TECHNICAL NOTE R-58

A METHOD FOR DIGITAL CALCULATION OF
THERMODYNAMIC PROPERTIES OF

Prepared By

V. L. Reed

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BROWN ENGINEERING COMPANY
HUNTSVILLE

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A METHOD FOR DIGITAL CALCULATION OF EQUILIBRIUM THERMODYNAMIC PROPERTIES OF AIR

July, 1963

Prepared For

ADVANCED PROPULSION SECTION
PROPULSION AND MECHANICS BRANCH
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GEORGE C. MARSHALL SPACE FLIGHT CENTER

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ABSTRACT

The thermodynamic properties of air at equilibrium are obtained using the principles of classical (Boltzmann) statistical mechanics, the laws of mass action and the values of the spectroscopic and molecular data available.

The accuracy of the method is within a few per cent of the more rigorous methods of Chapman and Enskog, i.e., the neglect of intermolecular potentials and the utilization of a hard sphere gas model are the principle differences. It should be established that, although these seem to be quite restrictive, the data obtainable from the following method is accurate to within only a few per cent and may be utilized to a great advantage in routines and procedures in connection with high speed digital computational programs.

author

TABLE OF CONTENTS

INTRODUCTION

The thermodynamic properties of air at equilibrium are obtained using the principles of classical (Boltzmann) statistical mechanics, the laws of mass action and the values of the spectroscopic and molecular data available.

The accuracy of the method is within a few per cent of the more rigorous methods of Chapman and Enskog, i.e., the neglect of intermolecular potentials and the utilization of a hard sphere gas model are the principle differences.

Several assumptions have been used of which the most severe is the neglect of relaxation and other nonequilibrium effects. The principle assumptions that were utilized are

1. Classical mechanics are valid; i.e. quantum effects are neglected.
2. No interparticle potentials exist.
3. The gas is of such a nature that a hard sphere model is a valid assumption.
4. Only oxygen and nitrogen and their reactions are considered.
5. Neglect the effect of nitric oxide (NO) since most endeavors will be to analyze vehicles at high altitude where this reaction is negligible.
6. Reactions are assumed to progress at an infinitely fast rate.

These assumptions are the principle ones that are considered here. It should be established that, although these seem to be quite restrictive, the data obtainable from the following method is accurate to within only a few per cent and may be utilized to a great advantage in routines and procedures in connection with high speed digital computational programs.

ANALYSIS

Equational Development

The equations are those of classical statistical mechanics and may be found in any text on this subject[1]. The primary development is taken from Hansen[2] and the basic theory presented here is his theory.

The partition functions of a gas may be shown to be

$$Q = \sum_i g_i \, e^{-\frac{\epsilon_i}{kT}} \quad , \tag{1}$$

where

Q - partition function,

g_i - degeneracy of the ith state,

ϵ_i - energy of the ith state,

k - Boltzmann's constant,

T - temperature.

Then it may be shown that

$$Q = q_t \, q_r \, q_v \, q_e \quad ,$$

where all other energy states are neglected and the subscripts refer to the translational, rotational, vibrational, and electronic molecular partition functions respectively.

It can be shown that for hard sphere gases

$$q_t = \left[\frac{2\pi m kT}{h^2}\right]^{\frac{3}{2}} \frac{RT}{p} \quad , \tag{2}$$

$$q_r = \sum_{J=0}^{\infty} (2J + 1) \exp\left(-\frac{h^2 J (J + 1)}{8\pi^2 I k T}\right) \quad , \tag{3}$$

$$q_r \approx \frac{8\pi^2 I k T}{\sigma h^2} \quad , \tag{4}$$

$$q_v = \sum_{n=0}^{\infty} e^{-\frac{n h\nu}{kT}} = \left(1 - e^{-\frac{h\nu}{kT}}\right)^{-1} \quad , \tag{5}$$

$$q_e = \sum_{n=0}^{\infty} g_n \exp\left(-\frac{\varepsilon_n}{kT}\right) \quad , \tag{6}$$

where

m - mass of the particle,

h - Planck's constant,

R - gas constant,

p - pressure,

J - rotational quantum number,

I - polar moment of inertia,

σ - symmetry number,

ν - wave number.

Table One displays the pertinent values of the molecular and spectroscopic constants of oxygen and nitrogen.

Performing the logarithms of both sides of Equation 2 through 6, expanding and substituting in the numerical values where applicable yields

$$\ell n\, Q_{N_2} = \frac{7}{2}\, \ell n\, T - 0.42 - \ell n \left(1 - e^{-\frac{3390}{T}}\right) - \ell n\, p \quad , \tag{7}$$

$$\ell n\, Q_{O_2} = \frac{7}{2}\, \ell n\, T + 0.11 - \ell n \left(1 - e^{-\frac{2270}{T}}\right) + \ell n \left(3 + 2\, e^{-\frac{11390}{T}} + e^{-\frac{18990}{T}}\right) - \ell n\, p \quad , \tag{8}$$

$$\ell n\, Q_N = \frac{5}{2}\, \ell n\, T + 0.30 + \ell n \left(4 + 10\, e^{-\frac{27700}{T}} + 6\, e^{-\frac{41500}{T}}\right) - \ell n\, p \quad , \tag{9}$$

$$\ell n\, Q_O = \frac{5}{2}\, \ell n\, T + 0.50 + \ell n \left(5 + 3\, e^{-\frac{228}{T}} + e^{-\frac{526}{T}} + 5\, e^{-\frac{22800}{T}} + e^{-\frac{48600}{T}}\right) - \ell n\, p \tag{10}$$

$$\ell n\, Q_{N^+} = \frac{5}{2}\, \ell n\, T + 0.30 + \ell n \left(1 + 3\, e^{-\frac{70.6}{T}} + 5\, e^{-\frac{188.9}{T}} + 5\, e^{-\frac{22000}{T}} + e^{-\frac{47000}{T}} + 5\, e^{-\frac{67900}{T}}\right) - \ell n\, p \quad , \tag{11}$$

$$\ell n\, Q_{O^+} = \frac{5}{2}\, \ell n\, T + 0.50 + \ell n \left(4 + 10\, e^{-\frac{38600}{T}} + 6\, e^{-\frac{58200}{T}}\right) - \ell n\, p, \tag{12}$$

TABLE ONE

PARTITION FUNCTION CONSTANTS FOR THE MAJOR COMPONENTS OF AIR

Particle	Molecular Weight M gm/mol	Rotational Constant $\frac{\sigma h^2}{8\pi^2 I k}$ °K	Vibrational Constant $\frac{h\nu}{k}$ °K	Dissociation Energy $\frac{D}{k}$ °K	Electronic Degeneracy g_n none	Electronic Energy $\frac{\epsilon_n}{k}$ °K	Ionization Energy $\frac{I}{k}$ °K
N_2	28	5.78	3390.	113200.	1.0	0.0	n/a
O_2	32	4.16	2270.	59000.	3.0	0.0	n/a
					2.0	11390.	
					1.0	18990.	
O	16	none	none	none	5.0	0.0	158000.
					3.0	228.	
					1.0	326.	
					5.0	22800.	
					1.0	48600.	
N	14	none	none	none	4.0	0.0	168800.
					10.0	27700.	
					6.0	41500.	
O^+	16	none	none	none	4.0	0.0	n/a
					10.0	38600.	
					6.0	58200.	
N^+	14	none	none	none	1.0	0.0	n/a
					3.0	70.6	
					5.0	188.9	
					5.0	22000.	
					1.0	47000.	
					5.0	67900.	
e^-	$\frac{1.0}{1820}$	none	none	none	2.0	0.0	n/a

$$\ell n\, Q_{e^-} = \frac{5}{2}\, \ell n\, T - 14.24 - \ell n\, p \quad , \tag{13}$$

where T is in degrees Kelvin absolute and p is in atmospheres. The internal energy and enthalpy are defined as

$$\frac{E - E_o}{RT} = T \left.\frac{\partial\, \ell n\, Q}{\partial\, T}\right]_\rho = T\, \frac{d\, \ell n\, Q_c}{dT} \quad , \tag{14}$$

$$\frac{H - E_o}{RT} = T \left.\frac{\partial\, \ell n\, Q}{\partial\, T}\right]_p = T\, \frac{d\, \ell n\, Q_p}{dT} \quad , \tag{15}$$

and the specific heats are

$$C_v = \left.\frac{\partial\, E}{\partial\, T}\right]_\rho \quad , \tag{16}$$

$$C_p = \left.\frac{\partial\, H}{\partial\, T}\right]_p \quad , \tag{17}$$

where

$$Q_c = \frac{p}{RT}\, Q \quad , \tag{18}$$

and

$$Q_p = p\, Q \quad . \tag{19}$$

Thus,

$$\left[\frac{E - E_o}{RT}\right]_{t\,+\,e^-} = \frac{3}{2} + \frac{\sum_n \frac{\varepsilon_n}{kT}\, g_n\, e^{-\frac{\varepsilon_n}{kT}}}{\sum g_n\, e^{-\frac{\varepsilon_n}{kT}}} \quad , \tag{20}$$

$$\left[\frac{H - E_o}{RT}\right]_{t+e} = \left[\frac{E - E_o}{RT}\right]_{t+e} + 1 \quad , \tag{21}$$

and the specific heats may be written as

$$\left(\frac{C_v}{R}\right)_{t+e} = \frac{3}{2} + \frac{\sum_n \left(\frac{\varepsilon_n}{kT}\right)^2 g_n e^{-\frac{\varepsilon_n}{kT}}}{\sum_n g_n e^{-\frac{\varepsilon_n}{kT}}} - \left[\frac{\sum_n \frac{\varepsilon_n}{kT} g_n e^{-\frac{\varepsilon_n}{kT}}}{\sum_n g_n e^{-\frac{\varepsilon_n}{kT}}}\right]^2 \quad , \tag{22}$$

$$\left(\frac{C_p}{R}\right)_{t+e} = \left(\frac{C_v}{R}\right)_{t+e} + 1 \quad . \tag{23}$$

This provides the energy, enthalpy, and specific heats which are due to the translational and electronic energy for atoms or molecules. The contributions of rotational and vibrational energy must be included for the molecular particles. These are

$$\left(\frac{E}{RT}\right)_{r+v} = 1 + \frac{h\nu}{kT}\left(e^{-\frac{h\nu}{kT}} - 1\right)^{-1} \quad , \tag{24}$$

$$\left(\frac{C}{R}\right)_{r+v} = 1 + \left(\frac{h\nu}{2kT}\right)^2 \left[\sinh\left(\frac{h\nu}{2kT}\right)\right]^{-2} \quad , \tag{25}$$

and should be added to Equations 20, 21, 22 and 23 respectively for the diatomic molecules of oxygen and nitrogen.

The entropy of the pure gas may be represented as (at unit pressure)

$$\frac{S}{R} = \ell n\, Q + T \left(\frac{\partial\, \ell n\, Q}{\partial\, T}\right)_p \quad , \tag{26}$$

or

$$\frac{S}{R} = \ell n\, Q_p + \frac{H - E_o}{RT} \quad . \tag{27}$$

The entropy at constant density as well as the energy, enthalpy and specific heats may be calculated in the same manner with appropriate change of the partition function and the constants.

The equilibrium constants for the reaction

$$\sum_i a_i\, A_i \rightleftarrows \sum_j b_j\, B_j \quad , \tag{28}$$

where

A_i indicates the reactant,

a_i indicates the stoichiometric constant of the reactant,

B_i indicates the products,

b_i indicates the stoichiometric constant of the product,

or

$$K_p = \frac{\prod_i p^{b_i}\, (B_i)}{\prod_i p^{a_i}\, (A_i)} \quad , \tag{29}$$

and

$$\ell n\, K_p = - \frac{\Delta E_o}{RT} + \sum_i b_i\, \ell n\, Q_p\,(B_i) - \sum_i a_i\, \ell n\, Q_p\,(A_i) \quad , \tag{30}$$

where

$$\Delta E_o \triangleq \sum b_i\, E_o\,(B_i) - \sum a_i\, E_o\,(A_i) \tag{31}$$

is the zero point energy of the products less the reactants both referred to their standard states.

Using the values in Table One and expanding Equation 30 yields

$$\ell n\, K_p\,(O_2 \rightarrow 2O) = - \frac{59000}{T} + 2\, \ell n\, Q_p\,(O) - \ell n\, Q_p\,(O_2) \quad , \tag{32}$$

$$\ell n\, K_p\,(N_2 \rightarrow 2N) = - \frac{113200}{T} + 2\, \ell n\, Q_p\,(N) - \ell n\, Q_p\,(N_2) \quad , \tag{33}$$

$$\ell n\, K_p\,(O \rightarrow O^+ + e^-) = - \frac{158000}{T} + \ell n\, Q_p\,(O^+) + \ell n\, Q_p\,(e^-) - \ell n\, Q_p\,(O) \quad , \tag{34}$$

$$\ell n\, K_p\,(N \rightarrow N^+ + e^-) = - \frac{168800}{T} + \ell n\, Q_p\,(N^+) + \ell n\, Q_p\,(e^-) - \ell n\, Q_p\,(N) \quad , \tag{35}$$

The concentration equilibrium constant is defined by

$$K_c = \frac{\prod_i n^{b_i}\,(B_i)}{\prod_i n^{a_i}\,(A_i)} \quad , \tag{36}$$

and

$$K_c = K_p (RT)^{\left(\sum_i a_i - \sum_i b_i\right)} \quad . \tag{37}$$

The equation of state may be defined as

$$\frac{p}{\rho} = \frac{Z\,RT}{M_o} \quad , \tag{38}$$

where

M_o - molecular weight of the undissociated air,

Z - compressibility .

The reactions of importance are

$$N_2 \rightarrow 2N \quad , \tag{39}$$

$$O_2 \rightarrow 2O \quad , \tag{40}$$

$$N \rightarrow N^+ + e^- \quad , \tag{41}$$

$$O \rightarrow O^+ + e^- \quad , \tag{42}$$

If ε_1 is the fraction of molecules which dissociate into oxygen atoms, ε_2 is the fraction of molecules which dissociate into nitrogen atoms, and ε_3 the fraction of atoms which are ionized, then the compressibility is

$$Z = 1 + \varepsilon_1 + \varepsilon_2 + 2\,\varepsilon_3 \quad . \tag{43}$$

The partial pressures for the three components are

$$p\,(N_2) = x\,(N_2)\,p = \frac{0.8}{1+\varepsilon_1}\,p \quad , \tag{44}$$

$$p\,(O_2) = x\,(O_2)\,p = \frac{0.2-\varepsilon_1}{1+\varepsilon_1}\,p \quad , \tag{45}$$

$$p\,(O) = x\,(O)\,p = \frac{2\,\varepsilon_1}{1+\varepsilon_1}\,p \quad . \tag{46}$$

The equilibrium constant for the oxygen dissociation reaction is

$$K_{p_{(O_2 \rightarrow 2O)}} = \frac{p^2\,(O)}{p\,(O_2)} = \frac{4\,\varepsilon_1^2\,p}{(1+\varepsilon_1)\,(0.2-\varepsilon_1)} \quad . \tag{47}$$

Solving for ε_1,

$$\varepsilon_1 = \frac{-0.8 + \sqrt{0.64 + 0.8\left(1 + \dfrac{4\,p}{K_{p_{(O_2 \rightarrow 2O)}}}\right)}}{2\left(1 + \dfrac{4\,p}{K_{p_{(O_2 \rightarrow 2O)}}}\right)} \quad . \tag{48}$$

The negative value of the square root is of no interest. One point of trouble is where $K_{p_{(O_2 \rightarrow 2O)}}$ goes to zero at low temperatures; however, ε_1 reaches a limit of zero at this point, i.e. there is no dissociation at low temperature. At intermediate temperatures, ε_1 reaches a limit of 0.2 as $K_{p_{O_2 \rightarrow 2O}}$ goes to infinity, i.e., there exists complete dissociation of oxygen molecules into oxygen atoms. Here nitrogen dissociation begins and we have

$$p\,(N_2) = x\,(N_2)\,p = \frac{0.8 - \varepsilon_2}{1.2 + \varepsilon_2}\,p \quad , \tag{49}$$

$$p\,(N) = x\,(N)\,p = \frac{2\,\varepsilon_2}{1.2 + \varepsilon_2}\,p \quad , \tag{50}$$

$$p\,(O) = x\,(O)\,p = \frac{0.4}{1.2 + \varepsilon_2}\,p \quad . \tag{51}$$

The equilibrium constant for the nitrogen dissociation is

$$K_{p_{(N_2 \rightarrow 2N)}} = \frac{p^2\,(N)}{p\,(N_2)} = \frac{4\,\varepsilon_2^{\,2}\,p}{(1.2 + \varepsilon_2)\,(0.8 - \varepsilon_2)} \quad . \tag{52}$$

Solving for ε_2 ,

$$\varepsilon_2 = \frac{-0.4 + \sqrt{0.16 + 3.84\left(1 + \dfrac{4p}{K_{p_{(N_2 \rightarrow 2N)}}}\right)}}{2\left(1 + \dfrac{4p}{K_{p_{(N_2 \rightarrow 2N)}}}\right)} \quad . \tag{53}$$

Here again there are two important limits, i.e. ε_2 approaches 0.8 as $K_{p_{(N_2 \rightarrow 2N)}}$ approaches infinity and ε_2 is zero where $K_{p_{(N_2 \rightarrow 2N)}}$ is zero. Again the negative square root is of no importance.

The last reactions to consider have partial pressures as follows

$$p\,(N) = x\,(N)\,p = \frac{1 - \varepsilon_3}{1 + \varepsilon_3}\,p \quad , \tag{54}$$

$$P\,(N^+) = x\,(N^+)\,p = \frac{\varepsilon_3}{1 + \varepsilon_3}\,p \quad , \tag{55}$$

$$p\,(e^-) = x\,(e^-)\,p = \frac{\varepsilon_3}{1 + \varepsilon_3}\,p \quad , \tag{56}$$

and the equilibrium constant is

$$K_{p_{(\text{ionize})}} = \frac{p\,(N^+)\,p\,(e^-)}{p\,(N)} = \frac{\varepsilon_3^{\,2}\,p}{1 - \varepsilon_3^{\,2}} \quad . \tag{57}$$

Solving for ε_3,

$$\varepsilon_3 = \frac{1}{1 + \dfrac{p}{K_{p_{(\text{ionize})}}}} \quad , \tag{58}$$

where the negative square root is unimportant and

$$K_{p_{\text{ionize}}} = 0.2\,K_{p_{(O \rightarrow O^+ + e^-)}} + 0.8\,K_{p_{(N \rightarrow N^+ + e^-)}} \quad . \tag{59}$$

Here again the limits are imposed, i.e., ε_3 is zero where $K_{p_{\text{ionize}}}$ is zero and ε_3 is one where $K_{p_{(\text{ionize})}}$ is infinity.

The mol fractions are found by

$$x\,(N_2) = \frac{0.8 - \varepsilon_2}{Z} \quad , \tag{60}$$

$$x\,(O_2) = \frac{0.2 - \varepsilon_1}{Z} \quad , \tag{61}$$

$$x\,(N) = \frac{2\,\varepsilon_2 - 1.6\,\varepsilon_3}{Z} \quad , \tag{62}$$

$$x\,(O) = \frac{2\,\varepsilon_1 - 0.4\,\varepsilon_3}{Z} \quad , \tag{63}$$

$$x\,(N^+ + O^+) = x\,(X^+) = x\,(e^-) = \frac{2\,\varepsilon_3}{Z} \quad , \tag{64}$$

The energy, enthalpy, entropy, speed of sound, and the specific heats may be found for the equilibrium mixture. The energy is just the sum of the components or

$$\frac{E}{RT} = \sum_j x_j \frac{E_j}{RT} \quad , \tag{65}$$

and the enthalpy

$$\frac{H}{RT} = \frac{E}{RT} + 1 \quad . \tag{66}$$

The entropy is found by

$$\frac{S}{R} = \sum_j x_j \frac{S_j}{R} - \sum_j x_j \ln x_j - \ln p \quad , \tag{67}$$

and the specific heats are obtained from

$$\frac{C_v}{R} = \frac{1}{ZR} \frac{\partial ZE}{\partial T}\Big]_\rho = \sum_i x_i \frac{C_i}{R} + \frac{T}{Z} \sum_i \left(\frac{E_i}{RT}\right) \left(\frac{\partial Z\, x_i}{\partial T}\right)_\rho \quad , \tag{68}$$

where

$$C_i = \frac{d\,E_i}{dT} \quad , \tag{69}$$

and

$$\frac{\partial Z_x(O_2)}{\partial T}\Big]_\rho = \frac{-\partial \varepsilon_1}{\partial T}\Big]_\rho \quad , \tag{70}$$

$$\frac{\partial Z_x(N_2)}{\partial T}\Big]_\rho = -\frac{\partial \varepsilon_2}{\partial T}\Big]_\rho \quad , \tag{71}$$

$$\frac{\partial Z_x(N)}{\partial T}\Big]_\rho = \frac{2\,\partial \varepsilon_2}{\partial T}\Big]_\rho - 1.6\,\frac{\partial \varepsilon_3}{\partial T}\Big]_\rho \quad , \tag{72}$$

$$\frac{\partial Z_x(O)}{\partial T}\Big]_\rho = \frac{2\,\partial \varepsilon_1}{\partial T}\Big]_\rho - 0.4\,\frac{\partial \varepsilon_3}{\partial T}\Big]_\rho \quad , \tag{73}$$

$$\frac{\partial Z_x(N^+ + O^+)}{\partial T}\Big]_\rho = \frac{\partial Z_x(e^-)}{\partial T}\Big]_\rho = \frac{2\,\partial \varepsilon_3}{\partial T}\Big]_\rho \quad , \tag{74}$$

where

$$\frac{\partial \varepsilon_1}{\partial T}\Big]_\rho = \frac{\frac{d}{dT}\left(\ell n\, K_{c(O_2 \rightarrow 2O)}\right)}{\frac{2}{\varepsilon_2} + \frac{1}{0.2 - \varepsilon_1}} \quad , \tag{75}$$

$$\frac{\partial \varepsilon_2}{\partial T}\Big]_\rho = \frac{\frac{d}{dT}\left(\ell n\, K_{c(N_2 \rightarrow 2N)}\right)}{\frac{2}{\varepsilon_2} + \frac{1}{(0.8 - \varepsilon_2)}} \quad , \tag{76}$$

$$\frac{\partial \varepsilon_3}{\partial T}\Big]_\rho = \frac{\frac{d}{dT}\left(\ell n\, K_{c(\text{ionize})}\right)}{\frac{2}{\varepsilon_3} + \frac{1}{1 - \varepsilon_3}} \quad , \tag{77}$$

where

$$\frac{d}{dT}\left(\ell n\, K_{c_i}\right) = \frac{1}{T}\left[\frac{\Delta E_o}{RT} + \sum_i b_i \left(\frac{E - E_o}{RT}\right)_{B_i} - \sum_i a_i \left(\frac{E - E_o}{RT}\right)_{A_i}\right] . \qquad (78)$$

The corresponding specific heat at constant pressure is

$$\frac{C_p}{R} = \frac{1}{ZR}\frac{\partial Z H}{DT}\Big]_p = \sum_i x_i \left(\frac{C_i}{R} + 1\right) + \frac{T}{Z}\sum_i \left(\frac{E_i}{RT} + 1\right)\left(\frac{\partial Z x_i}{\partial T}\right)_p , \qquad (79)$$

where

$$\frac{\partial Z x (N_2)}{\partial T}\Big]_p = -\frac{\partial \varepsilon_2}{\partial T}\Big]_p , \qquad (80)$$

and similarly for O_2, O, N, $(N^+ + O^+)$ and e^- noting that a p is used instead of a ρ in Equations 70 through 74. However Equations 75 through 78 are changed and they are

$$\frac{\partial \varepsilon_1}{\partial T}\Big]_p = \frac{\frac{d}{dT}\left(\ell n\, K_{p(O_2 \rightarrow 2O)}\right)}{\frac{2}{\varepsilon_1} - \frac{1}{(1 + \varepsilon_1)} + \frac{1}{(0.2 - \varepsilon_1)}} , \qquad (81)$$

$$\frac{\partial \varepsilon_2}{\partial T}\Big]_p = \frac{\frac{d}{dT}\left(\ell n\, K_{p(N_2 \rightarrow 2N)}\right)}{\frac{2}{\varepsilon_2} - \frac{1}{(1.2 + \varepsilon_2)} + \frac{1}{(0.8 - \varepsilon_2)}} , \qquad (82)$$

$$\frac{\partial \varepsilon_3}{\partial T}\Big]_p = \frac{\frac{d}{dT}\left(\ell n\, K_{p(\text{ionize})}\right)}{\frac{2}{\varepsilon_3} - \frac{1}{(1 + \varepsilon_3)} + \frac{1}{(1 - \varepsilon_3)}} , \qquad (83)$$

and

$$\frac{d}{dT}\ (\ell n\ K_{p_i}) = \frac{d}{dT}\ (\ell n\ K_{c_i}) + \frac{1}{T}\ \left[\sum_i b_i - \sum_i a_i\right] \quad . \tag{84}$$

The specific heat ratio, γ, is just

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{C_p}{R}}{\frac{C_v}{R}} \quad . \tag{85}$$

The corrected gas constant (contains molecular weight change effects) is just

$$\frac{C_p}{R} - \frac{C_v}{R} = 1 + \frac{T}{Z} \sum_i \left[\frac{H_i}{RT} \left(\frac{\partial\ Z\ x_i}{\partial\ T}\right)_p - \frac{E_i}{RT} \left(\frac{\partial\ Z\ x_i}{\partial\ T}\right)_\rho \right] \quad . \tag{86}$$

The speed of sound may be found by

$$a^2 = -\gamma \frac{\frac{\partial\ p}{\partial\ T}\Big]_\rho}{\frac{\partial\ \rho}{\partial\ T}\Big]_p} \quad . \tag{87}$$

Then

$$\frac{a^2\ \rho}{p\ \gamma} = \frac{1 + \frac{T}{Z} \frac{\partial\ Z}{\partial\ T}\Big]_\rho}{1 + \frac{T}{Z} \frac{\partial\ Z}{\partial\ T}\Big]_p} \quad . \tag{88}$$

This completes the development of the equations used in the computer subroutine "PARFN" which is based on classical statistical mechanics.

Estimation of Error

The solutions obtained by this method have been compared with those obtained by the more exact method of Hilsenrath and Beckett[3]. The percentage deviation of certain properties has been shown in Figures 1, 2, 3, and 4. These figures show that the data is good at low density (within 2%) while at higher densities the data goes to a maximum error of about 6%.

Note that the use of the term Amagat is convenient here since one Amagat is the density at standard temperature and pressure.

Since primarily the utilization of this program will be in the analysis of re-entry bodies at high altitudes, the per cent error in the thermodynamic properties should be less than two per cent. Thus, this program should provide a very successful means of solving equilibrium flow properties for re-entry bodies.

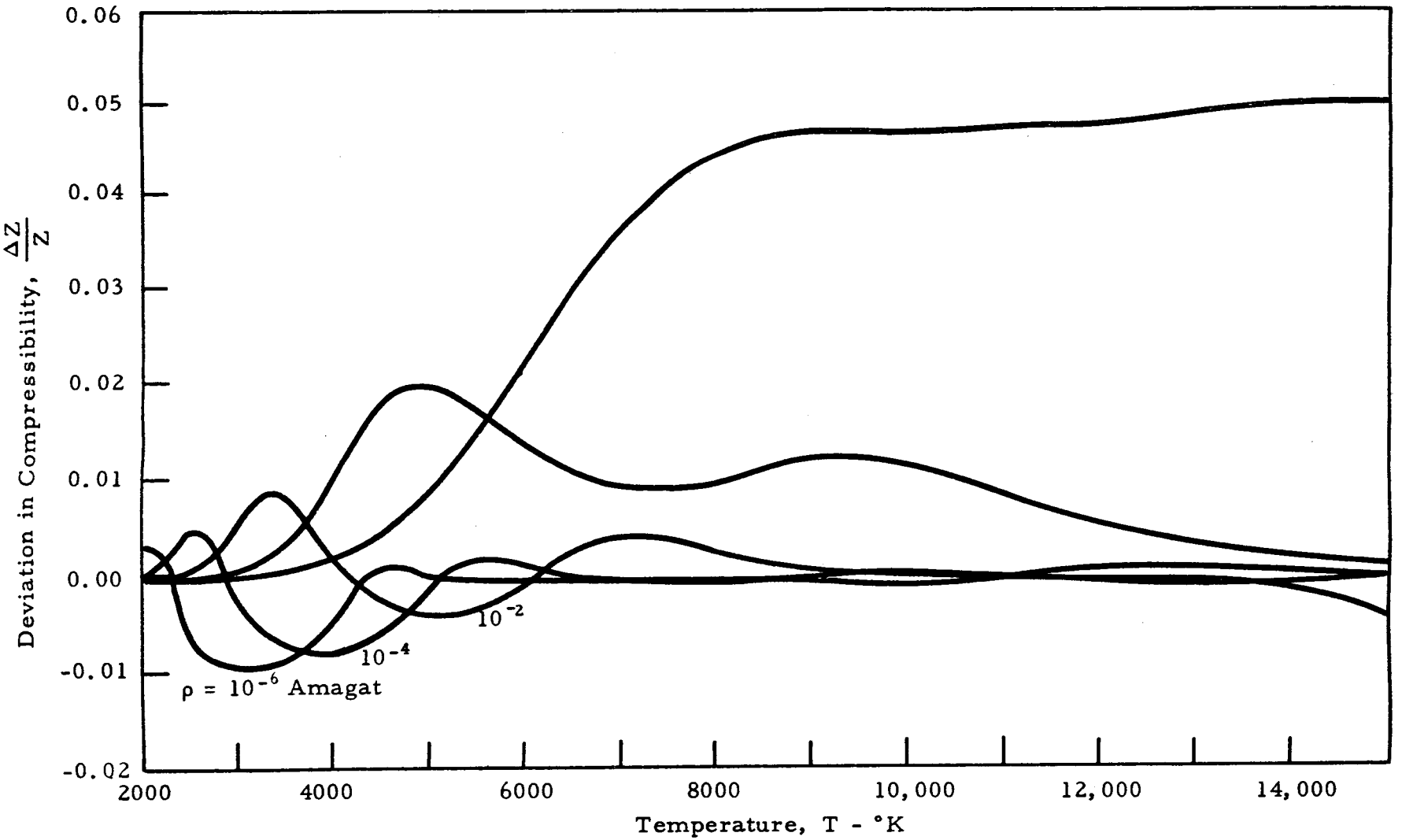

Figure 1. Error in Compressibility as a Function of Temperature and Density

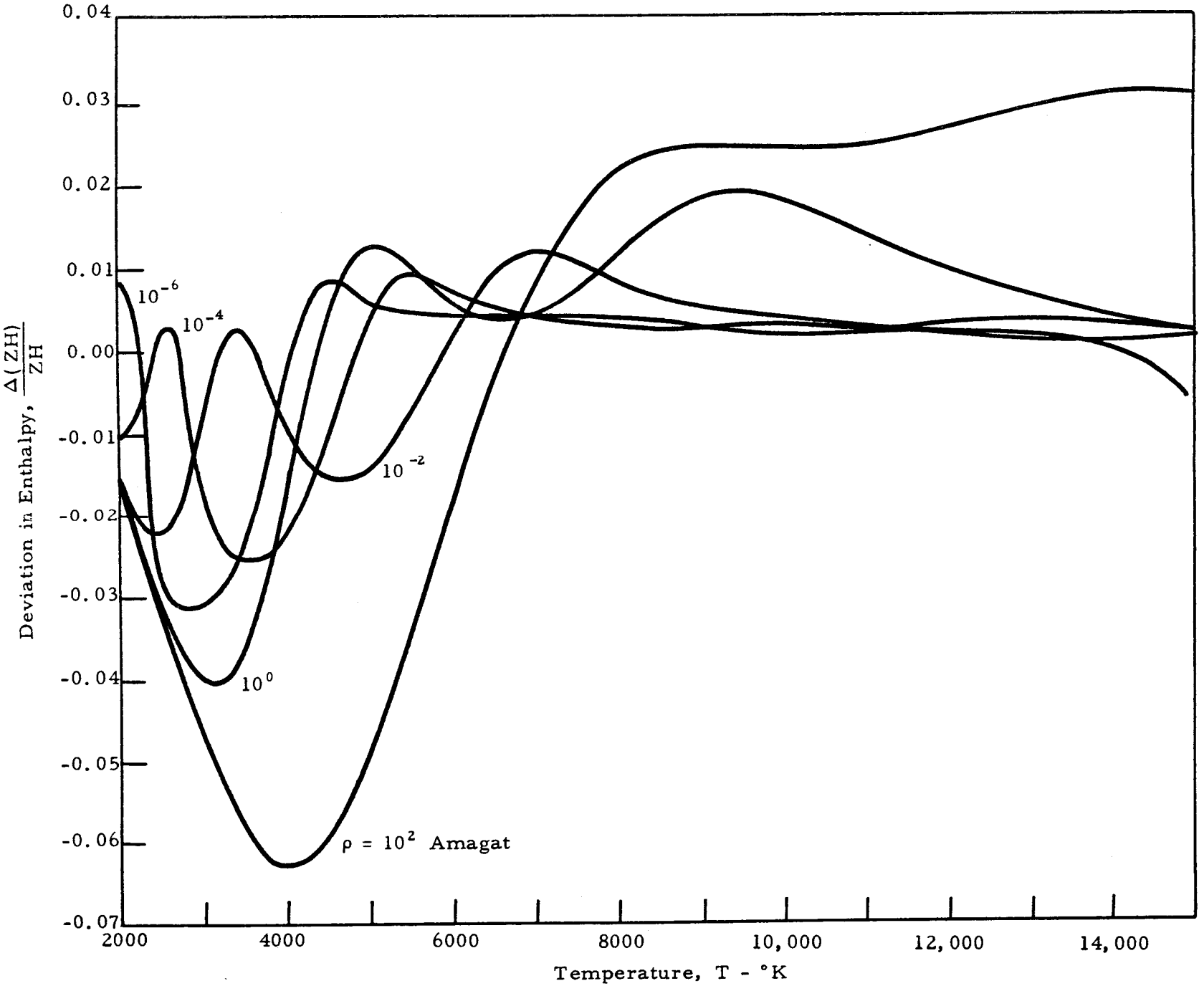

Figure 2. Error in Enthalpy as a Function of Temperature and Density

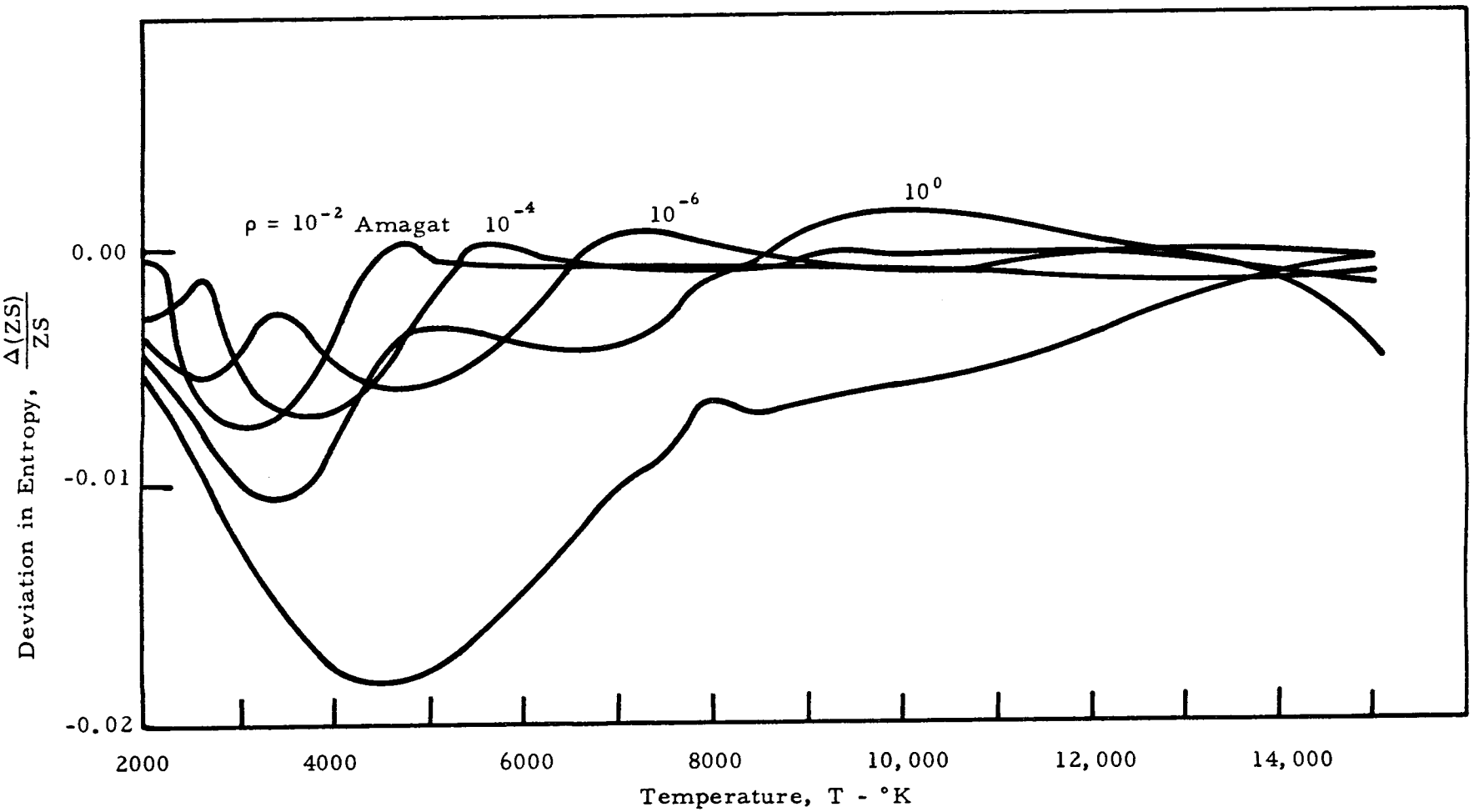

Figure 3. Error in Entropy as a Function of Temperature and Density

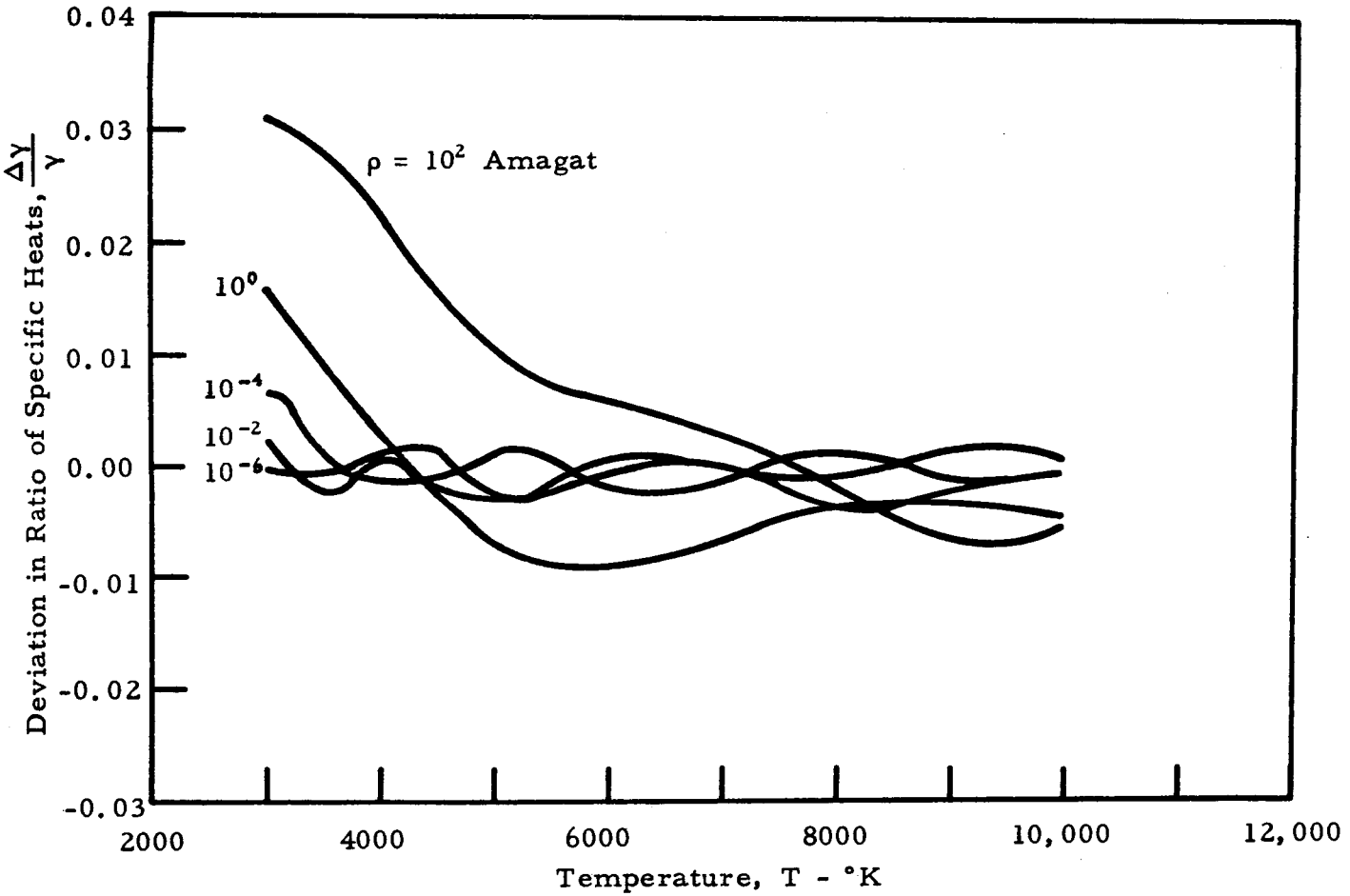

Figure 4. Error in Polytropic Exponent as a Function of Temperature and Density

CONCLUSIONS

The use of classical Boltzmann statistical mechanics provides an adequate thermodynamic approximation to the equilibrium properties of atmospheric air at low densities, i. e., high altitudes. The development of the FORTRAN digital computer subroutine has allowed versatility in the utilization of high speed computational techniques for various compressible flow problems.

REFERENCES

1. Davidson, N., Statistical Mechanics, McGraw Hill Book Company, N. Y. (1962).

2. Hansen, C. F., "Approximations for the Thermodynamic and Transport Properties of High-Temperature Air," NASA TR-R-50 (1959).

3. Hilsenrath, J. and Beckett, C. W., "Tables of Thermodynamic Properties of Argon-Free Air to 15000 °K," RAND Report RM-1543 (1955).

LIST OF FORTRAN PROGRAM

SUBROUTINE PARFN

```
      SUBROUTINE PARFN %TT,P,GAMMA,Z,RC,ASND,ZH,ZS¤
      I#TT
C     CALCULATION OF ENTROPY,ENTHLPY,SOUND SPEED,CP,CV,GAMMA,EQUILIBRIUM
C
C     CONSTANTS,PARTITION FUNCTIONS,MOL FRACTIONS,ELECTRON COCENTRATIONS
C     AND SEVERAL OTHER PARAMETERS FOR AIR IN THERMAL EQUILIBRIUM GIVEN
C     TEMPERATURE AND PRESSURE OF THE STREAM
      ECHRG#4.80286E-10
      BK#    1.384056E-16
      RU#.082054
      XXX#RU*288.
      AVNO#6.025E23
 4002 TLN # LOGF%T¤
      PLN # LOGF%P¤
      RT#RU*T
      CRT # P/RT
      RUN#LOGF%CRT¤
      Q  N2 # 3.5*LOGF%T¤-0.42-LOGF%1.-EXPF%-3390./T¤¤ -LOGF%P¤
     OQ O2 # 3.5*  TLN   &0.11-LOGF%1.-EXPF%-2270./T¤¤ & LOGF%3.&2.*EXPF
     1%-11390./T¤ &EXPF%-18990./T¤¤ - PLN
```

LIST OF FORTRAN PROGRAM

SUBROUTINE PARFN

```
OQ O1 # 2.5* TLN      & 0.5& LOGF%5.&3.*EXPF%-228./T¤&EXPF%-326./T¤&
15.*EXPF%-22800./T¤&EXPF%-48600./T¤¤-PLN
OQ N1 # 2.5*TLN     &0.3 &LOGF%4.&10.*EXPF%-27700./T¤ & 6.*EXPF%-415
100./T¤¤ - PLN
OQ OP # 2.5*TLN      &0.5 &LOGF%4.& 10.*EXPF%-38600./T¤ & 6.* EXPF%-
158200./T¤¤ - PLN
OQ NP # 2.5*TLN      &0.3 & LOGF%1.&3.*EXPF%-70.6/T¤&5.*EXPF%-188.
19/T¤ & 5.*EXPF%-22000./T¤ &EXPF%-47000./T¤ & 5.*EXPF%-67900./T¤¤ -
2PLN
OQ E # 2.5 * TLN      - 14.24 - PLN
 QC N2 #RLN & Q N2
 QC O2 #RLN & Q O2
 QC O1 #RLN & Q O1
 QC N1 #RLN & Q N1
 QC NP #RLN & Q NP
 QC OP #RLN & Q OP
 QC E  #RLN  &Q  E
 QP N2 #PLN & Q  N2
 QP O2 #PLN & Q  O2
 QP O1 #PLN & Q  O1
```

LIST OF FORTRAN PROGRAM

SUBROUTINE PARFN

```
      QP OP #PLN & Q  OP
      QP N1 #PLN & Q  N1
      QP NP #PLN & Q  NP
      QPE   #PLN & Q  E
C
C
C                          NOTE- GAS INPUT NUMBERS
C          1-N2,      2-O2,      3-O,      4-N,      5-N&      6-O&      7-E-
C
C
      A1#1.5
      R#3390./2./T
      B1#EXPF%R□
      B2#EXPF%R*%-1.□□
      SINH#0.5*%B1-B2□
      CV1#2.5&%1695./T/SINH□**2
      A7 # 1.5
      CV7 # 1.5
      A#2.*EXPF%-11390./T□
      CV2 #%11390./T□**2 * A
```

LIST OF FORTRAN PROGRAM

SUBROUTINE PARFN

```
A2# 11390./T * 2.* EXPF%-11390./T¤
A2P # A2 • T/11390. & 3.
A#EXPF%-18990./T¤
A2P#A2P & A
CV2 # %18990./T¤**2 • A & CV2
A2 # A2 & 18990.* EXPF %-18990./T¤/T
CV3# %2270./2./T¤
BB1#EXPF%CV3¤
BB2#EXPF%CV3*%-1.¤¤
SINH#0.5*%BB1-BB2¤
CV2#2.5&CV2/A2P-%A2/A2P¤**2&%CV3/SINH¤**2
A2 # 1.5 & A2/A2P
A # EXPF%-228./T¤ • 3.
CV3#%&228./T¤**2*A
A3 #228./T*A
A3P #A&5.
A # EXPF %-326./T¤
CV3#CV3&%326./T¤**2*A
A3 # A3 & 326./T • A
A3P # A3P & A
```

LIST OF FORTRAN PROGRAM

SUBROUTINE PARFN

```
A # EXPF%-22800./T□ * 5.
CV3#CV3&%22800./T□**2*A
A3 # A3 & 22800./T *A
A3P # A3P & A
A # EXPF%-48600./T□
CV3#CV3&%48600./T□**2*A
A3 # A3 & 48600./T * A
A3P # A3P & A
CV3#1.5&CV3/A3P-%A3/A3P□**2
A3 # 1.5 & A3/A3P
A # 10./ EXPF%27700./T□
CV4#%27700./ T□**2 * A
A4 #27700./T*A
A4P #A&4.
A # 6./EXPF%41500./T□
CV4 # %41500./T□**2 * A & CV4
A4 # A4 & 41500./T * A
A4P # A4P & A
CV4 # 1.5 & CV4/A4P - %A4/A4P□**2
A4 # 1.5 & A4/A4P
```

LIST OF FORTRAN PROGRAM

SUBROUTINE PARFN

```
A # 3./EXPF%70.6/T□
CV5 # %70.6/T□**2 • A
A5#70.6/T*A
A5P#A&1.
A#5.* EXPF%-188.9/T□
CV5 # CV5 & %188.9/T□**2 * A
A5 # A5 & 188.9/T *A
A5P # A5P &A
A # 5.*EXPF%-22000./T□
CV5 # CV5 & %22000./T□**2 • A
A5 # A5 & 22000./ T * A
A5P # A5P & A
A # EXPF%-47000./ T□
CV5#CV5 & %47000./T□**2* A
A5 # A5 & 47000./T *A
A5P # A5P & A
A#EXPF%-67900./T□*5.
CV5 # CV5 & %%67900.□/T□**2*A
A5 # 67900./T * A & A5
A5P # A5P &A
```

LIST OF FORTRAN PROGRAM

SUBROUTINE PARFN

```
CV5 # 1.5 & CV5/A5P - %A5/A5P□**2
A5 # 1.5 & A5/A5P
A # EXPF%-38600./T□ • 10.
CV6 # %38600./T□**2 • A
A6 #38600./T*A
A6P#A&4.
A # EXPF%-58200./T□ • 6.
CV6 # %58200./T□**2 • A & CV6
A6 # A6 & 58200./T • A
A6P # A6P & A
CV6#1.5&CV6/A6P-%A6/A6P□**2
A6 # 1.5 & A6/A6P
A1#2.5&3390./T/%EXPF%3390./T□-1.□
A2#A2&1.&2270./T/%EXPF%2270./T□-1.□
H1 # A1 &1.
H2 # A2 &1.
H3 # A3&1.
H4 # A4&1.
H5 # A5&1.
H6 # A6&1.
```

LIST OF FORTRAN PROGRAM

SUBROUTINE PARFN

```
H7 # A7&1.
CP1 # CV1 &1.
CP2 # CV2 &1.
CP3 # CV3 &1.
CP4 # CV4 &1.
CP5 # CV5 &1.
CP6 # CV6 &1.
CP7 # CV7 &1.
S1 # QPN2 & H1
S2 # QPO2 & H2
S3 # QPO1 & H3
S4 # QPN1 & H4
S5 # QPNP & H5
S6 # QPOP & H6
S7 # QPE & H7
AKP1#-59000./T &2.* QPO1-QPO2
AKP2#-113200./T&2.• QPN1-QPN2
AKP3#0.2*%-158000./T& QPOP & QPE - QPO1¤
AKP3#AKP3 & 0.8 *%-168800./T & QPNP & QPE - QPN1¤
C#LOGF%RT¤
```

LIST OF FORTRAN PROGRAM

SUBROUTINE PARFN

```
      AKC1#AKP1-C
      AKC2#AKP2-C
      AKC3#AKP3-C
      TDKC1 # 59000./T & 2.*A3-A2
      TDKC2 #113200./T & 2.*A4 - A1
      TDKC3 #0.2*%158000./T & A7&A6-A3¤
      TDKC3 # TDKC3 & 0.8*%168800./T & A7 &A5-A4¤
      TDKP1 # TDKC1 & 1.
      TDKP2 # TDKC2 & 1.
      TDKP3 # TDKC3 & 1.
      IF%AKP1¤50,60,50
50    AK # ABSF%AKP1¤
      AKR # AKP1 / AK
      IF%AK-85.¤60,70,70
70    IF%AKR¤71,71,72
71    EP1#0.
      DEP 1 P # 0.
      DEP 1 R # 0.
      GO TO 40
72    EP1#.2
```

LIST OF FORTRAN PROGRAM

SUBROUTINE PARFN

```
      DEP 1 P # 0.
      DEP 1 R # 0.
40    IF%AKP2¤51,61,51
51    AK # ABSF%AKP2¤
      AKR # AKP2 / AK
      IF%AK-85.¤61,74,74
74    IF%AKR¤75,75,76
75    EP2#0.
      DEP 2 P # 0.
      DEP 2 R # 0.
      GO TO 41
76    EP2#.8
      DEP 2 P # 0.
      DEP 2 R # 0.
41    IF%AKP3¤52,62,52
52    AK # ABSF%AKP3¤
      AKR # AKP3 / AK
      IF%AK-85.¤62,90,90
90    IF%AKR¤91,91,92
91    EP3#0.
```

LIST OF FORTRAN PROGRAM

SUBROUTINE PARFN

```
      DEP 3 P # 0.
      DEP 3 R # 0.
      GO TO 42
92    EP3#1.
      DEP 3 P # 0.
      DEP 3 R # 0.
      GO TO 42
60    A#4.*P/EXPF%AKP1¤
      EP1 #%- 0.8 & SQRTF%0.64&0.8*%1.& A¤¤¤ / 2./%1.&A¤
      IF%EP1-0.2¤77,72,77
 77   DEP1P#TDKP1/T/%2./EP1-1./%1.&EP1¤&1./%0.2-EP1¤¤
      DEP1R # TDKC1/T/ %2./EP1 & 1./%0.2-EP1¤¤
      GO TO 40
61    A#4.*P/EXPF%AKP2¤
      EP2 # %-0.4 & SQRTF%0.16 & 3.84 * %1.&A¤¤¤/2./%1.&A¤
      IF%EP2-0.8¤88,76,88
 88   DEP2P # TDKP2/T/%2./EP2-1./%1.2&EP2¤ & 1./%0.8-EP2¤¤
      DEP2R # TDKC2/T/%2./EP2& 1./%0.8-EP2¤¤
      GO TO 41
62    EP3#1./%SQRTF%1.&P/EXPF%AKP3¤¤¤
```

LIST OF FORTRAN PROGRAM

SUBROUTINE PARFN

```
      IF%EP3-1.0¤99,92,99
   99 DEP3P # TDKP3/T/%2./EP3-1./%1.&EP3¤&1./%1.-EP3¤¤
      DEP3R # TDKC3/T/%2./EP3&1./%1.-EP3¤¤
   42 Z # 1. & EP1 &EP2 & 2.*EP3
      ZCRT#CRT/Z/XXX
      XO2 # %0.2 - EP1¤/Z
      X N2 # %0.8 - EP2¤/Z
      XO1 # %2.*EP1 - 0.4*EP3¤/Z
      X N1 # %2.*EP2 - 1.6*EP3¤/Z
      X PI # 2. * EP3/Z
      X E # XPI
      XNI#0.8*XPI
      XOI#0.2*XPI
     OE # XN2*A1&XO2*A2&XO1*%A3&29500./T¤&XN1*%A4&56600./T¤
     1&XOI*%187500./T&A6¤&XNI*%225400./T&A5¤&XE*A7
      ZE # Z*E
      ZH # ZE& Z
      S # XN2*S1&XO2*S2&XO1*S3&XN1*S4&XE*%0.2*S6&0.8*S5 &S7¤
      IF%XN2¤1,1,2
    1 T1#0.
```

LIST OF FORTRAN PROGRAM

SUBROUTINE PARFN

```
      GO TO 10
    2 T1#XN2*LOGF%XN2¤
   10 IF%XO2¤3,3,4
    3 T2#0.
      GO TO 11
    4 T2#XO2*LOGF%XO2¤
   11 IF%XN1¤5,5,6
    5 T3#0.
      GO TO 12
    6 T3#XN1*LOGF%XN1¤
   12 IF%XO1¤7,7,8
    7 T4#0.
      GO TO 13
    8 T4#XO1*LOGF%XO1¤
   13 IF%XE¤9,9,14
    9 T5#0.
      GO TO 15
   14 T5#XE*LOGF%XE¤*2.
   15 XLN#T1&T2&T3&T4&T5
      ZS # Z * %S - XLN - PLN¤
```

LIST OF FORTRAN PROGRAM

SUBROUTINE PARFN

```
      CZE # XN2*CV1&XO2*CV2&XN1*CV4 &XO1*CV3&XE*%0.2*CV6&0.8*CV5&CV7¤
     ODZE #-DEP1R*A2-DEP2R*A1&%2.*DEP1R-0.4*DEP3R¤*%A3&29500./T¤&%2.*DEP
     12R-1.6*DEP3R¤*%A4& 56600./T¤&2.*DEP3R*%0.2*%A6&187000./T¤&0.8*%A5&
     2225400./T¤ & A7¤
      ZCV # Z*CZE & T* DZE
      CZE # CZE  & 1     .
     ODZE #-DEP1P*A2-DEP2P*A1&%2.*DEP1P -0.4*DEP3P¤*%A3&29500./T¤&%2.*DE
     1P2P-1.6*DEP3P¤*%A4& 56600./T¤&2.*DEP3P*%0.2*%A6&187500./T¤&0.8*%A5
     2&225400./T¤&A7¤
     ODZE # DZE & %2.*DEP1P-.4*DEP3P¤-DEP1P-DEP2P&%2.*DEP2P-1.6*DEP3P¤&
     14.*DEP3P
      ZCP # T* DZE & Z* CZE
      RC # %ZCP - ZCV¤/ Z
      GAMMA # ZCP/ZCV
C     ASND # A**2*CRT/P
     OASND # GAMMA*%%1.& T/Z*%DEP1R &DEP2R&DEP3R¤¤/%1.&T/Z*%DEP1P&DEP2P&
     1DEP3P¤¤¤
      RETURN
      END
```