

2a

Gibbs Thomsen Equation derivation.

Question 2. 80/100  $T_m(H) = T_T^b + \frac{2(\gamma_{lw} - \gamma_{sw})}{f_s \Delta_m H}$

$$\Delta T_m(x) = T_{m_0} - T_m(x)$$

$$\Rightarrow \mu_s(T_m) = \mu_L(T_m)$$

$$\rightarrow du = -s dT + v dp$$

$$\Rightarrow u = TS - pA_w H + 2\gamma A_w + \mu_H$$

Part a is done below

Considering  
No  
width  
influence  
we

$$\Rightarrow \Delta P \Rightarrow P_L - P_S = \frac{2(\gamma_{lw} - \gamma_{sw})}{H} \left\{ \begin{array}{l} u_L = u - TS - \mu_H \\ = -pA_w H + 2\gamma A_w \end{array} \right\}$$

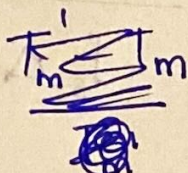
$$\Rightarrow \mu_L(T_m) + \int_{T_m}^{T_m'} -S_L dT = \mu_S(T_m) + \int_{T_m}^{T_m'} -S_S dT + \int_{P_0}^P V_S dp.$$

$$\Rightarrow - \int_{T_m}^{T_m'} (S_L - S_S) dT = \int_{P_0}^P V_S dp.$$



$$\Rightarrow -\Delta_{\text{fus}} S (T_m' - T_m) = V_s \Delta P$$

$$\Rightarrow -\Delta S (T_m' - T_m) = \frac{V_s (2(r_{\text{LW}} - r_{\text{SW}}))}{H}$$



$$\Rightarrow \frac{T_m - T_m'}{T_m'} = \frac{2(r_{\text{LW}} - r_{\text{SW}})}{H \rho_m h}$$

\* this accommodates the  $\gamma$  of nanoparticle with the fluid.

(2b)  $\Omega = U - TS - \mu N = -PA_{\text{W}}H + 2\gamma A_{\text{W}}$

$$U = TS - PA_{\text{W}}H + 2\gamma A_{\text{W}} + \mu N$$

From thermodynamic Square

$$\begin{matrix} -S & U & V \\ H & & F \end{matrix}$$

$$\begin{matrix} -P & G & T \end{matrix}$$

$$\begin{matrix} -S & U & V \\ H & & F \end{matrix}$$

$$\begin{matrix} -P & G & T \end{matrix}$$

$$\begin{matrix} -S & U & V \\ H & & F \\ -P & G & T \end{matrix}$$

$$\underline{U = F + TS} \quad \left| \quad du = -pdv + Tds + \mu dn \right. \\ \underline{F = U - TS}$$

$$\Delta H = Tds + Vdp$$

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

Helmholtz



(2c)

$$\frac{dp}{dT} = \frac{pL}{T^2 R} \quad \left| \quad \ln \left( \frac{p(r)}{p} \right) = \frac{2\gamma V_{\text{molecule}}}{k_B T \gamma} \right.$$

$$\frac{1}{p} \frac{dp}{dT} = \frac{\Delta H}{RT^2}$$

$$\int \frac{dp}{p} = \int \frac{\Delta H}{RT^2} dT$$

$$\ln p = \frac{\Delta H}{RT}$$

$$\frac{1}{p} dp = \frac{\Delta H}{RT^2} \times dT$$

$$\int \frac{1}{p} dp = \int \frac{\Delta H}{RT^2} \times dT$$

$$\ln p = \frac{\Delta H}{RT}$$

$$\ln \left( \frac{p(r)}{p} \right) = \frac{2\gamma V_{\text{molecule}}}{k_B T \gamma}$$

$$\frac{\Delta H}{RT} = \frac{\Delta p 2\gamma V}{k_B T \gamma} = \Delta T_m = \frac{T_m' 2\gamma}{H R}$$

Ostwald - Freundlich Equation



$$x_{app} = x_0 \cdot e \left( \frac{2 \cdot V_m \cdot \sigma_{SL}}{R \cdot T \cdot r} \right)$$

$x_0$  = Thermodynamic mole fraction

$x_{app}$  = apparent mole fraction

$\sigma_{SL}$  = Interfacial Energy between solid and liquid

$r$  = particle radius

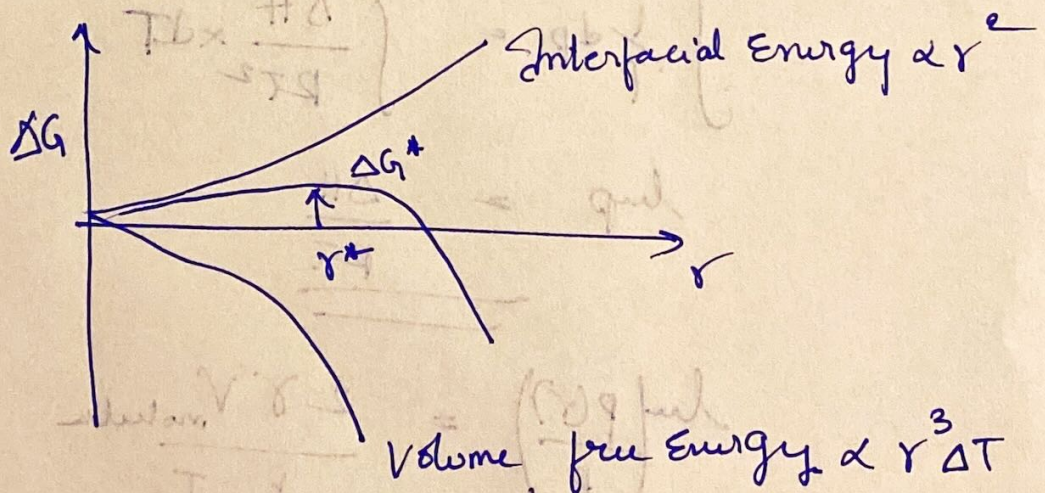
$V_m$  = molar ~~mass~~ volume

$R$  = universal gas constant

$T$  = temperature.

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Homogeneous nucleation.



$G_1 \Rightarrow \text{liq}$

$G_2 \Rightarrow \text{liq} + \text{particle}$



$$\Rightarrow G_1 = (V_S + V_L) \cdot G_L$$

$$\Rightarrow G_2 = V_S \cdot G_S + V_L \cdot G_L + A_{SL} \cdot \gamma_{SL}$$

$$\Delta G = G_2 - G_1 = V_S (\Delta G_V) + A_{SL} \cdot \gamma_{SL}$$

If the solid form is sphere "radius"

$$\Rightarrow \Delta G = \underbrace{\frac{4}{3}\pi R^3}_{\text{Vol}} \Delta G_V + \underbrace{4\pi R^2}_{A_{SL}} \gamma_{SL}$$

This is part "a" and "e"

term 1

term 2

$$\text{If } r \approx 0 \quad r^2 \rightarrow r^3$$

$$\text{at max } \Delta G \quad \frac{dG}{dr} = 0 \Rightarrow r^*$$

$$0 = \frac{4}{3}\pi \times 3R^2 \Delta G_V + 4\pi \times 2R \gamma_{SL}$$

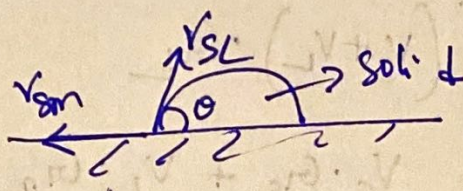
$$r^* = \frac{-2\gamma_{SL}}{\Delta G_V}$$

$$\Delta G^* = \frac{4}{3}\pi \left( \frac{-2\gamma_{SL}}{\Delta G_V} \right)^3 \Delta G_V + 4\pi \left( \frac{-2\gamma_{SL}}{\Delta G_V} \right)^2 \Delta G_V$$

$$\Delta G_V \quad \Delta G^* = \frac{16}{3} \pi \frac{\gamma_{SL}^3}{\Delta G_V^2}$$



Heterogeneous



$$\gamma_{sm} + \gamma_{LS} \cos \theta = \gamma_{Lm}$$

$$\Delta G_{Heter} = V_S \Delta G_V$$

$$\Delta G_{Heter} = V_S \Delta G_V + A_{SL} \gamma_{SL} + A_{sm} (\gamma_{sm} - \gamma_{Lm})$$

Sphere

$$V_S = \frac{\pi R^3}{3} (2 - 3 \cos \theta + \cos^3 \theta)$$

$$A_{SL} = 2\pi R^2 (1 - \cos \theta)$$

$$A_{sm} = \pi R^2 \sin^2 \theta$$

$$\Delta G_{Heter} = \left( \frac{4}{3} \pi R^3 \Delta G_V + 4\pi R^2 \gamma_{LS} \right) \left( \frac{2 - 3 \cos \theta + \cos^3 \theta}{4} \right)$$

$$\Delta G_{Heter} = \Delta G_{Hom} S(\theta)$$

Here the influence of solid surfaces like walls effect the morphology of the particle thus bringing a change in the free Energy.

Part "d" is missing -20



**Question 1 30/100**

①

① \* A State function is a property whose value does not depend on the path taken to reach a value.

**Knows state function and Hess's law but didn't apply it -5**

\* Hess Law → The heat of reaction  $\Delta H_f^\circ$  for a specific reaction is equal to the sum of the heats of reaction for any set of reactions which are equivalent to the reaction.

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②

Second-order transitions have discontinuous

Second derivative

**Repeats definition of second order but can't apply it. -5**

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③

**cde missing -60**