Dr. L. K. Mishra
Deptt of Chemistry

67

Deg II. Chem. Hons, Paper – III

Topic :- Thermodynamics

Entropy increase during Isothermal mixing of Ideal gases (Rest Portion)

If these two gases A and B are allowed to mix at same temperature and Pressure, the total entropy is givenby

$$S_{Total} = S_A + S_B$$

$$= n_A(S^0_A - R \log p_A) + n_B(S^0_B - R \log p_B) \quad \text{—(6)}$$

Where p_A and p_B represent the partial Pressure of gas A and B after mixing. The Value of p_A and p_B are Connected to the total Pressure P by Dalton's Law of Partial Pressure

$$p_A = \frac{n_A}{n_A + n_B} \cdot P = X_A \cdot P \quad \text{—(7)}$$

$$p_B = \frac{n_B}{n_A + n_B} \cdot P = X_B \cdot P \quad \text{—(8)}$$

where X_A = Mole fraction of A

X_B = Mole fraction of B

∴ Total change in entropy (ΔS) is given by

$$\Delta S = S_T - (S_A + S_B)$$

$$= n_A(s^0_A - R\log p_A) + n_B(s^0_B - R\log p_B)$$

$$= -[n_A(s^0_A - R\log P) + n_B(s^0_B - R\log P)]$$

from equation (4), (5) & (6)

$$= -n_A R\log\frac{p_A}{P} - n_B R\log\frac{p_B}{P}$$

$$= -n_A R\log X_A - n_B R\log X_B \quad \text{—(9)}$$

From (7) & (8)

Equation (9) gives two values of change in entropy when one mole of a mixture is formed.

In general $\Delta S_m = -R\sum_m X_m \log X_m$ — (10)

where ΔS_m = Increase of entropy on mixing ideal gases

standard entropy of a gas

If the entropy of the gas at one atmospheric Pressure is expressed in terms of ideal gas at the same pressure, then this value is termed as the standard entropy of gas.

Work & Free energy function

In addition to internal energy (E), Enthalpy (H) and Entropy (S), there are two fundamental thermodynamic Properties which also depend upon the state of the system only. These Properties are known as work and free energy function represented by A and G respectively

Helmholtz work function → A

Gibbs free energy function → G

They are defined by the equation

$$A = E - TS \quad \text{——} (1)$$

$$G = H - TS \quad \text{——} (2)$$

Since E, H and S depend only upon the state of the System (temperature is included in the state), It is clear that function A and G also depend upon the state only.