Influence of Differences in Thermochemistry Data upon High-Temperature Gas Composition

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A simple analysis is presented which allows the assessment of changes in thermochemistry data in the form of heat of formation, partition functions, specie free-energy, or specie specific heat upon the composition of high-temperature gas mixtures. The analysis is used to determine the level of sophistication required when treating polyatomic species, diatomic species, and atomic species.

Introduction

IN the analysis of propulsion, re-entry, and plasma dynamics problems one is interested in equilibrium thermodynamic properties and gas composition. For gas dynamic experiments directed at measuring thermochemistry, radiative, or kinetic properties of high-temperature gases, an accurate prediction of chemical equilibrium properties is important in the reduction of data. In these situations property gradients, the density levels, and radiative processes in the gas may arouse questions as to the existence of thermodynamic equilibrium and the description of the gas in terms of Boltzmann statistics. Nevertheless, the subject of equilibrium properties of dissociated and ionized gases has been an active area of investigation as witnessed by the literature in this area. This literature can be categorized as dealing primarily with: 1) the physics of the subject, 2) the computational or formulational aspects of the subject, 3) the presentation of thermochemistry data, and 4) the presentation of property and composition data for mixtures of gases which are undergoing dissociation and ionization.

In the view of many observers the physics governing high-temperature gases is treated thoroughly in standard texts.[1–4] Numerous workers have treated the formulation of the problem of computing the composition and thermodynamic properties of high-temperature gas mixtures and several approaches are available as computer programs so that general multicomponent mixtures can be treated.[5–10] These programs require thermochemistry data for each chemical species either in the experimental form of 1) energy levels, ionization potentials, dissociation energies, or in the computed form of 2) partition functions, specific heats, molar free-energies, molar enthalpies, and heats of formation. Several compilations of thermochemistry data are available.[11–17] However, for some species a significant uncertainty exists in the experimental data. As improved values are published a revision of the computed thermochemistry data becomes necessary. Furthermore, there are numerous approximations which can be used in computing partition functions, free-energies, and specific heats. Thus the following questions arise. How does the improvement in experimental thermochemistry data effect gas composition for a problem in which mixture properties have been computed? How do the approximations which are used in computing thermochemistry data effect gas composition? What accuracy in thermochemistry data is required to be compatible with the accuracy of a multicomponent mixture computer program?

Despite the considerable amount of worthy effort that has been expended on the subject of equilibrium composition and thermodynamic properties of multicomponent high-temperature gas mixtures, a general systematic analysis of the influence of changes (due to uncertainties or errors) in thermochemical data upon composition and mixture properties is not available. If one unguided by a theory attempts to approach this problem by simply comparing various published compilations of thermodynamic properties and composition of mixtures as a function of the different types of thermochemical data that were used to generate them, one is confronted with a nearly impossible task. This arises from the fact that compositions are usually presented in diverse forms i.e., some are tabulated as functions of temperature and pressure while others use temperature and density. The composition can be presented in the form of several different types of mole fractions or in several different units. Thus the errors arising from cross plotting or interpolation frequently outweigh other considerations.

An additional source of frustration in an attempt to draw some conclusion about the level of sophistication required from a comparison of published data is that while one may have several sets of data presented in an easy to compare form, each computed using different approximations for the determination of thermochemical properties, these results may have been generated with different energy level data or heat of formation data.

The intent of the following is to develop a simple procedure which will predict differences in gas composition which result from thermochemistry data uncertainties. The procedure will apply best to trace species for which differences in concentration do not influence the thermodynamic properties of the gas mixture. It is developed and applied to gases of moderate to low pressures for which the assumption of an ideal mixture of ideal gases is valid. Questions arising from nonideal behavior resulting from van der Waal or Coulomb type interactions are not considered. The procedure developed here will be used to examine problems arising in computing thermochemistry data for polyatomic, diatomic, and atomic species.

Analysis

To aid in the development of the arguments given below we shall consider three temperature intervals. In the lowest temperature interval (up to 5000°K) the primary problems arising in thermochemical data will be for polyatomic species. It is well known that differences in thermochemistry data which are a function of the level of sophistication used in evaluating the internal partition function increase with temperature. Thus, in this lowest interval no appreciable problems arise in determining accurate partition functions for most atomic and diatomic species. In the upper portion of this interval differences in the internal partition function for

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Received February 2, 1970; revision received April 12, 1971. This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract NAS7-100 sponsored by NASA.

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polyatomic molecules become significant, but at the upper limit of this interval most polyatomic molecules are dissociated. The second interval extends from 5000 to 10,000°K where uncertainties in diatomic properties are significant. Again the errors continue to increase with temperature; however, most diatomic molecules are dissociated by 10,000°K. The last interval is above 10,000°K. The chief error is due to the atomic properties until ionized species become significant. The exact values of the temperatures for the above interval limits are not important; however, from the above arguments, it is clear that the source of uncertainty is the data for a specie which is disappearing from the mixture. Thus the chief error occurs in regions where the concentration of the specie in question is small, and the error in composition has a negligible influence upon the thermodynamic properties.

Now consider the problem of equilibrium for the simple reaction $XY \rightleftarrows X + Y$ which may represent the dissociation of a polyatomic molecule or a diatomic molecule or the ionization on an atom. The mass action and mass balance equations take the form

$$n_{XY}/n_X n_Y = K \tag{1a}$$

$$n_X = n_Y \tag{1b}$$

$$n_{XY} + 2n_X = N \tag{1c}$$

where N is a constant. Now in terms of the mole fraction χ_{XY} of specie XY the solution to the aforementioned is

$$\chi_{XY} = n_{XY}/N = (1 + \alpha) - (2\alpha + \alpha^2)^{1/2} \tag{2}$$

where $\alpha = 2/KN$.

Now for α large the previous expression can be approximated by

$$\chi_{XY} = 1/2\alpha \tag{3}$$

which in the limit $\alpha \to \infty$, $\chi_{XY} \to 0$. This limit corresponds to complete dissociation or ionization. With the previous expression the question of errors in values of the mole fraction χ_{XY} which result from uncertainties in the equilibrium constant K can be examined.

Consider two values K_1 and K_2 such that $K_1 = \delta K_2$ and for which the mole fractions are, respectively, $(\chi_{XY})_1$ and $(\chi_{XY})_2$. Thus for large α we have

$$(\chi_{XY})_1/(\chi_{XY})_2 = \delta = K_1/K_2 \tag{4}$$

The ratio of equilibrium constants δ can be expressed in terms of partition functions as

$$\delta = [(q_1/q_2)_{XY}/(q_1/q_2)_X(q_1/q_2)_Y] \exp(\Delta\epsilon_{f_2} - \Delta\epsilon_{f_1})/kT \tag{5a}$$

or in terms of free-energies

$$\delta = \exp(\Delta F/RT) \exp(\Delta H/RT) \tag{5b}$$

with

$$\Delta F = \Delta F_{XY} - \Delta F_X - \Delta F_Y$$

$$\Delta F_{XY} = [-(F^\circ - H_0{}^\circ)_{XY}]_1 - [-(F^\circ - H_0{}^\circ)_{XY}]_2$$

$$\Delta F_X = [-(F^\circ - H_0{}^\circ)_X]_1 - [-(F^\circ - H_0{}^\circ)_X]_2$$

$$\Delta F_Y = [-(F^\circ - H_0{}^\circ)_Y]_1 - [-(F^\circ - H_0{}^\circ)_Y]_2$$

$$\Delta H = \Delta H_{XY} - \Delta H_X - \Delta H_Y$$

$$\Delta H_{XY} = [(H_0{}^\circ)_{XY}]_2 - [(H_0{}^\circ)_{XY}]_1$$

$$\Delta H_X = [(H_0{}^\circ)_X]_2 - [(H_0{}^\circ)_X]_1$$

$$\Delta H_Y = [(H_0{}^\circ)_Y]_2 - [(H_0{}^\circ)_Y]_1$$

Although the above was developed for a simple mixture of three components, it can be demonstrated that the ratio of mole fractions and equilibrium constants would result from an analysis of a general system of equations, which describe a complex mixture, providing the concentration of the specie in question is small. The fact that the concentration is small allows us to treat certain of the mass action equations independent of the mass balance equations.

From the aforementioned argument, it follows that the most likely region in which errors are to be examined will be for large α; so, we find that expressions Eqs. (4–5) are appropriate. However, a word of caution is appropriate at this point in that the previous arguments are good for low and moderate pressure. At high pressure the dissociation or ionization of a specie is delayed until higher temperature as it takes smaller values of K to yield large α values, and thus the influence of errors becomes more important in the range where the concentration of the species is large. Thus, Eq. (4) will form the basis for assessing the influence of changes in thermochemistry data upon the composition of high-temperature mixtures.

Now to substantiate the previous analysis let us attempt through Eqs. (4) and (5), to correlate two sets of concentrations which were computed with slightly different thermochemical data. The concentrations taken from Ref. 18 and from computations made with a program[10] are ratioed in column 2 of Table 1. We have also listed differences in free energies and heats of formation used. The values

$$\exp(\Delta F/RT)$$

and

$$\exp(\Delta H/RT)$$

give the relative errors due to the differences in free-energy and heats of formation. As is clear from a comparison of the second and the last columns for this case of air, the correlation is very good. Similar comparisons for other temperatures and pressures have also confirmed the aforementioned analysis. In some cases $\Delta F/RT$ is so small that

$$(\chi_1 - \chi_2)/\chi_2 = \Delta F/RT \tag{6}$$

Now to examine the problems which give rise to uncertainties in the evaluation of the partition function.

Uncertainties with Atomic and Ionic Species

Perhaps the best known aspect of the atomic species problem is that, for a completely free atom, the partition function series is a divergent infinite series. This is easily understood if one realized that for an isolated atom there are an infinite number of electronic energy levels which converge to the ionization limit. Thus, near the ionization limit the exponential factor $\exp(-\epsilon_i/kT)$ remains constant while the degeneracy g_i increases with each additional term. At low temperature this problem is circumvented by the apparent convergence of the series. Thus, for low temperatures investi-

Table 1 Comparison of concentrations[a] and sources of differences for air at 6000°K and $P/P_0 = 0.0007365$

Specie	χ_1/χ_2	$\Delta F/RT$	exp ($\Delta F/RT$)	$\Delta H/RT$	exp ($\Delta H/RT$)	exp ($\Delta F/RT$)- exp ($\Delta H/RT$)
$O_2{}^+$	1.38	−0.015	0.985	0.322	1.38	1.36
$N_2{}^+$	0.971	−0.054	0.948	−0.002	0.998	0.95
NO^+	0.974	−0.061	0.9406	0.013	1.013	0.955
O_2	0.970	−0.026	0.9742	−0.003	0.997	0.97
N_2	1.000	−0.002	0.998	−0.005	0.995	0.99
NO	0.976	−0.027	0.974	−0.004	0.996	0.969
N_2O	2.22	0.795	2.21	−0.005	0.995	2.20
NO_2	0.768	−0.268	0.764	−0.01	0.99	0.76
$O_2{}^-$	1.048	−0.316	0.728	0.379	1.46	1.06

[a] ( )$_1$ Concentration and properties from Ref. 10; ( )$_2$ concentration and properties from Ref. 18.

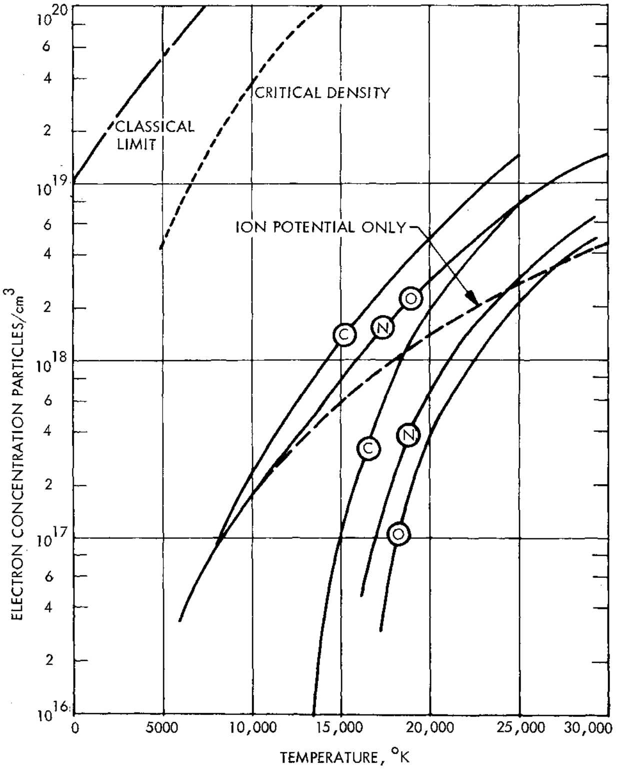

Fig. 1 Uncertainty curves for atomic concentration; the region between the above pairs of curves define the range of electron concentrations and temperatures for which the F.P.S. model atomic concentrations are accurate to ±10%.

gators have evaluated electronic partition functions by considering only the ground state,[19] by arbitrary truncation of the series at a preselected principal quantum number,[20] and by summing over-all observed energy levels, such as those in Moore's[21] compilation, as in Ref. 22. These three approaches yield the same values in a limited temperature range and implicit in them is some physical mechanism for reducing the number of electronic states.

In an ionized gas the presence of charged particles in the vicinity of a given ion or atom has the effect of altering the electric potential in which the bound electrons of the ion or atom move. Although there is still disagreement as to the precise description of this microfield, its role in the question of ionized gas properties is clear. The presence of this microfield gives rise to a perturbation term in the Hamiltonian for each specie which results in a finite number of energy levels which are shifted from their isolated species positions. In terms of property determination, this is manifested as a lowering of the ionization potential and a modification of the infinite sum partition function to a sum over only the finite number of bound states. Numerous papers have treated the ionizing gas property question from this point of view.[23-39] A review of this work is beyond the scope of this paper; however, it suffices to state that most investigators[4,23,25,26] now agree that in the moderate to low pressure range with

$$n_e \leq (1/2\pi)(kT/e^2)^3 \qquad (7)$$

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

$$\Delta I_z = (z+1)e^3\left[(4\pi/kT)\left(n_e + \sum_z z^2 n_z\right)\right]^{1/2} \qquad (8)$$

which is also used as a cutoff for truncating the partition function sum. For electron densities above this critical level, Eq. (7), the potential is dominated by interaction of the coulombic potentials of the test particle and its nearest neighbors according to the Unsold theory. A variety of other partition function cutoff procedures based upon characteristic plasma lengths are given by McChesney.[23]

To properly evaluate the partition function and apply the aforementioned cutoff criterion one must estimate those energy levels which are not given in tabulations such as Moore. This problem has been considered by several authors.[24,35,40] If the missing energy levels are estimated and their degeneracies included in the partition function evaluation one finds widely different values at high temperatures when different cutoff procedures are used.

If we consider conditions under which atomic concentrations differ due to differences in atomic partition functions and ionization potential lowering, we have from Eq. (4) for negligible difference in ion partition functions

$$\chi_d/\chi_i = (q_d/q_i)\exp-(\Delta I_d/kT) \qquad (9)$$

The d subscript denotes values obtained using Debye theory and i denotes the values obtained with the fixed ionization potential and the partition function summed over a finite number of energy levels, hereafter referred to as the F.P.S. model. The quantity q_i is only a function of temperature, and q_d and ΔI_d are functions of electron concentration and temperature. So, for fixed ratios of atomic concentrations this expression can be represented as a curve of electron concentration vs temperature.

Now two conditions are important: 1) At high temperatures and relatively low electron concentrations the influence of the micro field upon the lowering of the ionization potential is almost negligible, and the q_d series becomes large and $\chi_d > \chi_i$. 2) At high temperatures and high electron concentrations the influence of the micro field upon lowering the ionization potential is important and thus $\chi_d < \chi_i$. Therefore, we have considered χ_d/χ_i equal to 1.1 and 0.9 and generated two curves for each specie which in terms of electron concentration and temperature bound a region within which the atomic concentrations in an ionizing gas computed by the F.P.S. model differ by less than 10% from values obtained from the Debye theory. These curves are presented for atomic nitrogen, oxygen, and carbon in Fig. 1. For these curves the F.P.S. model values for the partition functions were obtained by summing the partition function series over all energy levels listed in Ref 21. The values for the partition function series truncated by the Debye theory were taken from Ref. 40 which includes missing energy levels. We have also shown in the figure three other important curves. The uppermost labeled "classical limit" represents the upper limit of electron concentrations for which the electron may be considered a classical particle. The next curve represents the critical electron density [Eq. (7)] below which the Debye-Huckel limiting laws apply to the plasma. The lowest curve is obtained by neglecting the influence of the partition functions in Eq. (9) and thus represents a 10% uncertainty in atomic concentration due to ionization potential lowering by the Debye theory.

Using solutions of the mass action and mass balance equation in which Debye theory was used, the curves of Fig. 1 have been confirmed in predicting the range in which the atomic concentrations are accurately given (±10%) by the F.P.S. model.[41] These solutions indicate the upper curves are in some cases too conservative. These cases occur for situations in which our original assumptions of small concentrations and low to moderate pressure are violated.

Uncertainties with Diatomic Species

Some of the problems encountered in atomic species are also important in diatomic species as discussed by Haar.[42] One approach to this apparent divergence in the diatomic partition function has been presented by Sinanoglu and Pitzer.[43]

Table 2 Shock parameters for wet air computed using different levels of approximation for the diatomic species: air with 4% H_2O initially at 10^{-3} atm; $M_0 = 28.53$

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

[a] First row for each temperature group: harmonic oscillator and rigid rotator.
[b] Second rows: electronic state correction.
[c] Third rows: electronic and anharmonic correction.

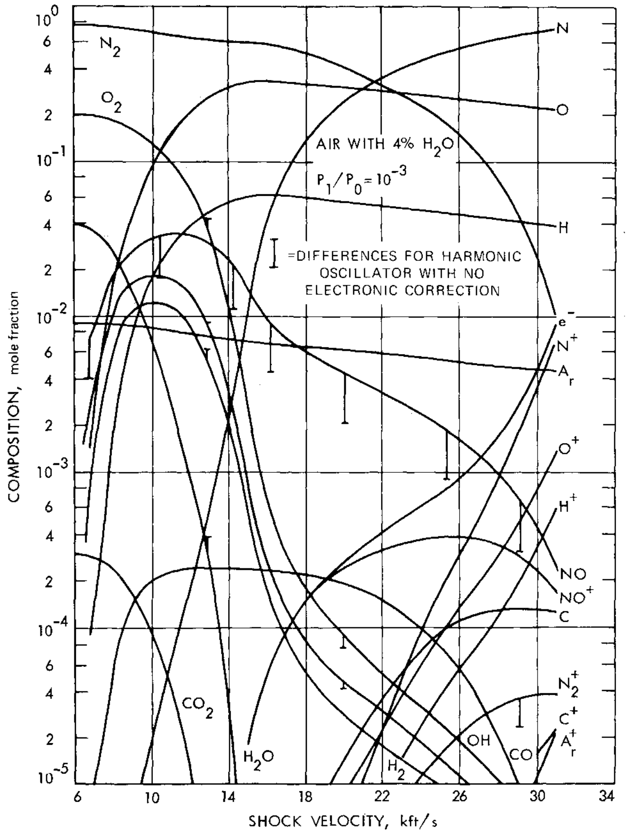

Fig. 2 Composition of humid shock heated air computed using anharmonic and electronic corrections; bars indicate differences in composition resulting from neglect of the anharmonic and electronic corrections.

In an earlier version of the JPL program,[8] tabulated data were used in which the diatomic species properties were computed using the anharmonic and rotational corrections in evaluating the contribution of the low lying states and were joined with a classical oscillator analysis to evaluate the contribution of the states near the dissociation limit. As the concentrations computed using the aforementioned properties agree closely with those computed using properties which neglected the correction for states near the dissociation limit, we have concluded that this divergence problem is not significant in the range of moderate to low pressures.

Another question considered by Stupochenko and treated in Ref. 35, is that of the effect of the rotational state upon the intramolecular potential. By performing detailed computations for O_2, Drellishak concluded that the inclusion of this effect produced partition functions which were within ±1% of those computed by the standard approach of computing properties with the harmonic oscillator-rigid rotator model with electronic, anharmonic, and rotational corrections.

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

From Table 2 one can observe the small effect that the differences in thermochemical properties, presented in Tables 3 and 4, have upon the shock parameters and equilibrium properties. In Fig. 2 one can observe the temperature range in which the various species are important. The data presented

Table 3 Free energies for diatomic species computed using different levels of approximation.

Specie	$-[(F - H_0)/RT]$											
	3000°K			5000°K			7000°K			9000°K		
O_2^+	29.934[a]	29.910[b]	29.910[c]	32.102	32.053	35.052	33.576	33.500	33.496	34.707	34.604	34.588
N_2^+	28.818	28.802	28.773	31.073	31.038	30.892	32.664	32.609	32.325	33.890	33.816	33.409
NO^+	28.814	28.799	28.799	30.937	30.906	30.906	32.383	32.335	32.333	33.490	33.425	33.414
CO^+	29.457	29.441	29.441	31.598	31.565	31.559	33.075	33.023	32.991	34.224	34.154	34.075
C_2	29.187	29.794	28.013	32.157	32.111	30.157	33.758	33.687	31.601	34.975	34.880	32.693
CH	26.943	26.891	26.891	29.081	28.974	28.972	30.564	30.398	30.387	31.721	31.496	31.460
OH	26.946	26.911	26.911	29.017	28.943	28.943	30.450	30.332	30.331	31.555	31.392	31.389
H_2	22.323	22.267	22.267	24.416	24.268	24.268	25.893	25.640	25.640	27.051	26.688	26.688
O_2	29.922	29.893	29.877	32.173	32.116	32.041	33.727	33.641	33.495	34.920	34.805	34.592
N_2	28.021	28.008	28.008	30.144	30.116	30.116	31.587	31.543	31.543	32.685	32.626	32.625
NO	30.468	30.447	29.783	32.642	32.599	31.923	34.113	34.047	33.366	35.231	35.141	34.456
CO	28.797	28.781	28.781	30.935	30.902	30.902	32.387	32.336	32.336	33.493	33.425	33.421
CN	29.452	29.435	29.408	31.713	31.677	31.536	33.306	33.251	32.974	34.535	34.461	34.061
O_2^-	30.541	30.495	30.493	32.793	32.703	32.680	34.351	34.215	34.144	35.562	35.381	35.247

[a] First vertical row: anharmonic and electronic correction.
[b] Second row: electronic correction only.
[c] Third row: rigid rotator; harmonic oscillator.

Table 4 Specific enthalpies for diatomic species computed using different levels of approximation

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

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

[b] Second row: electronic correction only.

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

in this figure were computed with thermochemical data which were computed using the electronic, anharmonic, and rotational corrections. Error bars indicate the differences in composition when the rigid rotator-harmonic oscillator approximation is considered. As the differences in concentration correlate with the expressions given earlier, we have another conformation of our analysis. Thus, in the discussion below we shall be guided by Eq. (5) with diatomic partition functions and free-energies used when considering diatomic species and only polyatomic properties considered when discussing polyatomic species.

For small $\Delta F/RT$ Eq. (6) indicates that the decimal differences in free-energy are directly proportional to the fractional differences in gas composition. With this in mind, Table 3 reveals that sizable errors, in excess of 20%, can result from neglecting corrections. With the exception of the species which have split ground states or extremely low electronic states, the electronic correction is usually less than the anharmonic correction. At a temperature of 7000°K the anharmonic correction results in an average uncertainty of about 10% in the composition of the various diatomic species. However, as shown in Fig. 2, most of the diatomic molecules are no longer present at this temperature. Notable exceptions are NO, and the positive diatomic ions. The large discrepancy in NO composition is due to the omission of the upper level of the 121 cm^{-1} split in the ground state in the harmonic oscillator-rigid rotator computations. Of particular interest in Table 3 is the approximately 30% difference in composition which results from neglect of electronic excitation in the two important trace species CN and N_2^+ at 7000°K.

Thus, to achieve a desirable accuracy for diatomic species both electronic and anharmonic corrections as given in Ref. 16 are necessary. We would like to note at this point that the free-energies and enthalpies given in Tables 3 and 4 were computed with old values of the spectroscopic constants and, therefore, do not necessarily compare with values which are currently used in Ref. 10. However, this does not detract from the usefuless of the data presented in the tables and figures as an internally consistent set of data for our purposes here.

Uncertainties with Polyatomic Species

For polyatomic species, the convention used by most investigators is to neglect electronic states and to follow the procedure of Pennington and Kobe.[44] This involves computing the thermochemical properties by a rigid rotator-harmonic oscillator approximation to which small corrections are added to account for anharmonicity, rotation-vibration interaction, centrifugal distortion, Fermi resonance, and Darling-Dennison resonance. This procedure has been used to compute properties for species of interest.[45–50]

Durand and Brandmaier[47] have performed computations for CO_2, H_2O, and N_2O in which all of the corrections just listed were considered. To make the results more meaningful, they have listed separately the contributions of the various correction terms to the specific heat at constant pressure for each of the aforementioned species over a range of temperatures (1000°K–7000°K). The results indicate the principal correction is due to the anharmonic terms. The influence of the corrections upon specie composition can be estimated by assuming a linear increase with temperature of the contribution of the corrections to specific heat. If we recall that

$$-\left(\frac{F^\circ - H_0^\circ}{RT}\right) = \int \frac{\int (c_p/R)dT}{T^2}\, dT \tag{10}$$

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

$$\Delta[-(F^\circ - H_0^\circ)/RT] \doteq \tfrac{1}{2}(\Delta C_p/R) \tag{11}$$

Thus to the approximation given by Eq. (6) we have

$$(\chi_1 - \chi_2)/\chi_2 \doteq \Delta C_p/2R \tag{12}$$

Durand and Brandmaier list the following correction at 5000°K to the specific heat in cal/mole-°K of CO_2, H_2O, and N_2O, respectively, (0.36, 0.78, 0.70). These would correspond to errors in concentrations of 9, 19, and 17%. At a lower temperature of 3000°K the errors in concentrations are only 6%, 10%, and 10%, respectively. Unless the pressure is high, most of these species will be fully dissociated at the highest temperature just cited and at 3000°K the concentrations will be nearly an order of magnitude below their undissociated values. This is confirmed by an examination of the data presented earlier for air with 4% H_2O.

A careful analysis in which published values of free energy are compared with those computed by the program of Ref. 10, using the analysis and data of Ref. 16 indicates smaller errors than previously presented. In the case of H_2O, using the approximation of Eq. (6), the JPL program concentrations would differ by 5 to 6% at 3000°K and 11 to 12% at 5000°K. The difference depends upon whether one uses the data tabulated in Ref. 47 or 49 for the comparison. For CO_2, using the data of Refs. 47 and 50, the concentration of this specie would differ by 2% at 3000°K and 5 to 6% at 5000°K from the JPL values. At these same temperatures, the concentration of N_2O would vary by 6 and 13% depending upon whether the data of Ref. 47 or the JPL data were used.

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

Uncertainties with Heats of Formation

Another important question, which should be explored here, is the accuracy of heat of formation data required for good results. To a first approximation, small errors can be evaluated through the use of an expression similar to Eq. (6),

$$(\chi_1 - \chi_2)/\chi_2 = [(H_0°)_2 - (H_0°)_1]/RT \qquad (13)$$

As the error in heat of formation is not temperature dependent, the effect of this error upon composition is reduced as the temperature increases. Furthermore, in the temperature range from 1000°K to 10,000°K, uncertainties of a few hundred calories per mole will introduce concentration errors of less than 10%. For the gases of primary interest, heats of formation are known to this accuracy. For certain trace species, the uncertainty is sufficient to warrant the retention of the exponential term in the evaluation of its uncertainty. Equation (5) has proven very useful in estimating the uncertainties in CN concentration which are due to the significant uncertainty in the dissociation energy for this species.

Concluding Remarks

To this point very little has been said concerning the influence of the uncertainties reviewed above upon the thermodynamic properties. This is because they will have negligible influence, at most a few percent, if we allow uncertainties in the composition of principal species of only a few percent and in the composition of trace species of about 10%. The property and shock parameter uncertainty will be dominated by the principal species. This conclusion is confirmed in Ref. 24 among others, and is supported by the shock parameters in Table 2 for the 4% H_2O and air calculations.

The aforementioned analysis developed for estimating the influence of differences in thermochemical data upon chemical composition reveals that to achieve the accuracy of 10% for trace species one can use: 1) a simple rigid rotator-harmonic oscillation model to describe the properties of polyatomic species, 2) the aforementioned model with anharmonic and electronic corrections to describe the properties of diatomic species, and 3) the isolated atom model with a finite number of energy levels and a fixed ionization potential to describe the properties of atomic and ionic species. Furthermore, the analysis and data just presented can be used to define quantitative limits of applicability for the aforementioned models in terms of temperatures and pressures for specific mixtures. With this theory one can answer those questions raised in the introduction of this paper concerning the influence of changes in thermochemistry data upon the composition of high-temperature gas mixtures for specific applications.

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