

THERMODYNAMICS phy

Ques -1 Partial molar free energy OR
Chemical potential.

→ If there is a small extensive property under study is free energy (G), \bar{G} will represent partial molar free energy

$$\bar{G}_1 = \left(\frac{\delta G}{\delta n_1} \right)_{T, P, n_2, n_3, \dots, n_j}$$

$$\bar{G}_j = \left(\frac{\delta G}{\delta n_j} \right)_{T, P, n_1, n_2, \dots, n_{j-1}}$$

Chemical potential represented by μ ,

$$\mu_1 = \bar{G}_1 = \left(\frac{\delta G}{\delta n_1} \right)_{T, P, n_2, \dots, n_j}$$

→ By definition the chemical potential of a given substance is the change in free energy of the system produced on addition of one mole of the substance at constant temperature and pressure to a large bulk of the mixture so that its composition does not undergo any change.

→ Greater the chemical potential of a system greater will be its escaping tendency.

Gibbs Duhem equation :-

→ G can be determined by fixing the variable T, P and no. of moles.

$$G = f(T, P, n_1, n_2, \dots, n_j) \quad \text{--- (1)}$$

Differentiating eqⁿ (1) we get,

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P, n_1, n_2, \dots, n_j} dT + \left(\frac{\partial G}{\partial P} \right)_{T, n_1, n_2, \dots, n_j} dP +$$

$$\left(\frac{\partial G}{\partial n_1} \right)_{T, P, n_2, \dots, n_j} dn_1 + \left(\frac{\partial G}{\partial n_2} \right)_{T, P, n_1, \dots, n_j} dn_2 + \left(\frac{\partial G}{\partial n_j} \right)_{T, P, n_1, n_2, \dots, n_{j-1}} dn_j$$

We know the chemical potential is given by

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_1, n_2, \dots} = \bar{G}_i$$

Substituting in eqⁿ (1) we get,

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P, n_1, n_2, \dots, n_j} dT + \left(\frac{\partial G}{\partial P} \right)_{T, n_1, n_2, \dots, n_j} dP +$$

$$\left(\mu_1 dn_1 + \mu_2 dn_2 + \mu_j dn_j \right) \quad \text{--- (2)}$$

→ for a closed system there is no change in the composition and eqⁿ (3) reduces to,

$$dG = \left(\frac{\delta G}{\delta T} \right)_{P, n_1, n_2, \dots, n_j} dT + \left(\frac{\delta G}{\delta P} \right)_{T, n_1, n_2, \dots, n_j} dP$$

We know,

$$dG = -SdT + VdP \quad \text{--- (5)}$$

$$\left(\because G = H - TS \right.$$

$$H = E + PV$$

$$G = dE + PdV + VdP - Tds - SdT$$

Comparing eqⁿ (4) and (5)

$$\left(\frac{\delta G}{\delta T} \right)_{P, n_1, n_2, \dots, n_j} dT = -S$$

$$\left(\frac{\delta G}{\delta P} \right)_{T, n_1, n_2, \dots, n_j} dP = +V$$

Putting these values in eqⁿ (3) we get

$$dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_j dn_j \quad \text{(6)}$$

At constant temperature and pressure

eqⁿ (6) reduces to,

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_j dn_j \quad \text{(7)}$$

Integrating eqⁿ (7) we get,

$$(G)_{TP} = \mu_1 n_1 + \mu_2 n_2 + \dots + \mu_j n_j \quad \text{--- (8)}$$

Differentiating eqⁿ (8) we get,

$$(dG)_{TP} = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 + \dots + \mu_j dn_j + n_j d\mu_j \quad \text{--- (9)}$$

Comparing eqⁿ (7) & (9)

$$n_1 d\mu_1 + n_2 d\mu_2 + \dots + n_j d\mu_j = 0$$

$$\sum n_j d\mu_j = 0 \quad \text{--- (10)}$$

eqⁿ (10) is Gibbs Duhem eqⁿ

② Ionic Strength

→ The ionic strength I of a soln. is a measure of the electrical intensity due to the presence of ions in the soln.

→ It is given by half of the sum of all the terms obtained by multiplying the molality of each ion by square of its valency.

$$I = \frac{1}{2} (m_1 z_1^2 + m_2 z_2^2 + m_3 z_3^2 + \dots) \quad (17)$$

where, m_1, m_2, m_3 are molalities
 z_1, z_2, z_3 are valencies of the various ions present in soln.

→ For a single electrolyte, for example, potassium chloride or zinc sulphate. it contains two terms, one for the cation and one for the anion.

$$I = \frac{1}{2} (m_+ z_+^2 + m_- z_-^2)$$

m_+ and m_- are the molalities
 z_+ and z_- are the valencies of the cation and the anion

→ The ionic strength of a solution which is 0.1 molal in NaCl and 0.01 molal in calcium chloride, assuming complete ionization, may be calculated as under

Molality of Na^+ ion,
 $m_1 = 0.1$

Molality of Ca^{+2} ion, $m_2 = 0.01$

Total molality of Cl^- ion,
 $m_3 = 0.1 + 0.02 = 0.12$

Accordingly,

$$I = \frac{1}{2} (0.1 \times 1^2 + 0.01 \times 2^2 + 0.12 \times 1^2)$$
$$= \underline{0.13}$$

★ Numericals (Ionic strength)

★ Calculate the ionic strength of

(i) 0.15 molar KCl soln.

(ii) 0.25 molar K_2SO_4 soln.

(iii) 0.2 molar $BaCl_2$ soln.

(iv) a soln. which is 0.1 molar in KCl and 0.2 molar in K_2SO_4 .

Ans (i) In 0.15 molar KCl soln., the molality of each ion = 0.15.
 $m_+ = 0.15$, $m_- = 0.15$, $z_+ = 1$, $z_- = 1$

$$I = \frac{1}{2} (0.15 \times 1^2 + 0.15 \times 1^2) = \underline{0.15}$$

(ii) K_2SO_4 produces two K^+ ion and one SO_4^{2-} ion, hence the molality of the ion is
 $m_+ = 2 \times 0.25$, $m_- = 0.25$, $z_+ = 1$, $z_- = 2$

$$I = \frac{1}{2} (0.5 \times 1^2 + 0.25 \times 2^2) \\ = \underline{0.75}$$

(iii) for 0.2 molar $BaCl_2$ soln.
 $m_+ = 0.2$, $m_- = 2 \times 0.2 = 0.4$
 $z_+ = 2$, $z_- = 1$

$$I = \frac{1}{2} (0.2 \times 2^2 + 0.4 \times 1^2) \\ = \underline{0.8}$$

(iv) 0.1 molal in KCl
0.2 molal in K_2SO_4 .

$$\frac{1}{2} (0.1 \times 1^2 + 0.1 \times 1^2) + \frac{1}{2} (2 \times 0.2 \times 1^2 + 0.2 \times 2^2)$$

$$= 0.1 + 0.6 = \boxed{0.7}$$

④ Discuss Fugacity :-

→ The concept of fugacity was given by Gilbert N. Lewis as a substitute for pressure in real gases.

→ Variation of free energy with pressure at constant temp. is given by

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{--- (1)}$$

If one mole of a gas is under consideration

$$(dG)_T = RT/dp \quad \frac{RT dp}{p} \quad \text{--- (2)}$$

for n moles of,

$$(dG)_T = \frac{nRT dp}{p} \quad \text{--- (3)}$$

$$= nRT \ln p \quad nRT d(\ln p) \quad \text{--- (3)}$$

Integration of eqⁿ (3),

$$G = G^{\circ} + nRT \ln p \quad \text{--- (4)}$$

G° , the integration constant, is the free energy of n moles of the ideal

The ideal gas at temp T , pressure p &

Integration of eqⁿ (3) betⁿ pressure P_1 and P_2 , at constant temperature T ,

$$\Delta G = \int_{P_1}^{P_2} nRT \frac{dp}{p}$$

$$\Delta G = nRT \ln \frac{P_2}{P_1} \quad \text{--- (5)}$$

for 1 mole of the gas,

$$\Delta G = RT \ln \frac{P_2}{P_1} \quad \text{--- (6)}$$

→ Eqⁿ (4) and (6) are not valid for real gases since v is not exactly equal to $\frac{RT}{p}$

So, Lewis introduced a new function f , called fugacity function.

It takes the place of P in eqⁿ (3)

$$f(dG)_T = nRT d(\ln f) \quad \text{--- (7)}$$

eqⁿ (4) may be represented as

$$G = G^\circ + nRT \ln f$$

Integrating eqⁿ (7) at constant temp. betⁿ fugacity f_1 & f_2

$$\Delta G = nRT \ln \left(\frac{f_2}{f_1} \right)$$

for 1 mole of the gas.

$$\Delta G = RT \ln \left(\frac{f_2}{f_1} \right)$$

★ Numericals

→ Calculate the free energy change accompanying the compression of 1 mole of a gas at 57°C from 25 to 200 atm. The fugacity of the gas at 57°C may be taken as 23 and 91 atm, respectively at pressure of 25 and 200 atm.

$$\Delta G = nRT \ln \frac{P_2}{P_1}$$

$$= 1 \times 8.314 \times 330 \ln \left(\frac{200}{25} \right)$$

$$= 5702.8 \text{ J}$$

$$\Delta G = nRT \ln \frac{f_2}{f_1}$$

$$= 1 \times 8.314 \times 330 \ln \left(\frac{91}{23} \right) = 3730. \text{ J}$$

⑤ ★ Determination of fugacity of a Gas.

$$\Rightarrow G = G^{\circ} + RT \ln f \quad \text{--- (1)}$$

differentiate the eqⁿ (1) with respect to pressure at constant temp. and constant number of moles of the various const

$$\left(\frac{\partial G}{\partial P} \right)_T = RT \left(\frac{\partial (\ln f)}{\partial P} \right)$$

$$\left(\frac{\partial G}{\partial P} \right)_T = V$$

$$\left(\frac{\partial (\ln f)}{\partial P} \right)_T = \frac{V}{RT} \quad \text{--- (2)}$$

$$RT d(\ln f) = V dp \quad \text{--- (2) \times}$$

$$V = \frac{RT}{P}$$

$$\alpha = \frac{RT}{P} - V \quad \text{--- (3)}$$

Multiplying by dp.

$$\alpha dP = RT \left(\frac{dP}{P} \right) - v dP \quad (4)$$

combining eqⁿ (2) and (3)

$$RT d(\ln f) = RT \left(\frac{dP}{P} \right) - \alpha dP$$

$$\text{or } d(\ln f) = d(\ln P) - \frac{\alpha dP}{RT} \quad (5)$$

Integrating eqⁿ (5) betⁿ pressures 0 and P

$$\ln \frac{f}{P} = -\frac{1}{RT} \int_0^P \alpha (dP)$$

★ Calculation of fugacity at low pressure.

→ It has been found that the experimental value of α at low pressure almost a constant value.

$$\ln \frac{f}{P} = -\frac{\alpha P}{RT}$$

$$f \approx P \quad \text{or} \quad \frac{f}{P} = 1$$

→ $\ln x$ is approximately equal to $x-1$

$$\ln \frac{f}{P} = \frac{f}{P} - 1$$

$$\frac{f}{p} = 1 + \ln \frac{f}{p}$$

$$\frac{f}{p} = 1 - \frac{\alpha p}{RT}$$

$$\frac{f}{p} = \frac{pV}{RT}$$

$$f = \frac{p^2 V}{RT}$$