PRESSURE-TEMPERATURE BOUNDARIES FOR

IDEAL DISSOCIATING AND IONIZING GASES

by

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LIST OF SYMBOLS

A, B   neutral atoms

A_2 homonuclear diatomic molecule

AB   heteronuclear diatomic molecule

A^+, A^{++}, etc.   singly-positive, doubly-positive, etc., atomic ions

amu   atomic mass unit, 1 gm mole^{-1} ($= 1.6598 \times 10^{-24}$ gm particle^{-1})

C_K equilibrium constant coefficient, 0.05118142 atm amu$^{-3/2}$ $^oK^{-5/2}$

c_2 second radiation constant, 1.43880 cm ^oK

e   base of the natural logarithm, 2.718 .....

e^- free electron

F_p pressure conversion factor, 0.9869233×10^{-6} atm cm^2 dyne^{-1}

G_ρ coefficient constant of characteristic density, 6.2354×10^{-4} gm cm^{-3} amu$^{-5/2}$ $^oK^{-3/2}$

g   degeneracy of quantum states

h   Planck's constant, 6.62517×10^{-27} erg sec

I   molecular moment of inertia; ionization potential (e v)

J   inner quantum number

j   rotational quantum number

K   equilibrium constant (atm)

k   Boltzmann's constant, 1.38044×10^{-16} erg $^oK^{-1}$

k_e equilibrium force constant (dyne cm^{-1})

M   total mass of mixture (gm)

m	particle mass (gm particle^{-1}); mass in amu; angular momentum component quantum number
N	total number of particles
N_O	Avogadro's number, 6.02486×10^{23} particles mole^{-1}
n	vibrational quantum number; non-negative integer
P	total static pressure of mixture (atm)
p	static partial pressure (atm)
Q	partition function
R_O	gas constant, 8.31696×10^7 erg mole^{-1} $^{\circ}$K^{-1}
r	equilibrium radius of separation between atoms ($\overset{\circ}{A}$)
S	total spin quantum number
s	species and/or particle type; spin quantum number
T	temperature of mixture ($^{\circ}$K)
T_e	equilibrium molecular electronic energy (cm^{-1})
V	volume (cm^3)
x	mole fraction
Y	initial number of moles
Z	number of electrons in neutral atom
α	degree of reaction
β	number of moles of constituent
ϵ	particle energy (cm^{-1})
μ	reduced mass (amu)
ν	vibrational frequency (sec^{-1})
ρ	density (gm cm^{-3})
σ	symmetry number for diatomic molecules

Superscripts

E	electronic
i	index
j	index
m	number of electrons stripped from neutral atom
n	index; ionization level
R	rotational
T	translational
V	vibrational
+, ++, etc.	positively charged first-level, second-level, etc., atomic ion

Subscripts

A, B	neutral atom
A_2	homonuclear diatomic molecule
AB	heteronuclear diatomic molecule
A^+, A^{++}, etc.	species and type A^+, A^{++}, etc., atomic ion
d	dissociation
i	index; ionization
i1, i2, etc.	first ionization level, second ionization level, etc.
j	index
L0	limit of dissociation level
L1, L2, etc.	limit of first ionization level, limit of second ionization level, etc.
n	index; non-negative integer

r	rotation
s	species and/or particle type
v	vibration
0	dissociation level (when attached to variables)
1, 2, etc.	first, second, etc., ionization level (when attached to variables)

I. INTRODUCTION

Since the advent of man's first successful flight in 1903 the magnitude and scope of problems within the field of Aerospace Engineering have steadily increased at a tremendous rate, a truth quite characteristic of many other scientific fields. In the aeronautical sciences this rapid advance can be attributed almost directly to the ever widening ranges of temperature and pressure with which the aerodynamicist is constantly faced. In the general areas of hypersonic aerodynamics and plasma flow, for example, the temperatures encountered may range from only a few degrees Kelvin to well over 10,000 degrees Kelvin, whereas the pressure may vary between near-zero values and several thousand atmospheres. In the study of gaseous systems subjected to such wide variations in temperature and pressure it becomes necessary to include real-gas effects when investigating the thermodynamic properties of such systems. Hence when temperatures are high enough and/or pressures low enough to cause dissociation and ionization of the gas, the gas no longer can be treated as a homogeneous fluid. In such cases the general problem is complicated by the necessity of treating large numbers of particle species, such as molecules, molecular ions, atomic ions, and electrons, all considered as components of the system mixture at specified conditions of temperature and pressure. As the number of different species increases the number of non-linear equations which

must be solved simultaneously to determine thermodynamic properties of the system also increases proportionately. Therefore it would be advantageous to have available simplified methods and theory which could be used to obtain at least first approximations to the thermodynamic properties of such real-gas systems.

For diatomic gaseous systems in which dissociation is the only real-gas effect considered, a simplified theory for determining approximate thermodynamic properties of the system under conditions of equilibrium has been developed by Lighthill (Ref. 11) and has found wide use in many recent applications. This theory, which is discussed briefly in Section III, applies to any diatomic ideal dissociating gas in equilibrium. The gas is referred to as ideal because the perfect-gas equation of state is retained in the theory, contributing in a large measure to its simplicity. The theory is limited to some range of pressure and temperature, however, since ionization effects are not considered.

For an ideal monatomic gas subjected to conditions of temperature and pressure which cause ionization of the gas, a simplified equilibrium theory similar to Lighthill's dissociation theory has been developed. This ideal ionizing gas theory is presented in Ref. 1 and briefly reviewed in Section IV. The perfect-gas equation of state is again utilized, but only first-level ionization is taken into account in this theory, so it too is limited to applications within some specified range of pressure and temperature.

Many fluid flow systems in which real-gas effects occur involve not only dissociation of the gas but single ionization and higher levels of ionization as well. It would be desirable to make use of the two theories mentioned above in determining the equilibrium thermodynamic properties of such systems, since the calculations then would be simplified considerably. However, it is apparent that certain additional assumptions will have to be made in order to combine the two separate theories in analyzing a single system. The most important of these new assumptions is that the processes of dissociation, single ionization, double ionization, and higher-level ionization all may be considered to take place independently of one another, though in a definite order, within the system. That is, the assumption is made that single ionization does not begin until dissociation of the gas is essentially complete. Similarly, for higher levels of ionization, it is assumed that ionization of the gas at the $(n + 1)$th level does not begin until nth level ionization is essentially complete. To the author's knowledge this assumption of independent gas processes within a single equilibrium system has not as yet received extensive analytical exploration. Truitt, however, in Ref. 16, has shown that at least in the case of a hydrogen plasma a simplified procedure of this type can be used to determine approximate thermodynamic properties under conditions of equilibrium flow.

If the assumption of independent gas processes can be considered to hold true for any particular gaseous system, then it is

quite reasonable to assume that during dissociation (provided the gas
under some conditions of temperature and pressure is diatomic) the
Lighthill theory can be used to determine approximate equilibrium
properties. When conditions of temperature and pressure have gone
beyond the extent of the ideal dissociating gas theory, and single
ionization begins to take place within the system, it should then be
possible to use the ideal ionizing gas theory for a monatomic gas to
determine approximate thermodynamic properties under equilibrium
conditions. At higher ionization levels the ideal ionizing gas
theory can be extended so that successive applications of the theory
can be made at each ionization level to determine approximate thermo-
dynamic properties of the fluid in equilibrium. This procedure then
can be carried to as high an ionization level as desired.

Even with the assumption of independent gas processes there
remains one other aspect of the problem to be investigated before a
simplified analysis of a single system can be carried out in the
manner discussed above. The pressure-temperature range of appli-
cation for each of the ideal real-gas theories must be determined.
Since the theories are to be applied independently of one another it
is necessary to know at what condition of pressure and temperature the
dissociation theory should terminate and the single-ionization
theory begin, for example. Similarly, at higher levels of ioni-
zation, it is necessary to determine the pressure-temperature
condition at which application of the nth level ionization theory

should be terminated and use of the (n + 1)th level ionization theory begun. Such a condition constitutes a pressure-temperature limit or division boundary separating the range of application of one theory from that immediately adjacent to it. It is the purpose of the present work to develop analytical expressions which will permit the determination of these pressure-temperature boundaries for ideal dissociating and ionizing gases.

II. DISCUSSION OF PARTITION FUNCTIONS

In determining the thermodynamic properties of a gaseous system

in which dissociation and ionization effects are to be considered,

it is advantageous to make use of quantum mechanical partition functions

as applied to each separate species of particle[1] comprising the system.

The total partition function Q_s for a particle of species s is a defined

quantity and is expressed by the infinite series

$$Q_s = \sum_j (g_s)_j \, e^{-\frac{(\epsilon_s)_j}{kT}} . \tag{1}$$

In this summation $(\epsilon_s)_j$ is the total energy of the jth energy level

of the particle and $(g_s)_j$ is the degeneracy of this level; that is,

the jth energy level is manifest by $(g_s)_j$ quantum states.

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[1] The word ''particle'' will be used in a somewhat broader sense
than that to which the physicist is usually accustomed. Material con-
stituents such as molecules, atoms, and ions all will be referred to
as particles, as well as more fundamental entities such as the electron.
When a particular kind of particle is being considered the word
''species'' will generally be used to make this distinction. For
example, the molecule is one species of particle, the atom an entirely
different species. The word ''type'' will be used to distinguish
between particles which are of the same species. For example, H_2, NO,
and HCl are all molecular species, but each is a different ''type''
of diatomic molecule. In the general case the subscript s will be used
to designate either species or type of particle, or both. It is not
anticipated that this duplication will present any difficulties,
however, since the meaning should be made clear by the text. In
specific cases the subscript s will be replaced by a chemical formula
or symbol representing the particle under consideration. Since both
species and type are specified by such formulas and symbols there is
no ambiguity in these cases.

Each system treated will contain a total of N particles which, in turn, may be made up of a number of different species, such as molecules, atoms, ions, and electrons. All molecular species to be considered are diatomic and will, in general, be represented by the symbol A_2 when homonuclear or AB when heteronuclear. Atoms may be designated A or B, singly-positive atomic ions A^+ (since ionization of homonuclear mixtures only will be considered), and e^- will be the symbol used to denote the electron[2]. Hence, for any homonuclear system which may contain only these four particular species of particles,

$$N = N_{A_2} + N_A + N_{A^+} + N_{e^-} \quad , \qquad (2)$$

where N_{A_2} is the number of diatomic homonuclear molecules A_2 present among the N particles, N_A is the number of type A atoms, N_{A^+} the number of type A^+ singly-positive atomic ions, and N_{e^-} is the number of electrons contained in the mixture.

Considering a particle of species s to have n degrees of freedom, and assuming that no interaction occurs among these degrees of freedom, the total energy of the particle at the jth energy level can be expressed

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[2] In Section VI certain generalizations are presented which apply at all levels of ionization of an initially neutral atom A, so it becomes necessary to consider ions of the type A^+, A^{++}, A^{+++}, etc., in that section. In order to condense the notation in Section VI the superscripted plus signs used to designate the atomic ions at successively higher levels of ionization are replaced by a positive integer which represents the number of plus signs deleted (i.e., the number of electrons removed from the initially neutral atom A).

$$(\epsilon_s)_j = \sum_{i=1}^{n} (\epsilon_s^i)_j \quad . \tag{3a}$$

The degeneracy of this level then can be written

$$(g_s)_j = \prod_{i=1}^{n} (g_s^i)_j \quad . \tag{3b}$$

Substituting these two equations into Eq. 1, the total partition function Q_s for this particle of species s becomes

$$Q_s = \sum_j \prod_{i=1}^{n} (g_s^i)_j \, e^{-\frac{(\epsilon_s^i)_j}{kT}} \quad . \tag{4}$$

Now if the positions of the summation and product operators in this equation could be exchanged then Eq. 4 would be written

$$Q_s = \prod_{i=1}^{n} \sum_j (g_s^i)_j \, e^{-\frac{(\epsilon_s^i)_j}{kT}} \quad , \tag{5}$$

and there would be associated with each degree of freedom a partition function Q_s^i having the same form as Eq. 1. However, such an exchange would be equivalent to assuming that the sum of a product is equal to the product of the sums, a mathematical statement which does not hold in the case of the infinite series of Eqs. 4 and 5. This becomes quite apparent when Eqs. 4 and 5 are expanded and their individual terms compared. It will be noted that each term in the infinite sum

of Eq. 4 is of the general form $\prod\limits_{i=1}^{n} a_j^i$, whereas the expansion of

Eq. 5 contains not only all of these terms but also terms of the type

$(a_i \, a_j \ldots\ldots)$, where $i \neq j$. Hence there are far more terms contained

in the expansion of Eq. 5 than in Eq. 4, clearly demonstrating the

inequality of these two expressions. Due to the facility of Eq. 5,

however, it becomes desirable to re-define the total partition

function Q_s in terms of this equation for any particle of species s

having more than one degree of freedom within any quantum state.

Hence, with this new definition, the quantity

$$Q_s^i = \sum_j (g_s^i)_j \; e^{-\dfrac{(\epsilon_s^i)_j}{kT}} \tag{6}$$

will be designated as a separate partition function associated with

only the ith degree of freedom of the s-type particle, and Eq.5 then

becomes

$$Q_s = \prod_{i=1}^{n} Q_s^i \; . \tag{7}$$

Four degrees of freedom will be considered, namely, translational,

rotational, vibrational, and electronic. Thus, in general, the particle

partition function of Eq. 7 can be written

$$Q_s = Q_s^{\;T} \, Q_s^{\;R} \, Q_s^{\;V} \, Q_s^{\;E} \; . \tag{8}$$

However, it should be noted that of the different species of particles

considered, only the molecules may possess all four degrees of freedom. The atoms, atomic ions, and electrons will have only translational and electronic degrees of freedom, so that for each of these species the particle partition function of Eq. 8 reduces to

$$Q_s = Q_s^T \, Q_s^E \quad .\tag{9}$$

Translational Partition Function

Employing Eq. 6, the translational partition function Q_s^T for a particle of species s becomes

$$Q_s^T = \sum_j (g_s^T)_j \; e^{-\dfrac{(\epsilon_s^T)_j}{kT}} \quad .\tag{10}$$

As shown in Ref. 3, the allowable translational energy levels for a particle of mass m_s having only translational motion within a box or enclosure of volume V can be determined from a solution of the Schrodinger time-independent wave equation, and are found to be

$$\epsilon_s^T = \frac{h^2}{8 \, m_s \, V^{2/3}} \, (n_1^2 + n_2^2 + n_3^2) \quad ,\tag{11}$$

where n_1, n_2 and n_3 are integers. Unfortunately, a simple formula for the degeneracies of the translational energy levels cannot be written, but with

$$n^2 = n_1^2 + n_2^2 + n_3^2\tag{12}$$

an approximate formula can be derived which is valid for large values of n. It is shown in many texts (see e.g. Ref. 17) that under this

assumption of large n the translational partition function of Eq. 10

can be reduced to the closed form[3]

$$Q_s^T = (\frac{2\pi \, m_s \, kT}{h^2})^{3/2} V \quad . \tag{13}$$

This is the expression which will be used throughout subsequent

developments for the translational partition function of a type s

particle.

Rotational Partition Function

For an asymmetric (heteronuclear) diatomic molecule AB, made up

of atoms A and B having masses m_A and m_B, respectively, the reduced

mass μ_{AB} is defined by

$$\mu_{AB} = \frac{m_A \, m_B}{m_A + m_B} \quad . \tag{14}$$

If, however, the molecule is symmetric (homonuclear) then

$$m_B = m_A \quad , \tag{15}$$

and the reduced mass becomes

$$\mu_{A_2} = \frac{m_A}{2} \quad , \tag{16}$$

each of the atoms being designated as type A since the two atoms are

indistinguishable in this class of molecule.

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[3]Since the assumption of large n is equivalent to assuming that the
particle is approaching classical behavior in its translational motion,
the classical phase integral also can be used to obtain the result of
Eq. 13. See, e.g., Ref. 8.

Assuming now a rather elementary model for the diatomic molecule, which can be represented by a simple dumbbell structure, the rotational energy levels can be found by treating the molecule as a rigid rotator in space. As shown in Ref. 7 these energy levels for a molecule of type s are given by[4]

$$(\epsilon_s^R)_j = j(j+1) \frac{\hbar^2}{2 I_s} \quad , \tag{17}$$

where j is the rotational quantum number, $\hbar$ is Planck's constant divided by 2π, and I_s is the moment of inertia about a point through the center of mass and perpendicular to the molecule, i.e.,

$$I_s = \mu_s r_s^2 \quad , \tag{18}$$

where μ_s is the reduced mass and r_s is the equilibrium radius of separation between the two atoms making up this molecule. If a characteristic temperature of rotation T_r is defined for the s-type molecule as

$$(T_r)_s = \frac{\hbar^2}{2k I_s} \quad , \tag{19}$$

then Eq. 17 can be written

$$(\epsilon_s^R)_j = j(j+1) k (T_r)_s \quad . \tag{20}$$

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[4]The energy expression of Eq. 17 is also developed from Schrodinger's steady-state wave equation in Ref. 8.

The quantum number j can take on successive integral values of 0, 1, 2, 3, etc. In solving the time-independent Schrodinger wave equation for the rigid rotator, of which the energy eigenvalues are given by Eq. 20, there arises a second quantum number m which quantizes one component of the angular momentum and hence permits only certain orientations of the rigid rotator in space. As shown in Ref. 8, m can take on the values

$$m = 0, \pm 1, \pm 2, \ldots, \pm j . \tag{21}$$

Thus, for each value of j there are $2j + 1$ possible orientations. This is the degeneracy of the jth rotational energy level, so that

$$\left(g_s^R\right)_j = 2j + 1 . \tag{22}$$

Substituting this and the energy expression of Eq. 20 into Eq. 6, the rotational partition function for a diatomic molecule of type s becomes

$$Q_s^R = \sum_{j=0}^{\infty} (2j + 1)\, e^{-j(j+1)\frac{(T_r)_s}{T}} . \tag{23}$$

As shown in Ref. 17 a first approximation to this infinite sum is given by

$$Q_s^R = \frac{T}{(T_r)_s} . \tag{24}$$

Higher approximations can be obtained by applying the Euler-Maclaurin summation formula (Ref. 9) to Eq. 23, as shown in Ref. 8.

For the present work the approximation given in Eq. 24 will prove sufficient.

The necessity of including spin factors in Eq. 23 is discussed in Ref. 3, and the conditions under which such factors can be ignored by introducing a symmetry number σ are noted in Ref. 4. Under these conditions the rotational partition function becomes

$$Q_s{}^R = \frac{1}{\sigma} \sum_{j=0}^{\infty} (2j + 1)\, e^{-j(j+1)\frac{(T_r)_s}{T}} , \qquad (25)$$

where σ is unity for diatomic molecules which are asymmetric (heteronuclear) and has a value of 2 for those which are symmetric (homonuclear). Hence, in the present work the final expression which will be used throughout all subsequent developments for the rotational partition function of a type s diatomic molecule will be

$$Q_s{}^R = \frac{1}{\sigma} \frac{T}{(T_r)_s} . \qquad (26)$$

Vibrational Partition Function

In classical mechanics the natural vibrational frequency ν of a simple one-dimensional harmonic oscillator without damping, having a mass m acted upon by a restoring force $F = - k_e x$, where k_e is here referred to as the equilibrium force constant (or spring constant) and x is the linear displacement of mass m from its equilibrium position, is found to be

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k_e}{m}} \ . \tag{27}$$

The quantum mechanical treatment of diatomic molecules, assuming the linear harmonic oscillator model, is discussed in many texts (see e.g. Refs. 7 and 13), and the vibrational energy levels for such a model are found to be

$$\epsilon^V = (n + \tfrac{1}{2}) \, h\nu \ , \tag{28}$$

where n is the vibrational quantum number, h is Planck's constant, and ν is the vibrational frequency given by Eq. 27 with m replaced by μ. If a characteristic temperature of vibration T_v is defined for the diatomic molecule of type s by the expression

$$(T_v)_s = \frac{h \, \nu_s}{k} \ , \tag{29}$$

where k in this equation is Boltzmann's constant, then the vibrational energy levels of Eq. 28 can be written

$$(\epsilon_s^V)_n = (n + \tfrac{1}{2}) \, k \, (T_v)_s \ . \tag{30}$$

It will be noted that the lowest vibrational energy level is obtained when the quantum number n has a value of zero (since n must be non-negative). This energy, which is given by

$$(\epsilon_s^V)_o = \tfrac{1}{2} \, k \, (T_v)_s \ , \tag{31}$$

is the absolute vibrational energy of the molecule when in its

vibrational ground state, and is often referred to as the zero-point
vibrational energy. It is customary to reference successively higher
energy levels of the vibrating molecule to this zero-point energy
of the ground state, so that in formulating the vibrational partition
function the energy expression to be used reduces to

$$(\epsilon_s^V)_n = (n + \frac{1}{2}) \; k \; (T_V)_s - (\epsilon_s^V)_o = nk \; (T_V)_s \; . \tag{32}$$

Since these energy levels are nondegenerate (i.e., $(g_s^V)_n = 1$),
substitution of Eq. 32 into Eq. 6 gives the following expression
for the vibrational partition function of an s-type diatomic molecule
assumed to be behaving like a simple harmonic oscillator:

$$Q_s^V = \sum_{n=0}^{\infty} e^{-n\frac{(T_V)_s}{T}} \; . \tag{33}$$

Clearly this sum converges to the limit

$$Q_s^V = \frac{1}{1 - e^{-\frac{(T_V)_s}{T}}} \tag{34}$$

for all non-zero, positive values of T_V/T. Equation 34 is the
expression which will be used throughout this work for the vibrational
partition function of a type s diatomic molecule.

Electronic Partition Function

Thus far, in developing the translational, rotational, and
vibrational partition functions, it has been possible to replace the

infinite series of Eq. 6 by some closed-form expression through use
of an assumed model for the species of particle under consideration
or by employing certain other simplifying approximations. With
regard to the electronic partition function, however, the situation
is somewhat complicated by the fact that only in very special cases
has it been possible to develop simple relationships for the energies,
degeneracies, and quantum numbers of the electronic states. In any
event, the infinite series of Eq. 6 does not converge, so it becomes
necessary to decide upon some point at which the series can be
terminated in any particular case. When the electronic partition
function is evaluated from experimental data this termination point
may be predetermined by the amount of data available. In other
instances a number of different factors influence the choice.
Several such factors are discussed in a subsequent paragraph.

Utilizing Eq. 6, the electronic partition function for a
particle of species s becomes

$$Q_s^E = \sum_{n=0}^{\infty} (g_s^E)_n \, e^{-\frac{(\epsilon_s^E)_n}{kT}} . \tag{35}$$

For hydrogen-like atoms (i.e., atoms in which a single valence
electron is located in an orbit some distance away from a positively
charged core which may be made up of additional electrons as well as
the positively charged nucleus), an explicit expression for the

electronic energy levels and degeneracies can be derived (see, e.g., Ref. 10). Even in these special cases, however, the resulting summation of Eq. 35 diverges[5], so it is still necessary to decide upon a termination point. For other species of particles, observed data are most frequently used to evaluate $Q_s{}^E$, and a termination point must usually be decided upon for each separate species.

To determine the electronic energy level degeneracies for homonuclear and heteronuclear diatomic molecules, the spectroscopist's ''term values'' (e.g. $^2\Sigma_g^+$, $^1\Pi_i$, $^3\Delta_u$) for the electronic states must be considered. As explained in Ref. 8, the left superscript in these term symbols indicates the ''spin multiplicity'' $2S + 1$, where S is the total spin quantum number of the molecule in the particular electronic state under consideration. In the case of electronic levels designated by the Σ symbol, the degeneracies for such levels are given directly by the left superscript; that is, for any diatomic molecule of type s (symmetric or asymmetric),

$$(g_s{}^E)_n = (2S + 1) \text{ for } \Sigma \text{ states }.\tag{36}$$

For electronic levels designated by any other symbols the left superscript of the term value must be doubled to give the degeneracy of the level; that is,

$$(g_s{}^E)_n = 2(2S + 1) \text{ for } \Pi, \Delta, \text{ etc. states }.\tag{37}$$

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[5]For a discussion of this divergence in the case of hydrogen-like atoms see, e.g., Ref. 10.

Table 39 of Ref. 7 is the most widely used source from which are taken energy values $(\epsilon_s{}^E)_n$ for the electronic energy levels of diatomic molecules. In this reference successive electronic levels are designated by term symbols[6], such as mentioned in the preceeding paragraph, and the energy of each level is given in units of (centimeter)$^{-1}$. This energy is denoted by T_e in Ref. 7, so adopting this notation, Eq. 35 can be written for any diatomic molecule as

$$Q^E = \sum_{n=0}^{\infty} (g^E)_n \, e^{-\frac{c_2 (T_e)_n}{T}} \quad , \tag{38}$$

where c_2 is the second radiation constant given by[7]

$$c_2 = 1.43880 \text{ cm deg.} \quad \cdot \tag{39}$$

For all diatomic molecules in Table 39 of Ref. 7 it will be noted that for the electronic ground state

$$(T_e)_0 = 0 \quad \cdot \tag{40}$$

For atoms and atomic ions the energies and degeneracies of the electronic energy levels are most readily obtainable from Ref. 12. For a type s atom or atomic ion the degeneracy $(g_s{}^E)_n$ of the nth

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[6]For a disucssion of electronic states which cannot be classified as Σ, Π, Δ, ... states see Ref. 7, p. 216.

[7]Except where otherwise stated, all physical constants used in the present work have been taken from Tables 8-6 and 8-7 of Ref. 2.

electronic energy level is given by

$$(g_s{}^E)_n = 2J + 1 \quad , \qquad (41)$$

where J is the ''inner'' quantum number of this nth level. Values of J and corresponding values of the energy $(\epsilon_s{}^E)_n$ are given in Ref. 12 for successive electronic levels beginning with the lowest level of the ground state. In all cases it will be noted that for this level

$$(\epsilon_s{}^E)_0 = 0 \quad . \qquad (42)$$

All energies for the electronic levels in Ref. 12 have the units (centimeter)$^{-1}$.

For many atoms and atomic ions there often occur electronic levels having energies which are very close together. For example, in the case of the hydrogen atom H, the first four entries of Ref. 12 (Vol. I) read

J	$(\epsilon_H{}^E)_n$	
1/2	0.000	cm^{-1}
1/2	82258.907	cm^{-1}
1/2	82258.942	cm^{-1}
1 1/2	82259.272	cm^{-1}

Using only these four levels, the electronic partition function of Eq. 35, for the hydrogen atom, would become

$$Q_H^E = 2 + 2e^{-\frac{82258.907\ c_2}{T}} + 2e^{-\frac{82258.942\ c_2}{T}} + 4e^{-\frac{82259.272\ c_2}{T}} .$$

$$(43)$$

If, however, a value of 82259 cm^{-1} is chosen for the energy of each of the three closely spaced levels, then Eq. 43 reduces to

$$Q_H^E = 2 + 8e^{-\frac{82259\ c_2}{T}} \qquad (44)$$

This procedure of using rounded-off values for the energies of closely spaced electronic levels is followed throughout the present work. With this consideration in mind, a comparison of the energies (and degeneracies) in the atomic hydrogen partition function

$$Q_H^E = 2 + 8e^{-\frac{82259\ c_2}{T}} + 14e^{-\frac{97492\ c_2}{T}} + 22e^{-\frac{102824\ c_2}{T}} + 32e^{-\frac{105292\ c_2}{T}}$$

$$(45)$$

with those tabulated for the hydrogen atom in Ref. 12 (Vol. I) will show that although only five terms have been given in the partition function of Eq. 45 there actually are included 18 average-valued energy levels above the ground state in this equation.

The question naturally arises as to how many terms should be retained in any particular electronic partition function, molecular as well as atomic. However, no concise answer is readily forthcoming. Certainly it depends in large measure upon the problem at hand and the temperature range involved. As noted by Lighthill in Ref. 11, the higher electronic states, though important from a spectroscopic point

of view, may be quite negligible thermodynamically. In Ref. 6, for example, Hansen elects to include in the electronic partition function only those exponential terms for which the energy levels $(\epsilon^E)_n$ are less than six times kT_{max}, where the maximum temperature T_{max} considered is 15,000 °K. In Ref. 14, all electronic levels located 100,000 cm^{-1} above the ground state are taken into account in computing electronic partition functions for molecular species, and for atoms and atomic ions all known levels (rounded off to three significant figures) are used. An opposite extreme appears in Ref. 1 in which electronic excitation of the atoms and ions is completely neglected, only the degeneracies of the ground-state energy levels being retained. It should be emphasized that in each of the references cited the problem requirements vary considerably. In Refs. 1 and 6, as their titles would imply, very highly detailed calculations are not the prime objective. In Ref. 14, however, considerable refinement has been retained in order that very accurate thermodynamic properties may be determined. It becomes apparent that in any particular investigation the decision on the part of the investigator as to the number of electronic levels to be retained in certain calculations may depend upon many factors. Even then the answer to the question can still remain in doubt. In the present work the general computing procedure followed is to add successively higher energy level terms to the electronic partition functions until change in the particular thermodynamic quantity being calculated, due to these additions,

becomes negligibly small. In Section IV this procedure is discussed further in connection with a particular application.

The only electronic degree of freedom which a free electron e^- may have is electron spin, which is independent of temperature. Hence, in this case,

$$J = s = 1/2 \quad ,$$

where s is the spin quantum number of the electron. The electronic partition function for the free electron then becomes simply

$$Q_{e^-}^E = 2 \quad . \tag{46}$$

III. LIGHTHILL'S IDEAL DISSOCIATING GAS

The equilibrium theory for an ideal dissociating gas, in which ionization effects are not considered, is developed and discussed in Ref. 11 and applied to the particular cases of oxygen and nitrogen dissociation over a temperature range of approximately 3000 °K to 7000 °K. Because of its simplicity this theory provides an excellent method for calculating approximate thermodynamic properties of dissociating diatomic gases in equilibrium so long as the assumptions of ''ideal'' behavior and negligible ionization can be considered applicable. Much of the simplification of this theory is achieved by replacing a particular temperature-dependent function, having the dimensions of density, by a constant value ρ_d, referred to as characteristic density of dissociation, which has been averaged over the temperature range of interest. As noted in Ref. 11, this approximation is equivalent to taking the vibrational modes of motion of the molecules as being excited to only one half their full classical energy content at all temperatures throughout the range over which ρ_d is averaged.

In view of the assumption of negligible ionization effects, it may be difficult to justify the choice of an upper limit to the temperature range over which this theory is considered to apply for any particular diatomic gas. A selection based upon certain physical considerations of the problem at hand, as was made in Ref. 11, still involves a certain amount of arbitrariness. In Section V a method

is presented for removing this uncertainty and analytically determining
an upper limit for this temperature as a function of pressure. To
aid in this development the ideal dissociating gas theory will be
reviewed and certain thermodynamic quantities will be formulated from
it for further use. Because of subsequent considerations, appli-
cation of the ideal dissociating gas theory will be restricted to
homonuclear diatomic molecules only, as was done in Ref. 11, although
the extension to include diatomic molecules which are asymmetric is
quite straightforward.

Before presenting any formulas a word should be said about the
notation to be used. The development in this section is restricted
to the dissociation process only, and that in Section IV deals solely
with first-level ionization. However, in Section V the processes of
dissociation and single ionization are both considered simultaneously,
and in Section VI certain generalized relationships are developed
which apply at all ionization levels. Hence, it is desirable to
employ a notation which will maintain continuity throughout all
sections. Toward this aim the subscript d is used in this section
to denote all constants which are unique to the dissociation range.
In Section IV the subscript i1 is used in a similar manner with
regard to the first-level ionization process, and this is extended
in Section VI where constants unique to the higher ionization levels
are subscripted i2, i3, i4, . . ., in, . . . etc. Many of the
variables arising in this section, e.g. T, P, V, β_A, N_A, x_A, α, etc.,

are also encountered in Section IV. However, since these two sections are quite distinct, additional subscripting will not be attached to such variables until Sections V and VI. In Section V the variables associated with first-level ionization are subscripted simply with the numeral 1, whereas those variables in that section which are associated with the dissociation process are subscripted 0, which is indicative of a zero-ionization level. In Section VI variables for the higher ionization levels are subscripted 2, 3, . . ., n, . . . etc.

The reaction equation for Y_d moles of type A_2 molecules dissociating into their atomic components can be written

$$Y_d \, A_2 \rightarrow \beta_{A_2} \, A_2 + \beta_A \, A \quad , \tag{47}$$
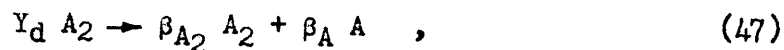
where β_{A_2} and β_A are the moles of A_2 molecules and A atoms, respectively, contained in the mixture at any given temperature and pressure. The numbers of particles of the mixture constituents can be expressed

$$N_{A_2} = N_o \, \beta_{A_2} \tag{48a}$$

and

$$N_A = N_o \, \beta_A \tag{48b}$$

Hence, from Eqs. 47 and 48, a mass balance yields

$$2Y_d = 2\beta_{A_2} + \beta_A = \frac{2N_{A_2} + N_A}{N_o} \quad . \tag{49}$$

Following Zemansky (Ref. 18), the degree of reaction α (which in this case becomes the degree of dissociation) can be defined for reaction (47) in terms of the A_2 molecules as

$$\alpha = \frac{Y_d - \beta_{A_2}}{Y_d - 0} \quad . \tag{50}$$

Using Eqs. 48 and 49, Eq. 50 can be written

$$\alpha = \frac{\beta_A}{2\beta_{A_2} + \beta_A} = \frac{N_A}{2N_{A_2} + N_A} \quad . \tag{51}$$

Thus the mole fractions of mixture constituents A_2 and A are given by

$$x_{A_2} = \frac{\beta_{A_2}}{\beta_{A_2} + \beta_A} = \frac{1 - \alpha}{1 + \alpha} \tag{52}$$

and

$$x_A = \frac{\beta_A}{\beta_{A_2} + \beta_A} = \frac{2\alpha}{1 + \alpha} \quad . \tag{53}$$

Writing now the partial pressures for this ideal dissociating gas,

$$p_{A_2} = \beta_{A_2} R_1 \frac{T}{V} = N_{A_2} k_1 \frac{T}{V} \tag{54a}$$

and

$$p_A = \beta_A R_1 \frac{T}{V} = N_A k_1 \frac{T}{V} \quad , \tag{54b}$$

where R_1 is the gas constant given by

$$R_1 = R_0 F_p \approx 82.082 \frac{\text{atm cm}^3}{\text{mole } {}^\circ K} \quad , \tag{55}$$

F_p is a pressure conversion factor (Appendix, Ref. 15) given by

$$F_p = 1 = 0.9869233 \times 10^{-6} \frac{\text{atm cm}^2}{\text{dyne}} , \qquad (56)$$

and $k_1 = k\, F_p$.

Combining Eqs. 54a and 54b, the total pressure of the mixture becomes

$$P = p_{A_2} + p_A = (N_{A_2} + N_A)\, k_1\, \frac{T}{V} . \qquad (57)$$

There is associated with Eq. 47 the governing dissociation reaction for equilibrium

$$A_2 \rightleftharpoons 2A , \qquad (58)$$

for which a dissociation equilibrium constant K can be defined in terms of partial pressure as

$$K = \frac{p_A^2}{p_{A_2}} . \qquad (59)$$

Using Eqs. 51, 54, and 57, Eq. 59 can be expressed

$$K = \frac{4\alpha^2\, P}{1 - \alpha^2} , \qquad (60)$$

and the mole fraction of A atoms present in the mixture, from Eq. 53, then can be written

$$x_A = \frac{K}{2P} \left[\sqrt{1 + \frac{4P}{K}} - 1 \right] . \qquad (61)$$

Employing the relationships of Ref. 11 and Section II, the equilibrium constant of Eq. 60 becomes

$$K = C_K \, (\mu^{3/2} \, T_r)_{A_2} \left[1 - e^{-\frac{(T_v)_{A_2}}{T}} \right] \frac{(Q_A^E)^2}{Q_{A_2}^E} \, T^{3/2} \, e^{-\frac{T_d}{T}} \quad , \quad (62)$$

showing the dependence of K upon temperature alone. When μ_{A_2} is given in atomic mass units (physical scale) the constant C_K has a value of approximately 0.05118 atm $\text{mole}^{3/2} \, \text{gm}^{-3/2} \, {}^\circ\text{K}^{-5/2}$. This constant may be expressed in more familiar terms as

$$C_K = 2k_1 \left(\frac{2\pi \, k}{N_o \, h^2} \right)^{3/2} = 2R_1 \, \exp \left(\frac{S_o}{R_o} - \frac{5}{2} \right) \quad , \quad (63)$$

where $\frac{S_o}{R_o}$ is the Sackur-Tetrode constant of Table 8-7, Ref. 2. The equilibrium constant K can be expressed in terms of the characteristic density ρ_d of Ref. 11 as

$$K = R_1 \left(\frac{\rho_d}{\mu} \right)_{A_2} T \, e^{-\frac{T_d}{T}} \quad , \quad (64)$$

where ρ_d is treated as a constant; however, in the developments of Section V, the more involved Eq. 62 will be used in order to retain the greater dependence of K upon temperature in that expression.

The principal dissociation relationships to be used in Section V are Eqs. 61 and 62, so there is no need in the present work to develop further expressions for thermodynamic properties such as total internal energy, enthalpy, entropy, and the like, for the ideal dissociating gas. Relationships which can be used to calculate such quantities as these are given in Ref. 11.

IV. THE IDEAL IONIZING GAS

The theory for an ideal ionizing monatomic gas is outlined in Ref. 1, and application is made to the cases of equilibrium and frozen flow of argon through nearly conical nozzles within a temperature range of 10,000 °K to 20,000 °K. In Ref. 1 the only mixture components considered to result from the ionization of such a gas in this temperature range are neutral atoms, singly-positive ions, and free electrons. Under these conditions the reaction equation for first-level ionization of Y_{i1} moles of atoms A can be written

$$Y_{i1} A \longrightarrow \beta_A A + \beta_{A^+} A^+ + \beta_{e^-} e^- \quad ; \qquad (65)$$
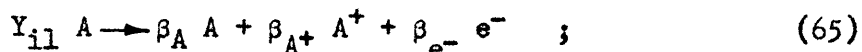
where the β's are the numbers of moles of constituents in the gas mixture at any given temperature and pressure. Proceeding in a manner similar to that of Section III, the numbers of constituent particles in the mixture are given by

$$N_A = N_0 \beta_A \quad , \qquad (66a)$$

$$N_{A^+} = N_0 \beta_{A^+} \quad , \qquad (66b)$$

and

$$N_{e^-} = N_0 \beta_{e^-} \quad . \qquad (66c)$$

Hence, conservation of atomic nuclei, from Eq. 65, yields

$$Y_{i1} = \beta_A + \beta_{A^+} = \frac{N_A + N_{A^+}}{N_0} \quad . \qquad (67)$$

The degree of first-level ionization α, defined similarly to the degree of dissociation but in this case taken with respect to the type A atoms, will be

$$\alpha = \frac{Y_{i1} - \beta_A}{Y_{i1} - 0} .$$ (68)

Using Eqs. 66 and 67, Eq. 68 can be written

$$\alpha = \frac{\beta_{A^+}}{\beta_A + \beta_{A^+}} = \frac{N_{A^+}}{N_A + N_{A^+}}$$ (69)

Thus, noting that conservation of electric charge in Eq. 65 requires $\beta_{A^+} = \beta_{e^-}$, the mole fractions of the mixture constituents are given by

$$x_A = \frac{\beta_A}{\beta_A + 2\beta_{A^+}} = \frac{1 - \alpha}{1 + \alpha}$$ (70)

and

$$x_{A^+} = x_{e^-} = \frac{\alpha}{1 + \alpha} .$$ (71)

It will be noted that Eq. 70 represents the second expression developed for x_A in terms of degree of reaction, the first such relationship being Eq. 53 of Section III. Of course the two expressions are quite different since one is developed under considerations of a process involving only dissociation, while the other arises in connection with the simplified first-level ionization of a monatomic gas. However, in Section V, a useful relationship will be developed as a result of the mathematical equality of these two functions under certain presumed conditions.

The total mass M of the gas mixture may be expressed

$$M = N_A m_A + N_{A^+} (m_{A^+} + m_{e^-}) \quad . \tag{72a}$$

If the mass equivalent of the bonding energy of an outer-shell electron in the type A atom can be neglected, then

$$m_A \approx m_{A^+} + m_{e^-} \quad ,$$

and Eq. 72a becomes

$$M = (N_A + N_{A^+}) m_A \quad . \tag{72b}$$

Hence, the density for the gas contained in volume V will be

$$\rho = \frac{M}{V} = (N_A + N_{A^+}) \frac{m_A}{V} \quad . \tag{73}$$

Writing now the partial pressures for this ideal ionizing gas,
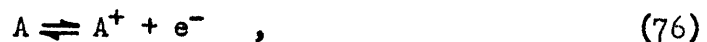
$$p_A = N_A k_1 \frac{T}{V} \tag{74a}$$

and

$$p_{A^+} = p_{e^-} = N_{A^+} k_1 \frac{T}{V} \quad . \tag{74b}$$

Combining these equations, the total pressure of the gas mixture becomes

$$P = p_A + p_{A^+} + p_{e^-} = (N_A + 2N_{A^+}) k_1 \frac{T}{V} \quad . \tag{75}$$

There is associated with Eq. 65 the governing ionization equilibrium reaction

$$A \rightleftharpoons A^+ + e^- \quad , \tag{76}$$

for which the law of mass action gives

$$\frac{N_{A^+}\, N_{e^-}}{N_A} = \frac{Q_{A^+}\, Q_{e^-}}{Q_A}\, e^{-\frac{T_{i1}}{T}} \quad , \tag{77}$$

where $T_{i1} = \dfrac{I_{i1}}{k_2}$, the quantity I_{i1} being the ionization potential (in electron volts) for first-level ionization, and k_2 being Boltzmann's constant given by (Table 8-7, Ref. 2)

$$k_2 = 8.6167 \times 10^{-5} \text{ ev/}^{\circ}K \quad .$$

Employing Eqs. 69, 73, and 77, an equation analogous to Eq. 13 of Ref. 11 can be developed for the ideal ionizing gas, and is given by

$$\frac{\alpha^2}{1-\alpha} = \frac{1}{\rho}\left[\frac{m_A}{V}\ \frac{Q_{A^+}\, Q_{e^-}}{Q_A} \right] e^{-\frac{T_{i1}}{T}} \quad , \tag{78}$$

which is sometimes referred to as Saha's equation. Making use of Eqs. 9, 13, and 46 from Section II, Eq. 78 also can be written

$$\frac{\alpha^2}{1-\alpha} = \frac{1}{\rho}\left[\frac{2m_A}{V}\ \left(\frac{Q_{A^+}{}^T\, Q_{e^-}{}^T}{Q_A{}^T} \right) \left(\frac{Q_{A^+}{}^E}{Q_A{}^E} \right) \right] e^{-\frac{T_{i1}}{T}}$$

$$= \frac{1}{\rho}\left[2m_A \left(\frac{2\pi\, \mu_{i1}\, kT}{h^2} \right)^{3/2} \left(\frac{Q_{A^+}{}^E}{Q_A{}^E} \right) \right] e^{-\frac{T_{i1}}{T}} \quad , \tag{79}$$

where

$$\mu_{i1} = \frac{m_{A^+}\, m_{e^-}}{m_A} \approx \frac{m_{A^+}\, m_{e^-}}{m_{A^+} + m_{e^-}} \quad .$$

It will be noted that the bracketed quantity in Eq. 79 has the dimensions of density. As mentioned in Ref. 1, however, this quantity cannot be treated as a characteristic density of ionization in the same sense that ρ_d was treated as a characteristic density of dissociation, primarily because of the presence of the $T^{3/2}$ term. Following Ref. 1, the variable temperature can be removed from the bracketed function by replacing it with the constant temperature of first-level ionization T_{i1}, so that Eq. 79 then becomes

$$\frac{\alpha^2}{1-\alpha} = \frac{1}{\rho}\left(\frac{T}{T_{i1}}\right)^{3/2}\left[\frac{m_A\,C_K}{R_1}(\mu_{i1}\,T_{i1})^{3/2}\left(\frac{Q_{A^+}^E}{Q_A^E}\right)\right]e^{-\frac{T_{i1}}{T}}, \tag{80}$$

where m_A is the mass of the type A atom expressed in atomic mass units (physical scale) and $\dfrac{C_K}{R_1}$ can be determined from Eq. 63. It is the bracketed quantity in Eq. 80 which is taken as the characteristic density of ionization ρ_i in Ref. 1, except that in that reference only the degeneracies of the ground-state energy levels are retained in the electronic partition functions $Q_{A^+}^E$ and Q_A^E, and the units of ρ_i in Ref. 1 are slugs ft^{-3} rather than gm cm^{-3} as in Eq. 80. In the present work ρ_{i1} will be taken as

$$\rho_{i1} = G_\rho\, m_A\, (\mu_{i1}\, T_{i1})^{3/2}\,\frac{Q_{A^+}^E}{Q_A^E}\quad, \tag{81}$$

where

$$G_\rho = \frac{C_K}{R_1} = 2\exp\left(\frac{S_o}{R_o} - \frac{5}{2}\right)\quad. \tag{82}$$

Since it is intended that ρ_{11} be treated as a constant, some discussion of the electronic partition-function ratio appearing in Eq. 81 is in order. There immediately arises the question of how many terms should be retained in the two infinite series of these partition functions. In Ref. 1, as has already been mentioned, only the degeneracies of the ground-state energy levels are retained in each sum for the case of first-level argon ionization, and it is shown in that reference that such an approximation does not introduce appreciable errors into the calculations for this particular gas within the temperature range of interest. However, it is possible to treat the partition-function ratio in Eq. 81 in such a way that it can be replaced by a constant value which in many cases will reduce the error below that introduced by the method of Ref.1, and this will generally hold true when the present method is applied to similar partition-function ratios at any ionization level in the case of most all gases. To develop the method certain properties of the electronic partition function of Eq. 35 will first be discussed.

Expanding the infinite series of Eq. 35, and taking into account the condition given by Eq. 42, the electronic partition function for an atomic species s can be written

$$Q_s^E = (g_s^E)_0 + (g_s^E)_1 \ e^{-\frac{(T_s^E)_1}{T}} + (g_s^E)_2 \ e^{-\frac{(T_s^E)_2}{T}} +$$
$$(g_s^E)_3 \ e^{-\frac{(T_s^E)_3}{T}} + \ldots , \qquad (83)$$

where $(T_s{}^E)_n = \dfrac{(\epsilon_s{}^E)_n}{k}$.

For any given temperature T the function $\dfrac{(T_s{}^E)_n}{T}$ is a monotone in-
creasing function of h, and beyond the point at which $T < (T_s{}^E)_n$
the contribution of terms having successively higher values of n in
Eq. 83 becomes quite small. A cut-off point is easily determined
in any particular case since there is no need to retain terms which
produce only negligible changes in $Q_s{}^E$. For any finite temperature
range $T_{min} \leqq T \leqq T_{max}$ it is apparent that the maximum number of
terms which need be included in Eq. 83 for any temperature within
the range can be determined by letting $T = T_{max}$ and deciding upon a
cut-off point at this condition. This reduces the problem to one
involving electronic partition functions which are series having
only a finite number of terms. Now clearly, from Eq. 83, $Q_s{}^E(T)$
is a monotone increasing function of T for any particle of species
s. Hence, in Eq. 81, although each of the two partition functions
$Q_{A+}{}^E$ and $Q_A{}^E$ will increase separately with increasing temperature,
the ratio $\dfrac{Q_{A+}{}^E}{Q_A{}^E}$ will not, in general, vary significantly. This is
shown for the cases of oxygen, nitrogen, fluorine, and chlorine in
Fig. 1. Thus an average value can be selected for this ratio over
the temperature range in which the first-level ionization theory is
considered to hold, and $\dfrac{Q_{A+}{}^E}{Q_A{}^E}$ in Eq. 81 can then be replaced by this
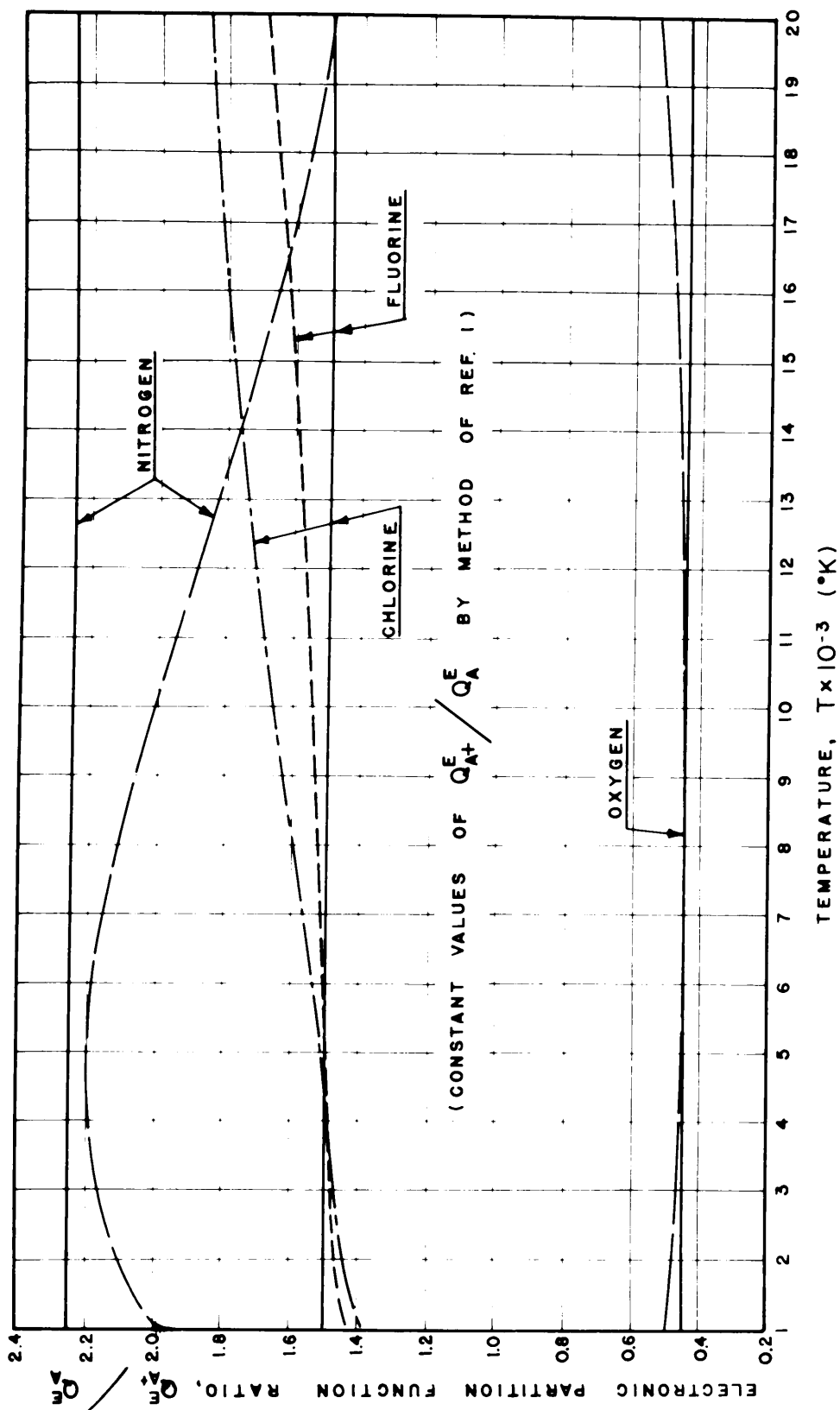value in order to remove the temperature dependence of the electronic

FIGURE I.   VARIATIONS   IN   THE   RATIO   OF   ELECTRONIC   PARTITION   FUNCTIONS

partition functions in ρ_{i1}. For each of the four gases shown in Fig. 1 it will be noted that selecting an average value for

$\dfrac{Q_{A^+}{}^E}{Q_A{}^E}$ over the probable temperature range of first-level ionization

results in overall errors which in general will be less than the errors introduced by retaining only the degeneracies of ground-state

energy levels in $\dfrac{Q_{A^+}{}^E}{Q_A{}^E}$.

For the reaction 76 an ionization equilibrium constant K can be defined in terms of partial pressures as

$$K = \frac{p_{A^+} \, p_{e^-}}{p_A} = \frac{p_{A^+}{}^2}{p_A} \quad . \tag{84}$$

Using Eqs. 69, 74 and 75, Eq. 84 can be expressed

$$K = \frac{\alpha^2 \, P}{1 - \alpha^2} \quad , \tag{85}$$

and the mole fraction of A atoms present in the mixture, from Eq. 70, then can be written

$$x_A = 1 - \frac{2K}{P} \left[\sqrt{1 + \frac{P}{K}} - 1 \right] \quad . \tag{86}$$

Employing Eqs. 9, 13, 46, 74 and 77, the equilibrium constant of Eq. 84 becomes

$$K = C_K \, \mu_{i1}{}^{3/2} \, T^{5/2} \, \frac{Q_{A^+}{}^E}{Q_A{}^E} \, e^{-\frac{T_{i1}}{T}} \quad , \tag{87}$$

where C_K is given by Eq. 63. This equilibrium constant may also be expressed in terms of the characteristic density ρ_{i1} of Eq. 81 as

$$ K = R_1 \left(\frac{\rho_{i1} \, T_{i1}}{m} \right)_A \left(\frac{T}{T_{i1}} \right)^{5/2} e^{-\frac{T_{i1}}{T}} \quad , \qquad (88) $$

where ρ_{i1} and T_{i1} are constants, and m_A is expressed in atomic mass units. In Section V, however, Eq. 87 will be used in preference to Eq. 88.

Expressions for other thermodynamic properties of the ideal ionizing gas are presented in Ref. 1. There is no need to repeat them here since they will not be used in the present work.

V. PRESSURE-TEMPERATURE BOUNDARIES FOR IDEAL DISSOCIATING AND SINGLY-IONIZING GASES

In gaseous systems subjected to wide variations in temperature and pressure, such as are encountered in the general cases of hypersonic aerodynamics and plasma flow, it is often necessary to treat the processes of both dissociation and ionization within a single system. At specified conditions of temperature and pressure the total number of particles comprising the system mixture may consist of many different species resulting from dissociation and ionization, such as is the case in Eq. 2, and the general problem is quite complicated when all such species are considered simultaneously. A considerable simplification in calculating the thermodynamic properties of such systems is achieved by assuming that the processes of dissociation, single ionization, double ionization, and higher-level ionization all take place independently of one another, though in a definite order within the system. That is, the assumption is made that single ionization cannot take place until dissociation of the gas is essentially complete (degree of dissociation near 100 percent), beyond which point only single ionization of the atoms is considered until a high degree of single ionization is reached, beyond which point only double ionization (i.e. single ionization of singly-positive atomic ions) is considered until a high degree of double ionization is reached, and so on throughout successively higher levels of ionization. A simplified procedure of this type is

employed in Ref. 16 to determine the thermodynamic properties of a hydrogen plasma and the results are shown to be in agreement with Ref. 5 in which the governing equations are solved with the processes of dissociation and ionization considered simultaneously.

If the assumption of independent gas processes can be presumed to hold true for any particular gaseous system, which under some conditions is diatomic, then Lighthill's equilibrium theory for an ideal dissociating gas can be applied to determine thermodynamic properties of the system within the dissociation range, and within the range of single ionization the ideal ionizing gas theory of Ref. 1 can be used to calculate system properties[8]. Use of these theories within their respective ranges of application results in calculation procedures which are straightforward and considerably simplified. However, difficulties arise in attempting to define the limits or boundaries of the ranges involved, since neither theory exactly specifies such limits. In the development to follow a method is presented for determining the boundary conditions of temperature and pressure which constitute an upper limit for Lighthill's ideal dissociating gas theory and a lower limit for the ideal ionizing gas theory of Ref. 1 when applied to a system in which both dissociation and single ionization are considered. Since

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[8]As noted in Ref. 1, the ideal ionizing gas theory of that reference cannot be extrapolated to the ionization of more complex molecules. Hence, only homonuclear systems will be considered in the present work.

it will be necessary to utilize equations and variables from Sections III and IV which are similar in form and notation, as has already been mentioned previously, the subscript o will be used to designate dissociation variables taken from Section III, and the subscript 1 will denote first-level ionization variables taken from Section IV.

Mathematically the two functions K_o and K_1 of Eqs. 62 and 87, respectively, are both generally increasing functions of temperature, each having a value of zero at zero temperature. As temperature becomes infinite little can be said about the behavior of either function since in the limit the electronic partition function Q_s^E becomes

$$\lim_{T \to \infty} Q_s^E = \sum_{n=0}^{\infty} (g_s^E)_n \ , \qquad (89)$$

which is a divergent series. Hence the ratio of electronic partition functions appearing in K_o and K_1 becomes indeterminate at this condition. If this ratio is assumed to be finite then both K_o and K_1 become infinite in the limit. Of course no physical significance can be attached to either function at or within the immediate vicinity of these extremes. However, consideration of the extremes has been included in order to help fully define the mathematical behavior of the two functions $(x_A)_o$ and $(x_A)_1$ of Eqs. 61 and 86, respectively.

The general behavior of $(x_A)_o$ and $(x_A)_1$, with total pressure P treated parametrically, is shown in Fig. 2. The function $(x_A)_o$
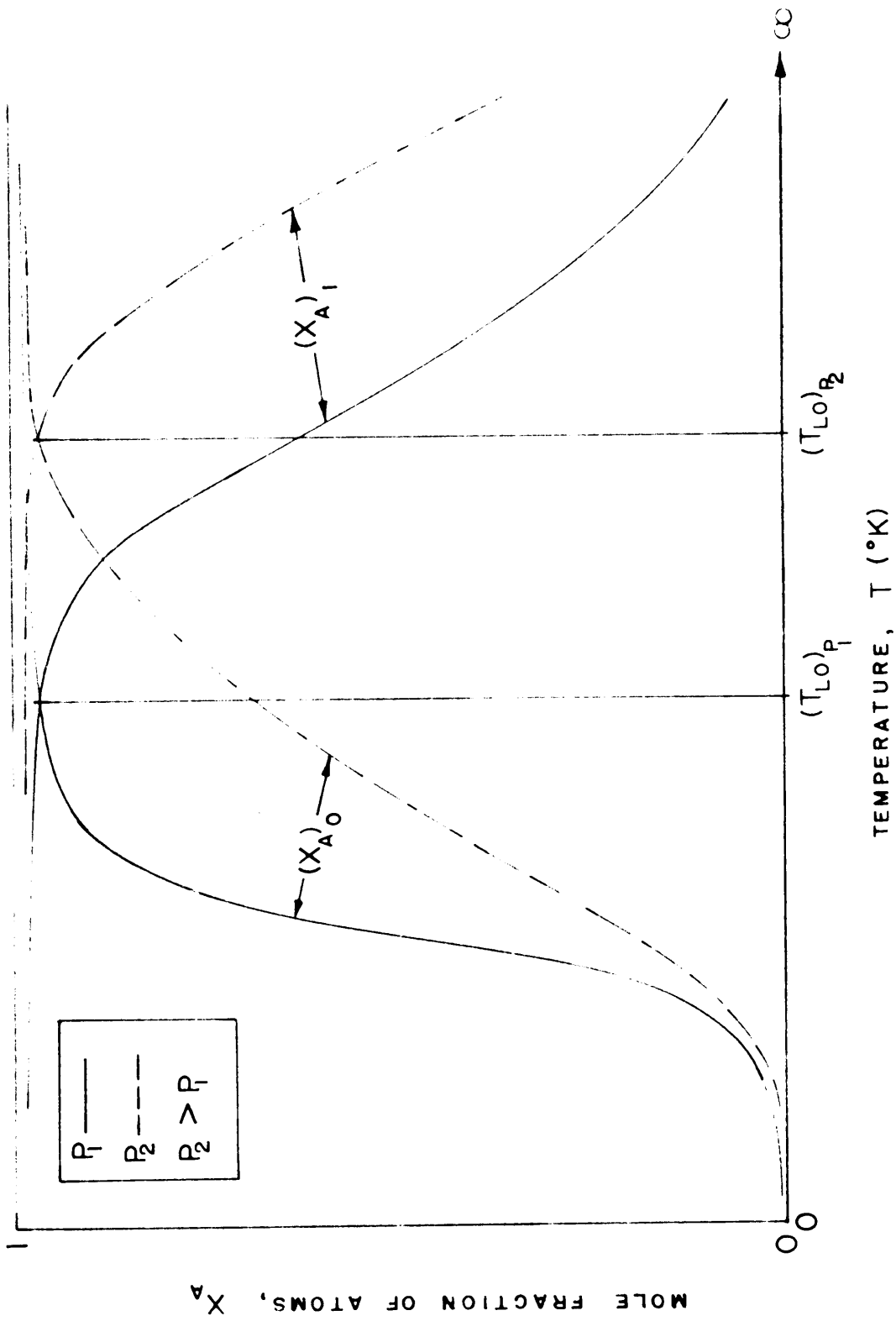
FIGURE 2. GENERAL BEHAVIOR OF THE MOLE-FRACTION FUNCTION

vanishes at zero temperature and approaches unity asymptotically as T becomes infinite. The function $(x_A)_1$, on the other hand, has a value of unity at zero temperature and is a decreasing function approaching zero asymptotically as T becomes infinite. Each of these functions is quite amenable to physical interpretation. Dissociation of the diatomic gas does not occur to any appreciable extent at the lower temperatures, so the mole fraction of atoms present in the mixture remains quite small. Once a temperature is reached at which increased dissociation begins to take place, the number of atomic components within the mixture multiplies rapidly within a certain temperature range, which may be called the predominant range of dissociation. At temperatures beyond this range, a high degree of dissociation having been attained, the number of additional atoms being formed drops off considerably since few molecules remain in the mixture. The change in $(x_A)_o$ with temperature becomes small and the asymptotic approach of this function to unity is quite gradual from this point on. If T_{LO} is the temperature representing this upper limit of the predominant dissociation range, then at temperatures much above this value the function $(x_A)_o$ becomes invalid since ionization of the atomic species must occur if pressure remains unchanged. Increasing pressure causes a general flattening of the $(x_A)_o$ curve; that is, the predominant range of dissociation is widened and the entire dissociation process takes place much more gradually with increasing temperature.

In considering the function $(x_A)_1$ it must be kept in mind that the first-level ionization theory is developed for an ideal gas which is initially monatomic. Hence, if the theory is to be used in the ionization region for a gas which is diatomic in its natural state, then the low-temperature portion of $(x_A)_1$ must be disregarded. However, beyond the temperature T_{LO} the mole fraction of atoms present in the gas mixture should be given to a close approximation by $(x_A)_1$. As can be seen from Fig. 2 the general behavior of $(x_A)_1$ is quite similar to that of $(x_A)_o$ in that an increase in pressure tends to flatten the curve, widening the predominant range of first-level ionization.

In a continuous solution carried well into the ionization temperature range the function x_A would be everywhere a differentiable function of temperature (with pressure held constant), and would appear somewhat similar to a combination of the functions $(x_A)_o$ and $(x_A)_1$ in Fig. 2. (See, e.g., Ref. 5.) Of course the calculations involved in such a continuous solution become quite lengthy. If the differentiability requirement is relinquished at the point T_{LO} then a continuous function x_A, closely approximating the mole fraction of A atoms present in the mixture over the entire temperature range, can be generated by letting $x_A = (x_A)_o$ for $T_o < T_{LO}$ and $x_A = (x_A)_1$ for $T_1 > T_{LO}$. In view of the general behavior of the two functions $(x_A)_o$ and $(x_A)_1$, and other considerations discussed above, it seems quite reasonable to establish the criterion

that $T_o = T_1 = T_{LO}$ when $(x_A)_o = (x_A)_1$. From Eqs. 61 and 86 this leads to the relationship

$$P^3 - 12\ K_o\ K_1\ P - 4\ K_o\ K_1\ (K_o + 4K_1) = 0 \quad , \qquad (90)$$

where
$$P = P_o = P_1 \quad , \qquad (91)$$

$$K_o = K_o(T_{LO}) = C_K(\mu^{3/2}\ T_r)_{A_2} \left[1 - e^{-\frac{(T_v)_{A_2}}{T_{LO}}} \right] \frac{(Q_A{}^E)^2}{Q_{A_2}{}^E}\ T_{LO}{}^{3/2}\ e^{-\frac{T_d}{T_{LO}}} \quad , \qquad (92a)$$

$$K_1 = K_1(T_{LO}) = C_K\ \mu_{i1}{}^{3/2}\ T_{LO}{}^{5/2}\ \frac{Q_{A^+}{}^E}{Q_A{}^E}\ e^{-\frac{T_{i1}}{T_{LO}}} \quad , \qquad (92b)$$

$$Q_{A_2}{}^E = Q_{A_2}{}^E\ (T_{LO}) \quad , \qquad (92c)$$

$$Q_A{}^E = Q_A{}^E\ (T_{LO}) \quad , \qquad (92d)$$

and
$$Q_{A^+}{}^E = Q_{A^+}{}^E\ (T_{LO}) \quad . \qquad (92e)$$

In Eq. 90 the limit temperature T_{LO} is an implicit function of pressure P because of the transcendental nature of Eqs. 92. Hence, for given value of P, a numerical (or iterative) solution is required to determine T_{LO}. However, Eq. 90 is a reduced cubic in P and as such is easily solved to give P as the following explicit function of T_{LO}:

$$P = (4 K_o{}^2 K_1)^{1/3} + (16 K_o K_1{}^2)^{1/3} \quad . \tag{93}$$

A plot of the limit temperature T_{L0} as a function of pressure P is shown in Fig. 3 for the two diatomic gases N_2 and O_2.
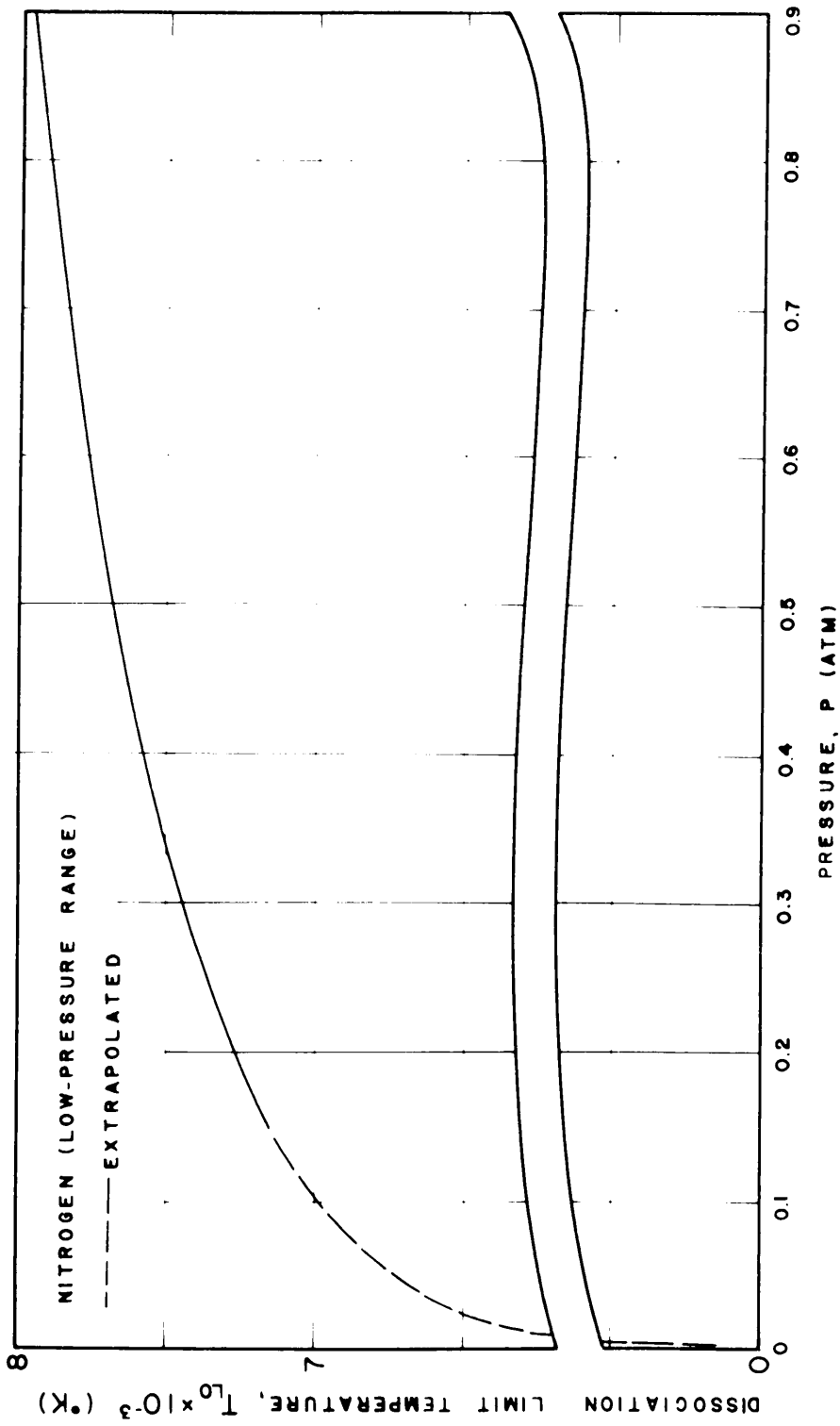
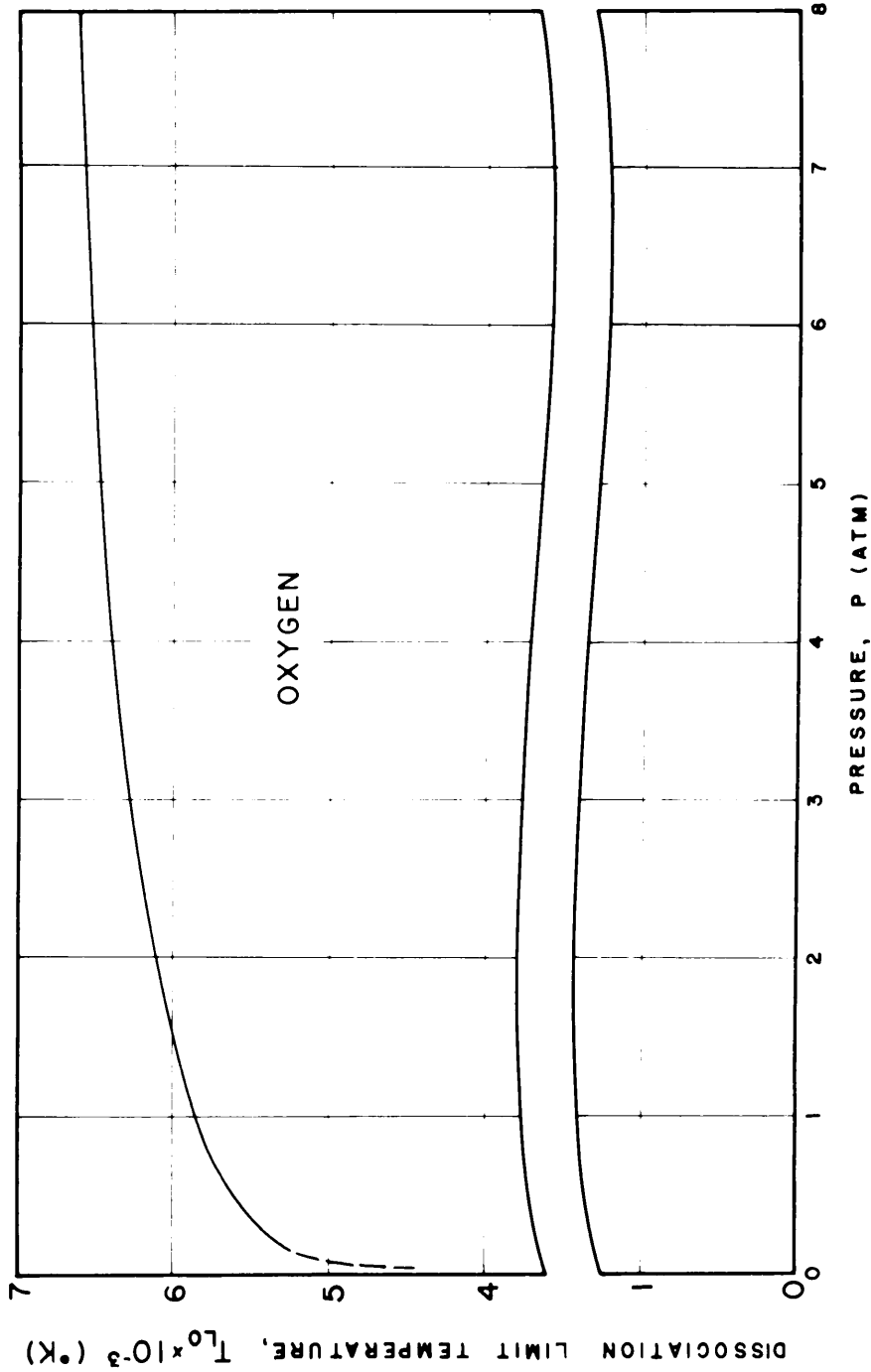FIGURE 3. LIMITING DISSOCIATION TEMPERATURE AS FUNCTION OF PRESSURE

FIGURE 3(CONT'D). LIMITING DISSOCIATION TEMPERATURE AS FUNCTION OF PRESSURE

VI. <u>PRESSURE-TEMPERATURE BOUNDARIES FOR ANY IONIZATION LEVEL OF THE IDEAL IONIZING GAS</u>

Employing the assumption of independent ionization processes at successively higher levels of ionization, the method of Section V for determining a boundary temperature as a function of pressure can be extended and generalized so as to include all possible ionization levels of the initially neutral atoms. The equilibrium reactions for the n + 1 levels of ionization to be considered will be written

| <u>Ionization Level</u>	<u>Equilibrium Reaction</u>
1	$A \rightleftharpoons A^+ + e^-$
2	$A^+ \rightleftharpoons A^{++} + e^-$
.	. . .
.	. . .
.	. . .
n	$A^m \rightleftharpoons A^{m+1} + e^-$
n + 1	$A^n \rightleftharpoons A^{n+1} + e^-$

where m is a positive integer representing the number of electrons which have been stripped from the initially neutral atom A. (Since m = n - 1, it will prove more convenient to write the (n + 1)th equilibrium reaction in terms of n rather than in terms of m + 1.) If the original number of electrons contained in the neutral atom

is given as Z, then clearly the last boundary which can be determined is that between the (Z - 1)th and Zth level, since the last equilibrium reaction which can be written is that for the Zth level.

From Eq. 65 the reaction equation for the first-level ionization is

$$Y_{i1}A \rightarrow \beta_A A + \beta_{A^+}A^+ + \beta_{e^-}e^- \quad . \qquad (94)$$
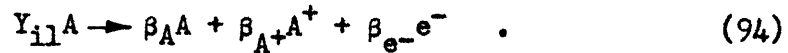
Hence, a comparable reaction equation for the nth ionization level becomes

$$Y_{i1}A^m \rightarrow \beta_{A^m}A^m + \beta_{A^{m+1}}A^{m+1} + \beta_{e^-}e^- \quad . \qquad (95)$$
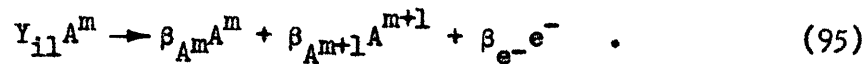
Defining degree of ionization for this level in the usual way, α_n will be given by

$$\alpha_n = \frac{Y_{i1} - \beta_{A^m}}{Y_{i1} - 0} \quad . \qquad (96)$$

By conservation of atomic nuclei, the mass balance for reaction equation 95 can be written

$$Y_{i1} = \beta_{A^m} + \beta_{A^{m+1}} \quad . \qquad (97)$$

Hence, since n = m + 1, the degree of ionization for the nth ionization level becomes

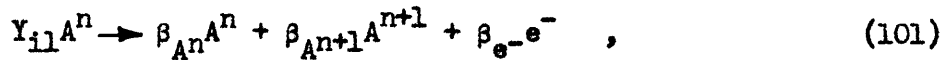$$\alpha_n = \frac{\beta_{A^n}}{Y_{i1}} \quad . \qquad (98)$$

Now at this level the number of moles of free electrons present in the mixture is given by

$$\beta_{e^-} = (n - 1) Y_{i1} + \beta_A n \quad . \tag{99}$$

Hence, the mole fraction of A^{m+1} ions becomes

$$(x_{A^{m+1}})_n = \frac{\alpha_n}{n + \alpha_n} \quad . \tag{100}$$

At the next highest energy level, the $(n + 1)$th, a reaction equation similar to Eq. 95 can be written as

$$Y_{i1} A^n \longrightarrow \beta_A n A^n + \beta_{A^{n+1}} A^{n+1} + \beta_{e^-} e^- \quad , \tag{101}$$

and the equilibrium reaction for this level becomes

$$A^n \rightleftharpoons A^{n+1} + e^- \quad . \tag{102}$$

Hence, at the $(n + 1)$th level, the mole fraction of A^n ions is given by

$$(x_{A^n})_{n+1} = \frac{1 - \alpha_{n+1}}{n + 1 + \alpha_{n+1}} \quad , \tag{103}$$

where α_{n+1} is the degree of ionization of the $(n + 1)$th level.

By developing equilibrium constants for the two levels n and $n + 1$, and expressing $(x_{A^{m+1}})_n$ and $(x_{A^n})_{n+1}$ in terms of these constants, the variations of the two functions $(x_{A^{m+1}})_n$ and $(x_{A^n})_{n+1}$ with temperature and pressure can be observed. With this aim in mind we proceed in a manner similar to that of Section IV.

The partial pressures at the nth ionization level are given by

$$p_{A^m} = N_{A^m} k_1 \frac{T_n}{V_n} \quad , \tag{104a}$$

$$p_{A^{m+1}} = N_{A^{m+1}} k_1 \frac{T_n}{V_n} \quad , \tag{104b}$$

and

$$p_{e^-} = N_{e^-} k_1 \frac{T_n}{V_n} \quad . \tag{104c}$$

Hence, the total pressure of the nth level mixture becomes

$$P_n = (N_{A^m} + N_{A^{m+1}} + N_{e^-}) k_1 \frac{T_n}{V_n} \quad . \tag{105}$$

An equilibrium constant K_n for this level is defined in terms of the partial pressures as

$$K_n = \frac{p_{A^{m+1}} \, p_{e^-}}{p_{A^m}} \quad , \tag{106}$$

which can be written

$$K_n = \frac{N_{A^{m+1}} \, N_{e^-}}{N_{A^m}} k_1 \frac{T_n}{V_n} \quad . \tag{107}$$

The law of mass action for the nth ionization level gives

$$\frac{N_{A^{m+1}} \, N_{e^-}}{N_{A^m}} = \frac{Q_{A^{m+1}} \, Q_{e^-}}{Q_{A^m}} e^{-\frac{T_{in}}{T_n}} \quad , \tag{108}$$

where $T_{in} = \dfrac{I_{in}}{k_2}$. Hence, substituting Eq. 108 into Eq. 107, and utilizing the relationships of Eqs. 9, 13, 46, and 63, the equilibrium constant K_n for the nth level becomes

$$K_n = C_K \, \mu_{in}^{3/2} \, T_n^{5/2} \, \frac{Q_{A^{m+1}}^E}{Q_{A^m}^E} \, e^{-\frac{T_{in}}{T_n}} \, , \qquad (109)$$

where

$$\mu_{in} = \frac{m_{A^{m+1}} \, m_{e^-}}{m_{A^m}} \approx \frac{m_{A^{m+1}} \, m_{e^-}}{m_{A^{m+1}} + m_{e^-}}$$

Similarly, for the $(n + 1)$th ionization level, it is easily shown that

$$K_{n+1} = C_K \, \mu_{in+1}^{3/2} \, T_{n+1}^{5/2} \, \frac{Q_{A^{n+1}}^E}{Q_{A^n}^E} \, e^{-\frac{T_{in+1}}{T_{n+1}}} \, , \qquad (110)$$

where

$$T_{in+1} = \frac{I_{in+1}}{k_2}$$

and

$$\mu_{in+1} = \frac{m_{A^{n+1}} \, m_{e^-}}{m_{A^n}} \approx \frac{m_{A^{n+1}} \, m_{e^-}}{m_{A^{n+1}} + m_{e^-}}$$

Recalling that $N_{Aj} = N_o \, \beta_{Aj}$, Eqs. 97, 98, 99, 104, 105, and 106 can be combined to express the equilibrium constant K_n of the nth ionization level in terms of the degree of ionization α_n of that level as

$$K_n = \frac{\alpha_n(n - 1 + \alpha_n)P_n}{(1 - \alpha_n)(n + \alpha_n)} \quad ; \tag{111}$$

or, solving for α_n ,

$$\alpha_n = \left[\frac{n}{1 + \dfrac{P_n}{K_n}} + \left(\frac{n - 1}{2} \right)^2 \right]^{1/2} - \left(\frac{n - 1}{2} \right) \quad . \tag{112}$$

Substituting this expression into Eq. 100, the mole fraction of A^{m+1} ions at the nth ionization level can be written in terms of the equilibrium constant K_n and total static pressure P_n at that level as

$$(x_{A^{m+1}})_n = \frac{K_n}{2 P_n} \left\{ \left[1 + n + (n - 1) \frac{P_n}{K_n} \right]^2 + \frac{4 P_n}{K_n} \right\}^{1/2} -$$

$$\frac{1}{2} \left[n - 1 + (n + 1) \frac{K_n}{P_n} \right] \quad . \tag{113}$$

Similarly, for the $(n + 1)$th ionization level, the following three expressions are obtained:

$$K_{n+1} = \frac{(n + \alpha_{n+1}) \, \alpha_{n+1} \, P_{n+1}}{(1 - \alpha_{n+1})(n + 1 + \alpha_{n+1})} \quad , \tag{114}$$

$$\alpha_{n+1} = \left[\frac{n + 1}{1 + \dfrac{P_{n+1}}{K_{n+1}}} + \frac{n^2}{4} \right]^{1/2} - \frac{n}{2} \quad , \tag{115}$$

and

$$(x_A n)_{n+1} = 1 -$$

$$\frac{n^2 P_{n+1} + (n + 2)^2 K_{n+1}}{2(n + 1) P_{n+1}} \left\{ \left[1 + \frac{4(n + 1) P_{n+1}}{n^2 P_{n+1} + (n + 2)^2 K_{n+1}} \right]^{1/2} - 1 \right\}. \qquad (116)$$

It will be noted that when $n + 1 = 1$ (i.e., $n = 0$), Eq. 116 corresponds to the first ionization level with respect to $(x_A)_1$ discussed in Section IV. Hence, under this condition, Eq. 116 reduces to Eq. 86 of that section.

The behavior of the two functions $(x_A m+1)_n$ and $(x_A n)_{n+1}$ differs from that of Eqs. 61 and 86 in that $(x_A m+1)_n$ approaches the value $1/(n + 1)$ asymptotically as temperature becomes infinite ($\alpha_n \rightarrow 1$), and $(x_A n)_{n+1}$ approaches $1/(n + 1)$ asymptotically at zero temperature ($\alpha_{n+1} \rightarrow 0$). The asymptotic value $1/(n + 1)$ decreases with increasing n because the number of free electrons present in the gas mixture grows increasingly larger as higher ionization levels are attained, whereas the number of atomic nuclei in volume V_n remains unchanged. However, this decrease in the value of the upper asymptote does not interfere with the determination of boundary temperatures at the higher ionization levels. Mathematically it is necessary only that $(x_A m+1)_n$ and $(x_A n)_{n+1}$ both have the same upper and lower asymptotes and that the two functions each be single-valued at least within the region of the boundary temperature

(point of intersection), $(x_{Am+1})_n$ being an increasing function and $(x_{An})_{n+1}$ a decreasing function of temperature within this region.

To determine the pressure-temperature boundary between the nth and (n + 1)th ionization levels it is again assumed that at this limit $P_n = P_{n+1} = P$, $T_n = T_{n+1} = T_{Ln}$, and $(x_{Am+1})_n = (x_{An})_{n+1}$. Hence, equating the functions 113 and 116 and simplifying, there is obtained the relationship

$$2n^3 (n + 1) P^3 + (n + 2)\left[n^3 K_n + (n^2 - 1)(n + 2) K_{n+1}\right] P^2 -$$

$$2(n + 2)^2 (n^2 + n + 1) K_n K_{n+1} P - (n + 2)^2 K_n K_{n+1}$$

$$\left[(n + 1)^2 K_n + (n + 2)^2 K_{n+1}\right] = 0 \quad , \tag{117a}$$

where

$$K_n = K_n (T_{Ln}) = C_K \mu_{in}^{3/2} T_{Ln}^{5/2} \frac{Q_{Am+1}^E}{Q_{Am}^E} e^{-\frac{T_{in}}{T_{Ln}}} \quad , \tag{117b}$$

$$K_{n+1} = K_{n+1} (T_{Ln}) = C_K \mu_{in+1}^{3/2} T_{Ln}^{5/2} \frac{Q_{An+1}^E}{Q_{An}^E} e^{-\frac{T_{in+1}}{T_{Ln}}} \quad , \tag{117c}$$

$$Q_{Am}^E = Q_{Am}^E (T_{Ln}) \quad , \tag{117d}$$

$$Q_{Am+1}^E = Q_{Am+1}^E (T_{Ln}) = Q_{An}^E (T_{Ln}) \quad , \tag{117e}$$

and

$$Q_{An+1}^E = Q_{An+1}^E (T_{Ln}) \quad . \tag{117f}$$

For a given pressure P Eqs. 117 can be solved iteratively to give the boundary temperature T_{Ln}, which constitutes an upper temperature limit for the nth ionization level and a lower temperature limit for the (n + 1)th ionization level. It should be noted that even though the dissociation range was assigned the value n = 0 in Section V, this value cannot be substituted into Eqs. 117 to give the relationships of Eqs. 90, 91, and 92, since Eqs. 117 apply only to a pressure-temperature boundary between two ionization levels.

VII. CONCLUSIONS

In view of the results presented in Sections IV, V, and VI of this analysis, the following conclusions can be reached:

1. In thermochemical calculations involving the use of electronic partition functions it is necessary to investigate the effects of higher-energy terms in determining the degree of accuracy of final results obtained from such calculations. A constant value determined for the ratio of electronic partition functions with several energy levels above the ground state retained, and averaged over the temperature range of interest, can vary significantly from that which would be obtained using only ground state degeneracies.

2. In order to make use of existing ideal gas theories in the analysis of systems which undergo both dissociation and ionization effects over wide ranges of temperature and pressure it is necessary to impose the assumption of independent gas processes in addition to those assumptions already inherent in each of the separate theories.

3. The pressure-temperature relationship which defines the boundary between dissociation and first-level ionization of an initially diatomic gas provides a means for determining theoretically

the upper limit of the ideal dissociating gas theory under
equilibrium conditions, whether the gas be carried into the ioni-
zation range or not.

4. Although the assumptions made in extending the ideal
ionizing gas theory to higher levels of ionization may prove
severe in the case of some gases, the pressure-temperature boundary
relationship developed under these assumptions still can be used
to provide a theoretical determination of the predominant ranges
of ionization at least to a first approximation.

VIII. SUMMARY

The problem of determining thermodynamic properties of gaseous systems in which real-gas effects must be considered can be greatly simplified through use of existing ideal-gas theories for the processes of dissociation and ionization. Since, however, the ideal dissociating gas theory neglects ionization effects and the ideal ionizing gas theory does not take into account dissociation, an additional assumption must be made in order to use these two theories within a single system experiencing both effects. The added assumption which is made is that the processes of dissociation, single ionization, and higher levels of ionization all occur independently of one another though in a definite order within the system. With this linearizing assumption of independent gas processes the ideal gas theories then can be applied within their respective ranges of application in order to calculate the thermodynamic properties of any system under equilibrium conditions, provided the ranges of application can be determined. Neither the ideal dissociating gas theory nor the ideal ionizing gas theory explicitly defines the pressure-temperature region throughout which the theory is applicable. In the present work an analytic expression is developed which gives the limiting temperature as a function of pressure for the ideal dissociating gas theory. The method is then generalized in the ionization range so

as to provide pressure-temperature boundaries for all levels of
ionization within the assumption of independent first-level,
second-level, and higher-level ionization processes.

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PRESSURE-TEMPERATURE BOUNDARIES FOR
IDEAL DISSOCIATING AND IONIZING GASES

by

William Pendleton Harrison, Jr.

ABSTRACT

With the assumption of independent gas processes
the ideal dissociating gas theory of Lighthill and
the ideal ionizing gas theory can be used to analyze
real-gas systems in equilibrium experiencing the ef-
fects of dissociation and ionization, provided the
range of application of each theory is known. In
this work an analytical expression is developed which
gives the limiting temperature as a function of pres-
sure for the ideal dissociating gas theory, the re-
sulting values constituting a pressure-temperature
division boundary separating the range of application
of the ideal dissociating gas theory from that of the
first-level ideal ionizing gas theory. The ideal
ionizing gas theory is then extended so as to include
all levels of ionization, and a generalized expression
is developed which permits the determination of pres-
sure-temperature boundaries at any ionization level.