

CALCULATION OF THERMODYNAMIC PROPERTIES OF  
GAS MIXTURES AT HIGH TEMPERATURES

By

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## V. INTRODUCTION

Planetary entry and other hypersonic flow problems currently being investigated are dependent on equilibrium thermodynamic properties of high-temperature gas mixtures. The atmospheres of Mars and Venus are believed to be composed primarily of the elements nitrogen, carbon, oxygen, and argon as is the earth's atmosphere. It is therefore desirable to be able to accurately compute equilibrium thermodynamic properties of mixtures of gases derivable from given elements. A method for making such computations is described in this paper.

Properties for air have been computed by many investigators such as Gilmore (ref. 1) and Browne (ref. 2) who included vibrational-rotational energy corrections in compact form for diatomic species. A thorough discussion of the calculation of properties for air, including interparticle electrostatic contributions, is given in reference 3. Properties of Martian and Venusian model atmospheres are presented in references 4 and 5. Nitrogen and oxygen plasma properties are discussed in reference 6. Also, pure diatomic gas properties have been computed by Gurvich and Yungman (ref. 7), Browne (refs. 8 and 9), and others.

Equilibrium thermodynamic properties are calculated in the present work for two mixtures of ideal gases, air and a recent model atmosphere of Mars. The mixtures include species of the following types: atoms and atomic ions, diatomic and linear triatomic molecules and ions, and electrons. For each species, the partition function and its temperature derivative are computed and used to determine thermodynamic properties.

Translational, electronic, vibrational, and rotational energies are considered. The vibrational and rotational energies of the diatomic species include vibrational anharmonicity, vibration-rotation interaction, and rotational stretching corrections. Whereas the translational and electronic energies are handled in the usual way, the vibrational and rotational energies are given more careful treatment. The double summation over the vibrational and rotational energies in the partition function for diatomic molecules and ions is carried out for each electronic state. This was possible since the computations were done by an IBM 7094 computer.

The equilibrium composition of the gas mixture at a given temperature and pressure is determined by minimizing the Gibbs free energy subject to constraints on the components (elements and electrons) of the gas. Thermodynamic properties of the mixture are then computed from the equilibrium composition. Temperatures up to  $15,000^{\circ}$  K and pressures from  $10^{-4}$  to  $10^2$  atmospheres are considered.

VI. LIST OF SYMBOLS

$A_{ik}$	number of atoms of component $k$ per particle of species $i$
$B_k$	number of (free and combined) atoms of component $k$ in the mixture
$c$	speed of light
$D_0$	dissociation energy, $\text{cm}^{-1}$
$e_i$	internal energy per particle of species $i$
$E$	internal energy of the mixture
$f_i$	Gibbs free energy per particle of species $i$
$F$	Gibbs free energy of the mixture
$g$	degeneracy of an energy $\epsilon$
$h_i$	enthalpy per particle of species $i$
$h$	Planck's constant
$H$	enthalpy of the mixture
$H_{0i}$	heat of formation at $0^\circ \text{K}$ per particle of species $i$
$j$	rotational quantum number
$k$	Boltzmann constant
$m$	mass per particle of a pure gas
$M$	molar mass
$N_i$	number of particles of species $i$ in the mixture
$N$	total number of particles in the mixture
$N_e$	electron density
$N_0$	Avogadro's number
$p$	pressure

$p_0$	atmospheric pressure
$Q$	partition function
$s_i$	entropy per particle of species $i$
$S$	entropy of the mixture
$T$	temperature, $^{\circ}\text{K}$
$v$	vibrational quantum number
$V$	volume of the mixture
$Z$	molecular weight ratio
$\epsilon$	energy
$v_{\text{ele}}$	electronic energy level, $\text{cm}^{-1}$
$\rho$	mass density
$\rho_0$	atmospheric mass density
$\omega_e, \omega_e x_e, B_e, \alpha_e, D_e$	spectroscopic constants, $\text{cm}^{-1}$
Subscripts:	
A	vibrational anharmonicity
ele	electronic
H	harmonic oscillator
i	species index number
int	internal
I	vibration-rotation interaction
k	component index number
$l$	total number of components, maximum value of $k$
$n$	total number of species considered, maximum value of $i$
q	quantum-mechanical energy state
rot	rotational

R	rigid rotor
S	rotational stretching
tr	translational
vib	vibrational
w	vibrational frequency of triatomic species

## VII. THEORY

Calculation of thermodynamic properties of an equilibrium gas mixture are made as follows. First, the thermodynamic properties of each individual species are determined from the quantum-mechanical partition function. Since temperature and pressure are held constant, the Gibbs free energy of the mixture is computed and then minimized to determine the equilibrium composition. Finally, the thermodynamic properties of the mixture in equilibrium are calculated.

### Species Properties

The Gibbs free energy, internal energy, enthalpy, entropy, and all other thermodynamic properties of a species, that is a pure gas, can be derived in terms of the partition function. The expressions for these quantities can be found in textbooks on statistical mechanics.

The internal energy per particle of species  $i$  is taken to be

$$e_i = kT^2 \left( \frac{\partial \ln Q_i}{\partial T} \right)_V + H_{oi} = \frac{kT^2}{Q_i} \left( \frac{\partial Q_i}{\partial T} \right)_V + H_{oi} \quad (1)$$

where  $Q_i$  is the partition function and  $H_{oi}$ , the heat of formation at  $0^\circ \text{K}$ ,\* is the ground-state energy of one particle of species  $i$ . Eq. (1) implies that the lowest energy level in the partition function is taken

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\*The heat of formation of a molecule includes the energy needed to form the molecule from its components. Certain species, such as  $\text{N}_2$ ,  $\text{O}_2$ , and Ar are assigned zero heats of formation and the others are determined relative to these (see appendix A).

to be zero as discussed below. Following references 1, 2, and 10, the entropy per particle is taken to be

$$s_i = k \left( \frac{\partial T \ln Q_i}{\partial T} \right)_V + k = k \ln Q_i + \frac{kT}{Q_i} \left( \frac{\partial Q_i}{\partial T} \right)_V + k \quad (2)$$

The enthalpy and the Gibbs free energy per particle are, respectively,

$$h_i = e_i + kT \quad (3)$$

$$f_i = h_i - Ts_i = -kT \ln Q_i + H_{oi} \quad (4)$$

#### Partition Functions

The partition function per particle of a pure gas is defined as

$$Q = \sum_q g_q \exp[-\epsilon_q/kT] \quad (5)$$

with the summation taken over all distinct energy states (of energy  $\epsilon_q$  and degeneracy  $g_q$ ) of the particle. By definition

$$\lim_{T \rightarrow 0} e_i = \text{the ground-state energy} = H_{oi} \quad (6)$$

On the other hand, taking the limit of Eq. (1), one can easily show that

$$\begin{aligned} \lim_{T \rightarrow 0} e_i &= \lim_{T \rightarrow 0} \frac{kT^2}{Q_i} \left( \frac{\partial Q_i}{\partial T} \right)_V + H_{oi} \\ &= g_0 \min \{ \epsilon_q \} + H_{oi} \end{aligned} \quad (7)$$

It follows, then, that the lowest  $\epsilon_q$  must be taken to be zero

$$\min \{ \epsilon_q \} = 0 \quad (8)$$

as stated earlier.

Since the translational energies are independent of the internal energies, the partition function for species  $i$  can be written as

$$Q_i = Q_{tr} Q_{int} \quad (9)$$

The translational partition function per particle  $Q_{tr}$  for a pure ideal gas of  $N_i$  particles of mass  $m_i$ , confined in a volume  $V$ , and at a (partial) pressure  $p_i$  is (ref. 10)

$$Q_{tr} = \frac{(2\pi m_i kT)^{3/2}}{h^3} \frac{V}{N_i} \quad (10)$$

in which  $k$  is the Boltzmann constant and  $h$ , Planck's constant. The equations of state for species  $i$  and for the mixture can be written as

$$\frac{V}{N_i} = \frac{kT}{p_i} = \frac{NkT}{N_i p} \quad (11)$$

where

$$N = \sum_{i=1}^n N_i = \text{total number of particles} \quad (12)$$

Clearly, Eqs. (10) and (11) show the following functional dependence of  $Q_{tr}$

$$Q_{tr} = Q_{tr}(p_i, T) = Q_{tr}(N_i p / N, T) \quad (13)$$

The internal partition function  $Q_{\text{int}}$  includes contributions from vibrational, rotational, and electronic energies. Thus,

$$Q_{\text{int}} = \sum_{\text{ele}} \sum_{\text{vib}} \sum_{\text{rot}} g_{\text{ele,vib,rot}} \exp[-\epsilon_{\text{ele,vib,rot}}/kT] \quad (14)$$

An atom or atomic ion has no vibrational or rotational energy so that

$$Q_{\text{int}} = \sum_{\text{ele}} g_{\text{ele}} \exp[-\epsilon_{\text{ele}}/kT] \quad (15)$$

The cutoff criterion for this summation is discussed in appendix B. However, a molecule or a molecular ion has a set of vibrational and rotational energies corresponding to each of its electronic states. Therefore,

$$Q_{\text{int}} = \sum_{\text{ele}} (Q_{\text{vib,rot}})_{\text{ele}} g_{\text{ele}} \exp[-\epsilon_{\text{ele}}/kT] \quad (16)$$

For a given electronic state

$$(Q_{\text{vib,rot}})_{\text{ele}} = \frac{1}{\sigma} \sum_{\text{vib}} \sum_{\text{rot}} g_{\text{vib,rot}} \exp[-\epsilon_{\text{vib,rot}}/kT] \quad (17)$$

where  $\sigma$ , the symmetry number, is 1 for unsymmetrical and 2 for symmetrical linear molecules. In the latter case, only even or odd values of the rotational quantum number  $j$  occur. Instead of omitting every other term, the rotational summation is divided by  $\sigma = 2$ , since many terms contribute and adjacent terms are nearly equal. The quantities  $\sigma$ ,  $\epsilon_{\text{ele}}$ , and  $g_{\text{ele}}$  can be found in the literature (see appendix A). Now the problem is reduced to determining  $Q_{\text{vib,rot}}$  for diatomic and linear triatomic species.

According to second-order perturbation calculations (refs. 11, 12, and 13), the vibrational-rotational energy  $\epsilon_{\text{vib,rot}}$  is given by

$$\epsilon_{\text{vib,rot}} = hc \left[ \omega_e v + B_e j(j+1) - \omega_e x_e (v^2 + v) - \alpha_e \left( v + \frac{1}{2} \right) j(j+1) - D_e j^2 (j+1)^2 \right] \quad (18)$$

where  $v, j = 0, 1, 2, \dots$  are quantum numbers. Eq. (18) has been written in a form such that the ground state ( $v = j = 0$ ) has zero energy (see Eq. (8)). The first two terms of Eq. (18) represent the independent vibrational and rotational energies while the other terms represent second-order corrections. It should be remembered that  $\omega_e$ ,  $\omega_e x_e$ ,  $B_e$ ,  $\alpha_e$ , and  $D_e$  are all positive constants and that  $\omega_e \gg \omega_e x_e$  and  $B_e \gg \alpha_e \gg D_e$ . The perturbation calculation gives (ref. 13)

$$\alpha_e = \frac{6B_e^2}{\omega_e} \left[ \sqrt{\frac{\omega_e x_e}{B_e}} - 1 \right] \quad (19)$$

and

$$D_e = \frac{4B_e^3}{\omega_e^2} \quad (20)$$

However, it is better to use experimental values of  $\alpha_e$  and  $D_e$ , whenever available, since they empirically include high-order corrections. The value of  $D_e$  is very small and difficult to measure, so Eq. (20) for  $D_e$  will be used throughout the discussions. Substituting Eq. (20) into Eq. (18) and collecting coefficients of powers of  $v$  and  $j(j+1)$ , one obtains

$$\epsilon_{\text{vib,rot}} = \epsilon_H + \epsilon_R - \epsilon_A - \epsilon_I - \epsilon_S \quad (21)$$

where

$$\left. \begin{aligned} \epsilon_H &= hc(\omega_e - \omega_e x_e)v \\ \epsilon_R &= hc\left(B_e - \frac{1}{2}\alpha_e\right)j(j+1) \end{aligned} \right\} \quad (22)$$

$$\left. \begin{aligned} \epsilon_A &= hc\omega_e x_e v^2 \\ \epsilon_I &= hc\alpha_e v j(j+1) \\ \epsilon_S &= hc \frac{4B_e^3}{\omega_e^2} j^2(j+1)^2 \end{aligned} \right\} \quad (23)$$

which is equivalent to an empirical development in powers of the quantum numbers (ref. 12, pp. 160-161). It is convenient to call  $\epsilon_H$  the harmonic-oscillator energy,  $\epsilon_R$  the rigid-rotor energy,  $-\epsilon_A$  the vibrational anharmonicity energy,  $-\epsilon_I$  the vibration-rotation interaction energy, and  $-\epsilon_S$  the rotational stretching energy. The degeneracy  $g_{\text{vib,rot}}$  for a given  $v$  and  $j$  is simply

$$g_{\text{vib,rot}} = (2j + 1) \quad (24)$$

Substitution of Eqs. (21) and (24) into Eq. (17) gives the expression for  $Q_{\text{vib,rot}}$  for diatomic molecules. As pointed out in reference 12 (pp. 162-163), the summations in  $Q_{\text{vib,rot}}$  diverge when summed to  $v, j = \infty$  because Eq. (18) is invalid for large quantum numbers. The problem is alleviated there by making an approximation which allows the summations to be written in a compact form. However, this approximation is not valid for diatomic species at temperatures around  $5,000^\circ$  K. In

the present work, a direct summation was carried out instead. To terminate the summations over  $v$  and  $j$  the following scheme was used. All values of  $v$  and  $j$  are allowed for which the harmonic-oscillator energy plus the rigid-rotor energy is less than the dissociation energy  $hcD_0$  (energy required to separate the two atoms of a diatomic molecule). That is,  $v_{\max}$  and  $j(v)_{\max}$  are determined from the relation

$$(\omega_e - \omega_e x_e)v + \left( B_e - \frac{1}{2} \alpha_e \right) j(j+1) < D_0 \quad (25)$$

The upper limit  $v_{\max}$  is the largest integer  $v$  for which Eq. (25) is satisfied for  $j = 0$ . For all  $v \leq v_{\max}$ ,  $j(v)_{\max}$  is the largest integer  $j$  such that Eq. (25) holds. Thus, the expression for  $Q_{\text{vib,rot}}$  for diatomic molecules becomes

$$Q_{\text{vib,rot}} = \frac{1}{\sigma} \sum_{v=0}^{v_{\max}} \sum_{j=0}^{j(v)_{\max}} (2j+1) \exp[-\epsilon_{\text{vib,rot}}/kT] \quad (26)$$

where  $\epsilon_{\text{vib,rot}}$  is given by Eq. (21). The values of  $v_{\max}$  and  $j(v)_{\max}$  are approximate since no correction terms are included in the vibrational-rotational energy in Eq. (25). However, it was found that the summations over  $v$  and  $j$  are not very sensitive to the exact values of  $v_{\max}$  and  $j(v)_{\max}$ . This observation justifies the use of the above scheme for determining  $v_{\max}$  and  $j(v)_{\max}$ , provided that  $D_0$  for each electronic state is known. Whereas  $D_0$  for the ground electronic state is usually known, it is generally not known (i.e., has not been measured) for excited states. Approximate  $D_0$  values can be obtained (see ref. 13, p. 100) by considering the energy expression at  $j = 0$ ,

$$\epsilon(v,0)_{\text{vib,rot}} = hc \left[ (\omega_e - \omega_e x_e)v - \omega_e x_e v^2 \right] \quad (27)$$

Note that  $\epsilon(v,0)_{\text{vib,rot}}$  has a maximum. This maximum energy is taken to be the approximate dissociation energy  $hcD_0$ , and  $D_0$  is then given by

$$D_0 = \frac{(\omega_e - \omega_e x_e)^2}{4\omega_e x_e} \quad (28)$$

Use of this approximation is discussed in detail in appendix C. It should be mentioned at this point that for diatomic species, only electronic states with

$$v_{\text{ele}} < 90,000 \text{ cm}^{-1}$$

were considered. Higher states do not contribute a significant amount to the partition function below about  $15,000^\circ \text{ K}$ .

For linear triatomic species,  $Q_{\text{vib,rot}}$  is computed from the harmonic-oscillator, rigid-rotor model. Since a linear triatomic species has four independent vibrational frequencies and the rotations are independent of the vibrations, Eq. (17) becomes

$$Q_{\text{vib,rot}} = \frac{1}{\sigma} \prod_{w=1}^4 \left( \sum_{v=0}^{\infty} \exp[-\epsilon_{\text{H}w}/kT] \right) \sum_{j=0}^{\infty} (2j+1) \exp[-\epsilon_{\text{R}}/kT] \quad (29)$$

where  $\epsilon_{\text{H}}$  and  $\epsilon_{\text{R}}$  are defined by Eqs. (22). The summation over  $v$  can be written in a closed form and the summation over  $j$  can be changed to an integral over the variable  $j(j+1)$  to give

$$\sum_{j=0}^{\infty} (2j+1) \exp[-\epsilon_{\text{R}}/kT] \cong \frac{1}{\frac{hc}{kT} \left( B_e - \frac{1}{2} \alpha_e \right)} \quad (30)$$

Therefore, Eq. (29) becomes

$$Q_{\text{vib,rot}} = \frac{1}{\sigma} \prod_{w=1}^4 \left\{ \frac{1}{1 - \exp\left[-\frac{hc}{kT}(\omega_e - \omega_e x_e)_w\right]} \right\} \frac{1}{\frac{hc}{kT} \left( B_e - \frac{1}{2} \alpha_e \right)} \quad (31)$$

In conclusion, the partition function per particle of species  $i$  is

$$Q_i = Q_{\text{tr}} Q_{\text{int}} \quad (9)$$

in which  $Q_{\text{tr}}$  has the functional dependence

$$Q_{\text{tr}} = Q_{\text{tr}}\left(\frac{N_{i,p}}{N}, T\right) \quad (13)$$

For atomic species

$$Q_{\text{int}} = \sum_{\text{ele}} g_{\text{ele}} \exp\left[-\epsilon_{\text{ele}}/kT\right] \quad (15)$$

and for molecular species

$$Q_{\text{int}} = \sum_{\text{ele}} (Q_{\text{vib,rot}})_{\text{ele}} g_{\text{ele}} \exp\left[-\epsilon_{\text{ele}}/kT\right] \quad (16)$$

with  $(Q_{\text{vib,rot}})_{\text{ele}}$  given by Eq. (26) or Eq. (31), respectively, for diatomic or linear triatomic species.

Once the partition function  $Q_i$  is given as a function of  $T$  and  $V$ , calculation of the temperature derivative

$$\left(\frac{\partial Q_i}{\partial T}\right)_V$$

is straightforward.

### Gibbs Free Energy of a Gas Mixture

According to Eqs. (4) and (13), the Gibbs free energy of species  $i$  at its partial pressure  $p_i$  has the following functional dependence:

$$f_i = f_i(p_i, T) = f_i\left(\frac{N_i p}{N}, T\right) \quad (32)$$

More explicitly,

$$f_i = f_i(p, T) + kT \ln \frac{N_i}{N} \quad (33)$$

Since the Gibbs free energy is an additive quantity, the total Gibbs free energy for the mixture is simply

$$F = \sum_{i=1}^n N_i f_i = \sum_{i=1}^n N_i \left[ f_i(p, T) + kT \ln \frac{N_i}{N} \right] \quad (34)$$

In the calculations that follow,  $p$  and  $T$  will be treated as constants, while the  $N_i$  are being adjusted to minimize  $F$ .

### Minimization Method

To determine the equilibrium composition of the gas mixture at a given temperature and pressure, the Gibbs free energy of the mixture is minimized subject to the constraints on the components of the mixture. The components are just the atomic elements (and electrons) which combine chemically to form the species. The constraint equations are

$$B_k = \sum_{i=1}^n A_{ik} N_i \quad k = 1, 2, \dots, l \quad (35)$$

where the  $B_k$  are conserved quantities. The above quantities are:  $B_k$ , the number of (free and combined) atoms of component  $k$  in the mixture;  $A_{ik}$ , the number of atoms of component  $k$  per particle of species  $i$ ;  $N_i$ , the number of particles of species  $i$  in the mixture; and  $l$ , the number of components in the mixture.

The minimization of the Gibbs free energy, Eq. (34), subject to Eqs. (35), lends itself to the use of the method of Lagrange multipliers. However, application of the Lagrange multiplier method to  $F$  gives  $n$  nonlinear and  $l + 1$  linear equations in  $n + l + 1$  unknowns which must be solved simultaneously. A numerical method developed in reference 14 has been used to solve the set of nonlinear equations. Note that if  $F$  were a quadratic expression, the Lagrange multiplier method would produce  $n + l + 1$  linear equations in  $n + l + 1$  unknowns. In the numerical method of reference 14,  $F$  is expanded in a Taylor series about an initial guess for the  $N_i$  in which terms of first and second power in the  $N_i$  are retained. This quadratic approximation is then easily minimized. A better quadratic approximation for  $F$  is made by expanding about the new values for the  $N_i$ . This procedure is continued until the minimum is reached giving the equilibrium values of the  $N_i$ . Numerically, this point is reached when no  $N_i$  changes in successive iterations by more than a small number,  $NM \times 10^{-7}$ . Appendix D gives the computational equations used in the numerical method (ref. 14). In reference 15, it is shown that this numerical calculation converges.

### Equilibrium Properties

Once the equilibrium concentrations have been determined, the mixture properties are easily computed. The Gibbs free energy has already been discussed. The enthalpy of the mixture is also additive and is given by

$$H = \sum_{i=1}^n N_i h_i \quad (36)$$

The entropy of the mixture is related to  $F$  and  $H$  through

$$S = \frac{H}{T} - \frac{F}{T} \quad (37)$$

The term "original mixture" will be used to refer to the mixture at about room temperature and atmospheric pressure, since under these conditions no significant dissociation or ionization of the particles takes place. The molar mass of the original mixture and of the equilibrium mixture can be defined, respectively, as

$$M' = N_O \frac{\text{Total mass of mixture}}{N'} = N_O \frac{\sum_{i=1}^n N_i' m_i}{N'} \quad (38)$$

and

$$M = N_O \frac{\text{Total mass of mixture}}{N} = N_O \frac{\sum_{i=1}^n N_i m_i}{N} \quad (39)$$

where the primed quantities are for the original mixture and  $N_O$  is Avogadro's number. A quantity of interest in some applications is the molecular weight ratio  $Z$  which is given by

$$Z = \frac{M'}{M} = \frac{N}{N'} \quad (40)$$

The mass density of the mixture is

$$\rho = \frac{MN}{N_0 V} = \frac{Mp}{N_0 kT} \quad (41)$$

Finally, the electron density  $N_e$  is given by

$$N_e = \frac{N_1}{V} = \frac{N_1 p}{NkT} \quad (42)$$

with the subscript 1 referring to the electrons.

#### Temperature and Pressure Limits

The assumptions made in the present computational method restrict the temperature and pressure ranges in which it should be used. At temperatures above 15,000<sup>o</sup> K, inaccuracies enter because the high electronic energy levels of the atoms and ions are approximate (see appendix B) and coulomb interactions have been neglected (see ref. 2). At pressures above about 10<sup>2</sup> p<sub>0</sub> (p<sub>0</sub> = atmospheric pressure), departures from the ideal-gas law begin to occur. Below about 10<sup>-4</sup> p<sub>0</sub>, collisions between gas particles may not occur frequently enough to maintain chemical equilibrium in practical applications such as planetary entry and other hypersonic flow problems.

### VIII. RESULTS AND DISCUSSION

Thermodynamic properties were calculated using the constants which are listed in appendix A. Gibbs free energy and enthalpy were computed for diatomic species at atmospheric pressure  $p = p_0$  (figs. 1-20). Enthalpy, entropy, molecular weight ratio, mass density, and electron density were computed (figs. 21-30) for the following two mixtures: air and a model atmosphere of Mars which consists of 25 percent  $N_2$ , 43 percent  $CO_2$ , and 32 percent Ar by volume.

For diatomic species at  $p = p_0$ , the properties were computed as described in chapter VII. Hereafter, this method will be referred to as the corrected method. Next, they were computed using the uncorrected (harmonic-oscillator, rigid-rotor) model. In these uncorrected computations the diatomic species were treated exactly as the linear triatomic species in chapter VII, except for the number of independent vibrational frequencies (which for a diatomic species is one). The third method is a compromise between the corrected method and the one using the form of the partition function given in reference 12, pages 162-163. This third method is described in appendix E. Results obtained using these three methods and the results of Browne (refs. 8 and 9) are presented and discussed under the subheading "Diatomic Species Properties."

The thermodynamic properties for mixtures were computed using both the corrected and uncorrected methods for diatomic species. The third method (appendix E) was not used for computing mixture properties. Some representative results are given for two mixtures under the subheading "Mixture Properties."

For air, thermodynamic properties computed herein are compared with those as computed by Browne (ref. 2) and Gilmore (ref. 1). These are discussed under the subheading "Comparison With Existing Results."

In all figures (1-30) the corrected property is presented in the upper graph. In the lower graph, the value of the quantity calculated by a given method minus that from the corrected method is plotted. This difference is denoted by  $\Delta f_i$ ,  $\Delta h_i$ , etc.

#### Diatomic Species Properties

Results for diatomic species at atmospheric pressure  $p = p_0$  are presented in figures 1 through 20. The diatomic species which were considered are  $N_2$ ,  $O_2$ ,  $NO$ ,  $CO$ ,  $CN$ ,  $N_2^+$ ,  $O_2^+$ ,  $O_2^-$ ,  $NO^+$ , and  $CO^+$ . Figure 1 shows that for  $N_2$  the uncorrected free-energy difference increases steadily up to  $15,000^\circ K$ . Figure 2 shows that for  $O_2$  the uncorrected free-energy difference increases at a faster rate than for  $N_2$  and starts decreasing at  $9,000^\circ K$ . The rate of increase of this difference measures the sensitivity of the species to its corrections. On the other hand, the temperature at which this difference starts decreasing depends strongly on the dissociation energy of the species. Computations for gas mixtures show that a given diatomic species generally will dissociate before this difference starts decreasing. At still higher temperatures, this difference depends almost entirely on the fact that  $v$  and  $j$  were summed to infinity for the uncorrected properties, but were cut off in the corrected calculations (see Eq. (25)). In general, this free-energy difference is seen to be about 0.2 or 0.3 percent of the free energy itself.

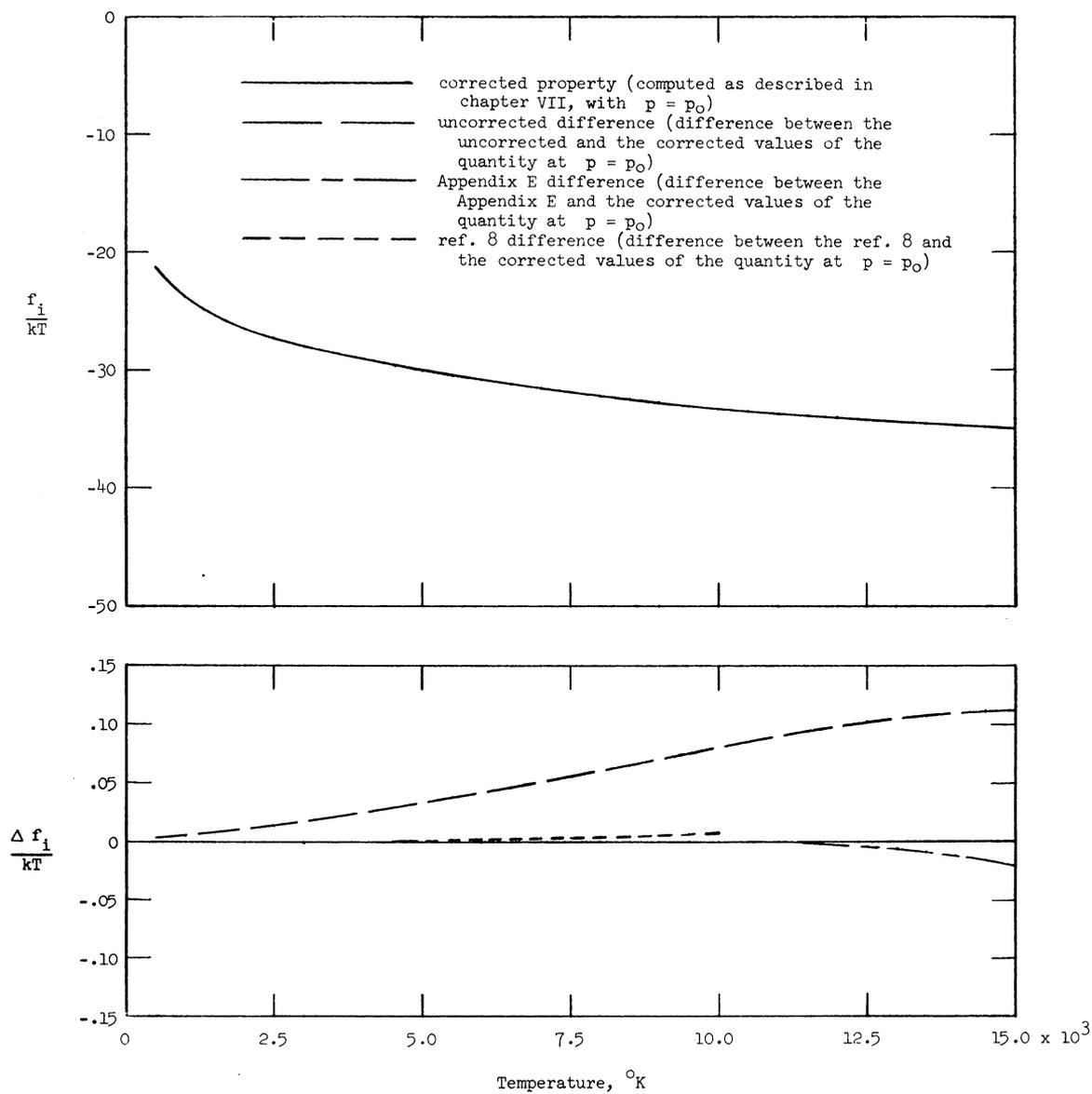


Figure 1.— Free energy of  $N_2$  and comparisons with other results.

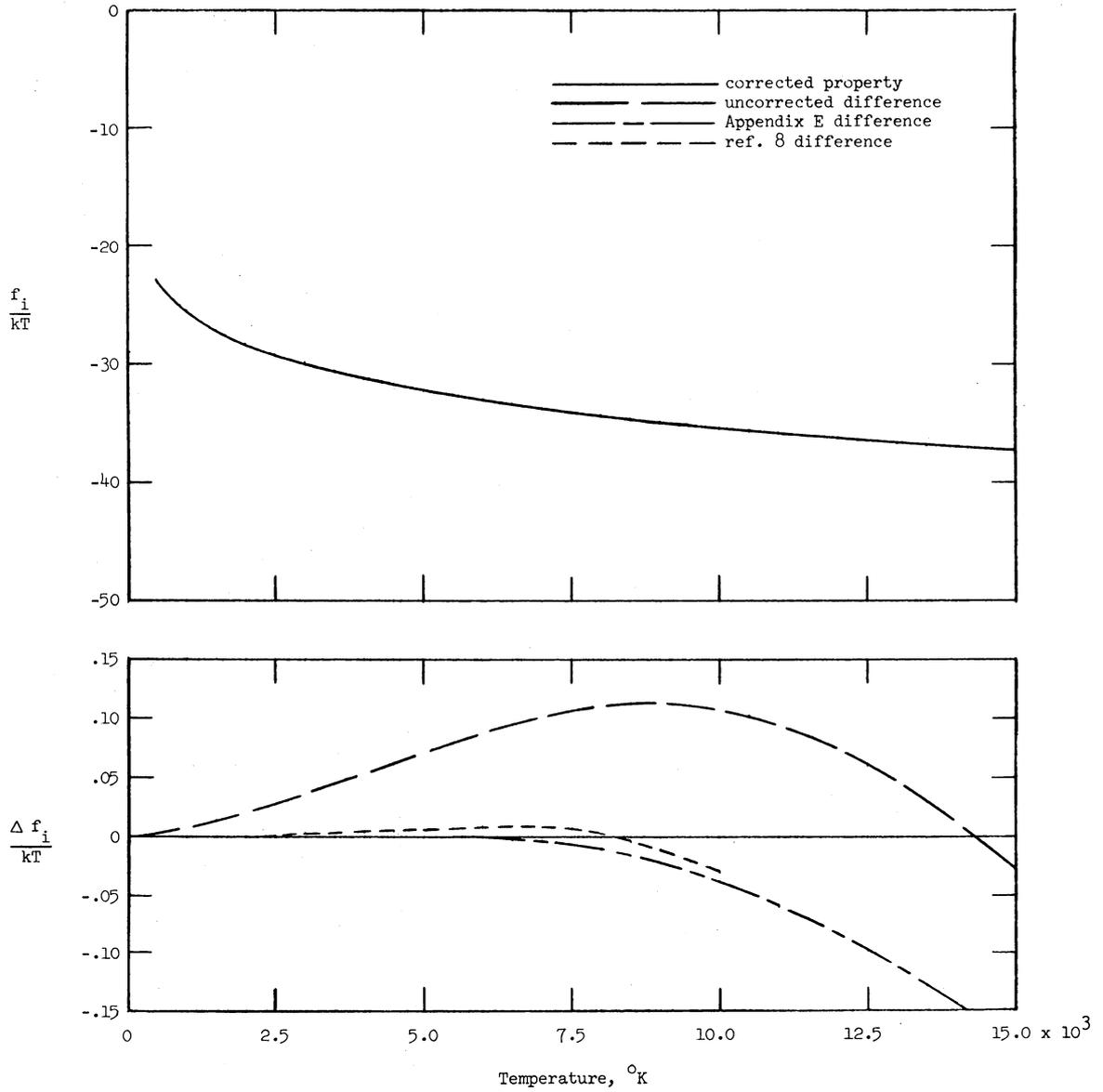


Figure 2.- Free energy of  $O_2$  and comparisons with other results.

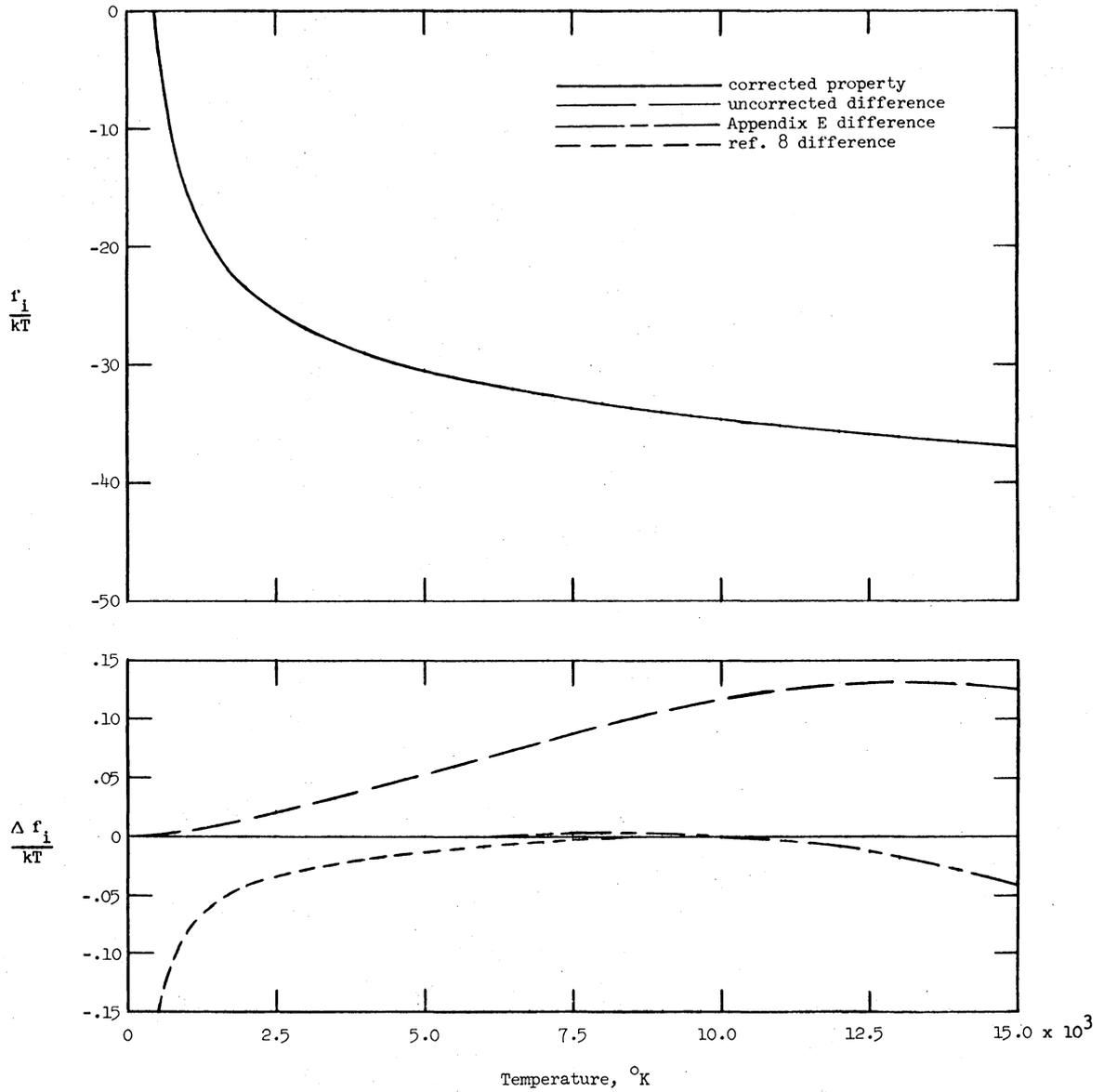


Figure 3.— Free energy of NO and comparisons with other results.

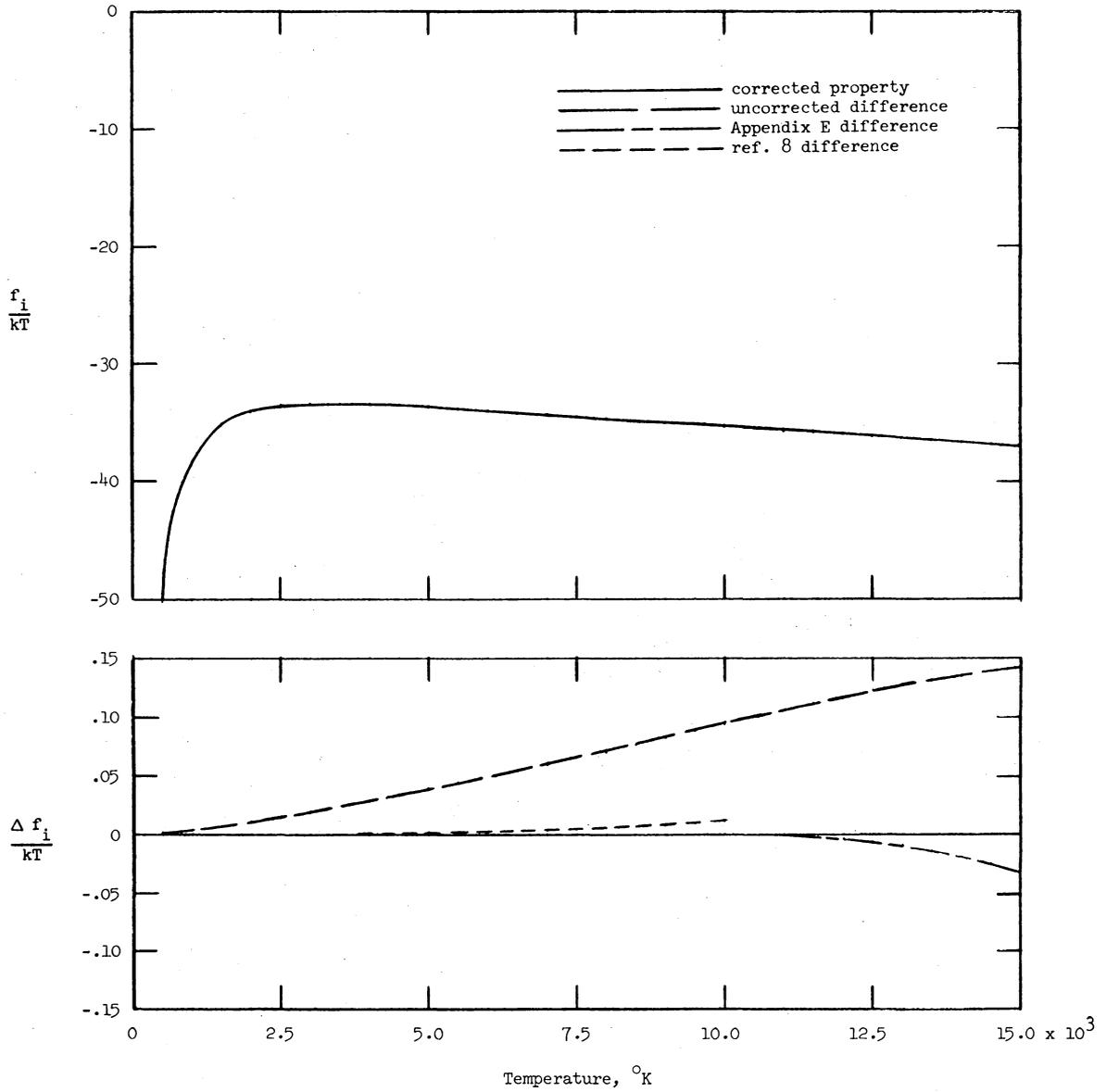


Figure 4.- Free energy of CO and comparisons with other results.

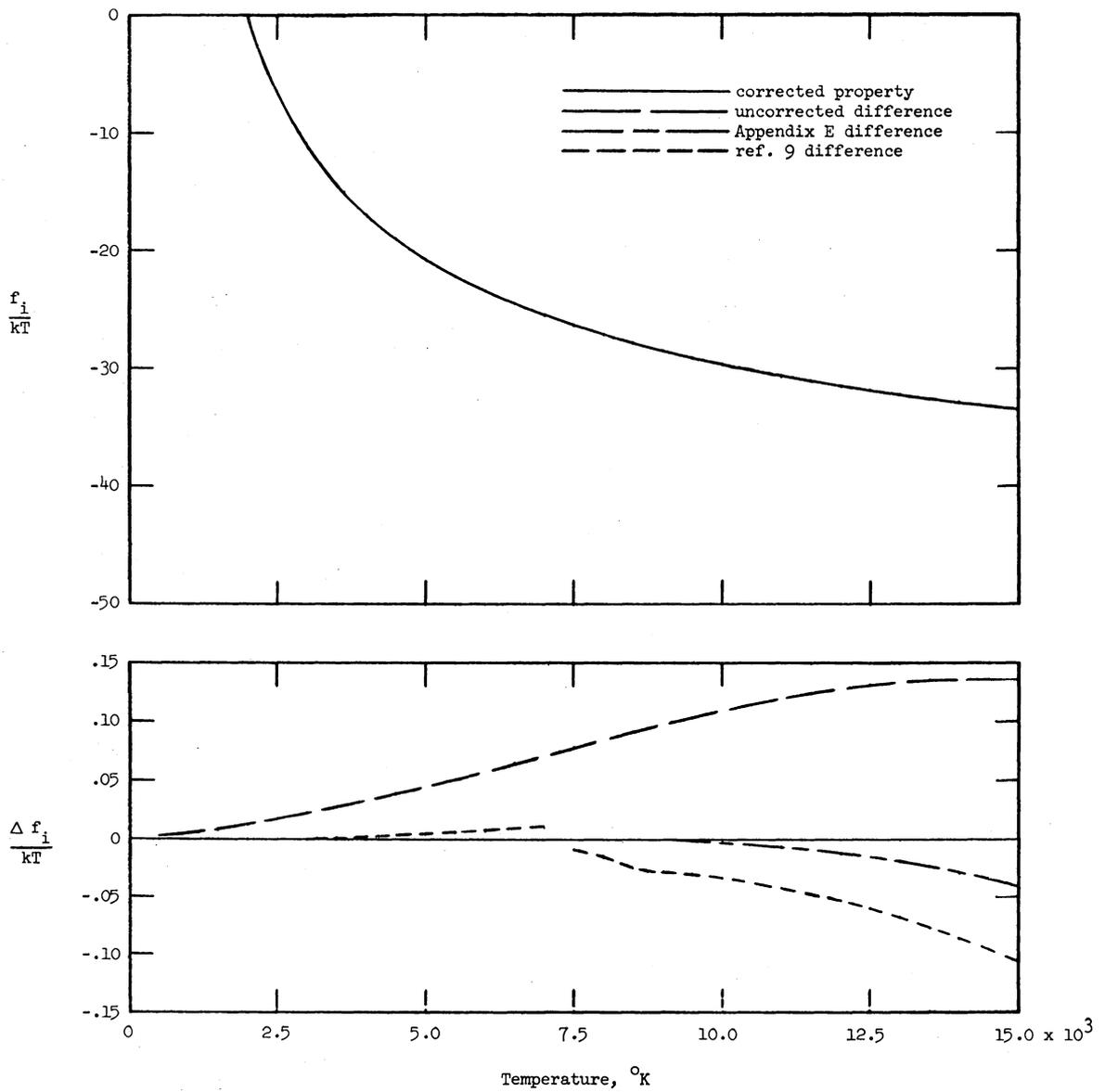


Figure 5.- Free energy of CN and comparisons with other results.

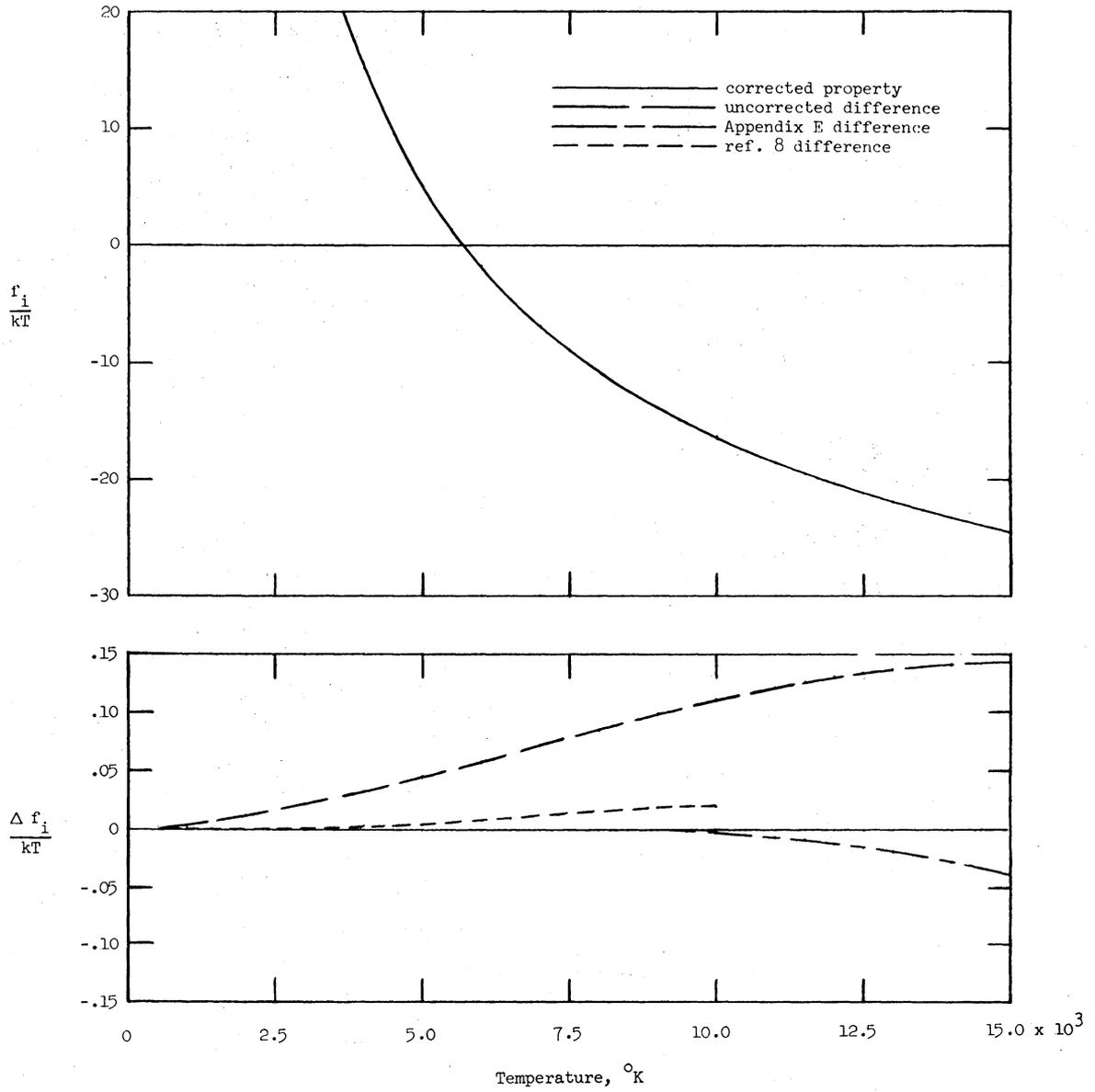


Figure 6.— Free energy of  $\text{N}_2^+$  and comparisons with other results.

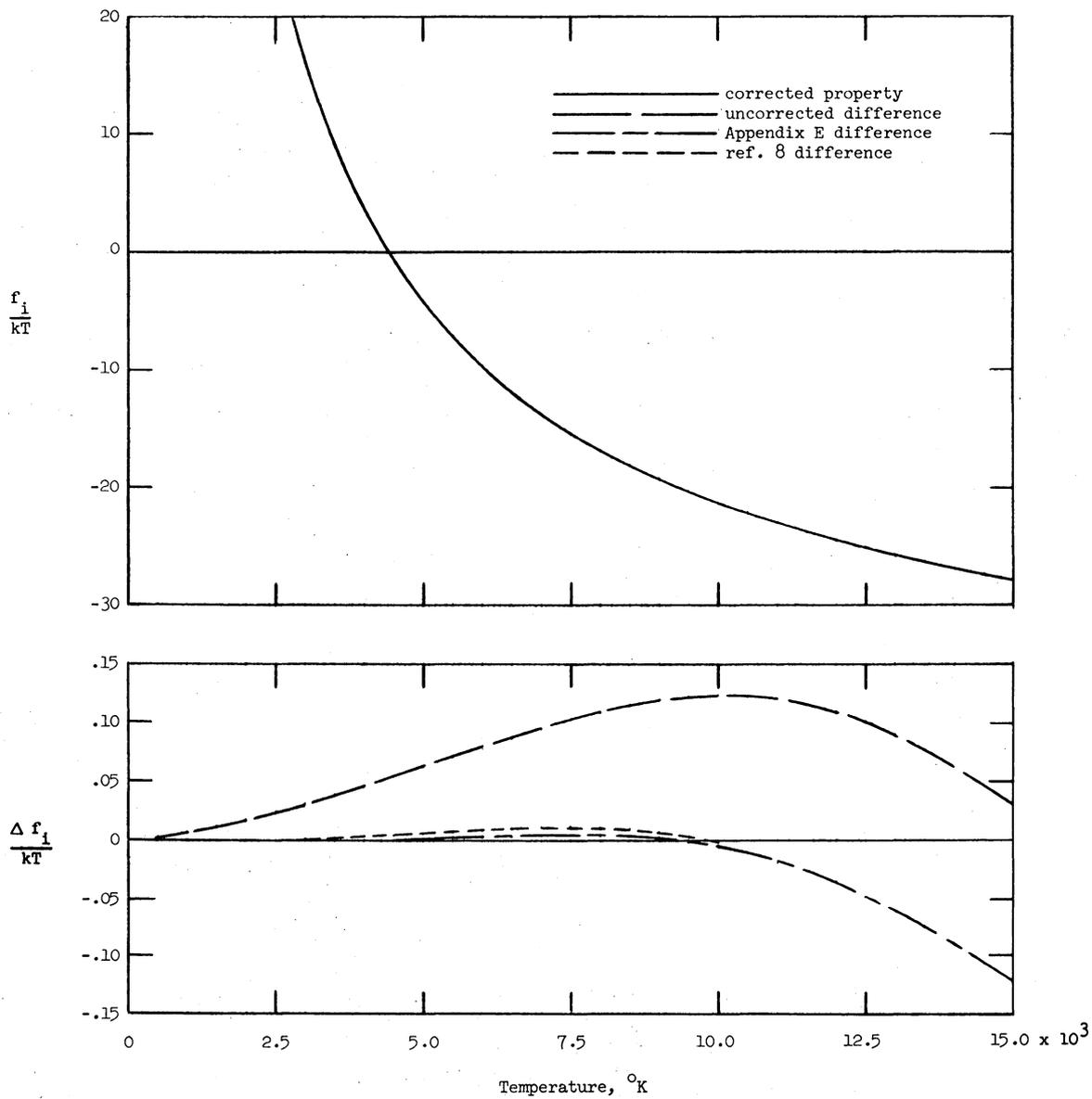


Figure 7.- Free energy of  $O_2^+$  and comparisons with other results.

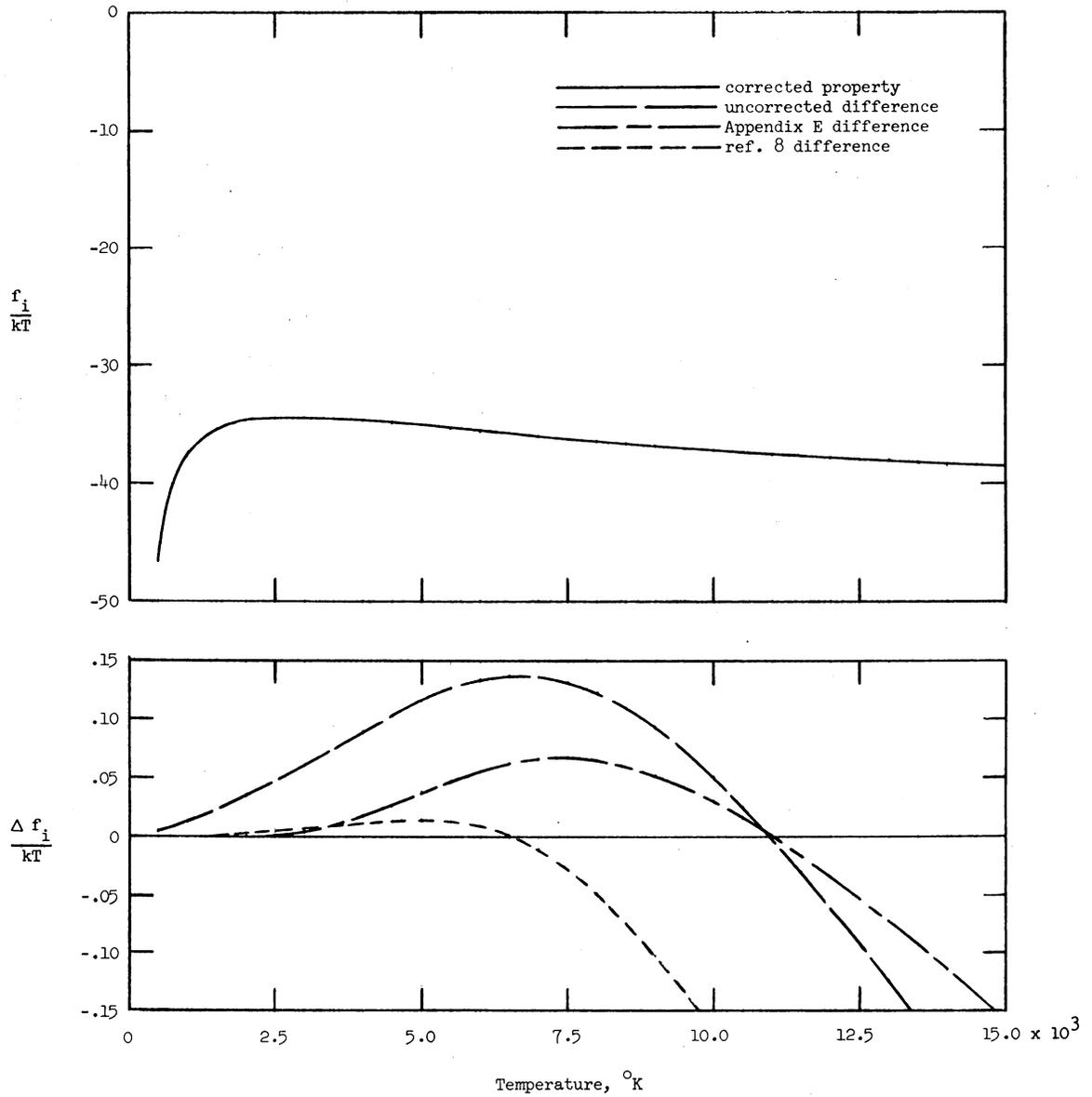


Figure 8.— Free energy of  $\text{O}_2^-$  and comparisons with other results.

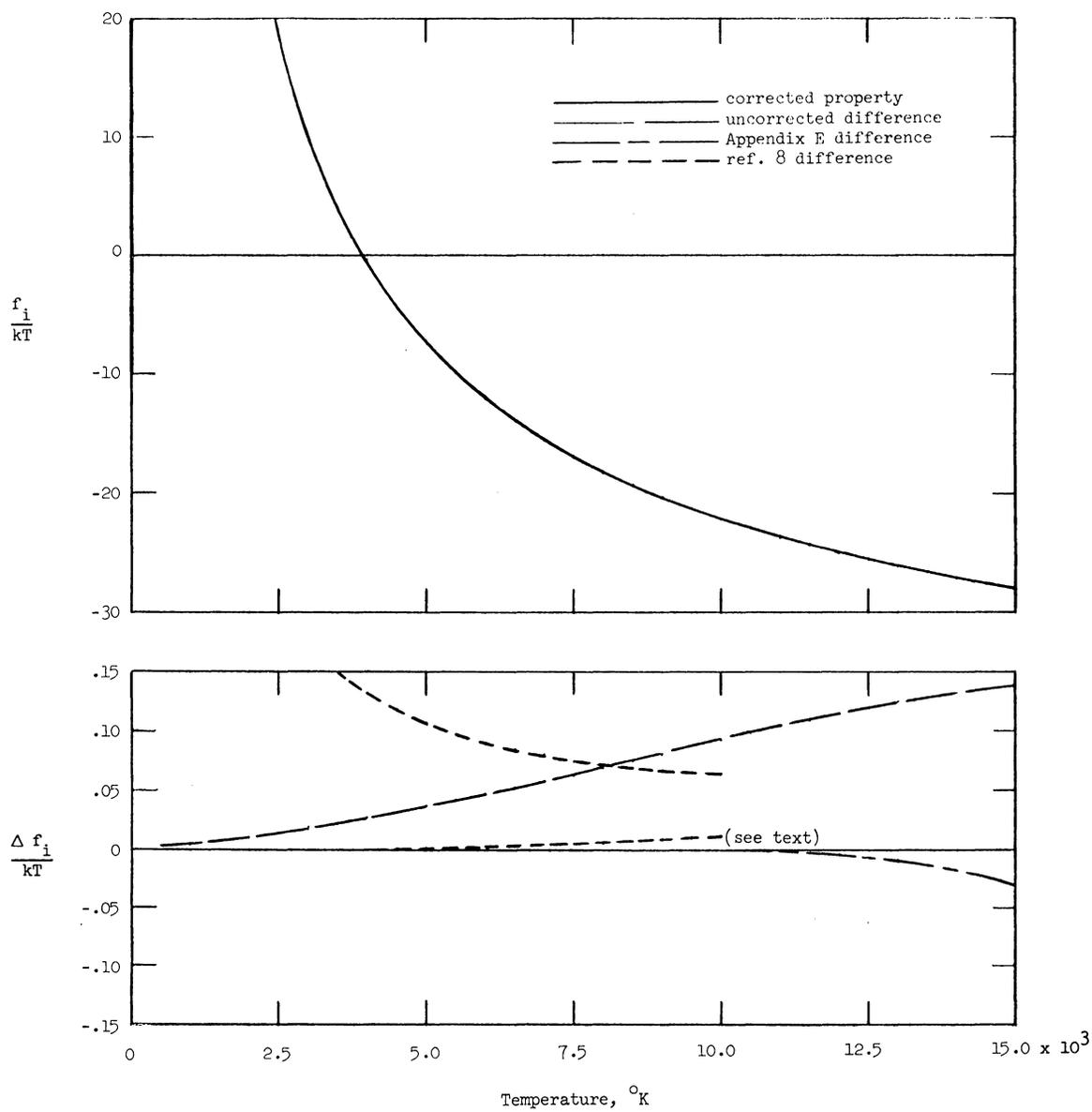


Figure 9.— Free energy of  $\text{NO}^+$  and comparisons with other results.

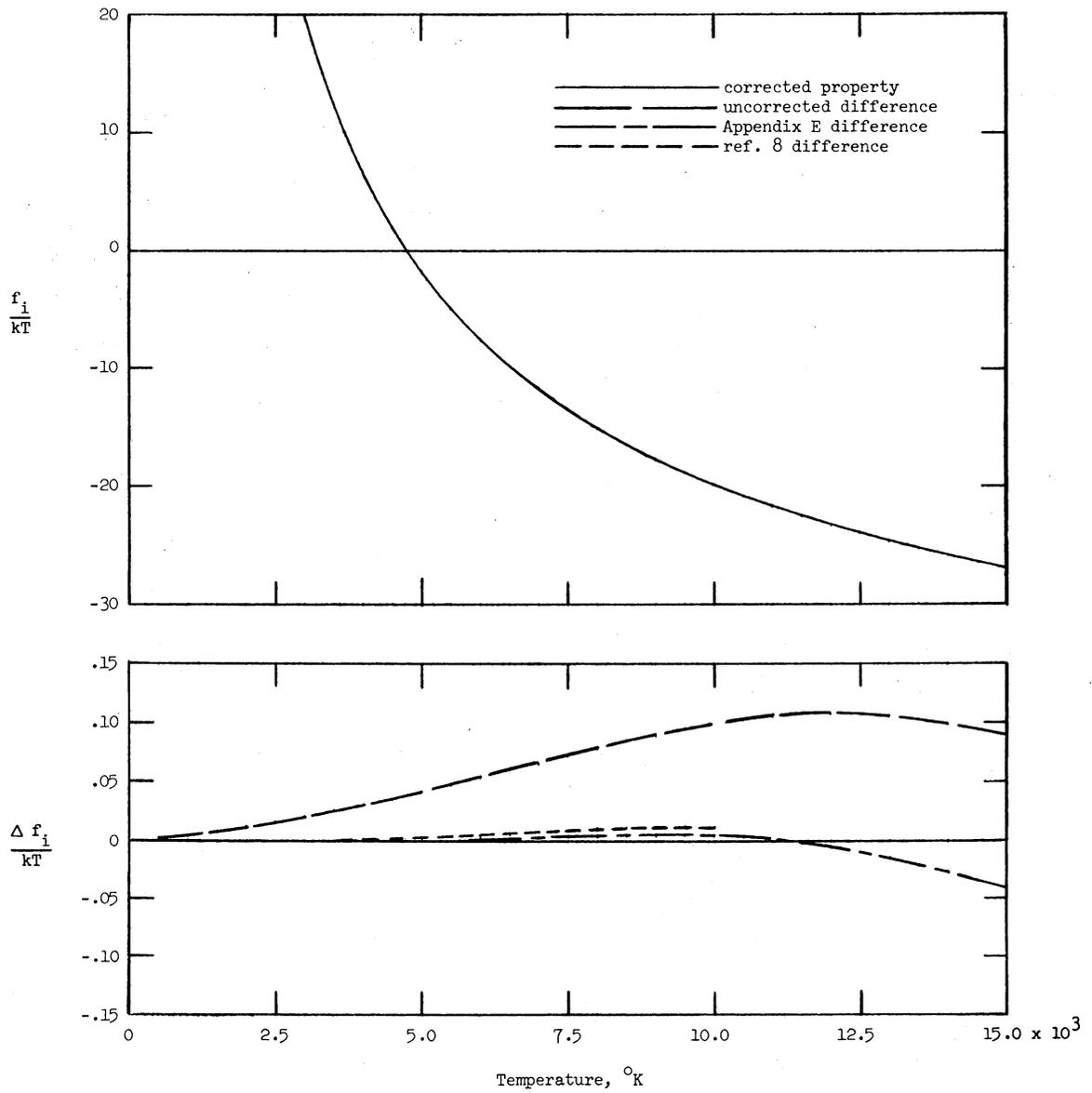


Figure 10.— Free energy of  $\text{CO}^+$  and comparisons with other results.

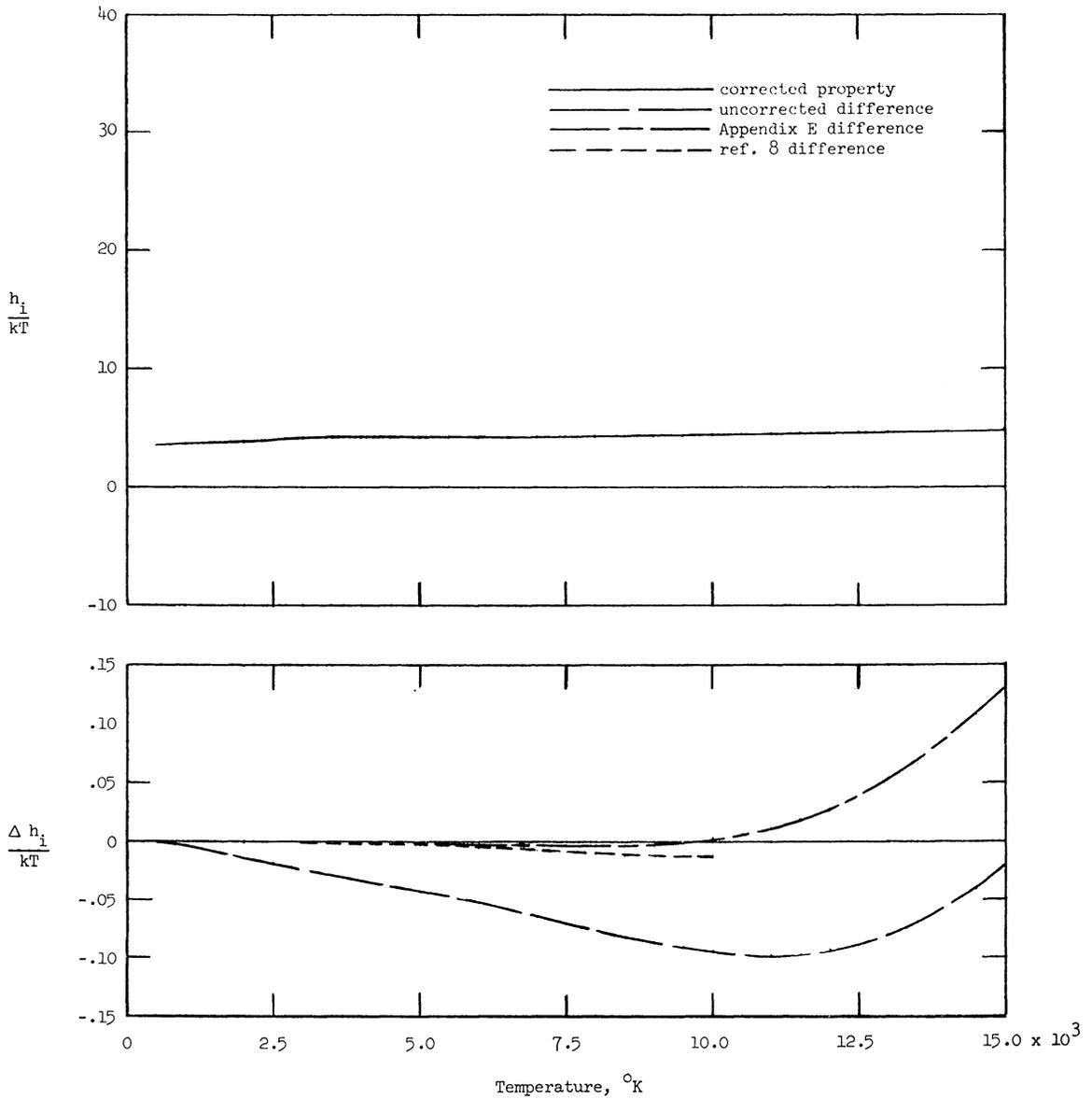


Figure 11.- Enthalpy of  $N_2$  and comparisons with other results.

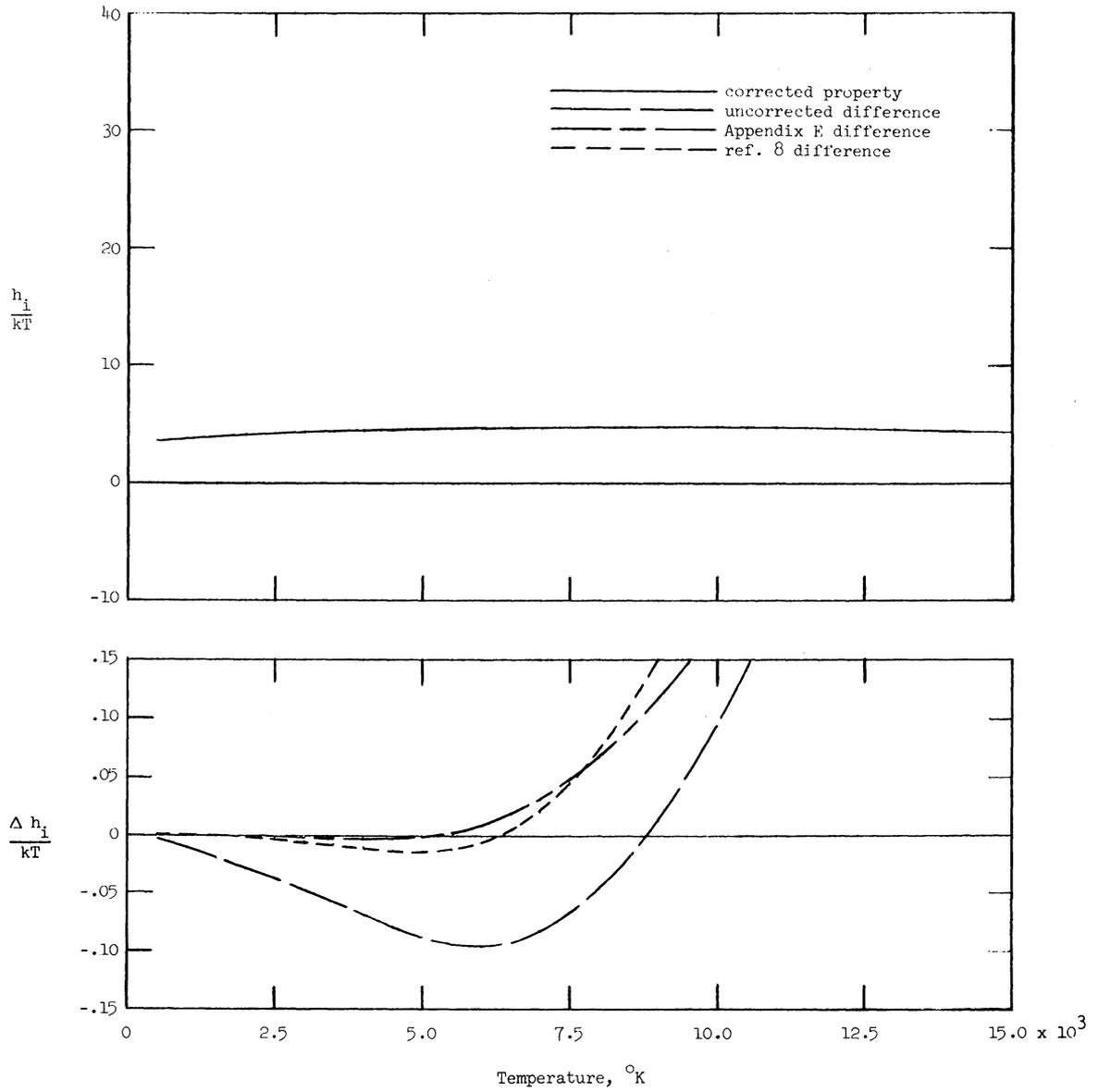


Figure 12.- Enthalpy of  $O_2$  and comparisons with other results.

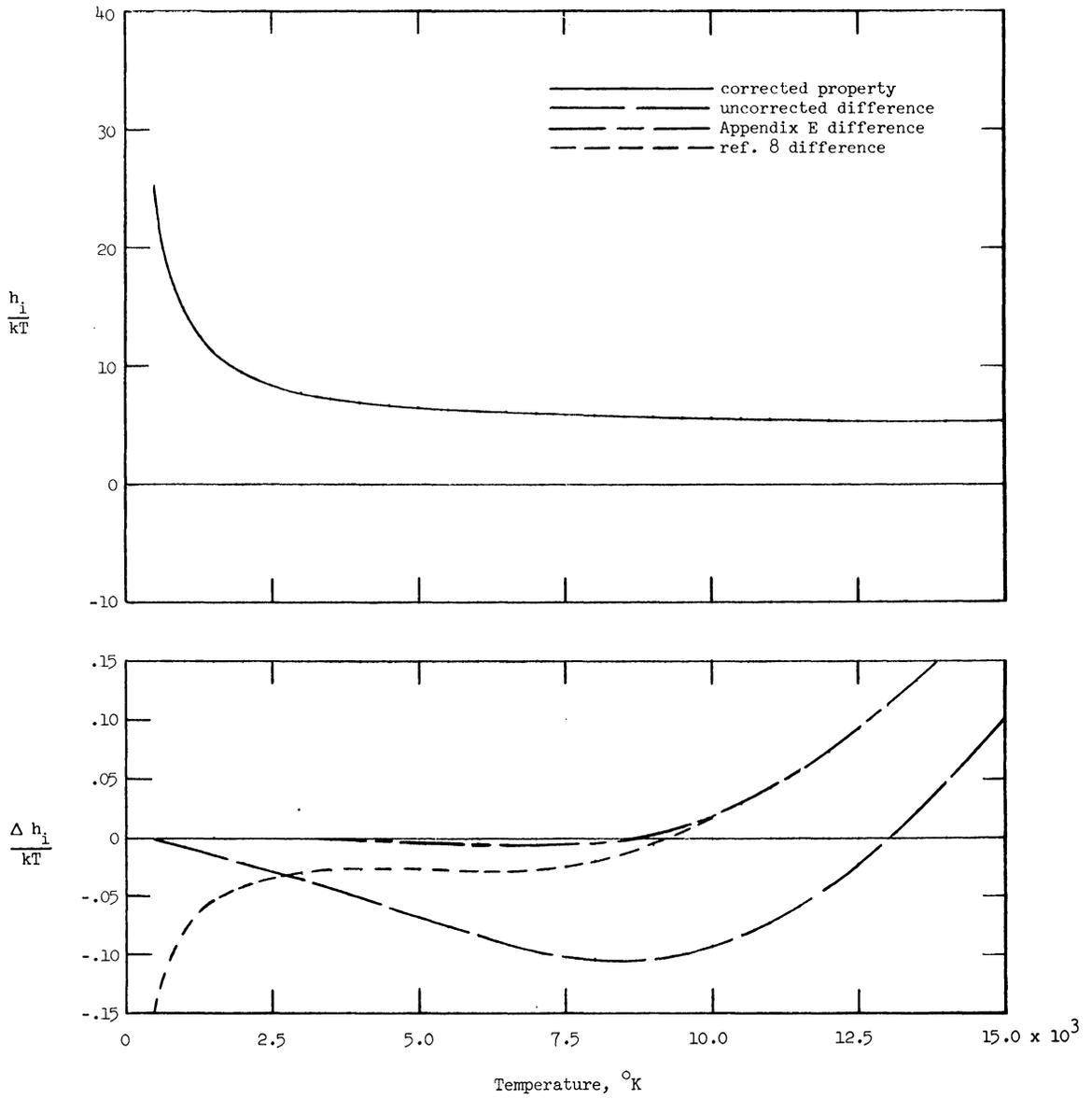


Figure 13.- Enthalpy of NO and comparisons with other results.

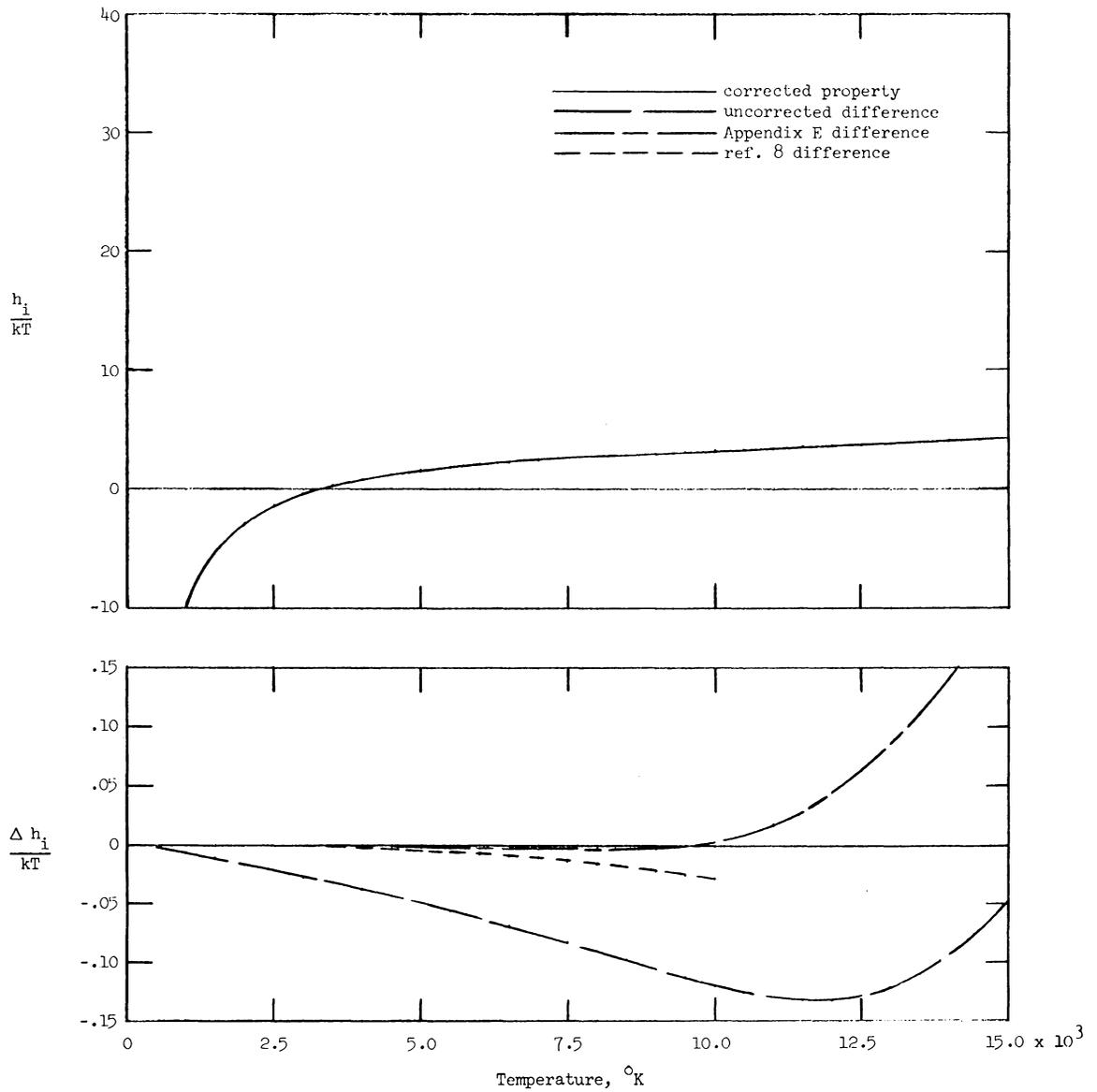


Figure 14.— Enthalpy of CO and comparisons with other results.

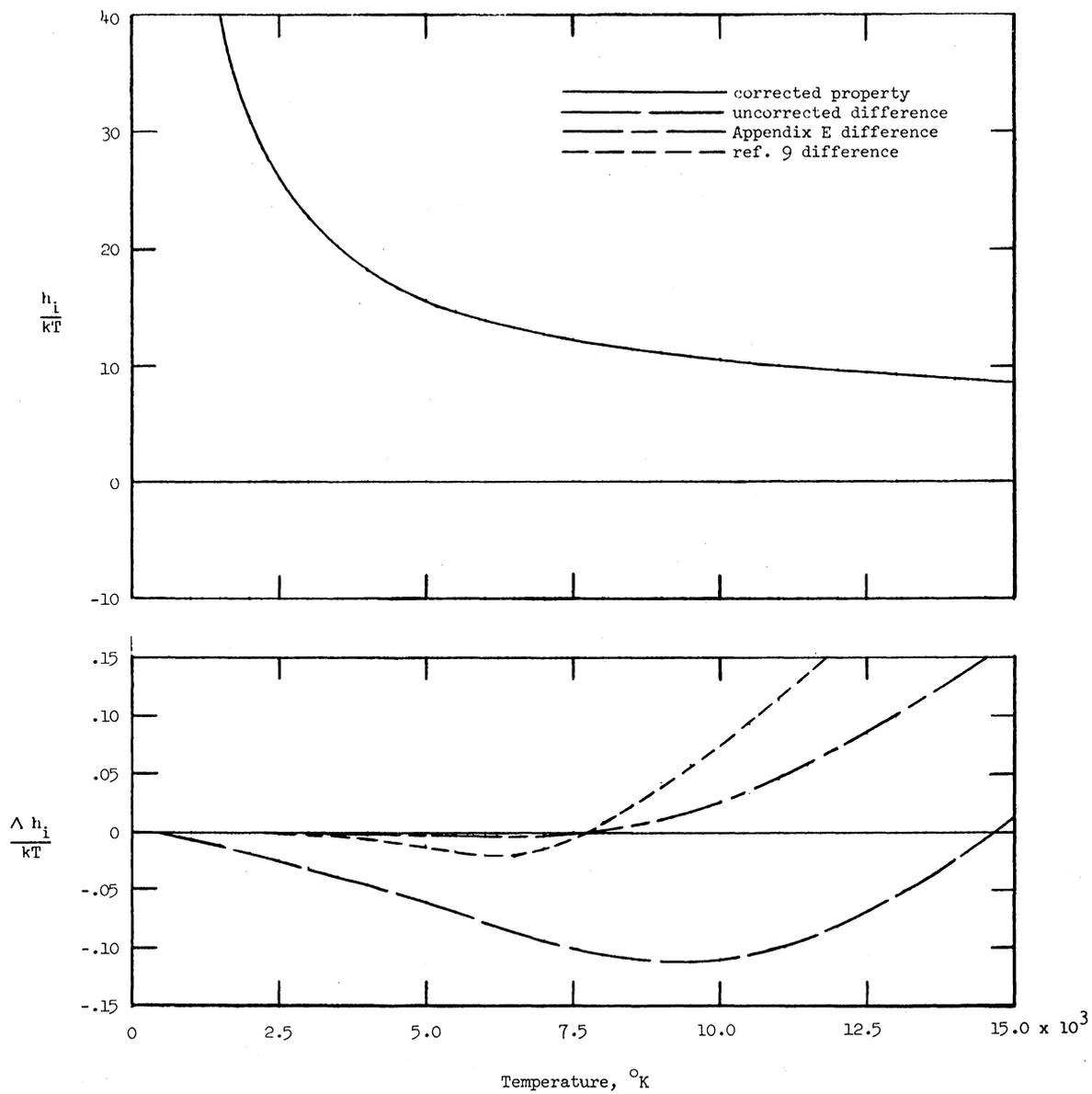


Figure 15.- Enthalpy of CN and comparisons with other results.

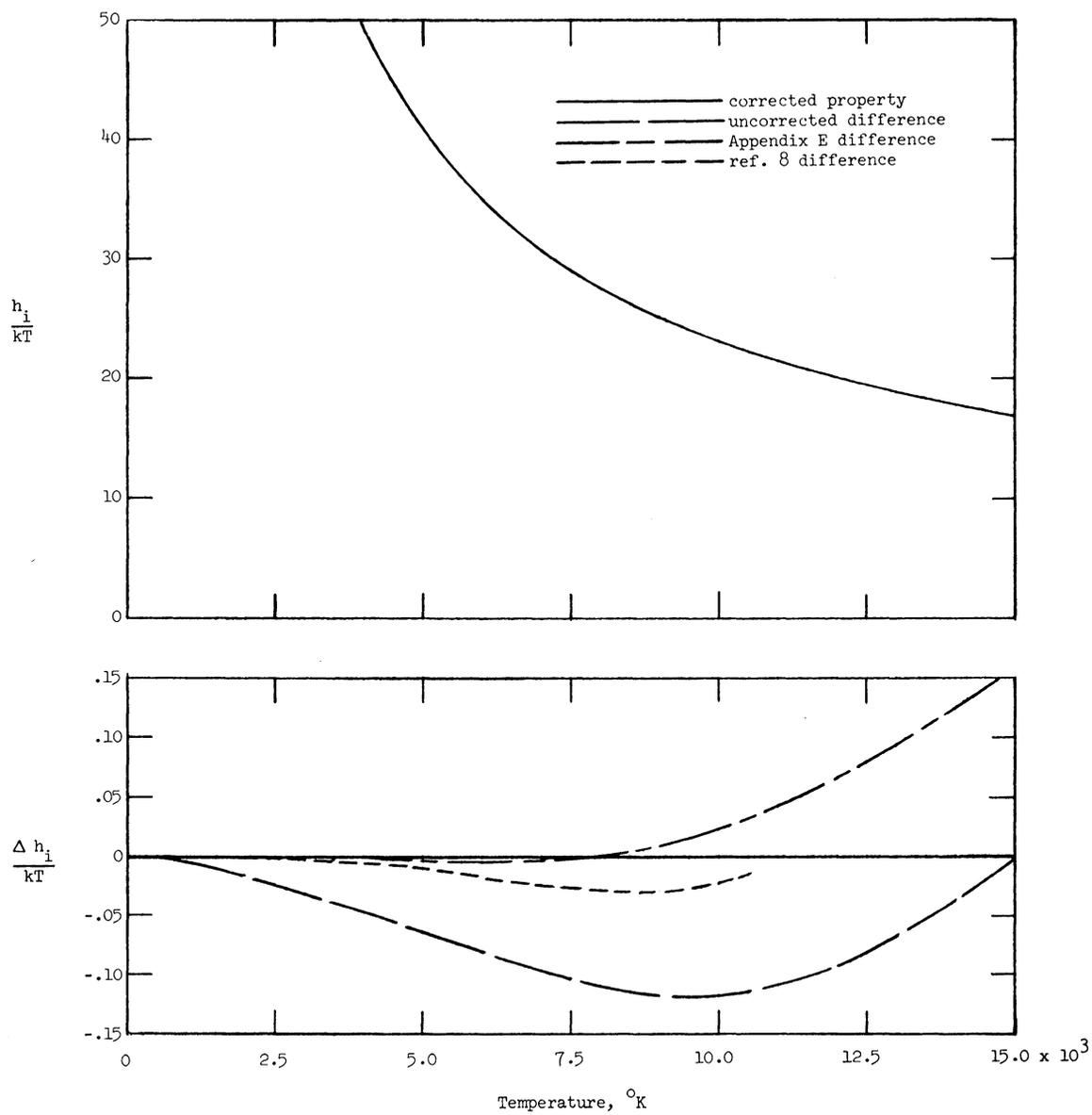


Figure 16.- Enthalpy of  $N_2^+$  and comparisons with other results.

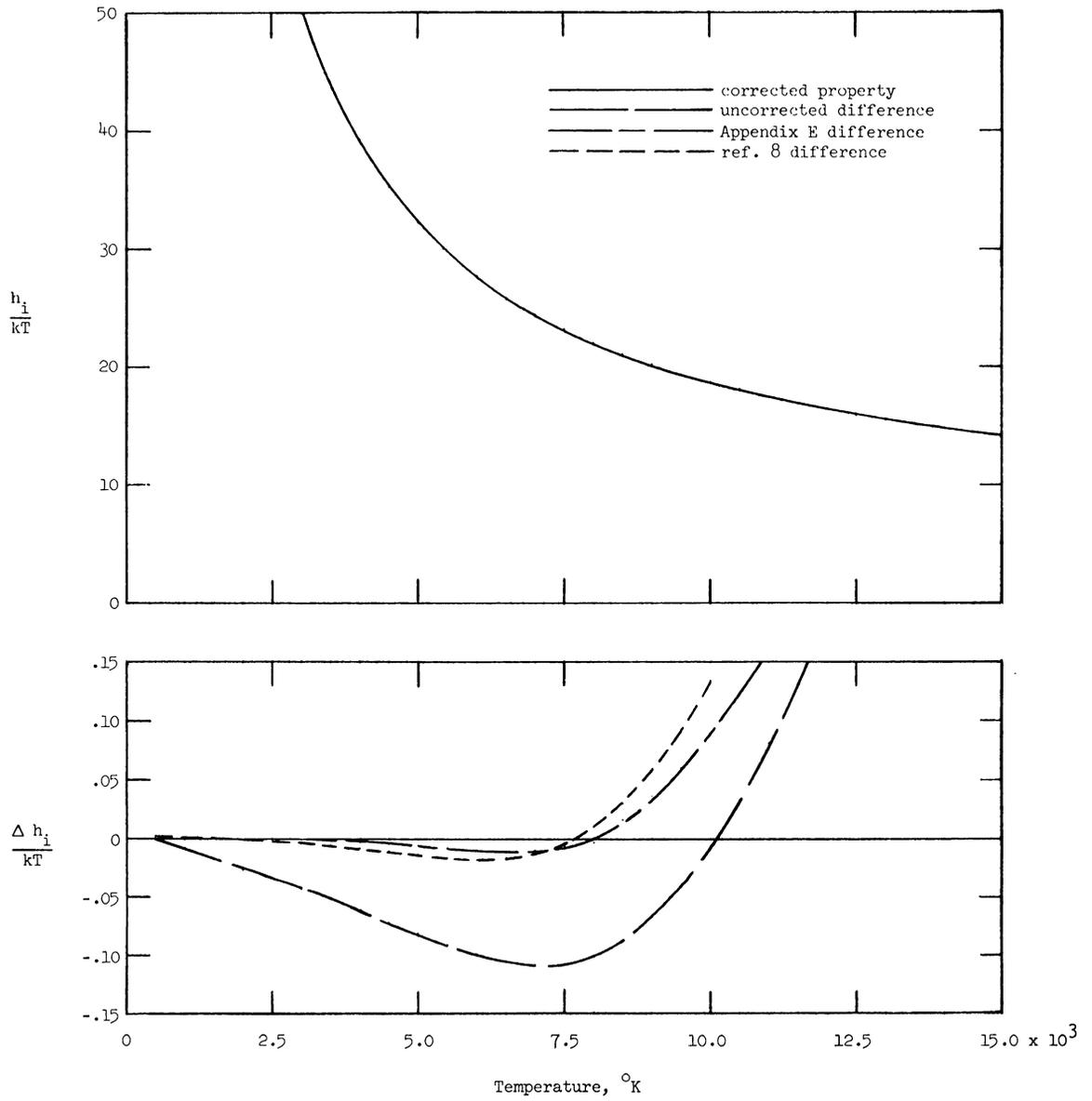


Figure 17.- Enthalpy of  $\text{O}_2^+$  and comparisons with other results.

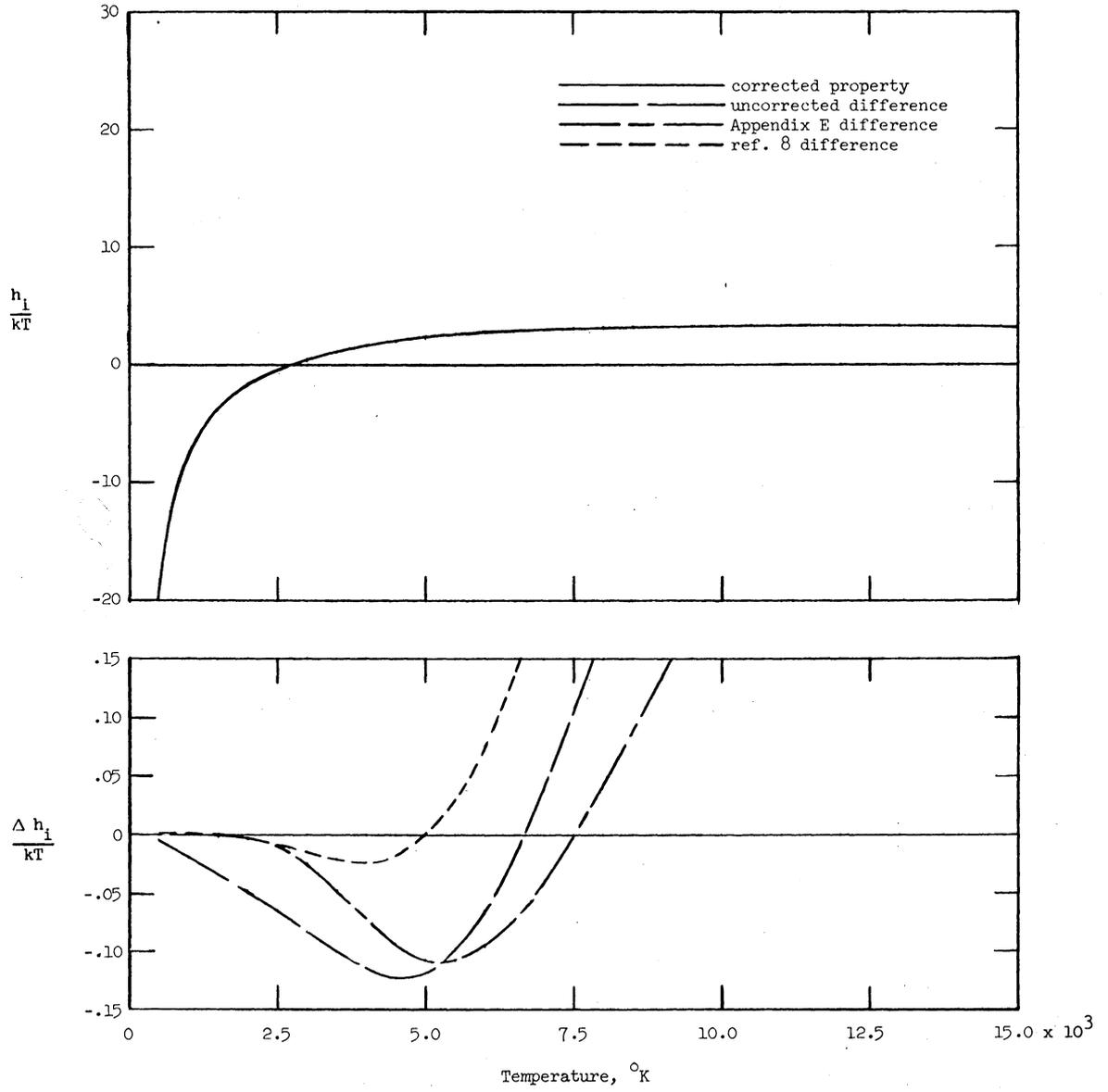


Figure 18.— Enthalpy of  $\text{O}_2^-$  and comparisons with other results.

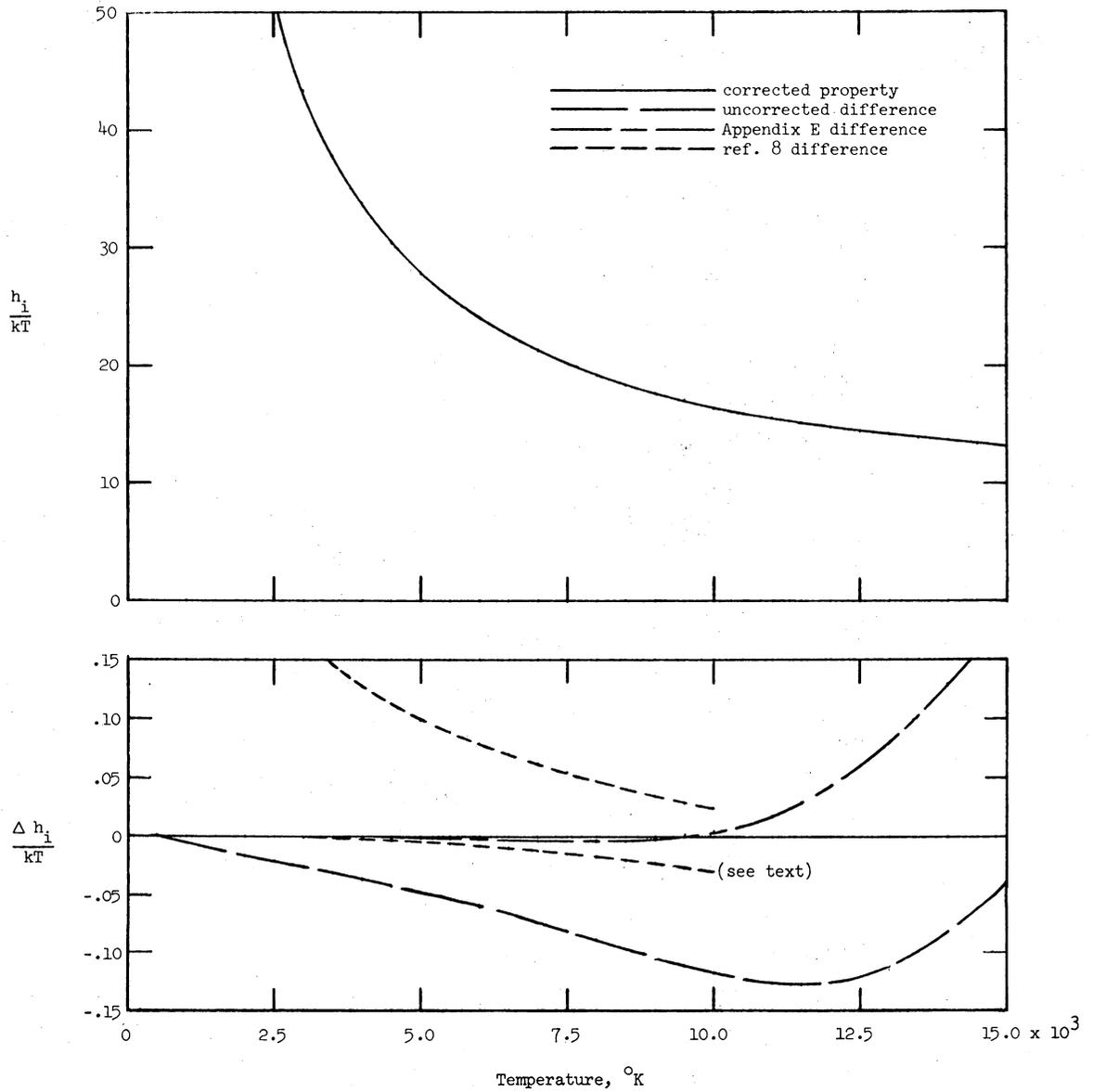


Figure 19.- Enthalpy of  $\text{NO}^+$  and comparisons with other results.

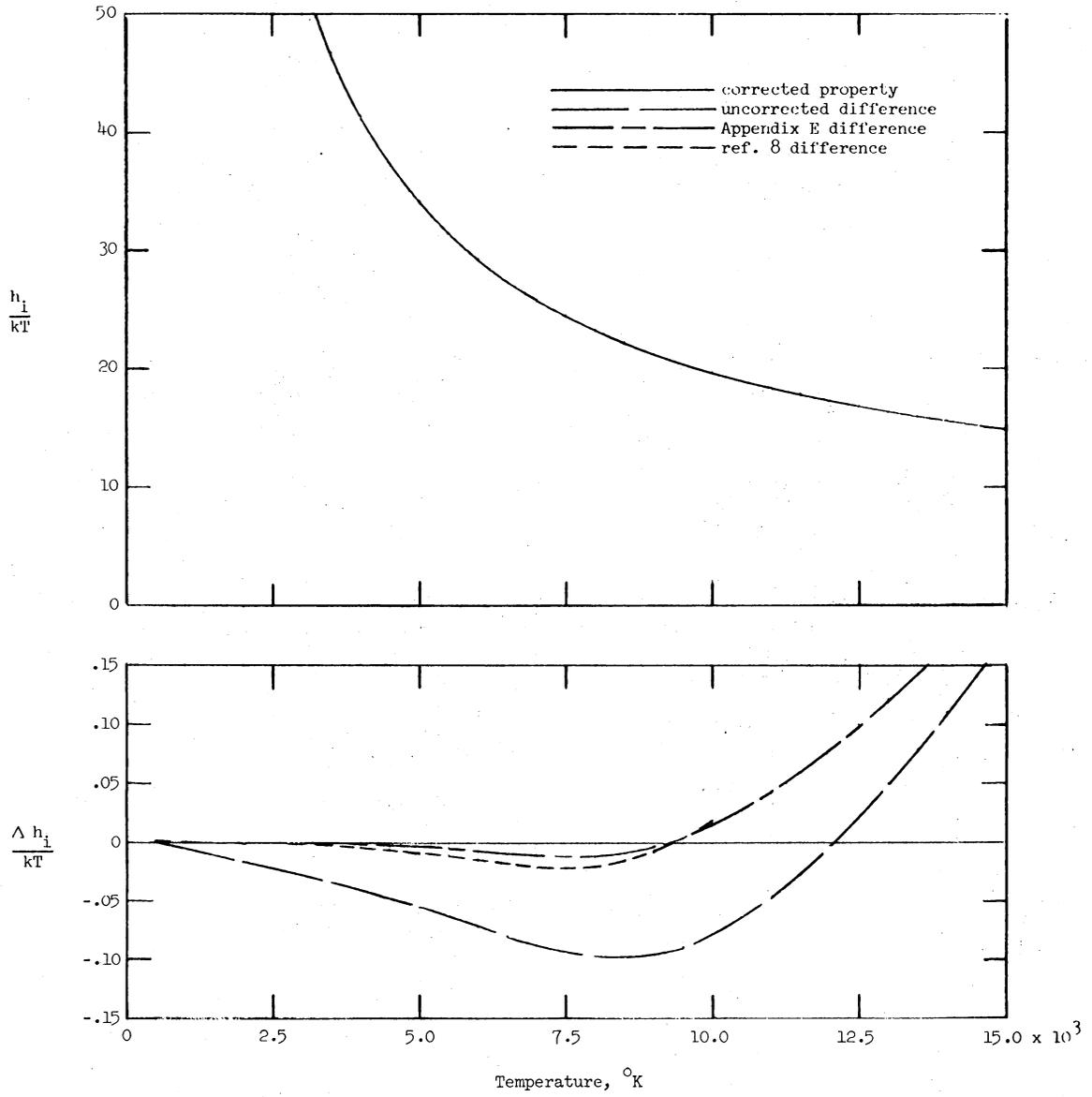


Figure 20.- Enthalpy of  $\text{CO}^+$  and comparisons with other results.

Figures 11 through 20 show that the uncorrected enthalpy difference is negative for most temperatures. The same comments that were made about the increase and decrease of the free-energy difference apply to the absolute value of the enthalpy difference. This difference is generally seen to be about 1 or 2 percent of the enthalpy itself.

As previously noted, appendix E describes an alternate partition function for diatomic species in which  $j$  is summed to infinity analytically, but  $v$  is still summed to  $v_{\max}$ . The difference based on this approximation is also given in figures 1 through 20. Large values of this difference occur only for temperatures at which a given species is usually dissociated. For lower temperatures this difference is very small, which indicates that the approximation in appendix E is useful for practical applications. However, in the present work, no mixture properties were computed in this manner.

W. G. Browne (refs. 8 and 9) computed thermodynamic properties of diatomic species based on the rigid-rotor, harmonic-oscillator model with corrections added to the properties. These corrections were based on partition functions in which both  $v$  and  $j$  were summed to infinity analytically. The difference between Browne's properties and the corrected properties is shown in figures 1 through 20. Since the spectroscopic and thermochemical constants for diatomic species in the present work (see appendix A) are the same as those used by Browne, this difference is due only to the different computational method. The present computational method is felt to be more accurate than that used by Browne, except where Browne used the virial coefficient formalism. In figure 5,

the discontinuity in the difference is believed to be caused by a change to the virial coefficient formalism at high temperatures in Browne's computations for CN (ref. 9). In reference 8, Browne did not use the virial coefficient formalism. The differences between Browne's results and the corrected results is very small for most species. Note, however, that there is a large difference between Browne's results and the corrected results for NO at low temperatures in figures 3 and 13. The difference between the present results and Gilmore's results (ref. 1) for NO in the range 1,000-3,000° K was found to be negligible when plotted in figures 3 and 13. Figures 9 and 19 for NO<sup>+</sup> show two difference curves due to Browne. The upper curve is from reference 8 data, while the lower curve is from the same data plus a correction on the heat of formation of NO<sup>+</sup> as given by Browne in reference 16.

#### Mixture Properties

Reciprocal molecular weight ratio, nondimensional enthalpy and entropy per unit mass, logarithm of density ratio, and logarithm of electron density are presented in figures 21 through 30 for air and a model atmosphere of Mars. The composition of air is the same as in references 1 and 2 except that neon has been omitted: 78.086 percent N<sub>2</sub>, 20.947 percent O<sub>2</sub>, 0.934 percent Ar, and 0.033 percent CO<sub>2</sub> by volume. The model atmosphere of Mars was proposed by Kaplan in July 1963:\* 25 percent N<sub>2</sub>,

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\*Communication from Jet Propulsion Laboratory to NASA, Langley Research Center containing preliminary conclusions based on observations later reported in reference 17.

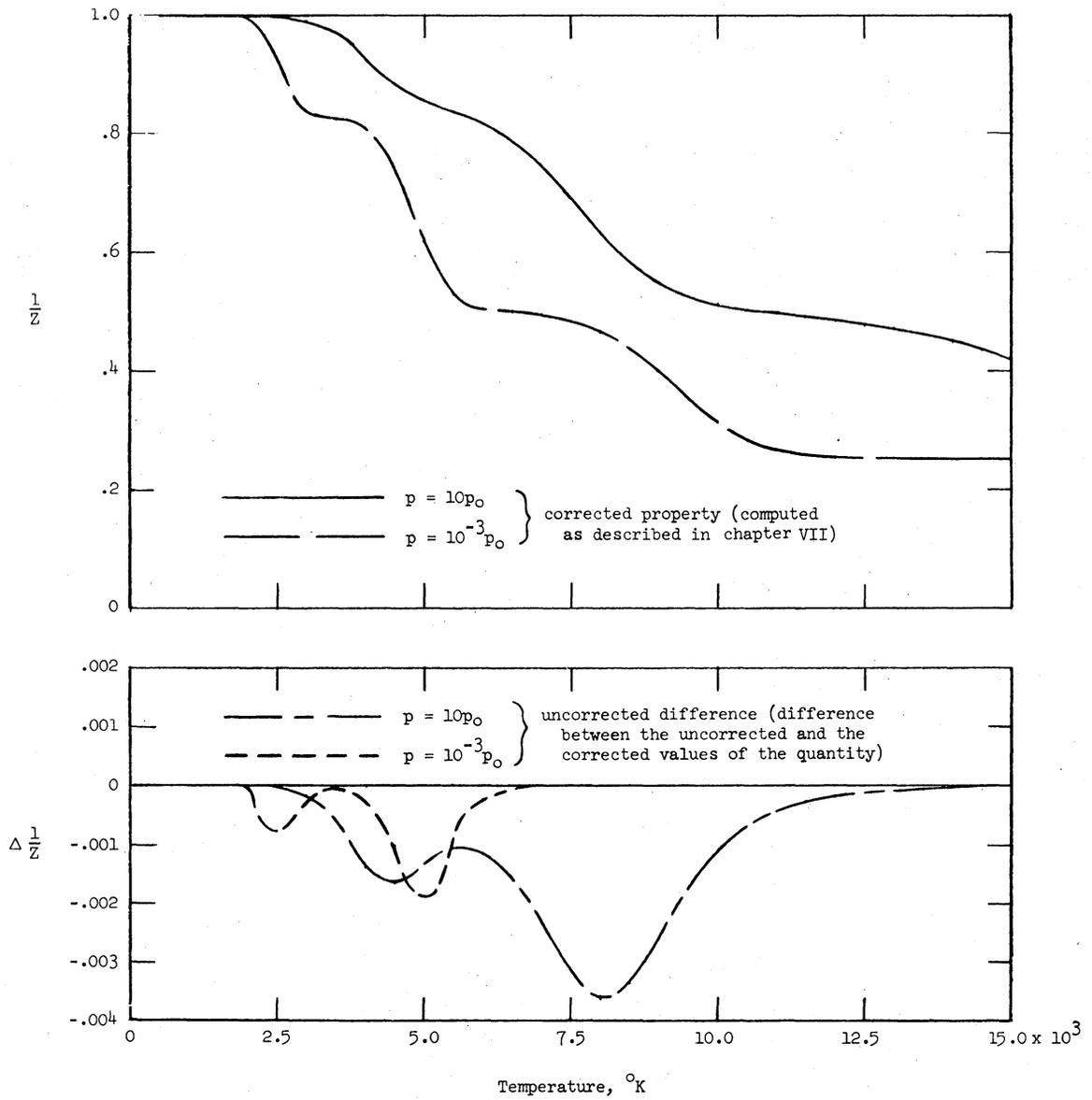


Figure 21.— Reciprocal molecular weight ratio of air.

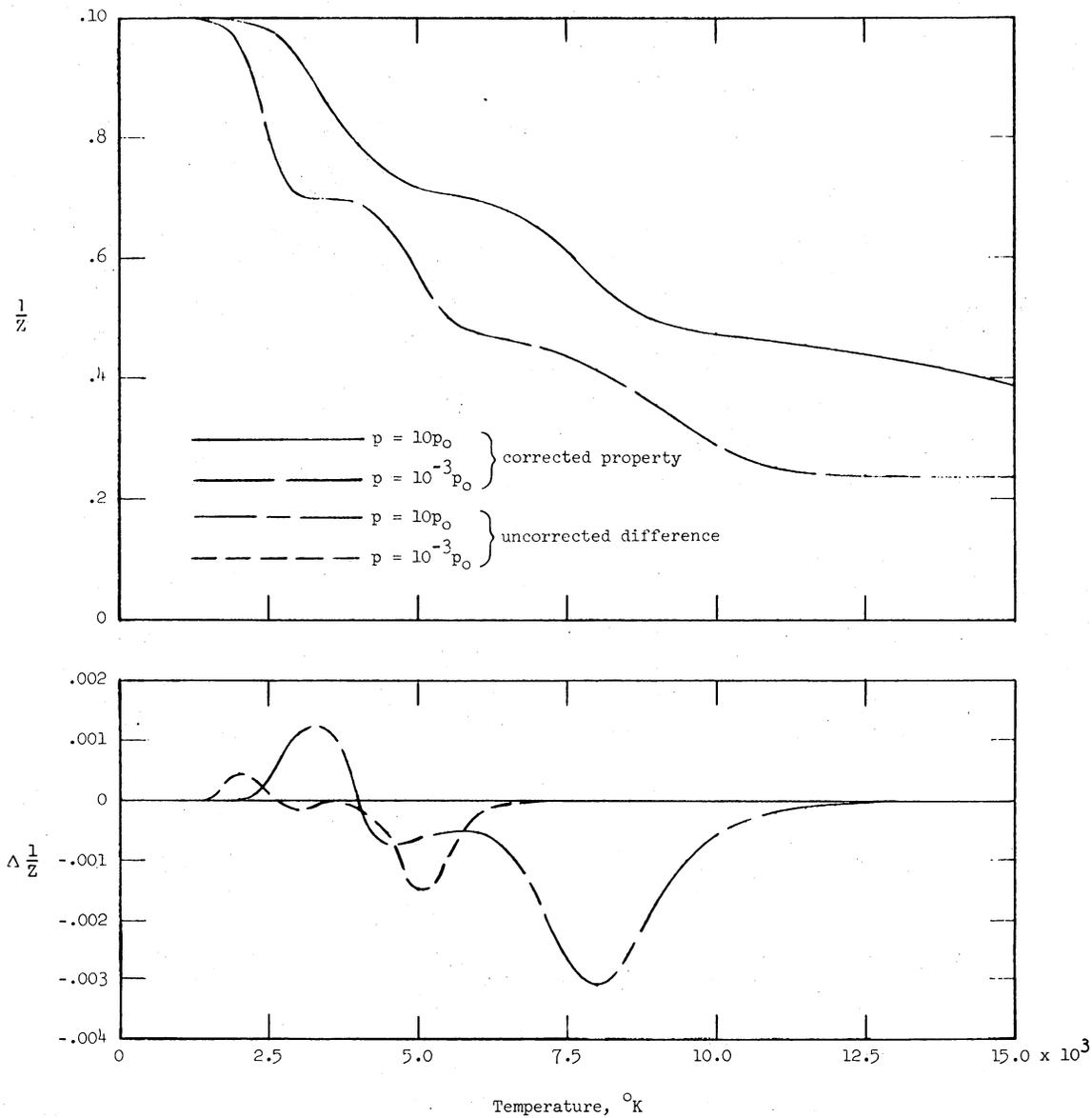


Figure 22.— Reciprocal molecular weight ratio of Mars model atmosphere.

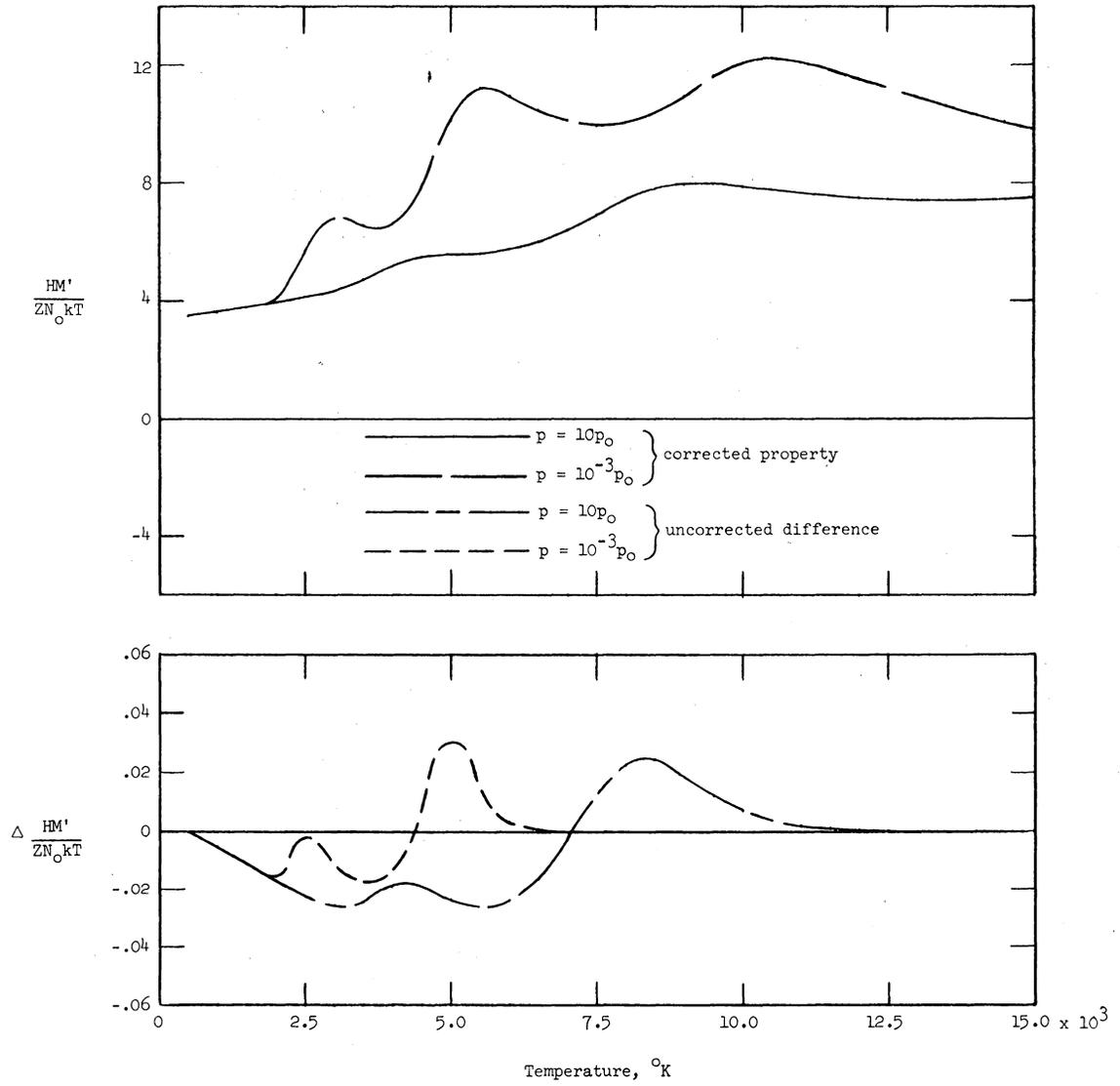


Figure 23.— Enthalpy of air.

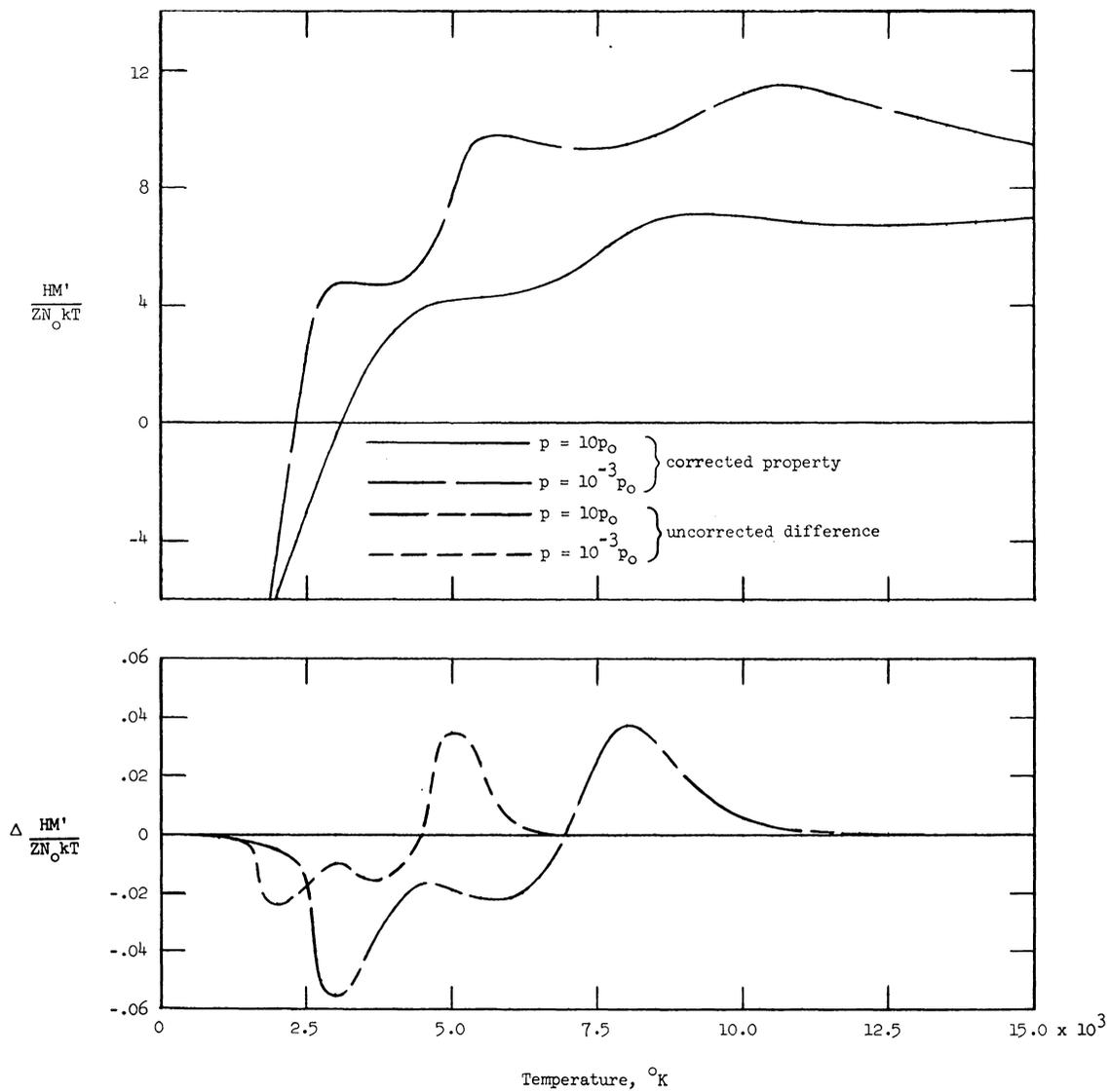


Figure 24.— Enthalpy of Mars model atmosphere.

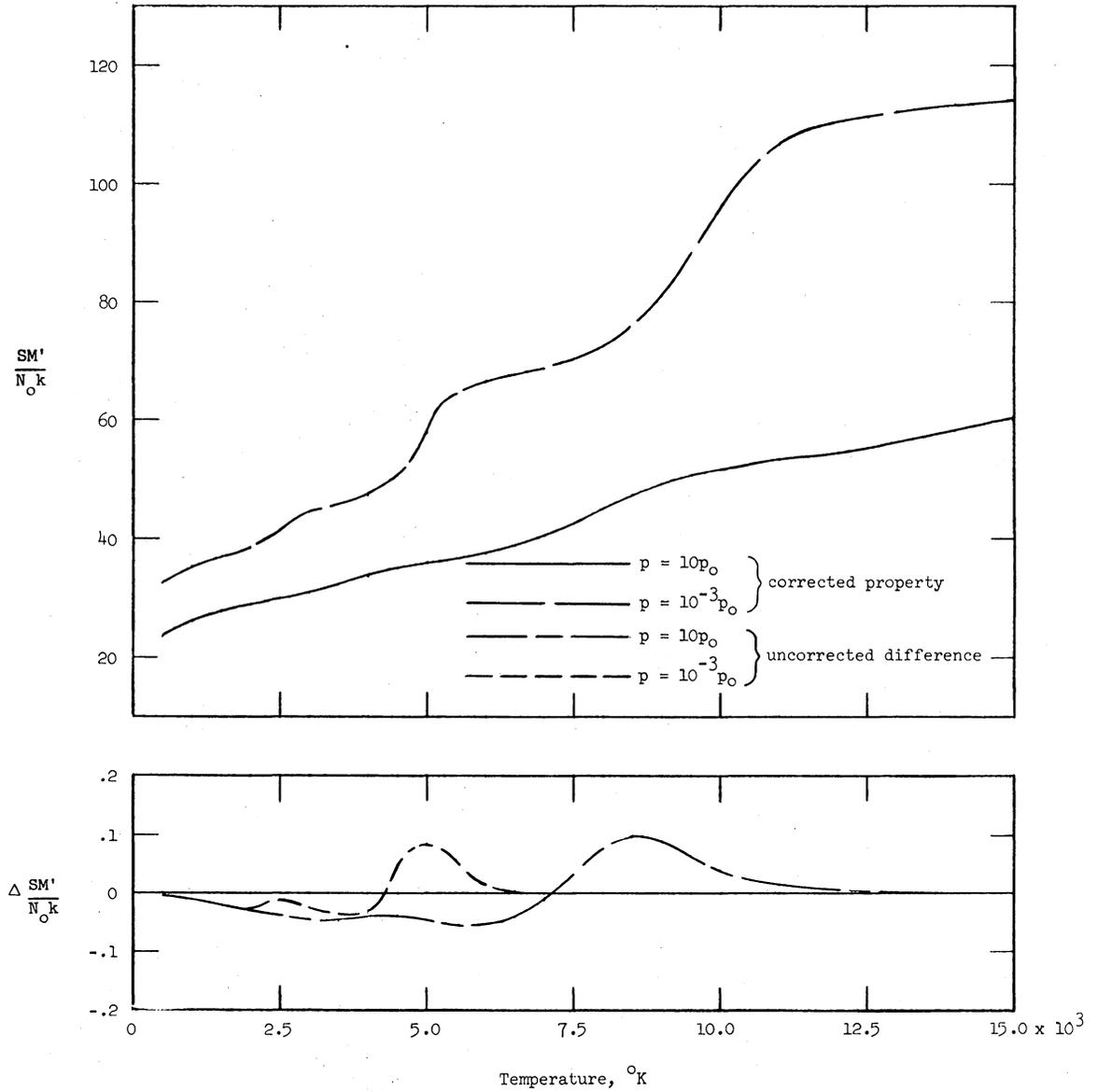


Figure 25.— Entropy of air.

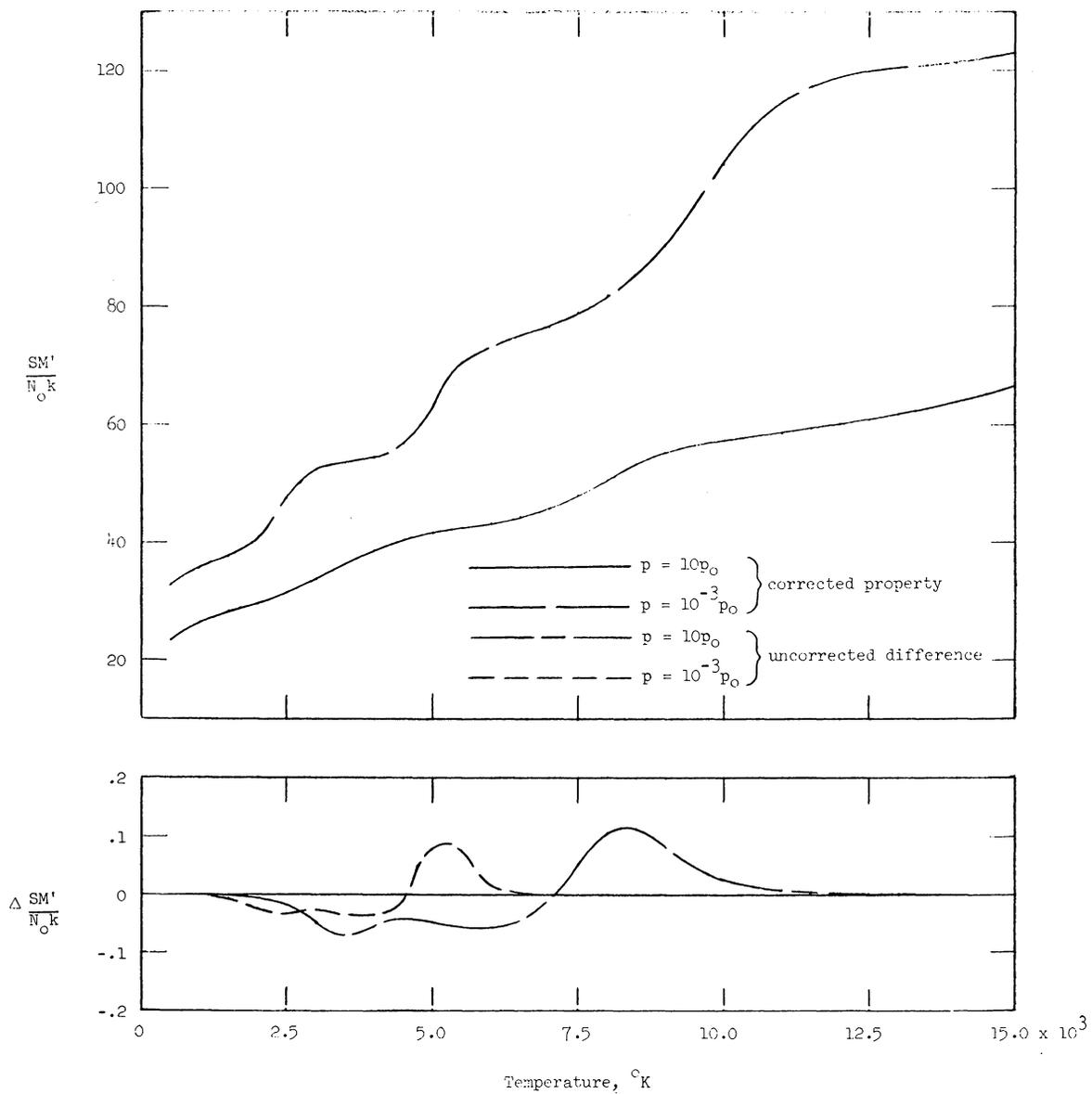


Figure 26.- Entropy of Mars model atmosphere.

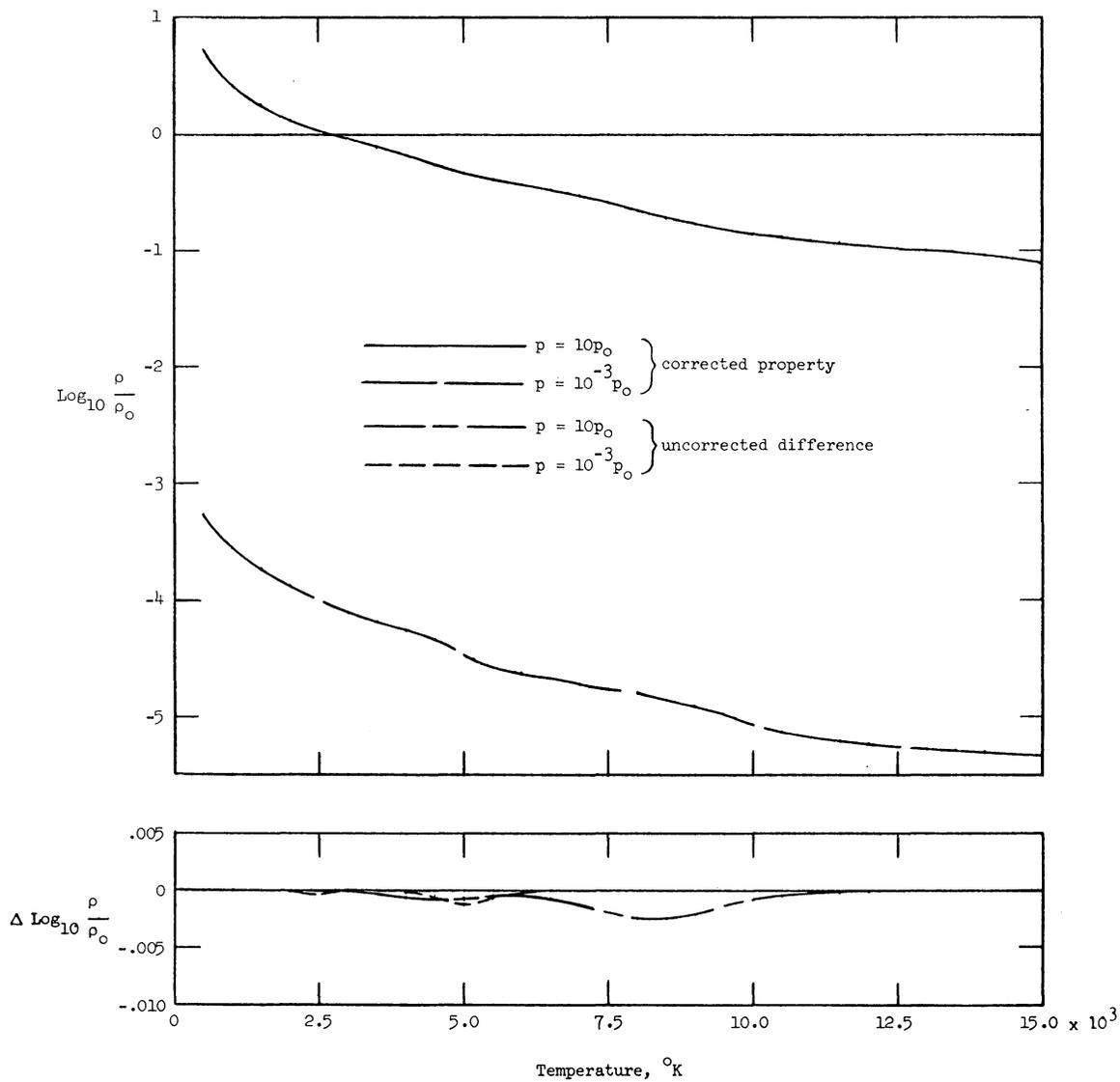


Figure 27.— Mass density of air.

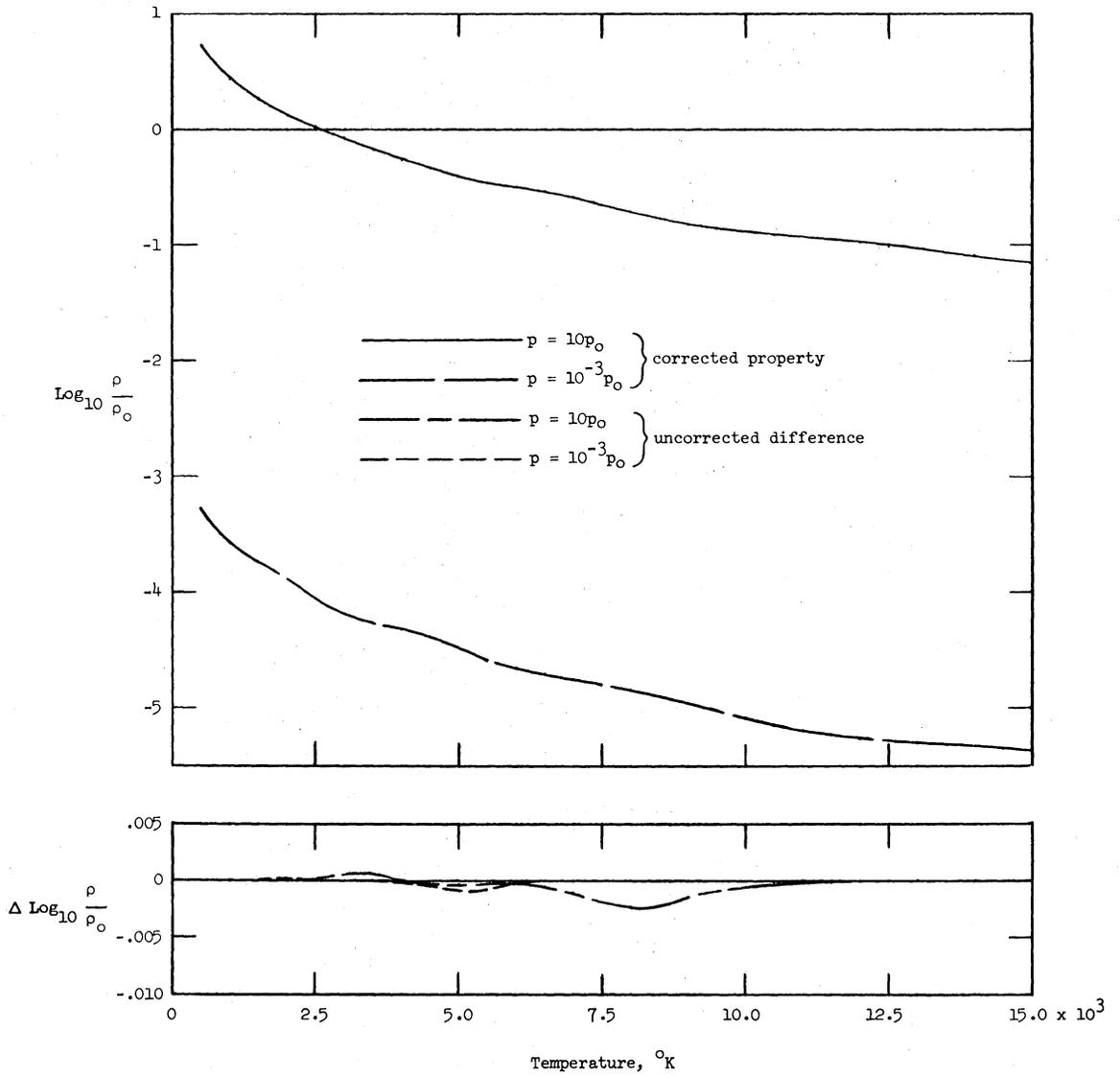


Figure 28.— Mass density of Mars model atmosphere.

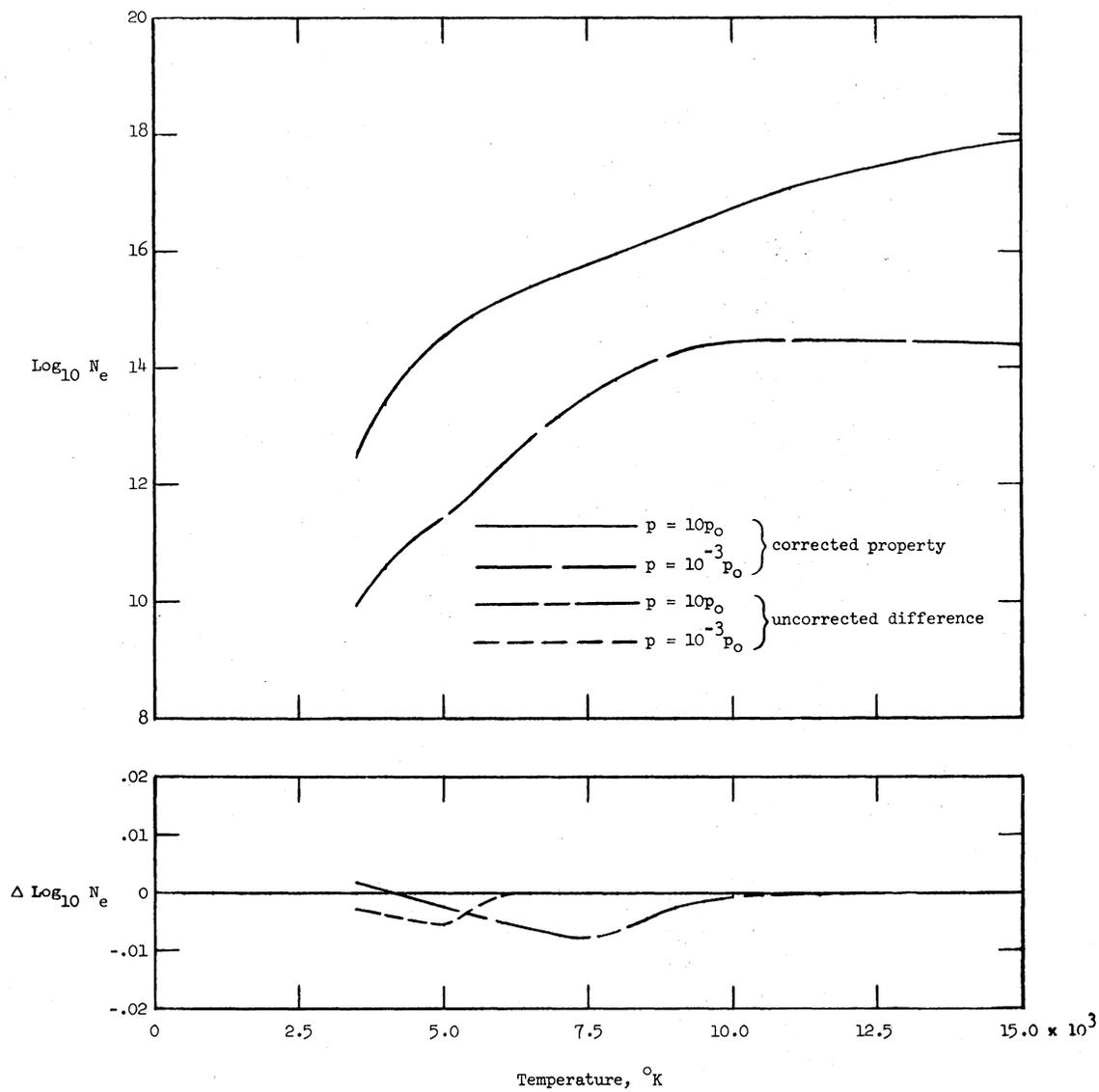


Figure 29.— Electron density of air.

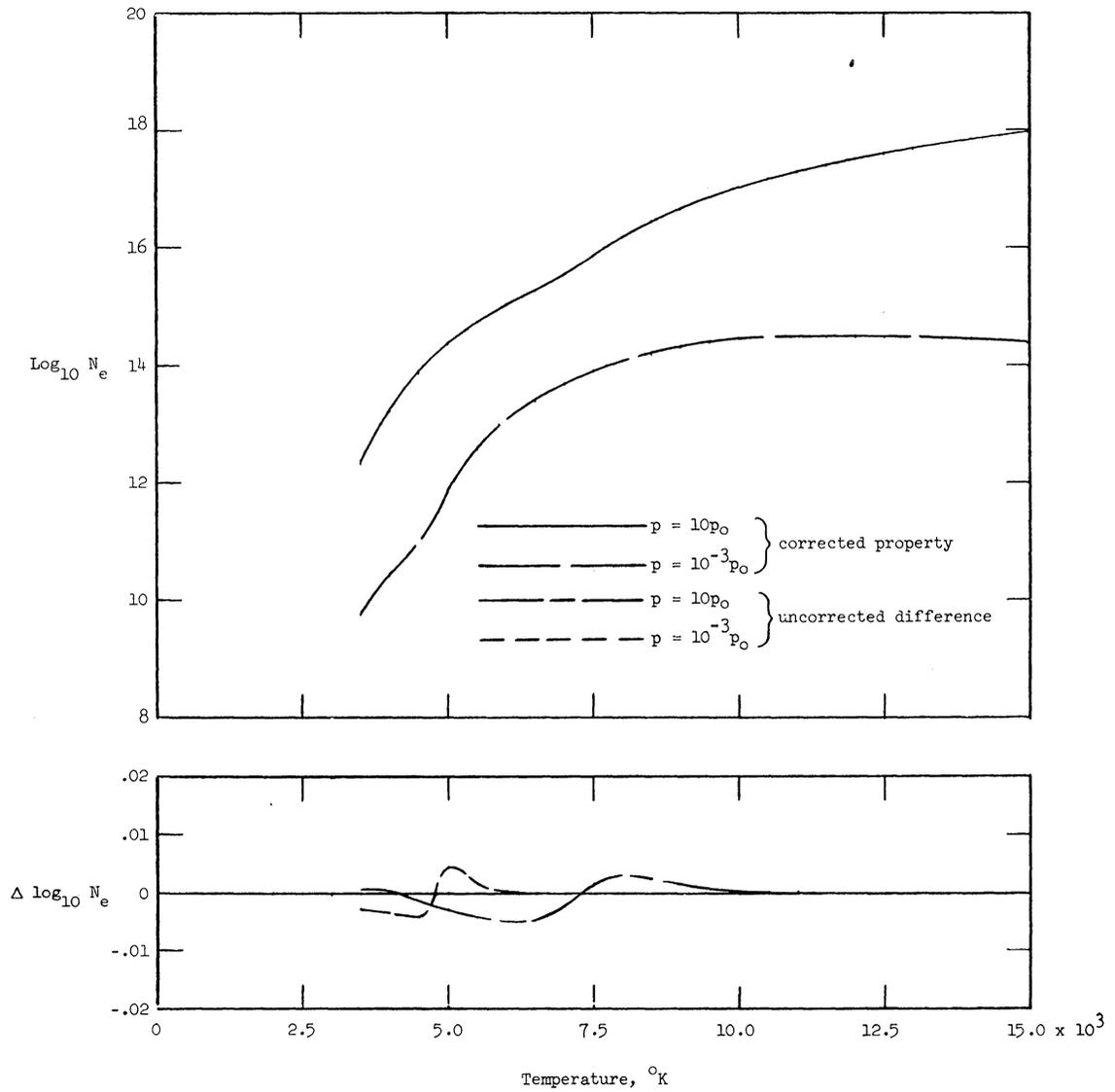


Figure 30.— Electron density of Mars model atmosphere.

32 percent Ar, and 43 percent CO<sub>2</sub> by volume. Results are presented for temperatures up to 15,000° K for two representative pressures. The only difference shown for the mixtures is the uncorrected property difference.

Figures 21 and 22 present reciprocal molecular weight ratio. Eq. (40) shows that  $1/Z$  is equal to the number of particles of original mixture divided by the number of particles of equilibrium mixture. Thus,  $1/Z$  measures the amount of dissociation that has taken place in the equilibrium gas mixture. The shape of each of the  $1/Z$  curves reveals some information about certain dissociation processes, especially for the low pressure  $p = 10^{-3} p_0$ . If all the O<sub>2</sub> in the air were dissociated, for every 100 particles of original air there would be approximately 121 particles consisting of 78 of N<sub>2</sub>,  $2 \times 21 = 42$  of O, and 1 of Ar. Then  $1/Z$  would be equal to  $100/121$  or 0.83. Notice that, for  $p = 10^{-3} p_0$  in figure 21,  $1/Z$  decreases rapidly, then levels off at  $1/Z \approx 0.83$ . This rapid decrease between 2,000° K and 3,000° K is caused primarily by dissociation of O<sub>2</sub>. The level part between 3,000° K and 4,000° K indicates little further dissociation. Between 4,000° K and 6,000° K most of the N<sub>2</sub> dissociates. At about 6,500° K,  $1/Z = 0.50$  indicating that the air is composed almost entirely of atoms. When  $1/Z = 0.25$ , singly ionized atoms and electrons predominate. In order to illustrate the above comments, the mass fractions,  $N_i M_i / \sum N_i M_i$ , of all major species are presented in table 1 for air at temperatures corresponding to  $1/Z \approx 1, 0.83, 0.50,$  and  $0.25$  for both pressures. In the model atmosphere of Mars, first CO<sub>2</sub> dissociates into CO and O ( $1/Z = 0.70$ ), next N<sub>2</sub> and CO dissociate to N, C, and O ( $1/Z = 0.47$ ), and finally the mixture ionizes

TABLE 1.- MASS FRACTIONS FOR AIR,  $N_i M_i / \sum N_i M_i$

Species	$p = 10^{-3} p_0$			
	T = 1,000	T = 3,500	T = 6,500	T = 15,000
e <sup>-</sup>	< 10 <sup>-10</sup>	0.00001 × 10 <sup>-5</sup>	0.01971 × 10 <sup>-5</sup>	3.7723 × 10 <sup>-5</sup>
N	< 10 <sup>-5</sup>	0.00327	0.74684	0.00092
N <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00385	0.75242
N <sup>++</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00182
O	< 10 <sup>-5</sup>	0.22853	0.23047	0.00049
O <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00123	0.23123
O <sup>++</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00003
O <sup>-</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
C	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00009	< 10 <sup>-5</sup>
C <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00005	0.00013
C <sup>++</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00001
C <sup>-</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
Ar	0.01288	0.01288	0.01286	0.00001
Ar <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00002	0.01247
Ar <sup>++</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00039
N <sub>2</sub>	0.75521	0.74985	0.00448	< 10 <sup>-5</sup>
N <sub>2</sub> <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
O <sub>2</sub>	0.23138	0.00065	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
O <sub>2</sub> <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
O <sub>2</sub> <sup>-</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
NO	0.00004	0.00450	0.00002	< 10 <sup>-5</sup>
NO <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00009	< 10 <sup>-5</sup>
CO	< 10 <sup>-5</sup>	0.00032	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
CO <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
CN	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
CO <sub>2</sub>	0.00050	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>

TABLE 1.- MASS FRACTIONS FOR AIR,  $N_i M_i / NM$  - Concluded

Species	p = 10 p <sub>0</sub>			
	T = 1,000	T = 6,000	T = 10,500	T = 15,000
e <sup>-</sup>	< 10 <sup>-10</sup>	0.00029 × 10 <sup>-5</sup>	0.04489 × 10 <sup>-5</sup>	0.71067 × 10 <sup>-5</sup>
N	< 10 <sup>-5</sup>	0.03415	0.71458	0.60049
N <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00940	0.15411
N <sup>++</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
O	< 10 <sup>-5</sup>	0.20947	0.22886	0.20188
O <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00187	0.02976
O <sup>++</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
O <sup>-</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00001	0.00003
C	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00012	0.00007
C <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00002	0.00007
C <sup>++</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
C <sup>-</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
Ar	0.01288	0.01288	0.01275	0.00957
Ar <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00013	0.00331
Ar <sup>++</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
N <sub>2</sub>	0.75521	0.70466	0.03013	0.00041
N <sub>2</sub> <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00025	0.00012
O <sub>2</sub>	0.23138	0.00337	0.00003	< 10 <sup>-5</sup>
O <sub>2</sub> <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
O <sub>2</sub> <sup>-</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
NO	0.00004	0.03500	0.00133	0.00006
NO <sup>+</sup>	< 10 <sup>-5</sup>	0.00016	0.00054	0.00012
CO	< 10 <sup>-5</sup>	0.00032	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
CO <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
CN	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
CO <sub>2</sub>	0.00050	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>

TABLE 2.- MASS FRACTIONS FOR MARS MODEL ATMOSPHERE,  $N_i M_i / \text{NM}$

Species	$p = 10^{-3} p_0$			
	T = 1,000	T = 3,500	T = 6,000	T = 14,000
e <sup>-</sup>	< 10 <sup>-10</sup>	0.00001 × 10 <sup>-5</sup>	0.02651 × 10 <sup>-5</sup>	2.9872 × 10 <sup>-5</sup>
N	< 10 <sup>-5</sup>	0.00150	0.17933	0.00057
N <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00005	0.18028
N <sup>++</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00007
O	< 10 <sup>-5</sup>	0.17626	0.34806	0.00194
O <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00012	0.35349
O <sup>++</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00001
O <sup>-</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
C	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.12229	0.00009
C <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00565	0.13217
C <sup>++</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00115
C <sup>-</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
Ar	0.33019	0.33019	0.33017	0.00084
Ar <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00002	0.32749
Ar <sup>++</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00185
N <sub>2</sub>	0.18093	0.17859	0.00151	< 10 <sup>-5</sup>
N <sub>2</sub> <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
O <sub>2</sub>	< 10 <sup>-5</sup>	0.00044	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
O <sub>2</sub> <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
O <sub>2</sub> <sup>-</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
NO	< 10 <sup>-5</sup>	0.00180	0.00002	< 10 <sup>-5</sup>
NO <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00001	< 10 <sup>-5</sup>
CO	< 10 <sup>-5</sup>	0.31103	0.01270	< 10 <sup>-5</sup>
CO <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00001	< 10 <sup>-5</sup>
CN	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00004	< 10 <sup>-5</sup>
CO <sub>2</sub>	0.48887	0.00018	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>

TABLE 2.- MASS FRACTIONS FOR MARS MODEL ATMOSPHERE,  
 $N_i M_i / NM$  - Concluded

Species	p = 10 p <sub>0</sub>			
	T = 1,000	T = 6,000	T = 10,000	T = 15,000
e <sup>-</sup>	< 10 <sup>-10</sup>	0.00017 × 10 <sup>-5</sup>	0.04118 × 10 <sup>-5</sup>	0.66109 × 10 <sup>-5</sup>
N	< 10 <sup>-5</sup>	0.01521	0.17491	0.14765
N <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00080	0.03320
N <sup>++</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
O	< 10 <sup>-5</sup>	0.16797	0.34515	0.31465
O <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00102	0.04063
O <sup>++</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
O <sup>-</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00003	0.00006
C	< 10 <sup>-5</sup>	0.00042	0.11940	0.07064
C <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00713	0.06271
C <sup>++</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
C <sup>-</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00001	0.00001
Ar	0.33019	0.33019	0.32911	0.25337
Ar <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00108	0.07682
Ar <sup>++</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
N <sub>2</sub>	0.18093	0.15894	0.00417	0.00003
N <sub>2</sub> <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00001	0.00001
O <sub>2</sub>	< 10 <sup>-5</sup>	0.00247	0.00011	0.00001
O <sub>2</sub> <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00001
O <sub>2</sub> <sup>-</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>
NO	< 10 <sup>-5</sup>	0.01422	0.00093	0.00003
NO <sup>+</sup>	< 10 <sup>-5</sup>	0.00009	0.00017	0.00005
CO	< 10 <sup>-5</sup>	0.30937	0.01486	0.00007
CO <sup>+</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	0.00014	0.00003
CN	< 10 <sup>-5</sup>	0.00019	0.00098	0.00002
CO <sub>2</sub>	0.48887	0.00092	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>

to  $N^+$ ,  $C^+$ ,  $O^+$ , and  $Ar^+$  ( $1/Z = 0.24$ ). Table 2 presents mass fractions of all major species for the Mars model atmosphere at temperatures corresponding to the above  $1/Z$  values for both pressures.

Figures 21 and 22 show that the uncorrected  $1/Z$  difference is greatest for temperatures at which dissociation processes are occurring. In figures 23 through 30, the peaks and dips in the uncorrected differences for other properties occur at these same temperatures. This means that these mixture property differences are caused mainly by different amounts of dissociation. In general, the mixture property differences are less than 1/2 percent of the corresponding properties.

#### Comparison with Existing Results

The results in tables 3 through 6 are for air at various temperatures and two representative densities. Since the present work requires temperature and pressure (not density) as inputs, the data in tables 3 through 6 were generated by inputting the pressures computed by Browne (or Gilmore). Tables 3 through 6 compare corrected properties with Browne (ref. 2) and Gilmore (ref. 1). The fact that the present corrected results agree better with Browne than with Gilmore is due to the use of atomic and molecular constants which agree well with those used in the more recent work of Browne. Below about  $10,000^{\circ}$  K, the differences between the present work and Browne's results are primarily due to the different treatment of the vibration-rotation partition function  $Q_{vib,rot}$  for diatomic species. Except for the highest densities, diatomic species dissociate below about  $10,000^{\circ}$  K and thus do not contribute to mixture

TABLE 3.- COMPARISON RESULTS FOR RECIPROCAL MOLECULAR WEIGHT RATIO,  $1/Z$

T, °K	$\rho = \rho_0$				$\rho = 10^{-3} \rho_0$			
	Uncorrected	Corrected	Ref. 2	Ref. 1	Uncorrected	Corrected	Ref. 2	Ref. 1
1,000	1.00000	1.00000	---	1.0000	1.00000	1.00000	---	1.0000
2,000	.99994	.99994	---	1.0000	.99822	.99824	---	.9983
3,000	.99268	.99281	0.99285	.9929	.88062	.88161	0.88168	.8818
4,000	.93946	.94068	.94082	.9409	.82578	.82595	.82604	.8260
5,000	.87173	.87338	.87329	.8735	.76321	.76422	.76418	.7645
6,000	.83307	.83443	.83452	.8344	.59852	.60079	.60067	.6009
7,000	.78516	.78715	.78715	.7875	.51513	.51581	.51578	.5159
8,000	.71099	.71440	.71423	.7142	.49944	.49957	.49960	.4998
10,000	.56532	.56904	.56857	---	.46274	.46275	.46292	---
12,000	.50971	.51105	.51041	.5110	.37816	.37816	.37847	.3794
15,000	.47734	.47758	.47765	---	.27861	.27861	.27872	---
18,000	.43746	.43752	.43771	.4378	.25576	.25576	.25578	.2558
21,000	.39112	.39113	.39151	---	.25097	.25097	.25098	---
24,000	.35006	.35006	.35078	.3490	.24168	.24168	.24170	.2414

TABLE 4.- COMPARISON RESULTS FOR ENTHALPY,  $HM'/ZN_0kT$

T, °K	$\rho = \rho_0$				$\rho = 10^{-3} \rho_0$			
	Uncorrected	Corrected	Ref. 2	Ref. 1	Uncorrected	Corrected	Ref. 2	Ref. 1
1,000	3.6248	3.6305	---	3.630	3.6248	3.6305	---	3.630
2,000	3.9438	3.9607	---	3.962	3.9897	4.0061	---	4.007
3,000	4.3448	4.3708	4.3724	4.371	6.1247	6.1285	6.1273	6.127
4,000	5.0664	5.0879	5.0867	5.088	6.2416	6.2607	6.2592	6.263
5,000	5.4665	5.4905	5.4898	5.488	7.0627	7.0642	7.0629	7.061
6,000	5.5683	5.5964	5.5932	5.591	9.3740	9.3452	9.3458	9.346
7,000	5.9182	5.9361	5.9335	5.932	9.7463	9.7383	9.7384	9.744
8,000	6.5392	6.5351	6.5342	6.531	9.1941	9.1929	9.1922	9.196
10,000	7.3807	7.3599	7.3650	---	8.8180	8.8179	8.8147	---
12,000	7.2244	7.2178	7.2254	7.224	9.4070	9.4070	9.4036	9.399
15,000	6.8395	6.8386	6.8410	---	9.4986	9.4986	9.5006	---
18,000	6.7477	6.7475	6.7568	6.709	8.6410	8.6410	8.6439	8.650
21,000	6.7565	6.7563	6.7790	---	7.8908	7.8908	7.8932	---
24,000	6.6931	6.6930	6.7261	6.616	7.5887	7.5888	7.5901	7.609

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TABLE 5.- COMPARISON RESULTS FOR ENTROPY,  $SM'/N_0k$

T, °K	$\rho = \rho_0$				$\rho = 10^{-3} \rho_0$			
	Uncorrected	Corrected	Ref. 2	Ref. 1	Uncorrected	Corrected	Ref. 2	Ref. 1
1,000	27.024	27.034	---	26.83	33.932	33.942	---	33.74
2,000	29.262	29.291	---	29.29	36.225	36.253	---	36.26
3,000	30.951	30.998	31.000	30.98	40.656	40.669	40.666	40.65
4,000	33.000	33.043	33.042	33.03	43.003	43.045	43.041	43.05
5,000	34.860	34.907	34.906	34.91	46.115	46.128	46.125	46.11
6,000	36.186	36.244	36.238	36.25	54.107	54.013	54.016	54.00
7,000	37.862	37.904	37.898	37.88	59.556	59.518	59.519	59.51
8,000	40.320	40.307	40.305	40.32	61.219	61.213	61.209	61.20
10,000	45.958	45.856	45.872	---	65.341	65.340	65.324	---
12,000	49.050	49.005	49.034	49.00	74.163	74.163	74.128	74.03
15,000	51.789	51.781	51.783	---	88.438	88.438	88.422	---
18,000	54.990	54.988	55.003	54.88	93.399	93.399	93.398	93.38
21,000	58.710	58.709	58.755	---	95.394	95.394	95.395	---
24,000	62.328	62.328	62.396	62.09	98.812	98.812	98.809	98.93

TABLE 6.- COMPARISON RESULTS FOR ELECTRON DENSITY,  $N_e$

T, °K	$\rho = \rho_0$				$\rho = 10^{-3} \rho_0$			
	Uncorrected	Corrected	Ref. 2	Ref. 1	Uncorrected	Corrected	Ref. 2	Ref. 1
1,000	---	---	---	---	---	---	---	---
2,000	---	---	---	---	---	---	---	---
3,000	0.1843 +12	0.1830 +12	0.1802 +12	0.195 +12	0.5584 +10	0.5591 +10	0.5571 +10	0.605 +10
4,000	.3055 +14	.3047 +14	.3038 +14	.328 +14	.3406 +12	.3431 +12	.3424 +12	.369 +12
5,000	.5203 +15	.5226 +15	.5216 +15	.562 +15	.3633 +13	.3676 +13	.3672 +13	.396 +13
6,000	.2987 +16	.3018 +16	.3011 +16	.324 +16	.1875 +14	.1900 +14	.1893 +14	.198 +14
7,000	.1005 +17	.1020 +17	.1021 +17	.109 +17	.1085 +15	.1087 +15	.1080 +15	.108 +15
8,000	.2608 +17	.2657 +17	.2645 +17	.280 +17	.5139 +15	.5140 +15	.5110 +15	.503 +15
10,000	.1526 +18	.1538 +18	.1532 +18	---	.4581 +16	.4581 +16	.4562 +16	---
12,000	.6732 +18	.6744 +18	.6727 +18	.669 +18	.1755 +17	.1755 +17	.1751 +17	.173 +17
15,000	.3020 +19	.3021 +19	.3015 +19	---	.4295 +17	.4295 +17	.4294 +17	---
18,000	.7987 +19	.7988 +19	.7971 +19	.795 +19	.5158 +17	.5158 +17	.5159 +17	.516 +17
21,000	.1522 +20	.1522 +20	.1518 +20	---	.5359 +17	.5359 +17	.5360 +17	---
24,000	.2324 +20	.2324 +20	.2313 +20	.235 +20	.5771 +17	.5771 +17	.5771 +17	.579 +17

NOTE: 0.1843 +12 means  $0.1843 \times 10^{12}$ , etc.

properties at higher temperatures. Above about  $10,000^{\circ}$  K, the differences between the present work and Browne's results are primarily due to the different electronic energy level data used in the partition functions for atoms and atomic ions (see appendix B). Browne (ref. 2) included all energy levels up to and beyond the ionization limit as tabled in Moore (ref. 18).

In table 6, electron density  $N_e$  is given rather than  $\log_{10} N_e$ . A comparison of the uncorrected and corrected values of  $N_e$  shows that this difference is almost 2 percent in some cases. Electron density is sensitive to the corrections because it depends on the concentrations of all the ionized species in the mixture. There is a need for accurate values of  $N_e$  since radio transmission through a hot gas (such as that surrounding an entry vehicle) can be greatly attenuated by electron density. The difference between the present corrected value of  $N_e$  and Browne's (ref. 2) is greater than 0.5 percent in some cases.

## IX. CONCLUSIONS

As would be expected, the sensitivity of different diatomic species to the correction terms in the vibrational-rotational energy is not the same. The following conclusions concerning diatomic species properties are based on discussions in chapter VIII. These conclusions hold only for temperatures up to that for which a given diatomic species is almost completely dissociated in a mixture of ideal gases. For example, at  $p = 10 p_0$ ,  $O_2$  is almost completely dissociated at  $6,000^\circ K$  whereas for  $N_2$  this occurs at  $11,000^\circ K$ .

1. In general, the correction terms changed the free energy of a diatomic species up to about 0.3 percent from its rigid-rotor, harmonic-oscillator value. The enthalpy of a diatomic species is generally changed up to about 2 percent from its rigid-rotor, harmonic-oscillator value when the correction terms are considered.

2. Comparisons of the present corrected diatomic species results with those of Browne (refs. 8 and 9) indicated differences which were about 1/10 the size of those quoted above in conclusion 1.

3. In applications where computer time is an important consideration, the method used by Browne (refs. 8 and 9) for diatomic species is recommended instead of the present corrected method in view of conclusion 2.

4. The compromise method for diatomic species described in appendix E gives accuracy for mixture properties comparable to that of the present corrected method. Furthermore, the required computer time should be comparable to that of the method used by Browne.

The remaining conclusions apply to mixtures of ideal gases and are based on the mixture results as discussed in chapter VIII.

5. The molecular weight ratio, enthalpy, and entropy of the mixtures were generally changed by less than 1/2 percent by considering the correction terms for the diatomic species. Electron density, however, was changed by about 2 percent in some cases when the correction terms for the diatomic species were considered.

6. The effect of the corrections on the mixture was to shift the amount of dissociation at a given temperature and pressure. This shift was the primary cause of changes in the mixture properties.

7. Comparison of the present corrected mixture properties with the results of Browne (ref. 2) and Gilmore (ref. 1) shows agreement to within a few tenths of a percent except for electron density.

8. The present corrected electron density agrees with that of Browne (ref. 2) to about 1/2 percent. The 1.5 percent difference at  $p = p_0$  and  $T = 3,000^\circ \text{K}$  (see table 6) appears to be caused by numerical round-off error in the electron concentration variable  $N_1$  (see appendix D) which is very small for high-density, low-temperature conditions. The electron density of Gilmore (ref. 1) disagrees with both the present corrected results and those of Browne (ref. 2) by as much as 8 percent in some cases.

In view of the two mixtures considered, it appears that the corrections change the properties of a mixture by only a few percent. For many practical applications, this small difference is considered unimportant and the additional computer time required by the corrections is unwarranted.



XI. REFERENCES

1. Gilmore, F. R.: Equilibrium Composition and Thermodynamic Properties of Air to 24,000° K. RM-1543, The Rand Corporation, Aug. 24, 1955.
2. Browne, W. G.: Thermodynamic Properties of the Earth's Atmosphere. Radiation and Space Phys. Tech. Memo. No. 2, MSD, General Electric, Nov. 15, 1962.
3. Denton, Jesse C.: Thermodynamic Properties of Air Including Interparticle Electrostatic Contributions. Ph. D. Dissertation, Texas A and M University, 1963.
4. Browne, W. G.: Equilibrium Thermodynamic Properties of the Environment of Mars. Adv. Aerospace Phys. Tech. Memo. No. 2, MSVD, General Electric, Mar. 26, 1962.
5. Browne, W. G.: Thermodynamic Properties of the Venusian Atmosphere. Adv. Aerospace Phys. Tech. Memo. No. 13, MSVD, General Electric, June 11, 1962.
6. Drellishak, Kenneth S.: Partition Functions and Thermodynamic Properties of High Temperature Gases. (AEDC-TDR-64-22, ASTIA No. AD 428210), Gas Dynamics Laboratory, Northwestern University, Jan. 1964.
7. Gurvich, L. V.; and Yungman, V. S.: Thermodynamic Functions of Monatomic and Diatomic Gases Over a Wide Temperature Range.  
II. Method of Calculating the Thermodynamic Functions of Ideal Diatomic Gases. Russian Jour. of Phys. Chem., vol. 35, no. 9, Sept. 1961, pp. 947-951.

8. Browne, W. G.: Thermodynamic Properties of Some Diatomic and Linear Polyatomic Molecules. Engineering Phys. Tech. Memo. No. 3, General Electric, undated.
9. Browne, W. G.: Thermodynamic Properties of the Species CN, C<sub>2</sub>, C<sub>3</sub>, C<sub>2</sub>N<sub>2</sub>, and C<sup>-</sup>. Adv. Aerospace Phys. Tech. Memo. No. 9, MSVD, General Electric, May 14, 1962.
10. Rocard, Y. (C. R. S. Manders, trans.): Thermodynamics. Sir Isaac Pitman and Sons, Ltd., London, 1961.
11. Landau, L. D.; and Lifshitz, E. M. (J. B. Sykes and J. S. Bell, trans.): Quantum Mechanics. Addison-Wesley Publishing Co., Inc., Reading, Mass., 1958.
12. Mayer, Joseph E.; and Mayer, Maria G.: Statistical Mechanics. John Wiley and Sons, Inc., New York, 1940.
13. Herzberg, Gerhard: Spectra of Diatomic Molecules. D. Van Nostrand Co., Inc., New York, 1950.
14. White, W. B.; Johnson, S. M.; and Dantzig, G. B.: Chemical Equilibrium in Complex Mixtures. J. of Chem. Phys., vol. 28, no. 5, May 1958, pp. 751-755.
15. Zeleznik, Frank J.; and Gordon, Sanford: An Analytical Investigation of Three General Methods of Calculating Chemical-Equilibrium Compositions. NASA TN D-473, 1960.
16. Browne, W. G.: Comparison of Thermal Functions Generated for Species in the High Temperature Air System With Literature Values. Adv. Aerospace Phys. Tech. Memo. No. 10, MSVD, General Electric, May 28, 1962.

17. Kaplan, Lewis D.; Münch, Guido; and Spinrad, Hyron: An Analysis of the Spectrum of Mars. The Astrophysical Journal, vol. 139, no. 1, Jan. 1964, pp. 1-15.
18. Moore, Charlotte E.: Atomic Energy Levels. Vol. I. National Bureau of Standards, Circular 467, June 15, 1949.
19. Hodgman, Charles D.: Handbook of Chemistry and Physics. Thirty-seventh ed., Chemical Rubber Publishing Co., Cleveland, 1955.
20. Knight, Herbert T.; and Rink, John P.: Dissociation Energy of Cyanogen and Related Quantities by X-Ray Densitometry of Shock Waves. J. of Chem. Phys., vol. 35, no. 1, July 1961, pp. 199-208.
21. Seman, Michael L.; and Branscomb, Lewis M.: Structure and Photo-detachment Spectrum of the Atomic Carbon Negative Ion. Phys. Rev., vol. 125, no. 5, Mar. 1962, pp. 1602-1608.
22. Schexnayder, Charles J., Jr.: Tabulated Values of Bond Dissociation Energies, Ionization Potentials, and Electron Affinities for Some Molecules Found in High-Temperature Chemical Reactions. NASA TN D-1791, 1963.
23. Mulliken, R. S.: The Energy Levels of the Nitrogen Molecule. The Threshold of Space, M. Zelikoff, ed., Pergamon Press, New York, 1956.
24. Beckett, Charles W.; and Haar, Lester: Thermodynamic Properties at High Temperatures. Proceedings of the Joint Conference on Thermodynamic and Transport Properties of Fluids, July 1957; published by the Institution of Mechanical Engineers, London, 1958.

25. Herzberg, G.: Forbidden Transitions in Diatomic Molecules.  
III. New  ${}^1\Sigma_u^- \leftarrow {}^3\Sigma_g^-$  and  ${}^3\Delta_u \leftarrow {}^3\Sigma_g^-$  Absorption Bands of  
the Oxygen Molecule. Can. J. Phys., vol. 31, 1953, pp. 657-669.
26. Konowalow, Daniel D.; and Hirschfelder, Joseph O.: Morse Potential  
Parameters for O-O, N-N, and N-O Interactions. Phys. Fluids,  
vol. 4, no. 5, May 1961, pp. 637-642.
27. Barrow, R. F.; and Miescher, E.: Fine Structure Analysis of NO  
Absorption Bands in the Schumann Region. Proc. Phys. Soc., vol. 70,  
no. 447A, Mar. 1957, pp. 219-222.
28. Lagerqvist, A.; and Miescher, E.: Absorptionsspektrum des NO-  
Moleküls Feinstruktur-Analyse der  $\delta$ - und  $\beta$ -Banden und homogene  
Störung  $C^2\Pi - B^2\Pi$ . Helvetica Physica Acta, vol. 31, 1958,  
pp. 221-262.
29. Miescher, E.: Rotationsanalyse der  $\beta'$ -Banden ( $B'^2\Delta - X^2\Pi$ ) des NO-  
Moleküls. Helvetica Physica Acta, vol. 29, 1956, pp. 401-409.
30. Herzberg, Gerhard: Infrared and Raman Spectra of Polyatomic  
Molecules. D. Van Nostrand Co., Inc., New York, 1945.
31. White, H. E.: Introduction to Atomic Spectra. McGraw-Hill Book Co.,  
Inc., New York, 1934.

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XIII. APPENDICES

A. SPECTROSCOPIC AND THERMOCHEMICAL CONSTANTS

The input constants used in the computation of the properties presented in this thesis are listed and their sources are indicated.

TABLE 7.- ATOMIC AND MOLECULAR CONSTANTS

<u>Species</u>	<u>Symmetry number, <math>\sigma</math></u>	<u>M gm/mole</u>	<u><math>N_0 H_0</math> ergs/mole</u>	<u><math>D_0</math> for the ground state <math>\text{cm}^{-1}</math></u>
$e^-$	---	$5.4847 \times 10^{-4}$	0	---
N	---	14.008	$4.70729 \times 10^{12}$	---
$N^+$	---	14.007	$18.72607 \times 10^{12}$	---
$N^{++}$	---	14.007	$47.28830 \times 10^{12}$	---
O	---	16.000	$2.46741 \times 10^{12}$	---
$O^+$	---	15.999	$15.60389 \times 10^{12}$	---
$O^{++}$	---	15.999	$49.47996 \times 10^{12}$	---
$O^-$	---	16.001	$1.05410 \times 10^{12}$	---
C	---	12.011	$7.11238 \times 10^{12}$	---
$C^+$	---	12.010	$17.97182 \times 10^{12}$	---
$C^{++}$	---	12.010	$41.49225 \times 10^{12}$	---
$C^-$	---	12.012	$5.89944 \times 10^{12}$	---
Ar	---	39.944	0	---
$Ar^+$	---	39.943	$15.20235 \times 10^{12}$	---
$Ar^{++}$	---	39.943	$41.85170 \times 10^{12}$	---
$N_2$	2	28.016	0	78740

TABLE 7.- ATOMIC AND MOLECULAR CONSTANTS - Concluded

<u>Species</u>	<u>Symmetry number, <math>\sigma</math></u>	<u>M gm/mole</u>	<u><math>N_0H_0</math> ergs/mole</u>	<u><math>D_0</math> for the ground state <math>cm^{-1}</math></u>
$N_2^+$	2	28.015	$15.03336 \times 10^{12}$	70420
$O_2$	2	32.000	0	41260
$O_2^+$	2	31.999	$11.62808 \times 10^{12}$	52270
$O_2^-$	2	32.001	$-0.96232 \times 10^{12}$	37480
NO	1	30.008	$0.89860 \times 10^{12}$	52350
$NO^+$	1	30.007	$9.82403 \times 10^{12}$	85500
CO	1	28.011	$-1.13813 \times 10^{12}$	89610
$CO^+$	1	28.010	$12.38367 \times 10^{12}$	68000
CN	1	26.019	$4.56056 \times 10^{12}$	60900
$CO_2$	2	44.011	$-3.93146 \times 10^{12}$	---

M for  $e^-$  is from reference 19, page 3083.

$N_0H_0$  for CN is from reference 20;  $N_0H_0$  for  $C^-$  is derived from reference 21;  $N_0H_0$  for all other species are from reference 16.

The ground-state dissociation energies  $D_0$  for diatomic species are from reference 22.

TABLE 8.- COMPONENT COEFFICIENTS

The  $A_{ik}$  (see appendix D) corresponding to the above list of species are:

Component		N	O	C	A	$e^-$
k		1	2	3	4	5
Species	i					
$e^-$	1	0	0	0	0	1
N	2	1	0	0	0	0
$N^+$	3	1	0	0	0	-1
$N^{++}$	4	1	0	0	0	-2
O	5	0	1	0	0	0
$O^+$	6	0	1	0	0	-1
$O^{++}$	7	0	1	0	0	-2
$O^-$	8	0	1	0	0	1
C	9	0	0	1	0	0
$C^+$	10	0	0	1	0	-1
$C^{++}$	11	0	0	1	0	-2
$C^-$	12	0	0	1	0	1
Ar	13	0	0	0	1	0
$Ar^+$	14	0	0	0	1	-1
$Ar^{++}$	15	0	0	0	1	-2
$N_2$	16	2	0	0	0	0
$N_2^+$	17	2	0	0	0	-1
$O_2$	18	0	2	0	0	0

TABLE 8.- COMPONENT COEFFICIENTS - Concluded

Species	Component	N	O	C	A	e <sup>-</sup>
	k	1	2	3	4	5
	i					
O <sub>2</sub> <sup>+</sup>	19	0	2	0	0	-1
O <sub>2</sub> <sup>-</sup>	20	0	2	0	0	1
NO	21	1	1	0	0	0
NO <sup>+</sup>	22	1	1	0	0	-1
CO	23	0	1	1	0	0
CO <sup>+</sup>	24	0	1	1	0	-1
CN	25	1	0	1	0	0
CO <sub>2</sub>	26	0	2	1	0	0

In table 8 note that some of the  $A_{ik}$  are negative. Since neutral species are considered to have zero electrons, positive ions are considered to have a negative number of electrons.

TABLE 9.- ATOMIC ENERGY LEVEL CONSTANTS

The electronic energy levels and degeneracies (see appendix B) for atomic species are:

<u>Species</u>	<u>g<sub>ele</sub></u>	<u>v<sub>ele</sub></u> <u>cm<sup>-1</sup></u>	<u>Species</u>	<u>g<sub>ele</sub></u>	<u>v<sub>ele</sub></u> <u>cm<sup>-1</sup></u>
e <sup>-</sup>	2	0	N	16	107600
N	4	0		54	109600
	10	19225		12	109860
	6	28840		106	110350
	12	83330		132	111600
	6	86180		136	112200
	12	88140		6	112310
	2	93582		68	112820
	20	94800		30	112910
	12	95500		2	113600
	4	96752		10	113900
	10	96810		14	117000
	6	97800	N <sup>+</sup>	9	0
	10	99660		5	15316
	18	104000		1	32687
	34	104700		5	47168
	56	105000		15	92245
	22	106600		9	109220
	16	107200		5	144189

TABLE 9.- ATOMIC ENERGY LEVEL CONSTANTS - Continued

<u>Species</u>	<u>g<sub>ele</sub></u>	<u>v<sub>ele</sub></u> <u>cm<sup>-1</sup></u>	<u>Species</u>	<u>g<sub>ele</sub></u>	<u>v<sub>ele</sub></u> <u>cm<sup>-1</sup></u>
N <sup>+</sup>	12	149000	N <sup>+</sup>	5	234250
	3	155130	N <sup>++</sup>	6	0
	3	164612		12	57280
	18	166650		10	101026
	3	168893		2	131044
	9	170620		6	145920
	5	174212		4	186802
	1	178274		10	203078
	41	187090		2	221302
	16	189100		6	230407
	3	190121		6	245690
	12	197200		10	267242
	30	203000		12	287650
	21	205700		6	297210
153	210500		2	301088	
	12	214828	32	310500	
	12	218000	4	314224	
546	220500		22	317550	
	37	223000	14	320288	
	15	226000	10	321040	
	15	228000	30	329000	
	14	230300	22	333300	

TABLE 9.- ATOMIC ENERGY LEVEL CONSTANTS - Continued

<u>Species</u>	<u>g<sub>ele</sub></u>	<u>v<sub>ele</sub></u> <u>cm<sup>-1</sup></u>	<u>Species</u>	<u>g<sub>ele</sub></u>	<u>v<sub>ele</sub></u> <u>cm<sup>-1</sup></u>
N <sup>++</sup>	22	336290	0	15	99094
	20	339550		9	99680
	48	343000		9	100000
	24	348000		15	101140
	32	364000		5	102116
	12	368620		3	102412
	22	374000		5	102662
	52	379000		25	102865
	2	380700		15	102908
0	5	0		9	103869
	3	159		15	104000
	1	227		25	105385
	5	15868		15	105408
	1	33792		56	106000
	5	73768		56	107000
	3	76795	0 <sup>+</sup>	4	0
	15	86630		10	26820
	9	88630		6	40465
	5	95476		12	120000
	3	96226		10	165990
	36	97420		12	185400
	15	97488		6	189000

TABLE 9.- ATOMIC ENERGY LEVEL CONSTANTS - Continued

<u>Species</u>	<u>g<sub>ele</sub></u>	<u>v<sub>ele</sub></u> <u>cm<sup>-1</sup></u>	<u>Species</u>	<u>g<sub>ele</sub></u>	<u>v<sub>ele</sub></u> <u>cm<sup>-1</sup></u>
0 <sup>+</sup>	2	195710	0 <sup>+</sup>	24	283000
	2	203942	0 <sup>++</sup>	9	0
	42	207600		5	20271
	26	212800		1	43184
	2	226851		5	60312
	24	230000		15	120050
	80	232700		9	142383
	16	233900		5	187049
	18	239600		3	197087
	40	245500		3	210459
	20	248000		12	270000
	6	250300		9	283900
	32	251900		26	294000
	44	254000		14	303000
	84	255500		1	313801
	116	256000		50	327000
	18	258100		10	332000
	10	259300		15	338700
	72	261500		1	343303
	166	265500		9	350200
	134	270000		12	357500
	142	276500		46	365000

TABLE 9.- ATOMIC ENERGY LEVEL CONSTANTS - Continued

<u>Species</u>	<u>g<sub>ele</sub></u>	<u>v<sub>ele</sub></u> <u>cm<sup>-1</sup></u>	<u>Species</u>	<u>g<sub>ele</sub></u>	<u>v<sub>ele</sub></u> <u>cm<sup>-1</sup></u>
0 <sup>++</sup>	48	370500	C	1	73976
	158	380000		9	75256
	62	394000		5	77681
	90	398000		9	78130
	558	403400		21	78230
	72	425000		18	78320
	311	430000		10	78600
	48	438000		9	79318
	15	442710		18	80400
0 <sup>-</sup>	6	0		12	81200
C	9	0		5	81770
	5	10194		1	82252
	1	21648		53	83800
	5	33735		103	84000
	9	60360		30	84940
	3	61982		6	85400
	15	64090		503	86400
	3	68858		19	86500
	15	69700	C <sup>+</sup>	6	0
	3	70744		12	43030
	9	71365		10	74931
	5	72611		2	96494

TABLE 9.- ATOMIC ENERGY LEVEL CONSTANTS - Continued

<u>Species</u>	<u>g<sub>ele</sub></u>	<u>v<sub>ele</sub></u> <u>cm<sup>-1</sup></u>	<u>Species</u>	<u>g<sub>ele</sub></u>	<u>v<sub>ele</sub></u> <u>cm<sup>-1</sup></u>
c <sup>+</sup>	6	101800	c <sup>+</sup>	12	186450
	6	110650		10	188600
	2	114900		30	195500
	2	116538		20	196572
	14	119400	c <sup>++</sup>	1	0
	6	131731		9	52360
	12	135800		3	102351
	20	136000		9	137420
	4	142024		5	145875
	10	145551		1	182520
	10	150465		3	238161
	2	157234		1	247170
	6	162522		3	258931
	12	167000		9	259662
	10	168124		15	269960
	20	168900		5	276843
	2	173348		15	309100
	6	175293		1	311721
	16	178350		12	318700
	32	179000		61	322550
	26	182000		5	324212
	4	184689		12	328000

TABLE 9.- ATOMIC ENERGY LEVEL CONSTANTS - Continued

<u>Species</u>	<u>g<sub>ele</sub></u>	<u>v<sub>ele</sub></u> <u>cm<sup>-1</sup></u>	<u>Species</u>	<u>g<sub>ele</sub></u>	<u>v<sub>ele</sub></u> <u>cm<sup>-1</sup></u>
C <sup>++</sup>	31	333000	Ar	8	107220
	15	337626		4	108000
	13	340000		4	111280
	7	341368		16	111750
	3	343256		8	112900
	30	345000		20	113550
	60	346600		16	114750
	7	348000		8	115000
	12	376600		3	116660
	18	381500		12	116960
	13	384345		8	117170
	34	386000		1	117563
C <sup>-</sup>	6	0		16	118530
Ar	1	0		36	119300
	5	93144		56	120250
	3	93751		20	120700
	1	94554		32	121750
	3	95400		36	122200
	3	104102		56	122700
	12	105500		20	123500
	8	106150		28	124136
	1	107054	Ar <sup>+</sup>	6	0

TABLE 9.- ATOMIC ENERGY LEVEL CONSTANTS - Continued

<u>Species</u>	<u>g<sub>ele</sub></u>	<u>v<sub>ele</sub></u> <u>cm<sup>-1</sup></u>	<u>Species</u>	<u>g<sub>ele</sub></u>	<u>v<sub>ele</sub></u> <u>cm<sup>-1</sup></u>
Ar <sup>+</sup>	2	108723	Ar <sup>+</sup>	84	196000
	20	132400		48	200000
	12	134800		18	205000
	6	138600		6	208593
	28	142700		220	210000
	6	145200		50	215000
	12	147650		70	220000
	10	148750	Ar <sup>++</sup>	5	0
	10	150000		3	1112
	12	155160		1	1570
	30	158300		5	14010
	12	161000		1	33267
	2	167309		9	114400
	14	170600		10	128000
	26	173000		28	144650
	38	174800		15	156950
	6	179700		5	174375
	40	183000		15	182000
	60	186000		75	189500
	62	190200		15	196600
	34	192200		5	200000
	120	194000		18	204700

TABLE 9.- ATOMIC ENERGY LEVEL CONSTANTS - Concluded

<u>Species</u>	<u><math>\xi_{ele}</math></u>	<u><math>\nu_{ele}</math> <math>cm^{-1}</math></u>	<u>Species</u>	<u><math>\xi_{ele}</math></u>	<u><math>\nu_{ele}</math> <math>cm^{-1}</math></u>
Ar <sup>++</sup>	21	208300	Ar <sup>++</sup>	91	251000
	27	210800		24	258000
	33	214500		127	270000
	46	224500		121	278500
	9	231500		116	282000
	5	235000		111	286000
	26	240000		524	302000
	50	246036			

TABLE 10.\*- MOLECULAR ENERGY LEVEL CONSTANTS

The electronic, vibrational, and rotational constants for the molecular species are:

Species	Electronic state	$g_{ele}$	$\nu_{ele}$ cm <sup>-1</sup>	$B_e$ cm <sup>-1</sup>	$\alpha_e$ cm <sup>-1</sup>	$\omega_e$ cm <sup>-1</sup>	$\omega_e x_e$ cm <sup>-1</sup>	Reference
N <sub>2</sub>	X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	1	0	1.998	0.017	2358.07	14.19	23
	A <sup>3</sup> Σ <sub>u</sub> <sup>+</sup>	3	49757	1.440	.013	1460.37	13.89	23
	B <sup>3</sup> Π <sub>g</sub>	6	59314	1.638	.0184	1734.11	14.47	23
	a <sup>1</sup> Π <sub>g</sub>	2	68953	1.6182	.0183	1693.70	13.83	23
	a' <sup>1</sup> Σ <sub>u</sub> <sup>-</sup>	1	70700	1.480	.0164	1530.00	12.00	23
	C <sup>3</sup> Π <sub>u</sub>	6	87984	1.8258	.0197	2035.10	17.08	23

\*All constants in table 10 were assembled by W. G. Browne in references 8 and 9. His source references are given in this table for convenience.

TABLE 10.- MOLECULAR ENERGY LEVEL CONSTANTS - Continued

Species	Electronic state	$g_{e\ell}$	$\nu_{e\ell}$ cm <sup>-1</sup>	$B_e$ cm <sup>-1</sup>	$\alpha_e$ cm <sup>-1</sup>	$\omega_e$ cm <sup>-1</sup>	$\omega_e x_e$ cm <sup>-1</sup>	Reference
N <sub>2</sub> <sup>+</sup>	X <sup>2</sup> Σ <sub>g</sub> <sup>+</sup>	2	0	1.9322	0.0202	2207.23	16.22	24
	A <sup>2</sup> Π <sub>u</sub>	4	9020	1.722	.0180	1902.84	14.91	24, 1
	B <sup>2</sup> Σ <sub>u</sub> <sup>+</sup>	2	25570	2.083	.0195	2419.84	23.19	24, 13
	C <sup>2</sup> Σ <sub>g</sub> <sup>+</sup>	2	64550	1.650	.0500	2050.00	14.92	24, 13, 8
O <sub>2</sub>	X <sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	3	0	1.4457	0.0158	1580.36	12.07	13
	a <sup>1</sup> Δ <sub>g</sub>	2	7882.4	1.4264	.0171	1509.30	12.90	13
	b <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	1	13120.9	1.4004	.0182	1432.69	13.95	13
	A <sup>3</sup> Σ <sub>u</sub> <sup>+</sup>	3	35713.0	1.0500	.0357	819.00	22.50	13, 8

TABLE 10.- MOLECULAR ENERGY LEVEL CONSTANTS - Continued

Species	Electronic state	$g_{ele}$	$\nu_{ele}$ cm <sup>-1</sup>	$B_e$ cm <sup>-1</sup>	$\alpha_e$ cm <sup>-1</sup>	$\omega_e$ cm <sup>-1</sup>	$\omega_e x_e$ cm <sup>-1</sup>	Reference
O <sub>2</sub>	<sup>1</sup> Σ <sub>u</sub> <sup>-</sup>	1	36212.7	0.8260	0.0205	650.40	17.03	25
	B <sup>3</sup> Σ <sub>u</sub> <sup>-</sup>	3	49363.1	.8190	.0110	700.36	8.00	13
O <sub>2</sub> <sup>+</sup>	X <sup>2</sup> Π <sub>g</sub>	4	0	1.6722	0.0198	1876.40	16.53	13
	a <sup>4</sup> Π <sub>u</sub>	8	31500	1.1047	.0158	1035.69	10.39	24, 13
	A <sup>2</sup> Π <sub>u</sub>	4	38300	1.0617	.0191	900.00	13.40	24, 13
	b <sup>4</sup> Σ <sub>g</sub> <sup>-</sup>	4	48100	1.2873	.0221	1196.77	17.09	24, 13

TABLE 10.- MOLECULAR ENERGY LEVEL CONSTANTS - Continued

Species	Electronic state	$g_{ele}$	$\nu_{ele}$ cm <sup>-1</sup>	$B_e$ cm <sup>-1</sup>	$\alpha_{e-1}$ cm <sup>-1</sup>	$\omega_e$ cm <sup>-1</sup>	$\omega_e x_e$ cm <sup>-1</sup>	Reference
O <sub>2</sub> <sup>-</sup>	<sup>2</sup> Π <sub>g</sub>	4	0	1.200	0.016	1300.00	14.00	1
	<sup>4</sup> Σ <sub>u</sub> <sup>-</sup>	4	13400	.970	.017	990.00	15.00	1
	<sup>2</sup> Δ <sub>u</sub>	4	24200	.920	.027	560.00	13.00	1
NO	X <sup>2</sup> Π <sub>1/2</sub>	2	0	1.7046	0.0178	1904.03	13.97	13
	X <sup>2</sup> Π <sub>3/2</sub>	2	120.9	1.7046	.0178	1903.68	13.97	13
	A <sup>2</sup> Σ <sup>+</sup>	2	44200	1.9972	.0193	2374.80	16.46	24, 26, 27
	B <sup>2</sup> Π	4	45440	1.1260	.0152	1037.68	7.603	13
	D <sup>2</sup> Σ <sup>+</sup>	2	53290	2.0026	.0218	2323.90	22.885	24, 26, 27

TABLE 10.- MOLECULAR ENERGY LEVEL CONSTANTS - Continued

Species	Electronic state	$g_{ele}$	$\nu_{ele}$ cm <sup>-1</sup>	$B_e$ cm <sup>-1</sup>	$\alpha_e$ cm <sup>-1</sup>	$\omega_e$ cm <sup>-1</sup>	$\omega_e^x$ cm <sup>-1</sup>	Reference
NO	C $^2\Pi$	4	52376	2.0020	0.0300	2395.00	15.000	26, 28
	E $^2\Sigma^+$	2	60860	1.9863	.0182	2373.60	15.850	13
	B' $^2\Delta$	4	60020	1.3300	.0190	1216.60	15.880	26, 29
NO <sup>+</sup>	X $^1\Sigma^+$	1	0	2.002	0.0202	2377.10	16.35	1
	$^3\Pi$	6	39982	1.680	.0190	1740.00	14.50	1
	$^3\Sigma^+$	3	58523	1.330	.0160	1220.00	9.50	1
	$^3\Pi$	6	72384	1.260	.0170	1140.00	7.60	1
	A $^1\Pi$	2	73083.8	1.587	.0240	1608.90	23.30	1

TABLE 10.- MOLECULAR ENERGY LEVEL CONSTANTS - Continued

Species	Electronic state	$g_{ele}$	$\nu_{ele}$ cm <sup>-1</sup>	$B_e$ cm <sup>-1</sup>	$\alpha_e$ cm <sup>-1</sup>	$\omega_e$ cm <sup>-1</sup>	$\omega_e x_e$ cm <sup>-1</sup>	Reference
CO	X $^1\Sigma^+$	1	0	1.9313	0.01748	2170.21	13.461	13
	a $^3\Pi_r$	6	48473.9	1.6810	.01930	1739.25	14.470	13
	a' $^3\Sigma^+$	3	55380.0	1.3310	.01600	1218.00	9.500	13
	d $^3\Pi_i$	6	61784.6	1.2615	.01700	1137.79	7.624	13
	A $^1\Pi$	2	64746.5	1.6116	.02229	1515.61	17.2505	13
	b $^3\Sigma^+$	3	83831.0	2.0750	.03300	2198.00	13.476	13, 8
	B $^1\Sigma^+$	1	86917.8	1.9610	.02700	2082.07	12.092	13, 8

TABLE 10.-- MOLECULAR ENERGY LEVEL CONSTANTS - Continued

Species	Electronic state	$g_{ele}$	$\nu_{ele}$ cm <sup>-1</sup>	$B_e$ cm <sup>-1</sup>	$\alpha_e$ cm <sup>-1</sup>	$\omega_e$ cm <sup>-1</sup>	$\omega_e x_e$ cm <sup>-1</sup>	Reference
CO <sup>+</sup>	X $^2\Sigma^+$	2	0	1.9772	0.01896	2214.24	15.164	13
	A $^2\Pi_i$	4	20407.5	1.5894	.01942	1562.06	13.530	13
	B $^2\Sigma^+$	2	45633.5	1.7999	.03025	1734.18	27.927	13
CN	X $^2\Sigma^+$	2	0	1.8996	0.01735	2068.705	13.144	13
	A $^2\Pi_i$	4	9114.59	1.7165	.01746	1814.430	12.883	13
	B $^2\Sigma^+$	2	25797.85	1.9701	.02215	2164.130	20.250	13

TABLE 10.- MOLECULAR ENERGY LEVEL CONSTANTS - Concluded

Species	Electronic state	$g_{ele}$	$\nu_{ele}$ cm <sup>-1</sup>	$B_e$ cm <sup>-1</sup>	$\alpha_e$ cm <sup>-1</sup>	$\omega_e$ cm <sup>-1</sup>	$\omega_e x_e$ cm <sup>-1</sup>	Reference
CO <sub>2</sub>	1 $\Sigma$	1	0	0.3906	0.0022	667.33	0	30, 8
						667.33	0	8
						1342.86	0	8
						2349.30	0	8

The following relations were used when necessary to convert from constants given in the references to the constants in table 10.

$$\omega_0 = \omega_e - \omega_e x_e \quad (\text{ref. 12})$$

$$B_0 = B_e - \frac{1}{2} \alpha_e \quad (\text{ref. 12})$$

$$\nu_{ele} = \nu_e + \frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e - \left[ \frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e \right]_{\text{ground state}} \quad (\text{ref. 13})$$

TABLE 11.- PHYSICAL CONSTANTS

The following physical constants were also used in the computations:

$$h = 6.62517 \times 10^{-27} \text{ erg-sec}$$

$$k = 1.38044 \times 10^{-16} \text{ ergs/deg}$$

$$N_0 = 6.02322 \times 10^{23} \text{ particles/mole}$$

$$c = 2.99793 \times 10^{10} \text{ cm/sec}$$

$$p_0 = 1.013250 \times 10^6 \text{ dynes/cm}^2$$

## B. ATOMIC ENERGY LEVELS

The internal partition function for an atom or an atomic ion is

$$Q_{\text{int}} = \sum_{\text{ele}} g_{\text{ele}} \exp\left[-\epsilon_{\text{ele}}/kT\right] \quad (15)$$

where the sum is taken over all electronic energy levels  $\epsilon_{\text{ele}}$  of the species. The degeneracy of  $\epsilon_{\text{ele}}$  is  $g_{\text{ele}}$ . The sum should include all energy levels which actually exist. For an atom or ion in an infinite volume there would be an infinite number of electronic energy levels. The energies of these levels would approach the ionization limit of the atom, and  $Q_{\text{int}}$  would be a divergent sum. However, since there is a finite volume available to an atom or ion in a gas,  $Q_{\text{int}}$  will have a finite number of terms and will thus be a finite sum. Gilmore (ref. 1) points out that a density-dependent cutoff criterion can be used to terminate the energy level summation, causing  $Q_{\text{int}}$  to depend on density as well as temperature, thus complicating the calculations. He adds that for the highest density considered ( $\rho/\rho_0 = 10^1$ ), energy levels corresponding to the atom or ion having one electron excited to the  $n = 5$  shell should be included. For the lowest density considered ( $\rho/\rho_0 = 10^{-6}$ ), the summation should be extended to levels having a principal quantum number of  $n = 64$ . Below  $10,000^\circ$  K the difference in the summations to  $n = 5$  and  $n = 64$  is negligible. Above  $10,000^\circ$  K most of the atoms become ionized and the difference for the ions is small. Gilmore decided to break off the summation at energies corresponding to the atom or ion having one electron excited

to the  $n = 5$  shell. In the present work all levels whose principal quantum number is  $n \leq 5$  and whose energy is less than the ionization limit were included. These levels include those tabulated in Moore (ref. 18) as well as the missing levels which could be approximated by extrapolating along the isoelectronic sequence (ref. 31). Levels whose energies were large were lumped together with other levels of approximately the same energies by assigning the same energy to all of them and adding their degeneracies. This saved computer storage space since there are many levels whose energies are close together near the ionization limit. The above procedure was used for all atoms and positive atomic ions. Negative ion data were taken from reference 1 for  $O^-$  and reference 9 for  $C^-$ . The energy levels and corresponding degeneracies for all atoms and atomic ions considered are given in appendix A.

The notation used there is

$$\epsilon_{ele} = hc\nu_{ele}$$

and  $\nu_{ele}$  in  $cm^{-1}$  is tabulated.

Note that electrons are treated as an atomic species. The internal partition function for an electron is just 2, its spin degeneracy. Thus it has a "ground-state" degeneracy of 2 and of course no electronic excitation states.

C. APPROXIMATE DISSOCIATION ENERGIES FOR EXCITED STATES

The purpose of this appendix is to show that the use of the approximation

$$D_0 = \frac{(\omega_e - \omega_e x_e)^2}{4\omega_e x_e} \quad (28)$$

for the dissociation energy of excited electronic states of diatomic species introduces no significant error in the properties of a gas mixture. Since  $O_2$  is strongly anharmonic and has low dissociation energies it is more sensitive to the anharmonicity corrections and the dissociation energies than  $N_2$ ,  $NO$ ,  $CO$ , or  $CN$ . Therefore numerical values for  $O_2$  will be used to illustrate certain points. The quantities presented will be evaluated at  $5,000^{\circ}$  K, since most  $O_2$  molecules in a mixture dissociate at this or a lower temperature.

To simplify the notation Eq. (26) can be written as

$$Q_{\text{vib,rot}} = \frac{1}{\sigma} \sum_{v=0}^{v_{\text{max}}} \sum_{j=0}^{j(v)_{\text{max}}} (2j + 1) \exp[-A(v,j) + B(v,j)]$$

where  $A(v,j)$  and  $B(v,j)$  are both positive and

$$A(v,j) = (\epsilon_H + \epsilon_R)/kT$$

and

$$B(v,j) = (\epsilon_A + \epsilon_I + \epsilon_S)/kT$$

From Eqs. (22) and (23), respectively, it can be seen that  $A(v,j)$  is the harmonic-oscillator, rigid-rotor energy and  $B(v,j)$  is the negative of the correction terms. Therefore  $B(v,j)$  should always be small compared to  $A(v,j)$  since  $B(v,j)$  contains only correction terms and  $A(v,j)$  is known to be a good approximation to the actual energy. Notice, however, that  $B(v,j)$  depends on the square of  $v$  and  $j(j+1)$ ; thus for large  $v$  and  $j$ ,  $B(v,j)$  will not be small compared to  $A(v,j)$ . The problem that this can cause arises since the terms of the sum in  $Q_{\text{vib,rot}}$

$$(2j + 1) \exp[-A(v,j) + B(v,j)]$$

decrease at first but increase when  $v$  and  $j$  become too large. This problem occurs when  $v_{\text{max}}$  and  $j(v)_{\text{max}}$  are determined from Eq. (25) by using a dissociation energy which is too large. Since the dissociation energies for excited electronic states are not generally known, the ground state  $D_0$  was used for the excited states in trial computations. Trouble was caused by the fact that the ground state  $D_0$  is much too large for some of the excited states. This resulted in values of  $Q_{\text{vib,rot}}$  which were too large for some electronic states. For  $O_2$ , dissociation energies have been computed from intermolecular potential curves in reference 6. These dissociation energies were used for  $O_2$  and the results, compared with the previous results, are shown in table 12. Also included in table 12 are  $O_2$  results using the approximate  $D_0$  values

$$D_0 = \frac{(\omega_e - \omega_{xe})^2}{4 \omega_{xe}} \quad (28)$$

TABLE 12.- RESULTS FOR O<sub>2</sub> AT T = 5,000° K

Electronic state	Ground state D <sub>0</sub> , cm <sup>-1</sup>	(Q <sub>int</sub> ) <sub>ele</sub>	Ref. 6 D <sub>0</sub> , cm <sup>-1</sup>	(Q <sub>int</sub> ) <sub>ele</sub>	Eq. (28) D <sub>0</sub> , cm <sup>-1</sup>	(Q <sub>int</sub> ) <sub>ele</sub>
X 3Σ <sub>g</sub> <sup>-</sup>	41260	0.107045 +05	41260	0.107045 +05	41260	0.107045 +05
a 1Δ <sub>g</sub>	41260	.787039 +03	33378	.785169 +03	43396	.787251 +03
b 1Σ <sub>g</sub> <sup>+</sup>	41260	.942521 +02	28139	.934146 +02	36072	.940958 +02
A 3Σ <sub>u</sub> <sup>+</sup>	41260	.978009 +02	5568	.470850 +00	7049	.600859 +00
1Σ <sub>u</sub> <sup>-</sup>	41260	.632230 +03	5040	.188339 +00	5878	.223310 +00
B 3Σ <sub>u</sub> <sup>-</sup>	41260	.349264 -01	7764	.174641 -01	14980	.263812 -01
		<u>Q<sub>tr</sub> Q<sub>int</sub></u>		<u>Q<sub>tr</sub> Q<sub>int</sub></u>		<u>Q<sub>tr</sub> Q<sub>int</sub></u>
		0.100897 +15		0.948995 +14		0.949236 +14
		<u>h<sub>i</sub>/kT</u>		<u>h<sub>i</sub>/kT</u>		<u>h<sub>i</sub>/kT</u>
		4.68418		4.56153		4.56387
		<u>f<sub>i</sub>/kT</u>		<u>f<sub>i</sub>/kT</u>		<u>f<sub>i</sub>/kT</u>
		-32.2451		-32.1838		-32.1841

NOTE: (Q<sub>int</sub>)<sub>ele</sub> = (Q<sub>vib,rot</sub>)<sub>ele</sub> g<sub>ele</sub> exp [- ε<sub>ele</sub>/kT] and 0.107045 +05 means 0.107045 × 10<sup>5</sup>, etc.

It is obvious from table 12 that use of the ground state  $D_0$  in the excited states causes significant errors in the results. However, the  $O_2$  results indicate that use of the approximate  $D_0$  values for excited electronic states introduces no significant errors in the species properties, since use of the more accurate  $D_0$  values from reference 6 gives essentially the same species properties.

To further justify the use of approximate  $D_0$  values, consider the  $j = 0$  case. For this case,

$$A(v,0) = \frac{hc}{kT} [(\omega_e - \omega_e x_e)v] = \frac{\epsilon_H}{kT}$$

and

$$B(v,0) = \frac{hc}{kT} [\omega_e x_e v^2] = \frac{\epsilon_A}{kT}$$

The upper limit for  $v$ ,  $v_{\max}$ , is the largest whole number such that, from Eqs. (25) and (28),

$$(\omega_e - \omega_e x_e)v_{\max} < D_0 = \frac{(\omega_e - \omega_e x_e)^2}{4\omega_e x_e}$$

Assuming for convenience that  $v_{\max}$  does not have to be a whole number,

$$(\omega_e - \omega_e x_e)v_{\max} = \frac{(\omega_e - \omega_e x_e)^2}{4\omega_e x_e}$$

so that

$$v_{\max} = \frac{\omega_e - \omega_e x_e}{4\omega_e x_e}$$

The maximum values of  $A(v,0)$  and  $B(v,0)$  are

$$A(v_{\max},0) = \frac{hc}{kT} \left[ (\omega_e - \omega_e x_e) \frac{(\omega_e - \omega_e x_e)}{4\omega_e x_e} \right] = \frac{hc}{kT} \frac{(\omega_e - \omega_e x_e)^2}{4\omega_e x_e}$$

and

$$B(v_{\max},0) = \frac{hc}{kT} \left[ \omega_e x_e \frac{(\omega_e - \omega_e x_e)^2}{16(\omega_e x_e)^2} \right] = \frac{1}{4} A(v_{\max},0)$$

Thus, the correction term  $B(v,0)$  never gets larger than one-fourth of  $A(v,0)$  as  $v$  increases from zero to  $v_{\max}$ .

D. MINIMIZATION EQUATIONS

The following equations were used to minimize the Gibbs free energy of the mixture. They are equivalent to those in reference 14. From Eq. (34), the nondimensional free energy of the gas mixture can be written

$$\frac{F}{kT} = \sum_{i=1}^n N_i \left[ \frac{f_i(p,T)}{kT} + \ln \frac{N_i}{N} \right]$$

The equilibrium value of the set  $\{N_i\}$  is determined by an iterative procedure in which the nondimensional free energy is minimized subject to the constraints on the components of the mixture

$$B_k = \sum_{i=1}^n A_{ik} N_i \quad k = 1, 2, \dots, l \quad (35)$$

To start this procedure, an initial guess for  $\{N_i\}$ , referred to as  $\{\eta_i\}$ , is required. Any positive set,  $\{\eta_i\}$ , which satisfies Eqs. (35) can be used. An improved set,  $\{N_i\}$ , is obtained by solving the following equations:

$$N_i = -\eta_i \left[ \frac{f_i(p,T)}{kT} + \ln \frac{\eta_i}{\eta} \right] + \frac{\eta_i}{\eta} N + \eta_i \sum_{k=1}^l \Pi_k A_{ik}$$

where

$$\eta = \sum_{i=1}^n \eta_i$$

The Lagrange multipliers  $\Pi_1, \Pi_2, \dots, \Pi_l$  and  $N$  are obtained by solving the  $l + 1$  linear equations:

$$r_{11}\Pi_1 + r_{12}\Pi_2 + \dots + r_{1l}\Pi_l + B_1u = \sum_{i=1}^n A_{i1}\eta_i \left[ \frac{f_i(p,T)}{kT} + \ln \frac{\eta_i}{\eta} \right]$$

$$r_{21}\Pi_1 + r_{22}\Pi_2 + \dots + r_{2l}\Pi_l + B_2u = \sum_{i=1}^n A_{i2}\eta_i \left[ \frac{f_i(p,T)}{kT} + \ln \frac{\eta_i}{\eta} \right]$$

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$$r_{l1}\Pi_1 + r_{l2}\Pi_2 + \dots + r_{ll}\Pi_l + B_lu = \sum_{i=1}^n A_{il}\eta_i \left[ \frac{f_i(p,T)}{kT} + \ln \frac{\eta_i}{\eta} \right]$$

$$B_1\Pi_1 + B_2\Pi_2 + \dots + B_l\Pi_l + 0 \cdot u = \sum_{i=1}^n \eta_i \left[ \frac{f_i(p,T)}{kT} + \ln \frac{\eta_i}{\eta} \right]$$

where

$$N = (1 + u)\eta$$

and

$$r_{kk'} = r_{k'k} = \sum_{i=1}^n (A_{ik}A_{ik'})\eta_i \quad k, k' = 1, 2, \dots, l$$

The improved set,  $\{N_i\}$ , is then treated as the starting set,  $\{\eta_i\}$ , and the above equations are used again. This iterative procedure continues until  $\{N_i\}$  reaches the equilibrium set. Convergence is determined numerically when no  $N_i$  changes by  $10^{-7}$  NM in successive iterations,

that is, when

$$\frac{|\eta_i - N_i|}{NM} < 10^{-7}$$

for all species,  $i = 1, 2, 3, \dots, n$ .

The above equations were programed for an IBM 7094 computer. Also, a short additional step was programed to eliminate the possibility of negative  $N_i$  and to test the directional derivative of the free energy as suggested in reference 14.

It is shown in reference 15 that the above iterative procedure converges.

E. ALTERNATE PARTITION FUNCTION

Certain approximations can be made to simplify the vibrational-rotational partition function for diatomic species, Eq. (26). In reference 12 (pp. 162-163), the approximations

$$e^{+\epsilon_S/kT} \cong 1 + \epsilon_S/kT \quad (E-1)$$

and

$$e^{+\epsilon_A/kT} \cong 1 + \epsilon_A/kT \quad (E-2)$$

are made and Eq. (26) is summed to  $v, j = \infty$  to obtain a compact form for  $Q_{\text{vib,rot}}$ . Use of Eqs. (E-1) and (E-2) introduces error at temperatures around  $5,000^\circ$  K and higher, especially in Eq. (E-2), since  $\epsilon_A$  is larger than  $\epsilon_S$ . In chapter VII, both summations are carried out directly up to certain cutoff terms. In this appendix, the summation over  $v$  is carried out directly, and the summation over  $j$  is simplified by using the Euler-Maclaurin summation formula and Eq. (E-1).

Substitution of Eq. (21) into Eq. (26) yields

$$Q_{\text{vib,rot}} = \frac{1}{\sigma} \sum_{v=0}^{v_{\text{max}}} \exp\left[\frac{-(\epsilon_H - \epsilon_A)}{kT}\right] \sum_{j=0}^{j(v)_{\text{max}}} (2j + 1) \exp\left[\frac{-(\epsilon_R - \epsilon_I)}{kT} + \epsilon_S/kT\right] \quad (E-3)$$

The Euler-Maclaurin summation formula is given in reference 12 (p. 152) as

$$\sum_{j=a}^{\infty} f(j) = \int_a^{\infty} f(j) dj + \frac{1}{2} f(a) - \frac{1}{12} f'(a) + \frac{1}{720} f'''(a) - \dots \quad (E-4)$$

Applying Eq. (E-4) to the second summation in Eq. (E-3), neglecting the third and higher derivatives, one obtains

$$\sum_{j=0}^{\infty} (2j + 1) \exp\left[\frac{-(\epsilon_R - \epsilon_I)}{kT} + \frac{\epsilon_S}{kT}\right] \approx \int_0^{\infty} (2j + 1) \exp\left[\frac{-(\epsilon_R - \epsilon_I)}{kT} + \frac{\epsilon_S}{kT}\right] dj + \frac{1}{3} + \frac{(\epsilon'_R - \epsilon'_I)}{12kT} \quad (E-5)$$

where  $(\epsilon'_R - \epsilon'_I) = hc\left(B_e - \frac{1}{2} \alpha_e - \alpha_{ev}\right)$ . Use of Eq. (E-1) changes the integral to

$$\int_0^{\infty} (2j + 1) \exp\left[\frac{-(\epsilon_R - \epsilon_I)}{kT}\right] \left(1 + \frac{\epsilon_S}{kT}\right) dj$$

and gives the result

$$Q_{\text{vib,rot}} = \frac{1}{\sigma} \sum_{v=0}^{v_{\text{max}}} \exp\left[\frac{-(\epsilon_H - \epsilon_A)}{kT}\right] \left[ \frac{kT}{(\epsilon'_R - \epsilon'_I)} + \frac{\epsilon''_S (kT)^2}{(\epsilon'_R - \epsilon'_I)^3} + \frac{1}{3} + \frac{(\epsilon'_R - \epsilon'_I)}{12kT} \right] \quad (E-6)$$

where

$$\epsilon''_S = \frac{hc8B_e^3}{\omega_e^2}$$

Eq. (E-6) is a good approximation to Eq. (26) except for very high temperatures.

The corresponding approximation for the temperature derivative of  $Q_{\text{vib,rot}}$  is needed in the derivative of  $Q_i$  for diatomic species. Differentiation of Eq. (26) and application of the Euler-Maclaurin formula to the summation over  $j$  in the derivative is straightforward.

In Eq. (E-6) and the derivative,  $v_{\max}$  is the largest integral value of  $v$  such that

$$(\omega_e - \omega_e x_e)v < D_0 \quad (\text{E-7})$$

which is Eq. (25) with  $j = 0$ .

When using the equations in this appendix, care must be taken to avoid a certain difficulty. Notice that the integral below Eq. (E-5) exists only if

$$(\epsilon_R - \epsilon_I) > 0 \quad (\text{E-8})$$

Use of Eqs. (22) and (23) in Eq. (E-8) results in

$$hc \left( B_e - \frac{1}{2} \alpha_e \right) j(j+1) - hc \alpha_e v j(j+1) > 0$$

which is equivalent to

$$\frac{B_e - \frac{1}{2} \alpha_e}{\alpha_e} > v \quad (\text{E-9})$$

This inequality must be satisfied for all values of  $v$  up to and including  $v_{\max}$ . For every electronic state of each diatomic species as given in table 10 of appendix A, the inequality is satisfied by  $v_{\max}$  with only one exception: the  $C^2\Sigma^+$  state of  $N_2^+$ . This can be shown by substituting Eq. (28) into Eq. (E-7) to get

$$(\omega_e - \omega_e x_e)v < \frac{(\omega_e - \omega_e x_e)^2}{4\omega_e x_e}$$

and using the constants in table 10 to get

$$v < \frac{\omega_e - \omega_e x_e}{4\omega_e x_e} = \frac{2050.00 - 14.92}{4(14.92)} = 34.1$$

so that

$$v_{\max} = 34$$

Since, in Eq. (E-9)

$$\frac{B_e - \frac{1}{2} \alpha_e}{\alpha_e} = \frac{1.650 - 0.025}{0.050} = 32.5$$

it can be seen that  $v_{\max}$  is too large. In the calculations,  $v_{\max}$  for the  $C^2\Sigma^+$  state of  $N_2^+$  was changed to

$$v_{\max} = 30$$

to satisfy Eq. (E-9).

Properties of the diatomic species were computed using the equations of this appendix in place of Eq. (26) and its derivative and all other equations were unchanged. The property difference due to the above change is presented in each of the figures for the diatomic species. This difference is equal to the property based on the equations of this appendix minus the property computed exactly as described in chapter VII. No mixture properties were computed using the equations of this appendix.

CALCULATION OF THERMODYNAMIC PROPERTIES OF  
GAS MIXTURES AT HIGH TEMPERATURES

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By

Dennis Otto Allison

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CALCULATION OF THERMODYNAMIC PROPERTIES OF  
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ABSTRACT

Thermodynamic properties are calculated for mixtures of ideal gases in equilibrium for temperatures up to 15,000° K. Results for air and a model Mars atmosphere are given. The equilibrium composition of a gas mixture at a given temperature and pressure is determined by minimizing the Gibbs free energy. Species of the following types are included in the mixture: atoms and atomic ions, diatomic and linear triatomic molecules and ions, and electrons. Quantum statistical mechanics is used to determine thermodynamic properties of each species. For the diatomic species, accurate evaluations of vibrational anharmonicity, vibration-rotation interaction, and rotational stretching corrections are carried out. Comparisons are made between results with and without the above corrections.