THE CALCULATION OF CHEMICAL AND

IONIZATION EQUILIBRIUM IN A

CONVENTIONAL SHOCK TUBE

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by

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ABSTRACT

The equations describing a plasma in local thermodynamic equilibrium are presented and applied to a conventional shock tube. If conditions of local thermodynamic equilibrium exist, these equations give the number densities of the atoms, molecules, ions and electrons that make up the plasma.

For practical results an effective iteration scheme is presented for the computer solution of such equations.

I. Introduction

One of the fundamental problems of astrophysics is the determination of absolute absorption coefficients and oscillator strengths of atomic and molecular systems. For all molecular and all but the simplest of atomic systems we must rely on the experimental determination of these values. Toward the solution of many of these problems a shock tube may be used successfully. One particular advantage of shock tubes is the high temperature at which the experiment may be performed. The most important advantage, however, is that shock tubes produce a volume of gas that is usually in local thermodynamic equilibrium (LTE), a fact allowing an experimenter to determine more or less precisely the number of emitters or absorbers in the line of sight. This report will exhibit those equations describing the situation of thermodynamic equilibrium which predict the equilibrium number densities of the various chemical species present. A practical method of solution will be explained.

The equilibrium theory is valid for all practical ranges of temperature and pressure, subject to certain steady state and relaxation arguments. The relaxation time, in conjunction with the specific design of the shock tube, will dictate the range of thermodynamic parameters over which experiments may

be performed. Thus, when we are forced to limit our discussion to specifics, we will be directing our attention to those conditions found in the reflected shock produced in a conventional tube in the laboratory. In such tubes, one has a low molecular weight gas at high pressure separated by a diaphragm from a high molecular weight inert gas at low pressure. Usually a small percentage of the atom or molecule in question has been mixed with the inert gas. When the diaphragm is broken, a shock travels down through the low pressure gas and reflects back from the end of the tube. The conditions behind this reflected shock are steady over a few hundred microseconds and all measurements are made in or through the gas behind the reflected shock. The reader is referred to Gaydon and Hurle (1963) for a more complete description of reflected shock techniques. In short, we are addressing our primary attention to a uniform volume of gas characterized by the following ranges of parameters:

$$\text{Delay after shock:} \quad \geqslant 100 \ \mu\text{sec} \qquad (1)$$

$$\text{Temperature:} \quad 3500 - 7500°\text{K} \qquad (2)$$

$$\text{Total particle density:} \quad 5 \times 10^{18} - 10^{20} \text{cm}^{-3} \quad (3)$$

At lower temperatures and densities, many molecular systems may not have had time to relax within the allowed time. Higher temperatures and densities are more or less limited by the

experimental technique. Finally, the particular method of solution discussed in this paper becomes less efficient beyond both the upper and lower limits of the above thermodynamic parameters.

II. Equilibrium Relations

Consider a uniform volume of gas in complete thermodynamic equilibrium. We will make the assumption that the gas is an ideal one such that

$$p = NkT \quad , \tag{4}$$

where p is the pressure, N is the total number of particles per unit volume, k is Boltzmann's constant, and T is the absolute temperature (°K). The assumption of an ideal gas is quite reasonable because of the restrictions imposed by relations (2) and (3). It can be shown, for instance, that coulomb effects on the pressure are negligible. We let the gas be composed of various atomic and molecular species that may react chemically with each other in equilibrium. Such interactions may involve the simple dissociation-recombination of species A and B,

$$A + B \rightleftharpoons AB \quad .$$

Of course one may postulate more complicated chemical interactions such as

$$AB + CD \rightleftharpoons AC + BD$$

or

$$A + B + C \rightleftharpoons ABC \quad ,$$
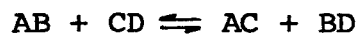
but these can ultimately be expressed in the forms of simple

dissociation-recombination reactions, viz.,

$$(AB) + (CD) \rightleftharpoons (ABCD) \rightleftharpoons (AC) + (BD)$$

$$(A + B) + C \rightleftharpoons (ABC) \quad .$$

In the identical framework we can consider ionization-recombina-

tion processes:

$$A^+ + e \rightleftharpoons A \quad .$$

Statistical mechanics (e.g., Fowler and Guggenheim, 1952)

provides the fundamental relations from which all chemical

equilibria may be calculated. For any species A and B (where

A or B may be an atom, molecule, ion or electron) in equilibrium

with their compound AB, the number densities n_A, n_B and n_{AB}

of species A, B, and AB are related by

$$\frac{n_A n_B}{n_{AB}} = \frac{Q_A Q_B}{Q_{AB}} \tag{5}$$

where Q_A is the partition function, or state sum, of species

A, etc. In all cases the partition function is simply a weighted

sum, over all discrete and continuous energy states, of the

probability of finding the molecule in each state (molecule is

used here in the general sense). It may be thought of as a

normalization factor for the ways of distributing the energy in

the states. Classical statistics, which apply to all particles

of present interest in normal ranges of temperature and pressure,

give the partition function as

$$Q = \sum_{\text{all levels}} g_i e^{-E_i/kT} \tag{6}$$

where g_i is the statistical weight of level i, and E_i is the energy of the ith level above the reference level. Equation (6) is applicable to any molecule, but its detailed calculation is in general prohibitively difficult. For any sort of practical application, the calculation of the partition function must be broken down and simplified.

With the assumption of a perfect gas we may introduce an immediate simplification to equation (6). As the individual particles do not interact with each other, except for short-term collisions, the internal energy of the molecule will be essentially decoupled from the external, or kinetic energy of the molecule. The partition function is then written

$$Q = \sum_{\text{external}} g_i e^{-E_i/kT} \cdot \sum_{\text{internal}} g_i e^{-E_i/kT} = Q_{ext} \cdot Q_{int} . \tag{7}$$

Q_{ext} is sometimes called the translational partition function and is readily evaluated from elementary quantum mechanics by considering the classical problem of the particle in the box. Details may be found in Morse (1964). The result is a familiar one:

$$Q_{ext} = \left(\frac{2\pi MkT}{h^2} \right)^{\frac{3}{2}} \tag{8}$$

where M is the mass of the molecule, k is Boltzmann's constant, and h is Planck's constant.

Except for the case of simple atoms, the evaluation of Q_{int} remains a difficulty. The standard procedure for non-monatomic molecules is, first of all, to invoke the Born-Oppenheimer approximation (1927), which allows one to neglect the electrons when considering the remaining degrees of freedom of the molecule. In other words, the Born-Oppenheimer approximation permits the separation of the molecular wave function, ψ, as

$$\psi = \psi_{nuclei} \; (\eta) \cdot \psi_{elec} \; (\zeta, \; \eta) \quad , \tag{9}$$

where η represents the coordinates of the two nuclei and ζ represents electron coordinates.* The next approximation is the assumption of the separability of the modes of the nuclei such that

$$\psi_{nuclei}(\eta) = \psi(r, \theta, \varphi) = \frac{1}{r} \, \psi_{vib}(r) \cdot \psi_{rot}(\theta, \varphi) \; . \tag{10}$$

This approximation requires treating a pure vibration and a rigid rotation independently. In these approximations the energy contributions of the various modes are simply additive:

$$E_{int} = E_{vib} + E_{rot} + E_{elec} \quad , \tag{11}$$

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* Note, however that ψ_{nuclei} is in fact determined primarily by the electronic structure.

and the internal partition function is the corresponding product:

$$Q_{int} = Q_{vib} \cdot Q_{rot} \cdot Q_{elec} \qquad \text{[diatomic and poly-} \qquad (12)$$
$$\text{atomic molecules].}$$

Toward higher temperatures the validity of equation (10) begins

to break down and the system is better treated as an anharmoni-

cally vibrating rotator (see Mayer and Mayer, 1940). For diatomic

molecules the rotational-vibrational part of the partition

function can be evaluated for the anharmonic oscillator (and if

necessary, for the non-rigid rotator) without the simplification

of equation (10); and a discussion of this is presented in the

Appendix. For many problems the simpler approximations are

adequate, and we continue the development from that point of

view with its extensions to polyatomic molecules.

The nuclear spins of the atoms comprising a molecule each

contribute a constant factor $(2S_{nuc} + 1)$ to the statistical

weight, and this same degeneracy is retained as the atoms form

a molecule, so long as the atoms are distinguishable (i.e., the

molecule is heteronuclear). For such cases, these contributions

obviously cancel in equation (5), and they need not be carried

through the analysis for evaluation. However, for molecules

containing indistinguishable component atoms the nuclear spins

play an additional, more complicated role that restricts the

rotational eigenvalues. This in turn is manifested in Q_{rot},

the rotational partition function (see Fowler and Guggenheim, 1952).

The rotational partition function,

$$Q_{rot} = \sum_{rot.\ levels} g_i e^{-E_i/kT} \quad , \tag{13}$$

can be evaluated with the assumption that the molecule is a rigid rotator (see Pauling and Wilson, 1935). For a hetero-nuclear diatomic molecule the energy eigenvalues are given by

$$E_J = J\ (J + L)\ \frac{h^2}{8\pi^2 \mu r_e^2} \qquad [\text{diatomic, heteronuclear}] \tag{14}$$

where J is the rotational quantum number, and r_e is the equilibrium separation between the two nuclei, evaluated for the lowest vibrational level of the ground electronic state. Here

$$\mu = \frac{M_A \cdot M_B}{M_A + M_B} \tag{15}$$

is the reduced mass, M_A and M_B being the masses of the component nuclei. Each level, E_J, has a statistical weight $(2J + 1)$. We can immediately generalize equation (14) to include polyatomic linear molecules by identifying μr_e^2 with the transverse moment of inertia, I_A. Then equation (13) leads to

$$Q_{rot} = \sum_{J=0}^{\infty} (2J + 1) \cdot e^{-J(J + 1)\ h^2/8\pi^2 I_A kT} \qquad [\text{linear, heteronuclear}] \tag{16}$$

For shock tube temperatures a direct summation is unreasonable as well as unnecessary, and equation (16) may instead be evaluated by an asymptotic series (see Herzberg, 1945) or by

simply replacing the sum by an integral over J. In either case

the result is the same and is equal to the result one obtains

from classical statistics:

$$Q_{rot} = \frac{8\pi^2 I_A kT}{h^2} \qquad \text{[linear, heteronuclear]} \qquad (17)$$

For a diatomic homonuclear molecule the summation in equation

(16) must omit every other J-value because of symmetry require-

ments; and while the details of which J-values are to be omitted

depend on the value of the nuclear spin, the difference is

purely an academic one at high temperatures, with the result

in either case being a factor of two in Q_{rot}. We can thus

generalize equation (17) to apply to all linear molecules:

$$Q_{rot} = \frac{8\pi^2 I_A kT}{\sigma h^2} \quad , \qquad \text{[linear]} \qquad (18)$$

where σ, the symmetry factor, is the number of indistinguishable

orientations of the molecule. Unfortunately, attempts to cal-

culate the Q_{rot} for non-linear polyatomic molecules in the

same manner, as developed in equations (14) through (18), are

not successful, because there are no explicit formulae for the

energy levels (Herzberg, 1945). However, because of the high

shock tube temperature, we are well justified in simply adopting

the classical result (see Mayer and Mayer, 1940):

$$Q_{rot} = \frac{16\pi^3}{\sigma h^3} \cdot \sqrt{2\pi I_A I_B I_C (kT)^3} \quad , \quad \text{[non-linear]} \qquad (19)$$

where I_A, I_B and I_C are the principal moments of inertia, and σ is the symmetry number defined above. The moments of inertia are deduced from spectroscopic data.

The vibrational partition function

$$Q_{vib} = \sum_{vib.\ levels} g_i e^{-E_i/kT} \tag{20}$$

can be easily evaluated if we assume the molecules to behave as a simple harmonic oscillator. Again, the problem is one from elementary quantum mechanics. The energy eigenvalues are given by

$$E_v = hc\omega (v + \tfrac{1}{2}) \quad v = 0, 1, 2 \ldots, \tag{21}$$

where c is the velocity of light and ω is the fundamental vibration frequency of the molecule in its ground electronic state. ω is obtained experimentally from spectroscopic data. Since the statistical weight of all levels is unity, the vibrational partition function for diatomic molecules is given by

$$Q_{vib} = \sum_{v=0}^{\infty} e^{-hc\omega v/kT} = \left(1 - e^{-hc\omega/kT} \right)^{-1} \quad \text{[diatomic]} \tag{22}$$

Note that in writing the vibrational energy in this fashion we have arbitrarily set the zero energy of the molecule at the lowest vibrational level rather than the minimum of the vibrational potential well. Equation (22) applies only to diatomic molecules. For a polyatomic molecule, the calculation

of the vibrational partition function is a more complicated

process. The common procedure is to assume that each mode of

vibration is decoupled from the other, and that therefore the

total partition function is given by the products of individual

vibrational partition functions. This is expressed generally as

$$Q_{vib} = \prod_{i=1}^{3n-x} \left(1 - e^{-hc\omega_i/kT}\right)^{-1} \quad , \quad [polyatomic] \quad (23)$$

where n is the number of atoms in the molecule, and x is 5 for

linear molecules and 6 for non-linear molecules. Mathematically,

equation (22) can be considered a special case of (23).

The electronic partition function

$$Q_{elec} = \sum_{elec. \ levels} g_i e^{-E_i/kT} \quad (24)$$

is evaluated by considering the levels combined in spectroscopic

terms. The term energies are obtained experimentally and are

completely similar to atomic terms, with the convention that

the term energy is evaluated for the $v = 0$ vibrational level.

The evaluation of the statistical weights, the g_i's, is, however,

not analogous to the $(2S + 1)(2L + 1)$ factor appropriate to

atoms. The reason for this is that orbital angular momentum

of multi-atomic molecules is primarily a rotational phenomenon.

The correct electronic statistical weight of a molecular term is

$$g = (2S + 1)(2 - \delta_{0\Lambda}) \quad , \quad (25)$$

where (2S + 1) is the normal spin multiplicity, δ represents the Dirac delta function, and Λ is the quantum number of the angular momentum of the electrons about the internuclear axis (e.g., $\Lambda = 0$ for Σ terms, $\Lambda = 1$ for Π terms, etc.). This latter contribution to the degeneracy is a manifestation of the so-called Λ-doubling (see Herzberg, 1950). From a computational viewpoint there is no difficulty including higher terms, but in most practical cases only the ground term contributes significantly to the partition function. Should a particular molecule (MgO, for instance) have extremely low-lying electronic levels that contribute to the sum in equation (24), then the question of the validity of the Born-Oppenheimer approximation must be examined.

For atoms and their ions there are no rotational and vibrational degrees of freedom, and the internal partition function is the usual sum over all electronic energy levels:

$$Q_{int} = Q_{elec} = \sum_{\substack{all \\ levels}} (2J_i + 1) \, e^{-E_i/kT} \quad [atoms] \qquad (26)$$

Particularly in the shock tube, this sum will not be infinite because of plasma effects that lower the ionization potential, and there is no difficulty in the evaluation of equation (26). For practical purposes Drawin and Felenbok (1965) have computed elaborate tables of the internal partition function of atoms

and their ions.

In the Saha equation [the ionization counterpart of the chemical equilibrium relation (5)] the partition function of the free electron enters; this always takes the value 2 to account for the two possible spin orientations.

In all the foregoing developments we have referenced the arbitrary energy scale to the ground level of the atom or molecule. The most important point of the equilibrium relation (5) is that the energy scales of components A and B and their compound AB must be referenced to the same common energy. If we arbitrarily set the zero energy at the ground level of the separated components, then the ground state of the compound is at $-D_{AB}$, the dissociation energy* of the molecule (or $-I_A$, the ionization energy* of the neutral), and to the energies in the partition function (6) of the compound there must be added the appropriate constant.

Summarizing the foregoing, we obtain the following equation:

$$\frac{n_A + n_e}{n_A} = \left(\frac{2\pi m_e kT}{h^3} \right)^{\frac{3}{2}} \frac{Q_{int,A+} \cdot 2}{Q_{int,A}} \cdot e^{-I_A/kT} \tag{27}$$

where m_e is the mass of the electron; A+ refers to the ion of species A; $Q_{int,A}$ refers to the internal partition function appropriate to species A (equations 12 - 26), etc.; and

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* Both I_A and D_{AB} may be subject to plasma effects that cause an effective lowering of the theoretical values.

I_A is the ionization potential of species A. Here species A

is taken in the general sense and can be either a molecule or

a single atom. Equation (27) is known as the Saha equation.

We may also write

$$\frac{n_A n_B}{n_{AB}} = \left(\frac{2\pi\mu kT}{h^2} \right)^{\frac{3}{2}} \frac{Q_{int,A} \cdot Q_{int,B}}{Q_{int,AB}} e^{-D_{AB}/kT} \qquad (28)$$

where μ is the reduced mass defined by equation (14) and D_{AB}

is the dissociation energy of the A, B, AB reaction. Again,

A and B themselves can be either molecules or single atoms.

There exist three additional types of equations that will

completely determine the equilibrium concentrations of the

various species of the plasma. Charge neutrality requires

that

$$n_e = \sum_A n_{A+} \qquad , \qquad (29)$$

where we include all appropriate atomic and molecular ions.

Conservation of atomic nuclei requires that

$$N_\alpha = n_\alpha + n_{\alpha+} + \sum_A \nu_{A,\alpha} (n_A + n_{A+}) \qquad (30)$$

where α, alone, refers to a single atomic species (not a molecule)

and N_α is the total density of nuclei of type α (occurring in

atoms, ions and molecules). The summation is over all molecules

and molecular ions that contain atom α, with the coefficient

$\nu_{A,\alpha}$ the number of atoms α in molecule A. The necessary

normalization is given by the perfect gas law, following the basic assumption of equation (4):

$$n_e + \sum_A (n_A + n_{A+}) = \frac{p}{kT} \quad , \tag{31}$$

where the summation is over all molecules and atoms, and p and T are the measured pressure and temperature. Absolute values of the densities of atomic nuclei, N_α, are then obtained from equation (31) once the _relative_ nuclear densities are given as part of the problem specification.

The foregoing set of equations, (27) through (31), are sufficient for problem solution. However, where ionization of diatomic and polyatomic molecules is considered, the problem is generally overdetermined because there are at least three energy-equivalent ways of forming molecular ions:

1) $A + B \rightarrow AB$; $AB - e \rightarrow AB^+$,

2) $A - e \rightarrow A^+$; $A^+ + B \rightarrow AB^+$,

3) $B - e \rightarrow B^+$; $A + B^+ \rightarrow AB^+$.

As a convention, we must select one path; sequence (1) is usually the least ambiguous. Similar problems enter with polyatomic molecules that can dissect themselves several different ways. Again, we must specify only one such possibility.

The solution of equations (27) through (31) is one of iteration, and one such method will be discussed in Section IV, below.

III. The Validity of LTE

A full discussion of the validity of the assumption of
LTE is beyond the scope of this report; to discuss this matter
adequately here would subvert the purpose. In fact, an adequate
discussion would lead from a small report to a large treatise.
However, we will briefly attempt to summarize the situation.

The great usefulness of the shock tube lies in the belief
that LTE holds, and there is considerable evidence supporting
this assumption. The readily observed fact that in a wide
variety of cases there exists a period (usually a few hundred
μsec) during which a steady temperature and pressure can be
measured certainly indicates that a type of equilibrium exists.
In recent years a number of experiments have been performed
which, for the most part, support the assumption of LTE; the
reader is referred to Greene and Toennies (1964) and Losev
and Osipov (1961) for a more complete discussion and excellent
bibliographies. Particular attention is called to the recent
work of Parkinson and Reeves (1964) and of Garton, Parkinson
and Reeves (1965), which indicates LTE among the bound and free
electronic levels of Ca I and Ca II.

For a theoretical discussion the reader is referred to
the work of Griem (1964) and to the paper of Losev and Osipov
(1961). The former is particularly enlightening and includes

a discussion of both steady state and relaxation problems. It is of interest to note that, while generally favorable, the theories do not always predict LTE in the shock tube.

Finally, we must add a general warning: situations may exist in which complete LTE does not obtain. Particular difficulties can arise with powered solids, with first ionization species, and with strongly bound molecules. The first of these, powdered solids, can suffer severely from inhomogeneities and relaxation difficulties. The second, ionized species, may not be in equilibrium because of relaxation problems with the ionization equilibrium. Lastly, molecules can constitute a very real equilibrium problem because many (particularly those with a high dissociation energy) are known to be very slow to dissociate. Greene and Toennies (1964) reproduce experimental results that dictate this conclusion and indicate that many molecules will not have relaxed dissociatively at the lower temperatures and densities given in relations (2) and (3); and molecules like N_2 and CO will prove to be problems at even higher temperatures and densities.

IV. The Method of Solution

Where equilibrium prevails, equations (27) through (31) constitute the problem to be solved. We will rewrite these

equations for convenience. Equations (27) and (28) yield

$$\frac{n_{A+} \cdot n_e}{n_A} = S_A \qquad (32)$$

$$\frac{n_A \cdot n_B}{n_{AB}} = K_{AB} \qquad (33)$$

Here again, A and B can refer to either atoms or molecules. To keep the problem properly defined we must have only one relation (32) for each molecular ion A+, and only one relation (33) for each compound AB. Equations (29) through (31) can be rephrased with

$$n_e = \sum_A n_{A+} \quad , \qquad (34)$$

where the summation is over all atoms and molecules, and

$$n_\alpha = N_\alpha - n_\alpha \left[\frac{S_\alpha}{n_e} + \sum_A \nu_{A,\alpha} \left(\frac{n_A}{K_{\alpha A}} + \frac{S_{\alpha A}}{n_e} \right) \right] , \qquad (35)$$

where α refers to atoms only. The particular arrangement of this equation is discussed below. The solution is normalized by the constraining equations

$$N_\alpha = R_\alpha \sum_\alpha N_\alpha \qquad (36)$$

and

$$2n_e + \sum_A n_A = C \quad . \qquad (37)$$

The specification of $\nu_{A,\alpha}$, C, R_α, S_A and K_{AB} defines the problem; the small n's constitute the unknowns.

These equations can be solved by a systematic iteration procedure. A number of schemes will suffice, but we have used one that is particularly suitable for shock tube problems outlined by relations (2) and (3). Under these conditions most of the atomic nuclei present will usually appear as free, neutral atoms rather than as ions or molecular components. The procedure, then, is to iterate on the number densities of the free, neutral atoms (n_α in the present notation). The scheme is as follows:

1) An initial guess is made for n_e. Using equations (32) for atoms only

$$n_e = (\sqrt{N_A S_A})_{max} \tag{38}$$

is determined, where N_A, as a first guess, assumes only neutral atoms exist.

2) An initial guess is made for each n_α. First, with n_α arbitrary, all equations (32) and (33) are investigated, and a label is associated with n_α denoting whether this atom tends more toward ionization or dissociation. If it is ionization-inclined, an initial guess is made for n_α:

$$n_\alpha = \frac{n_\alpha}{(1 + S_\alpha/n_e)} \tag{39}$$

If molecule-inclined, the initial guess is made as

$$n_\alpha = (K_{\alpha\beta} N_\alpha)^{\frac{1}{2}} \quad , \tag{40}$$

where $\alpha\beta$ is the dominating molecule containing atom α. n_β is initialized similarly. The right hand sides of equations (35) should be positive; if not, small adjustments in the n_α are made until this is so.

3) Densities of ions and molecules are computed according to equations (32) and (33), and a new trial electron density is computed according to (34).

4) $n_{\alpha(max)}$ and $n_{\alpha(min)}$, the maximum and minimum values for the atom densities are originally set at N_α and n_α, respectively.

5) The iteration proceeds on the right hand side of equation (35), as constrained by equations (36) and (37). As improved values of the n_α are calculated, the $n_{\alpha(max)}$ and $n_{\alpha(min)}$ are brought closer together until specified accuracy criteria are met. New trial values of n_α are calculated in the procedure by taking <u>geometric</u> means of the extreme values.* Number densities of ions and molecules are calculated as by-products. Electron densities from equations (32) and (34) are successively improved by taking geometric means.

This iteration scheme has been found to work well for a large number of shock tube problems. One percent accuracies are often obtained in three or four iterations; one-tenth

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* This procedure was suggested by G. Newsom.

percent accuracies in six or seven iterations. However, the scheme will not converge directly for problems with a high degree of ionization (some S_A large) or for problems with considerable molecular formation (some K_{AB} small), and as the iteration proceeds, checks on the convergence must be made, with the limits $n_{\alpha(min)}$ or $n_{\alpha(max)}$ adjusted appropriately. If the problem is such that this indirect path to convergence is necessary, it can take ten and twenty iterations to converge to one percent and one-tenth percent accuracy, respectively, for stubborn many-component problems. Thus, for unusually cool or unusually hot plasmas the iteration is less efficient, and similar statements apply to unusually dense or rare plasmas. However, while the efficiency will be somewhat poor, this scheme can be used successfully with most any laboratory or astrophysical plasma. For example, stellar atmosphere equilibrium can easily be treated, with certain limits placed on the number of possible reacting components. For extensive problems of this type it is usually advantageous to use more elaborate schemes such as the Newton-Raphson method (see Dolan, 1965).

V. Summary

We have presented the equations to be solved in the determination of the number densities of atoms, electrons, ions and

molecules in a shock tube, and a method of solution. The

brief discussion given here emphasizes the applicability of

the equilibrium physics described by these equations in a wide

variety of problems, yet points to possible deviations from

equilibrium--particularly with dissociating molecules.

Finally, the physics and mathematics discussed in this

report have been programmed in FORTRAN II for solution on an

IBM 7094 computer. The program is known as EXCIT4, and a copy

of the source deck with a set of operating instructions can

be obtained from this laboratory. The program has the option

of calculating the internal partition functions as discussed

in this report, or of interpolating these from tables. The

only restriction limiting its immediate use by others is that

the FORTRAN includes some half-dozen non-standard features

found on the Smithsonian Astrophysical Observatory FORTRAN

Monitor System.

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Appendix

The Validity of the Uncoupled Approximations

In the evaluation of internal partition functions of diatomic and polyatomic molecules in Section II, we have simplified the calculation by uncoupling the various modes from each other (cf. equations 11 and 12). As stated, this approximation gets worse at high temperatures. Here we briefly examine this effect.

We will assume the Born-Oppenheimer approximatiom holds, or, equivalently, that any important excited electronic states have rotational or vibrational constants and electronic degeneracies identical to those of the ground electron state-- generally a reasonable assumption. The problem is essentially that of analyzing the extent to which the harmonic oscillator approximates the anharmonic (Morse) oscillator.* For practical reasons we must restrict this discussion to diatomic molecules.

We examine three common molecules having rather different molecular constants: H_2, OH and CO. The behavior of these is indicative of the behavior of other molecules, although certain cases deserve special attention. With the molecular constants in Herzberg (1950), the coupled and uncoupled calculations have

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* It can be shown that any effects due to non-rigid rotation are entirely negligible.

been carried out and are displayed in Table 1. The comparisons illustrate that for the lower temperatures and the heavier molecules the harmonic oscillator approximation is generally adequate for the calculation of the partition functions. However, for lighter molecules (particularly H_2) and for higher temperatures, the approximations deteriorate. Whether or not one uses the harmonic approximation depends on a number of practical questions, since such a calculation is a simple one and the anharmonic one is a sum of several exponentials.* Attempts to calculate the partition function more accurately than this latter approximation usually encounter difficulties because of inadequacies in theory as well as in experimentally determined molecular data.

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* For a few of the most common diatomic molecules such calculations have been made by J. B. Tatum, to be published shortly in Volume 12 of the Pub. Dom. Ap. Obs. (1966).

<div align="center">

TABLE 1

</div>

		4000°K	5000°K	6000°K
H_2	$Q_{harmonic}$	29.5	40.8	53.9
	Q_{Morse}	31.0	43.8	59.5
OH	$Q_{harmonic}$	203	285	381
	Q_{Morse}	214	305	418
CO	$Q_{harmonic}$	2667	3891	5345
	Q_{Morse}	2734	4018	5564

The rotational-vibrational partition function of H_2, OH and CO. The harmonic oscillator approximation is given by

$$Q_{harmonic} = \frac{kT}{\sigma B_o hc} \cdot \left(1 - \exp\left[-\frac{hc\omega_e}{kT}\right]\right)^{-1}$$

The anharmonic oscillator approximation is given by

$$Q_{Morse} = \exp\left[\frac{hc}{2kT}\left(\omega_e - \tfrac{1}{2}\omega_e x_e\right)\right] \sum_{v=0}^{\frac{\omega_e}{2\omega_e x_e} - \frac{1}{2}} \frac{kT}{\sigma hc}\left(\frac{1}{B_e - \alpha_e(v-\tfrac{1}{2})}\right) \cdot$$

$$\cdot \exp\left[-\frac{hc}{kT}\left\{\omega_e(v+\tfrac{1}{2}) - \omega_e x_e(v+\tfrac{1}{2})^2\right\}\right].$$

Notation and molecular constants are taken from Herzberg (1950).

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13. ABSTRACT

The equations describing a plasma in local thermodynamic equilibrium are presented and applied to a conventional shock tube. If conditions of local thermodynamic equilibrium exist, these equations give the number densities of the atoms, molecules, ions and electrons that make up the plasma.

For practical results an effective iteration scheme is presented for the computer solution of such equations.

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