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**CHEMICAL EQUILIBRIA IN HOT AIR
WITH MOISTURE, SALT, AND VAPORIZED METAL CONTAMINANTS**

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John Zinn and C. Dexter Sutherland

ABSTRACT

This report describes computations of thermodynamic equilibrium chemical species concentrations in hot (300-6000 K) air with and without moisture, salt, and metallic contaminants. The importance of the salt and metal vapors stems from the fact that small concentrations can lead to greatly enhanced levels of ionization. Estimated thermodynamic functions are tabulated for 46 different complex molecular and polyatomic ions, and these ions are included in the equilibrium computations. The thermodynamic parameters are used for generating reaction rate coefficients for otherwise uninvestigated reactions which are the reverses of known reactions.

I. INTRODUCTION

This report describes computations of equilibrium chemical composition of hot air in the temperature range 300 to 6000 K. They are not the first computations of their kind, similar ones having been reported earlier by Gilmore,^{1,2} Hilsenrath,^{3,4} and others. However, they are probably unique in the number of molecular species that they include. We also include estimates of specific heats, entropies, and free energies of formation for a number of complex ions.

Our motivation for this work grew out of a need to compute electron and ion densities in hot air in various nuclear radiation environments. This is the first of a pair of reports on that general subject. The second, which is in preparation, describes the nonequilibrium chemical kinetics.⁵

In hot air the list of important rate processes includes many reactions which are unimportant at lower temperatures, and whose rates are not easily measurable. A satis-

factory computation of the time dependence of the chemical composition would have to include all of the important reactions. An obvious practical test of the completeness of a set of reactions for chemical kinetics computations at a given temperature is that the thermodynamic equilibrium set of species concentrations should turn out to be a stable solution to the rate equations. That is, if the equilibrium concentrations are introduced as initial conditions, and if there are no nonequilibrium sources or sinks (no nonequilibrium radiation fluxes, for example), the rates of change of the concentrations should come out to be zero. To perform this computational experiment, it is of course necessary to compute the equilibrium composition--hence these computations.

To be able to pass the above test, the chemical reaction set must be complete in the sense that each reaction is matched by a corresponding reverse reaction, and the

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ratio of each pair of forward and reverse rate coefficients is the equilibrium constant. In most cases, published rate coefficient data are for exothermic reactions, and rate coefficients for the reverse, endothermic, reaction paths are not given. To complete the set, therefore, we must furnish the set of reverse rate coefficients, and to do this we must calculate equilibrium constants. The latter task is simpler than the computation of equilibrium species concentrations. However, it requires the same set of input thermodynamic parameters, and is therefore within the context of this report.

Section II of this report describes the mathematics and numerical scheme for the computations of chemical equilibria. Section III gives the input thermodynamic parameters and the prescriptions used for estimating some that were not otherwise known. Section IV describes computed equilibrium compositions for hot air at various temperatures for various values of pressure and relative humidity. We also discuss the effects on electron and ion densities produced by atmospheric NaCl aerosol and vaporized metal contaminants. Section V contains a description of the calculation of equilibrium constants and reverse reaction rate coefficients.

II. COMPUTATIONS OF CHEMICAL EQUILIBRIA

A. Mixtures of Ideal Gases at Constant

Temperature and Pressure

For any system at constant temperature T and pressure P the state of thermodynamic equilibrium is the state of minimum Gibbs free energy F . We shall consider a mixture of ideal gases in which the numbers of moles N_i of individual constituent molecular species (subscript i) are variable, subject to the constraints of constant T and P and constant numbers of gram atoms n_j of constituent chemical elements (subscript j). The free energy of an ideal gas mixture of variable composition is given by

$$F = \sum_i N_i \bar{F}_i$$

$$= \sum_i N_i \left[\bar{F}_i^0 + RT \ln \left(P N_i / \sum_k N_k \right) \right] \quad (1)$$

where $\bar{F}_i$ is the molar free energy of species i , $\bar{F}_i^0$ is the standard molar free energy, and P is the pressure in atmospheres.* The constraint that the total amounts of the constituent elements are constant is expressed as

$$\sum_i a_{ij} N_i - n_j = 0 \quad (2)$$

where the a_{ij} are stoichiometric coefficients (number of atoms of element j in compound i). The equilibrium state is the state of minimum F consistent with the constraints. We shall find the equilibrium set of N_i by the method of Lagrange multipliers.

We define a set of constraint functions

$$Q_j \equiv \sum_i a_{ij} N_i - n_j \quad (3)$$

and Lagrange multipliers λ_j . Since the constraints require that $Q_j = 0$ (for all j), a minimum of F consistent with the constraints implies a minimum of the function

$$G \equiv F + \sum_j \lambda_j Q_j \quad (4)$$

A necessary condition for a minimum of G is that the partial derivatives of G with respect to the N_i and the λ_j are all zero. This leads to the equations

$$\frac{\partial G}{\partial N_i} = \bar{F}_i^0 + RT \ln \left(P N_i / \sum_k N_k \right) + \sum_j \lambda_j a_{ij}$$

$$= 0 \quad (5)$$

*Footnote: We have selected the convention that the heats of formation of elements in their reference states are zero at all temperatures. The same convention is used in the JANAF⁶ thermochemical tables.

and

$$\frac{\partial G}{\partial \lambda_j} = \sum_i a_{ij} N_i - n_j = 0 \quad (6)$$

where T , P , the $\bar{F}_i^0$, n_j , and a_{ij} are all given quantities, $i = 1, 2, \dots, i_{\max}$ and $j = 1, 2, \dots, j_{\max}$. The above constitute $i_{\max} + j_{\max}$ equations for the $i_{\max} + j_{\max}$ unknowns N_i and λ_j .

The condition of charge conservation is incorporated naturally in these equations. The net charge is treated as a chemical element of zero concentration, with stoichiometric coefficients which are negative for electrons or negative ions, zero for neutrals, and positive for positive ions.

Equations (5) and (6) are, of course, nonlinear. To find solutions, we employ a Newton-Raphson iterative procedure. Let us denote the unknown quantities by X_j , the set of equations by $Y_i(X_j) = 0$, and the zeros of the equations by $\bar{X}_j$ ($i, j = 1, \dots, i_{\max} + j_{\max}$). A set of initial guesses $X_j^{(0)}$ is made for a sequence $X_j^{(N)}$, converging to $\bar{X}_j$. The equations are approximated by first-order Taylor series expansions about $\bar{X}_j$. Define $X_j^{(N)} - \bar{X}_j = \Delta X_j$ and note that $Y_i(\bar{X}_j) = 0$. Then the Taylor expansions are

$$Y_i(X_j^{(N)}) = \sum_{j=1}^{i_{\max}+j_{\max}} \left. \frac{\partial Y_i}{\partial X_j} \right|_{X_j^{(N)}} \Delta X_j \quad (7)$$

($i=1, \dots, i_{\max}+j_{\max}$)

These equations are solved for the ΔX_j by standard linear algebra methods. The ΔX_j are then used to obtain sequential values of $X_j^{(N+1)}$ [replacing $\bar{X}_j$ by $X_j^{(N+1)}$].

$$X_j^{(N+1)} = X_j^{(N)} - \Delta X_j \quad (8)$$

subject to the added condition that none of

the $X_j^{(N)}$ may be less than zero. The sequence of corrections is terminated when $|\Delta X_j/X_j^{(N+1)}|$ is sufficiently small. The procedure is coded for the CDC 7600.

The general subject of chemical equilibrium computations is described in many places including the book by Van Zeggeren and Storey.⁷ The Lagrange multiplier method is treated along with other methods.

Basic input data for the computer code include standard free energies $\bar{F}_i^0$ for the $i_{\max}$ chemical species, as well as the stoichiometric coefficients a_{ij} . The $\bar{F}_i^0$ are derived mostly from the JANAF tabulations⁶ of molar enthalpy, free energy, etc. Some additional tabulations are available, including those of Gilmore,⁸ Hilsenrath et al.,⁹ Gurvich,¹⁰ and Clifton.¹¹ In cases where data do not exist, we have made our own estimates. These matters are elaborated in Section III.

B. Constant Density Nonideal Gas Systems

A version of the equilibrium code has been constructed for nonideal gas systems, with provision for including first and second virial coefficients and Debye-Hückel correction factors. This version is applicable to systems at constant volume rather than constant pressure, and can be used for ideal gases at constant volume, if desired. The Helmholtz free energy is minimized instead of the Gibbs free energy. Further discussion is beyond the scope of this report. The computed results described in Section IV are all for ideal gas systems.

III. THERMODYNAMIC DATA

A. JANAF Tables and Fits

Thermodynamic data in the JANAF tables⁶ include, for individual chemical species, tabulations of standard molar heat capacity $\bar{C}_p^0$, molar enthalpy of formation $\bar{H}_0^0$, enthalpy (in the form $\bar{H}^0 - \bar{H}_{298}^0$), entropy $\bar{S}^0$, free energy function $-(\bar{F}^0 - \bar{H}_{298}^0)/T$, etc., all as functions of temperature, for temperatures up to 6000 K. Input data for the equilibrium code are in the form of polynomial fits to these functions. The enthalpy is fitted as

$$\bar{H}^0 - \bar{H}_{298}^0$$

$$= (\bar{H}_0^0 - \bar{H}_{298}^0) + RT(A + BT + CT^2 + DT^3 + ET^4) \quad (9)$$

(i.e. simply a 5th-degree polynomial in T). It then follows that

$$\begin{aligned} & (\bar{F}^0 - \bar{H}_{298}^0)/T \\ &= R\{A(1 - \ln T) - BT - CT^2/2 - DT^3/3 - ET^4/4 - J\} \\ &+ (\bar{H}_0^0 - \bar{H}_{298}^0)/T, \end{aligned} \quad (10)$$

introducing a sixth parameter, J. The coefficients A through E and J can be derived from the tabulated $\bar{H}^0 - \bar{H}_{298}^0$ and $(\bar{F}^0 - \bar{H}_{298}^0)/T$. The fitting procedure is adapted from a report by Bird, Duff, and Schott.¹² These fits are valid only within the range of the tabulated data--usually $298 \text{ K} \leq T \leq 6000 \text{ K}$. Having $\bar{H}_0^0$ and coefficients A...E and J from the tables, one can generate values of standard free energy at any temperature via

$$\bar{F}^0 = \bar{H}_0^0 + RT\{A(1 - \ln T) - BT - CT^2/2 - DT^3/3 - ET^4/4 - J\} \quad (11)$$

B. Estimation of Thermodynamic Parameters for Strange Species

The next section (III-C) will include a listing of the fitted thermodynamic coefficients A, B, C, D, E, and J as well as $\bar{H}_0^0$ for each species included in the code, and comments on sources of information.

For purposes of generating matched forward and reverse rate coefficients for the kinetics code, it is necessary to include several compounds and complex ions that have negligible concentrations at equilibrium. Examples are hydrated ions and complexes such as CO_4^- , O_4^+ , and O_4^- . To compute equilibrium constants for these species we need to provide values of free energies of formation. The latter are frequently not available in the literature, and must be estimated.

To provide entries in the table where published thermodynamic data are not available, we proceed by estimating first the standard heat of formation $\bar{H}_0^0$, the specific heat $\bar{C}_p^0$, and the 298 K entropy $\bar{S}_{298}^0$. In some cases published values of $\bar{H}_0^0$ are available while $\bar{C}_p^0$ and $\bar{S}^0$ are not. We have had to estimate heats of formation only for some hydrated ions and for water dimer and trimer. In the absence of other information we have assumed that the heats of hydration of negative ions are all -18.4 kcal/mole for the first attached water molecule and -10.7 kcal/mole for the second. The value of -18.4 kcal/mole is the alleged heat of hydration of O_2^- ,¹³ (which corresponds, incidentally, to the ion-dipole attraction energy that would exist between a unit point charge and the 1.85 Debye water dipole at a separation distance of 2.2 Å). The -10.7 kcal/mole is the average water-water association energy obtained from the heat of vaporization of water. We have chosen the same value for the heat of dimerization of water and for the hydration of the dimer to trimer. For positive ion monohydrates other than those of H^+ and H_3O^+ we have arbitrarily chosen -20 kcal/mole as the heat of hydration. For the case of H^+ , H_3O^+ , $\text{W}\cdot\text{H}_3\text{O}^+$ and $\text{W}_2\text{H}_3\text{O}^+$ (where W means hydrate), published heats of hydration are available (Kearley et al.).¹⁴ The heat of hydration of H_3O^+ to $\text{W}\cdot\text{H}_3\text{O}^+$ is given as -36 kcal/mole, for hydration of $\text{W}\cdot\text{H}_3\text{O}^+$ to $\text{W}_2\text{H}_3\text{O}^+$ it is -22.3 kcal/mole, and for higher hydrates it decreases monotonically, becoming -10.3 kcal/mole for the eighth hydrate. (The -10.3 kcal/mole is close to our assumed value of -10.7 kcal/mole for the heat of association of water.) For formation of dihydrates of positive ions other than H^+ or H_3O^+ we assume $\Delta H = -22.3 \text{ kcal/mole}$ --i.e. the same as the published ΔH for hydration of $\text{W}\cdot\text{H}_3\text{O}^+$ to $\text{W}_2\text{H}_3\text{O}^+$.

We turn next to the problem of estimating $\bar{C}_p^0$, $\bar{S}_{298}^0$, and the related coefficients A, B, C, D, E, and J. According to Eq. (9) the

heat capacity is

$$\bar{C}_p^0 = R(A + 2BT + 3CT^2 + 4DT^3 + 5ET^4) \quad (12)$$

At normal temperatures (ca 298 K) the contributions to $\bar{C}_p^0$ arising from translational and rotational degrees of freedom are effectively saturated in all but the lightest molecules. Certain internal rotation, torsion, and molecular bending modes also contribute to the 298 K heat capacity. Using the equipartition principle, we assume therefore that

$$\begin{aligned} \bar{C}_p^0(298 \text{ K}) &\approx C_{\text{trans}} + C_{\text{rot}} + C_{\text{torsion}} + C_{\text{bend}} \\ &\approx R(4 + n_{\text{torsion}} + n_{\text{bend}}) \text{ for non-} \\ &\quad \text{linear molecules,} \end{aligned}$$

and

$$\bar{C}_p^0(298 \text{ K}) \approx R(7/2 + n_{\text{bend}}) \text{ for linear molecules.}$$

Here n_{torsion} represents the effective number of torsion and internal rotation modes populated at 298 K and n_{bend} represents the number of populated bending modes. Comparisons with published values of $\bar{C}_p^0(298 \text{ K})$ for a number of compounds lead us to conclude that these approximations have an accuracy of about $\pm 1 \text{ cal deg}^{-1} \text{ mole}^{-1}$.

At higher temperatures the limiting heat capacity, excluding contributions of excited electronic states, is

$$\bar{C}_p^0(\text{lim}) = R(3n_{\text{atoms}} - 2)$$

Next we make the very drastic assumption that $\bar{C}_p^0(2298 \text{ K}) = \bar{C}_p^0(\text{lim})$ and that $\bar{C}_p^0$ varies linearly with T between 298 and 2298 K. The choice of 2298 K as the temperature where $\bar{C}_p^0 = \bar{C}_p^0(\text{lim})$ is arbitrary. For most compounds $\bar{C}_p^0$ is in fact close to

$\bar{C}_p^0(\text{lim})$ at this temperature. With this assumption we obtain, for nonlinear molecules,

$$\begin{aligned} \bar{C}_p^0(T) &\approx R \left[(4.9 + 1.15n_{t+b} - 0.45n_{\text{atoms}}) \right. \\ &\quad \left. + T(-0.003 - 0.0005n_{t+b} + 0.0015n_{\text{atoms}}) \right], \end{aligned}$$

and

$$\begin{aligned} \bar{C}_p^0(T) &\approx R \left[(4.4 + 1.15n_{t+b} - 0.45n_{\text{atoms}}) \right. \\ &\quad \left. + T(-0.003 - 0.0005n_{t+b} + 0.0015n_{\text{atoms}}) \right] \end{aligned}$$

for linear molecules, where we use n_{t+b} as shorthand for $(n_{\text{torsion}} + n_{\text{bend}})$. These expressions are intended to apply to the temperature range $298 < T < 2298 \text{ K}$. Above 2298 K, $\bar{C}_p^0 \approx \bar{C}_p^0(\text{lim})$. Accordingly, the coefficients of the fit become

$$A = \begin{cases} 4.9 + 1.15 n_{t+b} - 0.45 n_{\text{atoms}} & \text{(nonlinear molecules)} \\ 4.4 + 1.15 n_{t+b} - 0.45 n_{\text{atoms}} & \text{(linear molecules)} \end{cases}$$

$$B = -2.5 \times 10^{-4} (6 + n_{t+b} - 3n_{\text{atoms}}),$$

$$\text{and } C = D = E = 0. \quad (13)$$

These approximations are certainly very crude, but they have a relatively minor influence on the $\bar{F}^0$.

Now, since we set $C = D = E = 0$, it follows from Eqs. (9) and (10) that

$$J = \frac{\bar{S}^0}{R} - A \ln T - 2BT \quad (14)$$

Therefore J can be determined if we know the standard entropy $\bar{S}^0$ at some temperature. We have chosen to evaluate J for $T = 298 \text{ K}$. For cases where published values of $\bar{S}^0$ are not available, we must estimate a value.

The entropy of a polyatomic gas at normal temperature includes contributions from

translation, ground electronic state degeneracy, rotation, and certain internal rotation, torsion, and bending modes. By the Sackur-Tetrode equation, the combined translational and ground state degeneracy contributions are

$$\bar{S}_{\text{trans}}^0 = R(1.5 \ln M + 2.5 \ln T + \ln g_0 - 1.164) \quad (15)$$

where M is the molecular weight in a.m.u. and g_0 is the ground state statistical weight factor. (See, for example, S. Glasstone.)¹⁵ The rotational entropy is, for linear molecules,¹⁵

$$\bar{S}_{\text{rot}}^0 = R(\ln I + \ln T - \ln \sigma + 89.40) \quad (16a)$$

where I is the moment of inertia in g cm^2 and σ is the symmetry number. For nonlinear molecules the rotational entropy is

$$\bar{S}_{\text{rot}}^0 = R[0.5 \ln(abc) + 1.5 \ln T - \ln \sigma + 134.68] \quad (16b)$$

where a , b , and c are the three principal moments of inertia.

The vibrational entropy of small molecules at 298 K and below is usually small. For $3n-6$ simple harmonic vibrations with fundamental frequencies ω_i (cm^{-1}) the vibrational entropy is¹⁵

$$\bar{S}_{\text{vib}}^0 = R \left\{ \sum_{i=1}^{3n-6} \left[\frac{u_i}{\exp(u_i) - 1} - \ln[1 - \exp(-u_i)] \right] \right\} \quad (17)$$

where $u_i = h\nu_i/kT$.

The total entropy is

$$\bar{S}^0 = \bar{S}_{\text{trans}}^0 + \bar{S}_{\text{rot}}^0 + \bar{S}_{\text{vib}}^0 \quad (18)$$

In many cases we have neither the molecular structure information needed for computing I or abc nor the vibrational frequencies ω_i . For a number of cases we have guessed at moments of inertia (see Appendix), and the errors in $\bar{S}_{\text{rot}}^0$ (298 K) from errors in these estimates are probably within ± 2 cal/mole K. We have also guessed at

vibrational frequencies. For molecules with internal rotation, torsion, or bending modes, the potential errors in $\bar{S}_{\text{vib}}^0$ (298 K) from errors in these guesses may be as large as $\pm 3n_{t+b}$ cal/mole K. Details of the assumed structures, vibrational frequencies, etc. are given in the Appendix, along with calculated thermodynamic parameters.

C. Tabulation of the Thermodynamic Parameters

Table I is a listing, for each chemical species, of the coefficients A , B , C , D , E , and J derived from fits to published thermodynamic data or calculated by the recipes in the previous section. Also tabulated are the heats of formation $\bar{H}_f^0$, entropies $\bar{S}_{298K}^0$, and references to literature or other sources.

IV. EQUILIBRIUM COMPOSITION OF HOT AIR

We have performed seven sets of computations of the composition of air over a range of temperatures, and the results are displayed in graph form in Figs. 1 through 7. The computations include all of the chemical species listed in Table I.

Figures 1(a,b) represent a series of cases for pure dry air at 1 atmosphere pressure. The plot gives the mole fractions of constituent chemical species (in the range 10^{-7} to 1) as functions of temperature. In this set of calculations the atom fractions of N, O, Ar, and C are 0.784, 0.211, 4.7×10^{-3} , and 1.6×10^{-4} respectively, and no other elements are included. The computations are extended to 8000 K--slightly beyond the range of the thermodynamic data. The total particle density, by the ideal gas law, is $7.34 \times 10^{21}/T \text{ cm}^{-3}$.

Figures 2(a,b) represent a similar series of runs for moist air (1 mole % water) at 1 atmosphere pressure. Atom fractions of N, O, Ar, C, and H are respectively 0.773, 0.213, 4.6×10^{-3} , 1.6×10^{-4} , and 0.01.

Figures 3(a,b), 4(a,b) and 5(a,b) represent three sets of computations for moist air containing 1 ppm of NaCl. One ppm is approximately the NaCl concentration found

TABLE I
COMPUTER LIST OF THE THERMODYNAMIC PARAMETERS

SPECIES	A	B	C	D	E	J	HEAT OF FORMATION	S(298 K)	REFERENCES
E	2.50	-4.95E-07	2.46E-10	-4.82E-14	3.30E-18	-11.73	0	5.0	6
AL	2.71	-1.59E-04	5.70E-08	-9.84E-12	6.72E-16	4.35	77440	39.2	6
AL+	2.50	-5.97E-06	3.76E-09	-9.95E-13	9.38E-17	3.76	215432	35.8	6
ALOH	3.80	1.46E-03	-3.77E-07	5.00E-11	-2.64E-15	6.39	-52794	57.4	6
ALOH+	2.97	2.23E-03	-5.98E-07	8.18E-11	-4.40E-15	7.79	-41967	51.6	6
ALO	3.22	2.14E-03	-5.89E-07	8.17E-11	-4.44E-15	7.99	123524	54.7	6
ALO+	3.48	4.25E-04	1.04E-07	4.15E-11	-3.37E-15	6.19	20031	52.3	6
ALO+	3.22	2.75E-03	-1.23E-06	2.19E-10	-1.38E-14	5.72	237533	50.8	6
ALO2-	4.62	1.91E-03	-6.12E-07	9.30E-11	-5.33E-15	.86	-142580	56.1	6
ALO2	4.87	1.79E-03	-5.86E-07	8.93E-11	-5.18E-15	1.16	-43538	59.4	6
ALO2O	4.52	1.66E-03	-5.35E-07	8.16E-11	-4.72E-15	4.15	-32374	61.3	6
ALO2+	4.68	1.54E-03	-4.95E-07	7.54E-11	-4.35E-15	3.65	145000	62.0	6
ALO2O	4.93	3.31E-03	-1.06E-06	1.60E-10	-9.23E-15	2.21	-95666	64.4	6
ALO2O+	5.29	3.15E-03	-1.01E-06	1.55E-10	-8.93E-15	.96	130772	65.3	6
AR	2.50	-2.68E-07	7.40E-11	-6.75E-15	5.77E-20	4.36	0	37.0	8
AR+	2.49	2.24E-04	-1.00E-07	1.74E-11	-1.07E-15	5.71	363423	39.7	8, 17
C	2.61	-9.35E-05	3.23E-08	-3.35E-12	1.07E-16	4.17	163576	37.7	6
C+	2.62	-9.20E-05	3.14E-08	-4.93E-12	2.95E-16	3.64	429627	36.8	8, 17
CO	3.33	1.96E-03	-4.95E-07	6.50E-11	-3.41E-15	4.26	32393	48.3	6
CO+	3.33	1.83E-03	-4.90E-07	6.63E-11	-3.59E-15	6.89	10314	53.4	6
CO+	3.33	1.90E-03	-5.18E-07	6.90E-11	-3.64E-15	4.41	197709	48.7	6
CO-	3.17	5.63E-04	-1.35E-07	1.65E-11	-7.81E-16	5.07	15198	46.7	6
CO+	3.34	3.57E-04	-2.65E-08	4.27E-12	-4.74E-16	5.06	103215	48.3	6
CO	3.28	6.90E-04	-1.67E-07	2.27E-11	-1.26E-15	6.54	428601	50.9	6
CO	3.83	2.18E-03	-6.59E-07	9.64E-11	-5.40E-15	5.00	37989	55.7	6
CO	3.17	6.05E-04	-1.45E-07	1.80E-11	-8.90E-16	5.26	-27200	47.1	6
CO2-	3.60	2.01E-03	-6.03E-07	8.79E-11	-4.93E-15	7.28	-104100	57.4	6
CO2	3.42	2.33E-03	-6.74E-07	9.70E-11	-5.38E-15	5.02	-93965	51.3	6
CL-	2.50	-4.95E-07	2.46E-10	-4.82E-14	3.30E-18	4.19	-94800	36.6	6
CL+	2.67	9.25E-06	-2.19E-08	4.95E-12	-3.44E-16	4.71	28587	39.6	6
CL	2.81	-8.80E-05	4.82E-09	2.89E-12	-3.20E-16	4.27	328700	40.2	6
HCL	3.22	3.82E-04	-4.26E-08	4.77E-13	1.82E-16	3.82	-22019	44.5	6
NaCl	4.02	3.84E-04	-1.14E-07	1.78E-11	-1.04E-15	4.63	-43020	55.2	6
QLO	3.56	6.45E-04	-1.93E-07	3.03E-11	-1.74E-15	6.66	24211	54.3	6
CL2	3.82	5.13E-04	-1.63E-07	2.87E-11	-1.83E-15	4.90	0	53.5	6
FE	3.17	-4.84E-04	1.90E-07	-2.63E-11	1.47E-15	4.04	98838	43.4	6
FE+	2.94	1.68E-04	-1.04E-07	2.11E-11	-1.33E-15	5.12	280420	43.6	6
FE0	3.59	5.91E-04	-1.83E-07	3.14E-11	-2.01E-15	8.38	60000	57.9	6
H+	2.50	-4.95E-07	2.46E-10	-4.82E-14	3.30E-18	-1.15	34212	26.0	6
H	2.50	-4.95E-07	2.46E-10	-4.82E-14	3.30E-18	-4.6	51631	27.4	6
H+	2.50	-6.54E-07	3.22E-10	-6.31E-14	4.32E-18	-1.16	365236	26.0	6
HN	3.26	3.05E-04	-1.43E-08	-2.16E-12	2.75E-16	3.00	90150	43.2	6
HNO	3.39	1.76E-03	-4.66E-07	6.24E-11	-3.25E-15	6.13	24498	52.5	6
HNO2C	4.03	1.26E-03	-9.06E-07	1.28E-10	-7.08E-15	5.43	-16862	59.9	6
HNO2T	4.12	3.10E-03	-8.79E-07	1.24E-10	-6.85E-15	4.94	-17369	59.9	6
HNO3	4.28	4.91E-03	-1.45E-06	2.10E-10	-1.17E-14	5.25	-29755	64.3	6

TABLE I (continued)

SPECIES	A	B	C	D	E	J	HEAT OF FORMATION S(298 K)	REFERENCES
O ⁺	3.33	1.55E-04	4.34E-08	-1.33E-11	9.78E-16	1.62	-32846	41.1 6
OH	3.51	4.19E-05	8.20E-08	-1.93E-11	1.34E-15	2.01	9349	43.7 6
OH ⁺	3.22	3.74E-04	-3.63E-08	-3.26E-13	2.68E-16	3.34	313309	43.5 6
H ₂	3.53	1.53E-03	-4.06E-07	5.33E-11	-2.77E-15	6.31	5697	54.2 6
H ₂ ⁺	3.38	5.23E-05	8.33E-08	-1.83E-11	1.24E-15	-3.59	0	31.2 6
H ₂ O	3.47	9.21E-04	-8.26E-08	-3.06E-12	6.88E-16	2.29	-57103	44.9 6
H ₂ O ⁺	4.12	2.44E-03	-6.26E-07	8.31E-11	-4.33E-15	3.33	-31025	56.0 10, 6
H ₂ N	3.93	2.73E-03	-4.41E-07	4.33E-11	-1.70E-15	4.04	-9302	45.6 6
H ₂ O ⁺	3.08	2.34E-03	-2.05E-08	4.34E-12	-2.08E-16	4.27	143000	45.6 6, 26
N	2.48	3.53E-05	5.33E-08	-7.33E-12	4.06E-16	3.56	112520	36.6 6
N ⁺	2.75	-1.73E-04	-2.00E-07	2.83E-11	-1.54E-15	6.34	447692	38.0 10, 17
NO	3.23	7.00E-04	-1.33E-07	1.77E-11	-9.01E-16	5.86	20903	49.9 6
NO ⁺	3.34	5.57E-04	-1.10E-07	1.33E-11	-5.93E-16	5.33	21456	50.1 6
NO ₂	3.18	5.46E-04	-6.24E-07	9.30E-11	-5.20E-15	5.71	235180	47.2 6
NO ₂ ⁺	3.60	2.00E-03	-5.93E-07	8.63E-11	-4.83E-15	6.65	-46302	56.6 6
NO ₃	3.67	1.93E-03	-5.93E-07	8.63E-11	-4.83E-15	6.65	8586	57.3 6
NO ₃ ⁺	4.29	3.73E-03	-1.10E-06	1.78E-10	-1.03E-14	4.16	18329	61.0 6
NE	3.18	5.50E-04	-1.20E-07	1.33E-11	-6.11E-16	4.54	0	45.6 6
NE ⁺	3.35	3.05E-04	-9.26E-10	-2.43E-13	-1.93E-16	4.45	359297	47.1 10, 17
NEO	3.59	2.27E-03	-6.74E-07	9.78E-11	-5.47E-15	4.86	20430	52.8 6
NEO ⁺	4.11	2.07E-03	-6.36E-07	9.41E-11	-5.33E-15	3.68	317780	56.2 6
NEO ₃	5.79	4.14E-03	-1.27E-06	1.83E-10	-1.07E-14	2.34	21466	74.8 6
NEO ₄	6.43	5.93E-03	-1.63E-06	2.77E-10	-1.56E-14	-2.75	4473	73.9 6
NEO ₅	8.57	6.40E-03	-2.03E-06	3.17E-10	-1.84E-14	-9.64	5233	84.9 6
NA	2.52	-4.33E-05	3.03E-08	-9.83E-12	1.33E-15	4.13	25815	36.7 6
NA ⁺	2.50	-4.93E-07	2.46E-10	-4.83E-14	3.30E-18	3.54	144334	36.3 6
NAO	3.93	4.57E-04	-1.34E-07	2.03E-11	-1.20E-15	3.65	-27188	52.2 6
NAO ⁺	3.94	4.49E-04	-1.33E-07	2.03E-11	-1.20E-15	4.99	20326	56.0 6
NAOH	4.91	1.10E-03	-3.03E-07	4.03E-11	-2.19E-15	-0.80	-46395	56.3 6
NAOH ⁺	5.02	1.10E-03	-2.81E-07	3.73E-11	-1.97E-15	-0.28	161315	58.6 6
NAOH ₂	6.89	4.63E-03	-1.30E-06	1.83E-10	-1.00E-14	-4.35	-142154	74.6 6
O ⁻	2.63	-8.76E-05	2.88E-08	-4.40E-12	2.53E-16	4.04	25232	37.7 6
O	2.68	-1.18E-04	3.43E-08	-4.33E-12	2.33E-16	4.11	58089	38.4 6
O ⁺	2.50	5.77E-07	4.40E-10	-4.01E-13	7.33E-17	4.38	373021	37.0 10, 17
O ₂	3.38	7.14E-04	-2.14E-07	3.17E-11	-1.78E-15	5.46	-9920	49.9 6
O ₂ ⁺	3.30	6.11E-04	-1.43E-07	2.17E-11	-1.23E-15	5.48	0	48.9 6
O ₃	4.03	5.06E-04	-1.23E-07	1.48E-11	-6.73E-16	4.82	278178	48.9 10, 17
CO	3.17	6.05E-04	-1.43E-07	1.80E-11	-5.21E-15	5.95	34739	57.3 6
CO ₂	3.42	2.33E-03	-6.74E-07	9.10E-11	-8.90E-16	5.95	296000	48.4 APPENDIX
CO ₂ ⁺	3.38	5.20E-05	8.33E-08	-1.83E-11	1.24E-15	-2.16	223500	52.6 APPENDIX
CO ₃	3.47	9.21E-04	-8.26E-08	-3.06E-12	6.88E-16	2.98	355700	34.1 APPENDIX
NO ₂ ⁺	3.67	1.93E-03	-5.93E-07	8.63E-11	-4.83E-15	6.16	234200	46.2 APPENDIX
NO ₃	4.29	3.73E-03	-1.10E-06	1.78E-10	-1.03E-14	3.47	-66700	55.9 APPENDIX
O ₃ ⁺	4.03	1.93E-03	-5.93E-07	9.10E-11	-5.21E-15	5.51	-13000	59.6 APPENDIX
O ₃ ⁺	4.03	1.93E-03	-5.93E-07	9.10E-11	-5.21E-15	5.51	329900	58.7 APPENDIX

TABLE I (continued)

SPECIES	A	B	C	D	E	J	HEAT OF FORMATION S(298 K)	REFERENCES
O(1D)	2.50	-0.	0.	0.	0.	4.60	104330	APPENDIX
N(2D)	2.50	-0.	0.	0.	0.	5.10	167920	APPENDIX
N2	5.65	2.25E-03	0.	0.	0.	-1.40	-124900	APPENDIX
N3	6.60	4.00E-03	0.	0.	0.	-3.20	-192700	APPENDIX
N3+	3.55	7.50E-04	0.	0.	0.	6.10	378000	APPENDIX
N4+	4.25	1.25E-03	0.	0.	0.	7.10	345000	APPENDIX
O4-	4.25	1.25E-03	0.	0.	0.	8.00	268000	APPENDIX
O3-	4.25	1.25E-03	0.	0.	0.	8.10	-23500	APPENDIX
O4-	4.25	1.25E-03	0.	0.	0.	7.80	-115000	APPENDIX
O4+	4.25	1.75E-03	0.	0.	0.	9.20	-122300	APPENDIX
N4+	4.25	1.25E-03	0.	0.	0.	3.90	371000	APPENDIX
N4+	4.25	1.25E-03	0.	0.	0.	4.70	296000	APPENDIX
N4+	4.25	1.00E-03	0.	0.	0.	2.00	-50400	APPENDIX
O4BO+	5.65	2.25E-03	0.	0.	0.	-2.20	125300	APPENDIX
N3O2	6.55	7.50E-04	0.	0.	0.	-2.60	41400	APPENDIX
O4NO-	6.55	7.50E-04	0.	0.	0.	-2.20	-50000	APPENDIX
N3O2+	4.25	1.25E-03	0.	0.	0.	8.50	272500	APPENDIX
N3O2-	4.25	1.25E-03	0.	0.	0.	7.10	-43000	APPENDIX
N4BO+	7.50	2.50E-03	0.	0.	0.	8.50	-14500	APPENDIX
N4O+	6.10	1.50E-03	0.	0.	0.	-4.50	49300	APPENDIX
N4O2+	6.80	2.00E-03	0.	0.	0.	1.10	158000	APPENDIX
N4O2+	6.10	1.50E-03	0.	0.	0.	-40	157000	APPENDIX
N4O3-	6.10	1.50E-03	0.	0.	0.	1.70	283000	APPENDIX
N4O3-	7.50	2.50E-03	0.	0.	0.	2.00	201000	APPENDIX
N4O4-	8.20	3.00E-03	0.	0.	0.	-1.30	-181600	APPENDIX
N4O4+	6.10	1.50E-03	0.	0.	0.	-3.40	-193700	APPENDIX
N4O2-	6.80	2.00E-03	0.	0.	0.	.20	-112400	APPENDIX
N4O3-	7.50	2.50E-03	0.	0.	0.	1.10	-55000	APPENDIX
N4O3-	6.10	1.50E-03	0.	0.	0.	-40	-117700	APPENDIX
N4O3-	6.10	1.50E-03	0.	0.	0.	-2.10	-136300	APPENDIX
N4O3-	6.80	2.00E-03	0.	0.	0.	2.00	-69400	APPENDIX
N4O3-	7.50	2.50E-03	0.	0.	0.	.40	-66000	APPENDIX
N4BO+	7.30	4.50E-03	0.	0.	0.	-1.40	-99000	APPENDIX
N4O4+	5.90	3.50E-03	0.	0.	0.	-1.30	-29500	APPENDIX
N4O2+	5.90	3.50E-03	0.	0.	0.	4.20	78600	APPENDIX
N4O3-	7.30	4.50E-03	0.	0.	0.	5.00	122000	APPENDIX
N4O4+	8.00	5.00E-03	0.	0.	0.	-90	-258000	APPENDIX
N4O3-	7.30	4.50E-03	0.	0.	0.	.40	-265000	APPENDIX
N4O2-	5.90	3.50E-03	0.	0.	0.	5.00	-210000	APPENDIX
N4O4+	7.30	4.50E-03	0.	0.	0.	1.10	-157000	APPENDIX
N4O3+	5.90	3.50E-03	0.	0.	0.	3.60	-166900	APPENDIX
N4O4+	7.10	5.50E-03	0.	0.	0.	1.40	-104000	APPENDIX
N4O2-	5.70	5.50E-03	0.	0.	0.	6.90	4500	APPENDIX
N4O2-	5.70	5.50E-03	0.	0.	0.	7.60	-232200	APPENDIX

Fig. 1a,b. Equilibrium chemical composition of dry air as a function of temperature, for a constant pressure of 1 atmosphere. The total particle density is $7.34 \times 10^{21}/T \text{ cm}^{-3}$ (ideal gas law).

Fig. 2a,b. Equilibrium composition of moist air (1 mole % H_2O) as a function of temperature, for constant $P = 1$ atmosphere.

Fig. 3a,b. Equilibrium composition of salt air (1 mole % H_2O , 1 ppm NaCl) as a function of temperature, for constant $P = 1$ atmosphere.

Fig. 4a,b. Equilibrium composition of salt air (1 ppm H₂O, 0.1 ppm NaCl) at constant $P = 10^{-3}$ atmosphere.

Fig. 5a,b. Equilibrium composition of salt air (1 mole % H_2O , 1 ppm $NaCl$) at constant sea level density $\rho = 1.23 \times 10^{-3} \text{ g/cm}^3$.

Fig. 6a,b. Electron and negative ion number densities in air contaminated with sodium vapor. They are plotted vs sodium atom fraction for various values of temperature, at constant $P = 1$ atmosphere.

Fig. 7a,b. Electron and negative ion number densities in air contaminated with aluminum vapor. They are plotted vs aluminum atom fraction for various values of temperature, at constant $P = 1$ atmosphere.

in air over the oceans.¹⁶ Figure 3 is for a constant pressure of 1 atmosphere; Fig. 4 is for a pressure of 0.001 atmosphere; Fig. 5 is for a constant density of 1.23×10^{-3} g/cm³. The main effect of the NaCl is to increase the percentage ionization at temperatures between 2000 and 5000 K.

Figures 6(a,b) show electron and negative ion concentrations in air contaminated with elemental sodium. n_e and n_- are plotted vs Na atom fraction for various values of T, with P = 1 atmosphere. Figures 7(a,b) contain similar sets of plots for air contaminated with aluminum. The results bear on the question of enhanced ionization in a nuclear fireball produced by small quantities of vaporized bomb debris. Small quantities of sodium or aluminum can cause a very large increase in ionization. The effect of a given mole fraction of sodium is almost exactly the same as that of a similar fraction of NaCl, and electron-ion densities derived from Fig. 3b are within 10% of corresponding values from Figs. 6(a,b).

V. EQUILIBRIUM CONSTANTS AND REVERSE REACTION RATES

For a general forward-reverse pair of chemical reactions in an ideal gas system, viz:

the equilibrium constant in terms of number densities of reacting species is

$$K_n = (kT)^{-\Delta v} \exp(-\Delta F^0/RT) = \frac{n_L^l n_M^m \dots}{n_A^a n_B^b \dots} \quad (19)$$

where ΔF^0 is the standard free energy change for the given reaction at the given temperature T, Δv is the change in the total number of moles produced in the course of "1 mole" of the reaction as written

(i.e. $\Delta v = l + m - a - b - \dots$), k is Boltzmann's constant (1.36×10^{-22} cm³ atm/K),

and n_L is the number of molecules of L per cm³. From the fitted expression for F^0 [Eq. (11)] the standard free energy change for the reaction is given by

$$\Delta F^0/RT = \Delta H_0^0/RT + (\Delta A - \Delta J) - \Delta A \ln T - T\Delta B - T^2\Delta C/2 - T^3\Delta D/3 - T^4\Delta E/4, \quad (20)$$

where ΔA means $lA_L + mA_M - aA_A - bA_B$, etc. This can be combined with the previous equation to give an expression for K_n in terms of quantities listed in Table I, viz:

$$K_n = QT^{(\Delta A - \Delta v)} \exp(-\Delta H_0^0/RT) \quad (21a)$$

where

$$Q \equiv k^{-\Delta v} \exp(-\Delta A + \Delta J + T\Delta B + T^2\Delta C/2 + T^3\Delta D/3 + T^4\Delta E/4) \quad (21b)$$

It would be convenient if the expression for K_n were of the same functional form as the standard form for tabulating reaction rate coefficients, namely

$$k = a(T/300)^b e^{-c/T} \quad (22)$$

(see, for example, the DNA Reaction Rate Handbook).¹⁷ Such a functional form could be expected, at least as a reasonable approximation, since K_n is equal to the ratio of a corresponding pair of forward and reverse rate coefficients, both of which are of that form. That is,

$$\begin{aligned} K_n &= \kappa_f / \kappa_r \\ &= (a_f/a_r)(T/300)^{(b_f-b_r)} \exp[-(c_f-c_r)/T] \\ &\equiv a_{eq}(T/300)^{b_{eq}} \exp(-\Delta H_0^0/RT) \quad (23) \end{aligned}$$

Therefore, the quantity Q in Eq. (21b) should be approximately proportional to some small power of T.

We wish to generate reverse reaction

rate parameters (a_r , b_r , c_r) from known forward rate parameters (a_f , b_f , c_f) and computed equilibrium constants. Our procedure is to fit the quantities a_{eq} and b_{eq} [Eq. (23)] by least squares to a set of computed values of $QT^{(\Delta A - \Delta v)}$ [Eqs. (21)] over a specified temperature range, usually 300 - 3000 K. The reverse rate parameters a_r , b_r , and c_r are then derived from the a_f , b_f , c_f , a_{eq} , b_{eq} , and $\Delta H_0^0/R$ by Eq. (23).

Numerical values of the rate parameters will be given in the kinetics report.⁵

Equation (23) makes no special note of the fact that most reactions lead to products in excited electronic, vibrational, or rotational states. A reaction process that takes reactants to products with an *equilibrium population* of states is usually in actuality a sequence of reactions, where the first step is the "chemical" step, taking reactants to excited products, and subsequent steps are thermalizing collisions which bring the excited products into the equilibrium population. However, for computing reverse rate coefficients--i.e. coefficients for reaction processes that convert the thermal equilibrium products back to the thermal equilibrium reactants--detailed descriptions of the stepwise processes are usually unnecessary, and Eq. (23) gives correct results.

For example, consider the dissociative recombination reaction,

The first step is known to lead to an excited metastable $O(^1D)$ atom, subsequently converted to $O(^3P)$ by collisional deexcitation. The overall process can be described as consisting of the two steps

and

where M is the moderator. We wish to calculate the rate coefficient k_r for the reverse of the overall process [Eq. (24)], given the measured coefficient $k_f \equiv k_{1f}$ of the forward reaction.

The rate equations for the O_2^+ and $O(^1D)$ concentrations are

$$\frac{d[O_2^+]}{dt} = -k_{1f}[O_2^+][e] + k_{1r}[O(^1D)][O] \quad (27)$$

and

$$\begin{aligned} \frac{d[O(^1D)]}{dt} = & k_{1f}[O_2^+][e] - k_{2f}[O(^1D)][M] \\ & + k_{2r}[O][M] - k_{1r}[O(^1D)][O], \end{aligned} \quad (28)$$

where square brackets denote concentrations. Now let us invoke the steady state assumption $d[O(^1D)]/dt \approx 0$, which is equivalent to assuming that it is much smaller than any of the four separate terms on the right-hand side of Eq. (28). Then we can solve for $[O(^1D)]$, and substitute in Eq. (27) to obtain

$$\begin{aligned} \frac{d[O_2^+]}{dt} = & \left\{ -k_{1f}k_{2f}[O_2^+][e] + k_{1r}k_{2r}[O]^2 \right\} \times \\ & [M] / \left\{ k_{1r}[O] + k_{2f}[M] \right\} \end{aligned} \quad (29)$$

Now $k_{2f}[M]$ is almost certainly much larger than $k_{1r}[O]$. If this is true, and if we define the equilibrium constants $K_1 \equiv k_{1f}/k_{1r}$ and $K_2 \equiv k_{2f}/k_{2r}$, then Eq. (29) simplifies to

$$\frac{d[O_2^+]}{dt} \approx -k_{1f}[O_2^+][e] + (k_{1f}/K_1K_2)[O]^2 \quad (30)$$

This is exactly the rate equation corresponding to the overall reaction as described by Eq. (24), and $k_r = k_{1f}/K_1K_2$ is the same reverse rate coefficient for that process as we would have obtained directly with Eq. (23), without considering the stepwise reactions (25) and (26).

The above arguments rest on the assumption that $k_{2f}[M]$ is much larger than $k_{1r}[O]$, and the equivalent assumption can be made for most reactions. For the example cited, at 298 K, $k_{1f} = 2. \times 10^{-7} \text{ cm}^3/\text{s}$, $k_{2f} \approx 7. \times 10^{-11} \text{ cm}^3/\text{s}$ (Ref. 17), $K_1 = 10^{90}$, $k_{1r} = k_{1f}/K_1 = 2. \times 10^{-97} \text{ cm}^3/\text{s}$.

and $[M] \geq [O]$, so that $k_{2f}[M]$ is indeed $\gg k_{1r}[O]$.

Nevertheless, despite our conclusion that we can compute most overall reverse rate coefficients correctly with Eq. (23), it is frequently necessary in kinetics problems to consider detailed stepwise processes as in Eqs. (25) and (26). In particular, for stratospheric problems and fireball problems, it is necessary to follow concentrations of metastable atoms $O(^1D)$ and $N(^2D)$. For this reason we have included thermodynamic functions for these two species in the Appendix of this report.

APPENDIX

ASSUMED MOLECULAR STRUCTURES AND OTHER ASSUMPTIONS LEADING TO

ESTIMATED THERMODYNAMIC PARAMETERS

This appendix describes our assumptions leading to estimated thermodynamic parameters for some of the complex molecules and ions listed in Table I. The heat of formation values are in every case based on some experimental information. Most of the entropy estimates, on the other hand, are based on assumptions about molecular structures, moments of inertia, and low-frequency vibrational modes, which are more or less wild. In most instances the assumed structures and molecular dimensions will be defined, as will the ground state degeneracies g_0 , the symmetry numbers σ , molecular weights M , moment of inertia products abc , and the n_{t+b} lowest vibrational frequencies ω_i . The heats of formation $\bar{H}_0^0$ and the cal-

culated $\bar{C}_p$, $\bar{S}_{298}^0$, and parameters A-J will also be given.

If we commit a factor-of-four error in estimating abc , then we commit an error of only $\pm 1.4 \text{ cal/deg mole}$ in $\bar{S}_{\text{rot}}^0(298 \text{ K})$. On the other hand, the error in $\bar{S}_{\text{vib}}^0(298 \text{ K})$ may in some cases be rather large. The estimated uncertainties in the $\bar{H}_0^0$ and $\bar{S}_{298}^0$ will be indicated.

The order of listing of the species is: CO^+ , CO_2^+ , H_2^+ , H_2O^+ , NO_2^+ , NO_3^+ , O_3^- , O_3^+ , $\text{O}(^1D)$, $\text{N}(^2D)$, $(\text{H}_2\text{O})_2$, $(\text{H}_2\text{O})_3$, N_3^+ , N_4^+ , O_4^+ , O_4^- , CO_3^- , CO_4^- , $\text{N}^+\cdot\text{H}_2\text{O}$, $\text{O}^+\cdot\text{H}_2\text{O}$, $\text{OH}\cdot\text{H}_3\text{O}^+$, $(\text{NO})_2$, $\text{O}_2\cdot\text{NO}$, $\text{O}_2^+\cdot\text{N}_2$, $\text{O}_2^-\cdot\text{N}_2$, CO_3 , and miscellaneous hydrated polyatomic ions (Table AI). The ordering is roughly one of increasing uncertainty.

CO⁺

Moment of inertia, $\bar{C}_p^0$, and coefficients A through E assumed to be the same as for CO.

Ground state degeneracy $g_0 = 2$.

$$\bar{H}_0^0 = \bar{H}_0^0(\text{CO}) + 322.79 \\ = +296.0 \text{ kcal mole}^{-1} \text{ (Ref.17,18)}$$

$$\bar{S}_{298}^0 = \bar{S}_{298}^0(\text{CO}) + R \ln 2 \\ = 48.59 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = J(\text{CO}) + \ln 2 = 5.95$$

CO₂⁺

Moment of inertia, $\bar{C}_p^0$, and coefficients A through E assumed to be the same as for CO₂.

Ground state degeneracy $g_0 = 2$.

$$\bar{H}_0^0 = \bar{H}_0^0(\text{CO}_2) + 316.33 \\ = +223.5 \text{ kcal mole}^{-1} \text{ (Ref.17,18)}$$

$$\bar{S}_{298}^0 = \bar{S}_{298}^0(\text{CO}_2) + R \ln 2 \\ = 52.7 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = J(\text{CO}_2) + \ln 2 = 5.71$$

H₂⁺

$\bar{C}_p^0$ and coefficients A through E assumed to be the same as for H₂. Internuclear distance $r = 1.06 \text{ \AA}^{18}$ compared to $0.7416 \text{ \AA}$ for H₂. $g_0 = 2$.

$$\bar{H}_0^0 = +355.7 \text{ kcal mole}^{-1} \text{ (Ref.17,18)}$$

$$\bar{S}_{298}^0 = \bar{S}_{298}^0(\text{H}_2) + 2.80 = 34.01 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = -2.16$$

H₂O⁺

Moments of inertia, $\bar{C}_p^0$ and A through E assumed to be the same as for H₂O. $g_0 = 2$.

$$\bar{H}_0^0 = +233.9 \text{ kcal mole}^{-1} \text{ (Ref.17,18)}$$

$$\bar{S}_{298}^0 = 46.48 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = 2.98$$

NO₂⁺

Moments of inertia, $\bar{C}_p^0$ and A through E assumed to be the same as for NO₂. $g_0 = 1$, compared to 2 for NO₂.

$$\bar{H}_0^0 = +234.2 \text{ kcal mole}^{-1} \text{ (Ref.17,18)}$$

$$\bar{S}_{298}^0 = 55.96 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = 6.16$$

NO₃⁻

Moments of inertia, $\bar{C}_p^0$ and A through E same as for NO₃. $g_0 = 1$, compared to 2 for NO₃.

Electron affinity of NO₃ = 3.7 eV.¹⁹

$$\bar{H}_0^0 = -66.7 \text{ kcal mole}^{-1}$$

$$\bar{S}_{298}^0 = 59.0 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = 3.47$$

O₃⁻

Moments of inertia, $\bar{C}_p^0$ and A through E same as for O₃. $g_0 = 2$.

$$\bar{H}_0^0 = -13 \text{ kcal mole}^{-1} \text{ (Ref.17)}$$

$$\bar{S}_{298}^0 = 58.46 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = 5.51$$

O₃⁺

Moments of inertia, $\bar{C}_p^0$ and A through E same as for O₃. $g_0 = 2$.

$$\bar{H}_0^0 = +329.9 \text{ kcal mole}^{-1} \text{ (Ref.17)}$$

$$\bar{S}_{298}^0 = 58.46 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = 5.51$$

O(2¹D₂)

$$\bar{H}_0^0 = 104.33 \text{ kcal mole}^{-1} \text{ (see JANAF}^6)$$

$$\bar{S}_{298}^0 = 37.45 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{C}_p^0(298\text{K}) = 4.97 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$A = 2.5, B = C = D = E = 0$$

$$J = 4.60$$

N(2²D_{3/2,5/2})

$$\bar{H}_0^0 = 167.92 \text{ kcal mole}^{-1} \text{ (see JANAF}^6)$$

$$\bar{S}_{298}^0 = 38.43 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{C}_p^0(298\text{K}) = 4.97 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$A = 2.5, B = C = D = E = 0$$

$$J = 5.09$$

Water dimer (H₂O)₂

Molecular weight $M = 36$. $n_{\text{atoms}} = 6$. Multiplicity $g_0 = 1$. Heat of dimerization assumed to be $-10.7 \text{ kcal mole}^{-1}$ (from heat of vaporization). Assumed structure: planar. O - H' distance taken to be $1.5 \text{ \AA}$, consistent with assumed heat of dimerization. Symmetry number $\sigma = 2$. Important low-frequency modes $n_{t+b} = 3$, $\omega = 50, 200, 200 \text{ cm}^{-1}$.

Moments of inertia:

$$\begin{aligned} a &= 2 \times 10^{-40} \text{ g cm}^2 \\ b &= 9.5 \times 10^{-39} \text{ g cm}^2 \\ c &= 9.7 \times 10^{-39} \text{ g cm}^2 \\ abc &= 1.84 \times 10^{-116} \text{ g}^3 \text{ cm}^6 \end{aligned}$$

$$\bar{H}_0^0 = -124.9 \text{ kcal mole}^{-1} \mp 3$$

$$\bar{C}_p^0(298 \text{ K}) = 14 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$A = 5.65, B = 0.00225, C = D = E = 0$$

$$\bar{S}_{\text{trans}}^0(298 \text{ K}) = 36.66 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{rot}}^0(298 \text{ K}) = 18.39 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{vib}}^0(298 \text{ K}) = 8.7 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{298}^0 = 63.7 \mp 3 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = -1.4$$

Water trimer (H₂O)₃

$$M = 54. \quad n_{\text{atoms}} = 9. \quad g_0 = 1.$$

Assumed moment of inertia product

$$abc = 9.4 \times 10^{-115} \text{ g}^3 \text{ cm}^6. \quad \sigma = 1.$$

$$n_{t+b} = 5. \quad \omega = 20, 20, 100, 100, 100 \text{ cm}^{-1}.$$

$$\bar{H}_0^0 = -192.7 \text{ kcal mole}^{-1} \mp 4$$

$$\bar{C}_p^0(298 \text{ K}) = 18 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$A = 6.6, B = +0.004, C = D = E = 0$$

$$\bar{S}_{\text{trans}}^0(298 \text{ K}) = 37.87 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{rot}}^0(298 \text{ K}) = 23.68 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{vib}}^0(298 \text{ K}) = 11.7 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{298}^0 = 73.2 \mp 10 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = -3.2$$

N₃⁺

$$M = 42. \quad n_{\text{atoms}} = 3. \quad g_0 = 1.$$

Assumed structure: equilateral triangle resonance hybrid. $\sigma = 6$. Bond lengths

$$1.32 \text{ \AA}. \quad n_{t+b} = 0.$$

Moments of inertia:

$$a = b = 2.0 \times 10^{-39} \text{ g cm}^2$$

$$c = 4.0 \times 10^{-39} \text{ g cm}^2$$

$$abc = 1.65 \times 10^{-116} \text{ g}^3 \text{ cm}^6$$

$$\bar{H}_0^0 \leq 378 \text{ kcal mole}^{-1} \text{ (Ref. 20)}$$

$$\bar{C}_p^0(298 \text{ K}) = 8. \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$A = 3.55, B = 0.00075, C = D = E = 0$$

$$\bar{S}_{\text{trans}}^0(298 \text{ K}) = 37.12 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{rot}}^0(298 \text{ K}) = 16.10 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{vib}}^0(298 \text{ K}) = 0$$

$$\bar{S}_{298}^0 = 53.2 \text{ cal deg}^{-1} \text{ mole}^{-1} \mp 2$$

$$J = 6.10$$

M = 56. $n_{\text{atoms}} = 4$. $g_0 = 2$. Assumed structure: square resonance hybrid. $\sigma = 8$. Bond lengths 1.44 Å. $n_{t+b} = 1$. $\omega = 20 \text{ cm}^{-1}$.

Moments of inertia:

$$a = b = 4.8 \times 10^{-39} \text{ g cm}^2$$

$$c = 9.6 \times 10^{-39} \text{ g cm}^2$$

$$abc = 2.25 \times 10^{-115} \text{ g}^3 \text{ cm}^6$$

$$\bar{H}_0^0 \leq 345. \text{ kcal mole}^{-1} \text{ (Ref. 20)}$$

$$\bar{C}_p^0(298 \text{ K}) = 10. \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$A = 4.25, B = 0.00125, C = D = E = 0$$

$$\bar{S}_{\text{trans}}^0(298 \text{ K}) = 39.35 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{rot}}^0(298 \text{ K}) = 18.13 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{vib}}^0(298 \text{ K}) = 6.6 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{298}^0 = 64.1 \pm 3 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = 7.1$$

M = 64. $n_{\text{atoms}} = 4$. $g_0 = 2$. Assumed structure: square resonance hybrid. $\sigma = 8$. Bond lengths 1.6 Å. $n_{t+b} = 1$. $\omega = 20 \text{ cm}^{-1}$.

Moments of inertia:

$$a = b = 6.8 \times 10^{-39} \text{ g cm}^2$$

$$c = 1.36 \times 10^{-38} \text{ g cm}^2$$

$$abc = 6.3 \times 10^{-115} \text{ g}^3 \text{ cm}^6$$

$$\bar{H}_0^0 = 268. \pm 2 \text{ kcal mole}^{-1} \text{ (Ref. 21, 22)}$$

$$\bar{C}_p^0(298 \text{ K}) = 10. \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$A = 4.25, B = 0.00125, C = D = E = 0$$

$$\bar{S}_{\text{trans}}^0(298 \text{ K}) = 39.75 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{rot}}^0(298 \text{ K}) = 19.15 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{vib}}^0(298 \text{ K}) = 6.6 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{298}^0 = 65.5 \pm 3 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = 8.0$$

M = 64. $n_{\text{atoms}} = 4$. $g_0 = 2$. Assumed structure: square resonance hybrid. $\sigma = 8$. Bond lengths 1.7 Å. $n_{t+b} = 1$. $\omega = 20 \text{ cm}^{-1}$.

Moments of inertia:

$$a = b = 7.7 \times 10^{-39} \text{ g cm}^2$$

$$c = 1.53 \times 10^{-38} \text{ g cm}^2$$

$$abc = 9.0 \times 10^{-115} \text{ g}^3 \text{ cm}^6$$

$$\bar{H}_0^0 = -23.5 \text{ kcal mole}^{-1} \pm 0.2 \text{ (Ref. 22)}$$

$$\bar{C}_p^0(298 \text{ K}) = 10. \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$A = 4.25, B = 0.00125, C = D = E = 0$$

$$\bar{S}_{\text{trans}}^0(298 \text{ K}) = 39.75 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{rot}}^0(298 \text{ K}) = 19.50 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{vib}}^0(298 \text{ K}) = 6.6 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{298}^0 = 65.9 \pm 3 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = 8.1$$

M = 60. $n_{\text{atoms}} = 4$. $g_0 = 2$. Assumed structure: symmetric resonance hybrid. $\sigma = 6$. All C-O bonds of lengths 1.18 Å. $n_{t+b} = 1$. $\omega = 20 \text{ cm}^{-1}$.

Moments of inertia:

$$a = b = 5.5 \times 10^{-39} \text{ g cm}^2$$

$$c = 1.1 \times 10^{-38} \text{ g cm}^2$$

$$abc = 3.3 \times 10^{-115} \text{ g}^3 \text{ cm}^6$$

$$\bar{H}_0^0 \leq -115 \text{ kcal mole}^{-1} \text{ (Ref. 23, 24)}$$

$$\bar{C}_p^0(298 \text{ K}) = 10 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$A = 4.25, B = 0.00125, C = D = E = 0$$

$$\bar{S}_{\text{trans}}^0(298 \text{ K}) = 39.56 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{rot}}^0(298 \text{ K}) = 19.08 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{vib}}^0(298 \text{ K}) = 6.6 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{298}^0 = 65.2 \pm 3 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = 7.8$$

$M = 76$. $n_{\text{atoms}} = 5$. $g_0 = 2$. Assumed structure: planar. $\sigma = 2$. $n_{t+b} = 2$. $\omega = 20, 20 \text{ cm}^{-1}$.

Moments of inertia:

$$\begin{aligned} a &= 6.0 \times 10^{-39} \text{ g cm}^2 \\ b &= 1.65 \times 10^{-38} \text{ g cm}^2 \\ c &= 2.25 \times 10^{-38} \text{ g cm}^2 \\ abc &= 2.2 \times 10^{-114} \text{ g}^3 \text{ cm}^6 \end{aligned}$$

$$\bar{H}_0^0 = -122.3 \text{ kcal mole}^{-1} \mp 2 \text{ (Ref. 25)}$$

$$\bar{C}_p^0(298 \text{ K}) = 12 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$A = 4.95, B = 0.00175, C = D = E = 0$$

$$\bar{S}_{\text{trans}}^0(298 \text{ K}) = 40.27 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{rot}}^0(298 \text{ K}) = 23.15 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{vib}}^0(298 \text{ K}) = 13.2 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{298}^0 = 76.6 \mp 5 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = 9.2$$

$M = 32$. $n_{\text{atoms}} = 4$. $g_0 = 1$. Assumed structure: planar with 2.2 Å ion-dipole separation. $\sigma = 2$. $n_{t+b} = 1$. $\omega = 100 \text{ cm}^{-1}$.

Moments of inertia:

$$\begin{aligned} a &= 1.9 \times 10^{-40} \text{ g cm}^2 \\ b &= 6.55 \times 10^{-39} \text{ g cm}^2 \\ c &= 6.75 \times 10^{-39} \text{ g cm}^2 \\ abc &= 8.34 \times 10^{-117} \text{ g}^3 \text{ cm}^6 \end{aligned}$$

$$\bar{H}_0^0 = +371. \mp 5 \text{ kcal mole}^{-1} \text{ (based on assumed -18.4 kcal heat of hydration)}$$

$$\bar{C}_p^0(298 \text{ K}) = 10 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$A = 4.25, B = 0.00125, C = D = E = 0$$

$$\bar{S}_{\text{trans}}^0(298 \text{ K}) = 36.31 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{rot}}^0(298 \text{ K}) = 17.60 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{vib}}^0(298 \text{ K}) = 3.4 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{298}^0 = 57.3 \mp 4 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = 3.9$$

$M = 34$. $n_{\text{atoms}} = 4$. $g_0 = 2$. Assumed structure like $\text{N}^+ \cdot \text{H}_2\text{O}$. $\sigma = 2$. $n_{t+b} = 1$. $\omega = 100 \text{ cm}^{-1}$.

Moments of inertia:

$$\begin{aligned} a &= 1.9 \times 10^{-40} \text{ g cm}^2 \\ b &= 7.33 \times 10^{-39} \text{ g cm}^2 \\ c &= 7.52 \times 10^{-39} \text{ g cm}^2 \\ abc &= 1.04 \times 10^{-116} \text{ g}^3 \text{ cm}^6 \end{aligned}$$

$$\bar{H}_0^0 = +296. \mp 5 \text{ kcal/mole (based on assumed -18.4 kcal heat of hydration)}$$

$$\bar{C}_p^0(298 \text{ K}) = 10 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$A = 4.25, B = 0.00125, C = D = E = 0$$

$$\bar{S}_{\text{trans}}^0(298 \text{ K}) = 37.86 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{rot}}^0(298 \text{ K}) = 17.82 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{vib}}^0(298 \text{ K}) = 3.4 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{298}^0 = 59.1 \mp 4 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = 4.7$$

$M = 34$. $n_{atoms} = 4$. $g_0 = 2$. Assumed structure: planar with 2.2 ion-dipole separation. $\sigma = 2$. $n_{t+b} = 2$. $\omega = 20, 100 \text{ cm}^{-1}$.

Moments of inertia:

$$a = 1.9 \times 10^{-40} \text{ g cm}^2$$

$$b = 1.02 \times 10^{-38} \text{ g cm}^2$$

$$c = 1.04 \times 10^{-38} \text{ g cm}^2$$

$$abc = 2.0 \times 10^{-116} \text{ g}^3 \text{ cm}^6$$

$$\bar{H}_0^0 = -50.4 \text{ kcal mole}^{-1} \text{ (based on assumed}$$

$$-18.4 \text{ kcal heat of hydration)} \mp 3$$

$$\bar{C}_P^0 = 12 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$A = 5.4, B = 0.0010, C = D = E = 0$$

$$\bar{S}_{trans}^0(298 \text{ K}) = 37.86 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{rot}^0(298 \text{ K}) = 18.47 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{vib}^0(298 \text{ K}) = 10. \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{298}^0 = 66.3 \mp 6 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = 2.0$$

$M = 36$. $n_{atoms} = 6$. $g_0 = 2$. $\sigma = 3$.

$n_{t+b} = 3$. $\omega = 50, 50, 500 \text{ cm}^{-1}$.

$$abc = 4. \times 10^{-116} \text{ g}^3 \text{ cm}^6$$

$$\bar{H}_0^0 = 125.3 \text{ kcal mole}^{-1} \mp 5 \text{ (Ref. 26)}$$

$$\bar{C}_P^0 = 14 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$A = 5.65, B = 0.00225, C = D = E = 0$$

$$\bar{S}_{trans}^0(298 \text{ K}) = 38.03 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{rot}^0(298 \text{ K}) = 18.36 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{vib}^0(298 \text{ K}) = 10. \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{298}^0 = 66.4 \mp 10 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = -0.2$$

$M = 60$. $n_{atoms} = 4$. $g_0 = 1$. Assumed structure: planar (cis). $\sigma = 2$. $n_{t+b} = 3$. $\omega = 20, 100, 1000 \text{ cm}^{-1}$.

Moments of inertia:

$$a = 2.1 \times 10^{-39} \text{ g cm}^2$$

$$b = 1.45 \times 10^{-38} \text{ g cm}^2$$

$$c = 1.66 \times 10^{-38} \text{ g cm}^2$$

$$abc = 5.0 \times 10^{-115} \text{ g}^3 \text{ cm}^6$$

$$\bar{H}_0^0 = +41.4 \text{ kcal mole}^{-1} \mp 0.2 \text{ (Ref. 27)}$$

$$\bar{C}_P^0(298 \text{ K}) = 14 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$A = 6.55, B = 0.00075, C = D = E = 0$$

$$\bar{S}_{trans}^0(298 \text{ K}) = 38.19 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{rot}^0(298 \text{ K}) = 21.74 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{vib}^0(298 \text{ K}) = 10. \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{298}^0 = 69.9 \mp 6 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = -2.6$$

$M = 62$. $n_{atoms} = 4$. $g_0 = 1$. Assumed structure: planar. $\sigma = 1$. $n_{t+b} = 3$. $\omega = 20, 100, 1000 \text{ cm}^{-1}$.

Moments of inertia:

$$a = 8 \times 10^{-40} \text{ g cm}^2$$

$$b = 1.7 \times 10^{-38} \text{ g cm}^2$$

$$c = 1.7 \times 10^{-38} \text{ g cm}^2$$

$$abc = 2.3 \times 10^{-115} \text{ g}^3 \text{ cm}^6$$

OONO⁻ (continued)

$$\bar{H}_0^0 = -50.0 \text{ kcal mole}^{-1} \pm 8$$

Estimate. $\bar{H}_0^0 < -46.9$ kcal/mole from

Fehsenfeld et al.²⁸ $\bar{H}_0^0 > -59.2$ from DNA

Handbook¹⁷ Reaction XVI-15.

$$\bar{C}_p^0 = 14 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$A = 6.55, B = 0.00075, C = D = E = 0$$

$$\bar{S}_{\text{trans}}^0(298 \text{ K}) = 38.29 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{rot}}^0(298 \text{ K}) = 22.34 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{vib}}^0(298 \text{ K}) = 10. \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{298}^0 = 70.6 \pm 6 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = -2.2$$

O₂⁺·N₂

M = 60. $n_{\text{atoms}} = 4$. $g_0 = 2$. Assumed structure: planar trapezoid. $\sigma = 2$. $n_{t+b} = 1$. $\omega = 50 \text{ cm}^{-1}$.

Moments of inertia:

$$a = 5.5 \times 10^{-39} \text{ g cm}^2$$

$$b = 1.0 \times 10^{-38} \text{ g cm}^2$$

$$c = 1.5 \times 10^{-38} \text{ g cm}^2$$

$$abc = 8.25 \times 10^{-115} \text{ g}^3 \text{ cm}^6$$

$$\bar{H}_0^0 = +272.5 \text{ kcal/mole} \pm 2 \text{ (Ref. 22)}$$

$$\bar{C}_p^0 = 10 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$A = 4.25, B = 0.00125, C = D = E = 0$$

$$\bar{S}_{\text{trans}}^0(298 \text{ K}) = 39.56 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{rot}}^0(298 \text{ K}) = 22.17 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{\text{vib}}^0(298 \text{ K}) = 4.8 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\bar{S}_{298}^0 = 66.5 \pm 3 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = 8.5$$

O₂⁻·N₂

Dissociation energy $D(\text{O}_2^-\cdot\text{O}_2) = 13.6 \text{ kcal/mole}$.³⁰ We assume $D(\text{O}_2^-\cdot\text{N}_2) = 5 \text{ kcal/mole}$, and assume same $\bar{C}_p^0$ and $\bar{S}^0$ as for $\text{O}_2^+\cdot\text{N}_2$.

Therefore

$$\bar{H}_0^0 \approx -14.9 \pm 5 \text{ kcal mole}^{-1}$$

$$\bar{C}_p^0(298 \text{ K}) = 10. \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$A = 4.25, B = 0.00125, C = D = E = 0$$

$$\bar{S}_{298}^0 = 66.5 \pm 3 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = 8.5$$

CO₃

Moments of inertia, $\bar{C}_p^0$, A, and B same as those assumed for CO_3^- . $g = 1$.

$$\bar{H}_0^0 = -43 \pm 5 \text{ kcal/mole}^{24,31}$$

$$\bar{S}_{298}^0 = 63.8 \pm 3 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$J = 7.1$$

The remainder of the species in this list, all hydrated diatomic and polyatomic ions, are assumed to have no symmetry (i.e. $\sigma = 1$), and their moment of inertia products are assumed to be given by the approximation $abc = 7.4 \times 10^{-122} \text{ M}^3 n_{\text{atoms}}^2 (\text{g}^3 \text{ cm}^6)$. This is equivalent to assuming that the molecule behaves as a uniform sphere of mass $1.66 \times 10^{-24} \text{ M(g)}$ and volume $2 \times 10^{-24} n_{\text{atoms}} (\text{cm}^3)$. Furthermore, we assume that n_{t+b} is equal to the number of atoms minus twice the number of attached water molecules, and each of the n_{t+b} modes has the same fundamental frequency 100 cm^{-1} . The multiplicity g_0 is assumed to be 1 if the total number of electrons is even, and 2 if the number is odd. With these assumptions the 298 K entropy is given by

$$\bar{S}_{298}^0 = R \left[16.8 + 3 \ln M + 2n(n_{\text{atoms}}) + \ln g_0 + 1.7(1 + n_{\text{atoms}} - 2n_{\text{W}}) \right].$$

The 298 K specific heat is

$$\bar{C}_p^0(298 \text{ K}) = R(4 + n_{\text{atoms}} - 2n_{\text{water}}),$$

with a probable inaccuracy of about $\pm 5 \text{ cal deg}^{-1} \text{ mole}^{-1}$. Heats of formation are derived from those of the parent ions and the assumed heats of hydration specified in Section III. The results are listed in Table AI.

TABLE AI
CALCULATED THERMODYNAMIC PARAMETERS FOR THE MORE COMPLEX IONS

Ion	M	n_{atoms}	$\frac{1+n_{\text{atoms}}}{-2n_{\text{W}}}$	g_0	A	B	$\bar{S}_{298}^0$	J	$\bar{H}_0^0$	Ref
WH_3O^+	37	7	6	1	7.5	0.0025	79.	-4.5	+49.9	14
WNO^+	48	5	4	1	6.1	0.0015	73.	1.1	+158.	
WNO_2^+	64	6	5	1	6.8	0.0020	79.	-0.4	+157.	
WN_2^+	46	5	4	2	6.1	0.0015	74.	1.7	+282.	
WO_2^+	50	5	4	2	6.1	0.0015	75.	2.0	+201.	
WCO_3^-	78	7	6	2	7.5	0.0025	85.	-1.3	-181.6	24
WCO_4^-	94	8	7	2	8.2	0.0030	90.	-3.4	-193.7	29
WOH^-	35	5	4	1	6.1	0.0015	71.	0.2	-112.4	13
WNO^-	48	5	4	1	6.1	0.0015	73.	1.1	-55.	
WNO_2^-	64	6	5	1	6.8	0.0020	79.	-0.4	-117.7	29
WNO_3^-	80	7	6	1	7.5	0.0025	84.	-2.1	-136.3	29
WO_2^-	50	5	4	2	6.1	0.0015	75.	2.0	-85.4	13
WO_3^-	66	6	5	2	6.8	0.0020	80.	0.4	-85.	
WO_4^-	82	7	6	2	7.5	0.0025	85.	-1.4	-99.	
$\text{W}_2\text{H}_3\text{O}^+$	55	10	7	1	7.3	0.0045	86.	-1.3	-29.5	
W_2NO^+	66	8	5	1	5.9	0.0035	79.	4.2	+78.6	
W_2O_2^+	68	8	5	2	5.9	0.0035	81.	5.0	+122.	
W_2CO_3^-	96	10	7	2	7.3	0.0045	90.	1.1	-258.	
W_2CO_4^-	112	11	8	2	8.0	0.0050	95.	-0.9	-265.	
W_2NO_3^-	98	10	7	1	7.3	0.0045	89.	0.4	-210.	
W_2O_2^-	68	8	5	2	5.9	0.0035	81.	5.0	-159.7	13
W_2O_4^-	100	10	7	2	7.3	0.0045	90.	1.1	-167.	
W_2OH^-	53	8	5	1	5.9	0.0035	78.	3.6	-185.9	13
$\text{W}_3\text{H}_3\text{O}^+$	73	13	8	1	7.1	0.0065	91.	1.4	-104.	
W_3NO^+	84	11	6	1	5.7	0.0055	85.	6.9	+4.5	
W_3O_2^-	86	11	6	2	5.7	0.0055	86.	7.6	-232.2	13

REFERENCES

1. F. R. Gilmore, "Equilibrium Composition and Thermodynamic Properties of Air to 24000°K," Rand Corp. report RM-1543 (August 1955).
2. F. R. Gilmore, R&D Associates, Santa Monica, CA, private communication, March 1974.
3. J. Hilsenrath and M. Klein, "Tables of Thermodynamic Properties of Air in Chemical Equilibrium Including Second Virial Corrections from 1500°K to 15,000°K," Arnold Engineering Development Center, Air Force Systems Command report AEDC-TDR-63-161 (August 1963).
4. J. Hilsenrath, M. C. Green and C. W. Beckett, "Thermodynamic Properties of Highly Ionized Air," Air Force Special Weapons Center report AFSWC-TR-65-35 (April 1957).
5. C. D. Sutherland and J. Zinn, "Chemistry Computations in Irradiated Hot Air," Los Alamos Scientific Laboratory report in preparation.
6. D. R. Stull, JANAF Thermochemical Tables (Dept. of Commerce, National Bureau of Standards, Washington, DC, 1970).
7. F. Van Zeggeren and S. H. Storey, The Computation of Chemical Equilibria (Cambridge University Press, 1970).
8. F. R. Gilmore, "Thermal Radiation Phenomena," Vol. I, Lockheed Missiles and Space Co. report LMSC-3-27-67-1 (DASA-1917-1) (May 1967).
9. J. Hilsenrath, C. G. Messina, and W. H. Evans, "Tables of Ideal Gas Thermodynamic Functions for 73 Atoms and Their First and Second Ions to 10,000°K," National Bureau of Standards, Washington, DC, Air Force Weapons Laboratory report AFWL TDR-64-44 (August 1964).
10. L. V. Gurvich, Thermodynamic Properties for the Chemical Species of the Hydrogen-Air System (Publishing House of the Academy of Sciences of the USSR, Moscow, 1962).
11. David G. Clifton, "Approximate Thermodynamic Functions for the NO⁻(g), OH⁻(g), OH⁺(g) Ions," General Motors Defense Research Laboratories report TRGG-01C (April 1966).
12. P. G. Bird, R. E. Duff, and G. L. Schott, "HUG, a Fortran-FAP Code for Computing Normal Shock and Detonation Wave Parameters in Gases," Los Alamos Scientific Laboratory report LA-2980 (February 1964).
13. M. Arshadi and P. Kebarle, "Hydration of OH⁻ and O₂⁻ in the Gas Phase," J. Phys. Chem. 74, 1483 (1970).
14. P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, "The Solvation of the Hydrogen Ion by Water Molecules in the Gas Phase. Heats and Entropies of Solvation of Individual Reactions: H⁺(H₂O)_{n-1}+H₂O→H⁺(H₂O)_n," J. Am. Chem. Soc. 89, 6393 (1967).
15. S. Glasstone, Thermodynamics for Chemists (D. Van Nostrand Co., New York, NY, 1947).
16. R. M. Moyerman and K. E. Shuler, "The Concentration of Contaminant Alkali Salts in Ground Level Air," Science 118, 612 (1953).
17. Defense Nuclear Agency Reaction Rate Handbook, Second Edition, DNA 1948H, General Electric TEMPO (November 1972).
18. C. W. Allen, Astrophysical Quantities (University of London, The Athlone Press, 1963).
19. D. A. Parkes and T. M. Sugden, "Electron Attachment and Detachment in Nitric Oxide," Chemical Society of London, Faraday Transactions 2, 600 (1972).
20. A. Good, D. A. Durden, P. Kebarle, "Ion-Molecule Reactions in Pure Nitrogen and Nitrogen Containing Traces of Water, etc.," J. Chem. Phys. 52, 212 (1970).
21. D. A. Durden, P. Kebarle, A. Good, "Thermal Ion-Molecule Reaction Rate Constants, Reactions in Methane, Krypton, and Oxygen," J. Chem. Phys. 50, 805 (1969).
22. D. C. Conway and L. E. Nesbitt, "Stability of O₄," J. Chem. Phys. 48, 509 (1968).
23. J. T. Moseley, R. A. Bennett and J. R. Peterson, "Photodissociation of CO₃," USA Ballistic Research Laboratories report BRL CR 144 (March 1974).
24. E. E. Ferguson, F. C. Fehsenfeld and A. V. Phelps, "Comment on Photodetachment Cross Sections for CO₃ and Its First Hydrate," J. Chem. Phys. 59, 1565 (1973).
25. J. L. Pack and A. V. Phelps, "Electron Attachment and Detachment II. Mixtures of O₂ and CO₂ and of O₂ and H₂O," J. Chem. Phys. 45, 4316 (1966).
26. A. Good, D. A. Durden and P. Kebarle, "Mechanism and Rate Constants of Ion-Molecule Reactions Leading to Formation of H⁺·(H₂O)_n in Moist Oxygen and Air," J. Chem. Phys. 52, 222 (1970).

27. J. Billingsley and A. B. Callear, "Investigation of the 2050 Å System of the Nitric Oxide Dimer," *Trans. Far. Soc.* 67, 589 (1971).
28. F. C. Fehsenfeld, A. L. Schmeltekopf, H. I. Schiff and E. E. Ferguson, "Negative Ion Reactions of Atmospheric Interest," *Planet. Space Sci.* 15, 373 (1967).
29. J. D. Payzant, R. Yandagni, and F. Kurbale, "Hydration of CN^- , NO_2^- , NO_3^- and OH^- in the Gas Phase," *Can. J. Chem.* 49, 3105 (1971).
30. H. G. Adams, D. K. Bohme, D. W. Dunkin, F. C. Fehsenfeld, and E. E. Ferguson, "Flowing Afterglow Studies of Formation and Reactions of Cluster Ions of O_2^- , O_3^- , and O^- ," *J. Chem. Phys.* 52, 3133 (1970).
31. S. W. Benson, *Thermochemical Kinetics* (Wiley Publishing Co., New York, 1968).