상변태론 HW5. 20202238 권지혜

1. $dG = -SdT + Vdp + \sum \mu_i dn_i + \gamma dA = -(\mu_{vap} - \mu_{liq}) dn_{liq} + \gamma dA$

constant T.P

$\Delta G_v = -(\mu_{liq} - \mu_{vap})$: Driving force / volume of liquid.

r : liquid cluster radius.

$\Delta G = -\frac{4}{3}\pi r^3 \cdot \Delta G_v + 4\pi r^2 \cdot \gamma$

$\frac{4}{3}\pi r^3 = n \cdot v$. $\rightarrow r^2 = \left(\frac{3}{4\pi} \cdot nv\right)^{\frac{2}{3}}$

$\therefore \Delta G = -n \cdot v \cdot \Delta G_v + (36\pi)^{\frac{1}{3}} \cdot (n \cdot v)^{\frac{2}{3}} \cdot \gamma$.

2. a) $\Delta G = -n \cdot v \cdot \Delta G_v + (36\pi)^{\frac{1}{3}} \cdot (n \cdot v)^{\frac{2}{3}} \cdot \gamma$.

b) $\frac{\partial \Delta G}{\partial n} = 0 = -v \cdot \Delta G_v + \frac{2}{3} \cdot (36\pi)^{\frac{1}{3}} \cdot v^{\frac{2}{3}} \cdot \gamma \cdot n^{-\frac{1}{3}}$ (critical point)

$n^* = \frac{32\pi}{3v} \left(\frac{\gamma}{\Delta G_v}\right)^3$, $\Delta G^* = \frac{16}{3}\pi \frac{\gamma^3}{\Delta G_v^2}$

c) $dG_{gm} = -(\mu_{vap} - \mu_{gm}) dn_{gm} + \gamma_{gm} \cdot dA_{gm}$

$dG_{dis} = -(\mu_{vap} - \mu_{dis}) dn_{dis} + \gamma_{dis} dA_{dis}$

$\Rightarrow$ (1번공식)

$\Delta G_{gm} - \Delta G_{dis} = -n(G_{dis} - G_{gm}) + (36\pi)^{\frac{1}{3}} \cdot n^{\frac{2}{3}} \left(v_{gm}^{\frac{1}{3}} \cdot \gamma_{gm} - v_{dis}^{\frac{2}{3}} \cdot \gamma_{dis}\right) = 0$.

각 γ_{dis}에 대하여

$-n\left(0.02 eV/atom \times \left(1.602 \times 10^{-19} \frac{J}{eV}\right)\right) + (36\pi)^{\frac{1}{3}} \cdot n^{\frac{2}{3}} \cdot \left(\left(8 \times 10^{-30} m^3/atom\right)^{\frac{2}{3}} \cdot 3.1 \frac{J}{m^2}\right.$

$= -(3.204 \times 10^{-21} J/atom) \cdot n + (4.856 \times 10^{-20}) n^{\frac{2}{3}} \left(12.4 \frac{J}{atom} - 6^{\frac{2}{3}} \gamma_{dis}\right) - \left(6 \times 10^{-30} m^3/atom\right)^{\frac{2}{3}} \cdot \gamma_{dis}.$

1) $\gamma_{dis} = 3.6 J/m^2$: $n = 470$ atom

2) $\gamma_{dis} = 3.65 J/m^2$: $n = 146$ atom.

3) $\gamma_{dis} = 3.7 J/m^2$: $n = 21$ atom.

d) $\Delta G_{dia} - \Delta G_{gra} < 0$. for any size

$$n^* = \left\{ \frac{4.856\times10^{-20} \times (12.4 - 6^{\frac{1}{3}} \cdot \gamma_{dia})}{3.204\times10^{-21}} \right\}^3$$

예들들어 앞 (c) 에서 $n^* = 4$ 이기 때문에

n^*가 음수라면 모든 size 에서 핵이 형성한다.

$\therefore \gamma > 3.755\ J/m^2$.

e) (b) 에서 $n^* = \frac{32\pi}{3v}\left(\frac{\gamma}{\Delta G_v}\right)^3 = 100$

$$\frac{32\pi}{3.8\times10^{-30}\ \frac{m^3}{atom}} \cdot \left(\frac{3.1\ J/m^2}{\Delta G_v}\right)^3 = 100\ atom.$$

$$\Delta G_{v(gra)} = 1.077 \times 10^{10}\ J/m^3 .$$

f) $$\frac{I_{gra}}{I_{dia}} = \frac{\exp(-\Delta G^*_{gra}/kT)}{\exp(-\Delta G^*_{dia}/kT)} = \exp\left(\frac{\Delta G^*_{dia} - \Delta G^*_{gra}}{kT}\right)$$

$$\Delta G^*_{gra} = \frac{16\pi}{3}\frac{\gamma^3}{\Delta G_v^2} = 4.3\times10^{-18}\ J .$$

$V_{gra}\Delta G_{gra} - V_{dia}\Delta G_{dia} = G^\circ_{gra} - G^\circ_{dia}$ $= -0.102 eV/atom$

$\gamma_{dia} = 3.6\ J/m^2 \rightarrow 3.79\times10^{-18}\ J$: ΔG^*_{dia} ↓ $\Delta G_{dia} = 1.436 \times 10^{10}\ J/m^3$.

$\gamma_{dia} = 3.65\ J/m^2 \rightarrow 3.95\times10^{-18}\ J$.

$\gamma_{dia} = 3.7\ J/m^2 \rightarrow 4.11\times10^{-18}\ J$.

$T = 300K$ 라고하면. $k = 1.38\times10^{-23}\ J/K$.

$\frac{I_{gra}}{I_{dia}} = 3.16\times10^{-54}$ $\gamma = 3.6\ J/m^2$

$\frac{I_{gra}}{I_{dia}} = 1.92\times10^{-57}$ $\gamma = 3.65\ J/m^2$

$\frac{I_{gra}}{I_{dia}} = 1.17\times10^{-60}$ $\gamma = 3.7\ J/m^2$

g) γ_{dia}에 의해 $\left(\frac{I_{gm}}{I_{dm}}\right.$의 nucleation rate 비율 $\left.\text{}\right)$

diamond nucleation 비율이 조금 달라진다.

h). 대부분의 C가 graphite : $\frac{I_{gm}}{I_{dia}}$ 가 매우 매우 크다.

ΔG^*_{dia} 가 훨씬 조금 ΔG^*_{gm}가 훨씬 작다.

: ΔG_V의 관점에서 봤을 때, ΔG^*_{gm}가 훨씬 작기 위해서는,

$\Delta G^*_{gm} \propto \frac{1}{(\Delta G_V)^2}$: $\Delta G_{V(gm)}$가 훨씬 크다.

& (e)에서 n^*이 매우 작다.