4.11 PARTITION FUNCTION AND THERMODYNAMIC FUNCTIONS

We will now utilize the partition function and the distribution law to evaluate various thermodynamic functions including the equilibrium constant in chemical reactions.

(i) Internal Energy

Consider a system consisting of non-interacting molecules (e.g., ideal gas). the total energy of the system is given by

$$E = \Sigma n_i \epsilon_i \qquad \qquad \text{...... (4.3)}$$

According to Maxwell-Boltzmann law

$$n_i = g_i\, e^{-\alpha}\, e^{-\epsilon_i/kT}$$

Taking summation on both sides

$$\Sigma n_i = e^{-\alpha}\, \Sigma g_i\, e^{-\epsilon_i/kT} \qquad \qquad \text{...... (4.59)}$$

$$N = e^{-\alpha} Q$$

$$e^{-\alpha} = \frac{N}{Q} \qquad \qquad \text{...... (4.60)}$$

Putting the value of Σn_i from equation (4.59) into equation (4.3)

$$E = e^{-\alpha}\, \Sigma g_i\, e^{-\epsilon_i/kT}\, \epsilon_i \qquad \qquad \text{...... (4.61)}$$

Putting the value of $e^{-\alpha}$ from equation (4.60) into equation (4.61) we get

$$E = \frac{N}{Q} \Sigma g_i e^{-\epsilon_i/kT} \epsilon_i$$

$$\frac{EQ}{N} = \Sigma g_i e^{-\epsilon_i/kT}$$

.......(4.62)

Now $\quad Q = \Sigma g_i e^{-\epsilon_i/kT}$

Differentiate the above equation with respect to T at constant V, we get

$$\left(\frac{\partial Q}{\partial T}\right)_v = \frac{1}{kT^2} \Sigma g_i e^{-\epsilon_i/kT} \epsilon_i$$

or $\quad kT^2 \left(\frac{\partial Q}{\partial T}\right)_v = \Sigma g_i e^{-\epsilon_i/kT}$

.......(4.63)

Comparing equation (4.62) and (4.63)

$$\frac{EQ}{N} = kT^2 \left(\frac{\partial Q}{\partial T}\right)_v$$

$$E = \frac{NkT^2}{Q} \left(\frac{\partial Q}{\partial T}\right)_v$$

$$E = NkT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_v \qquad \therefore \quad \frac{1}{Q}\left(\frac{\partial Q}{\partial T}\right)_v = \left(\frac{\partial \ln Q}{\partial T}\right)_v$$

For one mole of a gas $N = N_A$ = Avogadro number

$$E = N_A kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_v$$

or $\quad E = RT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_v$

.......(4.64)

$\therefore \quad R = N_A k$

Thus, equation (4.64) is the relation between energy (E) and partition function of the system.

(ii) Heat Capacity

Heat capacity at constant volume is given by

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

.......(4.65)

and $\quad E = RT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_v$

Putting the value of E in equation (4.65), we get

$$C_v = \frac{\partial}{\partial T}\left[RT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_v \right]$$

$$C_v = R \left[2T \left(\frac{\partial \ln Q}{\partial T} \right)_v + T^2 \left(\frac{\partial^2 \ln Q}{\partial T^2} \right)_v \right]$$ ...... (4.66)

Equation (4.66) is the relation between the molar heat capacity (C_v) at constant volume of an ideal gas and partition function.

We also known

$$C_p = C_v + R$$

∴ $$C_p = R + \frac{\partial}{\partial T} \left[RT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_v \right]$$ ...... (4.67)

Equation (4.67) is the relation between molar heat capacity (C_p) at constant pressure of an ideal gas and partition function.

(iii) Entropy (S)

According to Boltzmann distribution law

$$\frac{n_i}{N} = \frac{g_i \, e^{-\epsilon_i/kT}}{Q}$$ ...... (4.21)

where n_i = Number of molecules having energy ϵ_i

N = Total number of molecules in the system

g_i = Statistical weight factor for energy level i

Taking logarithm of above equation on both sides

$$\ln n_i = \ln N + \ln g_i - \epsilon_i/kT - \ln Q$$

Multiplying the above equation by n_i both sides, we get

$$n_i \ln n_i = n_i \ln N + n_i \ln g_i - \frac{n_i \epsilon_i}{kT} - n_i \ln Q$$

or $$n_i \ln n_i = (n_i \ln N - n_i \ln Q) + n_i \ln g_i - \frac{n_i \epsilon_i}{kT}$$

or $$n_i \ln n_i = n_i \ln \left(\frac{N}{Q} \right) + n_i \ln g_i - \frac{n_i \epsilon_i}{kT}$$

By taking summation over all the energy-level (or quantum states) we get

$$\Sigma n_i \ln n_i = \Sigma n_i \ln \left(\frac{N}{Q} \right) + \Sigma n_i \ln g_i - \Sigma \frac{n_i \epsilon_i}{kT}$$

or $$\Sigma n_i \ln n_i = - \Sigma n_i \ln \left(\frac{Q}{N} \right) + \Sigma n_i \ln g_i - \Sigma \frac{n_i \epsilon_i}{kT}$$ ...... (4.68)

But according to modified definition of probability

$$W = \frac{(g_0)^{n_0}}{n_0!} \cdot \frac{(g_1)^{n_1}}{n_1!} \cdot \frac{(g_2)^{n_2}}{n_2!} \cdots \frac{(g_i)^{n_i}}{n_i!}$$

Taking logarithm on both sides of the equation

$$\ln W = (n_0 \ln g_0 - \ln n_0!) + (n_1 \ln g_1 - \ln n_1!) + \ldots (n_i \ln g_i - \ln n_i!)$$

$$\ln W = (n_0 \ln g_0 + n_1 \ln g_1 + \ldots n_i \ln g_i) - (\ln n_0! + \ln n_1! + \ldots \ln n_i!)$$

$$\ln W = \Sigma n_i \ln g_i - \Sigma \ln n_i! \qquad \ldots\ldots (4.69)$$

For any large values of n_i, as in the case with molecules, Stirling's formula may be used

$$\ln n_i! = n_i \ln n_i - n_i$$

$$\therefore \qquad \Sigma \ln n_i! = \Sigma n_i \ln n_i - \Sigma n_i$$

Hence $\Sigma \ln n_i! = \Sigma n_i \ln n_i - N$ $\qquad \ldots\ldots (4.70)$

From equation (4.69) and (4.70)

$$\ln W = \Sigma n_i \ln g_i - \Sigma n_i \ln n_i + N$$

or $\qquad \Sigma n_i \ln n_i = -\ln W + \Sigma n_i \ln g_i + N \qquad \ldots\ldots (4.71)$

From equations (4.68) and (4.71)

$$-\ln W + \Sigma n_i \ln g_i + N = -\Sigma n_i \ln \left(\frac{Q}{N}\right) + \Sigma n_i \ln g_i - \Sigma \frac{n_i \epsilon_i}{kT}$$

$$\ln W = \Sigma n_i \ln \left(\frac{Q}{N}\right) + \Sigma \frac{n_i \epsilon_i}{kT} + N \qquad \ldots\ldots (4.72)$$

Since in the summation $\Sigma n_i \ln \left(\frac{Q}{N}\right)$, the factor $\ln \left(\frac{Q}{N}\right)$ will come with each term

hence $\Sigma n_i \ln \left(\frac{Q}{N}\right) = \ln \left(\frac{Q}{N}\right) \Sigma n_i$

But $\qquad N = \Sigma n_i$

Hence $\Sigma n_i \ln \left(\frac{Q}{N}\right) = N \ln \left(\frac{Q}{N}\right) \qquad \ldots\ldots (4.73)$

Similarly

$$\Sigma \left(\frac{n_i \epsilon_i}{kT}\right) = \frac{1}{kT} \Sigma n_i \epsilon_i \qquad \ldots\ldots (4.74)$$

From equation (4.72), (4.73) and (4.74), we get

$$\ln W = N \ln \left(\frac{Q}{N}\right) + \frac{1}{kT} \Sigma n_i \epsilon_i + N \qquad \text{...... (4.75)}$$

But $E = NkT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_v$ $\therefore \; \Sigma n_i \epsilon_i = E$

$$\ln W = N \ln \left(\frac{Q}{N}\right) + \frac{NkT^2}{kT} \left(\frac{\partial \ln Q}{\partial T}\right)_v + N$$

$$\ln W = N \ln \left(\frac{Q}{N}\right) + NT \left(\frac{\partial \ln Q}{\partial T}\right)_v + N$$

Taking N as common

$$\ln W = N \left[\ln \left(\frac{Q}{N}\right) + T \left(\frac{\partial \ln Q}{\partial T}\right)_v + 1 \right] \qquad \text{...... (4.76)}$$

According to Boltzmann-Planck's equation

$$S = k \ln W$$

$$\ln W = \frac{S}{k}$$

Hence equation (4.76) becomes

$$\frac{S}{k} = N \left[\ln \left(\frac{Q}{N}\right) + T \left(\frac{\partial \ln Q}{\partial T}\right)_v + 1 \right]$$

$$S = kN \left[\ln \left(\frac{Q}{N}\right) + T \left(\frac{\partial \ln Q}{\partial T}\right)_v + 1 \right] \qquad \text{...... (4.77)}$$

Equation (4.77) is the relation between entropy and partition function for any number of molecules in the system. For one mole of an ideal gas; i.e., $N = N_A$, we get

$$S = kN_A \left[\ln \left(\frac{Q}{N}\right) + T \left(\frac{\partial \ln Q}{\partial T}\right)_v + 1 \right]$$

$$S = R \left[\ln \left(\frac{Q}{N}\right) + T \left(\frac{\partial \ln Q}{\partial T}\right)_v + 1 \right]$$

$$S = R \ln \left(\frac{Q}{N}\right) + RT \left(\frac{\partial \ln Q}{\partial T}\right)_v + R \qquad \text{...... (4.78)}$$

$R = kN_A$, where N_A is the Avogadro number. Equation (4.78) applies to one mole of an ideal gas.

(iv) Work Function

We know that,