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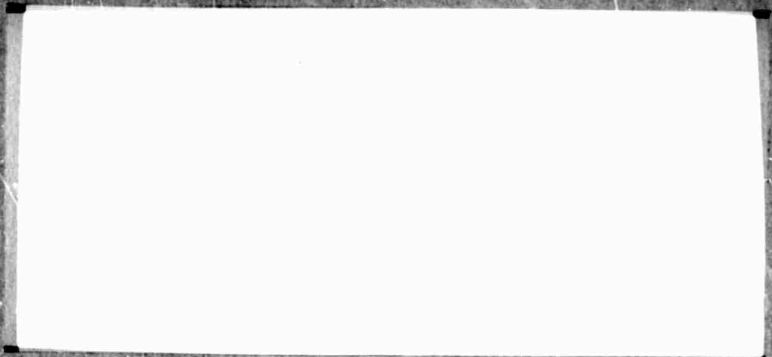


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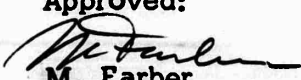
THERMODYNAMICS OF REACTIONS INVOLVING LIGHT METAL OXIDES AND PROPELLANT GASES

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ABSTRACT

The heat of formation of the trimer $(\text{BOF})_3(\text{g})$, which was reported in the preceding Quarterly Report, has been confirmed by transpiration experiments at 1000°K for the reaction $\text{B}_2\text{O}_3(\text{l}) + \text{BF}_2(\text{g}) = (\text{BOF})_3(\text{g})$. Employing the latest available thermodynamic data for the heats of formation of B_2O_3 and BF_3 values for $H_{f298\text{K}} = -567.8 \pm 0.5$ kcal/mole and $S_{298\text{K}} = 89.9 \pm 2$ cal/ $^\circ$ /mole for the trimer $(\text{BOF})_3(\text{g})$ are reported. Employing a new experimental technique, Molecular Flow Reaction Studies, a preliminary heat of formation $H_{f298\text{K}}$ of -145 ± 5 kcal/mole is reported for the monomer BOF.

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THERMODYNAMICS OF REACTIONS INVOLVING LIGHT METAL OXIDES AND PROPELLANT GASES

I. INTRODUCTION

It has been observed that the experimental performance of high energy propellants falls well short of the calculated theoretical performance, particularly in those propellants containing light metals such as aluminum or boron. This discrepancy in performance may very well be due to incorrect thermodynamic assumptions for the theoretical calculations, leading to excessively high predicted theoretical performance.

Such errors could be eliminated, with a resultant saving in time and testing, if more accurate thermodynamic information were available in certain areas. It is the purpose of this program to study the high temperature formation of oxyhalogens of aluminum and boron, such as BOF, $(BOF)_3$, $BOCl$, $AlOF$, and $AlOCl$. There is particular current interest in the gaseous BOF molecule. The formation of these compounds at high temperatures is a definite possibility when B_2O_3 and Al_2O_3 are in contact with the gaseous halogens or halide compounds (1 - 5). The formation of such compounds as exhaust products would influence the performance of the light metal solid propellants considerably. Hence, it is felt desirable to study the formation of these compounds and to measure their thermodynamic properties. It is also anticipated that similar reactions with beryllium oxide might occur and may be investigated after completion of the boron and aluminum studies.

A value for the heat of formation and entropy of the trimer $(BOF)_3$ has been determined by the transpiration method and reported in the preceding Quarterly Report (6). The work reported included a transpiration study of crystalline B_2O_3 with BF_3 in the temperature range of 300 to 500°K. Employing the latest available heats of formation from the National Bureau of Standards (7), the heat of reaction yielded a value of -567.8 kcal/mole for H_{f298K}

and 89.9 cal per degree per mole for S_{298K} . During this report period the transpiration study was extended to a temperature of $1000^{\circ}K$ utilizing liquid B_2O_3 with BF_3 as the transpiring gas. At a total pressure of one atmosphere the trimer $(BOF)_3$ is virtually stable with a negligible amount of dissociation occurring to the monomer. A heat of formation of -566.1 kcal/mole was obtained for $(BOF)_3$ at this temperature, employing theoretical values for the entropy and specific heat of $(BOF)_3$. This value is an excellent check on the "slope" data obtained during the last report period in the lower temperature range.

Partial pressure measurements utilizing BF_3 and argon mixtures have indicated no change in the equilibrium of the thermodynamic constants of the system in the temperature range studied. Evidence obtained from these experiments shows that no appreciable amount of the monomer $BOF(g)$ exists at a reaction pressure of one atmosphere. A study of surface area effects of glassy and crystalline boric oxide was made to determine their effect on the thermodynamic equilibrium.

During the latter part of this report period a new experimental technique, "Molecular Flow Reaction Studies", was developed for determining the thermodynamic data of the monomer. Essentially, this method involves an impinging gas at the temperature of the reaction, striking the reacting material at pressures allowing free molecular flow. Since the accommodation coefficient for temperature is therefore unity, the molecular concentration of new molecules is determined by the equilibrium constant. Upon the completion of the construction of the molecular flow reaction studies apparatus, several experiments were performed in the temperature range 1000 to $1200^{\circ}K$ to obtain a preliminary heat of formation for the monomer BOF . Since these data are preliminary and only a few points have been obtained to date, we shall report an approximate value only of -145 ± 5 kcal for the H_{f298K} of BOF . A more detailed experimental study is now under way and it appears that a definitive value for the heat of formation and the entropy of BOF may be reported shortly.

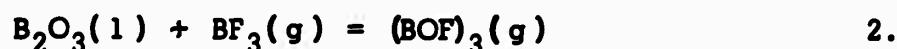
II. THERMODYNAMICS OF TRIMER (BOF)₃

The preceding Quarterly Report (6) disclosed experimental details of transpiration measurements of the equilibrium



The measurements were made over a temperature range of 300 to 500°K and at a total pressure of one atmosphere over the reaction vessel. A heat of reaction ΔH of 8 kcal was obtained for the equilibrium, Eq. 1. Employing the latest thermodynamic data from the National Bureau of Standards (7) of -305.3 kcal/mole for $\text{B}_2\text{O}_3(\text{c})$ and -270.0 kcal/mole for $\text{BF}_3(\text{g})$ at 298°K, a heat of formation, H_{f298K} of -567.8 kcal/mole for $(\text{BOF})_3(\text{g})$ is obtained. (A value of -561.7 kcal for H_{f298K} of $(\text{BOF})_3(\text{g})$ is reported in the 2nd Quarterly Report (6) since values of -300.98 and -268.7 kcal/mole (8, 9) were employed for $\text{B}_2\text{O}_3(\text{c})$ and $\text{BF}_3(\text{g})$ respectively.)

During this report period, transpiration experiments were performed at a temperature of 1000°K to obtain a verification of the lower temperature data. At a temperature of 1000°K and a total pressure of one atmosphere the equilibrium



was studied with several partial pressure mixtures of BF_3 and argon. These included mixtures of (5% BF_3 - 95% A), (10% BF_3 - 90% A), and (30% BF_3 - 70% A). A theoretical check of the equilibrium



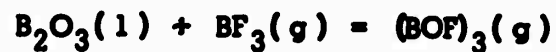
indicates that for an estimated heat H_{f298K} of -150 kcal/mole for the monomer BOF, the equilibrium constant K for Eq. 3 is approximately 10^{-10} at 1000°K and one atmosphere and 10^{-2} at 1500°K and one atmosphere. These calculations

were based on our measured heat of formation and entropy for $(\text{BOF})_3$ and theoretical thermodynamic values reported by Aeronutronic (10), for BOF. Therefore, the assumption that Eq. 2 represents the pertinent equilibrium at 1000°K would appear to be valid.

The experimental data obtained for these measurements employing the partial pressure mixtures reported above, are presented in Table I. A calculation made from this data, which is tabulated in Table II, indicates a heat of formation of -566.1 kcal/mole for $(\text{BOF})_3$ at 298°K . An uncertainty of at least ± 2 kcal for H_f must be attributed to the theoretical values of C_p and S data for $(\text{BOF})_3$ at 1000°K . This is in excellent agreement with the H_f of -567.8 kcal/mole calculated from the slope over a range of temperature (6). Based on these studies, including temperatures from $300 - 1000^\circ\text{K}$, it may be assumed that the value of -567.8 ± 0.5 kcal/mole for $H_{f298\text{K}}$ of $(\text{BOF})_3$ (6) is a definitive one and that a value of 89.9 ± 2 cal/ $^\circ$ /mole for $S_{298\text{K}}$ of $(\text{BOF})_3(\text{g})$ is also definitive.

TABLE I

**Experimental Data on Transpiration Study at a Temperature of 1000°K and
at a Pressure of One Atmosphere of Equilibrium:**



Run #	Gas Mixture	Flow (cc/min)	Time (hr)	$\Delta w/hr$ (mg)
1	5% BF_3 - 95% A	3.4	4	38.0
2	"	"	4	43.7
3	10% BF_3 - 90% A	3.1	1	78.3
4	"	"	2	66.1
5	"	"	2	65.0
6	"	"	7	58.5
7	"	"	4	70.8
8	"	"	4	71.3
9	"	"	25	48.4
10	30% BF_3 - 70% A	3.45	2	152.8
11	"	"	3	50.3
12	"	"	2	212.3
13	"	"	1	214.5
14	"	"	3	173.5
15	"	"	1	167.0
16	"	"	1	226.0
17	"	"	2	199.0
18	"	"	2	185.7
19	"	"	3	161.3
20	"	"	1	151.0
21	"	"	2	49.8

TABLE II

Thermodynamics for the Reaction

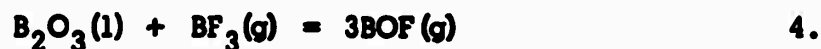


Equilibrium Constant K	11.8
ΔF of reaction at $1000^\circ K$	-4.89 kcal
ΔS of reaction at $1000^\circ K$	7.3 cal/°/mole
ΔH of reaction at $1000^\circ K$	2.4 kcal
ΔH of reaction at $298^\circ K$	4.9 kcal
$\Delta H_f (BOF)_3$ at $298^\circ K$	-566.1 kcal/mole

III. THERMODYNAMICS OF THE MONOMER BOF

A. Introduction

The trimer $(\text{BOF})_3$ is stable at 1000°K and dissociation to the monomer BOF does not appear appreciable below a temperature of 1500°K at pressures of one atmosphere. The study of the reaction,



at pressures approximating an atmosphere, by means of transpiration would have to be made in the temperature range between 1500 to 2000°K in order to obtain an appreciable amount of monomer. (Our transpiration apparatus is constructed with quartz and would need replacement with suitable high temperature materials for experimentation in this range). However, in the temperature range of 1000 to 1500°K the experiments that appear feasible for determination of the thermodynamic properties of the monomer are those that involve low pressure measurements.

As stated in Section II, the equilibrium constant for the dissociation of the trimer to the monomer, Eq. 3, is slight between 1000 and 1500°K at a pressure of one atmosphere. However, the great dependence of this dissociation on pressure is shown by the equilibrium constant

$$K = \frac{27x^3P^2}{(n+2x)^2(n-x)} \quad 5.$$

where x = moles of $(\text{BOF})_3$ dissociating

$n - x$ = moles of $(\text{BOF})_3$ undissociated

$3x$ = moles of BOF formed

P = reaction pressure

Rough calculations employing a value of -150 kcal/mole for H_f of BOF indicates complete dissociation of the trimer at pressures of 10^{-5}

atmospheres at temperatures below 1500°K . Therefore, the study of the reaction, Eq. 4, in the temperature range of 1000 to 1500°K , and at pressures in the micron range of mercury should yield BOF as the main constituent formed with only the formation of negligible amounts of $(\text{BOF})_3$.

Recently Minnesota Mining and Manufacturing Company (11) found that BOF existed as a monomer at 1000°K at very low pressures in a mass spectrometer tube. A mass spectrographic determination of this type is chiefly qualitative and does not lead to accurate measurements of the heat of formation. Aeronutronic (12, 13) has conducted some effusion studies employing a reaction of solid MgF_2 and liquid B_2O_3 in the cell. They report an upper limit for $H_{f298\text{K}}$ of -145 ± 5 kcal for BOF from these measurements. However, no definite evaluation of the extent of solid solution or of the accommodation coefficient has been made.

In order to eliminate some of the experimental problems inherent in the methods described above, a low pressure experiment for the determination of the heat of formation and entropy of BOF has been designed at this laboratory. For lack of a more suitable title, it may be called "Molecular Flow Reaction Studies". A description of the experiment, its theory and the results of some thermodynamic measurements, are discussed in the following sections.

B. Molecular Flow Reaction Studies

1. Theoretical Implications

Early experimenters (14, 15) discovered that rarefied gases do not obey Poisseuille's law of viscous flow. However, Knudsen in 1909 (16) first quantitatively derived and experimentally verified the laws of flow for rarefied gases. These laws are valid when the mean free path of gas molecules exceeds the least cross-sectional dimension of the tube through which gas is flowing. Knudsen's

derivation was based on classical kinetic theory of gases with the additional postulate that gas molecules are reflected from the tube walls according to the cosine law and independently of their direction before impact. In effect, the reflected molecules forget their direction of motion before impact. This generally accepted theory of heat conduction at low gas pressures involves a consideration of the mechanism of energy transfer by individual molecules incident on the hot surface. Knudsen introduced a constant α called the accommodation coefficient, which "can be defined as standing for the fractional extent to which those molecules that fall on the surface and are reflected or re-emitted from it, have their mean energy adjusted or 'accommodated' toward what it would be if the returning molecules were issuing as a stream out of a mass of gas at the temperature of the wall."

If a Maxwellian distribution is assumed, the number of molecules which strike a unit surface per second is

$$\int_0^{\infty} \frac{4n_0}{\sqrt{\pi}} \left(\frac{m}{2kT_1} \right)^{3/2} \left(\exp - \frac{mc^2}{2kT_1} \right) c^3 dc \quad 6.$$

where

- n_0 = number of molecules per cubic centimeter
- m = mass per molecule
- c = velocity of molecule
- k = Boltzmann's constant

The energy incident on unit surface per second is given as

$$\int_0^{\infty} \frac{4n_0}{\sqrt{\pi}} \left(\frac{m}{2kT_1} \right)^{3/2} \left(\exp - \frac{mc^2}{2kT_1} \right) c^3 (1/2 mc^2) dc \quad 7.$$

Integration of Equations 6 and 7 leads to an expression for the mean translational energy E_i of molecules incident on the surface

$$E_i = 2 kT_i \quad 8.$$

and for the number of molecules ν striking a unit area per second,

$$\nu = \left(\frac{n_i kT_i}{2\pi m} \right)^{1/2} \quad 9.$$

or, since $p = nkT$,

$$n_i = \frac{p}{\sqrt{2\pi mkT_i}} \quad 10.$$

It is noted that the mean translational energy per mole for molecules striking a surface is $2 kT$ instead of $3/2 kT$ for the average translational energy of all the molecules, and the total incident energy per unit area per second is $E_i = 2 kT_i$. The assumption that the velocity distribution of the incident molecules is Maxwellian is valid because all the molecules have come into temperature equilibrium with the walls before striking the surface.

Langmuir, (17), further developed the theory to include the conditions that a surface contains a number of "definite sites" and that a molecule striking this surface must remain for a period of time to acquire unit accommodation. (The theory of definite sites is discussed more fully in the Appendix.) In the molecular flow reaction study the impinging gas molecule is at the same temperature of the medium with which it may react. Therefore, no "sticking" time (i.e. unit temperature accommodation is achieved) is necessary for attainment of the equilibrium temperature as in the Langmuir type of experiment. Likewise, in the Knudsen effusion experiment, flow through the orifice may cause a

breakdown in the equilibrium pressure over the reactants in the cell, resulting in an accommodation coefficient of less than unity. Again, this is not the case for the molecular flow reaction and the pressure is maintained constant at all times over the reaction assuring unit accommodation. Therefore, the molecular flow reaction consists of a gas at a temperature T and pressure P impinging on a reacting medium at the same temperature T . The number of molecules leaving the surface unaltered, or those which react with the surface, is determined by the equilibrium constant,

$$K = e^{\frac{-\Delta H}{RT}} e^{\frac{\Delta S}{R}} \quad 11.$$

where the entropy term may be construed to represent the probability of reaction. This presumes, of course, that the mean free path is large enough (order of diameter of tube, 2-3 cm) to insure that collisions do not occur in the gas phase. Also, that the molecule formed in the reaction is not effected in an elastic collision with an inert wall. The calculation for the mean free path L can be made from critical constants as

$$L = \frac{2.33 \times 10^{-20} T}{p \delta^2} \quad 12.$$

where p is given in mm of Hg and δ is calculated from critical constants

$$\text{as } \delta = \frac{3b}{2\pi N} \quad , \text{ and} \quad 13.$$

$$b = \frac{RT_C}{8P_C} \quad 14.$$

T_C , P_C are the critical constants for temperature and pressure.

The number of molecules of incident gas striking a unit area of reacting surface is given by Eq. 10. For the equilibrium under consideration (Eq. 4) the following expressions lead to a derivation of the equilibrium constant:

let n_{BOF} = moles of BOF that leave the reaction zone in one hour and collected.

n'_{BOF} = moles of BOF formed or colliding with the reaction surface per hour.

$$n' = \frac{P_{\text{BOF}} (3600) A}{\sqrt{2 \pi N k T M_{\text{BOF}}}} \quad 15.$$

P_{BOF} = partial pressure of BOF

M_{BOF} = molecular wt of BOF

N = Avagadros number

A = Area of reacting surface

n_{BF_3} = moles of BF_3 that leave the reaction zone in one hour and collected

n'_{BF_3} = moles of BF_3 that strike the reaction surface per hour

$$n'_{\text{BF}_3} = \frac{P_{\text{BF}_3} (3600) A}{\sqrt{2 \pi N k T M_{\text{BF}_3}}} \quad 16.$$

P_{BF_3} = partial pressure of BF_3

M_{BF_3} = molecular weight of BF_3

$n_{\text{BOF}} / n'_{\text{BOF}}$ = Ratio of molecules collected to those formed and which enter the reaction zone during one hour.

$n_{\text{BF}_3} / n'_{\text{BF}_3}$ = Ratio of molecules collected to those striking the reaction surface in one hour.

The ratio of escape is independent of the type of molecule and depends only on length of reaction zone and pumping speed. (Similar to analogy of molecules effluxing through an orifice in an effusion cell) or

$$n'_{\text{BOF}} / n'_{\text{BF}_3} = n_{\text{BOF}} / n_{\text{BF}_3} \quad 17.$$

and substituting for n'_{BOF} and n'_{BF_3}

$$\frac{P_{\text{BOF}} A (3600)}{\sqrt{2\pi NkT} M_{\text{BOF}}} = \frac{P_{\text{BF}_3} A (3600)}{\sqrt{2\pi NkT} M_{\text{BF}_3}} \times \frac{n_{\text{BOF}}}{n_{\text{BF}_3}} \quad 18.$$

which yields

$$\sqrt{\frac{P_{\text{BOF}}}{M_{\text{BOF}}}} = \frac{n_{\text{BOF}}}{n_{\text{BF}_3}} \times \sqrt{\frac{P_{\text{BF}_3}}{M_{\text{BF}_3}}} \quad 19.$$

The total pressure P_D in dynes per sq. cm. over the reaction zone is

$$P_D = P_{\text{BOF}} + P_{\text{BF}_3} \quad 20.$$

Now, substituting Eq. 20 into Eq. 19, the following is obtained for the partial pressure,

$$P_{\text{BOF}} = \frac{\left(\frac{M_{\text{BOF}}}{M_{\text{BF}_3}}\right)^{1/2} \frac{n_{\text{BOF}}}{n_{\text{BF}_3}} P_D}{1 + \left(\frac{M_{\text{BOF}}}{M_{\text{BF}_3}}\right)^{1/2} \frac{n_{\text{BOF}}}{n_{\text{BF}_3}}} \quad 21.$$

and substituting Eq. 21 into Eq. 20 yields for the partial pressure,

$$P_{\text{BF}_3} = \frac{P_D}{1 + \left(\frac{M_{\text{BOF}}}{M_{\text{BF}_3}}\right)^{1/2} \frac{n_{\text{BOF}}}{n_{\text{BF}_3}}} \quad 22.$$

and substitution of these values for the partial pressures after conversion of partial pressures from dynes to atmospheres in the expression for the equilibrium constant

$$K_p = \frac{(P_{\text{BOF}})^3}{P_{\text{BF}_3}} \quad 23.$$

or

$$K_p = \frac{\left(\frac{M_{\text{BOF}}}{M_{\text{BF}_3}}\right)^{3/2} \left(\frac{n_{\text{BOF}}}{n_{\text{BF}_3}}\right)^3 (P_A)^2}{\left[1 + \left(\frac{M_{\text{BOF}}}{M_{\text{BF}_3}}\right)^{1/2} \left(\frac{n_{\text{BOF}}}{n_{\text{BF}_3}}\right)\right]^2} \quad 24.$$

2. Experimental Procedure

The molecular flow reaction studies were made in the transpiration

apparatus which was modified as shown in Figure 1. Leaks allowing pressures in the neighborhood of 10^{-5} atmospheres were constructed and calibrated at an absolute rate with a McLeod Gauge. The unreacted flow gas, BF_3 , and the BOF formed during the reaction were collected in a liquid nitrogen trap and analyzed at the conclusion of each experiment. The boat containing the B_2O_3 was weighed after each run for verification of the quantity of B_2O_3 reacting during the experiment. The incoming gas was heated to the experimental temperature by its passage over a bed of quartz beads thereby insuring a constant reaction temperature. Purification of reaction materials and analysis procedures were described in the preceding Quarterly Reports (6, 18).

3. Heat of Formation of BOF

In order to check the experimental apparatus and to establish the theoretical conceptions presented in the preceding Section III, B, 1., a few experiments were performed during the remaining few days of this report period. Seven runs were made at three temperatures, 1000, 1100 and 1200°K. At these temperatures leaks were chosen to yield a pressure of approximately 10^{-5} atmospheres. Time would not permit the study of several leaks at a given temperature in order to completely validate the theory. The experimental data obtained for these seven runs are presented in Table III. The theoretical value for ΔS of the reaction at 1000°K is 75.3 entropy units; while the theoretical value for ΔS at 1200°K is 73.8 entropy units (data taken from Aeronutronic Report (10). The theoretical difference in $T\Delta S$ between 1000°K and 1200°K is 13.2 kcals. The experimental data obtained in our preliminary experiments indicate a spread of 13.0 kcals for this temperature range. This would seem to indicate the constant value for the ΔH of reaction in this temperature range. A plot of the logarithm of the calculated value for the

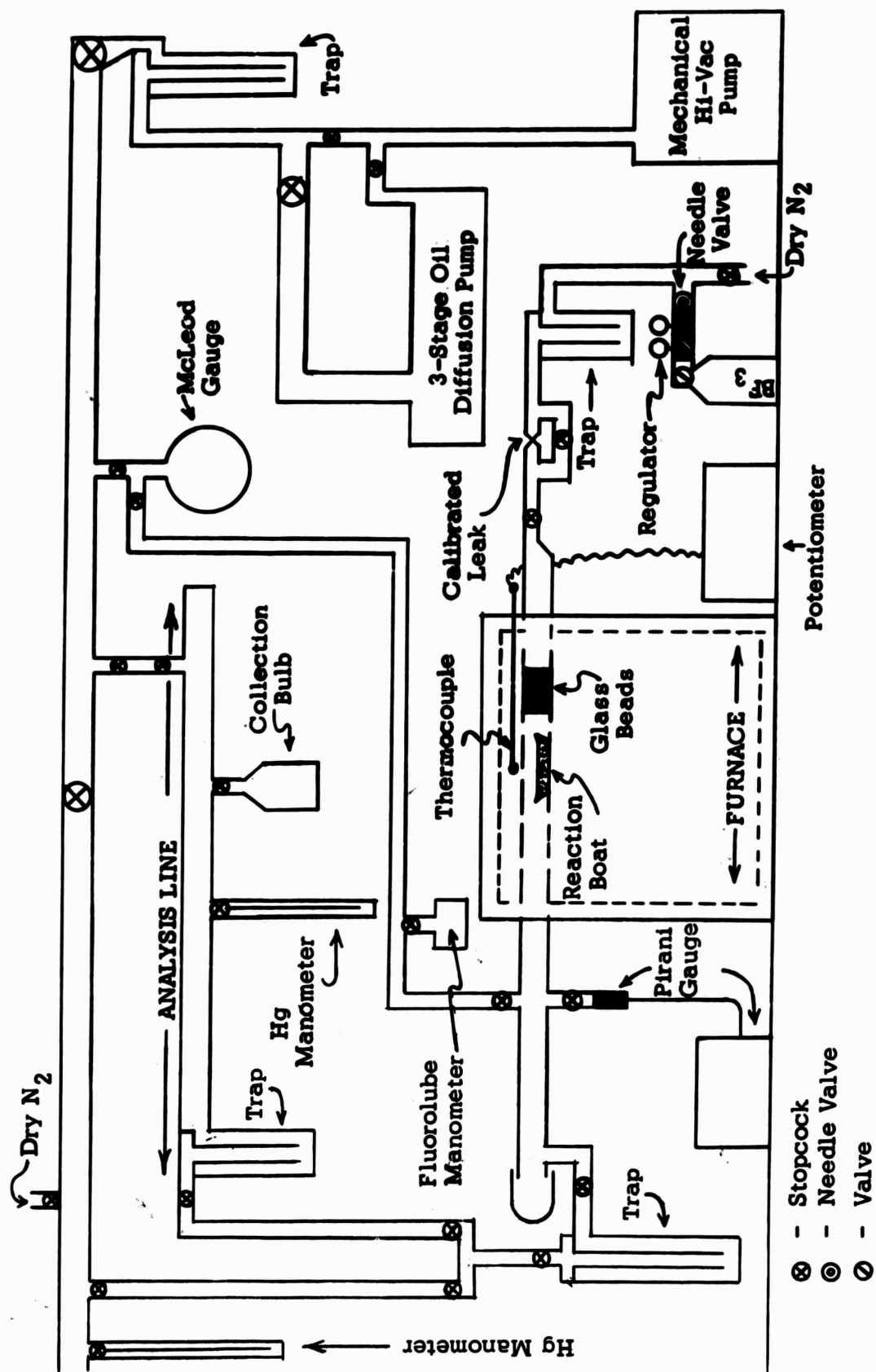
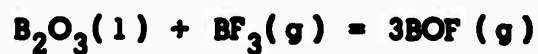


Fig. 1 Schematic Diagram of Molecular Flow Reaction Apparatus

TABLE III**PRELIMINARY Data for Molecular Flow Reaction Study of Equilibrium**

Leak Number	Temp °K	Pressure BF ₃ (atm)	Weight Loss B ₂ O ₃ moles/hr	Flow of BF ₃ moles/hr	K _p	ΔF kcal
V	1000	4.35 × 10 ⁻⁵	1.87 × 10 ⁻⁵	6.25 × 10 ⁻⁴	7.63 × 10 ⁻¹³	55.4 58.9
VI	1000	1.48 × 10 ⁻⁵	2.4 × 10 ⁻⁶	1.2 × 10 ⁻⁴	2.64 × 10 ⁻¹⁴	62.0
VI	1100	1.48 × 10 ⁻⁵	3.02 × 10 ⁻⁵	1.2 × 10 ⁻⁴	2.24 × 10 ⁻¹¹	53.5
VI	1100	1.48 × 10 ⁻⁵	2.3 × 10 ⁻⁵	1.2 × 10 ⁻⁴	1.77 × 10 ⁻¹¹	54.0
VI	1200	9.87 × 10 ⁻⁶	6.62 × 10 ⁻⁵	1.2 × 10 ⁻⁴	1.67 × 10 ⁻¹⁰	53.5
VI	1200	1.52 × 10 ⁻⁵	6.62 × 10 ⁻⁵	1.2 × 10 ⁻⁴	3.98 × 10 ⁻¹⁰	51.5
VI	1200	1.30 × 10 ⁻⁵	9.82 × 10 ⁻⁵	1.3 × 10 ⁻⁴	1.13 × 10 ^{-10⁹}	49.0

equilibrium constant K for Eq. 4, versus the reciprocal of the absolute temperature for these preliminary data are shown in Figure 2. Since these are preliminary data, it would be premature to present a definitive value of the heat of formation and entropy of BOF. However, the rough slope obtained from these data, as calculated from the van't Hoff equation,

$$\ln K_2 - \ln K_1 = - \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad 25.$$

is approximately 130 kcal in this temperature range. Employing the theoretical entropies and enthalpies for the reactants (10) a value of approximately -145 ± 5 kcal/mole is obtained for the H_{f298K} for the monomer BOF. No attempt to calculate the entropy is made at this time and should await further experiments. The preliminary value of -145 kcal/mole for H_{f298K} of BOF seems to agree with that expected from calculations based on estimates for the heat of polymerization of the trimer.

IV. FUTURE WORK

A detailed experimental evaluation of the reaction, $B_2O_3(l) + BF_3(g) = 3BOF(g)$, will be made in a temperature range of 1000 - 1500°K by means of the molecular flow reaction method. This should yield improved data for the H_f and S of the monomer BOF.

If time permits, experimental studies will be initiated to determine the thermodynamic properties of other high temperature molecules which are mentioned in the Introduction of this Report.

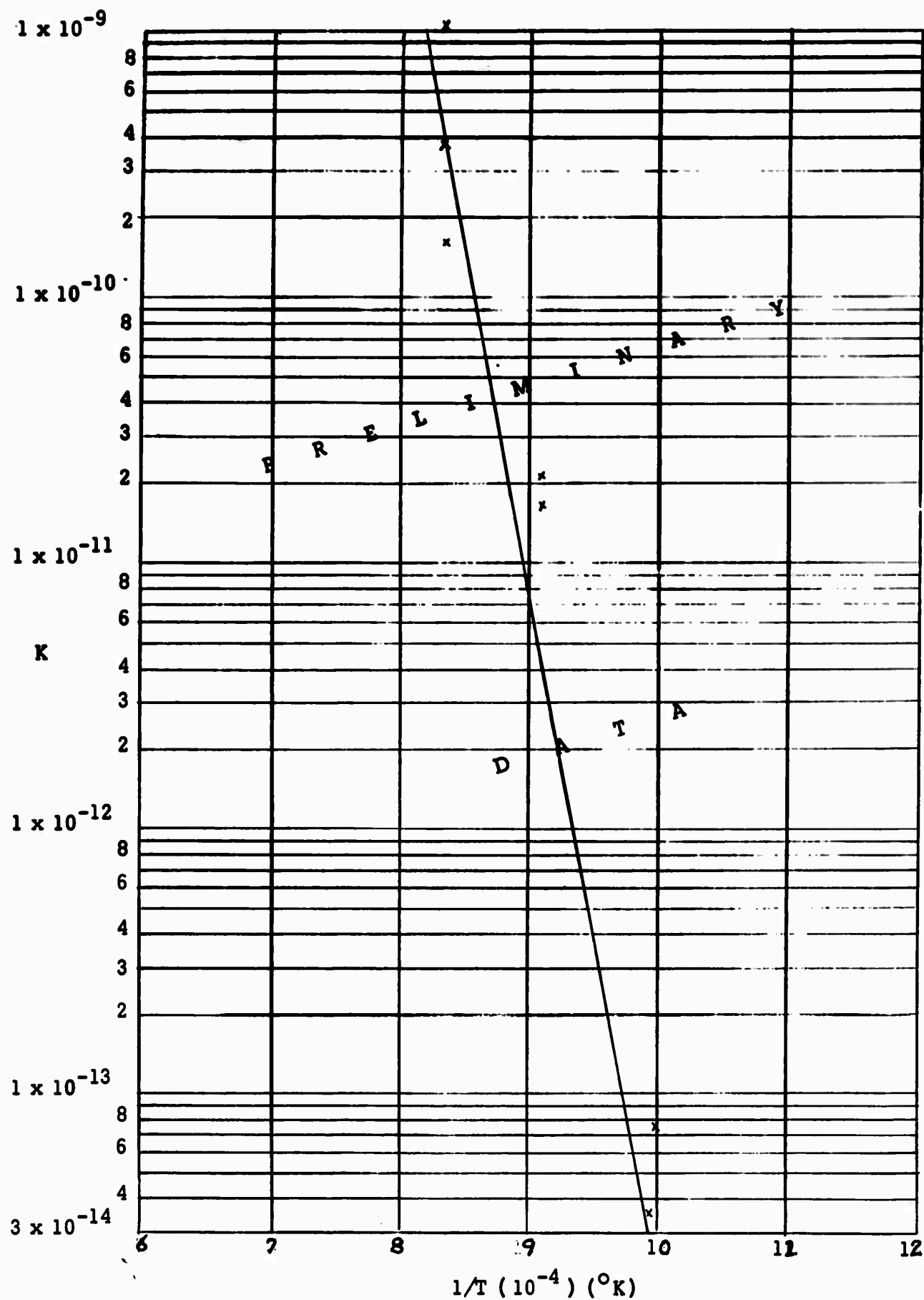


Fig. 2 The logarithm of K for the equilibrium $\text{B}_2\text{O}_3 (l) + \text{BF}_3 (g) = 3\text{BOF} (g)$ as a function of $1/T$.

APPENDIX

THEORETICAL CONSIDERATIONS FOR THE ACCOMMODATION COEFFICIENT

Some theoretical considerations of the accommodation coefficient are presented in this Appendix to support the theory of molecular flow reaction and to substantiate the use of unit accommodation for the experimental studies presented in the body of this report. The accommodation coefficient has had extensive study by Langmuir for both the Knudsen type of experiment (19) and the Langmuir hot wire experiment (17). The accommodation coefficient for molecules with an energy corresponding to a temperature somewhat lower than the temperature at which they react has been defined by Langmuir (17) as the ratio of molecules that leave the surface with a mean energy corresponding to the temperature of the surface to those that are incident upon the surface. Based on this theory, the temperature accommodation coefficient equals unity when the incident gas is at the temperature of the surface as is the case in the molecular flow reaction study described in Section III of this report.

Langmuir (17) further discusses in this theory of "definite sites", the accommodation of atoms or molecules on a surface. He states the surface atoms of a solid are held to the atoms in the interior by forces similar to those acting between the atoms inside the solid. But in the surface layer, because of the asymmetry at the boundary, the arrangement must always be somewhat different from that in the interior. These surface atoms are unsaturated chemically and thus have a strong field of force surrounding them. (The effective range is usually less than the diameter of the molecule.) From other considerations Langmuir concluded that, when gas molecules strike a solid or liquid surface, they condense on the surface because of the force field of the surface atoms. They may later evaporate from the surface but, in general, do not rebound elastically. The length of time between condensation and evaporation depends on the intensity of the surface forces. If the forces are strong, evaporation will be slow, and the surface of the solid will become saturated with a layer of the absorbed

gas. If the forces are weak, evaporation may occur so soon that only a small fraction of the surface will be covered at any instant. Since the range of the surface forces is small, the adsorbed molecules usually orient themselves in definite ways or on definite sites in the surface layer because they are held in position by forces acting between the surface atoms and particular atoms or groups of atoms in the molecule. It is apparent that the greater the surface area included in a given solid angle from a point outside the surface, the greater the number of positions on the surface which are attractive to the incident molecules. Thus more molecules will be condensed and evaporated per unit time, and the accommodation coefficient will be increased. It has been shown experimentally that the accommodation coefficient for a surface with a film of adsorbed gases is substantially larger than for a surface free from such a film. The latter condition (i.e., surface free from film) may be obtained by using a metal and a gas (for example, helium and platinum) which give rise to only weak surface forces; thus the molecules which condense on the surface evaporate rapidly, leaving only a small fraction of the surface covered by adsorbed molecules. Since it has been observed by Roberts (20), Mann (21), and others that the accommodation coefficient increases with time over the value for a clean surface, it may be assumed that this time effect results from the rate at which the molecules become adsorbed on the surface. Of course, the temperature of the surface and the pressure of the gas are important in determining the time required for this adsorption. If there are impurities in the gas, they will alter the situation also.

If the adsorption theory fits the physical situation, one might eliminate the surface forces almost entirely by allowing a gas with chemical affinity for the solid to form a monolayer at the surface in order to saturate chemically the surface atoms. If some comparatively inert gas were admitted, the surface forces originally causing condensation of the gas would be smaller, and evaporation would occur faster. Thus the molecules actually taking energy away from the surface (the inert gas) would not reside on the surface long enough to effect a very great energy transfer, and the accom-

modation coefficient would be expected to be quite small. This fact appears to be borne out in several instances. Langmuir (19) measured an α of hydrogen on bare tungsten as 0.5 at a filament temperature of 1200°K and pressure of 0.20 mm Hg, and α dropped to 0.09 when the tungsten had an adsorbed film of oxygen on it. Mann (21) noted later that an oxygen-treated platinum wire gave lower values of α with respect to helium than were obtained with pure platinum. The accommodation coefficient for pure platinum was about 0.05 and for oxygen-treated platinum, 0.035.

The available theory of definite sites nearly always dealt with an incident gas at a temperature lower than that of the surface. Since the adsorbed gases cause α to increase with time, the value of α for a clean surface is very difficult to measure directly because of the lag from the time the gas is admitted to the bulb to the time the readings are actually taken. The variation with time, however, can be made quite small by using very pure gas and operating at low pressures so that the rate of adsorption is quite slow. In this case a linear extrapolation to zero time is possible. Unless variation with time is almost negligibly small, this method is open to objection on the grounds that the extrapolation is being made over a period when α is changing most rapidly. Some of the uncertainties may be removed by considering the process by which adsorption takes place. If it is assumed that a certain number of available sites are uniformly distributed over the surface of the filament, the probability of capture of a gas atom in unit time is proportional to A_1 where

A_1 = number of unfilled sites on surface at any time t

A_0 = total number of sites at $t = 0$

therefore

$$-\frac{dA_1}{dt} = KA_1 \quad A_1$$

and

$$t = \frac{1}{K} (\ln A_1 + \ln C) \quad A 2$$

At the boundary conditions at $t = 0$ and $A_1 = A_0$

$$0 = \frac{1}{K} (\ln A_0 + \ln C) \quad A 3$$

then

$$t = \frac{1}{K} \ln (A_0/A_1) \quad A 4$$

In filling all the available sites A_0 , α will change from the initial value α_0 to a final value α_{∞} ; and in filling all the available sites A_1 at time t , α varies from α to α .

Therefore one may write

$$K t = \ln \frac{\alpha_{\infty} - \alpha_0}{\alpha_{\infty} - \alpha} \quad A 5$$

Since α_{∞} and $\alpha(t)$ may be measured, the exponential formula may be fitted to the data to obtain α_0 . Michels (22), using data given in an early paper by Roberts (23) in which α did not vary linearly with time, used a formula of this type to obtain α_0 . The values obtained by this extrapolation agreed with those obtained in later and better experiments by Roberts when the drift with time was negligibly small. Michels reports that, in practice, the linearity of the curve is extremely sensitive to the value of α_{∞} , and small adjustments of this quantity are sometimes necessary. However, in no case tried thus far has it been necessary to use a value which departs more than 2 or 3 per cent (a limit well within the experimental accuracy) from that obtained after heat losses seemed

and

$$t = \frac{1}{K} (\ln A_1 + \ln C) \quad A 2$$

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In filling all the available sites A_0 , α will change from the initial value α_0 to a final value α_∞ ; and in filling all the available sites A_1 at time t , α varies from α to α .

Therefore one may write

$$K t = \ln \frac{\alpha_\infty - \alpha_0}{\alpha_\infty - \alpha} \quad A 5$$

Since α_∞ and $\alpha(t)$ may be measured, the exponential formula may be fitted to the data to obtain α_0 . Michels (22), using data given in an early paper by Roberts (23) in which α did not vary linearly with time, used a formula of this type to obtain α_0 . The values obtained by this extrapolation agreed with those obtained in later and better experiments by Roberts when the drift with time was negligibly small. Michels reports that, in practice, the linearity of the curve is extremely sensitive to the value of α_∞ , and small adjustments of this quantity are sometimes necessary. However, in no case tried thus far has it been necessary to use a value which departs more than 2 or 3 per cent (a limit well within the experimental accuracy) from that obtained after heat losses seemed

reasonably steady.

The effect of the surface roughness was determined by Knudsen by measuring α first on a smooth platinum surface, then on a surface slightly coated with platinum black, and finally on a surface heavily coated with platinum black. The increase in surface roughness gave rise to an increase in α . This experiment was carried out for several gases, and the same trend was noted.

Roberts (20), using a tungsten wire in a bulb containing helium at a pressure of about 0.10 mm Hg, observed a decided increase in α on prolonged heating of the wire. He attributed this increase to the increase in surface roughness resulting from heating the wire. For a clean filament, that is, one which had been flashed at a temperature of about 2000°C to remove adsorbed gases from the surface, the α increased from 0.07 to 0.18. For a filament with adsorbed gases on the surface the accommodation coefficient increased from 0.19 to 0.55. It is reasonable that the increases in surface area which accompany increased surface roughness should allow greater exchange of energy of the gas molecules with the surface. Roberts (20) supposes that an incoming molecule may strike in a valley of the surface and be reflected from one surface to another before leaving. Using this simple notion and the data just given, he derived an empirical expression which predicts the number of times a molecule should strike the surface to give the observed α . His concept of molecularly rough surface is sometimes useful, i.e., a surface which gives $\alpha = 1$, (which would appear as reasonable for a liquid surface consisting of reacting material).

REFERENCES

- (1) Baumgarten, P. and Bruns, W., Ber. 72B, 1753, (1939) and Ber. 74B, 1232 (1941).
- (2) Ramser, H. and Wiberg, E., Ber., 63B, 1136 (1930).
- (3) Wiberg, E. and Sutterlin, W., Z. anorg. allgem. Chem. 202, 1, (1931).
- (4) Menzel, W. and Froehlich, M., Ber. 75B, 1055 (1942).
- (5) Goubeau, J. and Keller, H., Z. anorg. u. allgem. Chem., 267, 1 (1951).
- (6) Farber, M., et al, "Thermodynamics of Reactions Involving Light Metal Oxides and Propellant Gases", Rocket Power, 2nd Quarterly Report, QR-1987-2, ARPA, Aug - Nov. 1960.
- (7) Evans, W., "Thermodynamic Properties of Some Boron Compounds", National Bureau of Standards Report #4943, August 31, 1956; and Evans, W., "Thermochemistry and Thermodynamic Functions of Some Boron Compounds", National Bureau of Standards Report #6252, December 15, 1958.
- (8) Dobbins, T.O., "Thermodynamics of Rocket Propulsion and Theoretical Evaluations of Some Prototype Propellant Combinations", WADC Report TR-59-757, December 1959.
- (9) Private communication of late work in August 1960, by Professor John Margrave, University of Wisconsin.
- (10) Hildenbrand, D.L., "Study of Metal Additives for Solid Propellants", Aeronutronic Publication No. C-623, September 30, 1959.
- (11) Minnesota Mining and Manufacturing Company, Report No. 5, April - June 1960, SPIA File No. S 60-1115, Contract NOrd 18688.
- (12) Hildenbrand, D.L., "An Experimental Program for Obtaining the Thermodynamic Properties of Propellant Combustion Products", Aeronutronic, 1st Quarterly Report, U-985, ARPA, September 15, 1960.
- (13) Hildenbrand, D.L., "An Experimental Program for Obtaining the Thermodynamic Properties of Propellant Combustion Products", Aeronutronic, 2nd Quarterly Report, U-1085, ARPA, December 15, 1960.
- (14) Kundt, A. and Warburg, E., Pogg. Ann. 155, 337 and 525 (1875).
- (15) Warburg, E., Pogg. Ann. 159, 399 (1876).

- (16) Knudsen, M., Ann. Physik, 28, 75 (1909)
- (17) Langmuir, I., IACS, 40, 1361 (1918).
- (18) Rocket Power, First Quarterly Report for May - Aug 1960, QR-1987-1, ARPA, "Thermodynamics of Reactions Involving Light Metal Oxides and Propellant Gases".
- (19) Blodgett, K. B., and Langmuir, I., "Accommodation Coefficient of Hydrogen, " Physical Review, 40, 78-104, (1932).
- (20) Roberts, J.K., "The Exchange of Energy Between Gas Atoms and Solid Surfaces," Proceedings of the Royal Society (London), A129, 146-161 (1930); A135, 192, (1932); A142, 518-524, (1933).
- (21) Mann, W. B., "The Exchange of Energy Between a Platinum Surface and Gas Molecules", Proceedings of the Royal Society (London), A146, 776-791, (1934).
- (22) Michels, W. C., "Accommodation Coefficients of Helium and Argon Against Tungsten, " Physical Review, 40, 472, (1932).
- (23) Roberts, J. K., "The Adsorption of Hydrogen on Tungsten", Proceedings of the Royal Society (London), A152, 445-480, (1935).

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