

Substituting the value of E and P into equation (4.84), we get

$$\begin{aligned}
 H &= RT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_V + VRT \left( \frac{\partial \ln Q}{\partial V} \right)_T \\
 H &= RT \left[ T \left( \frac{\partial \ln Q}{\partial T} \right)_V + V \left( \frac{\partial \ln Q}{\partial V} \right)_T \right] \\
 H &= RT \left[ T \left( \frac{\partial \ln Q}{\partial \ln T} \right)_V + \left( \frac{\partial \ln Q}{\partial \ln V} \right)_T \right] \quad \dots\dots (4.85)
 \end{aligned}$$

Equation (4.85) is the relation between heat content and partition function.

#### 4.12 ENTROPY AND PROBABILITY (STATISTICAL TREATMENT OF ENTROPY)

Second law of thermodynamics has a statistical nature. At constant energy and volume a system is in the equilibrium when its entropy is maximum. Again, the thermodynamic probability is also maximum. It means that there exists some relationship between entropy and thermodynamic probability of the system. Boltzmann showed that entropy and thermodynamic probability are related by

$$S = k \ln W \quad \dots\dots (4.86)$$

where  $k$  is a Boltzmann constant  $= k = R/N_A$ ,  $R$  is the gas constant and  $N_A$  is the Avogadro number. Entropy is an additive property, whereas probability is multiplicative.

Consider two systems of identical particles for which the entropies are  $S_1$  and  $S_2$  and probabilities  $W_1$  and  $W_2$ . When these systems are combined the total entropy is  $S = S_1 + S_2$ , while the total probability becomes  $W_1 W_2$  and thus

$$S = f(W_1 W_2)$$

$$S = f(W_1) + f(W_2) = f(W_1 W_2)$$

The function which satisfies this relation must be logarithmic, namely,

$$S = K_1 \ln W + K_2 \quad \dots (4.87)$$

where  $K_1$  and  $K_2$  are the constants to be evaluated. If equation (4.87) has general validity, it should also apply to a perfect crystal at 0K. For such a crystal  $S = 0$ , by the 3rd law of thermodynamics. Again, since the crystal is perfect, there is only one arrangement for it and  $W = 1$ . On inserting these values in equation (4.87), we see that  $K_2 = 0$ , and here

$$S = K_1 \ln W \quad \dots (4.88)$$

The nature of  $K_1$  can be found by using equation (4.88) to calculate the translational entropy of an ideal gas. Using equation for thermodynamic probability ( $W$ ) with modification like insertion of statistical weights and quantum statistical recognition that identical particles are actually indistinguishable

$$W = \frac{(g_0)^{n_0}}{n_0!} \cdot \frac{(g_1)^{n_1}}{n_1!} \cdots \frac{(g_i)^{n_i}}{n_i!} \quad \dots (4.68)$$

Taking log on both sides and using Stirling's formula we get

$$\ln W = \sum n_i \ln g_i - \sum n_i \ln n_i + N \quad \dots (4.71)$$

According to most probable distribution

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

For translation motion, the above equation takes the form

$$n_i = \frac{N g_i e^{-\epsilon_t/kT}}{Q_t} \quad \dots (4.89)$$

Substituting the value of  $n_i$  into (4.71), we get

$$\ln W = \sum n_i \ln g_i - \sum n_i \ln \left[ \left( \frac{N}{Q_t} \right) g_i e^{-\epsilon_t/kT} \right] + N$$

$$\ln W = \sum n_i \ln g_i - \sum n_i \ln \left( \frac{N}{Q_t} \right) - \sum n_i \ln g_i + \frac{\sum n_i \epsilon_t}{kT} + N$$

$$\ln W = - \sum n_i \ln \left( \frac{N}{Q_t} \right) + \frac{1}{kT} \sum n_i \epsilon_t + N \quad \dots (4.90)$$

$$\text{But } \sum n_i \epsilon_t = E_t - E_{0(t)} = RT^2 \left( \frac{\partial \ln Q_t}{\partial T} \right)_V$$

Putting this value in equation (4.90) we get

$$\ln W = - \sum n_i \ln \left( \frac{N}{Q_t} \right) + \frac{RT^2}{kT} \left( \frac{\partial \ln Q_t}{\partial T} \right)_V + N$$

$$\ln W = N \ln \left( \frac{Q_t}{N} \right) + \frac{RT}{k} \left( \frac{\partial \ln Q_t}{\partial T} \right)_V + N \quad \dots\dots (4.91)$$

Multiplying equation (4.91) both sides by Boltzmann constant  $k$ , we get

$$k \ln W = Nk \ln \left( \frac{Q_t}{N} \right) + RT \left( \frac{\partial \ln Q_t}{\partial T} \right)_V + kN$$

For one mole of an ideal gas

$$k \ln W = N_A k \ln \left( \frac{Q_t}{N} \right) + RT \left( \frac{\partial \ln Q_t}{\partial T} \right)_V + N_A k$$

$$k \ln W = R \ln \left( \frac{Q_t}{N} \right) + RT \left( \frac{\partial \ln Q_t}{\partial T} \right)_V + R \quad \dots\dots (4.92)$$

$$k \ln W = S_t \quad \dots\dots (4.93)$$

$$\therefore S_t = R \ln \left( \frac{Q_t}{N} \right) + RT \left( \frac{\partial \ln Q_t}{\partial T} \right)_V + R \quad \dots\dots (4.93)$$

Therefore,

$$K_1 = k$$

Thus equation (4.93) becomes

$$S = k \ln W \quad \dots\dots (4.94)$$

Equation (4.94) represents the general relationship between entropy and probability.

#### 4.13 STATISTICAL EXPRESSION FOR EQUILIBRIUM CONSTANT

The free energy of a mole of an ideal gas can be related to the partition function. Since the methods of deriving partition functions for various types of molecules are available, at least in principle, it should be possible to calculate the free energies of the substances taking part in a chemical reaction. The free energy  $\Delta F^\circ$ , for reactants and products in the standard state, is related to the equilibrium constant  $K$  of the reaction by the equation

$$-\Delta F^\circ = RT \ln K \quad \dots\dots (4.95)$$