THE RELATION BETWEEN THE PARTITION FUNCTION AND THERMODYNAMIC PROPERTIES

by

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NOMENCLATURE

A	Helmholtz free energy
C_v	Specific heat at constant volume
C_p	Specific heat at constant pressure
C	$G_i e^{-\alpha}$
E	Internal energy of a system
E_i	Eigenvalue of the energy
G	Gibbs free energy
g	Statistical weight
H	Enthalpy of a system
H_i	Hamiltonian operator
h	Planck constant
I	Polar moment of inertia
i	Indicates the energy level
J	Quantum number of the energy level
K	Boltzmann constant
N	Total number of particles
N_i	Particles in energy level i
N_{ij}	Particles in energy level i of statistical weight j
N_o	Avogadro's number
N_x	Particles in the last group
m	Mass of a molecule
p	Pressure
Q	Partition function

R	Gas constant
r	interatomic distance
S	Entropy of a system
T	Absolute temperature
v	Specific volume
W	Thermodynamic probability
W_{max}	Maximum thermodynamic probability
x	Number or groups
x	$h\omega_e/KT$ Einstein function

Greek Letters

α	Lagrangian multiplier
β	Lagrangian multiplier
β_e	Equilibrium vibrational constant
ε_o	Energy of a molecule at ground level
ε_i	Energy of a molecule at energy level i
$\bar{\varepsilon}$	Internal energy per molecule
μ	Reduced mass
σ	The symmetry number
Ψ	Wave function
π	Universal constant (3.1416)
ω_e	Fundamental vibrational frequency

Operators

$\sum_i$ Summation over indices i

$\prod_i$ Multiplication over indices i

$\prod_j$ Multiplication over indices j

INTRODUCTION

The classical thermodynamic functions of a system are determined from the observable, macroscopic properties of a system. The macroscopic properties in turn may also be determined from the microscopic point of view by considering the properties and statistical behavior of the atoms and/or molecules in the system. The knowledge of molecules and the statistical characteristics necessary for the evaluation of the thermodynamic functions is incorporated in the partition function, and an understanding of the partition function permits the derivation of all the thermodynamic properties of a gaseous system in the statistical approach.

The partition function, by definition, is

$$Q = \sum_{i=0}^{\infty} g_i e^{-\frac{\varepsilon_i}{KT}} \qquad (1)$$

where Q is the partition function, g_i is the statistical weight, ε_i is a quantum-mechanically allowed energy level of the molecules which constitute the system, K is the Boltzmann constant, and T is the absolute temperature of the system.

Physically, the partition function is a pure number and might be evaluated for a system in any physical state, containing any number of molecules. It is a well defined function used to derive thermodynamic properties of a system from the state of atoms or molecules. As an example, the five basic thermodynamic properties S, E, H, A, and G, and the two derived thermodynamic properties, C_v and C_p, of a gaseous system can all be expressed in terms of the partition function. The definition of the partition function is the result of natural grouping of variables in the derivation of the Maxwell-Boltzmann distribution law, the law which describes the statistical behavior of any molecular gaseous system. It can be seen from the following sequence in this report that all the thermodynamic properties of a molecular gaseous system can be calculated on the basis

of a Maxwellian model with known spectroscopic information. The value of this kind of calculation lies in two facts; first, the thermodynamic properties of a system that may be unobtainable by macroscopic experiment can be evaluated using this method, and second, even though the macroscopic experiment can be carried out, the statistical method yields thermodynamic information with a higher accuracy and precision than the classical method.

I. Energy Level ε, and Statistical Weight g, in a System

Theoretical and experimental investigations, from the areas of quantum mechanics and spectroscopy, have yielded the pictures of the structure of individual molecules in the ideal gaseous state, that is, for the molecules at pressures sufficiently low that interactions between the molecules are negligible. From the Schrodinger wave equation (Ref. 6),

$$H\Psi = E\Psi \qquad (2)$$

where H is the Hamiltonian operator, Ψ is the wave function, i.e. the eigenfunction, and E_i is the energy, i.e. the eigenvalue, the well defined energy levels are established theoretically. Experimentally, the energy of a system can be found from the observed spectroscopic data. Assuming that there is no interaction between the translational, rotational, vibrational, and electronic contributions to the energy, the total energy of the system will simply be the sum of the various energy contributions. Moreover, a complete set of discrete quantum levels of energy is associated with each contribution. Each set of levels of energy may be represented schematically by the following diagram.

* The levels (discrete quantum levels) of energy are numbered

as indicated. The lowest or ground level is the minimum possible, or allowable, level of a molecule.

* The energy of each level is represented by $\varepsilon_0, \varepsilon_1, \cdots, \varepsilon_i$.
* The statistical weight (sometimes called degeneracy or multiplicity) is the number of individual states of virtually the same energy. It is given by the notation g_0, g_1, ..., g_i.

Schematic diagram of a set of levels of energy of a molecule

Level of Energy	No. of the given level	Energy of the given level	Statistical Weight
———	i	ε_i	g_i
———	.	.	.
———	.	.	.
.	.	.	.
———	2	ε_2	g_2
———	1	ε_1	g_1
———	0	ε_0	g_0

In order to evaluate the partition function, $\Sigma\, g_i \exp(-\varepsilon_i/KT)$, the g_i and ε_i for each energy level have to be known. However, it has been shown that only when the electronic contribution to the energy is significant, will the discrete values of ε_i and the corresponding g_i prove their usefulness. The following are examples of values of the g_i and ε_i that are available in the literature.

A. The set of electronic energy levels of monatomic hydrogen (Ref. 2) where J is the quantum number and (cm^{-1}) is the wave number which is the equivalent of an energy unit:

Energy Level	$g = (2J + 1)$	Energy (cm^{-1})
0	2	0
1	2	82258.907
2	2	82258.942
3	4	82259.272
4	2	97492.198
.	.	.

B. The set of energy levels of diatomic hydrogen (Ref.3)

Energy Level	$g = (2J + 1)$	Energy (cm^{-1})
0	1	0
1	2	91698.0
2	2	100043.0
3	2	100062.8
.	.	.

II. Thermodynamic Probability W and Maxwell-Boltzmann Distribution Law

The relationship between the thermodynamic properties of a system and the microscopic structure of the system, as proposed by Planck, is that the entropy of a system, S, may be expressed by the equation

$$S = K \ln W \qquad (3)$$

in which, K is the Boltzmann constant and W is the thermodynamic probability. This equation is a postulate; it is, moreover, a most important one, for it constitutes the bridge that connects the macroscopic thermodynamics with the microscopic thermodynamics. The thermodynamic probability is defined as the number of microscopically different ways in which a thermodynamic state can be realized, or the

number of different ways in which a statistical state can be attained.

As an example, let N distinguishable particles be arranged into x groups with N_1 in the first group, N_2 in the second group, and so on to N_x in the last group, and such that

$$N_1 + N_2 + \ldots\ldots\ldots + N_i + \ldots\ldots + N_x = N \qquad (4)$$

The total number of ways of distributing the N particles into x groups is N!. This includes, as different ways, the result of permutations of the N_i within the i group. However, permutations within a group do not result in "different" ways of distributing the N particles into the x groups. The number of such permutations within a group is $N_i!$. Therefore, the total number of "different" ways of distributing the N particles into N groups is obtained by dividing the N! ways by $\prod_i N_i!$. This result is the thermodynamic probability, W.

$$W = \frac{N!}{\prod_i N_i!} \qquad (5)$$

After knowing the thermodynamic probability, W, the following statement, shows how energy level, statistical weight, and thermodynamic probability are related to the Maxwill-Boltzmann energy distribution. At a given temperature, the distribution of molecules among the possible states of energy is described by the Maxwell-Boltzmann statistics, which the molecular system follows as proved by experiment. This distribution gives the average population of energy level ε_i in terms of the population of a state at the ground level having as energy ε_0.

A number of atoms or molecules will be distributed among energy levels with values denoted by ε_0, ε_1, ε_2, and so on. Sometimes it happens that certain of these levels are degenerate - that is, can be realized in more than one way or through more than one combina-

tion of quantum numbers. The number of different states having the same energy level is the "statistical weight" of that level. Statistical weight is equivalent to having several boxes of the mechanical analogue at the same height in the gravitational field. The number of such boxes at any one height, or the quantum number corresponding to any one level, is said to be the statistical weight of the energy level.

When a situation of this kind occurs, it is necessary that the energy be listed as many times as the value of the statistical weight of the level. To express the thermodynamic probability, it is desirable to employ double subscripts for the N's. Thus, if i specifies the energy level of ε_i, then N_{ij} will denote the number of particles in the jth representation of that level if j takes on the values 1, 2, ... , g_i, with g_i equal to the statistical weight. The thermodynamic probability of the system is

$$W = \frac{N!}{\prod_i N_i!} \frac{\prod_i N_i!}{\prod_i \prod_j N_{ij}!} \tag{6}$$

or

$$W = \frac{N!}{\prod_i \prod_j N_{ij}!} \tag{7}$$

and

$$\sum_{j=1}^{g_i} N_{ij} = N_i \tag{8}$$

where N_i is the total number of particles with energy ε_i.

With the foundation shown above, the Maxwell-Boltzmann distribution Law can be derived, which shows how distinguishable atoms or molecules are distributed among their energy levels. Consider N particles with allowable energy levels ε_0, ε_1, ε_2, etc., which have

statistical weights $\mathcal{E}_0$, $\mathcal{E}_1$, $\mathcal{E}_2$, etc.. The total energy of these particles is a fixed quantity, E. Since both the total number of molecules and the total energy are fixed, this statistical problem involves two conditions of constraint.

By using the method of Lagrangian multipliers, the maximum thermodynamic probability can be established.

Taking the logarithm of equation (7), there results

$$\ln W = N \ln N - N - \sum_i \sum_j (N_{ij} \ln N_{ij} - N_{ij}) \tag{9}$$

Moreover

$$N = \sum_i N_i = \sum_i \sum_j N_{ij} \tag{10}$$

and the total energy constraint is expressed as

$$E = \sum_i N_i \varepsilon_i = \sum_i \sum_j N_{ij} \varepsilon_i . \tag{11}$$

Taking variations of equation (9), (10), (11)

$$\delta \ln W = - \sum_i \sum_j \ln N_{ij} \delta N_{ij} \tag{12}$$

$$\delta N = \sum_i \delta N_i = \sum_i \sum_j \delta N_{ij} = 0 \tag{13}$$

$$\delta E = \sum_i \varepsilon_i \delta N_i = \sum_i \sum_j \varepsilon_i \delta N_{ij} = 0 \tag{14}$$

and multiplying equation (13) by α and (14) by β, the combination of (12), (13), and (14) gives

$$\delta \ln W - \alpha \delta N - \beta \delta E = - \sum_i \sum_j (\ln N_{ij} + \alpha + \beta \varepsilon_i) \delta N_{ij} . \tag{15}$$

To render ln W a maximum, the coefficient of each of the variations of the right-hand side equation of (15) is set equal to zero. The

result is that

$$\ln N_{ij} = -\alpha - \beta \varepsilon_i \tag{16}$$

or

$$N_{ij} = e^{-\alpha - \beta \varepsilon_i} \tag{17}$$

Since N_{ij} depends only on i (through ε_i) and not on j, the total number of particles with energy ε_i can be written as follows

$$N_i = \sum_{j=1}^{g_i} N_{ij} = g_i N_{ij} = g_i e^{-\alpha - \beta \varepsilon_i} \tag{18}$$

The two equations immediately above are statements of the Maxwell-Boltzmann energy distribution law.

The average energy, $\bar{\varepsilon}$, of the particles in the system can be found as

$$\bar{\varepsilon} = \frac{E}{N} = \frac{\sum_i \varepsilon_i N_i}{\sum_i N_i}$$

$$= \frac{\sum_i \varepsilon_i g_i e^{-\beta \varepsilon_i}}{\sum_i g_i e^{-\beta \varepsilon_i}} \tag{19}$$

The factor $e^{-\alpha}$ obviously drops out when equation (17) is substituted into the expression for the quotient, E/N. It is evident, therefore, that β depends only on the average molecular energy and hence must be an intensive variable.

β is identified by considering its relationship to the entropy.

$$S = K \ln W_{max} \tag{20}$$

The entropy for a system in equilibrium, one for which the thermodynamic probability is maximum, can be evaluated by multiplying equation (9) by K and replacing $\ln N_{ij}$ by $-\alpha - \beta \varepsilon_i$. The expression is thus

$$S = N K \ln N - N K + K \sum_i \sum_j N_{ij} (\alpha + \beta \varepsilon_i + 1) \qquad (21)$$

or

$$S = K \ln N! + N K \alpha + K \beta E + N K \qquad (22)$$

Differentiation of (22), while keeping N and all of the ε_i's constant, gives

$$dS = N K \, d\alpha + K E \, d\beta + K \beta \, dE \qquad (23)$$

Since

$$N = \sum_i N_i = \sum_i g_i e^{-\alpha - \beta \varepsilon_i} \qquad (24)$$

then

$$dN = 0 = \sum_i (-d\alpha - \varepsilon_i d\beta) \, g_i e^{-\alpha - \beta \varepsilon_i}$$

$$= - \sum_i N_i (d\alpha + \varepsilon_i d\beta)$$

$$= -N \, d\alpha - E \, d\beta \qquad (25)$$

Combining equation (23) and equation (25):

$$\left(\frac{\partial S}{\partial E} \right)_V = K \beta \qquad (26)$$

The differentiation of S is obtained by holding constant all independent variables except E. From classical thermodynamics,

$$\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T} \tag{27}$$

therefore, by comparison of (26) with (27)

$$\beta = \frac{1}{KT} \tag{28}$$

The Maxwell-Boltzmann distribution law equation (18) can be written in the following form

$$N_i = C\, e^{-\frac{\varepsilon_i}{KT}} \tag{29}$$

where C is the $g_i e^{-\alpha}$.

III. Expression of Thermodynamic Properties of a Gaseous System in Terms of Partition Function

1. Internal Energy E

From equation (19) and (28), the internal energy E of a system can be written as

$$E = \frac{N\sum_i \varepsilon_i N_i}{\sum_i N_i} = \frac{N\sum_i \varepsilon_i g_i e^{-\frac{\varepsilon_i}{KT}}}{\sum_i g_i e^{-\varepsilon_i/KT}}$$

$$= \frac{N\sum_i \varepsilon_i g_i e^{-\frac{\varepsilon_i}{KT}}}{Q} \tag{30}$$

where Q is the partition function,

$$Q = \sum_i g_i e^{-\frac{\varepsilon_i}{KT}} \tag{31}$$

Now taking the derivative of Q with respect to T,

$$\frac{dQ}{dT} = \frac{1}{KT^2} \sum_i \varepsilon_i g_i e^{-\frac{\varepsilon_i}{KT}} \tag{32}$$

From equations, (30) and (32), E can be expressed as

$$E = \frac{NK\ T^2}{Q} \frac{dQ}{dT}$$

or

$$E = NKT\left(\frac{\partial \ln Q}{\partial \ln T}\right)_V \tag{33}$$

2. Entropy S

The entropy of a system can likewise be easily computed. From

$$N = \sum_i N_i = \sum_i g_i e^{-\alpha - \beta\varepsilon_i}$$

and by use of the definition of Q,

$$Q = Ne^{\alpha}. \tag{34}$$

By subsitution of the internal energy or given by equation (33) and from equation (34) into equation (22), and by use Stirling's approximation, the entropy can be expressed in the following simple closed from:

$$\begin{aligned} S &= K \ln N! + NK\alpha + K\beta E + NK \\ &= K (N \ln N - N) + NK \ln Q - NK \ln N + NK\left(\frac{\partial \ln Q}{\partial \ln T}\right) + NK \\ &= NK \left(\ln Q + \frac{\partial \ln Q}{\partial \ln T}\right) \\ &= NK \frac{\partial}{\partial T} (T \ln Q) \end{aligned} \tag{35}$$

3. Helmholtz Free Energy, $A = E - TS$.

$$A = NKT \frac{\partial \ln Q}{\partial \ln T} - NKT \left(\ln Q + \frac{\partial \ln Q}{\partial \ln T}\right)$$

$$= - NKT \ln Q \qquad (36)$$

4. Enthalpy, H.

$$p = - \left(\frac{\partial A}{\partial v}\right)_T = - \frac{\partial}{\partial v} (- NKT \ln Q)$$

$$= NKT \left(\frac{\partial \ln Q}{\partial v}\right)_T \qquad (37)$$

Then the pv term is

$$pv = vNKT \left(\frac{\partial \ln Q}{\partial v}\right)_T$$

$$= NKT \left(\frac{\partial \ln Q}{\partial \ln v}\right)_T \qquad (38)$$

and from equation (33) and (38) the enthalpy H can be expressed as

$$H = E + pv$$

$$= NKT \left[\left(\frac{\partial \ln Q}{\partial \ln T}\right)_V + \left(\frac{\partial \ln Q}{\partial \ln v}\right)_T\right] \qquad (39)$$

5. Gibbs Free Energy, $G = H - TS$.

$$G = H - TS$$

$$= NKT \left[\left(\frac{\partial \ln Q}{\partial \ln T} \right)_V + \left(\frac{\partial \ln T}{\partial \ln v} \right)_T \right] - NKT \ln Q - NKT \left(\frac{\partial \ln Q}{\partial \ln T} \right)_V$$

$$= NKT \left[\left(\frac{\partial \ln Q}{\partial \ln v} \right)_T - \ln Q \right] . \qquad (40)$$

6. Specific Heat at Constant Volume, C_v, and Constant Pressure C_p.

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v$$

$$= \frac{\partial}{\partial T} \left[NKT \left(\frac{\partial \ln Q}{\partial \ln T} \right)_v \right]$$

$$= NK \left[\left(\frac{\partial \ln Q}{\partial \ln T} \right)_v + T \frac{\partial}{\partial T} \left(\frac{\partial \ln Q}{\partial \ln T} \right)_v \right]$$

$$= NK \left[\left(\frac{\partial \ln Q}{\partial \ln T} \right)_v + \frac{\partial}{\partial \ln T} \left(\frac{\partial \ln Q}{\partial \ln T} \right)_v \right]$$

$$= NK \left[\left(\frac{\partial \ln Q}{\partial \ln T} \right)_v + \left(\frac{\partial^2 \ln Q}{\partial \ln T^2} \right)_v \right] \qquad (41)$$

For a perfect gas, $R = pv/T = NK \left(\frac{\ln Q}{\ln v} \right)_T$, and $C_p = R + C_v$, hence

$$C_p = NK \left[\left(\frac{\partial \ln Q}{\partial \ln v} \right)_T + \left(\frac{\partial \ln Q}{\partial \ln T} \right)_v + \left(\frac{\partial^2 \ln Q}{\partial \ln T^2} \right)_v \right] \qquad (42)$$

IV. Calculation of Thermodynamic Properties

1. Procedure

A. Partition Function Q

a. Assuming that Q_{trans} can be approximated by replacing the summation of equation (1) by an integral, upon intergration the following equation results, (Ref. 4).

$$Q_{trans} = f_1 (m, T)$$

$$Q_{trans} = (2\pi mKT)^{3/2} V/h^3$$

b. Assuming that the diatomic molecule is a rigid rotator, upon replacing the sum of

$$Q_{rot} = \sum_i g_i e^{-\frac{\varepsilon_{irot}}{KT}}$$

the following equation is derivable. (Ref. 4)

$$Q_{rot} = f_2 (m, T, r)$$

$$Q_{rot} = \frac{8\pi^2 IKT}{\sigma h^2}$$

where r is the interatomic distance, $I = \mu r$, μ is the reduced mass, $m_1 * m_2/m_1 + m_2$ for diatomic molecules, and σ is the symmetry number.

c. Assuming that the diatomic molecule is harmonic oscillator, upon neglecting the higher terms of

$$Q_{vib} = \sum_i g_i e^{-\frac{ivib}{KT}}$$

the following equation is derivable. (Ref. 4).

$$Q_{vib} = f_3 (\beta_e, \omega_e)$$

$$Q_{vib} = \prod \frac{1}{1-e^{-\beta_e h \omega_e}}$$

where β_e is the equilibrium vibrational constant, and ω_e

is the fundamental vibrational frequency.

d. The exact Q_{elec} is as follows,

$$Q_{elec} = f_4(\varepsilon_i, g_i)$$

$$Q_{elec} = g_0 + g_1 e^{-\frac{\varepsilon_1}{KT}} + g_2 e^{-\frac{\varepsilon_2}{KT}} + \cdots\cdots\cdots$$

e. Q_{total} is the products of Q_{trans}, Q_{rot}, Q_{vib} and Q_{elec}.

$$Q_{total} = \text{II } Q$$

B. Internal Energy E, (Ref. 4)

$$E_{trans} = NKT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_v$$

$$= NKT^2 \frac{\partial}{\partial T}\left(\frac{3}{2} \ln \frac{2\pi mKT}{h^2} + \ln V\right)$$

$$= \frac{3}{2} NKT^2 \left(\frac{1}{T}\right)$$

$$= \frac{3}{2} NKT$$

$$= \frac{3}{2} RT$$

$$E_{rot} = RT$$

$$E_{vib} = RTx\left(\frac{1}{2} + \frac{1}{1-e^x}\right)$$

where x is equal to $h\omega_3/KT$, and ω_e is the fundamental vibration frequency.

$$E_{elec} = R \frac{\varepsilon_1}{K} g \frac{e^{-\frac{\varepsilon_1}{KT}}}{1 + g e^{-\frac{\varepsilon_1}{KT}}} \qquad g = \frac{g_0}{g_1}$$

$$E_{total} = \Sigma E$$

C. Enthalpy H

$$H_{total} = E_{total} + RT$$

D. Entropy S, (Ref. 4)

Upon substituting in all the numerical universal values of constants, such as h, K, and N_o, the following equation is obtained.

$$S_{trans} = 6.8635 \log m - 2.3141 + 11.4391 \log T$$

$$S_{rot} = 4.5757 \log\left(\frac{I \cdot 10}{\sigma}\right)^{39} - 0.7804 + 4.5757 \log T$$

$$S_{elec} = R \ln \left(1 + g e^{-\frac{\varepsilon_1}{KT}}\right) + \frac{R}{KT} \frac{g \varepsilon e^{-\frac{\varepsilon_1}{KT}}}{1 + g e^{-\frac{\varepsilon_1}{KT}}},$$

where $g = \frac{g_0}{g_1}$

$$S_{vib} = R \left[\ln\left(\frac{KT}{h\omega_e}\right) + 1\right]$$

$$S_{total} = \Sigma S$$

E. Helmholtz Free Energy A, (Ref. 4)

$$A = - RT \ln \left(\frac{Q}{N} + 1\right)$$

F. Gibbs Free Energy G, (Ref. 6)

$$G = - RT \ln \frac{Q}{N}$$

G. Specific Heat at Constant Volume C_v

$$C_{v\ trans} = \left(\frac{\partial E}{\partial T}\right)_v$$

$$= \frac{3}{2} NK$$

$$= \frac{3}{2} R$$

$$C_{v\ rot} = R$$

$$C_{v\ vib} = \frac{R\, x^2\, e^x}{(e^x - 1)^2}, \text{ where } x = \frac{h\omega_e}{KT}$$

$$C_{v\ ele} = R \left(\frac{\varepsilon_1}{KT}\right)^2 \frac{g_0}{g_1} \frac{e^{-\frac{\varepsilon_1}{KT}}}{1 + \frac{g_0}{g_1} e^{-\frac{\varepsilon_1}{KT}}}$$

$$C_{v\ total} = \Sigma\, C_v$$

H. Specific Heat at Constant Pressure C_p

$$C_{p\ total} = C_{v\ total} + R$$

2. Example 1.

Calculation of the properties of one mole of monoatomic hydrogen H ideal gas which is under the condition of temperature 273.16 K,

volume 22416 c.c. and pressure 1 atm.

For a monoatomic gas, only translational and electronic terms need to be calculated. Values of ε_0, ε_1, and ε_1 are obtained from "Atomic Energy Level" N. B. S. Circular 467 (Ref. 2).

A. Partition Function

$$Q_{trans} = \left(\frac{2\pi K}{h^2}\right)^{3/2} (mT)^{3/2} V$$

$$= \left(\frac{2\pi \times 1.38 \times 10^{-16}}{(6.26 \times 10^{-23})^2}\right)^{3/2} \left(\frac{1 \times 273.16}{6.02 \times 10^{23}}\right)^{3/2} (22416)$$

$$= 1.87 \times 10^{28}$$

$$Q_{rot} = 1$$

$$Q_{vib} = 1$$

$$Q_{elec} = \varepsilon_0 + \varepsilon_1 e^{-\frac{\varepsilon_1}{KT}} + \varepsilon_2 e^{-\frac{\varepsilon_2}{KT}} + \cdots\cdots\cdots$$

If T is low, $e^{-\frac{\varepsilon_1}{KT}} = e^{-\frac{82258.9 \times 1.98562 \times 10^{-16}}{1.38 \times 10^{-16} \times 273.16}} \approx 0$

$$Q_{elec} = 2$$

$$Q_{total} = \Pi Q_i = (1.87 \times 10^{28}) \times 2 = 3.74 \times 10^{28}$$

B. Internal Energy E

$$E_{trans} = \frac{3}{2} (1.987 \times 273.16) = 814 \text{ cal/mole}$$

$$E_{rot} = 0$$

$$E_{vib} = 0$$

$$E_{elec} = R \frac{\varepsilon_1}{K} \frac{g_1}{g_0} \frac{e^{-\frac{\varepsilon_1}{KT}}}{\frac{g_1}{g_0} e^{-\frac{\varepsilon_1}{KT}}}$$

$$\approx 0$$

$$E_{total} = \Sigma E_i \geq 814 \text{ cal./mole}$$

C. Enthalpy H

$$H_{total} = E_{total} + RT \geq 814 + (1.987 \times 273.16) \geq 1356 \text{ cal./mole}$$

D. Entropy S

$$S_{trans} = 6.8635 \log_{10} m - 2.3141 + 11.4391 \log_{10} T$$
$$= 25.7$$

$$S_{elec} = R \ln \left(1 + \frac{g_0}{g_1} e^{-\frac{\varepsilon_1}{KT}}\right) + \frac{R}{KT} \frac{\frac{g_0}{g_1} e^{-\frac{\varepsilon_1}{KT}}}{1 + \frac{g_0}{g_1} e^{-\frac{\varepsilon_1}{KT}}}$$

$$\approx 1.38$$

$$S_{total} \approx 25.7 + 1.38$$
$$\approx 27.08 \text{ cal./mole deg.}$$

E. Helmholtz Free Energy A

$$A = - RT \ln\left(\frac{Q}{N} + 1\right)$$

$$= - (1.987 \times 273.16) \ln\left[\frac{2.74 \times 10^{28}}{6.02 \times 10^{23}} + 1\right] = - 456$$

F. Gibbs Free Energy G

$$G = - RT \ln \frac{Q}{N}$$

$$= - (1.987 \times 273.16) \ln\left[\frac{2.74 \times 10^{28}}{6.02 \times 10^{23}}\right] = - 456 \text{ cal./mole}$$

G. Specific Heat at Constant Volume C_v

$$C_v = \frac{3}{2} R = \frac{3}{2} (1.987)$$

$$= 2.98 \text{ cal./mole deg.}$$

H. Specific Heat at Constant Pressure C_p

$$C_p = \frac{5}{2} R = \frac{5}{2} (1.987)$$

$$= 4.96 \text{ cal./mole deg.}$$

Example 2.

Calculation of the properties of one mole of diatomic hydrogen H_2 ideal gas which is under the condition of temperature 1500 K, volume 22416 c.c., and pressure 1 atm.

Since H_2 is a diatomic molecule, the translational, rotational, vibrational, and electronic terms have to be counted in the calculation. Values of I, σ, ω_e, ε_1, g_0, g_1, are obtained from "Spectra of Diatomic Molecule", Herzberg (Ref. 3)

A. Partition Function Q

$$Q_{trans} = \left[\frac{2\pi \times 1.38 \times 10^{-16}}{(6.62 \times 10^{-23})^2}\right]^{3/2} \left(\frac{2 \times 1500}{6.02 \times 10^{23}}\right)^{3/2} (22416)$$

$$= 3.74 \times 10^{30}$$

$$Q_{rot} = \frac{8\pi^2 IKT}{\sigma h^2}$$

$$= 2.48 \times 10^{38} \frac{IT}{\sigma}$$

where σ is 2 and I is 0.46×10^{-40} (g-cm^2)

$$Q_{rot} = 8.56$$

$$Q_{vib} = II\left(\frac{1}{1 - e^{-x}}\right)$$

where ω_e is 4395.2 (cm^{-1})

$$x = h\omega_e/KT = 4.21$$

$$Q_{vib} = \frac{1}{1 - 0.0015} = 1.02$$

$$Q_{elec} = \varepsilon_0 + \varepsilon_1 e^{-\frac{\varepsilon_1}{KT}} + \cdots\cdots\cdots$$

$$= 1 + e^{-\frac{91689 \times (1.98 \times 10^{-16})}{K\ 1500}}$$

$$\approx 1$$

$$Q_{total} = II\ Q = (3.74 \times 10^{30})(8.56)(1.02)(1)$$

$$= 3.27 \times 10^{31}$$

B. Internal Energy E

$$E_{trans} = \frac{3}{2} NKT$$

$$= \frac{3}{2} RT$$

$$= 4470$$

$$E_{rot} = RT = 2980$$

$$E_{vib} = RTx \left(\frac{1}{2} - \frac{1}{e^x - 1}\right)$$

$$= 6270$$

$$E_{elec} = R \frac{\varepsilon_1}{K} \frac{g_0}{g_1} \frac{e^{-\frac{\varepsilon_1}{KT}}}{1 + \frac{g_0}{g_1} e^{-\frac{\varepsilon_1}{KT}}} \approx 0$$

$$E_{total} = 13720 \text{ cal./mole}$$

C. Enthalpy H

$$H_{total} = E_{total} + RT$$

$$= 13720 + (1.987 \times 1500)$$

$$= 16700 \text{ cal./mole}$$

D. Entropy S

$$S_{trans} = 36.09$$

$$S_{rot} = 6.53$$

$$S_{vib} = 0.2$$

$$S_{elec} = 0$$

$$S_{total} = 42.82 \text{ cal./mole deg.}$$

E. Helmoltz Free Energy A

$$A = - RT \ln \left(\frac{Q}{N} + 1\right)$$

$$= - RT \ln \left(\frac{3.27 \times 10^{31}}{6.03 \times 10^{23}} + 1\right)$$

$$= - 53{,}000 \text{ cal./mole}$$

F. Gibbs Free Energy G

$$G = -RT \ln \left(\frac{Q}{N}\right)$$

$$= -53{,}000 \text{ cal./mole}$$

G. Specific Heat at Constant C_v

$$C_{v\ trans} = \frac{3}{2} R = 2.98$$

$$C_{v\ rot} = R = 1.98$$

$$C_{v\ vib} = \frac{Rx^2 e^x}{(e^x - 1)^2} = 0.536$$

$$C_{v\ elec} = R\left(\frac{\varepsilon_1}{KT}\right)^2 \frac{\frac{g_0}{g_1} e^{-\frac{\varepsilon_1}{KT}}}{1 + \frac{g_0}{g_1} e^{-\frac{\varepsilon_1}{KT}}}$$

$$C_{v\ total} = 5.503 \text{ cal./mole deg.}$$

H. Specific Heat at Constant Pressure C_p

$$C_p = C_v + R = 5.503 + 1.987 = 7.49 \text{ cal./mole deg.}$$

Example 3. Calculation of specific heat at constant pressure, C_p, and specific heat at constant volume, C_v, of H_2 as a function of temperatures from 600 K to 6000 K.

Calculation:

The total specific heat at constant volume, C_v, will be the sum of $C_{v\ trans}$, $C_{v\ rot}$ and $C_{v\ vib}$

$$C_{v\ total} = C_{v\ trans} + C_{v\ rot} + C_{v\ vib}$$

$$= \frac{3}{2} R + R + \frac{Rx^2 e^x}{(e^x - 1)^2}$$

where $x = \frac{\omega_e h}{KT}$

and the total specific heat at constant pressure, C_p, will be

$C_{p\ total} = C_{v\ total} + R$

TABLE I

T (°K)	$\frac{Rx^2e^x}{(e^x-1)^2}$	C_v		C_p	
		cal/mole,deg.			cal/mole,deg.
600	0.0031R	2.5031R	4.95	3.5031R	6.94
1200	0.1489R	2.6489R	5.24	3.6489R	7.23
1800	0.3974R	2.8974R	5.72	3.8974R	7.70
2400	0.5836R	3.0836R	6.10	4.0836R	8.08
3000	0.7035R	3.2035R	6.34	4.2035R	8.31
3600	0.7817R	3.2817R	6.50	4.2817R	8.48
4200	0.8318R	3.3318R	6.59	4.3318R	8.57
4800	0.8684R	3.3684R	6.65	4.3684R	8.65
5400	0.8950R	3.3950R	6.70	4.3950R	8.70
6000	0.9137R	3.4137R	6.75	4.4137R	8.80

TABLE II. GAS TABLE: KEENAN AND KAYE

T	C_v	C_p
°K	cal/mole,deg.	cal/mole,deg.
600	5.015	7.002
1200	5.415	7.402
1800	6.019	8.007
2400	6.472	8.459
3000	6.801	8.787

The results of calculation are plotted in Fig. 1, and compared with values from "Gas Tables" Keenan and Kaye on the same figure.

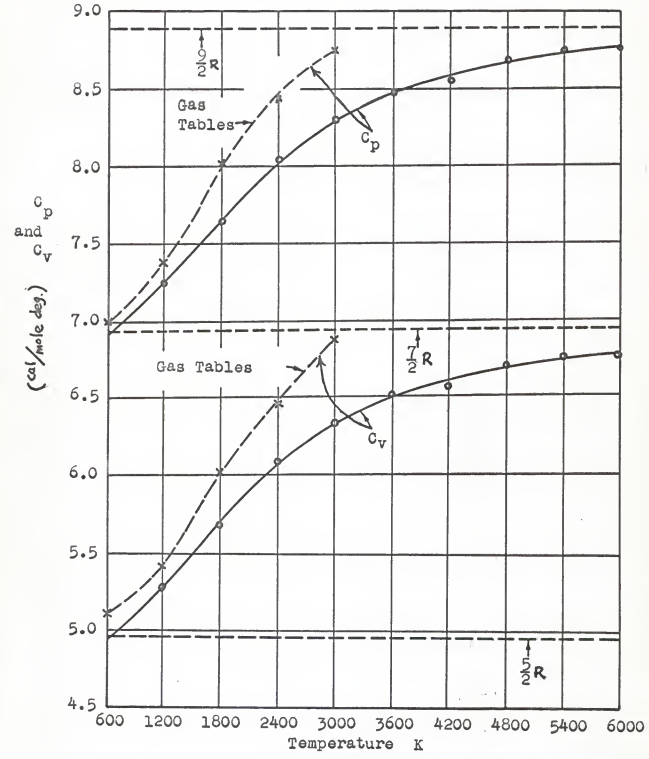

Fig. 1 Molar Specific Heat of H_2 as a Function of Temperature.

3. Discussion:

All the calculations are based upon a gaseous molecular model which follows exactly the Maxwell-Boltzmann distribution. This gaseous model is an ideal gas. Hence, the larger the volume of the gas the smaller the discrepency between the results calculated by this method and the properties of the real gas. Moreover, in this calculation the following relations are neglected, 1, the non-rigid rotating property of a diatomic molecule, 2, the anharmonicity of the vibrating property of the molecule, 3, the interacted vibrational rotating property of the molecule, 4, the electronic vibrating property of the molecule. The error introduced by the ideality can be classified as external error, while the errors due to non-rigidity, the anharmonicity, and the internal interactions can be classifed as internal error. A more precise analysis is possible, thus reducing the number of simplifications used but at the expense of much mathematical complexity.

As the temperature of the system goes higher, dissociation takes place according to the reaction, $H_2 = (1 - y)H_2 + 2yH$, and monatomic hydrogen will be present in the system. Moreover, when the temperature reaches certain rather higher values, which are always greater than for dissociation, then ionized hydrogen and free electrons will appear. In comparison of the specific heat at constant pressure, C_p, and the specific heat at constant volume, C_v, calculated by this statistical method with the data tabulated in "Gas Table", by Keenan and Kaye, the discrepency is relatively large at higher temperature. The reason for this is that H_2 dissociates appreciably at about 3000 K and this effect has been incorperated into the value tabulated in the "Gas Tables".

However, a more precise statistical method would remove this discrepency and has the further advantage of predicting thermodynamic properties up to very high temperatures, far above the experimental ranges.

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RELATIONS BETWEEN THE PARTITION FUNCTION AND THERMODYNAMIC PROPERTIES

by

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The purpose of this report is to show the relation between the thermodynamic properties of a gaseous system and the partition function. The partition function is defined as $Q = \sum_i g_i \, \mathrm{EXP}(-\varepsilon_i/KT)$. When the energy levels ε_i, the statistical weights g_i, and the temperature of a gaseous system are known, the partition function of the system is fixed. In statistical thermodynamics, all thermodynamic properties of a gaseous system can be written in terms of the partition function, hence, a thermodynamic property is merely a function of the partition function from this point of view.

In statistical thermodynamics, the concept, $S = K \ln W$, is first introduced, where S is the entropy of the system, K is Boltzmann constant, and W is the thermodynamic probability. By maximizing W, or rather ln W, the system will be in equilibrium. This is carried out by using the method of Lagrange Multipliers and the Stirling's Approximation. Consequently, the entropy, $S = NK \frac{\partial}{\partial T} (T \ln Q)$, can be obtained, where N is the number of particles in the system and T is the absolute temperature of the system.

From the Maxwell-Boltzmann energy distribution law and the partition function, the internal energy can be expressed as

$$E = \frac{N \sum_i \varepsilon_i N_i}{\sum_i N_i}$$

and finally, $E = NKT \, (\partial \ln Q / \partial \ln T)$ is obtained. According to the definitions, all other thermodynamic properties, such as A, G, H, C_v and C_p, can be obtained by using the known values of S and E.

The value of the microscopic statistical method to evaluate thermodynamic properties of a gaseous system lies in two facts; first, the thermodynamic properties of a gaseous system that may be unobtainable by macroscopic classical experiment can be evaluated using this method, and second, even though the macroscopic experiment can be carried out, the statistical method yields thermodynamic information with a higher accuracy and precision than the classical method.