Homework #5   20222980 정대훈.

1. a)

(n atoms, r radius)

$V_n = \frac{4}{3}\pi r_n^3 = n V_a$ (V_a : atomic volume)

$\rightarrow r_n = \left(\frac{3}{4\pi} n V_a\right)^{\frac{1}{3}}$

$$\Delta G = -n\Delta G_a + 4\pi r_n^2 \gamma$$

$$= -n\Delta G_a + 4\pi \cdot \left(\frac{3}{4\pi}\right)^{\frac{2}{3}} \cdot n^{\frac{2}{3}} \cdot v^{\frac{2}{3}} \cdot \gamma \quad (v = V_a)$$

$$= -n\Delta G_a + (4\pi)^{\frac{1}{3}} \cdot 3^{\frac{2}{3}} \cdot n^{\frac{2}{3}} \cdot v^{\frac{2}{3}} \cdot \gamma$$

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

b) $\left.\frac{\partial \Delta G}{\partial n}\right)_{n^*} = 0$.

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

$$\rightarrow n^{\frac{1}{3}} = \frac{2}{3} \cdot (36\pi)^{\frac{1}{3}} \cdot \frac{v^{\frac{2}{3}} \gamma}{\Delta G_a}$$

$$\therefore n^* = \frac{32\pi}{3} \cdot \frac{v^2 \gamma^3}{\Delta G_a^3}$$

$$\Delta G^* = -\frac{32\pi}{3} \cdot \frac{v^2 \gamma^3}{\Delta G_a^3} \cdot \Delta G_a + (36\pi)^{\frac{1}{3}} \cdot \left(\frac{32\pi}{3}\right)^{\frac{2}{3}} \frac{v^{\frac{4}{3}} \cdot \gamma^2}{\Delta G_a^2} \cdot v^{\frac{2}{3}} \cdot \gamma$$

$$= -\frac{32}{3}\pi \cdot \frac{v^2 \gamma^3}{\Delta G_a^2} + 16\pi \cdot \frac{v^2 \gamma^3}{\Delta G_a^2}$$

$$= \frac{16\pi}{3} \cdot \frac{v^2 \gamma^3}{\Delta G_a^2}$$

c) $\Delta G_{gra} = \Delta G_{dia}$ at n'.

$$-n'\Delta G^{a}_{gra} + (36\pi)^{\frac{1}{3}} V_{gra}^{\frac{2}{3}} \gamma_{gra} n'^{\frac{2}{3}} = -n'\Delta G^{a}_{dia} + (36\pi)^{\frac{1}{3}} V_{dia}^{\frac{2}{3}} \gamma_{dia} n'^{\frac{2}{3}}$$

$$\rightarrow \quad n'^{\frac{1}{3}} = \frac{(36\pi)^{\frac{1}{3}}\left(V_{dia}^{\frac{2}{3}}\gamma_{dia} - V_{gra}^{\frac{2}{3}}\gamma_{gra}\right)}{\Delta G^{a}_{dia} - \Delta G^{a}_{gra}}$$

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

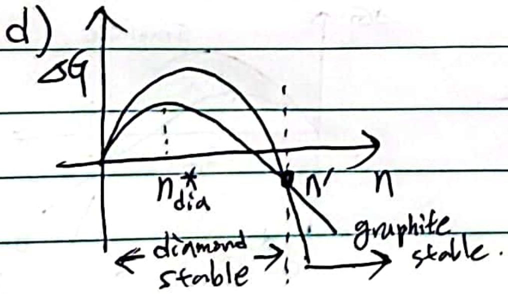
$$\left(\begin{aligned} \Delta G^{a}_{dia} &= -{}^{\circ}G_{dia} + {}^{\circ}G_{gas} \\ \Delta G^{a}_{gra} &= -{}^{\circ}G_{gra} + {}^{\circ}G_{gas} \\ \Delta G^{a}_{dia} - \Delta G^{a}_{gra} &= {}^{\circ}G_{gra} - {}^{\circ}G_{dia} \end{aligned}\right)$$

$$= 36\pi \left(\frac{\gamma_{dia} \times (6\times10^{-30})^{\frac{2}{3}} - 3.1\times(8\times10^{-30})^{\frac{2}{3}}}{-0.02 \times 1.6\times10^{-19}}\right)^{3} \text{ atom.}$$

① $\gamma_{dia} = 3.6\ J/m^2$ $\quad n'_1 = 4607$ atoms.

② $\gamma_{dia} = 3.65\ J/m^2$ $\quad n'_2 = 146$ atoms.

③ $\gamma_{dia} = 3.7\ J/m^2$ $\quad n'_3 = 22$ atoms.

d) 

For any size of clusters of diamond to be stable,

① $n' > 1$

② $n' > n^{*}_{dia}$

should be satisfied.

e) from b), $100 = \frac{32}{3}\pi \cdot \frac{V_{gra}^{2} \times \gamma_{gra}^{3}}{\Delta G_a^{3}}$

$$\rightarrow \Delta G_a = \left(\frac{32\pi}{300}\right)^{\frac{1}{3}} \times (8\times10^{-30})^{\frac{2}{3}} \times 3.1 \quad (J/atom)$$

$$= 8.61\times10^{-20}\ J/atom$$

$$= 0.54\ eV/atom.$$

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

from e), $\Delta G^a_{gra} = 8.61 \times 10^{-20}$ J / atom.

(ΔG^a_{gra} denotes the driving force for graphite per atom)

$$\Delta G^a_{dia} = \Delta G^a_{gra} - ({}^\circ G_{dia} - {}^\circ G_{gra})$$
$$= 8.61 \times 10^{-20} - 0.02 \times 1.6 \times 10^{-19} \text{ (J / atom)}$$
$$= 8.29 \times 10^{-20} \text{ (J / atom)}$$

$$\rightarrow \Delta G^*_{gra} = \frac{16}{3}\pi \times \frac{V_{gra}^2 \times \gamma_{gra}^3}{(8.61 \times 10^{-20})^2}, \quad \Delta G^*_{dia} = \frac{16}{3}\pi \times \frac{V_{dia}^2 \times \gamma_{dia}^3}{(8.29 \times 10^{-20})^2}$$

① $\gamma_{dia} = 3.6$ J/m², $$\frac{I_{gra}}{I_{dia}} = \exp\left(-\frac{(431 - 409) \times 10^{-20}}{1.38 \times 10^{-23} \times 300}\right)$$

$$= 8.35 \times 10^{-24}$$

② $\gamma_{dia} = 3.65$ J/m², $$\frac{I_{gra}}{I_{dia}} = \exp\left(-\frac{(431 - 427) \times 10^{-20}}{1.38 \times 10^{-23} \times 300}\right)$$

$$= 6.37 \times 10^{-5}$$

③ $\gamma_{dia} = 3.7$ J/m² $$\frac{I_{gra}}{I_{dia}} = \exp\left(-\frac{(431 - 445) \times 10^{-20}}{1.38 \times 10^{-23} \times 300}\right)$$

$$= 4.86 \times 10^{14}$$

g) During the CVD diamond process, clusters of diamond is more stable than graphite, and if γ_{dia} is sufficiently small, nucleation of diamond is much faster than that of graphite.