white phosphorus – P (cryst. white, α).

The enthalpy values of white phosphorus adopted in the Handbook

$$H°_{298.15} - H°_0 = 1236 \pm 10 \text{ cal/g.atom}$$

$$H°_{298.15} - H°_0 = 1264 \pm 10 \text{ cal/g.atom}$$

were calculated by Khachkuruzov [435] on the basis of the data existing in the literature on the specific heat of white phosphorus [1325, 1517, 4369],* its vapor pressure [1249, 2725] and the transformations of the β-modification of white phosphorous to the α-modification [934, 935].**

P (gas). The value of the heat of formation of monatomic phosphorus adopted in the Handbook

$$\Delta H^\circ f_0(P, \text{gas}) = 75{,}371 \pm 0{,}05 \text{ kcal/g-atom}$$

was calculated on the basis of the adopted thermochemical magnitudes for P_4 and P_2 (see further on).

P_2 (gas). Herzberg [2015] found the predissociation limit of the state $B^1\Sigma^+_4$ of the P_2 molecule to be equal to 51,959 ± 20 cm^{-1} and showed that it corresponds to the dissociation into phosphorus atoms $P(^4S) + P(^2D)$. The excited ^2D state of the phosphorus atom is a doublet and consists of the substates $^2D_{3/2}$ and $^2D_{5/2}$ with energies, equal to 11,861.7 and 11,376.5 cm^{-1}, respectively.

Data which would permit to determine unequivocally to which of these substates the state $B^1\Sigma$ of the molecule P_2 corresponds, are entirely lacking at present. Hence, the average value $D_0(P_2)$ = 51,959 −11,369 = 40,590 cm^{-1} or

$$D_0(P_2) = 116{,}057 \pm 0{,}09 \text{ kcal/mole}$$

is used in the Handbook.

To this corresponds

$$\Delta H^\circ f_0(P_2, \text{gas}) = 34{,}685 \pm 0{,}05 \text{ kcal/mole}$$

P_4 (gas). The P_4 molecule is the main product of the evaporation of phosphorus and its heat of formation can be calculated on the basis of the results of the vapor pressure measurements on phosphorus. A review of the works on the measurement of the vapor pressure of phosphorus is given in the work of Khachkuruzov [435]. The most accurate data were obtained by Dainton and Kimberley [1249]. The vapor

pressure of phosphorus has been measured in this work within the temperature range of 250-314°K by the tracer atom method. The value

$$\Delta H^\circ_f{}_0(P_4, \text{ газ}) = 15{,}751 \pm 0{,}05 \text{ kcal/mole}$$

adopted in the Handbook, was calculated on the basis of the results of the measurements of Dainton and Kimberley and the values of the thermodynamic functions of white phosphorus [435].

Preuner and Brockmoller [3317] and Stock, Gibson and Stamm [3866] measured the equilibrium constant of the dissociation reaction: P_4 (gas) $\rightleftarrows 2P_2$ (gas) within the temperature range of 1100-1500°K. As Stevenson and Yost showed [3864, 4365], the data of Stock et al are more reliable [3866]. On the basis of these data, the authors of the Handbook calculated $D_0(P_4 \rightarrow 2P_2) = 53.62 \pm 0.05$ kcal/mole. The mass-spectrometric study of the equilibria in phosphorus vapor carried out by Drowart and Goldfinger [1407] led to the magnitude $D_{298}(P_4 \rightarrow 2P_2) = 55.7 \pm 0.5$ kcal/mole, or $D_0(P_4 \rightarrow 2P_2) = 54.0$ kcal/mole. This magnitude agrees well with that calculated on the basis of the data of Stock et al. [3866], but isless accurate.

The value of the dissociation energy of the P_4 molecules into atoms

$$D_0(P_4) = 285{,}733 \pm 0{,}2 \text{ kcal/mole}$$

adopted in the Handbook is based on the Handbook values of $D_0(P_2)$ and the above given value of $D_0(P_4 \rightarrow 2P_2)$, calculated on the basis of the data of Stock et al [3866].

PO(gas). Linear extrapolation of the observed levels of the vibrational energies of the electronic ground state of the PO molecule leads to a clearly higher value $D_0(PO) = 57{,}000$ cm^{-1} or 163 kcal/mole [1705, 1402]. A more satisfactory value of $D_0(PO) = 143$ kcal/mole was calculated by Rumpf [3567] on the basis of the results of a spectroscopic study of the cold luminescence of white phosphorus. This

value with an uncertainty of ±12 kcal/mole has been recommended by Gaydon [1668].

Dressler [1402] found, by brief extrapolation of the vibrational energy levels of PO in the $B^2\Sigma^+$ state that the dissociation limit of this state coincides with the predissociation limit in the F state, which is situated above the level v = 0 of the state $X^2\Pi_r$, approximately at 55,000 cm^{-1}. Assuming erroneously, that the state B is a state of the type $^2\Pi$, in which PO dissociates into $P(^2D) + O(^3P)$, he obtained $D_0(PO) = 55,000-11,370 = 43,630$ cm^{-1} or 124.7 kcal/mole. However, because the state B is a state of the type $^2\Sigma^+$, the PO molecule in this state should dissociate into unexcited atoms [1402, 3314a], i.e., the dissociation limits of PO in the states $X^2\Pi_r$ and $B^2\Sigma^+$ should coincide. Hence Potter and Distefano [3314a] re-examined the problem of the magnitude of $D_0(PO)$. These authors pointed out the predissociation of PO in the states E and E' (see Table 116) at 49,000 cm^{-1}, observed by Durga and Rao [1422] and found that of one introduces into the value D'_0, obtained by linear extrapolation of the levels of the vibrational energy of PO in the state $B^2\Sigma^+$, the correction of Gaydon [1668], the value $D_0(PO) = 49,500$ cm^{-1} is obtained. In consequence, Potter and Distefano used in their work [3314a] the value $D_0(PO) = 49,000$ $cm^{-1} \cong 140$ kcal/mole, which agrees with the values of $D_0(PO)$, found by Rumpf [3567] and with the values of the dissociation energy of the molecules NO, SiO and SO, adopted in the Handbook (see Tables 115, 206, 88).

In the works [1422, 1402], transitions were observed only into the v = 0 levels in the states E and E', which was explained by Durga and Rao [1422] by a predissociation between the levels v = 0 and v = 1 of these states, which according to Potter and Distefano [3314a] coincides with the dissociation limits of the states $B^2\Sigma^+$ and $X^2\Pi_r$.

On the basis of the data, given in the work [1422], one can state in this case that the dissociation limit of the PO molecule in the $X^2\Pi_r$ state is 49,500 $\pm$ 700 cm^{-1} corresponding to

$$D_0(PO) = 141{,}5 \pm 2{,}0 \text{ kcal/mole}$$

This value of $D_0(PO)$ has been adopted in the present Handbook. To it corresponds

$$\Delta H^\circ f_0(PO, \text{ газ}) = -7{,}142 \pm 2 \text{ kcal/mole}$$

P_4O_6 (gas). The values of the heat of formation of P_4O_6 (cryst.) equal to -488 and -156 kcal/mole, respectively, are given in the works of Ogier [3118] and Berthelot [781]. The data on which these results were based and the methods of their measurement were not published.

Koerner and Daniels [2455] determined the heat of combustion of red phosphorus in a stream of NO. As the chemical analysis showed, the combustion products under these conditions consist of P_4O_{10} and P_4O_6, the P_4O_6 content varying from one experiment to another (between 22 and 34%). The values of the heat of formation of P_4O_6, equal to -540 $\pm$ 8 kcal/mole,* were calculated on the basis of the experiments by Koerner and Daniels. Skuratov and coworkers [35] corrected the inaccuracy, tolerated in the calculations of Koerner and Daniels and obtained the value -521 $\pm$ 22 kcal/mole. It should be pointed out that the use of the method of analyzing the combustion products, used in the work [2455] did not permit the determination of another known phosphorus oxide, P_4O_8, which may be the cause of the slight error.

The value of the heat of formation of P_4O_6 can be estimated by comparing the heats of formation of elements which are analogous to phosphorus. The ratio of the heats of formation of the trioxides and pentoxides of As, Sb and N [3509] is approximately 0.72. Assuming that this ratio will also apply to phosphorus, we obtain the value of the heat of formation of phosphorus trioxide as -516 kcal/mole which

practically coincides with that found in the work [35].

The value of the heat of sublimation of phosphorus trioxide, $\Delta H_{S_{298.15}}$ = 17 kcal/mole, was calculated on the basis of the data given by Kelley for the heat of fusion [2356] and the heat of evaporation [2355] of phosphorus trioxide and the thermodynamic functions of liquid phosphorus trioxide, calculated by the method of Wenner [127].

On the basis of the value $\Delta Hf°_{298.15}(P_4O_6$, cryst.) = -521 ± 22 kcal/mole [35] and the above given value of the heat of sublimation of P_4O_6, we find the magnitude

$$\Delta Hf°_{298.15}(P_4O_6, \text{ газ}) = -504 \pm 22 \text{ kcal/mole}$$

which has been adopted in the Handbook. To this corresponds

$$D_0(P_4O_6) = 1153{,}731 \pm 22 \text{ kcal/mole}$$

<u>P_4O_8 (gas)</u>. Emmett and Schultz [1481] determined the value of the equilibrium constant of the reaction

$$P_4O_8 \text{ (газ)} + 2CO_2 \text{ (газ)} = P_4O_{10} \text{ (газ)} + 2CO \text{ (газ)} \quad \text{(XV.1)}$$

within the temperature range of 1270-1300°K. Based on these data and the values of the thermodynamic properties of the reaction components, adopted in the present Handbook, the heat effect of the reaction (XV.1) ΔH_0 = 18 ± 6 kcal/mole and the heat of formation of phosphorus tetroxide were calculated:

$$\Delta Hf°_0(P_4O_8, \text{ газ}) = -563 \pm 8 \text{ kcal/mole}$$

which was adopted in the Handbook. To this value corresponds

$$D_0(P_4O_8) = 1336{,}38 \pm 8 \text{ kcal/mole}$$

<u>P_4O_{10} (gas)</u>. The results of the measurements of the heat of combustion of phosphorus, obtained prior to 1934, were examined by Bichowsky and Rossini [813]. The most reliable data were obtained by Giran [1756]. The calculations of Bichowsky and Rossini [813], based on these data, led to the value $\Delta H°f_{298.15}(P_4O_{10}$, solid) = -720 kcal/mole.

Koerner and Daniels [2455] measured the heat of combustion of

red phosphorus in a stream consisting of a mixture of nitrogen and oxygen, which enabled them to calculate $\Delta H°f_{298.15}(P_4O_{10}$, solid) = = -710 ± 4 kcal/mole. Skuratov and coworkers [35] again carried out the calculation on the basis of the data in the work [2455] and found a slightly larger value: $\Delta H°f_{298.15}(P_4O_{10}$, solid) = -714 ± 6 kcal/mole.

For the heat of formation of the low-temperature modification of phosphorus pentoxide we adopted the value $\Delta H°f_{298.15}$ = -717 ± 5 kcal/mole, which is the average of the values, calculated on the basis of the measurements of Giran [1756] and Koerner and Daniels [2455].

The most accurate measurements of the vapor pressure of phosphorus pentoxide were carried out by Hill, Faust and Hendricks [2073]. The value of the heat of sublimation of phosphorus pentoxide was calculated on the basis of these data as $\Delta Hs_{298.15}$ = 30.3 ± 1 kcal/mole.*

The value of the heat of formation of phosphorus pentoxide in the gaseous state

$$\Delta H°f_0(P_4O_{10}, \text{ газ}) = -887 \pm 5 \text{ kcal/mole}$$

calculated by means of the above given values of the heat formation and the heat of sublimation of P_4O_{10} (cryst.) were adopted in the Handbook. To this value corresponds

$$D_0(P_4O_{10}) = 1570.133 \pm 5 \text{ kcal/mole}$$

PH (gas). The value

$$D_0(PH) = 70 \pm 10 \text{ kcal/mole.}$$

adopted in the Handbook, has been estimated on the basis of the relation

$$\frac{D_0(PH)}{D_0(PH_3)} = \frac{D_0(NH)}{D_0(NH_3)}.$$

The values of the dissociation energy of NH and NH_3 from Table 114 and the value $D_0(PH_3)$, calculated on the basis of the value $\Delta H°f_{298.15}$ (PH_3, gas) = 2.21 kcal/mole, presented in the Handbook [3508] were

used in the calculation. To this value of the dissociation energy of PH corresponds

$$\Delta H^\circ f_0 (PH, \text{газ}) = 57{,}003 \pm 10 \text{ kcal/mole}$$

PF (gas). The value adopted in the Handbook

$$D_0 (PF) = 105 \pm 10 \text{ kcal/mole}$$

was estimated on the basis of the relation

$$\frac{D_0 (PF)}{D_0 (PF_3)} = \frac{D_0 (NH)}{D_0 (NH_3)}.$$

The values $D_0(NH)$ and $D_0(NH_3)$ from Table 114 and the value $D_0(PF_3)$ from Table 123 were used in the calculation. To the adopted value of the dissociation energy of PF corresponds

$$\Delta H^\circ f_0 (PF, \text{газ}) = -11{,}129 \pm 10 \text{ kcal/mole}$$

PF_2 (gas). The value adopted in the Handbook

$$D_0 (PF_2) = 215 \pm 10 \text{ kcal/mole}$$

has been estimated by means of a method proposed by Karapet'yants. The values of the dissociation energy of NH, NH_2 and NH_3 from Table 114 and of PF and PF_3 from Table 123 were used for plotting the curve.

To the adopted value $D_0(PF_2)$ corresponds

$$\Delta H^\circ f_0 (PF_2, \text{газ}) = -102{,}629 \pm 10 \text{ kcal/mole}$$

PF_3 (gas). Berthelot [788] measured the heat of solution of PF_3 in aqueous potash. However, because of the indeterminate nature of the reaction products, the value of the heat of formation of PF_3 could not be calculated on the basis of these data. An estimate of the heat of formation of PF_3 by the method of half-adding, described in the work [469], leads to the value

$$\Delta H^\circ f_{298,15} (PF_3, \text{газ}) = -215 \pm 10 \text{ kcal/mole}$$

which was adopted in the Handbook. The heats of formation of PCl_3 (gas) and PBr_3 (gas) on the basis of the data [3508] were used in the calculation. Estimates, carried out by the methods of Kapustinskiy and Karapet'yants, confirmed the adopted magnitude of the heat of forma-

tion of PF_3. To the adopted value $\Delta H°f_{298.15}$ (PF_3, gas) corresponds

$$D_0(PF_3) = 344{,}533 \pm 10 \text{ kcal/mole}$$

PF_5 (gas). Comparing the heats of formation of the fluorides of the elements in the second period of the Mendeleyev Table, Sue [3895] calculated the value of the heat of formation of phosphorus pentafluoride as -335 kcal/mole. A more reliable estimate was carried out by Kapustinskiy [209]. The value obtained by Kapustinskiy

$$\Delta Hf_{298.15}(PF_5, \text{gas}) = -315 \pm 10 \text{ kcal/mole}$$

confirmed by an estimate by the method of half-adding [469], was adopted in the Handbook. To this value corresponds

$$D_0(PF_5) = 479{,}88 \pm 10 \text{ kcal/mole}$$

POF_3 (gas). Ebel and Bretscher [1443] measured the heat effect of the reaction: PF_3 (gas) + 1/2 O_2 (gas) = POF_3 (gas), $\Delta H°_{298}$ = -70.6 ± 1.0 kcal. According to the value of the heat of formation of PF_3, adopted in the present Handbook, the data of Ebel and Bretscher lead to the following value for the heat of formation of POF_3:

$$\Delta Hf_{298.15}(POF_3, \text{gas}) = -286 \pm 10 \text{ kcal/mole}$$

This value, adopted in the present Handbook, is confirmed by the results of calculation by the method of half-adding [469].* To the adopted value of the heat of formation of POF_3 corresponds

$$D_0(POF_3) = 473{,}760 \pm 10 \text{ kcal/mole}$$

PCl (gas). The value adopted in the Handbook

$$D_0(PCl) = 68 \pm 10 \text{ kcal/mole}$$

has been estimated on the basis of the relation

$$\frac{D_0(PCl)}{D_0(PCl_3)} = \frac{D_0(NH)}{D_0(NH_3)}.$$

The values of the dissociation energies of NH and NH_3 (see Table 114) and PCl_3 (see Table 123) were used in the calculation. To the adopted value D_0(PCl) corresponds

$$\Delta H^\circ f_0 (PCl, \text{ газ}) = 35{,}921 \pm 10 \text{ ккал/моль}$$

PCl_3 (gas). Thomsen [3981] and Berthelot and Louguinine [794] measured the heat of hydrolysis of PCl_3 (liq.) and found $\Delta H_{291} = -65.1$ kcal/mole. Bichowsky and Rossini [813] calculated on the basis of these data the value of the heat of formation of PCl_3 (liq.) as -76.9 kcal/mole.

The heat of hydrolysis of PCl_3 (liq.) was also measured by Neale and Williams [3035a] and Charnley and Skinner [1091]. Similar values were obtained in these works for the heat of formation of PCl_3 (liq.) equal to -79.6 kcal/mole and -79.4 kcal/mole [1091]. The main source of error in the magnitudes, obtained by Neale and Williams [3035a] and Charnley and Skinner [1091] is the inaccurate value of the heat of formation of H_3PO_3, used in the calculations. Hence Neale and Williams [3036] carried out measurements of the heat of hydrolysis of PCl_3 (liq.) in an aqueous solution of bromine. Under these conditions the hydrolysis product of PCl_3 is H_3PO_4. Because the heat of formation of H_3PO_4 is known more accurately than the heat of formation of H_3PO_3, the value $\Delta H^\circ f_{298.15}(PCl_3, \text{ liq.}) = -74.4$ kcal/mole, found by Neale and Williams in the work [3036] is more accurate. This value and taking into account the heat of evaporation calculated by Kelle [2355] $\Delta Hv_{298}(PCl_3, \text{ liq.}) = 8.2 \pm 1$ kcal/mole leads to the value

$$\Delta H^\circ f_{298.15}(PCl_3, \text{ газ}) = -66{,}2 \pm 2 \text{ kcal/mole}$$

which has been adopted in the Handbook. To this value corresponds

$$D_0(PCl_3) = 226{,}483 \pm 2 \text{ kcal/mole}$$

PCl_5 (gas). Thomsen [3981] and Berthelot and Louguinine [794] measured the heat of dissolution of crystalline PCl_5 in water, which enabled Bichowsky and Rossini [813] to calculate $\Delta H^\circ f_{291.15}$ (PCl_5, cryst.) = -106.5 kcal/mole. The calculations in the work [3508] based on the use of the measurement results [3981, 794] and the more accur-

ate values of the heat of formation of the reaction components, led to the value $\Delta H°f_{298.15}(PCl_5$, cryst.) = -110.7 kcal/mole. To this value corresponds $\Delta H°f_{298.15}(PCL_5$, gas) = -95.2 kcal/mole, because $\Delta Hs_{298.15}(PCl_5$, cryst.) = 15.5 kcal/mole, according to the measurements of Fischer and Jubermann [1565].

Thomsen [3981] has also measured the heat of the reaction

$$PCl_3\,(liq.) + Cl_2\,(gas) = PCl_5\,(cryst.).$$

To this value of ΔH = -29.69 kcal/mole corresponds ΔHf (PCl_5, cryst.) = -104.1 kcal/mole and ΔHf (PCl_5, gas) = -89.6 kcal/mole.

The results of the measurement of the equilibrium constants for the reaction

$$PCl_5\,(gas) \rightleftarrows PCl_3\,(gas) + Cl_2\,(gas) \qquad (XV.2)$$

were examined by Bichowsky and Rossini [813] who calculated the heat effect of this reaction as 21 $\pm$ 2 kcal/mole. New, more accurate measurements of the equilibrium constant of the reaction (XV.2) within the range 422-502°K were carried out by Fischer and Jubermann [1565]. On the basis of the values of the thermodynamic functions of the equilibrium components of the reaction (XV.2), adopted in the Handbook, the value ΔH_0 = 21.45 $\pm$ 0.1 kcal/mole was found. Similar values were obtained by Wilmshurst and Bernstein [4284] and Stevenson and Yost [3864] on the basis of the data of Holland [2106] and Fischer and Jubermann [1565].

The value

$$\Delta H°f_0(PCl_5, gas) = -87 \pm 2 \text{ kcal/mole}$$

adopted in the Handbook, is based on the results of the measurement of the equilibrium constant of the reaction (XV.1). To this corresponds

$$D_0(PCl_5) = 305,121 \pm 2 \text{ kcal/mole}$$

<u>$POCl_3$ (gas)</u>. The results of the measurement of the heat of hydrolysis of liquid $POCl_3$, obtained by several researchers, are used for

the calculation of the heat of formation of $POCl_3$. The first measurements of the heat of hydrolysis of liquid $POCl_3$ were carried out by Berthelot and Louguinine [794] and Thomsen [3981]. The calculations of the heat of formation of liquid $POCl_3$, carried out on the basis of these data in the Handbooks [813, 3508], led to values of -147.1 kcal/mole (at T = 291.15°K) and -151 kcal/mole (at T = 298.15°K), respectively.

Considerably more accurate measurement results on the heat of hydrolysis of liquid $POCl_3$ were obtained by Neale and Williams [3035a] and Charnley and Skinner [1091]. Values of -144.4 and -143.8 kcal/mole were obtained in these works of $\Delta H°f_{298.15}$ ($POCl_3$, liq.). Hence, the mean value $\Delta H°f_{298.15}$ ($POCl_3$, liq.) = -144.1 kcal/mole was adopted in the present Handbook, which in conjunction with $\Delta Hv_{298.15}$ ($POCl_3$, liq.) = 9.5 kcal/mole [3508], leads to the value

$$\Delta H°f_{298.15}(POCl_3, \text{газ}) = -134{,}6 \pm 1 \text{ kcal/mole}$$

adopted in the Handbook. To this corresponds

$$D_0(POCl_3) = 353{,}234 \pm 1{,}5 \text{ kcal/mole}$$

PS (gas). The dissociation energy of the PS molecule has not been determined experimentally. The ratios of the dissociation energies of the molecules No and NS, SiO and SiS, SO and S_2 are 1.25 ± 0.05. Assuming that this ratio also applies to the corresponding diatomic compounds of phosphorus, the authors of the Handbook obtained

$$D_0(PS) = 100 \pm 10 \text{ kcal/mole}$$

The value of $D_0(PS)$ thus determined has been adopted in the Handbook. To it corresponds

$$\Delta H°f_0(PS, \text{газ}) = 40{,}058 \pm 10 \text{ kcal/mole}$$

PN (gas). As aresult of an unreliable interpolation for the levels of the vibrational energy of the ground ($X^1\Sigma$) and excited ($A^1\Pi$) electronic states of the PN molecule, two values were obtained for

D_0(PN), equal to 180 amd 145 kcal/mole. Smaller values were recommended in the monographs of Herzberg [2020] and Gaydon [1668].

The somewhat larger value $D_0(PN) = 152 \pm 7$ kcal/mole is obtained by calculations, based on the use of the heat of combustion of solid phosphorus nitride PN, measured by Wetroff [4226, 4225], ($\Delta Hc_{298.15}$ = = -166.8 ± 0.8 kcal/mole) and the value of its heat of sublimation ($\Delta Hs_{298.15} = 50 \pm 5$ kcal/mole), estimated in the work [416a].

The most accurate values of the thermochemical magnitudes for PN are based on the measurement results of Huffman et a. [2143] on the equilibrium constant of the reaction

$$P_2 (газ) + N_2 (газ) \rightleftarrows 2PN (газ) \qquad (XV.3)$$

within the temperature range of 900–2000°C. The calculations on the basis of the data in the work [2143] lead to values of the heat effect of the reaction (XV.3) $\Delta H_0 = 13.83$ kcal/mole and $D_0(PN) = 163.65$ kcal/mole. Practically the same value for D_0(PN) was obtained in the [2143]; its uncertainty is estimated as ± 1 kcal/mole. On the basis of these calculations

$$D_0(PN) = 164 \pm 1 \text{ kcal/mole}$$

has been adopted in the Handbook, to which corresponds:

$$\Delta H^\circ f_0 (PN, газ) = 23{,}907 \pm 1{,}0 \text{ kcal/mole}$$

TABLE 123

Adopted Values (in cal/mole) of the Thermochemical Values of Phosphorus and its Compounds

Вещество A	Состояние B	D_0	$\Delta H°f_0$	$\Delta H°f_{298.15}$	$\Delta H°f_{298.15}$	$H°_{298.15}-H°_0$	$H°_{298.15}-H°_0$
P	Крист., бел., α	—	0	0	0	1236	1264
P	Газ D	—	75 871	75 591	75 588	1456	1481
P_2	»	116 067	34 685	34 303	34 285	2090	2128
P_4	»	285 733	15 751	14 104	14 073	3297	3378
PO	»	141 809	—7 142	—7 192	—7 200	2206	2244
P_2O_3	»	1 153 731	—498 325	—503 957	—504 000	5432	5606
P_2O_5	»	1 336 380	—569 000	—569 696	—569 948	6208	6406
P_2O_{10}	»	1 570 133	—678 779	—686 940	—687 000	6983	7210
PH	»	70 000	57 003	56 767	56 757	1992	2027
PP	»	105 000	—11 129	—11 322	—11 331	2080	2118
PF_3	»	215 000	—102 629	—103 363	—103 377	2575	2627
PF_3	»	344 533	—213 662	—214 985	—215 000	3023	3092
PF_5	»	479 880	—312 009	—314 974	—315 000	3454	3550
POF_3	»	473 780	—283 902	—285 980	—286 000	3288	3370
PCl	»	9 000	35 921	35 765	35 757	2156	2197
PCl_3	»	3 483	—65 482	—66 197	—66 200	3731	3817
PCl_5	»	305 121	—87 000	—88 291	—88 287	5328	5462
$POCl_3$	»	353 234	—133 226	—134 595	—134 600	4117	4218
PS	»	109 000	40 052	40 184	40 169	2387	2428
PN	»	164 000	23 907	23 697	23 686	2044	2079

A) Substance; B) state; C) cryst., white, α; D) gas.

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[Footnotes]

779* It is possible that one more allotropic modification of phosphorus exists [115] but its properties have not been studied.

779** A systematic review of the literature data on the heats of transformation of the different crystalline modifications of phosphorus is given in the work [347a].

781* The magnitudes of the energy levels of the phosphorus atom have been determined with greater precision in 1959 on the basis of more accurate measurements of the spectrum of monatomic phosphorus in the work [2791]. The energies corresponding to the energy levels 0, 1, 2, 3, 4 of the phosphorus atom (see Table 115), according to the data [2791] are 0: 11360.9; 11376.4; 18722.65; and 18747.95 cm^{-1}, respectively.

782 Some bands of the system $B^1\Sigma_u^+ - X^1\Sigma_g^+$ were observed in absorption in the work [2031].

785 Sreeramamurty [3829a] first observed transitions to lower levels of vibrational energy of the $X^1\Sigma_g^+$ state of the P_2 molecule during a study of the band systym $B^1\Sigma_u^+ - X^1\Sigma_g^+$ in the emission spectrum of P_2. He succeeded in measuring the band edges of this system, corresponding to v' = 1-11 and v" = 0-6. The work [3829a] remained unnoticed in the literature, however, and the data obtained in it were not used for the calculation of the vibrational constants of the P_2 molecule.

787 The values of the following magnitudes were determined (in cm^{-1}) in the work [3747] for the state $X^2\Pi_r$ of the PO molecule: $\Delta G_{1/2}$ = 1220.32; B_e = 0.7348; α^1 = 0.0055; A = 223.99; p = 0.0077.

789* The conclusion to the effect that the upper state of the band system of PO, observed by Rumpf, is the state $^2\Sigma^+$ is also made in the work of Walsh [4146].

789** An incorrect assignment of the type of this electronic state is given in the book of Herzberg [2020] and in the handbook [649], and erroneous values of the vibrational constants, obtained in the work [1235] are given.

794 An unsuccessful attempt to obtain the emission bands of PF, PCl and PBr in a high-frequency discharge spectrum via PF_3, PCl_3 and PBr_3 was made by Howell and Rochester [2139].

795 These bands systems were designamted by Dressler as C → X

and $B \rightarrow X$ systems.

796 The accuracy of the determination of the zero lines of the PN bands with resolved rotational structure in the work [1235] is estimated as ± 0.08 cm^{-1} and for the bands with unresolved rotational structure, ± 0.6 cm^{-1}.

797 The band with the two absorption maxima at 1150 and 1173 cm^{-1} was identified in the work [1903] with the frequency $2\nu_2 + \nu_3$. The assumption has been expressed in the work [3250b] that these bands should be assigned to the frequencies $\nu_1 + 2\nu_3 - \nu_2$ and $2\nu_2 + \nu_3$.

800 In a private communication, the authors of the work [373] agreed to the above-indicated modifications in the interpretation of the infrared spectrum of liquid phosphorus trioxide proposed by them.

805 The force constants of PF_3, calculated on the basis of Eqs. (P4.38) and the values of the basic frequencies of PF_3, quoted in Table 119, are: $f_d = 4.694 \cdot 10^5$, $f_{dd} = 0.5124 \cdot 10^5$; $f_\alpha = 0.8040 \cdot 10^5$ dyne/cm.

809 To the frequencies ν_1, ν_2, ν_3 in the infrared spectra of POF_3 and $POCl_3$ correspond the parallel bands and in the Raman spectra, the polarized bands. To the frequencies ν_4, ν_5, ν_6 in the infrared spectra correspond the perpendicular bands and in the Raman spectra, the depolarized bands.

813* To the frequencies ν_3, ν_4 correspond the parallel bands, and to the frequencies ν_5, ν_6, ν_7, the perpendicular bands of the infrared spectra.

813** After the present chapter had been written, studies of the infrared spectrum of gaseous PF_5 [19a] were carried out at the state Optical Institute. The spectrum of PF_5 was obtained in this study in the region 220-5000 cm^{-1} on an apparatus with slightly greater dispersion than in the works [1904, 3215]. In the longwave region of the spectrum, the band $\nu_7 = 390$ cm^{-1} was observed. Otherwise the measurement results, obtained in the work [19a] are in agreement with the measurements of Gutowsky, Liehr [1904] and Pemsler, Planet [3215]. The authors of the work [19a], in contrast to Gutowsky and Liehr, proposed to assign the bands with the centers 576 and 948 cm^{-1} to the frequencies ν_6 and ν_3, using the assignment of the frequencies ν_4 and ν_5 proposed by Gutowsky and Liehr. The frequencies of the overtones and

the composite frequencies, observed in the infrared spectrum of PF_5 in the work [19a], were not interpreted.

815 This can be inferred on the basis of a comparison of the P-Cl bond length in the molecules PCl_3 and PCl_5 (see Page 806 and 815) and a comparison of the P-F bond length in the PF_3 molecule (see page 806) with the P-F bond length in the PF_5 molecule, found by Braune and Pinnow (see page 815).

817 The results of the researches of Siebert and Schumacher are given in the works [3719,4365].

820 After subtraction of the nuclear components.

839 In particular, this explains the greater value of $S°_{217.78}$ (SO_2F_2, gas) obtained in the work [845a] (see page 648)

840* The work [1325] gives data on the heat capacity of white phosphorus at 50°K, the work [1517] at 137, 233, 282°K and the work [4369] at 273.15-317.35°K. The literature contains indications on the measurements of the heat capacity of white phosphorus by Westrum [1041a] within the range of temperatures 15-320°K and by Morrow and Stephenson [2957] from 15 to 300°K. The results of these measurements have not been published, however.

840** According to the calculations in [435], based on the data of Bridgman [934, 935], the heat of transformation of the β modification of white phosphorus into the α modification at p = 1 atm is 109 cal/g-atom (T_{tr} = 196.3°K) and at p = = 6000 atm 139 cal/g-atom (T_{tr} = 270.8°K). An erroneous value of the last magnitude, equal to 1350 cal/g-atom, is given in the work [935] and in the Handbook [3508].

843 It can be inferred on the basis of the data in the work [2455] that this magnitude relates to phosphorus trioxide in the solid state. Charnley and Skinner [1091], however, relate it to the liquid state.

845 The magnitude ΔHs_{632} = 22.7 ± 0.5 kcal/mole was found in the work [2075]. Recalculation to 298.15°K was carried out by means of the heat capacities of phosphorus pentoxide in the crystalline state, estimated in the work [469].

847 Use was made in the calculations of the values of the heats of formation of $POCl_3$, given in the present Handbook, and of $POBr_3$ [3508]. The heat of sublimation of $POBr_3$ was determined by using various calculation methods discussed in the review [468].