Phase Transformation H.W. #3. 20152027 조민국

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

$nv = \frac{4}{3}\pi r^3 \Rightarrow \therefore r = \left(\frac{3nv}{4\pi}\right)^{1/3}$

$4\pi r^2 = 4\pi \cdot \left(\frac{3nv}{4\pi}\right)^{2/3} = (36\pi)^{1/3} n^{2/3} v^{2/3}$

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

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

$\therefore \frac{d\Delta G}{dn} = -v\Delta G_v + \left(\frac{32}{3}\pi\right)^{1/3} n^{-1/3} v^{2/3}\gamma$

b). $\frac{d\Delta G}{dn}\Big|_{n^*} = 0. = -v\Delta G_v + \left(\frac{32}{3}\pi\right)^{1/3} n^{*-\frac{1}{3}} v^{2/3}\gamma$

$n^{*-\frac{1}{3}} = \frac{v\Delta G_v}{\left(\frac{32}{3}\pi\right)^{1/3} v^{2/3}\gamma} \Rightarrow n^* = \frac{\frac{32}{3}\pi v^2 \gamma^3}{v^3 \Delta G_v^3} = \frac{32\pi\gamma^3}{3v\Delta G_v^3}$

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

$= -\frac{32\pi\gamma^3}{3\Delta G_v^2} + (36\pi)^{1/3}\left(\frac{32\pi\gamma^3}{3v\Delta G_v^3}\right)^{2/3} v^{2/3}\gamma$

$= -\frac{32\pi\gamma^3}{3\Delta G_v^2} + \left(36\pi \cdot \frac{1024\pi^2}{9v^2} \cdot v^2\right)^{1/3} \cdot \frac{\gamma^2}{\Delta G_v^2} \cdot \gamma$

$= -\frac{32\pi\gamma^3}{3\Delta G_v^2} + \frac{16\gamma^3\pi}{\Delta G_v^2} = \left(-\frac{32}{3} + 16\right) \cdot \frac{\pi\gamma^3}{\Delta G_v^2}$

$= \frac{16\pi\gamma^3}{3\Delta G_v^2}$

c). $\Delta G_{dia} - \Delta G_{gr} = 0.$

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

$-\left[-n({}^\circ G_{vap} - {}^\circ G_{gr}) + (36\pi)^{1/3} n^{2/3} V_{gr}^{2/3}\gamma_{gr}\right]$

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

$n = \left(\frac{(36\pi)^{1/3}\left(V_{gr}^{2/3}\gamma_{gr} - V_{dia}^{2/3}\gamma_{dia}\right)}{{}^\circ G_{dia} - {}^\circ G_{gr}}\right)^3$

$= 36\pi\left(\frac{\left(4\text{Å}^2/atom \times 3.1 J/m^2 - 6^{2/3}\text{Å}^2/atom \times \gamma_{dia}\right)(0.06242 eV/\text{Å}^2)}{(0.02 eV/atom) \cdot (1 J/m^2)}\right)^3$

i). $\gamma_{dia} = 3.6 J/m^2$: $n \simeq 464$ atoms.

ii) $\gamma_{dia} = 3.65 J/m^2$: $n \simeq 145$ atoms.

iii) $\gamma_{dia} = 3.7 J/m^2$: $n \simeq 21$ atoms.

d) $\Delta G_{dia} - \Delta G_{gr} < 0.$

e). $n^*_{gr} = 100 = \frac{32\pi\gamma_{gr}^3}{3V_{gr}\Delta G_v^{gr\,3}}$ ... from 2-b)

$\therefore \Delta G_v^{gr} = \left(\frac{32\pi\gamma_{gr}^3}{3V_{gr} n^*_{gr}}\right)^{1/3} = \sqrt[3]{\frac{32\pi \times (3.1 J/m^2 \cdot (0.06242 eV/atom))^3}{3 \times 8\text{Å}^3/atom \times 100}}$

$= 0.067202 eV/\text{Å}^3$

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

$\Delta G^*_{gr} - \Delta G^*_{dia} = \frac{16\pi}{3}\left(\frac{\gamma_{gr}^3}{\Delta G_v^{gr\,2}} - \frac{\gamma_{dia}^3}{\Delta G_v^{dia\,2}}\right)$ ... from 2-b)

$V_{gr}\Delta G_v^{gr} - V_{dia}\Delta G_v^{dia} = {}^\circ G_{dia} - {}^\circ G_{gr}$ ... from 2-c)

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

$\therefore \frac{I_{gr}}{I_{dia}} = \exp\left(-\frac{\frac{16\pi}{3}\left(\frac{\gamma_{gr}^3}{\Delta G_v^{gr\,2}} - \frac{\gamma_{dia}^3}{\left(\frac{V_{gr}\Delta G_v^{gr} - ({}^\circ G_{dia} - {}^\circ G_{gr})}{V_{dia}}\right)^2}\right)}{kT}\right)$

at 1200K

$\Delta G_v^{gr} = 0.067202 eV/\text{Å}^3$ ... from 2-e).

${}^\circ G_{dia} - {}^\circ G_{gr} = 0.02 eV/atom$ ... from 2-c).

i) $\gamma_{dia} = 3.6 J/m^2$: $\frac{I_{gr}}{I_{dia}} = 2.47 \times 10^{-6}$

ii) $\gamma_{dia} = 3.65 J/m^2$: $\frac{I_{gr}}{I_{dia}} = 8.41 \times 10^{-2}$

iii) $\gamma_{dia} = 3.7 J/m^2$: $\frac{I_{gr}}{I_{dia}} = 3.83 \times 10^3$

g) γ_{dia}가 작아질 수록 diamond가 graphite에 비해 더 안정해 지며 nucleation rate가 graphite 보다 커질 수 있다. 특히, 작은 양의 γ_{dia}의 변화로도 diamond growth에 큰 영향일 끼칠수 있다.

h). $CH_4 \rightarrow C + 2H_2$ 로의 분해 반응으로 인해 반응이 활발히 일어나는 곳에서 C의 농도가 증가하여 커다란 cluster를 형성할 확률이 높아진다. 이러한 큰 cluster들은 capillarity effect를 극복하기 때문에 graphite 상태가 더 안정해진다. 따라서 높은 C의 농도가 driving force로 작용한다.