

Evaluation of Lagrange's Multipliers.

To determine α and β and $n_i = g_i e^{-\alpha - \beta \epsilon_i}$

Undetermined

Consider $N = \sum_i n_i$

$$\sum_i g_i e^{-\alpha - \beta \epsilon_i} = N \quad \text{or} \quad e^{-\alpha} = N / \sum_i g_i e^{-\beta \epsilon_i} \quad (1)$$

Defining a quantity, called molecular partition function, as

$$q = \sum_i g_i e^{-\beta \epsilon_i} \quad (2)$$

we obtain $e^{-\alpha} = N/q$ (3)

Accordingly, the Boltzmann distribution law equation becomes

$$n_i = N g_i e^{-\beta \epsilon_i} / q \quad (4)$$

The partition function q is a quantity of immense importance in statistical thermodynamics. By evaluating the partition function for a system we can calculate the value of any thermodynamic function for that system.

To determine the constant β taking log of eqn $W = N! \prod \frac{g_i^{n_i}}{n_i!} \times \text{constant}$ and apply the Stirling approximation we get

$$\ln w = \ln N! + \sum_i (n_i \ln g_i - \ln n_i!) \quad (5)$$

$$= N \ln N - N + \sum_i (n_i \ln g_i - n_i \ln n_i + n_i) \\ = N \ln N + \sum_i n_i \ln g_i - \sum_i n_i \ln n_i \quad (6)$$

Taking logs of eqn (4), we have

$$\ln n_i = \ln N - \ln q + \ln g_i - \beta \epsilon_i \quad (7)$$

Substituting in eqn (6) we get

$$\ln w = N \ln N + \sum_i n_i \ln g_i - \sum_i n_i (\ln N - \ln q + \ln g_i - \beta \epsilon_i) \\ = N \ln N + \sum_i n_i \ln g_i - N \ln N + N \ln q - \sum_i n_i \ln g_i \\ + \beta \sum_i n_i \epsilon_i \quad (8) \\ = N \ln q + \beta U$$

Substituting the above result into Boltzmann eqn $S = k \ln w$

$$S = Nk \ln q + k\beta U \quad (9)$$

From the combined statement of First and the Second laws of Thermodynamics, we know

$$dU = T ds - PdV \quad (10)$$

At constant volume ($V = \text{constant}; dV = 0$), $dU = T ds$

$$\therefore \left(\frac{\partial S}{\partial U} \right)_V = 1/T \quad (11)$$

Differentiating eq (9) w.r.t U at constant V ,

$$\left(\frac{\partial S}{\partial U} \right)_V = \frac{Nk}{q} \left(\frac{\partial q}{\partial U} \right)_V + k\beta + kU \left(\frac{\partial \beta}{\partial U} \right)_V = \frac{Nk}{q} \frac{dq}{d\beta} \left(\frac{\partial \beta}{\partial U} \right)_V + k\beta + kU \left(\frac{\partial \beta}{\partial U} \right)_V$$

Also from eqn (2) $dq/d\beta = -Uq/N$ — (13)

Substitution of eqn (13) in eqn (12) results in in cancellation of the first and last terms giving

$$\left(\frac{\partial S}{\partial U}\right)_V = k\beta \quad \text{--- (14)}$$

Comparing eqns (11) and (14) we get

$$\beta = \frac{1}{kT} \quad \text{--- (15)}$$

Hence from eqn (2), the molecular function q becomes

$$q = \sum g_i e^{-\epsilon_i/kT} \quad \text{--- (16)}$$

and the Maxwell-Boltzmann equation becomes

$$n_i = (N g_i e^{-\epsilon_i/kT})/q \quad \text{--- (17)}$$

The Translational Partition Function

For a particle of mass m , moving in an infinite three dimensional box sides a, b and c assuming that the potential is zero within the box, the energy levels obtained by the solution of the Schrödinger are given by the expression

$$E_{n_x, n_y, n_z} = E_{tr} = \frac{h^2}{8m} \left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right] \quad (1)$$

where each of the quantum numbers n_x, n_y, n_z vary from one to infinity. Neglecting degeneracy the translational partition function is given by

$$q_{tr} = \sum_{n_x} \sum_{n_y} \sum_{n_z} \exp \left[- \frac{h^2}{8m k T} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right) \right] \quad (2)$$

where the triple summation is taken over all integral values of n_x, n_y and n_z from one to infinity. The motion of the particle in the three x, y , and z directions being independent, we can replace the triple summation as a product of three summations.

$$q_{tr} = \sum_{n_x=1}^{\infty} \exp \left[- \frac{n_x^2 h^2}{8m a^2 k T} \right] \times \sum_{n_y=1}^{\infty} \exp \left[- \frac{n_y^2 h^2}{8m b^2 k T} \right] \times \sum_{n_z=1}^{\infty} \exp \left[- \frac{n_z^2 h^2}{8m c^2 k T} \right] \quad (3)$$

It is well known that the spacing between the energy levels of a particle in a three-dimensional box is very small compared with the thermal energy kT . Hence we can replace the summation

by integration. Accordingly,

$$q_{\text{tr}} = \int_0^a \exp\left[-\frac{m_x^2 v_x^2}{8m_x^2 kT}\right] dv_x \times \int_0^b \exp\left[-\frac{m_y^2 v_y^2}{8m_y^2 kT}\right] dv_y \times \int_0^c \exp\left[-\frac{m_z^2 v_z^2}{8m_z^2 kT}\right] dv_z$$

From calculus, it is well known that the standard integral $\int_0^a e^{-ax^2} dx = \frac{1}{2} \left(\frac{\pi}{a}\right)^{1/2}$ — (5)

Using this result, three integrals in eqn (4) which are identical except for the constants a , b and c can be calculated, giving

$$q_{\text{tr}} = \frac{a}{h} (2\pi m kT)^{1/2} \times \frac{b}{h} (2\pi m kT)^{1/2} \times \frac{c}{h} (2\pi m kT)^{1/2}$$

$$= \left(\frac{2\pi m kT}{h^2}\right)^{3/2} \times abc = \left(\frac{2\pi m kT}{h^2}\right)^{3/2} \times V \quad \text{--- (6)}$$

where $V (= abc)$ is the volume of the box in which the molecule moves. Eqn (6) can be written as

$$q_{\text{tr}} = q_{\text{tr}}^{\circ} \times V \quad \text{--- (7)}$$

where q_{tr}° is the partition function per unit volume. The quantity $h / (2\pi m kT)^{1/2}$ in eqn (6) is called the thermal de Broglie wavelength and is represented by the symbol λ . Thus

$$q_{\text{tr}} = V / \lambda^3.$$

The Rotational Partitioning Function: 3

The simplest system that undergoes rotational motion is a diatomic molecule. The rotational energy levels of a rigid diatomic rotor (i.e., a rotor whose internuclear distance remains fixed during rotation), obtained by solving the Schrödinger wave equation, are

$$E_J = \frac{J(J+1)h^2}{8\pi^2 I} \quad \text{--- (1)}$$

where the rotational quantum number J has the values $0, 1, 2, 3, \dots$ and I is the moment of inertia of the molecule about an axis perpendicular to the internuclear axis.

The degeneracy, g_J of rotational energy levels is equal to $(2J+1)$. The rotational partition function of a rigid diatomic rotor is given by

$$q_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1) \exp\left[-\frac{J(J+1)h^2}{8\pi^2 I kT}\right] \quad \text{---}$$
$$= \sum_{J=0}^{\infty} (2J+1) \exp[-J(J+1)c] \quad \text{--- (2)}$$

where $c = h^2 / 8\pi^2 I kT$.

When $kT \gg h^2 / 8\pi^2 I kT$, the spacing between the neighbouring rotational energy levels is much

larger than that between the translational energy levels. Still it is found that for practically all diatomics, $h^2/8\pi^2 I kT$ is small so that the successive rotational energy levels are closer to one another. It is thus possible to replace the summation in eqn. (2) by integration. Accordingly

$$q_{rot} = \int_0^{\infty} (2J+1) \exp[-J(J+1)c] dJ \quad - (3)$$

Let $x = J^2 + J$ Therefore $dx = (2J+1)dJ$

$$q_{rot} = \int_0^{\infty} e^{-cx} dx = \frac{1}{c} [e^{-\infty} - e^0] = \frac{1}{c}$$

Substituting for c where

$$q_{rot} = 8\pi^2 I kT / h^2 \quad - (5)$$

The quantity $h^2 / (8\pi^2 I kT)$ in eqn(5) has the dimensions of temperature and is called characteristic rotational temperature which can be written as $\Theta_{rot} = T / q_{rot}$

eqn(5) can be applied to rotational degrees of freedom in which identical configurations occur only after a rotation of 2π . If the molecule has elements of symmetry such that identical configurations occur after a rotation of $2\pi/\sigma$ where σ is the symmetry number, then the rotational partition function is given by

$$q_{rot} = \frac{8\pi^2 I kT}{\sigma h^2} = \frac{T}{(\sigma \Theta_{rot})} \quad \text{--- (6)}$$

The symmetry number insures the avoidance of too many identical configurations being taken into account. For homonuclear diatomic molecules such as H_2, O_2, N_2 etc $\sigma = 2$ whereas for heteronuclear diatomic molecules such as CO, NO, HD, HCl etc $\sigma = 1$. We can also write eqn (6) as

$$q_{rot} = \frac{kT}{(\sigma h c B)} \quad \text{--- (7)}$$

where B is the rotational constant of diatomic rotor defined as $B = \frac{h}{8\pi^2 I c}$

The Vibrational Partition Function

For a diatomic molecule vibrating as a simple harmonic oscillator (S.H.O), the vibrational energy levels obtained by the solution of the Schrodinger wave equation, are given by

$$E_{vib} = (v + \frac{1}{2}) h\nu \quad \text{--- (1)}$$

where ν is the vibrational frequency and v is the vibrational quantum number which has the values $v = 0, 1, 2, 3, \dots$

The energy levels are non-degenerate, i.e the degeneracy g_v is unity. The vibrational partition function of the diatomic molecule is given by

$$q_{vib} = \sum_{v=0}^{\infty} \exp\left[-\frac{(v + 1/2) h\nu}{kT}\right]$$

$$= e^{-h\nu/2kT} \sum_{\nu=0}^{\infty} \exp[-\nu h\nu/kT] \quad (2)$$

In the case of simple harmonic oscillator, the spacing between the neighbouring energy levels is very large compared with the translational or the rotational energy levels. In other words $h\nu \gg kT$. Hence the summation cannot be replaced by integration. The summation can be carried out as follows. Let $x = h\nu/kT$. Then

$$\sum_{\nu=0}^{\infty} \exp[-\nu h\nu/kT] = \sum_{\nu=0}^{\infty} e^{-\nu x} = 1 + e^{-x} + e^{-2x} + \dots \quad (3)$$

$$= \frac{1}{1 - e^{-x}} = \frac{1}{1 - e^{-h\nu/kT}} \quad (4)$$

Hence from eqn (2)

$$q_{vib} = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}} \quad (5)$$

If we define Θ_{vib} , the characteristic vibrational temperature, of the oscillator as

$$\Theta_{vib} = h\nu/k \quad (6)$$

then, the vibrational partition function is given by

$$q_{vib} = \frac{e^{-\Theta_{vib}/2T}}{1 - e^{-\Theta_{vib}/T}} \quad (7)$$

If the temperature is very high or very low eqn (7) can assume a simpler form as given below.

Case (i). T is very low so that $\Theta_{\text{vib}}/T \gg 1$. 5

Then, $\exp(-\Theta_{\text{vib}}/T)$ is negligible compared with unity in the denominator of Eqn (7) and we get

$$q_{\text{vib}} = e^{-\Theta_{\text{vib}}/2T} \quad (\text{at low temperature})$$

Case (ii). T is very high so that $\Theta_{\text{vib}}/T \ll 1$

Then, the exponential in the denominator can be expanded as a series, retaining only the first two terms:

$$e^{-\Theta_{\text{vib}}/T} = 1 - \Theta_{\text{vib}}/T + \dots$$

$$\text{Hence } q_{\text{vib}} = \frac{T}{\Theta_{\text{vib}}} e^{-\Theta_{\text{vib}}/2T} \quad (\text{at high temperatures})$$

The value of ν and hence Θ_{vib} is obtained from the vibrational (infrared) spectrum of a molecule.

Application of Bose-Einstein Statistics to Black Body Radiation (ie Ideal Photon Gas)

Electromagnetic radiation in thermal equilibrium is called blackbody radiation. The radiation is emitted or absorbed in quanta (packets) of energy $E = h\nu$, where ν is the radiation frequency. Also the radiation travels as quanta of energy called photons. The photons do not interact with one another and hence form an ideal Bose-Einstein gas. The thermal equilibrium is brought about by the absorption and emission of photons by the matter present. Thus the number of photons N is not a fixed quantity and has to be determined from the condition of thermal equilibrium. In thermal equilibrium, the Helmholtz free energy is minimum for a given T and V ; thus the necessary condition is

$$\left(\frac{\partial A}{\partial N}\right)_{V,T} = 0 \quad \text{--- (1)}$$

$$\text{Since } \mu = \left(\frac{\partial A}{\partial N}\right)_{V,T} \quad \text{--- (2)}$$

so that the chemical potential μ , of the ideal photon gas is zero. i.e. $\mu = 0$.

For a photon (travelling with the speed of light, c) the momentum $p = \frac{h}{\lambda} = \frac{h\nu}{c}$, so that $dp = h d\nu/c$ and the number of states for photons with momenta between p and $p+dp$ is

$$g(p)dp = \frac{4\pi p^2 dp}{h^3/V} = \frac{4\pi V}{c^3} \nu^2 d\nu \quad (3)$$

where V is the volume of the enclosure for the blackbody radiation. As there are two independent directions of polarisation.

$$g(\nu)d\nu = \frac{8\pi V}{c^3} \nu^2 d\nu \quad (4)$$

for the total number of states lying in the frequency $d\nu$ at ν . The B.E distribution for photons is

$$dn = \frac{g(\nu)d\nu}{\exp(\alpha + \beta E) - 1} = \frac{8\pi V}{c^3} \frac{\nu^2 d\nu}{\exp(\alpha + \beta E) - 1} \quad (5)$$

where $E = h\nu$. The energy density $u d\nu = \left(\frac{dn}{V}\right) E$ in the specified energy range is

$$u d\nu = \frac{8\pi h \nu^3}{c^3} \cdot \frac{d\nu}{\exp(\alpha + \beta E) - 1} \quad (6)$$

The above equation is the Planck radiation formula if we put for photons

$$\alpha = 0, \quad \beta = 1/kT$$

The requirement $\alpha = 0$ (or $\mu = 0$) simply means dropping the condition $dn = \sum dn = 0$, for the fixed number of particles. Photons differ from other bosons in that their number is not conserved. Thus, for photons, the energy density is given by

$$u(\nu) = \frac{8\pi h \nu^3}{c^3} \frac{d\nu}{\exp(h\nu/kT) - 1} \quad - (7) \quad (3)$$

The total energy density is given by

$$\frac{U}{V} = \int_0^\infty u(\nu, T) d\nu = \frac{8\pi h}{c^3} \int_0^\infty \frac{\nu^3 d\nu}{\exp(h\nu/kT) - 1}$$

$$= \frac{8\pi h}{c^3} \left(\frac{kT}{h}\right)^4 \int_0^\infty \frac{x^3 dx}{e^x - 1} = bT^4, \quad b = \frac{8\pi^5 k^4}{15c^3 h^3} \quad - (8)$$

where $x = h\nu/kT$ and integral $\int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}$

Eqn (8) is called Stefan-Boltzmann Law.

with no restraint on n_i , the photon partition function is given by

$$Q_{ph}(T, V) = \sum_{n_1=0}^\infty \sum_{n_2=0}^\infty \dots \exp[-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)] \quad - (9)$$

$$= \prod_{i=0}^\infty \left[\sum_{n_i=0}^\infty \dots \exp(-\beta \epsilon_i n_i) \right] = \prod_{i=0}^\infty \frac{1}{1 - \exp(-\beta \epsilon_i)} \quad (10)$$

so that

$$\begin{aligned} \ln Q_{ph}(T, V) &= \sum_i \ln(1 - \exp(-\beta \epsilon_i)) \\ &= - \int \ln[1 - \exp(-\beta h\nu)] g(\nu) d\nu \quad - (11) \end{aligned}$$

The Helmholtz free energy is given by

$$A(V, T) = -kT \ln Q_{ph}(V, T)$$

$$= \frac{8\pi V kT}{c^3} \int_0^\infty \nu^2 d\nu \ln[1 - \exp(-\beta h\nu)]$$

$$= \frac{8\pi V kT}{c^3 \beta^3 h^3} \int_0^\infty x^2 dx \ln[1 - e^{-x}] = -\frac{1}{3} bVT^4 \quad (4)$$

The other thermodynamic quantities of the ideal photon gas

$$S = -\left(\frac{\partial A}{\partial T}\right)_V = (4/3) bVT^3$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = (1/3) bT^4$$

$$U = E = A + TS = bVT^4$$

Ideal Fermi-Dirac Gas (Electrons in metal)

A system of electrons in metal is an ideal Fermi-Dirac gas. To evaluate the thermodynamic properties of electrons in metal or electron gas consider non-interacting gas of Fermi-Dirac particles in a box volume V . The energy levels are then those of free particle in a 3-D box, that is

$$E_{n_x, n_y, n_z} = \frac{(n_x^2 + n_y^2 + n_z^2) h^2}{8m V^{2/3}} \quad (1)$$

where m is the mass of Fermi particles, in this case it is electron. The energy levels will be very close to each other for very large volume V . Therefore, the energy levels can be

considered almost continuous. For a Fermi-diract (5)
 gas the occupation number of any energy level E_i
 is n_i and can never be greater than 1, the
 distribution of which is given as

$$n_i = \frac{g_i}{\exp(E_i - \mu)/kT + 1} \quad - (2)$$

The number of quantum states between energy
 E and $E + dE$ is given by

$$W(E) dE = \frac{2\pi (2m)^{3/2} V E^{1/2} dE}{h^2} \quad - (3)$$

If the spin of the particle (electron) (ie degeneracy
 of electronic state) then number of quantum
 states will be

$$W(E) dE = 2\pi g V \left(\frac{2m}{h^2} \right)^{3/2} E^{1/2} dE \quad - (4)$$

where g is the degeneracy of the spin state. In
 case of electron $g = 2$. Hence

$$W(E) dE = 4\pi V \left(\frac{2m}{h^2} \right)^{3/2} E^{1/2} dE \quad - (5)$$

The mean number of particles in the system will be

$$\bar{N} = \frac{2\pi g V (2m)^{3/2}}{h^2} \int_0^\infty \frac{E^{1/2} dE}{e^{(E - \mu)/kT} + 1} \quad - (6)$$

when we set $E=0$ at $T=0\text{K}$, then $n_i=1$ and $n_i=0$ for $E > \mu_0$. The average number of particles in the system will be

$$\bar{N} = 4\pi V \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^{\mu_0} E^{1/2} dE \quad - (7)$$

At $T=0\text{K}$ $n_i=1$ and kinetic energy is

$$E = \sum E_i n_i$$

Replacing n_i by integral with a upper limit as Fermi energy, we get

$$E = 4\pi \left(\frac{2m}{\hbar^2} \right)^{3/2} V \int_0^{\mu_0} E^{3/2} dE = \frac{3}{5} \bar{N} \mu_0 \quad - (8)$$

$$E = \frac{3}{5} \bar{N} \frac{\hbar^2}{2m} \left(\frac{3\bar{N}}{4\pi gV} \right)^{2/3} \quad - (9)$$

$$= \frac{3}{10m} \bar{N} \hbar^2 \left(\frac{3\bar{N}}{4g\pi V} \right)^{2/3} \quad - (10)$$

and C_v specific heat of electron at 0K is zero

since

$$C_v = \left(\frac{\partial E}{\partial T} \right)_V = 0 \quad - (11)$$

at $T=0\text{K}$, all \bar{N} indistinguishable particles will be in the lowest \bar{N} quantum states and there is only one way to put these particles in various quantum

hence entropy, S at $T=0\text{K}$ is zero or

$$S = 0 \text{ at } T = 0\text{K}.$$

The kinetic energy of the electron gas and other thermodynamic properties at temperature T are given by the following equations.

$$E = \frac{3}{5} N \mu_0 \left[1 + \frac{5}{12} \pi^2 \left(\frac{kT}{\mu_0} \right)^2 - \frac{\pi^4}{16} \left(\frac{kT}{\mu_0} \right)^4 + \dots \right]$$

$$C_v = \left(\frac{\partial E}{\partial T} \right) = \frac{\pi^2}{2} N k \left(\frac{kT}{\mu_0} \right) \left(1 - \frac{3\pi^2}{10} \left(\frac{kT}{\mu_0} \right)^2 + \dots \right)$$

The above equation shows that the electronic heat capacity of metal is proportional to T and at 300K it is about 1%.

The entropy of electrons in a metal will be

$$S_T = \int_0^T \frac{C_v}{T} dT = \frac{N \mu_0}{T} \left[\frac{\pi^2}{2} \left(\frac{kT}{\mu_0} \right)^2 - \frac{\pi^4}{20} \left(\frac{kT}{\mu_0} \right)^4 + \dots \right]$$

Similarly, Helmholtz free energy, A, will be

$$A = E - TS$$

$$= \frac{3}{5} N \mu_0 \left[1 - \frac{5}{12} \pi^2 \left(\frac{kT}{\mu_0} \right)^2 + \frac{\pi^4}{48} \left(\frac{kT}{\mu_0} \right)^4 + \dots \right]$$

and the pressure will be

$$P = - \left(\frac{\partial A}{\partial V} \right)_T = \frac{2}{3} \frac{E}{V}$$