20182466
서경인

1

Nucleation (spherical nucleus)

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

at constant T, P

$$dG = \mu_{vap} dn_{vap} + \mu_{liq} dn_{liq} + \gamma dA = -\underline{(\mu_{vap} - \mu_{liq})} dn_{liq} + \gamma dA$$

$$\| $$

$\underline{\Delta G_{vap} \text{ ; per volume}}$

$$\therefore \Delta G = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \quad \cdots (1)$$

$$\frac{4}{3}\pi r^3 = nv$$

→ $n$: number of molecules in cluster (atoms)

→ $v$ : molecular volum (atomic)

$$r^3 = \frac{3nv}{4\pi}$$

$$4\pi r^2 = (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} v^{\frac{2}{3}}$$

→ 식 (1)에 대입,

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

2.

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

(b) $$\left.\frac{\partial \Delta G}{\partial n}\right|_{n=n^*} = -v\,\Delta G_v + \frac{2}{3}(36\pi)^{\frac{1}{3}} n^{-\frac{1}{3}} v^{\frac{2}{3}} \gamma = 0$$

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

$$\therefore\ n^* = \frac{\frac{8}{27} \times 36\pi \times v^2 \gamma^3}{v^3\,\Delta G_v^3} = \frac{32\pi\gamma^3}{3v\,\Delta G_v^3}$$

$$\Delta G^* = \frac{-32\pi\gamma^3}{3v\,\Delta G_v^3} v\,\Delta G_v + (36\pi)^{\frac{1}{3}} \left(\frac{32\pi}{3}\right)^{\frac{2}{3}} \frac{\gamma^2}{\cancel{v^{\frac{2}{3}}}\,\Delta G_v^2} \times \cancel{v^{\frac{2}{3}}}\gamma$$

$$= -\frac{32\pi}{3}\frac{\gamma^3}{\Delta G_v^2} + \pi \times 16 \times \frac{\gamma^3}{\Delta G_v^2}$$

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

(c)

Stability of diamond = graphite

$$\Delta G_{dia} = \Delta G_{gr}$$

$$-n_d \cancel{v_d}\left(\frac{{}^\circ G_g - {}^\circ G_{dia}}{\cancel{v_d}}\right) + (36\pi)^{\frac{1}{3}} n_d^{\frac{2}{3}} v_{dia}^{\frac{2}{3}} \gamma_{dia} = -n_{gr} \cancel{v_{gr}} \left(\frac{{}^\circ G_g - {}^\circ G_{gr}}{\cancel{v_d}}\right) + (36\pi)^{\frac{1}{3}} n_{gr}^{\frac{2}{3}} v_{gr}^{\frac{2}{3}} \gamma_{gr}$$

Consider $n_{gr} = n_{dia} = n'$

$$0 = n'\left({}^\circ G_{dia} - {}^\circ G_{gr}\right) + (36\pi)^{\frac{1}{3}} n'^{\frac{2}{3}} \left(v_{dia}^{\frac{2}{3}}\gamma_{dia} - v_{gr}^{\frac{2}{3}}\gamma_{gr}\right)$$

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

~~when~~

(i) $\gamma_{dia} = 3.6$ $\qquad 1eV = 1.6\times10^{-19}J$

$$n = 36\pi\left(\frac{(6\times10^{-30})^{\frac{2}{3}}\times\frac{3.6}{1.6\times10^{-19}} - (8\times10^{-30})^{\frac{2}{3}}\times\frac{3.1}{1.6\times10^{-19}}}{0.02}\right)^3$$

$\approx \underline{466}$

(ii) $\gamma_{dia} = 3.65$

$$n = 36\pi\left(\frac{(6\times10^{-30})^{\frac{2}{3}}\times\frac{3.65}{1.6\times10^{-19}} - (8\times10^{-30})^{\frac{2}{3}}\times\frac{3.1}{1.6\times10^{-19}}}{0.02}\right)^3$$

$\approx 147$

(iii) $\gamma_{dia} = 3.7$

$$n = 36\pi\left(\frac{(6\times10^{-30})^{\frac{2}{3}}\times\frac{3.7}{1.6\times10^{-19}} - (8\times10^{-30})^{\frac{2}{3}}\times\frac{3.1}{1.6\times10^{-19}}}{0.02}\right)^3$$

$\approx 22$

(d) more stable than graphite $\iff \Delta G_{dia} < \Delta G_{gr}$

$$n < n' \iff n < 36\pi\left(\frac{V_{dia}^{\frac{2}{3}}\gamma_{dia} - V_{gr}^{\frac{2}{3}}\gamma_{gr}}{{}^{\circ}G_{gr} - {}^{\circ}G_{dia}}\right)^3$$

$\Downarrow$

$\underline{2-(c)}$

(e)

$$n^* = 100$$

$$= \frac{32\pi}{3}\frac{\gamma^3}{v\,\Delta G_v^3} = \frac{32\pi}{3}\times\frac{(3.1J/m^2)^3}{8\,\mathring{A}^3/\text{atom}\ \Delta G_v^3}$$

$$\therefore \Delta G_v \approx 1.08\times10^{10}\,J/m^3$$

(f)

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

$$\Delta G^* = \frac{16\pi}{3}\frac{\gamma^3}{\Delta G_v^2} \Longrightarrow \frac{I_{gr}}{I_{dia}} = \exp\left(\frac{16\pi}{3kT}\left(\frac{\gamma_{dia}^3}{\Delta G_{v,dia}^2} - \frac{\gamma_{gr}^3}{\Delta G_{v,gr}^2}\right)\right)$$

$$\Delta G_{v,gr} = \frac{{}^\circ G_g - {}^\circ G_{gr}}{V_{gr}}, \quad \Delta G_{v,dia} = \frac{{}^\circ G_g - G_{dia}}{V_{dia}}$$

$$V_{dia}\,\Delta G_{v,dia} = V_{gr}\,\Delta G_{v,gr} + \left({}^\circ G_{gr} - {}^\circ G_{dia}\right)$$

$$\Delta G_{v,dia} = \frac{1.08\times10^{10}\,J/m^3 \times 8\,Å^3/atom - 0.02\,eV/atom}{6\,Å^3/atom}$$

$$\simeq 1.38\times10^{10}\,J/m^3$$

$$\therefore \frac{I_{gr}}{I_{dia}} = \exp\left(\frac{16\pi}{3kT}\left(\frac{\gamma_{dia}^3}{(1.38\times10^{10}\,J/m^3)^2} - \frac{(3.1\,J/m^2)^3}{(1.08\times10^{10}\,J/m^3)^2}\right)\right)$$

set. $T = 300K$, $k = 1.38\times10^{-23}$

(i) $\gamma = 3.6\,J/m^2$

$I_{gr}/I_{dia} \simeq \underline{9.3\times10^{-233}}$

(ii) $\gamma = 3.68\,J/m^2$

$I_{gr}/I_{dia} \simeq \underline{6.4\times10^{-5}}$

(iii) $\gamma = 3.7\,J/m^2$

$I_{gr}/I_{dia} \simeq \underline{4.8\times10^{14}}$

(g) $n$이 클 때는 graphite가 안정하나 $n$이 작은 경우에는 diamond가 더 안정하다. 또한 diamond의 nucleation rate은 surface E의 작은 변화에도 큰 영향을 받기에, nucleation 시 surface E에 주의 하여야 한다.

(h) graphite nucleation 과정의 driving force는 C의 높은 농도일 것이다. $CH_4 \rightarrow C + 2H_2$의 반응이 활발하게 일어나면 C의 농도가 증가할 것이고, 이로 인해 $n$이 큰 cluster가 형성될 확률이 높다. 이러한 cluster들은 capillary effect를 극복하기에 graphite 상태가 더 안정하게 된다.