상변태 과제 HW3

2016291B 차준호

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

since $nV = \frac{4}{3}\pi r^3$, $(nV)^{2/3} = r^2 \pi^{2/3} \left(\frac{16}{9}\right)^{1/3} \Leftrightarrow 4\pi r^2 / \left(\frac{16}{9}\right)^{1/3} \pi^{2/3} r^2 = 36^{1/3} \pi^{1/3}$

$\therefore \Delta G = -nV\Delta G_v + (36\pi)^{1/3} n^{2/3} V^{2/3} \gamma$

2. a) from 1. $\Delta G = -nV\Delta G_v + (36\pi)^{1/3} n^{2/3} V^{2/3} \gamma$

b) from $\frac{\partial \Delta G}{\partial n} = 0 = -V\Delta G_v + \frac{2}{3}(36\pi)^{1/3} n^{-1/3} V^{2/3} \gamma \Rightarrow n^* = \frac{32\pi}{3V}\left(\frac{\gamma}{\Delta G_v}\right)^3$

a)에서 n^*을 대입하면 $\Delta G = \Delta G^* = \frac{16}{3}\pi \frac{\gamma^3}{(\Delta G_v)^2}$

c) $\Delta G_{dia} = -n(^\circ G_{gra} - ^\circ G_{dia}) + (36\pi)^{1/3} n^{2/3} V_{dia}^{2/3} \gamma_{dia}$

$\Delta G_{gra} = -n(^\circ G_{gra} - ^\circ G_{gra}) + (36\pi)^{1/3} n^{2/3} V_{gra}^{2/3} \gamma_{gra}$

$\Delta G_{gra} - \Delta G_{dia} = 0 = -n(^\circ G_{dia} - ^\circ G_{gra}) + (36\pi n^2)^{1/3} \left(V_{gra}^{2/3}\gamma_{gra} - V_{dia}^{2/3}\gamma_{dia}\right)$

$= -n \cdot 0.02\,eV/atom + (36\pi n^2)^{1/3} \left((8\,Å^3/atom)^{2/3} \cdot 3.1\,J/m^2 - (6\,Å^3/atom)^{2/3} \cdot \gamma_{dia}\right)$

$\Leftrightarrow n^{1/3} = \frac{(36\pi)^{1/3}\left(4\times10^{-20}\times3.1\,J/atom - 6^{2/3}\times\gamma_{dia}\times10^{-20}\right)}{0.02\times1.6\times10^{-19}\,J/atom}$

i) $\gamma_{dia} = 3.6\,J/m^2 \Rightarrow n = 466$

ii) $\gamma_{dia} = 3.65\,J/m^2 \Rightarrow n = 145$

iii) $\gamma_{dia} = 3.7\,J/m^2 \Rightarrow n = 21$

d) $\Delta G_{gra} - \Delta G_{dia} > 0$ 이어야 되므로 i) $\gamma_{dia} = 3.6\,J/m^2$ 일 때는 $n < 466$

ii) $\gamma_{dia} = 3.65\,J/m^2$ 일 때는 $n < 145$

iii) $\gamma_{dia} = 3.7\,J/m^2$ 일 때는 $n < 21$.

e) $n^* = 100 = \frac{32\pi}{3V_{gr}}\left(\frac{\gamma_{gr}}{\Delta G_v}\right)^3 = \frac{32\cdot\pi}{3\times 8\times 10^{-30}\,m^3/atom}\left(\frac{2.1\,J/m^2}{\Delta G_v}\right)^3$

$\therefore \Delta G_v^{gr} = 1.08\times 10^{10}\,J/m^3$

f) $V_{gr}\Delta G_v^{gr} = {}^{\circ}G_{vap} - {}^{\circ}G_{gr}$

$V_{dia}\Delta G_v^{dia} = {}^{\circ}G_{vap} - {}^{\circ}G_{dia}$ $\Leftrightarrow \Delta G_v^{dia} = \frac{V_{gr}\Delta G_v^{gr} + ({}^{\circ}G_{gr} - {}^{\circ}G_{dia})}{V_{dia}}$

$= \frac{1.08\times 10^{10}\times 8\times 10^{-30} - 0.02\times 1.6\times 10^{-19}}{6\times 10^{-30}}$

$= 1.39\times 10^{10}\,J/m^3$

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

$\Delta G^*_{dia} = \frac{16}{3}\pi\frac{\gamma_{dia}^3}{(\Delta G_v)^2} = \frac{16\pi}{3}\frac{\gamma_{dia}^3}{(1.39\times 10^{10})^2}$

i) $\gamma_{dia} = 3.6\,J/m^2 \Rightarrow \Delta G^*_{dia} = 4.046\times 10^{-18}$

ii) $\gamma_{dia} = 3.65\,J/m^2 \Rightarrow$ " $= 4.217\times 10^{-18}$

iii) $\gamma_{dia} = 3.7\,J/m^2 \Rightarrow$ " $= 4.393\times 10^{-18}$

$\Delta G^*_{gr} = \frac{16\pi}{3}\frac{\gamma_{gr}^3}{\Delta G_v} = \frac{16\pi}{3}\cdot\frac{3.1^3}{(1.08\times 10^{10})^2} = 4.279\times 10^{-18}$

$T = 300K$ 라고 가정하면 $(k = 1.38\times 10^{-23}\,J/K)$

$I_{gra}/I_{dia} = \exp\left(\frac{\Delta G^*_{dia} - 4.279\times 10^{-18}}{1.38\times 300\times 10^{-23}}\right) \Rightarrow$

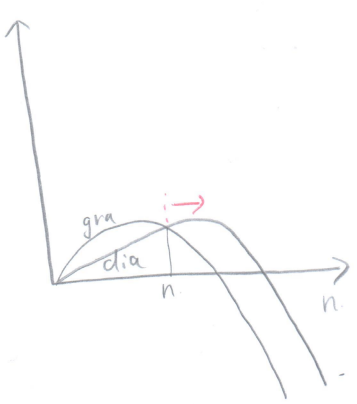
i) $\gamma_{dia} = 3.6\,J/m^2 \Rightarrow 3.61\times 10^{-25}$

ii) $\gamma_{dia} = 3.65\,J/m^2 \Rightarrow 3.13\times 10^{-1}$

iii) $\gamma_{dia} = 3.7\,J/m^2 \Rightarrow 9.10\times 10^{11}$

g) Surface energy가 $6.05\,J/m^2$ 정도만 달라져도 nucleation rate의 변화가 급변하는것으로 보아 surface energy에 nucleation rate가 아주 민감함을 알수 있고 γ_{dia} 값이 작아질수록 I_{gra} 값이 커짐을 알수있다.

h) $CH_4 \rightarrow C_{(g)} + 2H_2 \rightarrow C_{(gra)} + 2H_2$ 에서 graphite 가 생성되었다는 것은



고온일때 위의반응이 잘되어 P_c 값이올라
→ 방향으로 capillary effect 가 들어들어 graphite
가 생성됨을 알수있다.

여기서 driving force of graphite 는 높은 P_c 값이라
할수있다.