NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Technical Report 32-1425

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Preface

The author, T. E. Horton, is on the staff of the University of Mississippi. The work described in this report was performed under contract with the Jet Propulsion Laboratory with W. A. Menard and G. M. Thomas of the JPL Environmental Sciences Division as technical monitors.

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Abstract

The procedure for computing thermochemical data (specific free energy and specific enthalpy) from partition function is reviewed. Working expressions for approximate partition functions, specific free energy, and specific enthalpy of atomic, diatomic, and polyatomic species are presented.

A review of energy level and heat-of-formation data for atomic, ionic, diatomic, and polyatomic species is given. Species composed of carbon, nitrogen, oxygen, hydrogen, and the noble gases were considered.

A model for estimating the influence of differences in thermochemical data upon chemical composition is developed and used to assess the degree of approximation allowable for partition function computations.

The Computation of Partition Functions and Thermochemistry Data for Atomic, Ionic, Diatomic, and Polyatomic Species

I. Introduction

The procedures for computing partition functions from spectroscopic data and for using the partition function to compute thermochemical data have been enumerated in texts on statistical mechanics and thermodynamics such as Refs. 1, 2, and 3. Over the past 20 years numerous papers and computer programs have dealt with these computations and periodically compilations of such thermochemistry data have appeared (Refs. 4 and 5). As will be shown later, it is important that the approach which one uses in computing these data be standardized. Unfortunately, one does not always have this assurance when using compiled data.[1] Furthermore, as discussed in Ref. 8, such compilations are usually limited in temperature range.

Therefore, when a revision of Ref. 9 was undertaken, it was decided that the thermochemistry data for the new program should be computed systematically by means of a subroutine which could be easily modified and which would use spectroscopic data as input. In choosing between the various approximate procedures for evaluating partition functions the simplest procedures were used which would give the thermodynamic properties and the composition of principal species with only a few percent uncertainty and the composition of trace species to about 10% uncertainty for high-temperature gaseous mixtures encountered in shock tube research.

This report is to describe and justify the computational procedure used in the thermochemistry subroutine of the revised thermochemistry and normal shock program described in Ref. 8. The first half of this report presents the input data and procedure used in the subroutine to estimate the partition function, the specific free energy, and specific enthalpy. In the second half, the problems of correctly estimating the contribution to the partition function associated with the internal degrees of freedom of the various chemical species and the subsequent effect upon properties and chemical composition are discussed as a basis for justifying the procedure used in the subroutine.

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[1] For a critical appraisal of problems arising from use of compiled data see the paper by Durand and Brandmaire (Ref. 6) and the subsequent comments by W. H. Evans (Ref. 7).

II. Expressions and Data for Subroutine

A. The Partition Function

The relationship between the partition function and the equilibrium composition can be shown from Refs. 8 and 9 to be

$$\frac{n^{(i)}}{\prod\limits_{j=s+1}^{s+m} \left(n^{(j)}\right)^{\alpha_{ij}}} = \frac{\left(\dfrac{Q_i}{VA}\right)}{\prod\limits_{j=s+1}^{s+m} \left(\dfrac{Q_j}{VA}\right)^{\alpha_{ij}}} = \frac{K_i}{(RT)^{\Omega}} \tag{1}$$

with $\Omega = 1 - \sum\limits_{j=s+1}^{s+m} \alpha_{ij}$. Now, by comparing the expression

$$\ln K_i = -\frac{F_i^\circ}{RT} + \sum_{j=s+1}^{s+m} \alpha_{ij} \frac{F_j^\circ}{RT} \tag{2}$$

for the equilibrium constant in terms of classical thermodynamic variables, it can be shown that the specific or molal free energy takes the form

$$-\frac{F_i^\circ}{RT} = \ln RT + \ln \frac{Q_i}{VA} \tag{3}$$

The specific or molal enthalpy is given by

$$\frac{H_i^\circ}{RT} = 1 + T\left(\frac{\partial \ln Q_i}{\partial T}\right)_V \tag{4}$$

The partition function Q_i for the *i*th specie is defined as

$$Q_i = \sum_{j=1}^{P_i} g_j^{(i)} \exp\left(-\frac{\varepsilon_j^{(i)}}{kT}\right) \tag{5}$$

with P_i the number of energy levels $\varepsilon_1^{(i)}, \varepsilon_2^{(i)}, \varepsilon_3^{(i)}, \cdots, \varepsilon_{P_i}^{(i)}$ which have degeneracies $g_1^{(i)}, g_2^{(i)}, g_3^{(i)}, \cdots, g_{P_i}^{(i)}$ respectively.

Now, as the Hamiltonian for the motion of a molecule, atom, ion, or electron is separable into a translational term and a term representing the internal motion, it follows that there are a set of translational energy levels and a set of internal energy levels which are independent so that the total energy can be represented by

$$\varepsilon_{K,\ell} = (\varepsilon_{TR})_K + (\varepsilon_{INT})_\ell$$

Thus, dropping the super and subscript denoting a particular specie the partition function takes the form

$$\begin{aligned} Q &= \sum_{K,\ell} g_K g_\ell \exp\left(-\frac{\varepsilon_K + \varepsilon_\ell}{kT}\right) = \left[\sum_K g_K \exp\left(-\frac{\varepsilon_K}{kT}\right)\right]_{TR} \left[\sum_\ell g_\ell \exp\left(-\frac{\varepsilon_\ell}{kT}\right)\right]_{INT} \\ &= Q_{TR}\, Q_{INT} \end{aligned} \tag{6}$$

The internal partition function Q_{INT} can be further modified so that all energy levels for a specie are measured from the ground or lowest energy level. So if ε_0 is the lowest energy level and is measured from common bases for all the chemical species then

$$Q_{INT} = \left[\sum_{\ell=0}^{m} g_\ell \exp\left(-\frac{\varepsilon_{\ell 0}}{kT}\right)\right] \exp\left(-\frac{\varepsilon_0}{kT}\right) \tag{7}$$

where

$$\varepsilon_{\ell 0} = \varepsilon_\ell - \varepsilon_0$$

Thus for Eq. (6)

$$Q = Q_{TR}\, \tilde{q} \exp\left(-\frac{\varepsilon_0}{kT}\right) \tag{8a}$$

where

$$\tilde{q} = \sum_{\ell=0}^{m} g_\ell \exp\left(-\frac{\varepsilon_{\ell 0}}{kT}\right) \tag{8b}$$

The translational partition function for an isotropic family of translational wave functions takes the form

$$Q_{TR} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V \tag{9}$$

providing

$$\frac{N}{V} << \left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

That is, the de Broglie wave length for the motion of some average particle must be short compared to the dimensions of the system. It is clear that at very low temperatures the above discussion of the translational partition function fails. However, of greater interest here is the fact that even at very high temperatures the above expression can be violated provided the pressure is sufficiently high. At high temperatures the above semiclassical description of the translational partition function is most likely invalid in describing the electron gas due to its relatively small mass. Thus for electron concentrations exceeding or approaching

$$\frac{N_e}{V} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \tag{10}$$

the analysis used in this report and in the subroutine is invalid.

Perhaps one should recall at this point that in the development of the above expressions one assumes that the energies of the individual states are independent of variations in the chemical composition, that is, long range interactions of the van der Waal or the Coulomb types are neglected. The range of validity of this assumption determines the range of validity of the results given by the thermochemistry program. The question concerning coulombic type interactions will be deferred until a later section.

On the question of the range for which the neglect of van der Waal type forces is valid, a detailed analysis of this question has not been considered appropriate here as the pressure range over which this effect is important is not that of the usual shock tube experiment. However, one may acquire a quantitative feel for this problem by examining the work of Michels and Schneiderman (Ref. 10) and Hilsenrath and Klein (Ref. 11). A comparison of real (interacting species) and ideal (noninteracting species) computations reveals the influence of interactions is most pronounced at high pressure 100 to 1000 atm for temperatures below 10,000°K. A somewhat conservative rule of thumb is that for gas densities of the order of one amagat, imperfect behavior due to van der Waal forces can be neglected. Thus in terms of the translational and internal partition function expressions the specific or molal free energy becomes

$$-\frac{F^\circ - H^\circ_0}{T} = 5/2\,R\ln T + 3/2\,R\ln M + R\ln\tilde{q} - 7.2836 \tag{11}$$

where

$A\varepsilon_0 = H^\circ_0$ the heat of formation

M is the molecular weight

$R = 1.9872$ cal/mole − °K

$T =$ temperature in °K

and the specific or molal enthalpy is

$$\frac{H^\circ - H^\circ_0}{T} = 5/2\,R + RT\,\frac{\partial \ln\tilde{q}}{\partial T} \tag{12}$$

and the mass action equation can be written

$$\frac{n_i}{\prod\limits_{j=s+1}^{s+m} n_j^{a_{ij}}} = (0.312\,T^{3/2})^{\Omega}\left(\frac{M_i}{\prod\limits_{j=s+1}^{s+m} M_j^{a_{ij}}}\right)^{3/2}\cdot\frac{\tilde{q}_i}{\prod\limits_{j=s+1}^{s+m}\tilde{q}_j^{a_{ij}}}\exp\left(-\frac{\Delta\varepsilon_f}{kT}\right) \tag{13}$$

where

$$\Omega = 1 - \sum_{j=s+1}^{s+m}\alpha_{ij}$$

$$\Delta H_f = (H^\circ_0)_i - \sum_{j=s+1}^{s+m}\alpha_{ij}\,(H^\circ_0)_j$$

$$\Delta\varepsilon_f = \frac{\Delta H_f}{A}$$

Thus, we see the principal problem is the evaluation of the internal partition function.

Because of the differences in their internal motion, the atomic, diatomic, and polyatomic species will be discussed separately. However, before going into the discussion of the separate species let us examine a contribution to the partition function which is common to all species, that is, the contribution associated with the nuclear spin state of the species.

The nucleus of an atom, whether it is associated with others in molecular form or is alone, possesses an intrinsic spin of magnitude S_n measured in units of $h/2\pi$. The magnitude of S_n is an integer or one half an odd integer for even atomic weight isotopes, and an odd half integer for odd atomic weight isotopes. For even our highest temperature this magnitude may be considered fixed. The spin vector can have $(2S_n + 1)$ different space orientations. The magnitude of the magnetic moment associated with the spin is small and gives rise to no appreciable energy difference between states of different spin orientations. The slight differences are manifest as the hyperfine structure in spectra. Thus the only effect of the nuclear spin is to increase the number of particles in every energy level by $(2S_n + 1)$ for every atom present in a chemical specie. Thus, the internal partition function for the ith specie becomes

$$\tilde{q}_i = \left[\prod_{j=s+1}^{s+m} (2S_n^j + 1)^{\alpha_{ij}} \right] q_i$$

Now as

$$\ln \tilde{q}_i = \sum_{j=s+1}^{s+m} \alpha_{ij} \ln (2S_n^j + 1) + \ln q_i \tag{14}$$

we see that the derivative of the above with respect to temperature is not a function of the nuclear spin. Thus, the specific enthalpies are not affected by the nuclear spin. Also by examining the mass action Eq. (13), we see that the partition function portion of the expression is such that the nuclear spin terms cancel so

$$\frac{\tilde{q}_i}{\prod_{j=s+1}^{s+m} \tilde{q}_j^{\,\alpha_{ij}}} = \frac{q_i}{\prod_{j=s+1}^{s+m} q_j^{\,\alpha_{ij}}}$$

and the equilibrium constant and the chemical composition of the mixture are independent of the nuclear spin. However, one should take careful note of the fact that the free energy and therefore the entropy are functions of the nuclear spin. Thus when using free energy values from various references one must carefully note whether nuclear spin has been consistently included or ignored. As consistently ignoring or including nuclear spin has no effect upon the thermochemical behavior of a gaseous mixture, it is completely ignored in this work.

In the cases of three species of interest, He^{++}, H^{+}, and e^{-}, the internal partition functions consist only of the spin contribution. As we are neglecting nuclear spin, the value for the internal partition function of both He^{++}, H^{+} will be unity. However, as we are consistently keeping account of electron spin, which can have two values $\pm\frac{1}{2}\, h/2\pi$, the value of the internal partition function for a free electron must be $q = 2$.

Before discussing the expressions for the internal partition function for molecular, atomic and ionic species, the consideration of the energy level structure of their internal degrees of freedom is appropriate.

B. Energy Level Data

The energy level structure for atomic and atomic ion species was assumed in this work to be that of an isolated system with a finite number of electron states which correspond to those obtained by spectral observation. For the diatomic species the rotational-vibrational-electronic energy structure was accounted for by using the empirical constants of the type used by Herzberg (Ref. 12), which account for anharmonic corrections. For the polyatomic species a harmonic oscillator-rigid rotator model is used to represent the energy states with electronic structure neglected.

In the following material each of these three types of species will be discussed in detail. Appropriate numerical values which are necessary to evaluate the energy level models will be presented and discussed. These values make up a part of the library data used in the program described in Ref. 8.

*1. **Energy levels for atomic species.*** Let us first review the simple theory of the energy levels for an isolated ion or atom. Here by isolated we mean that potential fields associated with other charged particles are sufficiently weak so that energy levels for the specie in question are a function only of the position and charge of the nucleus and its associated electrons.

The simplest system which one can consider is that of hydrogen. As is well known for this and other single electron systems, the state of the atom is specified by four quantum numbers: n the principal quantum number which can take on any positive integer value, l the angular quantum number which can take on integer values ranging from 0 to $(n - 1)$, the magnetic quantum number which for each value of l can take on $(2l + 1)$ values, and the spin quantum number which can take on two values. As the energy levels for each state are determined only by the principal quantum number, the energy, in units of eV, is

$$\varepsilon_n = 13.595\left(1 - \frac{1}{n^2}\right) \qquad (15)$$

It can be shown that the degeneracy of an energy level is

$$(g_e)_n = 2n^2 \qquad (16)$$

Expressions of this type, Eq. (15) and (16) are good also for systems which possess only a single electron or for multielectron systems in which only one of the electrons is in a highly excited state. However, the usual picture for the multiple electron system is much more complex as the states of the system are determined not only by the interaction between nucleus and the electrons but also by interactions between electrons. Because of this complication the electronic energy levels (called "terms") are determined from spectroscopic observations and are taken from the tabulation in Ref. 13. The terms are characterized by their electron spin quantum number S and the orbital-angular momentum quantum number L. The value $(2S + 1)$ is called the multiplicity of the term. Terms with $L = 0, 1, 2, 3, 4$ are denoted by S, P, D, F, G respectively. Thus, a term with $L = 2$, $S = 1$ is denoted by ^3D and called a triplet-D term. In a tabulation of energy levels one finds many terms with the same L and S values. Their energy differences are due to the manner in which the orbital angular momentum and the spin angular momentum couple together to produce a resulting total angular momentum. This total angular momentum is characterized by the total angular momentum quantum number J. The degeneracy of a term is determined by the $(2J + 1)$ orientations in space which the total angular momentum vector of an atom may possess. In the absence of external fields all orientations have the same energy and so the degeneracy of the level is

$$g_e(L, S, J) = (2J + 1) \qquad (17)$$

A detailed discussion of the electron energy level structure can be found in Ref. 14.

Values for the atomic energy levels ε_i and term angular momentum quantum numbers J_i, used in this work were taken from Ref. 13. Because in some cases several hundred terms are listed for each specie, a modified tabulation which could conveniently be stored in the computer was devised. This reduced list of energy levels was obtained by replacing terms which were close together by a single energy level (that of the term of largest degeneracy) and an equivalent degeneracy which was the sum of the degeneracies. In this way a reduced list containing fewer than 70 values and capable of yielding values of the partition function and enthalpy $(H^\circ - H_0^\circ)$ which agree with those of the full tabulation to less than 0.1% in the temperature range of 300°K to 80,000°K were obtained. The species considered in this manner were He(I), C(I), C(II), C(III), C(IV), N(I), N(II), N(III), N(IV), O(I), O(II), O(III), O(IV), A(I), A(II), A(III), A(IV), Ne(I), Ne(II), Ne(III), Ne(IV). For H(I) and He(II) only those terms with principal quantum number of 5 or less were used in the reduced list. This number was chosen on the basis of extensive computations.

To estimate properties for H^-, C^-, N^-, and O^- energy levels for atomic specie of the same isoelectronic sequence were used. Thus H^- corresponds to the energy level of He(I) while C^-, N^-, and O^- correspond to N, O, and F respectively.

2. *Energy levels for diatomic species.* The energy level structure of diatomic ions and neutrals is characterized by a series of electronic levels similar to those for atomic systems but fewer in number. The electronic levels are subdivided into vibrational levels which in turn are subdivided into rotational levels. The energy difference between electronic excitation levels is of the order of 10^4–10^5 cm^{-1}. However, the energy difference between vibrational energy levels which differ by unity in their vibrational quantum numbers v is of the order of 10^3 cm^{-1}. For small rotational quantum numbers J, the energy difference between rotational energy levels of the same vibrational level is of the order of 10 cm^{-1}.

While the vibrational and rotational states are designated by the integer values of the quantum numbers v and J respectively, the designation of the electronic levels is considerably more complex. For the molecules considered in this work the electronic states are categorized by three quantities Λ, Σ, and Ω which are analogous to the L, S, and J quantities used to designate atomic electronic levels. The integer value of Λ, the component of the electronic angular momentum along the internuclear axis, is designated by the following translation of numeric to upper case Greek symbols:

$\Lambda = 0 \rightarrow \Sigma$ state

$\Lambda = 1 \rightarrow \Pi$ state

$\Lambda = 2 \rightarrow \Delta$ state

$\Lambda = 3 \rightarrow \Phi$ state

Now the electron spins combine to form a total spin angular momentum S which can have components denoted by Σ which are parallel to the internuclear axis such that $\Sigma = S, S - 1, \cdots, -S$. The electron spin multiplicity is designated by the quantity $(2S + 1)$ which is used as a left superscript to the state designation. The combination of Λ and Σ give the total angular momentum which is denoted by Ω. The numerical value is

$$\Omega = |\Lambda + \Sigma|$$

The actual value of $\Lambda + \Sigma$ is used as a right subscript in the state designation. Thus the ${}^4\Pi_{-1/2}$ state has $\Lambda = 1$, $S = 3/2$, $\Sigma = -3/2$ and $\Omega = +1/2$.

As in the case of atomic energy levels this designation for the different electronic levels can be translated into the electronic degeneracy or statistical weight $(g_e)_i$ for the *i*th electronic state. The degeneracy is related to the electronic spin multiplicity $(2S + 1)$ as follows:

$(g_e)_i = (2S_i + 1)$ if the *i*th is a Σ state

$(g_e)_i = 2\,(2S_i + 1)$ if the *i*th is a $\Pi, \Delta, \Phi, \cdots$ state.

Figure 1 depicts the vibrational levels for the ground state and the electronic state[2] for a molecule together with the interaction potentials between nuclei as a function of internuclear distance *r*. For such an anharmonic potential with the effects of centrifugal stretching and rotational-vibrational coupling upon rotational states taken into account, the energy of a particular electronic state with vibrational and rotational quantum number *v* and *J* respectively is given by an expression of the form

$$\begin{aligned}\varepsilon_{v,J} = T_e + \omega_e (v + \tfrac{1}{2}) - \omega_e x_e (v + \tfrac{1}{2})^2 + \cdots \\ + B_v J (J + 1) - D_v J^2 (J + 1)^2 + \cdots\end{aligned} \qquad (18)$$

This term representation is that used by Herzberg (Ref. 12). Because of their negligible contribution, the coefficients of terms other than those explicitly shown above will be neglected in future discussions. The quantity T_e represents the difference in energy between the minimum potential points on the excited electronic state potential curve and on the ground state potential curve. The ω_e is the small amplitude frequency of molecular vibration and the $\omega_e x_e$ accounts for the anharmonic effect. The B_v and D_v are the rotational terms which are functions of the vibrational quantum number *v*

$$B_v = B_e - \alpha_e (v + \tfrac{1}{2}) \qquad (19a)$$

$$D_v = D_e + \beta_e (v + \tfrac{1}{2}) \qquad (19b)$$

From the following work β_e is considered to be negligible and D_e equal to $\dfrac{4\,B_e^3}{\omega_e^2}$.

Figure 1 shows two representations for the term electronic energy *T* and the dissociation energy *D*. The rotational D_e used above should not be confused with the dissociative energy shown in the figure. In the computation of partition functions the convention of measuring all energy from the ground state is followed. Thus, the rearrangement of Eq. (18) applied to the *i*th electronic state takes the form

$$(\varepsilon_i)_{vJ} = (T_0)_i + (\omega_0)_i\, v - (\omega_0 x_0)_i\, v^2 + (B_0)_i\, J\,(J + 1)\left[1 + \left(\frac{D_e}{B_0}\right)_i J\,(J + 1) - \left(\frac{\alpha_e}{B_0}\right)_i v\right] \qquad (20)$$

where

$$(T_0)_i = (T_e)_i + \left(\frac{\omega_e}{2} - \frac{\omega_e x_e}{4}\right)_i - \left(\frac{\omega_e}{2} - \frac{\omega_e x_e}{4}\right)_x$$

$$(\omega_0)_i = \left(\omega_e - \frac{\omega_e x_e}{2}\right)_i$$

$$(\omega_0 x_0)_i = (\omega_e x_e)_i$$

$$(B_0)_i = \left(B_e - \frac{\alpha_e}{2}\right)_i$$

and the subscript $_x$ denotes constants for the ground electronic state.

All the above subscript *e* quantities are determined empirically from the spectroscopic data and they can be directly related to the interaction potential. The units used for these terms are cm^{-1}.

The primary source of data on diatomic energy levels is the classic work of Herzberg (Ref. 12); however, in the case of certain diatomic species either values were not available at the time of its publication or recent work

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[2] Rotational levels have not been shown.

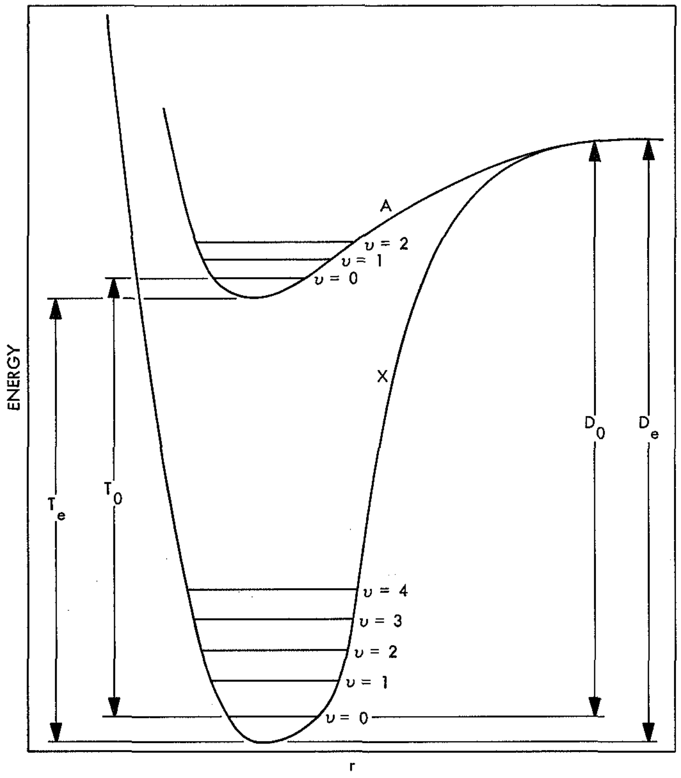

Fig. 1. Energy levels and nuclei interaction potentials for a diatomic molecule

has resulted in improved values. Thus, to have the best available data on diatomic species in the library of the program a review of sources of spectroscopic data was undertaken. However, because of the specialized nature of these data an exhaustive critical study was beyond the bounds of the current effort and we have relied heavily on recent compilations (Refs. 4, 5, and 15).

In our review we have considered neutral and singly charged positive and negative ion forms of diatomic molecules composed of hydrogen, oxygen, nitrogen, and carbon. In some cases, such as for N_2^-, CO^-, CN^+, CN^-, C_2^-, C_2^+, CH^+, and CH^-, either no stable form exists or insufficient data were available.

In most cases, electronic levels with terms above 30,000 cm^{-1} have been neglected. The contributions of states above this level should normally result in a negligible error in composition computations. Now, we shall discuss the different diatomic forms by isoelectronic sequence.

a. Sequence with 17 electrons. This sequence contains only the uninegative diatomic oxygen ion O_2^-. In the old JPL program the thermochemistry data were based upon the early work of Gilmore (Ref. 16). Our current values are based upon the work of Rolfe (Ref. 17).

O_2^- $\sigma = 2$

State	T_e	g_e	ω_e	$\omega_e x_e$	B_e	α_e
$X^2\Pi$	0.0	4.0	1170.0	8.5	1.247	0.013
$A^2\Pi$	29400	4.0	1170.0	8.5	1.247	0.013

Because the molecule is homonuclear, the symmetry number $\sigma = 2$. In the above listing the rotational and the vibrational constants for the ground state have been repeated for the excited state for want of better values. This will not result in a significant error in concentration. A comparison of computations made with the above values and with the previous library data reveals only 4% difference in O_2^- concentrations despite sizable differences in specific enthalpies and free energies. This is due to the compensating effect of the new estimate of the heat of formation of this specie.

b. Sequence with 16 electrons. This sequence contains the NO^- and O_2 species. For the diatomic oxygen O_2, energy levels listed in Herzberg have been used. References 4, 5, and 15 also cite these values:

O_2 $\sigma = 2$

State	T_e	g_e	ω_e	$\omega_e x_e$	B_e	α_e
$X^3\Sigma$	0.0	3.0	1580.36	12.073	1.4457	0.0158
$a^1\Delta$	7918.1	2.0	1509.0	12.0	1.4264	0.0171
$b^1\Sigma$	13195.2	1.0	1432.7	13.95	1.4004	0.0182
$A^3\Sigma$	36096.0	3.0	819.0	22.5	1.05	—

For the uninegative nitric oxide ion, NO^-, no electronic energy levels are available. Only Gilmore, Ref. 15, lists data for this specie and the constants are estimated from those for O_2. Because of the uncertainty only the ground state is listed:

NO^- $\sigma = 1$

State	T_e	g_e	ω_e	$\omega_e x_e$	B_e	α_e
$X^3\Sigma$	0.0	3.0	1600.0	12.0	1.4	0.016

c. Sequence with 15 electrons. This sequence contains the NO and O_2^+ species. For the nitric oxide molecule, the older ground state rotational-vibrational constants cited by Herzberg (Ref. 12) have been used; these are based upon the work of Gillette and Eyster (Ref. 18). The $a^4\Pi$ state is usually not listed. The ω_e and $\omega_e x_e$ values were reduced by the author from the work of Wallace (Ref. 19). The rotational constants were from W. Menard.[3] The T_e value for this state was reduced from data in Ref. 20.

NO $\sigma = 1$

State	T_e	g_e	ω_e	$\omega_e x_e$	B_e	α_e
$X^2\Pi$	0.0	2.0	1904.03	13.97	1.705	0.0178
$X^2\Pi$	121.1	2.0	1903.68	13.97	1.705	0.0178
$a^4\Pi$	38406.0	8.0	1017.0	12.0	1.22	0.0198
$A^2\Sigma$	43966.0	2.0	2371.0	14.5	1.995	0.0164

For the unipositive diatomic oxygen ion O_2^+, older works neglected the 0.02 eV splitting of the ground state. The spectroscopic constants used here were from Herzberg (Ref. 12) except for T_e of the ground state splitting and for the $a^4\Pi$ state. These values were reduced by the author from the compilation by Wallace (Ref. 19).

O_2^+ $\sigma = 2$

State	T_e	g_e	ω_e	$\omega_e x_e$	B_e	α_e
$X^2\Pi$	0.0	2.0	1876.4	16.53	1.6722	0.01984
$X^2\Pi$	200.0	2.0	1876.4	16.53	1.6722	0.01984
$a^4\Pi$	31900.0	8.0	1035.7	10.39	1.1047	0.01575
$A^2\Pi$	38795.0	4.0	900.0	13.4	1.0617	0.01906

d. Sequence with 14 electrons. This sequence contains CO, N_2, and NO^+. For the carbon monoxide molecule the data from the recent compilation by Krupenie (Ref. 21) were used. These values agree well with the work done by Herzberg (Ref. 22).

CO $\sigma = 1$

State	T_e	g_e	ω_e	$\omega_e x_e$	B_e	α_e
$X^1\Sigma$	0.0	1.0	2169.8	13.29	1.931	0.0175
$a^3\Pi$	48687.4	6.0	1743.6	14.47	1.691	0.0195

For the unipositive nitric oxide ion the ground state constants were taken from Gilmore (Refs. 15 and 16) and Wallace (Ref. 19). The values for the excited state are the estimates of Gilmore (Ref. 15) and no information on anharmonic or rotational constants was available.

NO^+ $\sigma = 1$

State	T_e	g_e	ω_e	$\omega_e x_e$	B_e	α_e
$X^1\Sigma$	0.0	1.0	2377.1	16.35	2.002	0.0202
$a^3\Sigma$	40332.0	3.0	1572.0	—	—	—

For the diatomic nitrogen molecule the data were taken from the Ref. 23 compilation.

N_2 $\sigma = 2$

State	T_e	g_e	ω_e	$\omega_e x_e$	B_e	α_e
$X^1\Sigma$	0.0	1.0	2358.1	14.19	1.99	0.017
$A^3\Sigma$	50206.0	3.0	1460.4	13.89	1.43	0.013

e. Sequence with 13 electrons. This sequence contains CO^+, CN, N_2^+. For unipositive carbon monoxide ion, CO^+, the spectroscopic constants were taken from the recent NBS compilation by Krupenie (Ref. 21).

CO^+ $\sigma = 1$

State	T_e	g_e	ω_e	$\omega_e x_e$	B_e	α_e
$X^2\Sigma$	0.0	2.0	2214.3	15.16	1.977	0.0190
$A^2\Pi$	20733.0	4.0	1562.1	13.53	1.589	0.0194
$B^2\Sigma$	45877.0	2.0	1734.2	27.93	1.800	0.0302

For cyanogen, CN, the values listed for the ground and excited states of this specie were reduced by the author from the data given in Ref. 19. These values are in agreement with the $X^2\Sigma$ values, $\omega_e = 2068.71$, $\omega_e x_e = 13.14$; and $\omega_e = 2068.61$, $\omega_e x_e = 13.11$ listed respectively by Herzberg (Ref. 12) and the JANAF tables (Ref. 4). The values for the $A^2\Pi$ and $B^2\Sigma$ states used in the present work differ as shown below:

	T_e	ω_e	$\omega_e x_e$	
$A^2\Pi$	9246.0	1812.6	12.7	Present work
	9241.7	1814.4	12.9	Herzberg
$B^2\Sigma$	25752.1	2163.66	20.05	Present work
	25751.8	2164.13	20.25	Herzberg

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[3] A JPL private communication.

CN $\sigma = 1$

State	T_e	g_e	ω_e	$\omega_e x_e$	B_e	α_e
$X^2\Sigma$	0.0	2.0	2068.8	13.19	1.90	0.018
$A^2\Pi$	9246.0	4.0	1812.6	12.7	1.72	0.017
$B^2\Sigma$	25752.1	2.0	2163.7	20.1	1.97	0.022

For the unipositive diatomic nitrogen ion N_2^+ the values were reduced by the author from the frequencies listed in Wallace (Ref. 24). These agree better with the observed frequencies than frequencies obtained using Ref. 23 constants for the $B^2\Sigma$ state. The other values agree closely.

N_2^+ $\sigma = 2$

State	T_e	g_e	ω_e	$\omega_e x_e$	B_e	α_e
$X^2\Sigma$	0.0	2.0	2207.6	16.9	1.93	0.020
$A^2\Pi$	9168.3	4.0	1902.8	14.6	1.74	0.018
$B^2\Sigma$	25452.9	2.0	2441.1	31.2	2.085	0.025

Although the JANAF tables list data for the C_2^- specie it will not be considered.

f. Sequence with 12 electrons. This sequence contains C_2 and CN^+. For the unipositive cyanogen ion insufficient data were available to reduce constants for this specie. For the diatomic carbon molecule the spectroscopic constants were from the work of E. Clementi (Ref. 25).

C_2 $\sigma = 2$

State	T_e	g_e	ω_e	$\omega_e x_e$	B_e	α_e
$a^1\Sigma$	0.0	1.0	1854.7	13.34	1.820	0.0176
$X^3\Pi$	716.2	6.0	1641.3	11.67	1.633	0.0164
$^3\Sigma$	6435.1	3.0	1470.4	11.19	1.499	0.0163
$b^1\Pi$	8391.1	2.0	1608.3	12.08	1.616	0.0169
$^1\Delta$	10186.3	2.0	1481	11.14	1.486	0.015
$^1\Sigma$	14181.5	1.0	1470	10.06	1.475	0.013
$^3\Sigma$	14282.1	3.0	1891	14.23	1.897	0.018
$A^3\Pi$	19950.3	6.0	1788.2	16.44	1.753	0.0161
$C^1\Pi$	34277.4	2.0	1809.1	15.81	1.733	0.012

g. Sequence with 10 electrons. This sequence contains only OH^-. For the uninegative hydroxyl ion OH^- the constants were obtained from the work of Branscomb (Ref. 26) as cited by the JANAF tables.

OH^- $\sigma = 1$

State	T_e	g_e	ω_e	$\omega_e x_e$	B_e	α_e
$X^1\Sigma$	0.0	1.0	3735.0	74.7	18.87	0.65

h. Sequence with 9 electrons. In this sequence only the hydroxyl molecule was considered. The data used for the reduction of the spectrographic constants came from Wallace (Ref. 19). Although these are based upon work done after Herzberg's text was published, the agreement of the values listed below with his are good.

OH $\sigma = 1$

State	T_e	g_e	ω_e	$\omega_e x_e$	B_e	α_e
$X^2\Pi$	0.0	4.0	3738.4	81.8	18.85	0.70
$A^2\Sigma$	32687.0	2.0	3179.7	103.3	17.23	0.78

i. Sequence with 8 electrons. This sequence consists of OH^+ and NH species. For the unipositive hydroxyl ion the constants for the $X^3\Sigma$ and $A^3\Pi$ states were reduced by the author from the Ref. 19 tabulation. These values differ by 300 cm^{-1} in the vibrational terms and 500 cm^{-1} in the electronic term from the values listed in Herzberg.

OH^+ $\sigma = 1$

State	T_e	g_e	ω_e	$\omega_e x_e$	B_e	α_e
$X^3\Sigma$	0.0	3.0	3229.0	131.0	16.74	0.73
$^3\Pi$	28459.0	6.0	2202.0	108.0	13.75	0.86

For the imidogen molecule NH, the constants were taken from the work of McBride (Ref. 5) and JANAF. McBride and JANAF cite the same source of the data but differ significantly on the ω_e and $\omega_e x_e$.

NH $\sigma = 1$

State	T_e	g_e	ω_e	$\omega_e x_e$	B_e	α_e
$X^3\Sigma$	0.0	3.0	3315.0	94.7	16.67	0.65
$a^1\Delta$	14970.0	2.0	3186.0	29.0	16.54	0.17
$b^1\Sigma$	23415.0	1.0	3480.0	—	16.40	—
$A^3\Pi$	29819.0	6.0	3232.5	99.2	16.69	0.74

j. Sequence with 7 electrons. This sequence consists of CH and NH^+. For methylidyne CH the values listed in the library were taken from Ref. 12.

CH $\sigma = 1$

State	T_e	g_e	ω_e	$\omega_e x_e$	B_e	α_e
$X^2\Pi$	0.0	2.0	2861.6	64.3	14.46	0.534
$X^2\Pi$	17.9	2.0	2861.6	64.3	14.46	0.534
$A^3\Delta$	23150.0	4.0	2921.0	90.4	14.91	0.67
$B^2\Sigma$	25949.0	2.0	2542.5	373.8	12.89	0.485
$C^2\Sigma$	31821.0	2.0	2824.1	105.8	14.63	0.74

For the unipositive imidogen ion NH^+, energy level data are available in Ref. 19; however, the specie was not considered of sufficient importance and was not included.

k. Sequence with 6 electrons. This sequence contains only the unipositive methylidyne ion CH^+ for which data were reduced by the author from the energy level data of Ref. 19.

CH^+ $\sigma = 1$

State	T_e	g_e	ω_e	$\omega_e x_e$	B_e	α_e
$X^1\Sigma$	0.0	1.0	2739.7	–	14.18	0.49
$A^1\Pi$	24171.3	2.0	1840.1	98.5	11.89	0.92

l. Sequences with 2 and 1 electrons. These sequences contain H_2 and H_2^+ and for these species the constants were taken from Ref. 12.

H_2 $\sigma = 2$

State	T_e	g_e	ω_e	$\omega_e x_e$	B_e	α_e
$X^1\Sigma$	0.0	1.0	4395.2	117.9	60.81	2.99

H_2^+ $\sigma = 2$

State	T_e	g_e	ω_e	$\omega_e x_e$	B_e	α_e
$X^2\Sigma$	0.0	2.0	2297.0	62.0	29.8	1.4

3. Energy levels for polyatomic species. The energy levels for polyatomic and diatomic species are similar, being characterized by electronic energy levels which are subdivided into vibrational and rotational states. In this analysis the electronic levels will be neglected on the assumption that most of the polyatomic species will be dissociated at temperatures for which electronic excitation becomes significant.

Furthermore, because of the relatively low temperature range in which these species are present it will be shown later that we are justified in assuming the vibrational-rotational states are those of a rigid rotator-harmonic oscillator.

The rotational aspect of polyatomic species motion is determined by the geometric configuration of the N nuclei. If they can all be placed in two intersecting planes (i.e., a linear molecule) then the rotational energy is quantitized according to

$$\varepsilon_J = B(J)(J+1)$$

And there are $3N - 5$ vibrational degrees of freedom which must be taken into account. Thus

$$\varepsilon_{J,v} = B(J)(J+1) + \sum_{i=1}^{3N-5} \omega_i v_i \qquad (21)$$

where the degeneracy of each rotational state is

$$g_J = 2J + 1 \qquad (22)$$

and ω_i comes from the set of $3N - 5$ vibrational frequencies for the specie.

For the polyatomic molecule with non-linear structure the rotational energy can be accounted for by assuming the molecule behaves as a classical asymmetric top with principal moments of inertia I_A, I_B, and I_C. The vibrational degrees of freedom are accounted for by considering $3N - 6$ vibrational frequencies of the specie.

As in the case of diatomic molecules a symmetry number σ must be considered to correctly account for rotational degeneracy. This number is equal to the number of distinct exchanges of identical atoms which can be accomplished by rotation about axes of symmetry.

Because of the large number of polyatomic species which can be constructed from C, N, O, and H, we have chosen to examine the constants of only CO_2, N_2O, NO_2, NH_3, H_2O, and CH_4 carefully. For the other polyatomic species the constants listed in the JANAF tables have been used. Work by Herzberg (Refs. 27 and 28) may prove helpful for improved values as well as the listing by McBride, et al. (Ref. 5).

4. Constants for polyatomic species. Constants, all from Ref. 28, are

(1) Carbon dioxide (CO_2)

$g = 1$ $\sigma = 2$ $B = 0.39021\ \text{cm}^{-1}$ $\omega_1 = 1388.17\ \text{cm}^{-1}$
$\omega_2 = 667.4$
$\omega_3 = 667.4$
$\omega_4 = 2349.16$

(2) Water (H_2O)

$g = 1$ $\sigma = 2$ $I_A = 1.004 \times 10^{-40}\ \text{gm-cm}^2$ $\omega_1 = 3657.0\ \text{cm}^{-1}$
$I_B = 1.929 \times 10^{-40}$ $\omega_2 = 1594.7$
$I_C = 3.015 \times 10^{-40}$ $\omega_3 = 3755.7$

(3) Ammonia (NH_3)

$g = 1$ $\sigma = 3$ $I_A = 2.964 \times 10^{-40}\ \text{gm-cm}^2$ $\omega_1 = 3336.2\ \text{cm}^{-1}$
$I_B = 2.964 \times 10^{-40}$ $\omega_2 = 949.87$
$I_C = 4.518 \times 10^{-40}$ $\omega_3 = 3443.9$
$\omega_4 = 3443.6$
$\omega_5 = 1627.4$
$\omega_6 = 1626.10$

(4) Dinitrogen Monoxide (N_2O)

$g = 1$ $\sigma = 1$ $B = 0.41901\ \text{cm}^{-1}$ $\omega_1 = 2223.7\ \text{cm}^{-1}$
$\omega_2 = 588.8$
$\omega_3 = 588.8$
$\omega_4 = 1284.9$

(5) Nitrogen Dioxide (NO_2)

$g = 2$ $\sigma = 2$ $I_A = 68.20 \times 10^{-40}\ \text{gm-cm}^2$ $\omega_1 = 1319.7\ \text{cm}^{-1}$
$I_B = 64.55 \times 10^{-40}$ $\omega_2 = 749.8$
$I_C = 3.498 \times 10^{-40}$ $\omega_3 = 1617.75$

(6) Methane (CH_4)

$g = 1$ $\sigma = 12$ $I_A = 5.340 \times 10^{-40}\ \text{gm-cm}^2$ $\omega_1 = 2916.5\ \text{cm}^{-1}$
$I_B = 5.340 \times 10^{-40}$ $\omega_2 = 1533.6$
$I_C = 5.340 \times 10^{-40}$ $\omega_3 = 1533.6$
$\omega_4 = 3019.49$
$\omega_5 = 3019.49$
$\omega_6 = 3019.49$
$\omega_7 = 1306.2$
$\omega_8 = 1306.2$
$\omega_9 = 1306.2$

5. Heat of formation. In addition to the energy level structure for each specie which has been discussed, the relative differences in ground state energy levels for all these species must be considered. The heat of formation is a measurement of this difference. The heat of formation is the energy difference between the ground state of the specie in question and ground states of reference species. Thus, the heat of formation of the reference species are usually taken to be zero. The number of reference species will always equal the number of elemental species considered. The heats of formation are functions of the more fundamental microscopic properties such as bond energies, ionization potentials, electron affinities, and dissociation energies.

The values for the heats of formation at one atmosphere and zero degrees absolute temperature used in this work are listed in Table 1 with the source of the data. For information on other species one may consult a compilation such as in Refs. 4, 5, 29 or 30.

Despite the considerable amount of effort which has been expended in measuring heats of formation, several

Table 1. Heat of formation tabulation

Specie	H_0° kcal/mole	Source
O_2^-	−13.37	Private communication[a]
O_2	0.0	—
NO^-	14.0	Ref. 15
NO	21.45	Ref. 29
O_2^+	278.178	Ref. 31
CO	−27.199	Ref. 29
NO^+	234.8	Ref. 29
N_2	0.0	—
CO^+	295.9	Ref. 29
CN	108.0	Ref. 29
N_2^+	359.297	Ref. 31
C_2	196.0	Ref. 32
OH^-	−32.9	Ref. 26
OH	9.25	Ref. 29
OH^+	316.0	↓
NH	79.0	↓
CH	141.6	↓
CH^+	398.1	↓
H_2	0.0	—
H_2^+	355.74	Ref. 29
CO_2	−93.963	↓
H_2O	−57.102	↓
NH_3	−9.34	↓
N_2O	20.435	↓
NO_2	8.60	↓
CH_4	−15.970	↓
C^-	144.0	Ref. 15
N^-	115.99	Ref. 33
O^-	25.20	Ref. 29
H^-	34.40	↓
C	169.98	↓
C^+	429.628	↓
C^{++}	991.900	↓
C^{+++}	2095.98	↓
N	112.534	↓
N^+	447.663	↓
N^{++}	1130.55	↓
N^{+++}	2224.52	↓
O	58.983	↓
O^+	373.019	↓
O^{++}	1183.73	↓
O^{+++}	2450.87	↓
H	51.626	↓
H^+	365.211	↓
He	0.0	—
He^+	566.978	Ref. 29
He^{++}	1821.07	Ref. 13
Ar	0.0	—
Ar^+	363.42	Ref. 29
Ar^{++}	1000.5	↓
Ar^{+++}	1943.9	↓
Ne	0.0	—
Ne^+	497.29	Ref. 29
Ne^{++}	1444.7	↓
Ne^{+++}	2915.0	↓

[a] A. R. Hochstim, Apr. 1968.

of those listed here remain uncertain by a significant amount. Some of these require comment.

In the previous JPL program (Ref. 9) a value of −23.0 kcal/mole was used for the heat of formation of O_2^-. This was based upon the electron affinity of 0.87 eV reported by Pritchard (Ref. 34). The value of −9.92 kcal/mole based upon Pack and Phelps (Ref. 35) value of 0.43 eV is frequently used. In a private communication, Hochstim indicated that the electron affinity of 0.58 eV or heat of formation of −13.37 kcal/mole is preferable.

For OH^-, Hochstim in a private communication suggested the value of 1.8 eV for electron affinity of OH instead of the older value of 2.7 eV. Both JANAF and Gilmore (Ref. 15) confirm this value of 1.83 which corresponds to a heat of formation of −32.9 kcal/mole. The measurement is attributed to the 1966 work of Branscomb (Ref. 26).

The heat of formation for N^- is based on the electron affinity of −0.15 eV by Edie and Rohrlich (Ref. 33).

Other species for which there seems to be a lack of agreement on the values of their heats of formation are NH, CN, C_2, NO^-, O_2^+, and NO^+.

C. Working Expressions

There are numerous approximations which can be used in computing the thermochemical quantities necessary to evaluate the concentration and properties of a multicomponent mixture. In the following section the approximate expressions used in evaluating the internal partition functions are given along with the resulting expressions for specific free energy and specific enthalpy. These are the expressions which are currently used in the thermochemical subroutine of the program discussed in Ref. 8.

1. Atomic species and atomic ions. The evaluation of the internal partition function for the atomic species and their ionic forms consists of simply summing over the electronic energy levels. The sum is over the finite list of levels given in Ref. 13 or the reduced list of levels, discussed earlier, which give the same result.

Thus, the internal partition function is

$$q = \sum_{i=1}^{n} g_i \exp\left(-\frac{\varepsilon_i}{kT}\right) \tag{23a}$$

The expression for free energy would be

$$-\left(\frac{F^\circ - H_0^\circ}{T}\right) = 5/2\,R\ln T + 3/2\,R\ln M + R\ln q - 7.2836 \tag{23b}$$

and for the specific enthalpy Eq. (12) becomes

$$\left(\frac{H^\circ - H_0^\circ}{RT}\right) = 5/2 + \frac{\sum_{i=1}^{n} \frac{\varepsilon_i}{kT}\, g_i \exp\left(-\frac{\varepsilon_i}{kT}\right)}{q} \tag{23c}$$

For the case of doubly ionized helium He(III) and ionized hydrogen H(II) the electric structure is lacking and nuclear spin by previous arguments is not considered. Thus

$$q = 1$$

so

$$-\left(\frac{F^\circ - H_0^\circ}{T}\right) = 5/2\,R\ln T + 3/2\,R\ln M - 7.2836 \tag{24}$$

For the special case of the electron the only contribution to the internal partition function is due to its spin, so

$$q = 2$$

and

$$-\left(\frac{F^\circ - H_0^\circ}{T}\right) = 5/2\,R\ln T + 3/2\,R\ln M - 5.9063 \tag{25}$$

The specific enthalpy for electrons He(III) and H(II) is

$$\left(\frac{H^\circ - H_0^\circ}{RT}\right) = 5/2 \tag{26}$$

2. Polyatomic species. The harmonic oscillation-rigid rotation approximation was used to describe the partition function of both the linear and non-linear polyatomic species. The description of the energy for these approximations was given earlier in Eqs. (21) and (22). Using these expressions for energy we have

$$q = \frac{g_e}{\sigma} \sum_{J, v_1, v_2, \ldots, v_n} (2J + 1) \exp\left(-\frac{\varepsilon_{J, v_1, v_2, \ldots, v_n}}{kT}\right)$$

where n is the number of vibrational degrees of freedom then

$$\varepsilon_{J, v_1, v_2, \ldots, v_n} = B(J)\,(J + 1) + \sum_{i=1}^{n} \omega_i v_i$$

Thus the partition function can be written as

$$q = \frac{g_e}{\sigma} q_R \prod_{i=1}^{n} (q_V)_i \tag{27}$$

For a harmonic oscillator

$$(q_V)_i = \sum_{v=0}^{\infty} \exp\left(-\frac{\omega_i v}{kT}\right) = \left[1 - \exp\left(-\frac{\omega_i}{kT}\right)\right]^{-1} \tag{28}$$

and for the rigid rotator where the energy levels are so closely spaced that the sum may be approximated by an integral we have

$$q_R = \frac{kT}{B} \tag{29}$$

Thus the free energy takes the form

$$-\left(\frac{F^\circ - H^\circ_0}{T}\right) = 7/2\,R \ln T + 3/2\,R \ln M - R \ln B + R \ln \frac{g_e}{\sigma} - \sum_{i=1}^{n} R \ln \times \left[1 - \exp\left(-\frac{\omega_i}{kT}\right)\right] - 8.0066 \tag{30a}$$

and the enthalpy is

$$\left(\frac{H^\circ - H^\circ_0}{RT}\right) = 7/2 + \sum_{i=1}^{n} \frac{\omega_i}{kT} \Big/ \left[\exp\left(\frac{\omega_i}{kT}\right) - 1\right] \tag{30b}$$

In the case of the polyatomic specie for which the rotational energy is that of a classical asymmetric top

$$q_R = \left[\pi \left(\frac{8\pi^2 kT}{h^2}\right)^3 I_A I_B I_C\right]^{1/2}$$

where I_A, I_B, and I_C are the principal moments of inertia in gm-cm². Thus the free energy becomes

$$-\left(\frac{F^\circ - H^\circ_0}{T}\right) = 4 R \ln T + 3/2\,R \ln M + 1/2\,R \ln (I_A I_B I_C \times 10^{120}) + R \ln \left(\frac{g_e}{\sigma}\right) - \sum_{i=1}^{n} R \ln \left[1 - \exp\left(-\frac{\omega_i}{kT}\right)\right] - 17.1614 \tag{31a}$$

and the specific enthalpy becomes

$$\left(\frac{H^\circ - H^\circ_0}{RT}\right) = 4 + \sum_{i=1}^{n} \frac{\omega_i}{kT} \Big/ \left[\exp\left(\frac{\omega_i}{kT}\right) - 1\right] \tag{31b}$$

3. ***Diatomic species.*** For the species considered and the temperature range in which they are significant, the representation of the diatomic specie as a harmonic oscillator-rigid rotator with anharmonic-stretching correction and electronic excitation is adequate. So

$$q = \frac{g_e}{\sigma} q_V\, q_R\, q_A\, q_E \tag{32a}$$

where

$$q_V = (1 - e^{-u})^{-1} \text{ with } u = \frac{\omega_e - 2x_e\omega_e}{kT}$$

$$q_R = \frac{kT}{B_0} \text{ with } B_0 = B_e - \frac{\alpha_e}{2}$$

$$q_A = 1 + \frac{8B_e}{\omega_e u} + \frac{\alpha_e / B_e}{e^u - 1} + \frac{2x_e\omega_e/\omega_e}{(e^u - 1)^2}$$

$$q_E = 1 + \sum_{i=1}^{P} \frac{(g_e)_i}{(g_e)_0} \exp\left(-\frac{\varepsilon_i}{kT}\right)$$

with

$$\varepsilon_i = (T_e)_i + \frac{(\omega_e)_i - (\omega_e)_0}{2} - \frac{(x_e\omega_e)_i - (x_e\omega_e)_0}{4}$$

Here the sum is taken over the P excited electronic states and $(\ )_0$ denotes a ground electronic state quantity. In the above we have assumed that in evaluating the electronic correction that the rotational and the vibrational partition functions for each electronic state are approximately equal to that of the ground state. Thus, their influence on the electron partition function can be neglected. The anharmonic correction is assumed small. Thus according to Eq. (11) free energy is given by

$$-\frac{F^\circ - H_0^\circ}{T} = 5/2\, R \ln T + 3/2\, R \ln M + R \ln q - 7.2836 \tag{32b}$$

where

$$\ln q = \ln \frac{(g_e)_0}{\sigma} + \ln q_R + \ln q_V + \ln q_A + \ln q_E$$

where the anharmonic contribution is approximated by

$$\ln q_A = \frac{8B_e}{\omega_e u} + \frac{\alpha_e/B_e}{e^u - 1} + \frac{2x_e\omega_e/\omega_e u}{(e^u - 1)^2}$$

And for the enthalpy Eq. (12) yields

$$\frac{H^\circ - H_0^\circ}{RT} = 5/2 + \frac{H_R}{RT} + \frac{H_V}{RT} + \frac{H_A}{RT} + \frac{H_E}{RT} \tag{32c}$$

where

$$\frac{H_R}{RT} = 1$$

$$\frac{H_V}{RT} = \frac{u}{e^u - 1}$$

$$\frac{H_A}{RT} = \frac{8B_e}{\omega_e u} + \frac{\left[\left(\frac{\alpha_e}{B_e}\right) e^u - \frac{2\omega_e x_e}{\omega_e}\right] u}{(e^u - 1)^2} + \frac{4\left(\frac{\omega_e x_e}{\omega_e}\right) u^2 e^u}{(e^u - 1)^3}$$

$$\frac{H_E}{RT} = \frac{\sum_{i=1}^{P} \frac{(g_e)_i}{(g_e)_0} \left(\frac{\varepsilon_i}{kT}\right) \exp\left(-\frac{\varepsilon_i}{kT}\right)}{q_E}$$

III. Analysis of the Influence of Thermochemical Uncertainties Upon Chemical Composition

A. Model for Estimating the Influence of Uncertainties Upon Composition

As there are many levels of sophistication which can be employed in computing partition functions, it is important to explore the question of how much increase in accuracy in predicting chemical composition results from different degrees of sophistication. If one attempts to simply compare various published compilations of thermodynamic properties and composition of mixtures as a function of the different types of thermochemical data that were used to generate them, one is confronted with a nearly impossible task. This arises from the fact that compositions are usually presented in diverse forms, i.e., some are tabulated as functions of T and P while others use T and ρ. The composition can be presented in the form of several different types of mole fractions or in several different units. Thus the errors arising from cross plotting or interpolation frequently outweigh other considerations. An example of this is given in Table 2 where the composition of high temperature argon computed by three different investigators are compared. The differences in the last column are indicative of the uncertainty resulting from a careful conversion of the values reported in Refs. 36–38 to a common basis for comparison.

An additional source of frustration in an attempt to draw some conclusion about the level of sophistication required from a comparison of published data, is that while one may have several sets of data presented in an easy to compare form, each computed using different approximations for the determination of thermochemical properties, these results may have been generated with different energy level data or heat of formation data. Thus, some of this difficulty could be eliminated if there were some simple theory to guide one in such comparisons.

The intent of the following is to develop such a simple theory which will predict the differences due to thermochemical uncertainties. The result will be an expression which can at least predict the order of magnitude influence of an improvement in the thermochemical data upon the chemical composition.

For purposes of analysis let us consider the mass action equation of the form

$$\frac{n_{XY}}{n_X n_Y} = K \tag{33a}$$

Table 2. Comparison of argon plasma composition at pressure of 1 atm as computed by different investigators

Temperature °K	Ref.	N_e, Particles/cm^3	N_A, Particles/cm^3	$N_A{}^+$, Particles/cm^3	$N_A{}^{++}$	N_{total}
10000	36	3.24×10^{16}	6.6×10^{17}	3.24×10^{16}	—	7.25×10^{17}
	37	1.30 ↓	7.0 ↓	1.30 ↓	—	7.26 ↓
	38	1.48	6.5	1.48	1.0×10^{8}	6.80
20000	36	1.78×10^{17}	3.1×10^{16}	1.77×10^{17}	4.1×10^{15}	3.62×10^{17}
	37	1.80 ↓	1.0 ↓	1.8 ↓	2.0 ↓	4.0 ↓
	38	1.96	0.50	1.9	3.0	3.94
30000	36	1.50×10^{17}	1.3×10^{15}	1.58×10^{16}	7.24×10^{16}	2.415×10^{17}
	37	1.60 ↓	1.5×10^{14}	2.7 ↓	6.5 ↓	2.6 ↓
	38	1.59	3.0×10^{13}	0.95	6.4	2.3

This type of expression is valid for simple dissociation or ionization. Furthermore we shall assume the species XY, X and Y to be the only species present so that

$$n_X = n_Y \tag{33b}$$

and

$$n_{XY} + 2n_X = N \tag{33c}$$

where N is a constant, i.e., it is a function of pressure and temperature and these are held constant.

Combining the above equations we find that

$$x^2 - \left(2 + \frac{4}{KN}\right) x + 1 = 0 \tag{34}$$

where $x = \dfrac{n_{XY}}{N}$. Thus x represents the mole-fraction of XY presented in the mixture. The solution of Eq. (34) is

$$x = (1 + \alpha) - (2\alpha + \alpha^2)^{1/2} \tag{35}$$

where

$$\alpha = \frac{2}{KN}$$

Now for α large the above expression reduces to

$$x \doteq \frac{1}{2\alpha} \tag{36a}$$

which in the limit $\alpha \to \infty$, $x \to 0$. This limit corresponds to complete ionization or dissociation. For α small the above expression reduces to

$$x \doteq 1 - (2\alpha)^{1/2} \tag{36b}$$

which in the limit $\alpha \to 0$, $x \to 1$. This limit corresponds to no ionization or dissociation.

Now the question of what errors in the values of the mole fraction x result from uncertainties in α which are a result of uncertainties in the equilibrium constant K can be examined. Consider two values α_1 and α_2 such that $\alpha_2 = \delta\alpha_1$ and for which the mole fractions are respectively x_1 and x_2. Thus for small α it can be shown that

$$1 - \frac{x_2}{x_1} = (2\alpha_1)^{1/2}(\delta^{1/2} - 1) \tag{37a}$$

Similarly for large α it can be seen that Eq. (36a) reduces to

$$\frac{x_2}{x_1} = \frac{1}{\delta} \tag{37b}$$

As α_1 and α_2 are evaluated at the same temperature and pressure, δ is simply the ratio of the equilibrium constants or

$$\delta = \frac{\left(\dfrac{q_1}{q_2}\right)_{XY}}{\left(\dfrac{q_1}{q_2}\right)_X \left(\dfrac{q_1}{q_2}\right)_Y} \exp\left[-\left(\frac{\Delta\varepsilon_{f1} - \Delta\varepsilon_{f2}}{kT}\right)\right] \tag{38a}$$

or in terms of free energies

$$\delta = \exp\left[\frac{\Delta(-F^\circ_{XY}) - \Delta(-F^\circ_X) - \Delta(-F^\circ_Y)}{RT}\right] \exp\left(-\frac{\Delta H^\circ_{f1}}{RT} + \frac{\Delta H^\circ_{f2}}{RT}\right) \tag{38b}$$

with $\Delta(-F^\circ) = -(F - H_0^\circ)_1 + (F - H_0^\circ)_2$.

Now we can categorize the reaction $XY \rightarrow X + Y$ in one of three cases.

1. The dissociation of polyatomic species into diatomic and atomic species. In this case the most probable sources of errors will be the polyatomic specie properties, i.e., the free energy of the polyatomic molecule $-\left(\frac{F - H_0^\circ}{RT}\right)_P$ or the internal partition function q_P and the dissociation energy

$$(D_0)_P = \frac{(H_0^\circ)_X + (H_0^\circ)_{XZ} - (H_0^\circ)_{XYZ}}{A}$$

with

$$(H_0^\circ)_{XYZ} = (H_0^\circ)_P$$

so for this case

$$\delta_{POLY} = \exp\left[\left(-\frac{F^\circ - H_0^\circ}{RT}\right)_{P_1} - \left(-\frac{F^\circ - H_0^\circ}{RT}\right)_{P_2}\right] \exp\left[\frac{(H_0^\circ)_{P_2} - (H_0^\circ)_{P_1}}{RT}\right] = \frac{q_{P_1}}{q_{P_2}} \exp\left[\frac{(D_0)_{P_1} - (D_0)_{P_2}}{kT}\right] \tag{39}$$

2. The dissociation of diatomic species into atomic species. In this case the most probable sources of errors will be the diatomic properties, i.e., the free energy of the diatomic molecule $-\left(\frac{F - H_0^\circ}{RT}\right)_D$ or the internal partition function q_D and the dissociation energy

$$(D_0)_D = \frac{(H_0^\circ)_X + (H_0^\circ)_Y - (H_0^\circ)_{XY}}{A}$$

with

$$(H_0^\circ)_{XY} = (H_0^\circ)_D$$

$$\delta_{DIATOMIC} = \exp\left[\left(-\frac{F^\circ - H_0^\circ}{RT}\right)_{D_1} - \left(-\frac{F^\circ - H_0^\circ}{RT}\right)_{D_2}\right] \exp\left[\frac{(H_0^\circ)_{D_2} - (H_0^\circ)_{D_1}}{RT}\right] = \frac{q_{D_1}}{q_{D_2}} \exp\left[\frac{(D_0)_{D_1} - (D_0)_{D_2}}{kT}\right] \tag{40}$$

3. The ionization of an atomic specie. In this case, the most probable sources of errors will be the atomic specie properties, i.e., the free energy of the atom $-\left(\frac{F - H_0^\circ}{RT}\right)_A$ or the internal partition function q_A and the ionization potential

$$I_0 = \frac{(H_0^\circ)_{A^+} + (H_0^\circ)_e - (H_0^\circ)_A}{A}$$

$$\delta_{ATOMIC} = \exp\left[\left(-\frac{F^\circ - H_0^\circ}{RT}\right)_{A_1} - \left(-\frac{F^\circ - H_0^\circ}{RT}\right)_{A_2}\right] \exp\left[\frac{(I_0)_{A_1} - (I_0)_{A_2}}{kT}\right] = \frac{q_{A_1}}{q_{A_2}} \exp\left[\frac{(I_0)_{A_1} - (I_0)_{A_2}}{kT}\right] \tag{41}$$

These three can be assigned to certain temperature ranges with Case 1 extending up to 5000°K. Errors which are a function of the degree of sophistication used in polyatomic partition function evaluation increase even more above this temperature; however, most polyatomic molecules are dissociated beyond this temperature. Case 2 extends from 5000°K to 10,000°K where uncertainties in diatomic properties are most significant. Again the errors continue to increase with temperature; however, most diatomic molecules are dissociated by 10,000°K. For Case 3, above 10,000°K is important. The chief error is due to the atomic properties until multiply ionized species become significant.

From the above arguments it is clear that the source of error is the property of a specie which is disappearing from the mixture. Thus the chief error is in the region where its concentration is small.

Some concern could be expressed at this point as to why the increasing error in the species which are disappearing does not affect the concentration of the others. This is due to the fact that as a specie disappears, its contribution to the mass balance equation becomes diminished, so that in effect the mass action and balance equations for this specie become decoupled. To illustrate this, consider a case in which only 1% CO_2 is undissociated in a mixture. If there is a 50% uncertainty in this figure the resulting uncertainty in the CO concentration is clearly less than 1%. From the above argument, it follows that the most likely region in which errors are to be examined will be for large α so we find that expressions of the type Eqs. (39–41) are appropriate. A word of caution is appropriate at this point in that the above arguments are good for low and moderate pressure. At high pressure the dissociation or ionization of a specie is delayed until higher temperature as it takes smaller values of K to yield large α values and thus the influence of errors becomes more important in the range where the concentration of the species is significant.

Now to substantiate the above arguments let us consider an illustrative example in which we shall attempt through Eqs. (37b) and (40), to correlate two sets of concentrations which were computed with slightly different thermochemical data. The concentration taken from Ref. 39 and from computations made with the program Ref. 9 are ratioed in column 2 of Table 3. We have also listed free energies and heats of formulation used. The values

$$\exp \frac{\Delta F}{RT}$$

and

$$\exp \frac{\Delta H_0^\circ}{RT}$$

give the relative errors due to differences in free energy and heats of formulation. As is clear for the last column for this case of air at 6000°K and a pressure of 0.000736 atm, the correlation is very good. In most cases

$$\frac{\Delta F}{RT}$$

is so small that

$$\frac{x_2 - x_1}{x_1} = \frac{(-F_2) - (-F_1)}{RT} \qquad (42)$$

Table 3. Comparison of concentrations[a] and sources of differences for air at 6000°K and $P/P_0 = 0.0007365$

Specie	n_1/n_2	$f = \frac{\Delta F_1 - \Delta F_2}{RT}$	exp(f)	$h = -(\Delta H_1 - \Delta H_2)$	exp(h)	exp(f) exp(h)
O_2^+	1.38	−0.015	0.985	0.322	1.38	1.36
N_2^+	0.971	−0.054	0.948	−0.002	0.998	0.95
NO^+	0.974	−0.061	0.9406	0.013	1.013	0.955
O_2	0.970	−0.026	0.9742	−0.003	0.997	0.97
N_2	1.000	−0.002	0.998	−0.005	0.995	0.99
NO	0.976	−0.027	0.974	−0.004	0.996	0.969
N_2O	2.22	0.795	2.21	−0.005	0.995	2.20
NO_2	0.768	−0.268	0.764	−0.01	0.99	0.76
O_2^-	1.048	−0.316	0.728	0.379	1.46	1.06

[a] $(\ )_1$ Concentration and properties from Ref. 9; $(\ )_2$ Concentration and properties from Ref. 39.

Although strictly applicable only to the three-component system for which they were derived, we shall (supported by the good correlation in Table 3), apply these expressions to the study of complex mixtures. Using this model we can examine the difference in mixture composition which will result from different levels of sophistication in partition function analysis. Let us next examine the questions which give rise to uncertainties in partition functions.

B. Problems With Atomic and Ionic Species

Perhaps the best known aspect of the atomic species problem is that, for a completely free atom, the partition function series is a divergent infinite series. This is easily understood if one realized that for an isolated atom there are an infinite number of electronic energy states which converge to the ionization limit. Thus, near the ionization limit the exponential factor $e^{-\epsilon_i/kT}$ remains constant while the degeneracy g_i increases with each additional term. At low temperature this problem is circumvented by the apparent convergence of the series. Thus, for low temperatures investigators have evaluated electronic partition functions by considering only the ground state Ref. 40, by arbitrary truncation of the series at a preselected principal quantum number, Ref. 16, and by summing over all observed energy levels such as those in Moore's compilation, as in Ref. 36. These three approaches yield the same values in a limited temperature range and implicit in them is some physical mechanism for reducing the number of electronic states.

In reality the atoms and ions in gases are not completely free but interact with the surrounding particles and are thus limited by the amount of space which they may occupy. Numerous models for truncating the partition function series which are based upon the volume of space occupied by an atom in an excited electronic state have been proposed and used. Some of these are Bethe's Ref. 41 scheme in which all energy levels are neglected for Bohr circular orbits greater than the mean distance between particles and the work of Rosenbaum and Levitt, Ref. 42, in which other than circular orbits were considered. McChesney's paper, Ref. 44, contains a critical review of the work of other such schemes.

In an ionized gas the presence of charged particles in the vicinity of a given ion or atom has the effect of altering the electric potential in which the bound electrons of an ion or atom move. Although there is still disagreement as to the precise description of this micro field, its role in the question of ionized gas properties is clear. The presence of this micro field gives rise to a perturbation term in the Hamiltonian for each specie which results in a finite number of energy levels which are shifted from their isolated species positions. In terms of property determination, this is manifested as a lowering of the ionization potential and a modification of the infinite sum partition function to a sum over only the finite number of bound states. Numerous papers have treated the ionizing gas property question from this point of view, see Refs. 43–59. A review of this work is beyond the scope of this report. It suffices to state that most investigators (Refs. 43, 45, 46, and 57) now agree that in the pressure and temperature range of most shock tube experiments

$$\frac{N_e}{V} \leq \frac{1}{2\pi}\left(\frac{kT}{e^2}\right)^3 \tag{43}$$

and the Debye-Huckel polarization theory describes the screened coulombic potential appropriate to Hamiltonian for each specie. The Debye theory predicts a lowering of the ionization potential of a z-times ionized specie by

$$\Delta I_z = (z+1)\, e^3 \left[\frac{4\pi}{kT}\,(n_e + \Sigma z^2 n_z)\right]^{1/2} \tag{44}$$

which is also used as a cutoff for truncating the partition function sum. For electron densities above this critical level (Eq. 43), the potential is dominated by interaction of the coulombic potentials of the test particle and its nearest neighbors according to the Unsold theory. A variety of other partition function cutoff procedures based upon characteristic plasma lengths are given by McChesney (Ref. 43).

To properly evaluate the partition function and apply the above cutoff criterion one must estimate those energy levels which are not given in tabulations such as Moore. This problem has been considered by several authors (Refs. 37, 44, and 60). If the missing energy levels are estimated and their degeneracies included in the partition function evaluation one finds widely different values at high temperatures when different cutoff procedures are used. This is dramatically illustrated by the plots of the partition function of atomic argon, neon, carbon, nitrogen, oxygen, and their ions in Figs. 2–6.

Hydrogen was chosen to examine the influence of the ionization potential lowering upon the composition of a system. Electron composition calculations were performed at various pressures with different principal quantum numbers used to truncate the series and to compute the amount by which the ionization potential should be modified. The results are shown in Figs. 7–9. These results

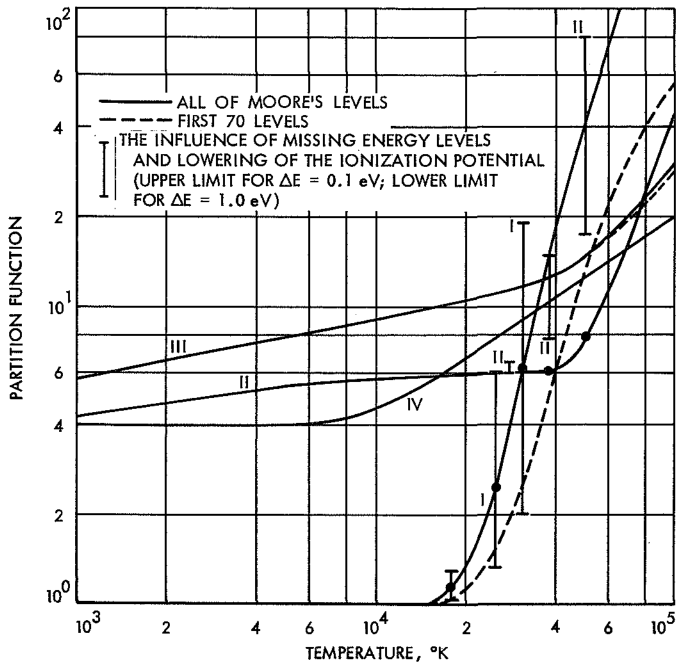

Fig. 2. Partition functions for argon

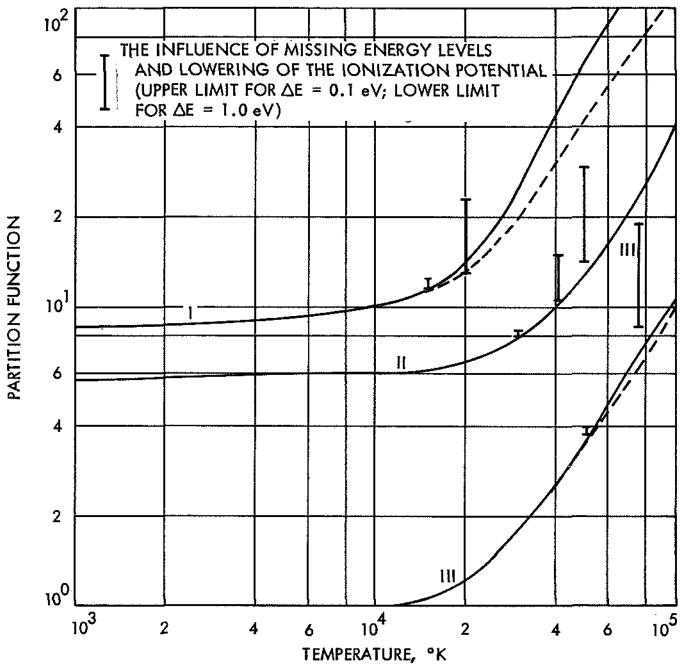

Fig. 4. Partition functions for carbon

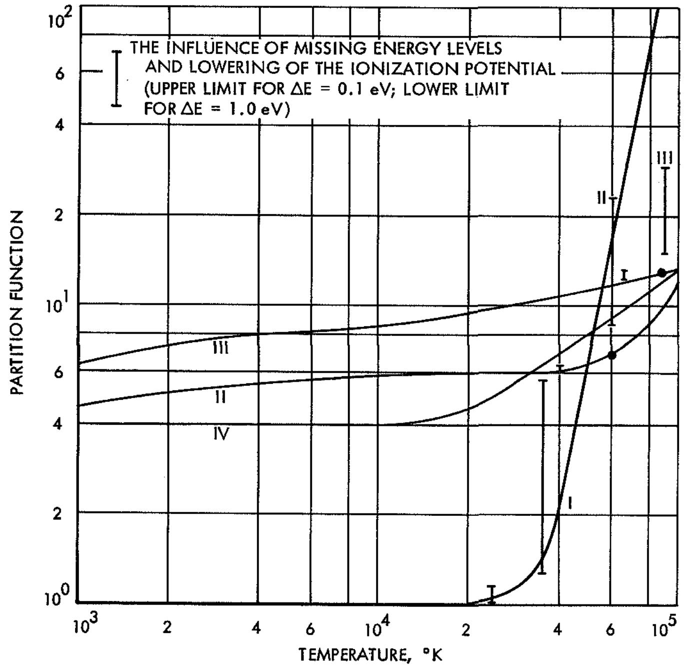

Fig. 3. Partition functions for neon

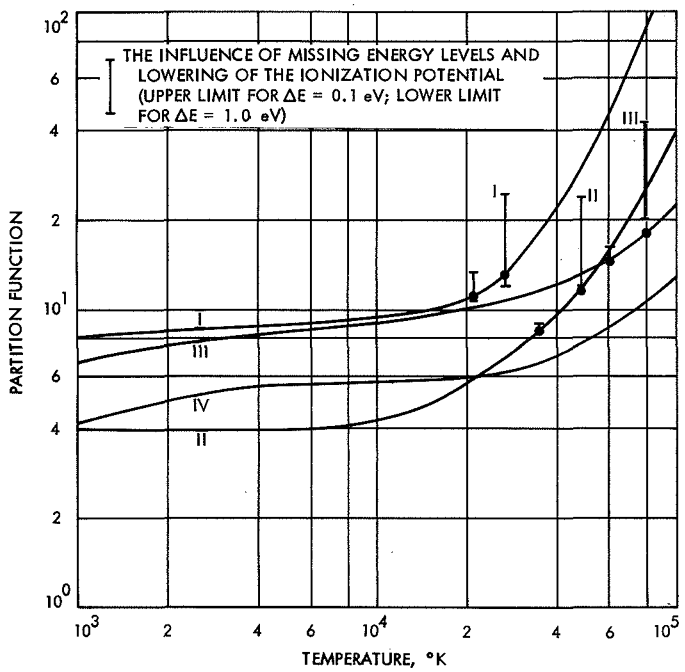

Fig. 5. Partition functions for oxygen

indicate the electron concentration at high temperatures and moderate to low pressures is independent of the ionization potential lowering since the gas is fully ionized. A careful examination of the computations reveals that at the low temperatures the differences in the concentration are due to the differences in the ionization potential as the partition functions all have the same value. At high temperatures, the effect of the partition function divergence is more pronounced. From these plots we see that the questions which were qualitatively discussed in earlier

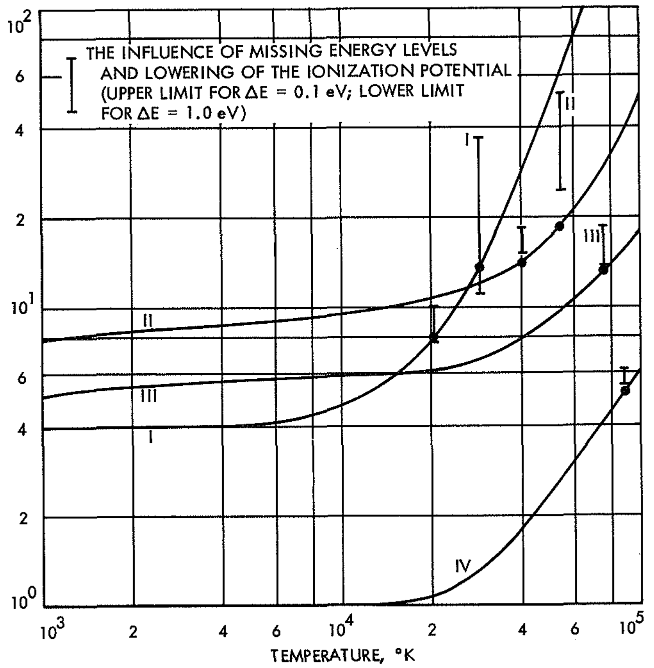

Fig. 6. Partition functions for nitrogen

paragraphs appear to have sizable effects upon plasma composition.

For additional comparison, electron concentrations were computed considering: (1) no lowering of the ionization potential and truncating the partition function series with the principal quantum number of 5 and; (2) the widely used Debye radius theory Refs. 37 and 43 to truncate the series and compute the lowering of the ionization potential. These results are also given in Figs. 8 and 9. Only one set of data is plotted at the lowest pressure as both sets agree closely. In the case of the Debye concentrations we see that at low temperatures and electron concentrations the ionization potential lowering is very small, and all partition functions are in agreement; thus, the good agreement with the computations in which no ionization potential lowering was considered. At high temperatures even at the highest pressure, the two cases are also in good agreement. In the intermediate and high temperature range, the Debye theory yields results such that the highest principal quantum number is about 5. Therefore, the slight difference, less than 10%, between the points in Figs. 8 and 9 is due to the ion potential lowering as in both cases the partition functions are virtually the same.

These results encouraged the use of partition functions evaluated by summing over a fixed number of energy levels and a fixed ionization potential for all species in the computational procedure used in the subroutine of Ref. 8. However, it is well to specify the thermodynamic condition for which this simple procedure would yield concentrations which differ by less than 10% from the more sophisticated Debye radius theory; the simple model developed in the previous section is ideal for this purpose.

If we consider conditions under which atomic concentrations differ due to differences in atomic partition functions and ionization potential lowering we have from Eqs. (37b) and (41)

$$\frac{x_d}{x_i} = \frac{q_d}{q_i} \exp\left(-\frac{\Delta I_d}{kT}\right) \tag{45}$$

The d subscript denotes values obtained using Debye theory and i denotes the values obtained with the fixed ionization potential and the partition function summed over the energy levels discussed in an earlier section and used in the Ref. 8 program. The quantity q_i is only a function of temperature, and q_d and ΔI_d are functions of electron concentration and temperature. So, for fixed ratios of atomic concentrations this expression can be represented as a curve of electron concentration vs temperature.

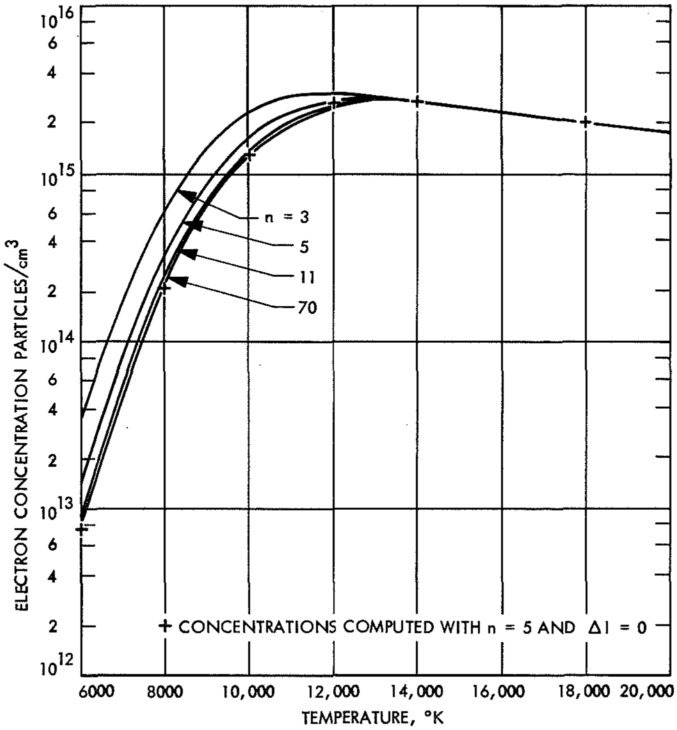

Fig. 7. Electron concentration as function of *n* at 0.01 atm

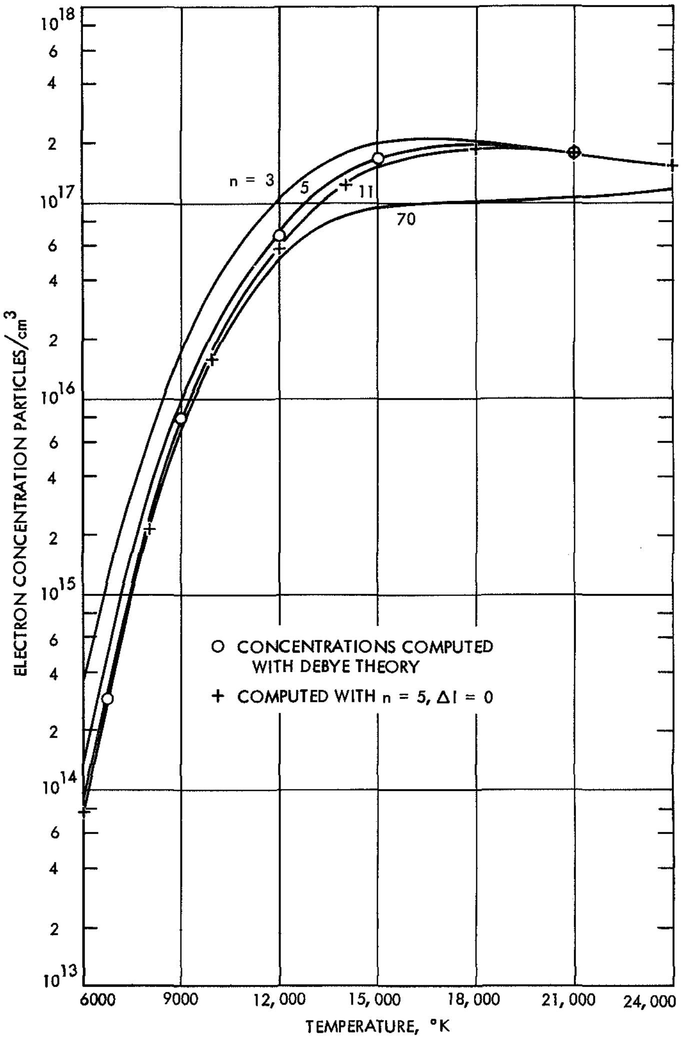

Fig. 8. Electron concentration as function of *n* at 1.0 atm

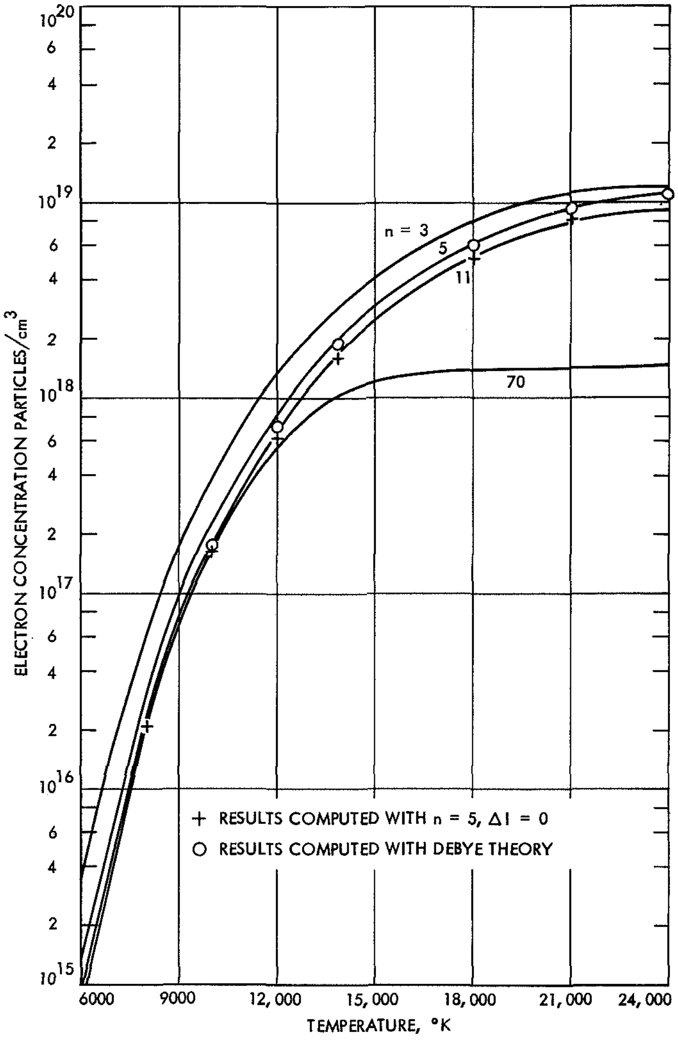

Fig. 9. Electron concentration as function of *n* at 100.0 atm

Now two conditions are important: (1) At high temperatures and relatively low electron concentrations the influence of the micro-field upon lowering of the ionization potential is almost negligible, and the q_d series becomes large and $x_d > x_i$; (2) at high temperatures and high electron concentrations the influence of the micro field upon lowering the ionization potential is important and thus $x_d < x_i$. Therefore, we have considered x_d/x_i equal to 1.1 and 0.9 and generated two curves for each specie which in terms of electron concentration and temperature bound a region within which the atomic concentrations in an ionizing gas computed by Ref. 8 differ by less than 10% from values obtained from the Debye theory. These curves are presented for atomic argon, nitrogen, oxygen, carbon, and hydrogen in Figs. 10 and 11. We have also shown in the first figure three other important curves. The uppermost labeled "classical limit" represents the upper limit of electron concentrations for which the electron may be considered a classical particle, i.e., Eq. (10). The next curve represents the critical electron density $\frac{1}{2\pi}\left(\frac{kT}{e^2}\right)^3$ below which the Debye-Huckel limiting laws apply to the plasma. The lowest curve is obtained by neglecting the influence of the partition functions in Eq. (45) and thus represents a 10% uncertainty in atomic concentration due to ionization potential lowering by the Debye theory.

Using limited solutions of the mass action and mass balance equation in which Debye theory was used, these curves have been confirmed in predicting the range in which the atomic and ionic approximations used in this report and Ref. 8 are appropriate. These solutions indicate the upper curves are in some cases too conservative. So, for high pressure mixtures in which electron concentrations computed by the program of Ref. 8 fall slightly above the upper bound curves, one may assume the atomic concentrations are accurate to 10%.

C. Problems With Diatomic Species

Some of the problems encountered in atomic species are also important in diatomic species as discussed by Haar in Ref. 61. One approach to this apparent divergence in the diatomic partition function has been presented by Sinanoglu and Pitzer, Ref. 62. In an earlier version of the JPL program (Ref. 9), tabulated data were used in which the diatomic species properties were computed using the anharmonic and rotational corrections given earlier in this report to evaluate the contribution of the low lying states joined with a classical oscillator analysis to evaluate the contribution of the states near the dissociation level. As the concentrations of the two programs for diatomic species agree closely when similar spectrographic and heat of formation data are used, we have concluded that this divergence problem is not significant in the range of temperatures and pressures where diatomic species are important in shock tube work.

Another question, treated in Ref. 37, is that of the effect of the rotational energy upon the intermolecular potential which is considered by Stupochenko. By performing detailed computations for O_2, Drellishak concluded that the inclusion of this effect produced partition functions which were within ±1% of those computed by the standard approach of harmonic oscillator-rigid rotator with corrections which were presented in an earlier section.

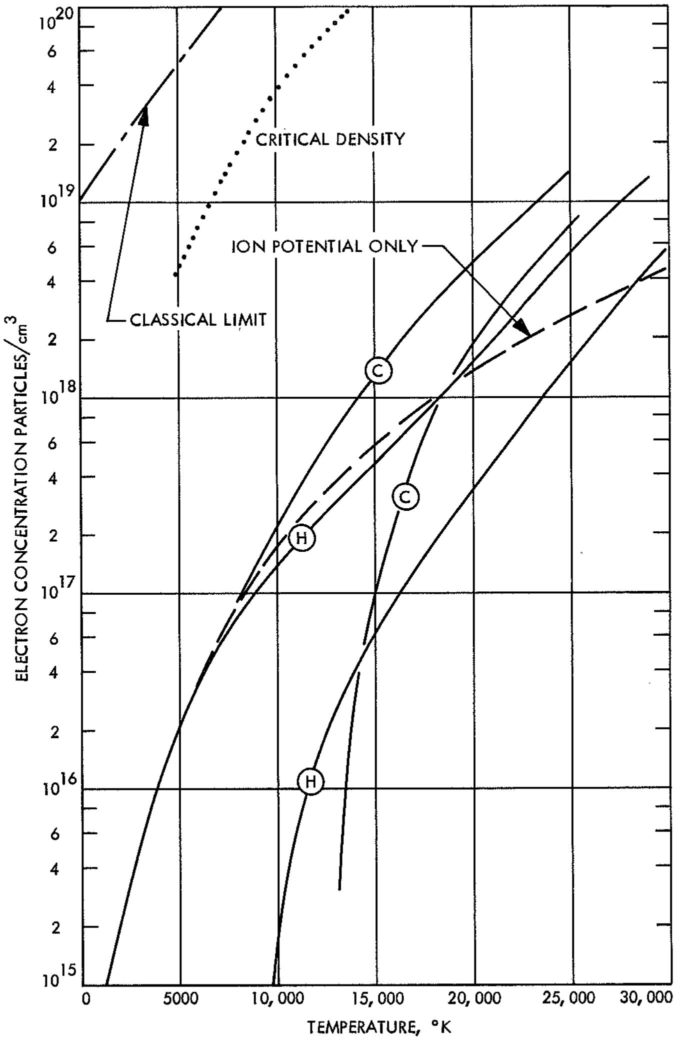

Fig. 10. Uncertainty analysis curves of hydrogen and carbon

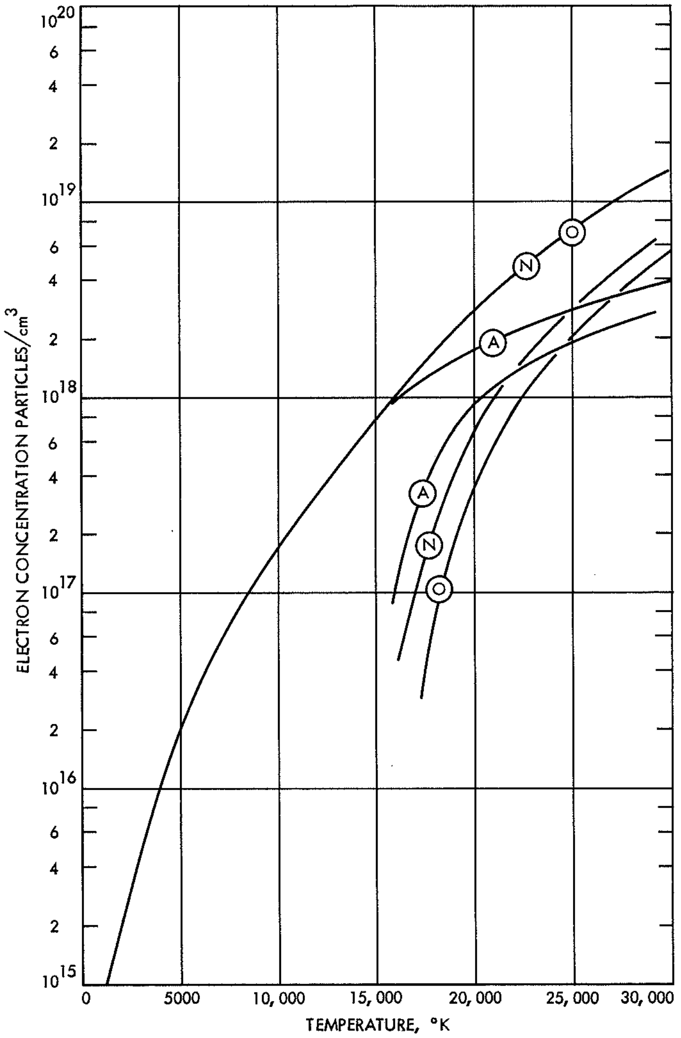

Fig. 11. Uncertainty analysis curves of nitrogen, oxygen, and argon

In view of the above, our main effort in investigating diatomic properties was confined to the influence of the correction term upon the thermochemical properties and chemical composition. To do this, computations of free energies and enthalpies, and the resulting mixture compositions were performed using: (1) the harmonic oscillator-rigid rotator approximation only and considering only the ground electronic state; (2) only the electronic excitation correction; and (3) both the anharmonic and electronic corrections. The results for a mixture initially composed of 4% H_2O and 96% air[4] are given in Tables 4–6, and Fig. 12.

For small $\frac{\Delta F}{RT}$ Eq. (42) indicates that the decimal differences in free energy are directly proportional to the fractional differences in gas composition. With this in mind, Table 5 reveals that sizable errors, in excess of 20%, can result from neglecting corrections. With the exception of the species which have split ground states or extremely low electronic states, the electronic correction is usually less than the anharmonic correction. At a temperature of 7000°K the anharmonic correction results in an average uncertainty of about 10% in composition of the various diatomic species. However, as shown in Fig. 12, most of the diatomic molecules are no longer present at this temperature. Notable exceptions are CO, NO, and the positive diatomic ions. The large discrepancy in NO composition is due to the omission of the upper level of the 121 cm^{-1} split in the ground state in the harmonic oscillator-rigid rotator computations. Of particular interest in Table 5 is the approximately 30% difference in composition which results from neglect of electronic excitation in the two important trace species CN and N_2^+ at 7000°K.

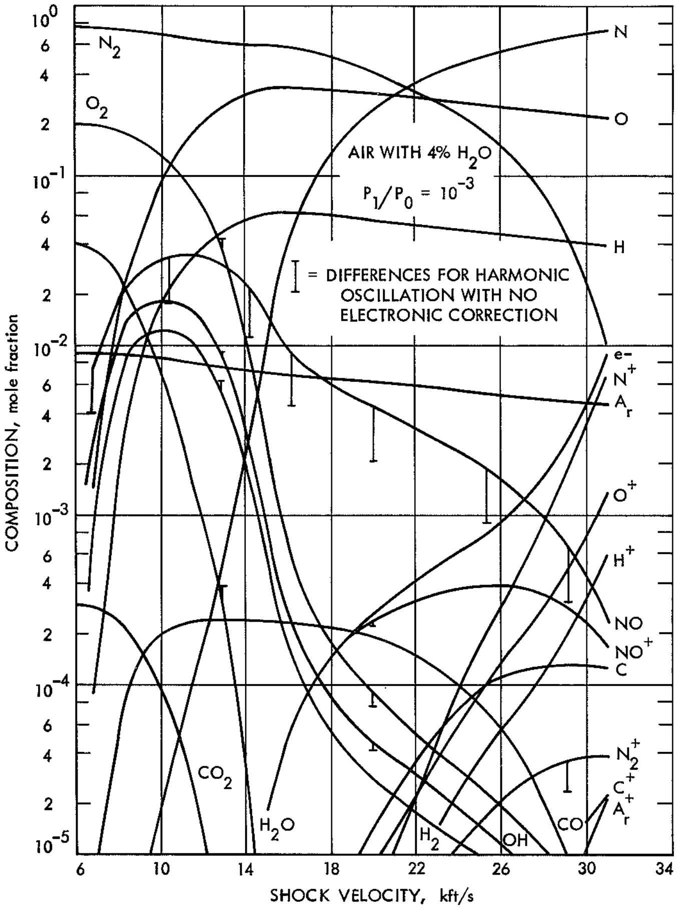

Fig. 12. Composition of wet shock heated air computed using anharmonic and electronic corrections

Thus, to achieve the accuracy desired for diatomic species, both electronic and anharmonic corrections were included. More sophisticated electronic corrections could have been used, but they would influence the above electronic correction by only a few percent. We would like to note at this point that the free energies and enthalpies given in Tables 5 and 6 were computed with old values of the spectroscopic constants and, therefore, do not necessarily compare with values which are currently used in the program. However, this does not detract from their usefulness as an internally consistent set of data for our purposes here.

D. Problems With Polyatomic Species

For polyatomic species, the convention used by most investigators is to neglect electronic states and to follow the procedure of Pennington and Kobe (Ref. 63). This involves computing the thermochemical properties by a rigid rotator-harmonic oscillator approximation to which small corrections are added to account for anharmonicity, rotation-vibration interaction, centrifugal distortion, Fermi resonance, and Darling-Dennison resonance. This procedure has been used to compute properties for species of interest in Refs. 64–69.

Durand and Brandmaier (Ref. 66) have performed computations for CO_2, H_2O, and N_2O in which all of the corrections listed above were considered. To make the results more meaningful, they have listed separately the contributions of the various correction terms to the specific heat at constant pressure for each of the above species over a range of temperatures (1000°K–7000°K). The results indicate the principal correction is that due

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[4] The 96% air was composed of 20.11% O_2, 74.96% N_2, 0.03% CO_2, and 0.9% A.

to the anharmonic terms. The influence of the corrections upon specie composition can be estimated by assuming a linear increase with temperature of contribution of the corrections to specific heat. If we recall that

$$-\frac{F^\circ - H_0^\circ}{RT} = \int \frac{\int \frac{C_P}{R}\,dT}{T^2}\,dT \qquad (46)$$

it follows that the difference in free energy due to the corrections to the rigid rotator-harmonic oscillator model is

$$\Delta\left(-\frac{F^\circ - H_0^\circ}{RT}\right) \doteq \tfrac{1}{2}\,\frac{\Delta C_P}{R} \qquad (47)$$

and from the combination of Eqs. (37b) and (39) to the approximation given by Eq. (42) we have

$$\frac{x_2 - x_1}{x_1} = \frac{\Delta C_P}{2R} \qquad (48)$$

Durand and Brandmaier list the following correction at 5000°K to the specific heat in cal/mole °K of CO_2, H_2O,

Table 4. Shock parameters for wet air computed using different levels of approximation for the diatomic species: air with 4% H_2O initially at 10^{-3} atm; $M_0 = 28.53$

Temperature, °K	Shock velocity	P_2/P_1	ρ_2/ρ_1	Z	n_e	H/RT_0	S/R
9000	30,970[a]	955.4	15.70	2.029	6.79×10^{15}	557.1	57.3
	30,970[b]	955.1	15.69	2.029	6.799×10^{15}	557.0	57.3
	30,960[c]	954.4	15.69	2.028	6.80×10^{15}	556.5	57.29
8000	29,160	849.0	16.33	1.950	2.06×10^{15}	493.9	55.49
	29,150	848.7	16.32	1.950	2.06×10^{15}	493.8	55.49
	29,110	846.3	16.31	1.946	2.06×10^{15}	492.3	55.45
7000	25,360	641.4	15.86	1.733	5.11×10^{14}	373.6	51.59
	25,350	640.6	15.85	1.732	5.12×10^{14}	373.4	51.59
	25,300	638.3	15.85	1.726	5.15×10^{14}	371.3	51.53
6000	20,000	394.7	13.57	1.455	1.23×10^{14}	231.7	46.40
	19,990	394.2	13.56	1.453	1.23×10^{14}	231.4	46.40
	19,950	392.8	13.54	1.451	1.24×10^{14}	230.9	46.40
5000	16,170	255.1	11.69	1.309	2.22×10^{13}	151.2	43.05
	16,160	254.7	11.70	1.307	2.20×10^{13}	150.8	43.03
	16,170	255.1	11.72	1.306	2.22×10^{13}	151.0	43.06
4000	14,240	198.2	11.79	1.261	1.99×10^{12}	117.1	41.31
	14,190	196.7	11.76	1.255	1.95×10^{12}	116.3	41.28
	14,200	197.1	11.79	1.254	1.969×10^{12}	116.4	41.30
3000	10,520	106.6	9.718	1.096	2.00×10^{10}	63.52	37.76
	10,550	107.1	9.791	1.094	1.97×10^{10}	63.78	37.80
	10,550	107.2	9.805	1.093	1.97×10^{10}	63.85	37.82
2000	6722	41.24	6.174	1.002	6.898×10^{5}	25.27	34.67
	6744	41.56	6.223	1.002	6.90×10^{5}	25.43	34.69
	6754	41.70	6.244	1.002	6.90×10^{5}	25.53	34.71

[a] First row for each temperature group: harmonic oscillator and rigid rotator.

[b] Second rows: electronic state correction.

[c] Third rows: electronic and anharmonic correction.

and N_2O respectively (0.36, 0.78, 0.70). These would correspond to errors in their concentrations of 9%, 19%, and 17%. At a lower temperature of 3000°K the errors in concentrations are only 6%, 10%, and 10%, respectively. Unless the pressure is large, most of these species will be fully dissociated at the highest temperature cited above and at 3000°K the concentrations will be nearly an order of magnitude below their undissociated values. This is confirmed by an examination of the air with 4% H_2O data presented earlier.

A more careful analysis in which published values of free energy are compared with those computed by the program of Ref. 8, using the analysis and data of an earlier section of this report, indicates smaller errors than presented above. In the case of H_2O, using the approximation of Eq. (42), the JPL concentrations would differ by 5 to 6% at 3000°K and 11 to 12% at 5000°K. The difference depends upon whether one uses the data tabulated in Ref. 66 or Ref. 68 for the comparison. For CO_2, using the data of Refs. 66 and 69, the concentration of this specie would differ by 2% at 3000°K and 5 to 6% at 5000°K from the JPL values. At these same temperatures, the concentration of N_2O would vary by 6% and 13% depending upon whether the data of Ref. 66 or the JPL data were used.

We can conclude that concentration errors in excess of our 10% limit will result if the rigid rotator-harmonic oscillator analysis for polyatomic species is used above 5000°K. Thus, pressure levels should be avoided which will result in a considerable concentration of polyatomic species above this temperature.

E. Concluding Remarks

To this point very little has been said concerning the influence of the uncertainties reviewed above upon the thermodynamic properties. This is because they will be negligibly influenced, at most a few percent, if the conditions presented in the introductory section are met. That is, if we have uncertainties in the composition of

Table 5. Free energies for diatomic species computed using different levels of approximation

Specie	$-\left(\frac{F-H_0}{RT}\right)$											
	3000°K			5000°K			7000°K			9000°K		
O_2^+	29.934[a]	29.910[b]	29.910[c]	32.102	32.053	32.052	33.576	33.500	33.496	34.707	34.604	34.588
N_2^+	28.818	28.802	28.773	31.073	31.038	30.892	32.664	32.609	32.325	33.890	33.816	33.409
NO^+	28.814	28.799	28.799	30.937	30.906	30.906	32.383	32.335	32.333	33.490	33.425	33.414
CO^+	29.457	29.441	29.441	31.598	31.565	31.559	33.075	33.023	32.991	34.224	34.154	34.075
C_2	29.817	29.794	28.013	32.157	32.111	30.157	33.758	33.687	31.601	34.975	34.880	32.693
CH	26.943	26.891	26.891	29.081	28.974	28.972	30.564	30.398	30.387	31.721	31.496	31.460
OH	26.946	26.911	26.911	29.017	28.943	28.943	30.450	30.332	30.331	31.555	31.392	31.389
H_2	22.323	22.267	22.267	24.416	24.268	24.268	25.893	25.640	25.640	27.051	26.688	26.688
O_2	29.922	29.893	29.877	32.173	32.116	32.041	33.727	33.641	33.495	34.920	34.805	34.592
N_2	28.021	28.008	28.008	30.144	30.116	30.116	31.587	31.543	31.543	32.685	32.626	32.625
NO	30.468	30.447	29.783	32.642	32.599	31.923	34.113	34.047	33.366	35.231	35.141	34.456
CO	28.797	28.781	28.781	30.935	30.902	30.902	32.387	32.336	32.336	33.493	33.425	33.421
CN	29.452	29.435	29.408	31.713	31.677	31.536	33.306	33.251	32.974	34.535	34.461	34.061
O_2^-	30.541	30.495	30.493	32.793	32.703	32.680	34.351	34.215	34.144	35.562	35.381	35.247

[a] First vertical row: anharmonic and electronic correction.

[b] Second row: electronic correction only.

[c] Third row: rigid rotator; harmonic oscillator.

Table 6. Specific enthalpies for diatomic species computed using different levels of approximation

Specie	$\left(\frac{H - H_0}{RT}\right)$											
	3000°K			5000°K			7000°K			9000°K		
O_2^+	4.158[a]	4.122[b]	4.122[c]	4.326	4.261	4.258	4.441	4.348	4.322	4.567	4.446	4.360
N_2^+	4.211	4.185	4.068	4.615	4.567	4.220	4.826	4.757	4.293	4.930	4.839	4.336
NO^+	4.063	4.041	4.041	4.243	4.201	4.200	4.353	4.293	4.278	4.474	4.394	4.324
CO^+	4.092	4.067	4.066	4.299	4.254	4.218	4.487	4.422	4.292	4.665	4.580	4.336
C_2	4.473	4.439	4.125	4.692	4.633	4.260	4.813	4.727	4.324	4.875	4.764	4.361
CH	4.060	3.984	3.984	4.312	4.169	4.158	4.512	4.304	4.245	4.706	4.434	4.297
OH	3.930	3.877	3.877	4.178	4.073	4.073	4.337	4.182	4.178	4.462	4.257	4.242
H_2	3.934	3.814	3.814	4.269	4.018	4.018	4.510	4.133	4.133	4.705	4.204	4.204
O_2	4.275	4.234	4.173	4.539	4.466	4.293	4.696	4.593	4.349	4.800	4.667	4.381
N_2	4.064	4.043	4.043	4.240	4.202	4.202	4.336	4.281	4.280	4.411	4.339	4.325
NO	4.176	4.145	4.117	4.328	4.271	4.254	4.415	4.334	4.320	4.484	4.378	4.358
CO	4.096	4.073	4.073	4.267	4.223	4.223	4.362	4.300	4.296	4.449	4.367	4.338
CN	4.227	4.202	4.089	4.624	4.577	4.235	4.833	4.766	4.305	4.936	4.848	4.346
O_2^-	4.301	4.237	4.226	4.530	4.418	4.328	4.735	4.576	4.375	4.905	4.699	4.402

[a] First vertical row: anharmonic and electronic correction.

[b] Second row: electronic correction only.

[c] Third row: rigid rotator; harmonic oscillator.

principal species of only a few percent and in the composition of trace species of about 10%, the property and shock parameter uncertainty will be dominated by the principal species. This conclusion is confirmed in Ref. 44, among others, and can be confirmed by reference to the shock parameters in Table 4 for the 4% H_2O and Air calculations.

Another important question, which should be explored here, is the accuracy in heat of formation data required for good results. To a first approximation, small errors can be evaluated through the use of an expression similar to Eq. (42).

$$\frac{x_2 - x_1}{x_1} = \frac{(H^\circ_0)_1 - (H^\circ_0)_2}{RT} \qquad (49)$$

As the error in heat of formation is not temperature dependent, the effect of this error upon composition is reduced as the temperature increases. Furthermore, in the temperature range from 1000°K to 10,000°K, uncertainties of a few hundred calories per mole will introduce concentration errors of less than 10%. For the gases of primary interest, heats of formation are known to this accuracy. For certain trace species, the uncertainty is of sufficient size to warrant the retention of the exponential term in the evaluation of its uncertainty.

Nomenclature

A	Avogadro's number
B	rotational constant for linear polyatomic species
D_0	dissociation energy
F°_i	specific or molal free-energy of the i^{th} specie at standard pressure
H°_i	molal or specific enthalpy of the i^{th} specie at standard pressure
h	Planck constant
H°_0	heat of formation at 0°K and standard pressure
H_R	rotational contribution to the molal or specific enthalpy
H_V	vibrational contribution to the molal or specific enthalpy
H_A	anharmonic contribution to the molal or specific enthalpy
H_E	excited electronic state contribution to the molal or specific enthalpy
I_A, I_B, I_C	principal moments of inertia for non-linear polyatomic molecules
J	rotational quantum number for diatomic species and the total angular momentum quantum number for atomic species
K_i	equilibrium constant for i^{th} specie
k	Boltzmann constant
L	the orbital-angular momentum quantum number for atomic specie
l	the angular quantum number for hydrogen
m	mass per particle
M	molecular weight
m_e	mass of the electron
n	principal quantum number
$n^{(i)}$	concentration of the ith specie in moles per liter
N_i	number of particles of the ith specie
N_e	number of electrons
Q_{TR}	translation partition function
Q_{INT}	total internal partition function
q	internal partition function without nuclear spin and with energy measured relative to the ground state
$\tilde{q}$	internal partition function with energy relative to ground state energy
q_V	vibration contribution to the partition harmonic oscillator
q_R	rotation contribution to the partition function (rigid rotator)
q_A	anharmonic contribution to the partition function
q_E	excited electronic state contribution to the partition function
R	gas constant per mole
S_n	nuclear spin
S	electron spin quantum number for atomic species
T	temperature
V	volume
v	vibrational quantum number
ω_e	Eq. (18)
$\omega_e x_e$	Eq. (18)
ω_0	Eq. (20)
$\omega_0 x_0$	Eq. (20)
ω_i	the i^{th} vibrational frequency for a polyatomic specie
σ	symmetry number
$\varepsilon^{(i)}_j$	energy of the j^{th} energy level of the i^{th} specie
ε_{itr}	energy of the i^{th} translation energy level
$\varepsilon_{j\,int}$	energy of the j^{th} internal energy level
ε_0	energy of the ground state
ε_{j0}	energy of the j^{th} energy level relative to the ground state
$\varepsilon_{J,v}$	energy for v^{th} vibration and J^{th} rotor state
α_{ij}	the number of atoms of the j^{th} numbered element in the molecule of the i^{th} numbered specie

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