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TECHNICAL REPORT ON
APPROXIMATE THERMODYNAMIC FUNCTIONS
FOR THE $\text{H}_3\text{O}^+(\text{g})$, $\text{HCO}^+(\text{g})$, AND $\text{CH}_3^+(\text{g})$ IONS

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CONTRACT NO. DA-04-495-ORD-3567(Z)
HYPERVELOCITY RANGE RESEARCH PROGRAM
A PART OF PROJECT "DEFENDER"



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GENERAL MOTORS CORPORATION

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APPROXIMATE THERMODYNAMIC FUNCTIONS
FOR THE $\text{H}_3\text{O}^+(\text{g})$, $\text{HCO}^+(\text{g})$, AND $\text{CH}_3^+(\text{g})$ IONS,

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FOREWORD

This report is one of a series of related papers covering various aspects of a broad program to investigate the flow-field variables associated with hypersonic-velocity projectiles in free flight under controlled environmental conditions. The experimental research is being conducted in the Flight Physics Range of GM Defense Research Laboratories, General Motors Corporation, and is supported by the Advanced Research Projects Agency under Contract No. DA-04-495-ORD-3567(Z). It is intended that this series of reports, when completed, will provide a background of knowledge of the phenomena involved in the basic study and thus aid in a better understanding of the data obtained in the investigation.

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ABSTRACT

Approximate values for the free-energy function, enthalpy function, entropy, and constant-pressure heat capacity have been calculated for the ions $\text{H}_3\text{O}^+(\text{g})$, $\text{HCO}^+(\text{g})$, and $\text{CH}_3^+(\text{g})$. A structural analysis of the ions based upon chemical valence considerations leads to the estimation and assignment of the spectroscopic constants, which are then used for the statistical thermodynamic calculations.

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SECTION I

INTRODUCTION

Any attempts at interpretation of the observables of a vehicle reentering the atmosphere or of the observables recorded in free-flight ranges require consideration of the coupling of the chemistry and gas dynamics of the system. Generally, the chemistry involves high-temperature air which may or may not be contaminated with additives introduced by ablation of the projectile. This chemical system is quite comparable to the chemical systems of flames, which have received considerable attention over the years; consequently, much recourse to the basic technology and analysis of flame chemistry is made. Observations of the reentry systems cover a broad band of the electromagnetic spectrum - radio, radar, infrared, optical, and ultraviolet waves - upon which ionization of the gaseous system has marked effects; therefore, closer analysis of ionic species and attendant chemical reactions is warranted.

Mass spectrometric studies of flames^{(1, 2, 3)*} show that there is ionization in most hydrocarbon systems, and many of the ions have been identified; for example, H_3O^+ , HCO^+ , CH_3^+ , C_2H_2^+ , C_3H_3^+ , and others. Very few, if any, tabulated values for the thermodynamic functions for these species exist; however, some reasonable values for the heats of formation of many have been provided by electron impact experiments. Two compilations and reviews of this latter data are given by Field and Franklin⁽⁴⁾ and Bernecker and Long.⁽⁵⁾ Knowledge of the thermodynamic functions and the heats of formation permit computations of equilibrium constants and the expected equilibrium concentrations of species for reactions of interest, which in turn are useful in the study of the kinetic behavior of the system.

* Raised numbers in parentheses indicate references, listed at the end of this report.

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In the work presented here analysis is made of the probable structure for some of these species from valence-bonding considerations, and consequent deductions from these structures give approximate values for the spectroscopic constants such as the fundamental vibrational frequencies, symmetry number, lowest-lying electronic state, and moments of inertia. These approximate constants are then used in the rigid-rotator harmonic-oscillator partition function relationships to generate the ideal-gas free-energy and enthalpy functions, the entropies, and the constant-pressure heat capacities over a range of temperatures.

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SECTION II

THE $\text{H}_3\text{O}^+(\text{g})$ ION

The stability of $\text{H}_3\text{O}^+(\text{g})$ may be explained by assuming that a proton H^+ , which is electron deficient, is attached to an H_2O molecule by sharing the electrons in the O atom $2p_z$ orbital which is perpendicular to the plane of the H_2O molecule. This gives a pyramidal molecular configuration similar to that of NH_3 , PH_3 , and AsH_3 , where there are three shared pairs and one unshared pair of electrons. The resulting H-O-H bond angles are expected to be greater than 90° as in the case of NH_3 , due to mutual repulsion of the H atoms or because of partial hybridization of the bonds. ^(6a, 7) Extension of this reasoning for the model allows the following approximations.

The O-H bond distance is shortened over that obtained from the addition of covalent bond radii because of the electric-charge effect. Use of the correction as proposed by Pauling ^(6b) gives an O-H distance of 0.95 Å.

The H-O-H bond angle may be approximated by extrapolation of a plot of bond length versus bond angle in radians for NH_3 and PH_3 to the assumed O-H bond length of 0.95 Å. This gives H-O-H equal to about 109° when the values of $106^\circ 47'$ and 1.014 Å for NH_3 and 99° and 1.40 Å for PH_3 are used. ^(8a)

Utilization of the NH_3 model ^(8b) for the calculation of the moments of inertia for $\text{H}_3\text{O}^+(\text{g})$ gives $I_C = I_B = 2.45 \times 10^{-40}$, and $I_A = 4.00 \times 10^{-40} \text{ gm cm}^2$.

An approximate value for the stretching force constant may be obtained from Badger's ⁽⁹⁾ empirical relationship between interatomic distance and the stretching force constant for diatomic molecules, $k_o = 1.86 \times 10^5 / (R - d_{ij})^3$ (where k_o is in dynes/cm, R is the O-H distance in Å, and d_{ij} is a constant with a value of 0.34 for H and a first-row element of the periodic table). For the $\text{H}_3\text{O}^+(\text{g})$ ion, $k_o = 8.19 \times 10^5 \text{ dynes/cm}$.

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Detailed analysis of the nonplanar XY_3 -type molecules assuming valence forces has been made by Herzberg.^(8c) The force constants for the vibrational modes were calculated analytically from the observed fundamental vibrational frequencies, with two values resulting for the "bending" force constant, k_δ/ℓ^2 , for each molecule considered. The two values were almost equal, the inequality being dependent upon which combination of input frequencies was chosen. The mean of the two values obtained for NH_3 and similarly for PH_3 were used in the following procedure. Extrapolation of a plot of the respective mean value of k_δ/ℓ^2 versus the product of the appropriate interatomic distance and the Y-X-Y bond angle in radians to the corresponding coordinate for the assumed $H_3O^+(g)$ parameters gives $k_\delta/\ell^2 = .54 \times 10^5$ dynes/cm for $H_3O^+(g)$.

Application of the analytical expressions as given by Herzberg⁽⁸⁾ for the valence force treatment of nonplanar XY_3 molecules to the $H_3O^+(g)$ structure, using the stretching and bending force constants of $k_0 = 8.19 \times 10^5$ and $k_\delta/\ell^2 = .54 \times 10^5$ dynes/cm respectively, gives the approximate fundamental vibrational frequencies of $\nu_1 = 3760$, $\nu_2 = 1050$, $\nu_3 = 3870$, and $\nu_4 = 1550$, in cm^{-1} , where the ν_3 and ν_4 are doubly degenerate as found for the NH_3 .

With the assumption that the ground electronic state of $H_3O^+(g)$ is a singlet (no unpaired electrons) and neglecting any excited electronic states, the total partition function is given by Equation (1).

$$Q = Q_{tr} Q_r Q_v = V(2\pi m k T/h^2)^{3/2} (\pi/B^2 A)^{1/2} (k T/hc)^{3/2} / \sigma \prod_{i=1}^4 \left((1 - \exp(-\omega_i hc/kT)) \right)^{d_i} \quad (1)$$

where the symbols are those defined by Herzberg.^(8d) The symmetry number σ is three, the rotational partition function is the classical value for a rigid symmetric top, and the vibrational partition function is that for a harmonic oscillator.

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The values for the thermodynamic functions, listed in Table I, were obtained by using Equation (1), the parameters quoted above, and the usual relationships between the partition function and the thermodynamic functions; the values for the fundamental constants used were those that have recently been adopted by the National Bureau of Standards⁽¹⁰⁾ with $R = 1.98717 \text{ cal/mole } ^\circ\text{K}$.

To see what effect variations in the input parameters A, B, and the ν_i 's of Equation (1) would have on the tabulated quantities, these parameters were varied separately by $\pm 10\%$. The enthalpy function and heat capacity are independent of changes in A and B; yet $\pm 10\%$ changes in A and B cause a maximum variation of $\mp .5\%$ at 300°K in the entropy and free-energy functions, with this variation decreasing as the temperature increases. Variations of $\pm 10\%$ in ν_1 or ν_2 give about the same maximum variations of $\mp .25\%$ in both the free-energy function and the entropy; similarly, $\pm 10\%$ in ν_3 and ν_4 give maximum variations of $\mp .45\%$. The enthalpy function H and heat capacity C are more sensitive to changes in the ν_i 's. The worst case is $\pm 10\%$ in ν_4 , which causes the variation in H and C to go through a maximum of $\mp 1.6\%$ at about 1000°K .

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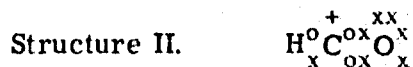
Table I
THERMODYNAMIC FUNCTIONS FOR $\text{H}_3\text{O}^+(\text{g})$, CAL/DEG MOLE

T °K	$-(F^\circ - H^\circ_0)/T$	$(H^\circ - H^\circ_0)/T$	S°	C_p
300	37.943	8.032	45.975	8.411
400	40.276	8.209	48.485	9.101
600	43.703	8.761	52.464	10.60
800	46.309	9.386	55.695	11.88
1000	48.470	10.000	58.470	13.00
1200	50.345	10.585	60.930	13.99
1400	52.019	11.135	63.154	14.86
1600	53.539	11.647	65.186	15.59
1800	54.939	12.121	67.060	16.20
2000	56.239	12.555	68.794	16.71
2200	57.454	12.952	70.406	17.13
2400	58.597	13.316	71.913	17.48
2600	59.676	13.647	73.323	17.77
2800	60.699	13.951	74.650	18.02
3000	61.671	14.229	75.900	18.22
3200	62.598	14.484	77.082	18.40
3400	63.483	14.719	78.202	18.55
3600	64.330	14.935	79.265	18.68
3800	65.143	15.135	80.278	18.79
4000	65.924	15.321	81.245	18.89
4200	66.676	15.492	82.168	18.97
4400	67.401	15.652	83.053	19.05
4600	68.100	15.801	83.901	19.11
4800	68.775	15.940	84.715	19.17
5000	69.428	16.071	85.499	19.22
5200	70.061	16.193	86.254	19.27
5400	70.674	16.307	86.981	19.31
5600	71.270	16.415	87.685	19.35
5800	71.847	16.517	88.364	19.38
6000	72.409	16.613	89.022	19.41

SECTION III

THE $\text{HCO}^+(\text{g})$ ION

The $\text{HCO}^+(\text{g})$ ion has 10 valence electrons or 5 electron pairs. Consideration of the most reasonable bonding which would lead to the stability of this species leads to the following two structures, which bear strong similarities to the bonding in the CO structure of aldehydes, CO , CO_2 , and also to the bonding in HCN.



In Structure I it is assumed that the bonding consists of digonal hybrids using the s and p_x orbitals of the carbon atom to form one σ bond for the C-H bond and one σ bond in the CO triple bond, with the other two bonds of the triple bond arising from two π bonds formed from the $\text{C}(p_z)$ and $\text{O}(p_z)$ and the $\text{C}(p_y)$ and $\text{O}(p_y)$ orbitals. The unshared pair of electrons are in the $\text{O}(s^2)$ orbital. Structure I compensates for the inherent instability of the residual positive charge on the more electronegative oxygen by the added stability of the triple bond.

Structure II again assumes digonal hybridization using the s and p_x orbitals of the carbon to form two σ bonds, while the second bond of the CO double bond is a π bond formed from the $\text{C}(p_z)$ and $\text{O}(p_z)$ orbitals; the two pairs of unshared electrons occupy the $\text{O}(s^2)$ and $\text{O}(p_y^2)$ orbitals. Structure II does not take advantage of all possible bonding orbitals but does relax the conflict of the electronegative O atom bearing the residual positive charge.

It is further assumed that we therefore have a linear ion with the probable resonance of Structures I and II.

An estimate of the interatomic distances can be obtained in the following way. The C-H distance in Structure I is the same as it is in acetylene, i. e. , 1.057 Å. The oxygen atom triple-bond covalent radius, 0.50 Å, is corrected for the effect of the positive charge^(6b) by -0.025 Å to give a value of 0.475 Å; the carbon atom triple-bond radius is taken to be 0.60 Å, resulting in the C-O triple-bond distance of 1.075 Å. For Structure II, the C-H bond length is taken to be 1.079 Å, similar to that in ethylene,^(7b) but is then corrected for the effects of the electric charge and the incomplete valence shell of the carbon atom (i. e. , corrections of -0.015 Å and -0.09 Å, respectively) to give 0.974 Å for the C-H distance. The O atom double-bond radius is taken to be 0.57 Å and the carbon atom double-bond radius of 0.67 Å is corrected for charge and incompleteness of the valence shell by -0.03 Å and -0.09 Å, respectively. This results in a carbon double-bond radius of 0.55 Å which gives a carbon-oxygen bond distance of 1.12 Å.

If it is assumed that resonance occurs and the two structures contribute equally, the interatomic distances corresponding to resonance can be obtained by averaging in such a manner as to weight the triple-bond structure twice that of the double-bond structure.^(6c) This gives 1.029 Å for the C-H and 1.090 Å for the C-O distances.

The bond distances and covalent radii quoted above are taken from Coulson.^(7b) More recent values for the C-H distance in ethylene are about 1.086 Å;⁽¹¹⁾ however, the calculations were performed using 1.079 Å. Because of the averaging used to account for resonance, this higher value for C-H changes the final C-H value very little; since the calculations are only an approximation, this slight error is insignificant.

Given the above bond lengths, the moment of inertia of the linear $\text{HCO}^+(\text{g})$ is calculated to be $17.95 \times 10^{-40} \text{ gm cm}^2$ and the rotational constant, B , equals 1.559 cm^{-1} .

Solution for K in Badger's empirical relationship of stretching force constants for diatomic molecules, $k_0 = K/(R-0.34)^3$ (which is for a hydrogen atom and an atom of the first row of the periodic table), making use of the stretching force constants for C-H in first acetylene and then in ethylene, and then using the average of these two K 's to compute the stretching force constant for $\text{HCO}^+(\text{g})$ gives a value of $k_0 = 6.5 \times 10^5 \text{ dynes/cm}$. Applying the same technique for the C-H stretching constant in HCN and then reversing the computation for $\text{HCO}^+(\text{g})$ gives about $6.65 \times 10^5 \text{ dynes/cm}$. A weighted average of these gives $6.60 \times 10^5 \text{ dynes/cm}$ as an approximate stretching force constant for the CH in $\text{CHO}^+(\text{g})$.

The stretching force constant for the CO bond in $\text{HCO}^+(\text{g})$ was obtained from a plot (which was essentially a straight line) of k -stretching versus $1/(R-d_{ij})^3$, where $d_{ij}^{(6d)}$ equals 0.68, for the series of molecules $\text{CO}(^3\pi)$, $\text{CO}(^1\Sigma)$, CO^+ , and $\text{NO}^{(8)}$, all of which have electronic structures similar to those postulated for the CO in HCO^+ . Extrapolation of this plot to the appropriate coordinate for $R = 1.090 \text{ \AA}$ gave a stretching constant for the C-O bond in $\text{HCO}^+(\text{g})$ of $23.5 \times 10^5 \text{ dynes/cm}$.

The force constant for the perpendicular vibrational mode of HCO^+ is taken to be the same as that of the similar molecule HCN: $k_0/\ell_1\ell_2 = 0.20 \times 10^5 \text{ dynes/cm}^{(8e)}$.

Insertion of the above parameters into the analytical expressions for the valence force treatment of XYZ-type linear molecules as given by Herzberg allow the solution of these expressions for the fundamental vibrational frequencies ν_1 , ν_2 , and ν_3 , where ν_2 is doubly degenerate. The values obtained are $\nu_1 = 2310$, $\nu_2 = 700$, and $\nu_3 = 3540 \text{ cm}^{-1}$, which are quite reasonable when compared with the corresponding experimental values for HCN.

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The above spectroscopic constants and the usual expressions for thermodynamic functions, as obtained from the partition functions for a classical rigid-rotator harmonic-oscillator linear molecule, yield the ideal-gas thermodynamic functions listed in Table II. The ground electronic state is a singlet; no excited electronic states were considered and the fundamental constants as cited above were used.

Table II.
THERMODYNAMIC FUNCTIONS FOR $\text{HCO}^+(\text{g})$, CAL/DEG MOLE

T °K	$-(F^\circ - H^\circ_0)/T$	$(H^\circ - H^\circ_0)/T$	S°	C_p
300	40.960	7.437	48.397	8.634
400	43.155	7.837	50.992	9.393
600	46.470	8.533	55.003	10.39
800	49.004	9.093	58.097	11.14
1000	51.085	9.568	60.653	11.78
1200	52.867	9.983	62.850	12.32
1400	54.434	10.349	64.783	12.76
1600	55.837	10.674	66.511	13.11
1800	57.111	10.961	68.072	13.40
2000	58.280	11.216	69.496	13.62
2200	59.360	11.443	70.803	13.80
2400	60.364	11.647	72.011	13.95
2600	61.304	11.829	73.133	14.07
2800	62.187	11.993	74.180	14.18
3000	63.019	12.141	75.160	14.26
3200	63.807	12.276	76.083	14.33
3400	64.555	12.399	76.954	14.39
3600	65.267	12.511	77.778	14.44
3800	65.946	12.614	78.560	14.49
4000	66.596	12.708	79.304	14.52
4200	67.218	12.796	80.014	14.56
4400	67.815	12.876	80.691	14.59
4600	68.389	12.951	81.340	14.61
4800	68.942	13.021	81.963	14.64
5000	69.475	13.086	82.561	14.66
5200	69.989	13.147	83.136	14.67
5400	70.486	13.203	83.689	14.69
5600	70.967	13.257	84.224	14.70
5800	71.433	13.307	84.740	14.72
6000	71.885	13.354	85.239	14.73

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In order to show the effects upon the free-energy function F , enthalpy function H , entropy S , and heat capacity C of different choices for the input frequencies $\nu_1 - \nu_3$ and rotational constant B , each of these parameters was varied separately by $\pm 10\%$ and the resulting changes in F , H , S , and C were noted. H and C are independent of B , but $\pm 10\%$ in B gives maximum variations of about $\mp 0.5\%$ in F and S at 300°K , and these decrease to about $\mp 0.25\%$ at 6000°K . If ν_1 or ν_3 is changed by $\pm 10\%$, both F and S have a maximum variation of about $\mp 0.25\%$ or less at 6000°K , both decreasing as temperature T decreases. A $\pm 10\%$ change in ν_2 causes a maximum variation of $\mp 0.6\%$ in F at 3000°K which decreases as T goes up or down, and the variation in S goes through a maximum of about $\mp 0.65\%$ at a temperature of about 1400°K with this decreasing as the temperature goes either up or down.

Both H and C are more sensitive to variations in the ν 's; these variations go through a maximum at some intermediate temperature, decreasing fairly rapidly as one moves away from this temperature, and the temperature of the maximum varies between the different ν 's. The values of the maxima of these variations and the temperatures of their occurrence are given in Table III.

Table III.
EFFECTS OF VARIATION OF INPUT PARAMETERS
ON THE ENTHALPY FUNCTION AND HEAT CAPACITY OF $\text{HCO}^+(\text{g})$

Input Parameter and Its Variation	Maximum Variation in % and Corresponding $T^\circ\text{K}$	
	H	C
ν_1 + 10%	-0.9 @ 1800°	-1.2 @ 1000°
	+0.9 @ 1400°	+1.2 @ 1000°
ν_2 + 10%	-1.9 @ 500°	-3.0 @ 300°
	+1.8 @ 300°	+3.2 @ 300°
ν_3 + 10%	-0.8 @ 2300°	-1.0 @ 1400°
	+0.9 @ 2000°	+1.1 @ 1300°

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SECTION IV

THE $\text{CH}_3^+(\text{g})$ ION

Recent studies^(12, 13) of the CH_3 radical have indicated it to be planar, which leads one to expect the unpaired electron to be in the p_z orbital of the carbon atom with essentially trigonal bonding of the atoms. If the $\text{CH}_3^+(\text{g})$ molecule-ion is visualized to result from the loss of this electron we then expect to have available for bonding six electrons or three carbon valence orbitals, one $2s$ and two $2p$ orbitals. The stability of $\text{CH}_3^+(\text{g})$ then may be postulated as resulting from sp^2 hybridization which forms trigonal bonds and gives a planar structure with bond angles of 120° , a structure similar to that of BF_3 .

An estimation of the C-H bond length is made by making appropriate corrections to the C-H bond length one finds in methane, $1.094 \text{ \AA}$. These are $-0.015 \text{ \AA}$ and $-0.09 \text{ \AA}$ for the effects of the charge and the incomplete valence shell of the carbon atom, respectively, and result in an approximate C-H distance in CH_3^+ of $0.989 \text{ \AA}$.

Similar to the analysis for planar XY_3 -type molecules, $\text{CH}_3^+(\text{g})$ would then be expected to be a planar symmetric top molecule with one principle moment of inertia about the three-fold axis and two equal principle moments of inertia in the molecular plane. These are readily calculable, and for the above bond distance are $I_A = 4.912 \times 10^{-40}$ and $I_B = I_C = 2.456 \times 10^{-40} \text{ gm/cm}^2$; or the rotational constants A and B become 5.698 and 11.397 cm^{-1} respectively.

Herzberg⁽⁸⁾ shows that for planar XY_3 -type molecules there are four fundamental vibrational frequencies, two of which are doubly degenerate. Following the nomenclature of Herzberg in the valence force treatment, the frequency ν_1 for XY_3 depends on the force constant k_1 which may be classified to be a C-H stretching mode in the $\text{CH}_3^+(\text{g})$. The frequency ν_2 depends on k_Δ

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which will be considered to be the force constant for out-of-plane "bending," while ν_3 and ν_4 , the doubly degenerate frequencies, depend upon k_1 and k_δ . The k_δ may be thought to be the force constant for the angular displacement of the H-C-H angles or "bending" in the plane for $\text{CH}_3^+(\text{g})$.

An estimate for the stretching force constant k_1 is obtained from Badger's formula, $k_1 = 1.86 \times 10^5 / (R - d_{ij})^3$. With $R = 0.989 \text{ \AA}$ and $d_{ij} = 0.34$, this becomes $k_1 = 6.80 \times 10^5 \text{ dyne/cm}$.

Herzberg^(8f) analyzes the ethylene molecule with the assumption of valence forces and from the observed fundamental frequencies obtains values for the out-of-plane bending and angular displacement force constants, k_β / ℓ^2 and k_δ / ℓ^2 , respectively, for the H-C-H group. The symbolism given here is that of Herzberg. Correction of these values for the shortened internuclear distance in $\text{CH}_3^+(\text{g})$ results in the choice of $k_\Delta / \ell^2 = 0.27 \times 10^5$ and $k_\delta / \ell^2 = 0.32 \times 10^5 \text{ dynes/cm}$ for the approximate values of the "bending" force constants of $\text{CH}_3^+(\text{g})$. Inspection of the trend of these types of force constants which come from experimental observations for the series of planar molecules BF_3 , BCl_3 , and BBr_3 confirms that the values for $\text{CH}_3^+(\text{g})$ would be expected to be larger than they are in ethylene, as are the values estimated here, because of the shortened bond length.

Substitution of the above parameters into the analytical expressions for the valence force treatment of planar XY_3 molecules⁽⁸⁾ results in approximate fundamental frequencies of $\nu_1 = 3385$, $\nu_2 = 754$, $\nu_3 = 3595$, and $\nu_4 = 1340 \text{ cm}^{-1}$.

These frequencies appear to be quite reasonable when they are assigned to the normal vibrations of a molecule with a structure like BF_3 . ν_1 is essentially a C-H stretching frequency, ν_2 is an out-of-plane bending, ν_4 is substantially an in-plane bending of H-C-H, and ν_3 is another stretching mode. The magnitudes compare favorably with the values observed for similar modes of vibration of the NH_3 molecule, which is to be expected because of the similarity of the masses of the atoms involved.

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With the assumptions of a singlet ground electronic state and no excited electronic states, a symmetry number of 3, and the statistical thermodynamic relationships for a classical rigid symmetric-top rotator and harmonic oscillator, the thermodynamic functions for CH_3^+ as tabulated in Table IV are obtained.

Table IV
THERMODYNAMIC FUNCTIONS FOR $\text{CH}_3^+(\text{g})$: CAL/DEG MOLE

T °K	$-(F^\circ - H^\circ_0)/T$	$(H^\circ - H^\circ_0)/T$	S°	C_p
300	37.497	8.188	45.685	8.951
400	39.892	8.487	48.379	9.821
600	43.466	9.198	52.664	11.36
800	46.209	9.896	56.105	12.59
1000	48.488	10.544	59.032	13.67
1200	50.464	11.147	61.611	14.63
1400	52.225	11.705	63.930	15.45
1600	53.822	12.217	66.039	16.13
1800	55.288	12.684	67.972	16.69
2000	56.647	13.108	69.755	17.15
2200	57.915	13.493	71.408	17.52
2400	59.104	13.842	72.946	17.83
2600	60.225	14.159	74.384	18.09
2800	61.285	14.448	75.733	18.30
3000	62.291	14.711	77.002	18.48
3200	63.248	14.951	78.199	18.63
3400	64.161	15.171	79.332	18.76
3600	65.034	15.373	80.407	18.87
3800	65.870	15.560	81.430	18.96
4000	66.673	15.732	82.405	19.04
4200	67.444	15.892	83.336	19.12
4400	68.187	16.040	84.227	19.18
4600	68.903	16.177	85.080	19.24
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5400	71.535	16.644	88.179	19.40
5600	72.142	16.743	88.885	19.43
5800	72.731	16.836	89.567	19.46
6000	73.303	16.924	90.227	19.49

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The effects of variations of the input parameters were studied. H and C are independent of B and A, yet $\pm 10\%$ variation in B causes maximum variations of about $\pm 0.5\%$ and $\pm 0.4\%$ in F and S, respectively, and $\pm 10\%$ in A gives $\pm 0.3\%$ and $\pm 0.2\%$ in F and S, respectively. These maxima all occur at 300°K and decrease as the temperature is raised.

Table V shows the effects of $\pm 10\%$ variations in the ν 's. H and C are more sensitive to these variations than F and S because of the way the ν 's enter into the partition-function expressions. The resulting maximum variations occur at different intermediate temperatures; in general, the variations decrease rather rapidly from the maximum values as one moves away from the stated temperatures.

Table V
EFFECTS OF VARIATION OF INPUT PARAMETERS ON
THE THERMODYNAMIC FUNCTIONS FOR $\text{CH}_3^+(\text{g})$

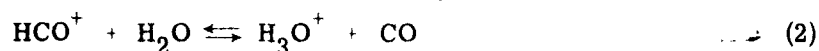
Input Parameter and Its Variation	Maximum Variation in % and Corresponding T $^\circ\text{K}$			
	F	H	S	C
ν_1 $+ 10\%$ $- 10\%$	-0.2 @ 6000°	-0.6 @ 3000°	-0.2 @ 6000°	-0.8 @ 1500°
	$+0.2$ @ 6000°	$+0.7$ @ 1400°	$+0.2$ @ 6000°	$+1.0$ @ 1000°
ν_2 $+ 10\%$ $- 10\%$	-0.3 @ 6000°	-0.6 @ 1000°	-0.3 @ 1000°	-1.3 @ 300°
	$+0.3$ @ 6000°	$+0.9$ @ 300°	$+0.3$ @ 1000°	$+1.6$ @ 300°
ν_3 $+ 10\%$ $- 10\%$	-0.3 @ 6000°	-1.1 @ 2700°	-0.5 @ 6000°	-1.6 @ 1500°
	$+0.4$ @ 6000°	$+1.3$ @ 2000°	$+0.5$ @ 6000°	$+1.9$ @ 1200°
ν_4 $+ 10\%$ $- 10\%$	-0.5 @ 6000°	-1.5 @ 800°	-0.5 @ 2000°	-2.4 @ 500°
	$+0.5$ @ 6000°	$+1.4$ @ 1000°	$+0.6$ @ 2000°	$+2.6$ @ 500°

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SECTION V

AN APPLICATION OF THE THERMODYNAMIC FUNCTIONS TO A REACTION OF COMBUSTION CHEMISTRY

It is of interest to use these newly acquired thermodynamic functions to compute the equilibrium constants for the reaction



which has been proposed by Green and Sugden⁽¹⁾ and other workers as the mechanism of formation of $\text{H}_3\text{O}^+(\text{g})$ ions in hydrocarbon flames.

To make these computations one must select the heats of formation for H_3O^+ and HCO^+ from several values which have been reported.

Green and Sugden chose 137 kcal/mole for ΔH_f of H_3O^+ as derived from a proton affinity for H_2O of -169 kcal/mole. This latter quantity was measured by Tal'rose and Frankevitch;⁽¹⁴⁾ the method of measurement and the results are described by N. N. Semenov.⁽¹⁵⁾

Field and Franklin⁽⁴⁾ tentatively recommend 195 kcal/mole for ΔH_f of H_3O^+ . This is a compromise from the two values of 193 and 196 kcal/mole which respectively come from electron impact measurements on H_2O beams and the appearance potential of H_3O^+ when $\text{C}_2\text{H}_5\text{OH}$ is subjected to electron bombardment.

Yet another ΔH_f for H_3O^+ of 207 kcal/mole is given by Bernecker and Long⁽⁵⁾ from their appearance-potential measurements for H_3O^+ from HCOOC_2H_5 .

For the ΔH_f of HCO^+ , Field and Franklin tentatively propose 203 kcal/mole, which is an average of 207 and 198 kcal/mole obtained from electron impact

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studies on cis- and trans-HCOOH. This reference also quotes a value of 230 kcal/mole from appearance-potential measurements on CH_3OH . Majer, Patrick, and Robb⁽¹⁶⁾ report a ΔH_f of 220 kcal/mole for HCO^+ from appearance-potential measurements on CH_3CHO .

Generally, errors in the heats of formation obtained from electron impact studies are such as to cause the quantities to be high because of unaccounted excitations or residual kinetic energy in the fragments; consequently, it is logical to prefer the low values, assuming the same reliability of the experiments. So, from the various electron impact studies, the values of 203 kcal/mole for HCO^+ and 195 kcal/mole for H_3O^+ are chosen. There is quite a discrepancy between the electron-impact-derived value of 195 kcal/mole for H_3O^+ and the 137 kcal/mole derived from the proton affinity.

Table VI displays a series of values of $\log K$ for reaction (2) at different temperatures calculated from the appropriate free-energy functions and using the two different values for ΔH_f of H_3O^+ .

Table VI
VALUES FOR $\log K$ FOR THE REACTION
 $\text{HCO}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CO}$

	$\Delta H_f \text{H}_3\text{O}^+ : 137,000$ $\Delta H_f \text{HCO}^+ : 203,000$	$\Delta H_f \text{H}_3\text{O}^+ : 195,000$ $\Delta H_f \text{HCO}^+ : 203,000$
$T^\circ \text{K}$	$\log K$	$\log K$
1500	5	-3.5
2000	3.6	-2.7
3000	2.3	-1.9
4000	1.6	-1.6

In the work of Green and Sugden⁽¹⁾ where reaction (2) is discussed, the authors made mass spectrometric detections of H_3O^+ and HCO^+ in a hydrogen-oxygen-nitrogen flame which had been doped with 1% acetylene. They found the intensity

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ratio of H_3O^+ to HCO^+ to be of the order of magnitude of 10^5 , therefore it is reasonable to assume the ratio of the partial pressures to be the same, i. e., about 10^5 . They also give an H_2O concentration for their flame conditions which leads to a partial pressure of the order of magnitude of tenths of atmospheres.

Computation of the expected equilibrium pressures of CO from the above experimental partial pressures of $p_{\text{H}_3\text{O}^+}/p_{\text{HCO}^+} = 10^5$ and $p_{\text{H}_2\text{O}} = 0.1$ atm and the two sets of equilibrium constants of Table I gives:

$$\begin{aligned} 1) \quad K &\approx 10^4 \text{ to } 10^2 \approx 10^6 p_{\text{CO}} & \therefore p_{\text{CO}} &= 10^{-2} \text{ to } 10^{-4} \text{ atm} \\ 2) \quad K &\approx 10^{-3} \text{ to } 10^{-2} \approx 10^6 p_{\text{CO}} & \therefore p_{\text{CO}} &= 10^{-9} \text{ to } 10^{-8} \text{ atm} \end{aligned}$$

where 1) is for 137 and 203 kcal/mole and 2) is for 195 and 203 kcal/mole.

In hydrocarbon flame systems the ratio of the partial pressures of CO to H_2O would normally be of the order of magnitude of 1 to 0.1; however, the flame under discussion here was an $\text{H}_2\text{-O}_2\text{-N}_2$ flame with about 1% acetylene, so it may be expected that the CO pressure would be reduced by a factor of 10^{-2} resulting in $p_{\text{CO}} \approx 10^{-2}$ or 10^{-3} atm. Thus, we see that the choice of ΔH_f for H_3O^+ of 137 kcal/mole and the assumption of equilibrium coupled with the experimental data for H_3O^+ , HCO^+ , and H_2O gives a p_{CO} which might be expected in the flame system considered.

Another argument for the value of 137 kcal/mole, or at least in that neighborhood, for ΔH_f of H_3O^+ is that if one chooses the higher values of 195 kcal/mole or 207 kcal/mole and computes the proton affinity for H_2O , one gets -111 or -99 kcal/mole respectively; both of these are extremely diverse from both the experimental value of -169 kcal/mole^(14, 15) and a result of -182 kcal/mole which was calculated theoretically by J. Sherman.⁽¹⁷⁾

It is granted that reaction (2) may not be in equilibrium under the experimental conditions cited above; however, if the partial pressure of the CO is truly of the order of magnitude of 10^{-2} to 10^{-4} atm the use of case 2) above makes it very difficult to explain the observed ratio of $\text{H}_3\text{O}^+/\text{HCO}^+$ without invoking the concept of a tremendous overshoot of the reaction in the forward direction.

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