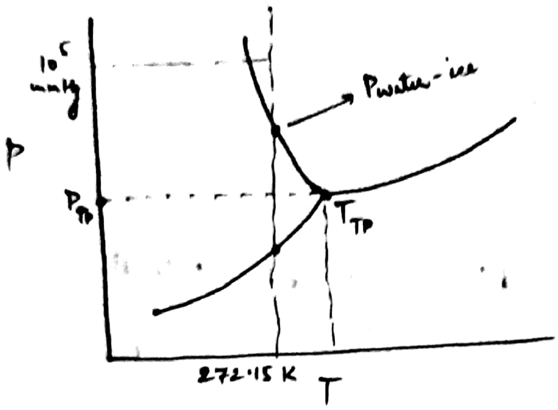
PH-207

Tutorial - 6

Q1 a)



Water at $-1°C = 272.15$ K

$P_{TP} = 4.6$ mm Hg

$v_{solid} = 1.12\ cm^3/g$

$v_{liquid} = 1\ cm^3/g$

Heat of melting = 80 Cal/g

" " vaporisation = 600 Cal/g

Water → Ice transformation

$$\frac{P - P_0}{T - T_0} = \frac{\Delta Q}{(v_{water} - v_{ice}) T_0} \Rightarrow P_{water-ice} = P_0 + \frac{\Delta Q}{v_{water} - v_{ice}} \cdot \frac{T - T_0}{T_0}$$

$P_0 = 4.6$ mm Hg

$T_0 = 273.16$ K

$T = 272.15$ K

1 mm of Hg = 133.322 Pa

$\Delta Q = 80$ Cal/g

$P_{water-ice} = 0.775 \times 10^5$ mm Hg

Solid → Vapor transformation

$V_{vapor} >> V_{ice}$

$$V_{vapor} = \frac{k_B T}{P\,m}$$

$$\frac{dP}{dT} \approx \frac{L}{T\,V_{vapor}} = \frac{m L P}{T^2 k_B}$$

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$$P_{ice\text{-}vapor} \approx P_0 \exp\left[\frac{mL}{k_B}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

$m = 18$ g/mol $\qquad P_{ice\text{-}vapor} = 4.4$ mm Hg

$L = 600$ Cal/g

b)

$$L = T(s_1 - s_2)$$

$$\frac{dL}{dT} = \frac{L}{T} + T\left(\frac{ds_1}{dT} - \frac{ds_2}{dT}\right)$$

$$dS_1 = \frac{C_{T_1}}{T}\,dT - \beta_1 V_1\,dP$$

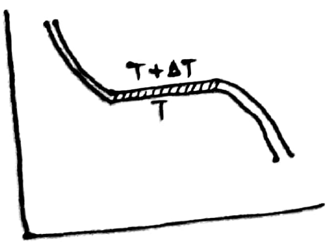
$$\beta_1 = \frac{1}{V_1}\left(\frac{\partial V_1}{\partial T}\right)_{P_1}$$

$$\frac{dL}{dT} = \frac{L}{T} + (C_{P_1} - C_{P_2}) - (\beta_1 V_1 - \beta_2 V_2)\,T\frac{dP}{dT}$$

$$\frac{dP}{dT} = \frac{L}{T(V_1 - V_2)}$$

$$\frac{dL}{dT} = \frac{L}{T} + (C_{P_1} - C_{P_2}) - (\beta_1 V_1 - \beta_2 V_2)\frac{L}{V_1 - V_2}$$

Q2 a)



$$\eta = \frac{W}{Q} = \frac{W}{L} = \frac{dT}{T}$$

$$W \approx dW = (P + dP)\Delta V - P\Delta V$$
$$= dP\,\Delta V$$

$$\frac{dP\,\Delta V}{L} = \frac{dT}{T} \Rightarrow \frac{dP}{dT} = \frac{L}{T\Delta V}$$

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b) $\Delta v = V_{gas} - V_{liquid} \approx V_{gas} = \frac{RT}{P}$

$$\frac{dP}{dT} = \frac{LP}{RT^2}$$

$$\ln \frac{P_0}{P_m} = \frac{L}{R}\left(\frac{1}{T_m} - \frac{1}{T_0}\right)$$

$$\cancel{T_m = \frac{T_0}{\left(1 + \frac{RT_0}{L}\right)}} \qquad T_m = \frac{T_0}{\left(1 + \frac{RT_0}{L}\ln\frac{P_0}{P_m}\right)}$$

3. Neglect v.p. of solvent

Equilibrium : $\mu_{gas}(P,T) = \mu_{gas}^{dissolved}(P,T,x)$

$x \Rightarrow$ Molar fraction of dissolved gas in solvent

$$\mu_{gas}^{dissolved}(P,T,x) = \mu_{gas}^{dissolved}(P,T,x_0) + k_B T \ln\frac{x}{x_0}$$

$x_0 \Rightarrow$ conc^n of ~~st~~ standard sol^n

$$\left.\frac{\partial \mu_{gas}}{\partial P}\right|_T dP = \left.\frac{\partial \mu_{gas}^{dissolved}}{\partial P}\right|_T dP = \left.\frac{\partial \mu_{gas}^{dissolved}}{\partial P}\right|_T dP + k_B T\, d\left\{\ln\frac{x}{x_0}\right\}$$

$$v_{gas}\, dP = v_{gas}^{dissolved}\, dP + k_B T\, d\left\{\ln\frac{x}{x_0}\right\}$$

$$\frac{d\left\{\ln\frac{x}{x_0}\right\}}{dP} = \frac{\left(v_{gas} - v_{gas,x_0}^{dissolved}\right)}{k_B T} \longrightarrow \text{vol difference in gaseous phase \& in sol}^n\text{ phase}$$

$$v_{gas,x_0}^{dissolved} << v_{gas} = \frac{k_B T}{P}$$

$$\Rightarrow \ln\frac{x}{x_0} = \ln\frac{P}{P_0} \Rightarrow x = x_0\frac{P}{P_0} \longrightarrow \text{Law of Henry \& Dalton}$$

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4. $\frac{\Delta P}{P} = x_{sub}$

$$\frac{\Delta P_1}{P_{1,0}} = x_2$$

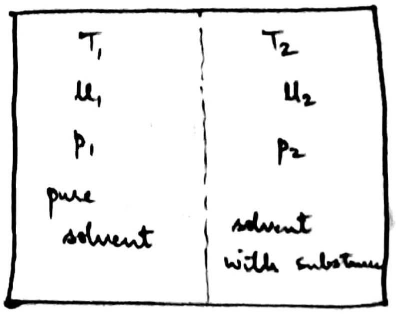
$$\frac{\Delta P_2}{P_{2,0}} = x_1$$

$$P_{1,0} - P_1 = x_2 P_{1,0} = (1 - x_1) P_{1,0}$$

$$P_{2,0} - P_2 = x_1 P_{2,0}$$

$$P = P_1 + P_2$$
$$= P_{2,0} + x_1 (P_{1,0} - P_{2,0})$$

5.



Equilibrium : $T_1 = T_2$

$$\mu_1^{pure} = \mu_2^{sol^n}$$
$$P_1 \neq P_2$$

$$\mu_1^{pure}(P_1, T) = \mu_2^{sol^n}(P_2, T, \underbrace{x_s}_{\text{solvent}})$$

$x_s = 1 - x_m \rightarrow$ solute

$$\mu_2^{sol^n}(P_2, T, x_s) = \mu_2^{pure}(P_2, T) + k_B T \ln x_s$$

$$\left.\frac{\partial \mu}{\partial P}\right|_T = v \Rightarrow \mu(P_2, T) = \mu(P_1, T) + \int_{P_1}^{P_2} v(P, T)\, dP$$

$$\Rightarrow \cancel{\mu_1^{pure}(P_1, T)} = \cancel{\mu_2^{pure}(P_1, T)} + k_B T \ln x_s + \int_{P_1}^{P_2} v(P, T)\, dP$$

$$\Rightarrow 0 = k_B T \ln x_s + v(P_2 - P_1)$$

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$$\pi v = -k_B T \ln(1 - x_m)$$

Osmotic pressure

$$\pi = P_2 - P_1$$

For $x_m \ll 1$,

$$\ln(1 - x_m) \approx -x_m$$

$$\pi v \approx x_m k_B T$$

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