상변태론 HW#5 20182347 김현석

1. $dG = -SdT + VdP + \sum \mu_i dn_i + \gamma dA$

$= -\underbrace{(\mu_{vap} - \mu_{liq})}_{\Delta G_v\text{. driving force per volume}} dn_{liq} + \gamma dA$

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

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

2.

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

(b) $\left.\frac{\partial \Delta G}{\partial n}\right|_{n^*} = \left. -v\Delta G_v + (36\pi)^{\frac{1}{3}} v^{\frac{2}{3}}\gamma \cdot \frac{2}{3} n^{-\frac{1}{3}} \right|_{n^*}$

$= 0.$

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

$n^* = \frac{8}{27} \cdot v^{-1} \cdot \gamma^3 \cdot 36\pi \cdot (\Delta G_v)^{-3}$

$= \frac{32}{3}\gamma^3 \pi \Big/ v(\Delta G_v)^3$

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

(c)

$\Delta G_{gra} = -(\mu_{vap} - \mu_{gra}) dn_{gra} + \gamma_{gra} dA_{gra}$

$-\Delta G_{dia} = -(\mu_{vap} - \mu_{dia}) dn_{dia} + \gamma_{dia} dA_{dia}$

$\Delta G_{gra} - \Delta G_{dia} = -n({}^\circ G_{dia} - {}^\circ G_{gra})$

$+ (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} \left(v_{gra}^{\frac{2}{3}}\gamma_{gra} - v_{dia}^{\frac{2}{3}}\gamma_{dia}\right)$

$= 0.$

$n = \frac{36\pi \left(v_{gra}^{\frac{2}{3}}\gamma_{gra} - v_{dia}^{\frac{2}{3}}\gamma_{dia}\right)^3}{({}^\circ G_{dia} - {}^\circ G_{gra})^3}$

$= \frac{36\pi \cdot \left((8\times10^{-30})^{\frac{2}{3}}\times3.1 - (6\times10^{-30})^{\frac{2}{3}}\times3.6\right)^3}{(0.02\times1.6\times10^{-18})^3}$

$\simeq 470$

For $\gamma_{dia} = 3.65\ \mathrm{J/m^2}$, $n \simeq 145$

" " $3.7\ \mathrm{J/m^2}$, $n \simeq 21$.

(d) $\Delta G_{dia} < \Delta G_{gra}$

$\Rightarrow n < 36\pi \left(\frac{v_{dia}^{\frac{2}{3}}\gamma_{dia} - v_{gra}^{\frac{2}{3}}\gamma_{dia}}{{}^\circ G_{gra} - {}^\circ G_{dia}}\right)^3$

(e) $n^* = \frac{32}{3}\gamma^3\pi \Big/ v(\Delta G_v)^3 = 100$

$= \frac{32}{3}\cdot(3.1)^3\cdot\pi \Big/ 8\times10^{-30}\times(\Delta G_v)^3$

$= 100$

$\Rightarrow \Delta G_v \simeq 1.08\times10^{10}\ \mathrm{J/m^3}$.

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

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

$\Delta G^*_{gra} = \frac{16\pi}{3} \cdot \frac{\gamma_{gra}^2}{(\Delta G_v^{gra})^2} = 4.3\times10^{-18}\ \mathrm{J}.$

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

$= \begin{cases} 4.1\times10^{-18} & (\gamma_{dia} = 3.6\ \mathrm{J/m^2}) \\ 4.3\times10^{-18} & (\gamma_{dia} = 3.65\ \mathrm{J/m^2}) \\ 4.46\times10^{-18} & (\gamma_{dia} = 3.7\ \mathrm{J/m^2}) \end{cases}$

Assuming $T = 300\mathrm{K}$,

$kT = 1.38\times10^{-23}\times300 = 4.14\times10^{-21}$

$\therefore \frac{I_{gra}}{I_{dia}} = \begin{cases} 3.68\times10^{-21} & (\gamma_{dia} = 3.6\ \mathrm{J/m^2}) \\ 5.28\times10^{-3} & (\text{"} = 3.65 \text{"}) \\ 2.61\times10^{16} & (\text{"} = 3.7 \text{"}) \end{cases}$

(g) The nucleation rate greatly depends on γ_{dia}

$\Rightarrow$ nucleation rate $\propto$ surface energy.

(h) Below the critical size, diamond can be more stable than graphite.

So, (e) works only in nanoscale.