CHAPTER – 6

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CH 2010 ASSIGNMENT

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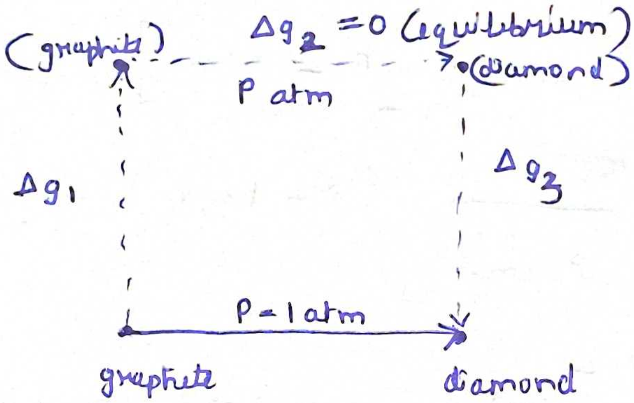
1) Consider the following path :



$\Rightarrow$ At const T (25°C)

$$\Delta g = 2866 \ \frac{J}{mol}$$

We have,

$$\Delta g = \Delta g_1 + \Delta g_2 + \Delta g_3$$

$$\Rightarrow \Delta g_1 + \Delta g_3 = 2866 \ J/mol \longrightarrow (1)$$

For finding Δg_1 and Δg_3

$dg_i = v_i \, dP - s \, dT$ (Fundamental relations)

$dg_i = v_i \, dP$ ($dT = 0 \rightarrow$ const temp 25°C)

$\Delta g_i = v_i \, \Delta P$ (graphite & diamond are solids, hence assumed incompressible $\therefore$ v_i is constant)

Δg_1 = (of graphite from 1 atm to P atm)

$$\Delta g_1 = \int_{1atm}^{P} V_{graphite}\, dP = V_{graphite}(P - 1atm) \rightarrow (2)$$

Δg_2 = (of diamond from P atm to 1atm)

$$\Delta g_2 = \int_{P}^{1atm} V_{diamond}\, dP = V_{diamond}(1 - P) \rightarrow (3)$$

Substituting (2) & (3) in (1)

$$\Rightarrow (V_{graphite} - V_{diamond})[P - 1atm] = 2866 \frac{J}{mol}$$

$$\Rightarrow \left[\frac{1}{\rho_{graphite}} - \frac{1}{\rho_{diamond}}\right](P - 1atm) = 2866 \frac{J}{mol}$$

$$\Rightarrow \left[\frac{1}{2.26} - \frac{1}{3.51}\right]\frac{cm^3}{g} \times \frac{12g}{mol} \times \frac{1m^3}{10^6 cm^3}(P - 1.01\times10^5 Pa) = 2866 \frac{J}{mol}$$

$$\Rightarrow P - 1.01\times10^5 = \frac{2866 \times 10^6}{1.890931}$$

$$\Rightarrow P = 1516 \text{ MPa} \quad \text{(approx)}$$

2) Assumptions

1: Assume molar volume of vapour (v_v) >> molar volume of liquid (v_l)

2: At 1500 K (high temperature), silver acts as an ideal gas

$$\frac{dp^{sat}}{dT} = \frac{\Delta h^{vap}}{T(v_v - v_l)} = \frac{\Delta h^{vap}}{T v_v} = \frac{(\Delta h^{vap})\, P}{RT^2}$$

⇒ Clausius – Clayperon equation

$$\frac{dp^{sat}}{dT} = \frac{\Delta h^{vap} \cdot p^{sat}}{RT^2} \longrightarrow (1)$$

According the question

$$\ln P = -\frac{14260}{T} - 0.458 \ln T + 12.23$$

differentiating wrt T

$$\frac{dP}{P} = \left(\frac{14260}{T^2} - \frac{0.458}{T}\right) dT$$

we need to find Δh_{vap} ⇒ put $P = p^{sat}$ and rearrange

$$\frac{dp^{sat}}{dT} = \left(\frac{14260}{T^2} - \frac{0.458}{T}\right) p^{sat} \longrightarrow (2)$$

comparing (1) and (2), we obtain

$$\left(\frac{14260}{T^2} - \frac{0.458}{T}\right) = \frac{\Delta h^{vap}}{RT^2}$$

$$\Rightarrow \Delta h^{vap} = R\,(14260 - 0.458\,T)$$

Putting $T = 1500\,K$,

$$\Delta h^{vap} = 8.314 \times (14260 - 0.458 \times 1500)$$

$$\boxed{\Delta h^{vap} = 112.846 \ \frac{kJ}{mol}}$$

3). We have

$P_1^{sat} = 400$ torr $\quad T_1 = 63.5\,°C$

$P_2^{sat} = 760$ torr $\quad T_2 = 78.4\,°C$

Assumptions (All assumptions of Clausius- Clapeyron eqn)

1: $V_v >> V_l$

2: ethanol vapour behaves as an ideal gas

3: Δh_{vap} is const (independent of T)

$\Rightarrow$ Clausius- Clapeyron eqn :

$$\ln\left(\frac{P_2^{sat}}{P_1^{sat}}\right) = \frac{-\Delta h^{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

using the values mentioned initially, we can find Δh_{vap} using the above eqn.

$$\Delta h_{vap} = \frac{-R \ln\left(\frac{P_2^{sat}}{P_1^{sat}}\right)}{\left[\frac{1}{T_2} - \frac{1}{T_1}\right]} = \frac{-8.314 \ln\left(\frac{760}{400}\right)}{\frac{1}{351.55K} - \frac{1}{336.65K}}$$

$$\Delta h_{vap} = 42.39 \frac{kJ}{mol}$$

Now, we can use the value of Δh_{vap} in clausius - Clapeyron eqn to find P_3^{sat} at $T_3 = 373.15$ K

using base as $T_2 = 351.55$ K

$$P_3^{sat} = P_2^{sat} \times e^{\left[\frac{-\Delta h_{vap}}{R}\left(\frac{1}{T_3} - \frac{1}{T_2}\right)\right]}$$

$$= 760 \times e^{\left[\frac{-42.39 \times 10^3}{8.314}\left(\frac{1}{373.15} - \frac{1}{351.55}\right)\right]}$$

$$\boxed{P_3^{sat} = 1760 \text{ torr}} \quad \text{at } T_3 = 100°C$$

4) $$\left[\frac{\partial\left(\frac{g_i}{T}\right)}{\partial T}\right]_P = \left[\frac{\left(\frac{T\,\partial g_i - g_i\,\partial T}{T^2}\right)}{\partial T}\right]_P \quad \text{(chain rule)}$$

$$= \frac{1}{T}\left(\frac{\partial g_i}{\partial T}\right)_P - \frac{g_i}{T^2} \rightarrow (1)$$

we know,

$$dg = -s\,dT + v\,dp$$

$$\Rightarrow \left(\frac{\partial g_i}{\partial T}\right)_P = -s_i$$

Substituting this value in (1)

$$\Rightarrow \left[\frac{\partial\left(\frac{g_i}{T}\right)}{\partial T}\right]_P = \frac{-Ts_i - g_i}{T^2} = \frac{-\cancel{Ts_i} - (h_i - \cancel{Ts_i})}{T^2}$$

(since $g_i = h_i - Ts_i \rightarrow$ defn)

$$\Rightarrow \left[\frac{\partial\left(\frac{g_i}{T}\right)}{\partial T}\right]_P = \frac{-h_i}{T^2}$$

5) From problem 4,

condition for equilibria : $\left(\frac{g_i}{T}\right)^{\alpha} = \left(\frac{g_i}{T}\right)^{\beta}$

$\Rightarrow$ Condition for phase equilibrium in this question

$$\left(\frac{g}{T}\right)_{Sn(s)} = \left(\frac{g}{T}\right)_{Sn(l)} \rightarrow (1)$$

<u>Enthalpy</u>

$\rightarrow$ Liquid state : (ref : T= 1500K)

$$h^l(T) = h^l(1500) + \int_{1500K}^{T} C_p\, dT$$

$$= 49179 + \int_{1500}^{T} 35.146\, dT = \underline{\underline{35.146T - 3540}}$$

→ Solid state : (ref : T = 900K)

$$h^s(T) = \cancel{h^s(900)}\ h^s(900) + \int_{900K}^{T} C_p\, dT$$

$$= 20285 + \int_{900}^{T} 37.656\, dT = \underline{\underline{37.656T - 16305.4}}$$

$\dfrac{g}{T}$ at reference states

$$\rightarrow \left(\frac{g^l}{T}\right)_{ref} = \frac{h^l - Ts^l}{T} = \frac{49179}{1500} - 116.64$$

$\downarrow$ T = 1500K

$$= \underline{\underline{-83.85 \frac{J}{mol\text{-}K}}}$$

$$\rightarrow \left(\frac{g^s}{T}\right)_{ref} = \frac{h^s - Ts^s}{T} = \frac{20285}{900} - 91.222$$

$\downarrow$ T = 900K

$$= \underline{\underline{-68.68 \frac{J}{mol\text{-}k}}}$$

using the above reference states, we can find $\left(\frac{g^l}{T}\right)$ and $\left(\frac{g^s}{T}\right)$ at any temperature :

$$\int d\left(\frac{g}{T}\right) = \int \left(\frac{\partial (g/T)}{\partial T}\right)_P dT = -\int \frac{h}{T^2}\, dT$$

(From Q4)

$\Downarrow$

Reason: P = constant for phase equilibria problems

Liquid

$$\int_{-83.85}^{g^l/T} d\left(\frac{g}{T}\right) = \int_{1500K}^{T} -\frac{(35.146T - 3540)}{T^2}\, dT$$

$$\Rightarrow \left(\frac{g^l}{T}\right) = -35.146 \ln T - \frac{3540}{T} + 176.04 \longrightarrow (2)$$

Solid

$$\int_{-68.68}^{g^s/T} d\left(\frac{g}{T}\right) = \int_{900K}^{T} -\frac{(37.656T - 16305.4)}{T^2}\, dT$$

$$\Rightarrow \left(\frac{g^s}{T}\right) = -37.656 \ln T - \frac{16305.4}{T} + 205.5 \longrightarrow (3)$$

Substituting (2) and (3) in (1)

$$\Rightarrow \left(\frac{g}{T}\right)_{Sn(s)} = \left(\frac{g}{T}\right)_{Sn(l)}$$ during phase transition

$$-35.146 \ln T - \frac{3540}{T} + 176.04 = -37.656 \ln T - \frac{16305.4}{T} + 205.5$$

$$\Rightarrow \boxed{T_{melt} = 1059.8\ K} \rightarrow$$ Temperature of phase transition

$$\Delta h^{fusion} = h^s(T_{melt}) - h^l(T_{melt})$$

$$= 37.656 \times 1059.8 - 16305.4 - [35.146 \times 1059.8 - 3540]$$

$$= 26.30 \times 10^3 - 33.71 \times 10^3 \ \frac{J}{mol}$$

$$\boxed{\Delta h^{fusion} = -7.41 \ \frac{kJ}{mol}}$$

6) From the Clausius-Clapeyron eqn,

$$\frac{dp^{sat}_{CS_2}}{dT} = \frac{\Delta h^{vap}}{T(v^v - v^l)}$$

$\boxed{\text{Assumption: } v^v >> v^l}$

$$\Rightarrow \frac{dp^{sat}_{CS_2}}{dT} = \frac{\Delta h^{vap}}{Tv^v} \longrightarrow (1)$$

According to the question,

$$\ln(p^{sat}_{CS_2}) = 62.7839 - \frac{4.7063\times10^3}{T} - 6.7794\ln T + 8.0194\times10^{-3}T \rightarrow (2)$$

At $T = 100°C$ (373K),

$$\ln(p^{sat}_{CS_2}) = 62.7839 - \frac{4.7063\times10^3}{373} - 6.7794\ln(373) + 8.0194\times10^{-3}(373)$$

$$\Rightarrow \boxed{p^{sat}_{CS_2}(T=373K) = 4.48\times10^5 \text{ Pa}} \rightarrow (3)$$

Taking derivative of (2) and substituting (3)

$$\Rightarrow \frac{dp^{sat}_{CS_2}}{p^{sat}_{CS_2}} = \left(\frac{4.7063\times10^3}{T^2} - \frac{6.7794}{T} + 8.0194\times10^{-3}\right)dT$$

$$\Rightarrow \frac{dp^{sat}_{CS_2}}{dT} = p^{sat}_{CS_2}\left[\frac{4.7063\times10^3}{T^2} - \frac{6.7794}{T} + 8.0194\times10^{-3}\right] \rightarrow (4)$$

Comparing ~~with~~ (1) and (4)

$$\Rightarrow \frac{\Delta h^{vap}}{T v^v} = p^{sat}_{CS_2}\left[\frac{4.7063\times10^{3}}{T^2} - \frac{6.7794}{T} + 8.01944\times10^{-3}\right]$$

Putting in the values at $T = 373\ K$:

$p^{sat}_{CS_2} = 4.48\times10^{5}$ Pa (From (3))

$\Delta h^{vap} = 24.050\times10^{3}$ J/mol (Given)

$$\Rightarrow v^v = 6.08\times10^{-3}\ \frac{m^3}{mol}$$

Virial equation

$$z = 1 + \frac{B}{v}$$

$$\frac{Pv}{RT} = 1 + \frac{B}{v}$$

Substituting $P = 4.48\times10^{5}$ Pa $T = 373\ K$

$R = 8.314\ \frac{J}{K\text{-}mol}$ $v = 6.08\times10^{-3}$

$$\Rightarrow \boxed{B = -7.4\times10^{-4}\ \frac{m^3}{mol} = -740\ \frac{cm^3}{mol}}$$

The magnitude is much larger than reported value of B

Reason:

We made assumptions like $v^v >> v^l$ and we assumed ~~v = v^v for a~~ v behaves like a gas all the time

7) $y_1 = \frac{n_1}{n_T} = \frac{1}{5} = \underline{\underline{0.2}}$ $y_2 = \frac{n_2}{n_T} = \underline{\underline{0.4}}$ $y_3 = \frac{n_3}{n_T} = \underline{\underline{0.4}}$

Calculation of v

From the available EOS, [$T = 500K$, $P = 50$ atm]

$$v = \frac{RT}{P}\left[1 + P^2\left[\frac{A}{RT}(y_1 - y_2) + \frac{B}{RT}\right]\right] \rightarrow (1)$$

$$v = \frac{82.06 \times 500}{50}\left[1 + 50^2\left(-9 \times 10^{-5}(0.2 - 0.4) + 3 \times 10^{-5}\right)\right]$$

$$\boxed{v = 919 \frac{cm^3}{mol}}$$

Calculation of V

$$V = n_T\, v = 5 \times 919 = \boxed{4595\ cm^3}$$

Calculation of v_1

$v_1 \rightarrow$ pure species volume of species 1

⇓

obtained by taking $y_1 = 1$, $y_2 = y_3 = 0$ in v (1)

$$v_1 = \frac{RT}{P}\left[1 + P^2\left[\frac{A}{RT}(1 - 0) + \frac{B}{RT}\right]\right]$$

$$v_1 = \frac{82.06 \times 500}{50}\left[1 + 50^2\left(-9 \times 10^{-5} + 3 \times 10^{-5}\right)\right]$$

$$\boxed{v_1 = 698 \frac{cm^3}{mol}}$$

Calculation of v_2

$v_2 \rightarrow$ pure species volume of species 2

$\Downarrow$

obtained by taking $y_1 = y_3 = 0,\ y_2 = 1$ in (1)

$$v_2 = \frac{RT}{P}\left[1 + P^2\left[\frac{A}{RT}(0-1) + \frac{B}{RT}\right]\right]$$

$$\boxed{v_2 = 1067\ \frac{cm^3}{mol}}$$

Calculation of v_3

$v_3 \rightarrow$ pure species volume of species 3

$\Downarrow$

obtained by taking $y_1 = y_2 = 0,\ y_3 = 1$ in (1)

$$v_3 = \frac{RT}{P}\left[1 + P^2\left[\frac{A}{RT}(0-0) + \frac{B}{RT}\right]\right]$$

$$\boxed{v_3 = 882\ \frac{cm^3}{mol}}$$

Calculation of $\overline{V_1}$

$$\overline{V_1} = \left(\frac{\partial V}{\partial n_1}\right)_{n_2,n_3,T,P} = \left(\frac{\partial (n_1+n_2+n_3)v}{\partial n_1}\right)_{n_2,n_3,T,P}$$

using (1),

$$\overline{V_1} = \frac{\partial}{\partial n_1}\left[\frac{RT}{P}\left[(n_1+n_2+n_3) + P^2\left(\frac{A}{RT}(n_1-n_2) + \frac{B}{RT}(n_1+n_2+n_3)\right)\right]\right]_{n_2,n_3,T,P}$$

$$\Rightarrow \overline{V_1} = \frac{RT}{P}\left[1 + P^2\left[\frac{A}{RT} + \frac{B}{RT}\right]\right]$$

$$\Rightarrow \bar{V}_1 = \frac{82.06 \times 500}{50}\left(1+50^2\left(-9\times10^{-5}+3\times10^{-5}\right)\right)$$

$$\Rightarrow \boxed{\bar{V}_1 = 697.5 \ \frac{cm^3}{mol}}$$

8)

(a) $\Delta h_{mix} = \sum x_i \bar{H}_i - \sum x_i h_i$

$$\Delta h_{mix} = \left(x_{cd}\bar{H}_{cd} + x_{sn}\bar{H}_{sn}\right) - \left(x_{cd} h_{cd} + x_{sn} h_{sn}\right)$$

$$\Delta H_{mix} = n_T\left(\Delta h_{mix}\right)$$

$$\Delta H_{mix} = \left(n_{cd}\bar{H}_{cd} + n_{sn}\bar{H}_{sn}\right) - \left(n_{cd} h_{cd} + n_{sn} h_{sn}\right)$$

$$\left(\Delta\bar{H}_{mix}\right)_{cd} = \left(\frac{\partial\left(\Delta H_{mix}\right)}{\partial n_{cd}}\right)_{n_{sn},T,P} = \bar{H}_{cd} - h_{cd}$$

(b) From (a),

$$\left(\Delta\bar{H}_{mix}\right)_{cd} = \bar{H}_{cd} - h_{cd}$$

Illy, we can prove

$$\left(\Delta\bar{H}_{mix}\right)_{sn} = \bar{H}_{sn} - h_{sn}$$

We have,

$$\left(\Delta\bar{H}_{mix}\right)_{cd} = \Delta h_{mix} - x_{sn}\frac{d\,\Delta h_{mix}}{d\,x_{sn}} \rightarrow (1)$$

$$\left(\Delta\bar{H}_{mix}\right)_{sn} = \Delta h_{mix} - x_{cd}\frac{d\left(\Delta h_{mix}\right)}{d\,x_{cd}} \rightarrow (2)$$

Eq (1) and (2) can be proved similar to eqn $\bar{V_1} = V - x_2 \frac{dv}{dx_2}$ we proved in class

$$\Delta h_{mix} = 13000\, x_{cd}\, x_{sn} \qquad [x_{sn} + x_{cd} = 1]$$

$$\Rightarrow \frac{d(\Delta h_{mix})}{dx_{sn}} = \frac{d}{dx_{sn}}\left(13000(1-x_{sn})(x_{sn})\right) = 13000(1-2x_{sn})$$

$$\Rightarrow \frac{d(\Delta h_{mix})}{dx_{cd}} = \frac{d}{dx_{cd}}\left(13000(x_{cd})(1-x_{cd})\right) = 13000(1-2x_{cd})$$

Substituting above values in (1) and (2)

$$\Rightarrow (\Delta\bar{H}_{mix})_{cd} = 13000\, x_{cd}\, x_{sn} - x_{sn}(13000)(1-2x_{sn})$$
$$= 13000\, x_{sn}^2$$

$$\Rightarrow (\Delta\bar{H}_{mix})_{sn} = 13000\, x_{sn}\, x_{cd} - x_{cd}(13000)(1-2x_{cd})$$
$$= 13000\, x_{cd}^2$$

Substituting $x_{sn} = \frac{2}{2+3} = 0.4$, $x_{cd} = 0.6$

$$\Rightarrow (\Delta\bar{H}_{mix})_{cd} = 2080 \frac{J}{mol}, \quad (\Delta\bar{H}_{mix})_{sn} = 4680 \frac{J}{mol}$$

$$\Rightarrow \boxed{\begin{aligned} \bar{H}_{cd} - h_{cd} &= (\Delta\bar{H}_{mix})_{cd} = 2080 \frac{J}{mol} \\ \bar{H}_{sn} - h_{sn} &= (\Delta\bar{H}_{mix})_{sn} = 4680 \frac{J}{mol} \end{aligned}}$$

(c) <u>Gibbs - Duhem Equation</u>

$$\Sigma\, n\, d\bar{K}_i = 0$$

Here, $\bar{K}_i = (\Delta \bar{H}_{mix})_i$

$$\Rightarrow n_{cd}\, d(\Delta \bar{H}_{mix})_{cd} + n_{sn}\, d(\Delta \bar{H}_{mix})_{sn} = 0$$

Dividing by dx_{cd}

$$\Rightarrow n_{cd}\left[\frac{d(\Delta \bar{H}_{mix})_{cd}}{dx_{cd}}\right] + n_{sn}\left[\frac{d(\Delta \bar{H}_{mix})_{sn}}{dx_{cd}}\right] = 0 \rightarrow (1)$$

In order to prove Gibbs–Duhem equation, we need to prove eqn (1) is satisfied

From (b), we have

$$(\Delta \bar{H}_{mix})_{cd} = 13000\, x_{sn}^2 = 13000\,(1-x_{cd})^2$$

$$\Rightarrow \frac{d(\Delta \bar{H}_{mix})_{cd}}{dx_{cd}} = (-26000)(1-x_{cd}) = -26000\, x_{sn}$$

$$(\Delta \bar{H}_{mix})_{sn} = 13000\, x_{cd}^2$$

$$\Rightarrow \frac{d(\Delta \bar{H}_{mix})_{sn}}{dx_{cd}} = 26000\, x_{cd}$$

∴ We have,

$$n_{cd}\left[\frac{d(\Delta \bar{H}_{mix})_{cd}}{dx_{cd}}\right] + n_{sn}\left[\frac{d(\Delta \bar{H}_{mix})_{sn}}{dx_{cd}}\right]$$

$$= n_T x_{cd} \left[-26000 + 26000 x_{cd}\right] + n_T (1-x_{cd}) 26000 x_{cd}$$

$$= n_T \left\{-26000 x_{cd} + 26000 x_{cd}^2 + 26000 x_{cd} - 26000 x_d^2\right\}$$

$$= \underline{\underline{0}}$$

$\Rightarrow$ Eq (1) is verified

$\Rightarrow$ Gibbs- Duhem eqn is verified