PH - 207

Problem Set - 5

1. a)

$$S = S(T, V)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$T\,dS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV$$

$$C_V = \left(\frac{dQ}{dT}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \qquad \therefore\ T\,dS = C_V\,dT + T\left(\frac{\partial S}{\partial V}\right)_T dV$$

$$T\,dS = C_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \qquad \text{(Maxwell relation)}$$

$$S = S(T, P)$$

$$T\,dS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP$$

$$= C_P\,dT - T\left(\frac{\partial V}{\partial T}\right)_P dP \qquad \text{(Maxwell relation)}$$

b)

$$C_P\,dT - T\left(\frac{\partial V}{\partial T}\right)_P dP = C_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

$$dT = \frac{T\left(\frac{\partial P}{\partial T}\right)_V dV}{C_P - C_V} + \frac{T\left(\frac{\partial V}{\partial T}\right)_P dP}{C_P - C_V}$$

$$dT = \left(\frac{\partial T}{\partial V}\right)_P dV + \left(\frac{\partial T}{\partial P}\right)_V dP$$

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_P = \frac{T\left(\frac{\partial P}{\partial T}\right)_V}{C_P - C_V}, \quad \left(\frac{\partial T}{\partial P}\right)_V = \frac{T\left(\frac{\partial V}{\partial T}\right)_P}{C_P - C_V}$$

$$\Rightarrow \quad C_p - C_v = T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial P}{\partial T}\right)_V$$

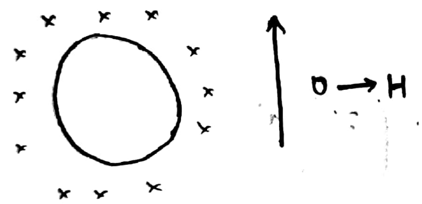
$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T$$

$$\Rightarrow \quad C_p - C_v = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T$$

$$= \frac{-T\left\{\frac{1}{V^2}\left(\frac{\partial V}{\partial T}\right)^2\right\}}{\frac{1}{V^2}\left(\frac{\partial V}{\partial P}\right)_T}$$

$$C_p - C_v = \frac{T\beta^2}{\frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T} \times V = \frac{TV\beta^2}{K}$$

2.



$$\Delta S = S(T,H) - S(T,0)$$

$$\Delta T = T(S,H) - T(S,0)$$

$$dU = TdS + HdM$$

$$G = U - TS - MH$$

$$dG = -SdT - MdH$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_H, \quad M = -\left(\frac{\partial G}{\partial H}\right)_T$$

Condition for total differential :

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H$$

$$\Delta S = S(T,H) - S(T,0) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH$$

$$\left(\frac{\partial S}{\partial H}\right)_T = -\left(\frac{\partial S}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_S = \left(\frac{\partial M}{\partial T}\right)_H$$

$$C_H = T\left(\frac{\partial S}{\partial T}\right)_H$$

$$\therefore \left(\frac{\partial T}{\partial H}\right)_S = -\frac{T}{C_H}\left(\frac{\partial M}{\partial T}\right)_H$$

$$\Delta T = T(S,H) - T(S,0) = -\int_0^H \frac{T}{C_H}\left(\frac{\partial M}{\partial T}\right)_H dH$$

3.

$$dG = VdP - SdT$$

$$V = \left.\frac{\partial G}{\partial P}\right|_T$$

Equilibrium (phase coexistence) : $G_D = G_G$

Under given condition : $G_D > G_G$

$V_D < V_G$

$$\left.\frac{\partial G}{\partial P}\right|_T^{\text{Diamond}} < \left.\frac{\partial G}{\partial P}\right|_T^{\text{Graphite}}$$

For const. T , $dG|_T = VdP|_T$

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

$$\int_{V_0}^{V} dV = \int_{P_0}^{P}\left(\frac{\partial V}{\partial P}\right)_T dP$$

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

$$V = V_0 - \int_{P_0}^{P} \underbrace{V}_{\text{Approx. } V_0} K\, dP$$

$$V = V_0 - V_0 K(P - P_0)$$

$$P >> P_0 \Rightarrow V \approx V_0 - V_0 K P$$

$$dG = VdP = V_0\, dP - V_0 K\, dP\, P$$

$$\int_{G_0}^{G} dG = V_0 \int_{P_0}^{P} dP - V_0 K \int_{P_0}^{P} P \, dP$$

$$G - G_0 \approx V_0 P - V_0 K \frac{P^2}{2}$$

$$G_G = V_0^G \left(P - K_G \frac{P^2}{2} \right) \quad (G_0 = 0)$$

$$G_D = G_0^D + V_0^D \left(P - K_D \frac{P^2}{2} \right)$$

$$G_G = G_D$$

$$P = \frac{0.00256 \pm 0.00256}{2 \times 0.010315} \times 10^9 \text{ Pa}$$

Take only positive sign

$$P = 0.249 \times 10^9 \text{ Pa}$$

$$= 248000 \text{ KPa} \qquad 1 \text{ atm} = 100 \text{ KPa}$$

$$= 2480 \text{ atm}$$

4. $$\Omega = -V P_0(T) \cdot \exp\left(\frac{\mu}{kT}\right)$$

$$\Omega = U - TS - \mu N$$

$$d\Omega = -S\,dT - P\,dV - N\,d\mu$$

$$P = -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu} , \quad N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V}$$

$$\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu} = -P_0(T) \cdot e^{\mu/kT}$$

$$\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} = \frac{-V P_0(T)}{kT} e^{\mu/kT}$$

$$= \frac{V}{kT} \left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu}$$

$$-N = \frac{-V}{kT} P \Rightarrow PV = NkT$$

5. a) P-T line (T, P same for both phases)

$$\frac{dP}{dT} = \frac{s^{(s)} - s^{(L)}}{v^{(s)} - v^{(L)}}$$

Equilibrium : $\mu^{(s)} = \mu^{(L)}$

For $T > T_{PT}$, $\mu^{(L)} < \mu^{(S)}$

$T < T_{PT}$, $\mu^{(L)} > \mu^{(s)}$

$T_{PT} \Rightarrow$ Temp. of phase transition

$$\Rightarrow \left(\frac{\partial \mu^{(L)}}{\partial T}\right)_P < \left(\frac{\partial \mu^{(s)}}{\partial T}\right)_P$$

$s^{(L)} > s^{(s)}$ always

For water, $v^{(s)} > v^{(L)}$

$\left(\frac{dP}{dT}\right)_{\text{phase line}} < 0$ (By Clausius-Clapeyron Eq^n)

$\Rightarrow$ Freezing temp. decreases with increase in pressure

b) $$\frac{P - P_0}{T_{min.} - T_0} = \frac{-h}{T_{min.} \cdot \Delta V}$$

$P_0 = 1$ atm

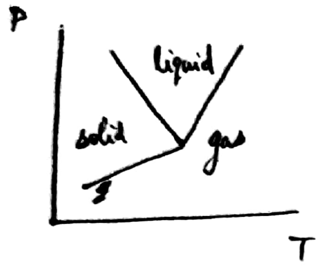
$T_0 = T_{TP} = 273.16$ K

$h = 80$ cal/g

$\Delta V = 0.091$ cm^3/g

$T_{min.} = -0.06°C$

6.



$$0 < \left(\frac{dP}{dT}\right)_{sub.} < \left(\frac{-dP}{dT}\right)_{fusion} < \left(\frac{dP}{dT}\right)_{vap.}$$

$$\Rightarrow \left(\frac{dP}{dT}\right)_{fusion} < 0$$

$$\Downarrow$$

Unusual property

$$\left(\frac{dP}{dT}\right)_{vap.} = \frac{s_{gas} - s_{liquid}}{v_{gas}}$$

$$\left(\frac{dP}{dT}\right)_{sub.} = \frac{s_{gas} - s_{solid}}{v_{gas}}$$

$$\underbrace{\left(\frac{dP}{dT}\right)_{vap.} > \left(\frac{dP}{dT}\right)_{sub.}}_{\text{violates 2nd law of thermodynamics}} \longrightarrow s_{solid} > s_{liquid}$$