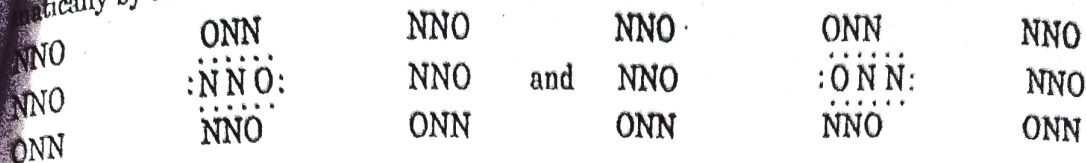


almost equal probabilities for the two orientations of a nitrous oxide molecule indicated schematically by the central molecules in the following arrangements :



Thus, close to 0K, each molecule can assume two states, so the entropy of a crystal containing  $N$  molecules ( $n$  moles) will be

$$\begin{aligned}
 S &= k \ln 2^n = nk \ln 2 \\
 &= R \times 2.303 \log 2 \\
 &= 8.314 \times 2.303 \times 0.301 \\
 &= 5.76 \text{ JK}^{-1} \text{ mol}^{-1}
 \end{aligned}$$

The observed residual entropies of nitrous oxide and carbon monoxide at 0K are close to the above calculated value.

The occurrence of residual entropy in ice is also attributed to the molecular disorder at 0K. In ice crystals, each water molecules is tetrahedrally co-ordinated to four other water molecules by hydrogen bonds. The hydrogen atoms of each hydrogen bond can exist in either of two potential energy minima. This enables the crystal to exist in many configurations at 0K. On this basis, the residual entropy can be calculated to be  $3.4 \text{ JK}^{-1} \text{ mol}^{-1}$ . This is in close agreement with the observed value.

In solid hydrogen, disorder exists because of the persistence of the hydrogen molecule in excited rotational states through nuclear spin.

**Problem 1 :** Calculate the molar residual entropy of a crystal in which the molecules can adopt 6 orientations of equal energy at 0K.

**Solution :** The residual entropy is given by,

$$S = k \ln W^n = nk \ln W$$

where

$$W = \text{number of orientations}$$

$$= \text{number of configurations} = 6$$

$$n = \text{number of particles} = N = 1 \text{ mol}$$

$$Nk = R = \text{gas constant}$$

$$= 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$S = R \ln 6 = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 2.303 \log 6$$

$$= 14.89 \text{ JK}^{-1} \text{ mol}^{-1}$$

## ■ PARTITION FUNCTION AND THERMODYNAMIC FUNCTIONS

We can utilise partition function and distribution law to find the values of various thermodynamic functions, as follows :

### (1) Internal Energy, $E$

The internal energy of a system of  $n$  molecules (in excess of that at the absolute zero), is given by,

$$\begin{aligned}
 E &= n_0 \epsilon_0 + n_1 \epsilon_1 + n_2 \epsilon_2 + \dots + n_i \epsilon_i + \dots \\
 &= \sum n_i \epsilon_i
 \end{aligned}$$

[From equation (10)]

$$= \sum \epsilon_i \left( \frac{n}{f} \cdot e^{-\epsilon_i/kT} \right)$$

or

$$E = \frac{n}{f} \cdot \sum \epsilon_i e^{-\epsilon_i/kT}$$

But

$$f = \sum e^{-\epsilon_i/kT}$$

or

$$\frac{df}{dT} = \frac{1}{kT^2} \sum \epsilon_i e^{-\epsilon_i/kT}$$

or

$$\sum \epsilon_i e^{-\epsilon_i/kT} = kT^2 \cdot \frac{df}{dT} \quad \dots(26)$$

Therefore, combining equations (25) and (26), we get,

$$E = \frac{nkT^2}{f} \cdot \frac{df}{dT}$$

or

$$E = nkT^2 \cdot \frac{d \log f}{dT} \quad \dots(27)$$

For 1 mole,  $n$  may be substituted by  $N$  (Avogadro's number), therefore,

$$E = NkT^2 \cdot \frac{d \log f}{dT} \quad \dots(28)$$

$$= RT^2 \cdot \frac{d \log f}{dT} \quad [\text{As } k = R/N] \quad \dots(29)$$

Expressions (23) and (24) give the value of internal energy in terms of partition function. The average of each molecule,

$$e = kT^2 \frac{d \log f}{dT} \quad \dots(30)$$

### (2) Entropy, S

From equation (13), we have entropy given by,

$$S = nk \log f + k\beta E \quad [\text{Taking } B = 0]$$

Since

$$\beta = \frac{1}{kT}, \text{ we have}$$

$$S = nk \log f + \frac{E}{T} \quad \dots(31)$$

From equations (27) and (31), we have,

$$S = nk \log f + nkT \frac{d \log f}{dT} \quad \dots(32)$$

Expression (32) gives the value of entropy in terms of partition function.

### (3) Work Function, A

We know that,

$$A = E - TS$$

Substituting the value of  $S$  from equation, (31), we have,

$$\begin{aligned} A &= E - T \left( nk \log f + \frac{E}{T} \right) \\ &= -nkT \log f \end{aligned} \quad \dots(33)$$



Expression (33) gives the relation between work function and partition function.

Pressure,  $P$

We know that, 
$$\left(\frac{dA}{dV}\right)_T = -P$$

Differentiating equation (33) with respect to volume, at constant temperature, we have,

$$\left(\frac{dA}{dV}\right)_T = -nkT \left(\frac{d \log f}{dV}\right)_T$$

$$P = nkT \left(\frac{d \log f}{dV}\right)_T \quad \dots(34)$$

Expression (34) gives the relation between pressure and partition function.

### 5) Heat Content, $H$

Since,

$$H = E + PV$$

$$\therefore H = nkT^2 \left(\frac{d \log f}{dT}\right) + V.nkT \left(\frac{d \log f}{dV}\right)_T$$

$$= nkT \left[ T \left(\frac{d \log f}{dT}\right) + V \left(\frac{d \log f}{dV}\right)_T \right]$$

$$= nkT \left[ \left(\frac{d \log f}{d \log T}\right) + \left(\frac{d \log f}{d \log V}\right) \right] \quad \dots(35)$$

$$\left[ \text{As, } \frac{dT}{T} = d \log T \text{ and } \frac{dV}{V} = d \log V \right]$$

Expression (35) gives the relation between heat content and partition function.

### (6) Free Energy, $F$

We know that,

$$F = H - TS \quad \dots(36)$$

Substituting the values of  $H$  and  $S$  from equations (35) and (32) in (36), we get,

$$G = nkT \left[ \left(\frac{d \log f}{d \log T}\right) + \left(\frac{d \log f}{d \log V}\right)_T \right] - T \left[ nk \log f + nkT \frac{d \log f}{dT} \right]$$

$$= nkT \left[ \left(\frac{d \log f}{d \log T}\right) + \left(\frac{d \log f}{d \log V}\right)_T \right] - nkT \log f - nkT^2 \frac{d \log f}{dT}$$

$$= nkT \left[ \left(\frac{d \log f}{d \log V}\right)_T - \log f \right] \quad \dots(37)$$

$$\left[ \text{As } -nkT^2 \frac{d \log f}{dT} = -nkT \frac{d \log f}{d \log T} \right]$$

Expression (37) gives the relation between free energy and partition function.

### 7) Heat Capacity, $C$

We know that,

$$C_V = \left(\frac{dE}{dT}\right)_V$$

Differentiating equation (27) with respect to temperature at constant volume, we get

$$\left(\frac{dE}{dT}\right)_V = \frac{d}{dT} \left[ nkT^2 \frac{d \log f}{dT} \right]$$

$$C_V = nk \frac{d}{dT} \left( T^2 \frac{d \log f}{dT} \right)_T$$

Expression (38) gives the relation between heat capacity and partition function.

### ■ MOLAR PARTITION FUNCTION

In the above systems, we considered  $n$  individual distinguishable particles distributed in different energy levels and  $f$  represented the molecular partition function. But for large scale systems, we have to take quantities in moles.

Consider a system supposed to consist of a large number of smaller ones each with one mole of the substance. In other words, the individual unit here is not the molecule but a mole. Let the energy levels for the whole system be  $E_1, E_2, E_3, \dots, E_i, \dots$ , and let there be  $x$  such systems in total. In each of these systems, there are  $N$  (Avogadro's number) number of molecules. Hence, the average energy,  $E$ , of such a unit is given by,

$$E = \frac{\sum x_i E_i}{\sum x_i}$$

If  $Z$  is the partition function of these systems, then,

$$Z = \sum e^{-E_i/kT}$$

Adopting the same procedure as used in deriving equation (30), we get,

$$E = kT^2 \cdot \frac{d \log Z}{dT} \quad \dots(39)$$

The function  $Z$  is known as **molar partition function**.

According to equation (28), the energy of a mole is given by,

$$E = NkT^2 \cdot \frac{d \log f}{dT} = kT^2 \frac{d \log f^N}{dT}$$

On comparison, this leads to  $Z = f^N$ .

The other thermodynamic functions may be written as :

$$\begin{aligned} \text{(i)} \quad G &= NkT \cdot \left[ \left( \frac{d \log f}{d \log V} \right)_T - \log f \right] \\ &= kT \left[ \left( \frac{d \log Z}{d \log V} \right)_T - \log Z \right] \quad \dots(40) \end{aligned}$$

$$\begin{aligned} \text{(ii)} \quad S &= Nk \log f + NkT \frac{d \log f}{dT} \\ &= k \log Z + kT \frac{d \log Z}{dT} \quad \dots(41) \end{aligned}$$

$$\text{(iii)} \quad H = NkT \left[ \left( \frac{d \log f}{d \log T} \right) + \left( \frac{d \log f}{d \log V} \right) \right]$$



$$= kT \left[ \left( \frac{d \log Z}{d \log T} \right) + \left( \frac{d \log Z}{d \log V} \right) \right] \quad \dots(42)$$

The above relations hold good for systems where all the molecules are distinguishable and can occupy energy levels without any restriction. Thus, the relations would be true in the case of a crystal, where the different atoms occupy fixed localised positions in the structure.

If the molecules are indistinguishable, as in the case of a perfect gas, the relation  $Z = f^N$  requires modification, for we have taken too many possible arrangements of the particles, hence the number of distribution would be much less. The  $N$ -particles in a  $g$  mole are all indistinguishable and these have  $N!$  permutations among themselves in as many energy levels. Hence, we should reduce the expression for  $Z$  by dividing it by  $N!$ . Therefore, for a perfect gas, (indistinguishable particles), the molar partition function,  $Z$  in the above three relations should be replaced by  $Z/N!$ . For a perfect gas, therefore, we have,

$$\begin{aligned} \text{(i)} \quad S &= k \log \frac{Z}{N!} + kT \frac{d}{dT} \left( \log \frac{Z}{N!} \right) \\ &= k \log Z + kT \frac{d \log Z}{dT} - k \log N! \end{aligned} \quad \dots(43)$$

$$\begin{aligned} \text{(ii)} \quad G &= kT \left[ \left( \frac{d \log Z/N!}{d \log V} \right)_T - \log \frac{Z}{N!} \right] \\ &= kT \left[ \left( \frac{d \log Z}{d \log V} \right)_T - \log Z + \log N! \right] \end{aligned} \quad \dots(44)$$

### THIRD LAW OF THERMODYNAMICS AND PARTITION FUNCTION

We can express the third law of thermodynamics in terms of partition function. As seen in preceding chapters we have

$$S_T - S_0 = \int_0^T \frac{C_P}{T} \cdot dT \quad \dots(45)$$

At very low temperatures,

$$S_T - S_0 = \int_0^T \frac{C_V}{T} \cdot dT; \quad [\because C_P \approx C_V] \quad \dots(46)$$

For 1 mole of a gas, equation (38) becomes,

$$\begin{aligned} C_V &= N \frac{R}{N} \frac{d}{dT} \left( T^2 \frac{d \log f}{dT} \right)_V \\ &= R \frac{d}{dT} \left( T^2 \frac{d \log f}{dT} \right)_V \end{aligned}$$

Substituting this value of  $C_V$  in equation (46), we get,

$$S_T - S_0 = \int_0^T \frac{R}{T} \frac{d}{dT} \left( T^2 \frac{d \log f}{dT} \right)_V \cdot dT$$

By integrating this expression by parts, we get,

$$S_T - S_0 = RT \left( \frac{d \log f}{dT} \right)_V + R \int \left( \frac{d \log f}{dT} \right)_V dT$$

From equation (29) at constant volume, we have,

$$\frac{E}{T} = RT \left( \frac{d \log f}{dT} \right)_V$$

Hence,

$$S_T - S_0 = \frac{E}{T} + R \int_0^T \left( \frac{d \log f}{dT} \right)_V dT$$

or

$$S_T - S_0 = \frac{E}{T} + R [\log f_T - \log f_0]$$

If temperature independent terms are introduced in this equation, we have,

$$S_0 - R \log f_0 = R \log g_0$$

where,  $g_0$  = statistical weight of the lowest energy state of the system.

For a perfect crystal at 0K, there is only one arrangement which means  $g_0 = 1$ . Hence,  $S_0 = 0$  which is the *third law of thermodynamics*. Equation (47) thus becomes,

$$S_T = \frac{E}{T} + R \log f_T \quad \dots(48)$$

In general, we can write,

$$S = \frac{E}{T} + R \log f \quad \dots(49)$$

## PARTITION FUNCTION FOR MOLECULES WITH DIFFERENT TYPES OF ENERGY

It has been observed that molecules are associated with energy of different types. All these forms of energy must be taken into account while mentioning partition function.

Consider a system containing  $N$  molecules of the same kind. All these molecules possess different forms of energy, e.g., translational, rotational, vibrational etc. Let the different types of energy be represented by  $t, r$  and  $v$ ... etc.

The allowed energy levels of the  $t$ -type are  $\epsilon_{t_1}, \epsilon_{t_2}, \epsilon_{t_3}$ ...

The allowed energy levels of the  $r$ -type are  $\epsilon_{r_1}, \epsilon_{r_2}, \epsilon_{r_3}$ ... and so on for other types.

The Boltzmann distributions will be represented by,

$$N_i^t = \frac{N}{f_t} \cdot e^{-\epsilon_{t_i}/kT}$$

$$N_i^r = \frac{N}{f_r} \cdot e^{-\epsilon_{r_i}/kT}$$

and

$$N_i^v = \frac{N}{f_v} \cdot e^{-\epsilon_{v_i}/kT}$$

where  $f_t, f_r$  and  $f_v$  are the partition functions corresponding to  $t, r$  and  $v$  types of energy.

The total energy ( $E_t$ ) of the system is given by,

$$E_t = \sum \epsilon_{t_i} N_i^t + \sum \epsilon_{r_i} N_i^r + \sum \epsilon_{v_i} N_i^v + \dots$$

$$= NkT^2 \frac{d}{dT} \log f_t + NkT^2 \frac{d}{dT} \log f_r + NkT^2 \frac{d}{dT} \log f_v$$

$$= NkT^2 \frac{d}{dT} \log (f_t \cdot f_r \cdot f_v)$$

... (50)



If  $f$  is the net molecular partition when every molecule is capable of freely taking any number of energy we can assume that,

$$E_t = NkT^2 \frac{d}{dT} \log f \quad \text{... (51)}$$

Comparing equations (50) and (51), we get,

$$f = f_t \cdot f_r \cdot f_v \quad \text{... (52)}$$

From equation (52), we can state that the net partition function is the product of the separate partition functions in respect of different types of energy independently associated with the molecules.

### APPLICATIONS OF PARTITION FUNCTION TO MONOATOMIC GASES

#### (i) Translation partition function

The partition function  $f_t(x)$  for a translational motion in one direction is given by,

$$f_t(x) = \sum g_t \cdot e^{-\epsilon_t/kT}$$

where  $\epsilon_t$  is the translational energy of molecule in  $x$  direction and  $g_t$  is the statistical weight of each translational level.

As the statistical weight of each level is unity, the partition function becomes,

$$f_t(x) = \sum e^{-\epsilon_t/kT} \quad \text{... (53)}$$

The translational energy is also quantised, though the difference in the energy levels are quite small. A particle would exhibit periodicity in translational motion only due to the impacts on the walls of the container. Consider a cube of length  $l$ . The molecule moving along  $x$ -axis will repeat its motion each time on traversing a distance of  $2l$ . Then if  $\lambda$  is the wavelength associated with the matter wave, we have,

$$n\lambda = 2l$$

where,  $n$  is an integer.

The translational energy ( $\epsilon_x$ ) along  $x$ -axis is given by,

$$\epsilon_x = \frac{1}{2} mc_x^2 = \frac{1}{2m} \cdot p_x^2$$

where,  $c_x$  and  $p_x$  represent the velocity and momentum of the moving particle.

According to de Broglie, there is associated with any particle of mass  $m$  moving with a velocity  $c_x$  in a single direction, a wavelength  $\lambda$ . Therefore,

$$\frac{h}{\lambda} = mc_x = p_x$$

Hence,

$$\epsilon_x = \frac{1}{2m} \left(\frac{h}{\lambda}\right)^2 = \frac{1}{2m} \left(\frac{hn}{2l}\right)^2 = \frac{n^2 h^2}{8 ml^2}$$

Substituting this value of  $\epsilon_x$  in equation (53), we get,

$$f_t(x) = \sum e^{-\epsilon_x/kT} = \sum e^{-(n^2 h^2 / 8 ml^2) / kT}$$

The energy levels are so closely spaced that the variation of energy may be taken to be continuous and then summation may be replaced by integration. Thus,

$$f_t(x) = \sum e^{-\epsilon_x/kT} = \sum e^{-(n^2 h^2 / 8 ml^2) / kT}$$

Put (14)

$$\frac{n^2 h^2}{8 ml^2 kT} = a^2 \quad \text{or} \quad nh = al (8 mkT)^{1/2}$$

$$dn = \frac{l}{h} (8 mkT)^{1/2} da$$

Therefore,

$$f_t(x) = \frac{(8 mkT)^{1/2} \cdot l}{h} \int_0^\infty e^{-a^2} \cdot da$$

$$= \frac{(8 mkT)^{1/2} l}{h} \sqrt{\left(\frac{\pi}{4}\right)}$$

[From integral calculus]

$$= \frac{(2\pi mkT)^{1/2} l}{h}$$

Similarly, the translational partition function for molecule in three directions  $x, y$  and  $z$  at right angles to each other is given by,

$$f_t = f_t(x) \cdot f_t(y) \cdot f_t(z)$$

$$= \frac{(2\pi mkT)^{1/2} \cdot l}{h} \cdot \frac{(2\pi mkT)^{1/2} \cdot l}{h} \cdot \frac{(2\pi mkT)^{1/2} \cdot l}{h}$$

$$= \frac{(2\pi mkT)^{3/2} \cdot V}{h^3}$$

 [As  $l^3 = \text{volume} = V$ ] ... (54)

In the case of a perfect monoatomic gas, the molar partition function,

$$Z = \frac{f^N}{N!} = \frac{1}{N!} \left[ \frac{(2\pi mkT)^{3/2} V}{h^3} \right]^N$$

or

$$Z = \left(\frac{e}{N}\right)^N \left[ \frac{(2\pi mkT)^{3/2} \cdot V}{h^3} \right]^N \quad \left[ \text{As Stirling's } N! = \left(\frac{N}{e}\right)^N \right]$$

or

$$Z = \left[ \frac{(2\pi mkT)^{3/2} Ve}{Nh^3} \right]^N$$

or

$$\log Z = N \log \frac{(2\pi mkT)^{3/2} Ve}{Nh^3} \quad \dots (55)$$

**Problem 1 :** Calculate the translational partition function for one mole of nitrogen at 2 atmospheres and  $27^\circ\text{C}$ , assuming the gas to behave ideally. Given that :

$N = 6.023 \times 10^{23}$ ;  $k = 1.38 \times 10^{-16}$  erg deg $^{-1}$  mole $^{-1}$ ;  $h = 6.624 \times 10^{-27}$  erg sec;  $R = 82.06$  c.c. atm deg $^{-1}$  mole $^{-1}$ .

**Solution :** From equation (54), we have,

$$f_t = \frac{(2\pi mkT)^{3/2} V}{h^3} = \frac{(2\pi mkT)^{3/2} RT}{h^3 P} \quad (\because PV = RT)$$

$$= \frac{\left( 2 \times 3.14 \times \frac{28}{6.023 \times 10^{23}} \times 1.38 \times 10^{-16} \times 300 \right)^{3/2} \times 82.06 \times 300}{(6.624 \times 10^{-27})^3 \times 2}$$

$$= 1.77 \times 10^{30}$$

**Problem 2 :** Calculate the translational partition function of a molecule of oxygen gas at 1 atm and 298 K moving in a vessel of volume 24.4 dm $^3$ .

**Solution :** Translational partition function  $q_t$  is given by equation (54).



$$q_t = \frac{(2\pi mkT)^{3/2}}{h^3} \cdot V$$

(15)

$$V = 24.4 \text{ dm}^3 = 24.4 \times 10^{-3} \text{ m}^3, \pi = 3.1416$$

$$T = 298 \text{ K}, k = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

$$h = 6.62 \times 10^{-34} \text{ Js}$$

$$m = 5.313 \times 10^{-26} \text{ kg for O}_2$$

$$q_t = \frac{(2 \times 3.1416 \times 5.313 \times 10^{-26} \times 1.38 \times 10^{-23} \times 298)^{3/2} \times 24.4 \times 10^{-3}}{(6.62 \times 10^{-34})^3}$$

$$= 4.28 \times 10^{30}$$

Therefore,  $10^{30}$  quantum levels are thermally accessible even at room temperature for  $\text{O}_2$  molecule.

**(II) Internal energy of a monoatomic gas**

The internal energy of a monoatomic gas can be obtained directly, as the rotational and vibrational energies are absent.

Taking logarithms of equation (54), we get,

$$\log f_t = \frac{3}{2} \log T + \log \frac{(2\pi mk)^{3/2} \cdot V}{h^3}$$

Differentiating this equation with respect to temperature at constant volume, we get,

$$\frac{d \log f_t}{dT} = \frac{3}{2T} \quad \dots(56)$$

From equation (39), we have,

$$E = kT^2 \frac{d \log Z}{dT} = NkT^2 \frac{d \log f_t}{dT} = RT^2 \frac{d \log f_t}{dT}$$

[Using translational partition function]

$$E = RT^2 \frac{3}{2T} = \frac{3}{2} RT$$

**(III) Entropy of monoatomic gas or vapour [Sackur-Tetrode equation]**

From equation (31), we have translational entropy given by,

$$S_t = \frac{E_t}{T} + Nk \log f_t = \frac{E_t}{T} + k \log Z = \frac{3}{2} R + Nk \log \frac{(2\pi mkT)^{3/2} V e}{Nh^3}$$

[From eqn. (55)]

(Neglecting the statistical weight factor)

$$S_t = R \log \frac{(2\pi mkT)^{3/2} V \cdot e^{5/2}}{Nh^3} = R \log \frac{(2\pi mk)^{3/2} T^{5/2} \cdot e^{5/2} R}{Nh^3 P}$$

$$k = \frac{R}{P}$$

[As  $PV = RT$ ]

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$$= R \log \frac{(2\pi M)^{3/2} (ek)^{5/2} T^{5/2}}{N^{3/2} h^3 P} \quad [\text{As } R = Nk; M = mN]$$

$$= R \log \frac{(2\pi)^{3/2} (ek)^{5/2}}{N^{3/2} h^3} + \frac{3}{2} R \log M + \frac{5}{2} R \log T - R \log P \quad \dots (57)$$

On inserting the values of natural constants, we see that the first term of equation (57) is  $-2.315 \text{ cal deg}^{-1}$

$$\therefore S_t = -2.315 + R \left( \frac{3}{2} \log M + \frac{5}{2} \log T - \log P \right) \quad \dots (58)$$

Equations (57) and (58) are known as *Sackur-Tetrode equations*.

In the above equations (57) and (58) we have not taken the contribution to the partition function due to the possible electronic state, but we have considered the concentration of translational energy only. If the former concession is also taken into account then equation (58) becomes,

$$S_t = -2.315 + R \left( \frac{3}{2} \log M + \frac{5}{2} \log T - \log P + \log f_e \right)$$

where,  $f_e$  is the electronic factor.

If the pressure  $P$  in equation (58) is taken as 1 atm., the entropy is that of the particular substance behaving as an ideal gas at this pressure, and hence represents the standard entropy,  $S^\circ$ . Equation (58) then gives the standard molar entropy of the gas in the same units, i.e.,  $\text{cal. deg}^{-1} \text{ mole}^{-1}$ . Thus,

$$S_t^\circ = -2.315 + R \left( \frac{3}{2} \log M + \frac{5}{2} \log T - \log P + \log f_e \right) \quad \dots (59)$$

**Problem 1 :** Calculate the entropy change of one mole of helium when it is heated from 300K to 600K at constant pressure.

Solution :  $S = R \log \left[ \frac{(2\pi M)^{3/2} (ek)^{5/2}}{N^{3/2} h^3 P} \cdot T^{5/2} \right] = R \log AT^{5/2}$

where,  $A = \frac{(2\pi M)^{3/2} (ek)^{5/2}}{N^{3/2} h^3 P}$

Now,  $S_{600} = R \log (A \cdot 600^{5/2})$

$\therefore S_{300} = R \log (A \cdot 300^{5/2})$

$$\begin{aligned} \Delta S &= R \log \left( \frac{600}{300} \right)^{5/2} \\ &= \frac{5}{2} \times 1.98 \times 2.303 \log_{10} 2 = 3.43 \text{ cal deg}^{-1} \text{ mole}^{-1} \end{aligned}$$

## PARTITION FUNCTION FOR DIATOMIC MOLECULES

### (I) Rotational partition function

The partition function for rotational energy of a diatomic molecule is given by,

$$f_r = \sum \epsilon_r e^{-\epsilon_r / kT} \quad \dots (60)$$

From quantum mechanical principles, the rotational energy ( $\epsilon_r$ ) for a diatomic molecule at the  $J$ th quantum level is given by,



$$\epsilon_r = J(J+1) \frac{h^2}{8\pi^2 I}$$

(17)

where,  $I = \text{moment of inertia} = \mu r^2$ .

As axis of rotation is defined by two coordinates, which means that there are two rotational degrees of freedom. Each quantum level of rotation will bring in two possible modes of distribution of rotational energy. Thus, the statistical weight factor in the rotational level  $J$  is given by  $(2J+1)$ . Hence, introducing the above arguments, we have from equation (44),

$$f_r = \sum (2J+1) \cdot e^{-[J(J+1)h^2]/8\pi^2 I k T}$$

Since the levels are closely spaced, the summation can be replaced by integration. Therefore,

$$\begin{aligned} f_r &= \int_0^{\infty} (2J+1) e^{-J(J+1) \frac{h^2}{8\pi^2 I k T} \cdot dJ} \\ &= \int_0^{\infty} (2J+1) e^{-J(J+1)\beta} \cdot dJ \end{aligned} \quad \dots(61)$$

where, 
$$\beta = \frac{h^2}{8\pi^2 I k T}$$

Suppose  $G = J(J+1)$ . On differentiating it we get,

$$dG = (2J+1) dJ$$

Hence, equation (61) becomes,

$$\begin{aligned} f_r &= \int_0^{\infty} e^{G\beta} dG \\ &= \frac{1}{\beta} = \frac{8\pi^2 I k T}{h^2} \end{aligned}$$

The value of  $f_r$  is valid for heteronuclear molecules like NO, HCl etc., whereas in the case of homonuclear molecules like  $O_2, N_2$  etc., where the molecule when reversed, becomes indistinguishable from initial state, the partition function is to be divided by the number of symmetry viz., 2. Therefore,

$$f_r = \frac{8\pi^2 I k T}{2 h^2}$$

In general, when the symmetry number is  $\sigma$ , the partition function is given by,

$$f_r = \frac{8\pi^2 I k T}{\sigma h^2} \quad \dots(62)$$

(Equation (62) holds good for diatomic molecules, other than hydrogen and deuterium) For polyatomic molecules, the principles involved in the evaluation of the partition function are quite similar to those described for diatomic molecules. It is, however, supposed that ground state of the polyatomic molecule consists of a single electronic level, and that excited states make no contribution to the total partition function. At all reasonable temperatures, the rotational levels of molecule containing more than two atoms are occupied sufficiently for the behaviour to be virtually classical in character. (Assuming the molecule to behave like a rigid rotator, the rotational partition function, excluding the nuclear spin factor, for a non-linear molecule is given by.)

$$f_r = \frac{8\pi^2 (8\pi^3 ABC)^{1/2} (kT)^{3/2}}{\sigma h^2}$$

where,  $A$ ,  $B$  and  $C$  are the moments of inertia of the molecule with respect to three perpendicular axes. For some molecules, e.g.,  $\text{NH}_3$ ,  $\text{PCl}_3$ ,  $\text{CH}_3\text{Cl}$ , etc., two of the three moments of inertia are equal.

Table-1. Moments of Inertia of polyatomic molecules

Molecule	Moment of Inertia
$\text{CO}_2^*$	71.9
$\text{N}_2\text{O}^*$	66.9
$\text{C}_2\text{H}_2^*$	23.
$\text{CH}_4$	5.27
$\text{CCl}_4$	5.20
$\text{H}_2\text{O}$	1.02, 1.90, $2.25 \times 10^{-40}$
$\text{H}_2\text{S}$	2.68, 3.08, $5.76 \times 10^{-40}$
$\text{NH}_3$	2.78, 2.78, $4.33 \times 10^{-40}$
$\text{CH}_3\text{Cl}$	5.46, 61.4, $61.4 \times 10^{-40}$

For spherically symmetrical molecule, e.g.,  $\text{CH}_4$ ,  $\text{CCl}_4$  etc., the values of  $A$ ,  $B$  and  $C$  are equal. If the non-linear molecule is planar, e.g.,  $\text{C}_6\text{H}_6$ ,  $\text{H}_2\text{O}$  etc., the sum of two of the moments of inertia is equal to the third, i.e.,  $A + B = C$ .

Problem 1 : Calculate the rotational partition function of  $\text{H}_2$  at  $0^\circ\text{C}$ . Given that :

$$h = 1.38 \times 10^{-16} \text{ erg deg}^{-1} \text{ mole}^{-1} ; h = 6.624 \times 10^{-27} \text{ erg sec. ;}$$

$$R = 0.206 \text{ c.c. atm. deg}^{-1} \text{ mole} ; \sigma = 2 ; I = 0.459 \times 10^{-40} \text{ g cm}^{-2}$$

Solution : From equation (62), we have,

$$f_r = \frac{8 \times (3.14)^2 \times 0.459 \times 10^{-40} \times 1.38 \times 10^{-16} \times 273}{2 \times (6.624 \times 10^{-27})^2} = 1.554$$

Problem 2 : Calculate the rotational partition function for hydrogen molecule at 300K. Moment of inertia of hydrogen molecule is  $4.59 \times 10^{-47} \text{ kg m}^2$ , symmetry number  $\sigma = 2$ .

Solution : The rotational partition function is :

$$\begin{aligned} q_r &= 8 \pi^2 I kT / \sigma h^2 \\ &= 8 \frac{(3.1416)^2 (4.59 \times 10^{-47} \text{ kg m}^2) (1.38 \times 10^{-23} \text{ JK}^{-1}) \times 300 \text{ K}}{2 (6.62 \times 10^{-34} \text{ Js})^2} \\ &= 1.71 \end{aligned}$$

### (III) Vibrational partition function

The partition function for vibrational energy of a diatomic molecule is given by,

$$f_v = \sum g_v \cdot e^{-\epsilon_v / kT}$$

As the statistical weight of each vibrational level is unity, we have,

$$f_v = \sum e^{-\epsilon_v / kT} \quad \dots(63)$$

At the  $n$ th quantum level, the vibrational energy of a diatomic molecule is given by,



$$\epsilon_v = \left( n + \frac{1}{2} \right) h\nu$$

where  $\nu$  = fundamental frequency of vibration,

$n$  = an integer, 0, 1, 2, 3 ... etc.

Therefore, from equation (63), we have

$$\begin{aligned} f_v &= \sum_0^{\infty} e^{-(n+1/2)h\nu/kT} \\ &= e^{-(1/2)h\nu/kT} [1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + \dots + e^{-i h\nu/kT} + \dots] \\ &= e^{-(1/2)h\nu/kT} [1 - e^{-h\nu/kT}]^{-1} \end{aligned} \quad \dots(64)$$

As  $(1 - e^{-x})^{-1} = 1 + e^{-x} + e^{-2x} + e^{-3x} + \dots + e^{-ix} + \dots$

The quantity  $h\nu/kT$  is very small and as a first approximation,

$$f_v = (1 - e^{-h\nu/kT})^{-1}$$

The value of  $\nu$  is equal to  $c\omega$ , where  $c$  is the velocity of light and  $\omega \text{ cm}^{-1}$  is the vibration frequency in wave number of the given oscillator. Hence,

$$\begin{aligned} f_v &= (1 - e^{-hc\omega/kT})^{-1} \\ &= (1 - e^{-1.439\omega/T})^{-1}; \text{ as } hc\omega/kT = 1.439\omega/T \end{aligned}$$

Table-2. Vibration frequencies of diatomic molecules.

Molecule	$\omega \text{ cm}^{-1}$	Molecule	$\omega \text{ cm}^{-1}$
H <sub>2</sub>	4405	HCl	2989
D <sub>2</sub>	3119	HBr	2650
O <sub>2</sub>	1580	HF	4141
N <sub>2</sub>	2360	HI	2309
Cl <sub>2</sub>	565	CO	2168
Br <sub>2</sub>	323	OH	3728
I <sub>2</sub>	214	NO	1907

Problem 1. Calculate the vibrational partition function of molecular hydrogen at 300K, assuming it to be harmonic oscillator. Given that  $\omega = 4405 \text{ cm}^{-1}$ .

Solution: We have,

$$\begin{aligned} f_v &= (1 - e^{-1.439\omega/T})^{-1} \\ &= (1 - e^{-1.439 \times 4405 / 300})^{-1} = (1 - e^{-21.23})^{-1} = 1.0000 \end{aligned}$$

### [[III]] Electronic partition function

Many monoatomic as well as polyatomic molecules have multiple electronic ground states. In other words, in their normal states there are two or more different electronic levels with energies so close together that they may be considered as a single level with a statistical weight factor greater than unity. In addition to this, there may be some excited electronic states whose energy may be considerably greater than that of the ground states. As we increase the temperature, such excited states become more and more occupied. Hence, electronic partition function is greater than unity and varies with temperature. The statistical weight factor for each electronic level, normal or excited is equal to weight factor for each electronic level, normal or excited is equal to  $(2j + 1)$ , where  $j$  is the resultant quantum number of the atom in the given state. Hence, the electronic partition function ( $f_e$ ) is given by,

$$f_e = \sum (2j + 1) e^{-\epsilon_e/kT}$$

where,  $\epsilon_e$  is the energy of the electronic state in excess of the lowest state, i.e., the ground state. In the ground state,  $\epsilon_e = 0$ , therefore,  $e^{-\epsilon_e / kT}$  becomes unity.

For helium, neon etc. and mercury, the value of  $j$  in the lowest energy state is zero, hence  $(2j + 1)$  becomes unity since no higher or excited level is required, therefore,  $f_e$  becomes unity and so can be disregarded.

For diatomic molecules and other atoms, one or more electronic states above the ground state are considerably occupied even at normal temperatures and so the appropriate terms must be included in the partition function. For example, in the lowest state of chlorine atom, i.e., when  $\epsilon_e = 0$ ;  $j = 3/2$ ; not very far above this is another state where  $j = 1/2$ . Thus, the value of  $f_e$  is given by,

$$f_e = \left(2 \times \frac{3}{2} + 1\right) e^{-0/kT} + \left(2 \times \frac{1}{2} + 1\right) e^{-\epsilon_1/kT} = 4 + 2e^{-\epsilon_1/kT}$$

where,  $\epsilon_1$  is the electronic energy of the upper level in excess of the value in the ground state. At higher temperatures, other terms for higher electronic levels have to be considered.

According to quantum theory, the energy,  $\epsilon$  corresponding to a frequency of  $\nu \text{ cm}^{-1}$  is represented by,

$$\epsilon = \nu hc$$

where  $h$  is Planck's constant and  $c$  is the velocity of light. For chlorine, it has been found from the spectrum of atomic chlorine, that the separation of two lines frequencies in wave numbers differ by  $881 \text{ cm}^{-1}$ . Substituting these assumptions, we get,

$$\begin{aligned} f_e &= 4 + 2e^{-881 h\nu / kT} \\ &= 4 + 2e^{-1268 / T} \end{aligned}$$

**Problem 1.** Calculate the electronic partition function of atomic chlorine at 300 K.

**Solution :** We know that,  $f_e = 4 + 2e^{-1268 / T}$

$$= 4 + 2e^{-1268 / 300} = 4.029$$

#### [IV] Complete partition function

The complete partition function of a diatomic molecule is expressed as,

$$\begin{aligned} f &= f_t \times f_r \times f_v \\ &= \frac{(2\pi m k T)^{3/2} \cdot V e}{N h^3} \cdot \frac{8\pi^2 I k T}{\sigma h^2} \cdot e^{-h\nu / kT} (1 - e^{-h\nu / kT})^{-1} \end{aligned}$$

#### [V] Rotational energy

The rotational energy of a diatomic molecule is given by,

$$\begin{aligned} E_r &= NkT^2 \frac{d \log f_r}{dT} \\ &= NkT^2 \frac{d}{dT} \log (8\pi^2 I k T / \sigma h^2) \\ &= NkT = RT \end{aligned}$$

...(65)

#### [VI] Vibrational energy

The vibrational energy of a diatomic molecule is given by,



$$E_v = NkT^2 \frac{d \log f_v}{dT} = NkT^2 \frac{d}{dT} \left[ e^{-h\nu/2kT} (1 - e^{-h\nu/kT})^{-1} \right]$$

$$= \frac{N\bar{h}\nu}{kT} + N\bar{h}\nu \frac{e^{-h\nu/kT}}{1 - e^{-h\nu/kT}} \quad \dots(66)$$

[VII] Total energy

The total internal energy is given by,

$$E = E_t + E_r + E_v$$

$$= \frac{3}{2}RT + RT + \frac{N\bar{h}\nu}{kT} + N\bar{h}\nu \cdot \frac{e^{-h\nu/kT}}{1 - e^{-h\nu/kT}}$$

$$= \frac{5}{2}RT + \frac{N\bar{h}\nu}{kT} + N\bar{h}\nu \cdot \frac{e^{-h\nu/kT}}{1 - e^{-h\nu/kT}}$$

(i)

21

v  
t

f

*complete.*

[VIII] Rotational entropy

From equation (31) we have,

$$S_r = \frac{E_r}{T} + nk \log f_r$$

or

$$S_r = R + NK \log \frac{8\pi^2 I k T}{\sigma h^2} = R \log \frac{8\pi^2 I k T e}{\sigma h^2}$$

$$= R \left( 1 + \log \frac{8\pi^2 I k T}{\sigma h^2} \right)$$

$$= R (1 + \log 8 + 2 \log \pi + \log I + \log k + \log T - \log \sigma - 2 \log h)$$

Substituting the values of  $\pi$ ,  $h$ ,  $k$  and  $R$  in the above equation, we get,

$$S_r = 4.576 (\log I + \log T - \log \sigma + 38.82) \quad \dots(67)$$

For a non-linear molecule, the rotational entropy is given by the following relation, after proceeding in the same way as above,

$$S_r = \frac{3}{2}R + \frac{R \log 8\pi^2 (8\pi^3 ABC)^2 (kT)^{3/2}}{\sigma h^2}$$

For a non-linear molecule,  $E_r = \frac{3}{2}RT$

Extracting the constants and converting the logarithms, in the usual manner, we see that,

$$S_r = 4.576 \left( \frac{1}{2} \log ABC + \frac{3}{2} \log T - \log \sigma + 58.51 \right) \quad \dots(68)$$

Problem 1 : Calculate the rotational entropy of CO at 25°C, if  $I = 14.48 \times 10^{-40} \text{ g cm}^{-2}$  and  $\sigma = 1$ .

Solution: From equation (67), we have,

$$S_r = 4.576 [(\log 14.48 \times 10^{-40}) + \log 298 - 1 + 38.82]$$

$$= 11.24 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Problem 2 : Calculate the rotational contribution to the molar entropy of ammonia at 25°C, if the moments of inertia are  $2.78 \times 10^{-40}$ ,  $2.78 \times 10^{-40}$  and  $4.33 \times 10^{-40} \text{ gm. cm}^{-2}$ , symmetry number = 3.

Solution : From equation (68), we have,

$$\begin{aligned}
 S_r &= 4.576 \left[ \frac{1}{2} \cdot \log (2.78 \times 10^{-40} \times 2.78 \times 10^{-40} \times 4.33 \times 10^{-40}) \right. \\
 &\quad \left. + \frac{3}{2} \cdot \log 298 - \log 3 + 58.51 \right] \\
 &= 11.5 \text{ cal deg}^{-1} \text{ mole}^{-1}
 \end{aligned}$$

## (i) Vibrational entropy

We know that,  $S_V = \frac{E_V}{T} + nk \log f_V$

or 
$$S_V = \frac{N h \nu}{k T^2} + \frac{N h \nu}{T} \frac{e^{-h \nu / k T}}{1 - e^{-h \nu / k T}} + N k \log (1 - e^{-h \nu / k T})^{-1} \quad \dots(69)$$

**Problem 1 :** Calculate the total standard entropy of nitrogen gas at 25°C. Given that :

Vibrational frequency = 2360 cm<sup>-1</sup>; Moment of inertia = 13.9 × 10<sup>-40</sup> g cm<sup>-2</sup>.

**Solution :** Since the ground state of molecular nitrogen is a singlet level,  $f_e$  is unity, and the molecular weight being 28, the combined translational and electronic entropy, the latter being actually zero, is given by equation (43.3) as,

$$\begin{aligned}
 S_t^0 &= 2.315 + 1.98 \left( \frac{3}{2} \log 28 + \frac{5}{2} \log 298 \right) \\
 &= 35.9 \text{ cal. deg}^{-1} \text{ mole}^{-1}
 \end{aligned}$$

The vibrational frequency is 2360 cm<sup>-1</sup> and hence  $h c \omega / k T$  is 11.4. Insertion of this result in equation (50.3) gives a value for  $S_V$  that is negligibly small. The vibrational contribution to the entropy of molecular nitrogen at 25°C may thus be taken as zero.

The rotational entropy ( $S_r$ ) is given by equation (67) taking  $\sigma = 2$ ; as the nitrogen molecule is symmetrical.

$$\begin{aligned}
 S_r &= 4.576 [\log 13.9 \times 10^{-40} + \log 298 - \log 2 + 38.82] \\
 &= 9.8 \text{ cal. deg}^{-1} \text{ mole}^{-1}
 \end{aligned}$$

∴ The total standard entropy = 35.9 + 9.8

$$= 45.7 \text{ cal. deg}^{-1} \text{ mole}^{-1}$$

**Problem 2 :** Calculate the vibrational contributions to  $H$ ,  $S$ ,  $C_v$  and  $G$  for O<sub>2</sub>(g) at 25°C. The vibrational frequency  $\bar{\omega} = 1580.2 \text{ cm}^{-1}$ .

**Solution :** Firstly, we will calculate the value of  $x$ .

$$\therefore x = h \omega / k = h c \bar{\omega} / k$$

$$h = 6.626 \times 10^{-34} \text{ Js, } c = 2.998 \times 10^8 \text{ ms}^{-1}$$

$$\bar{\omega} = 1580.2 \text{ cm}^{-1} = 1580.2 \times 10^2 \text{ m}^{-1}$$

$$k = 1.3806 \times 10^{-23} \text{ JK}^{-1}$$

$$x = \frac{(6.626 \times 10^{-34} \text{ Js})(2.998 \times 10^8 \text{ ms}^{-1})(1580.2 \times 10^2 \text{ m}^{-1})}{1.3806 \times 10^{-23} \text{ JK}^{-1}}$$

$$= 2273.64 \text{ K}$$

$$\text{For 1 mole of gas, } H_v = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \frac{2273.64 \text{ K}/298 \text{ K}^{-1}}{\exp(2273.64/298) - 1}$$

$$= 9.18 \text{ J mol}^{-1} = 0.009 \text{ kJ mol}^{-1}$$

$$S_v = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \left[ \frac{2273.64/298}{\exp(2273.64/298) - 1} - \ln \left\{ 1 - \exp \left( \frac{-2273.64}{298} \right) \right\} \right]$$

$$= 0.035 \text{ JK}^{-1} \text{ mol}^{-1}$$



$$G_p = H_p - TS_p$$

$$= 9.18 \text{ J mol}^{-1} - 298 \text{ K} \times 0.035 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$= -1.25 \text{ J mol}^{-1}$$

(18)

## EQUILIBRIUM CONSTANT AND PARTITION FUNCTION Assignment

We will now express the value of equilibrium constant ( $K$ ) of a reaction in terms of partition function. We know that,

$$E - E_0 = RT^2 \frac{d \log f}{dT}$$

where  $E_0$  is the zero point energy of the  $N$  molecules, while  $E$  is the total energy of the same molecular species.

Since the total internal energy of an ideal gas is independent of the pressure at a given temperature, the values  $E$  and  $E_0$  can be replaced by their standard state values  $E^\circ$  and  $E_0^\circ$ , respectively.

Thus, 
$$E^\circ - E_0^\circ = RT^2 \frac{d \log f^\circ}{dT}$$

$$E^\circ = E_0^\circ + RT^2 \frac{d \log f^\circ}{dT}$$

We also know that, 
$$G = E + PV - TS = E + RT - TS$$

$$G = E_0 - RT \log \frac{f}{N} \quad \dots(70)$$

If the pressure of the gas is unity, the value of  $G$  and  $f$  can be replaced by their standard values  $G^\circ$  and  $f^\circ$ , respectively. Thus, equation (70) becomes,

$$G^\circ = E_0^\circ - RT \log \frac{f^\circ}{N}$$

$$-\frac{G^\circ - E_0^\circ}{T} = RT \log \frac{f^\circ}{N} \quad \dots(71)$$

The left hand side is known as *free energy function of the substance*.

We know that, 
$$H = E + PV = E + RT$$

When the substance is in its standard state, then equation (72) becomes at 0K,

$$H_0^\circ = E_0^\circ \quad [\text{As } T = 0]$$

Substituting this value of  $E_0^\circ$  in equation (71), we get,

$$-\frac{G^\circ - H_0^\circ}{T} = R \log \frac{f^\circ}{N} \quad \dots(73)$$

The quantity  $\left(-\frac{G^\circ - H_0^\circ}{T}\right)$  is also known as *free energy function of the substance*.

Consider the gaseous reaction :



in which,

$$\Delta G^\circ = (pG^\circ_P + qG^\circ_Q + rG^\circ_R + \dots) - (lG^\circ_L + mG^\circ_M + nG^\circ_N + \dots) \quad \dots(74)$$

P    Q    R



three v  
3N d  
ator

19

If equation (64) is applied to the substances L, M, ... and P, Q etc., we get,

(5)

$$G^{\circ}_L = H^{\circ}_{0L} - RT \log \frac{f^{\circ}_L}{N}$$

$$G^{\circ}_M = H^{\circ}_{0M} - RT \log \frac{f^{\circ}_M}{N}$$

$$G^{\circ}_N = H^{\circ}_{0N} - RT \log \frac{f^{\circ}_P}{N}$$

.....  
.....

$$G^{\circ}_P = H^{\circ}_{0P} - RT \log \frac{f^{\circ}_P}{N}$$

$$G^{\circ}_Q = H^{\circ}_{0Q} - RT \log \frac{f^{\circ}_Q}{N}$$

$$G^{\circ}_R = H^{\circ}_{0R} - RT \log \frac{f^{\circ}_R}{N}$$

$$G^{\circ} = H^{\circ}_0 - RT \log \frac{F^{\circ}}{Z}$$

Substituting these values in equation (74) we get, (5)

$$\begin{aligned} \Delta G^{\circ} &= \left[ p \left( H^{\circ}_{0P} - RT \log \frac{f^{\circ}_P}{N} \right) + q \left( H^{\circ}_{0Q} - RT \log \frac{f^{\circ}_Q}{N} \right) + r \left( H^{\circ}_{0R} - RT \log \frac{f^{\circ}_R}{N} \right) + \dots \right. \\ &\quad \left. - \left[ l \left( H^{\circ}_{0L} - RT \log \frac{f^{\circ}_L}{N} \right) + m \left( H^{\circ}_{0M} - RT \log \frac{f^{\circ}_M}{N} \right) + n \left( H^{\circ}_{0N} - RT \log \frac{f^{\circ}_N}{N} \right) + \dots \right] \right. \\ &= (pH^{\circ}_{0P} + qH^{\circ}_{0Q} + rH^{\circ}_{0R} + \dots) - (lH^{\circ}_{0L} + mH^{\circ}_{0M} + nH^{\circ}_{0N} + \dots) \\ &\quad - RT \log \frac{(f^{\circ}_P/N)^p \cdot (f^{\circ}_Q/N)^q \cdot (f^{\circ}_R/N)^r \dots}{(f^{\circ}_L/N)^l \cdot (f^{\circ}_M/N)^m \cdot (f^{\circ}_N/N)^n \dots} \\ &= \Delta H^{\circ}_0 - RT \log \frac{(f^{\circ}_P/N)^p \cdot (f^{\circ}_Q/N)^q \cdot (f^{\circ}_R/N)^r \dots}{(f^{\circ}_L/N)^l \cdot (f^{\circ}_M/N)^m \cdot (f^{\circ}_N/N)^n \dots} \end{aligned}$$

We have,  $\Delta G^{\circ} = -RT \log K_p$

or  $\log K_p = -\frac{1}{RT} \Delta G^{\circ}$

or  $\log K_p = -\frac{1}{RT} \left[ \Delta H^{\circ}_0 - RT \log \frac{(f^{\circ}_P/N)^p \cdot (f^{\circ}_Q/N)^q \cdot (f^{\circ}_R/N)^r}{(f^{\circ}_L/N)^l \cdot (f^{\circ}_M/N)^m \cdot (f^{\circ}_N/N)^n} \right]$

$$= -\frac{\Delta H^{\circ}_0}{RT} + \log \frac{(f^{\circ}_P/N)^p \cdot (f^{\circ}_Q/N)^q \cdot (f^{\circ}_R/N)^r}{(f^{\circ}_L/N)^l \cdot (f^{\circ}_M/N)^m \cdot (f^{\circ}_N/N)^n \dots}$$

or  $K_p = \frac{(f^{\circ}_P/N)^p \cdot (f^{\circ}_Q/N)^q \cdot (f^{\circ}_R/N)^r \dots}{(f^{\circ}_L/N)^l \cdot (f^{\circ}_M/N)^m \cdot (f^{\circ}_N/N)^n \dots} \times e^{-(\Delta H^{\circ}_0)/RT} \dots (75)$

This is the expression relating the equilibrium constant in terms of partition function.

### HEAT CAPACITY OF SOLIDS AND PARTITION FUNCTION

The atoms in the crystalline solids are arranged in one set pattern and, therefore, have only vibrational motion, the electronic levels are assumed to be unexcited. For a single atom, there are