HW#5 20212568 강승연

$\boxed{1}$ $\Delta G = -V\Delta G_v + A\cdot\gamma$

spherical nucleus ; $V = \frac{4}{3}\pi r^3$ / $A = 4\pi r^2$

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

대입

$V = \frac{4}{3}\pi r^3 = n\upsilon \Rightarrow r = \left(\frac{3}{4\pi} n\upsilon\right)^{1/3}$

υ → atomic volume

n → # of atoms in cluster

$\therefore \Delta G = -n\upsilon\cdot\Delta G_v + 4\pi\cdot\left(\frac{3}{4\pi} n\upsilon\right)^{2/3}\cdot\gamma$

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

$\boxed{2}$

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

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

$\therefore n^* = \frac{32\pi}{3\upsilon}\left(\frac{\gamma}{\Delta G_v}\right)^3$

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

$= -\frac{32\pi}{3}\cdot\frac{\gamma^3}{(\Delta G_v)^2} + (4\times32^2)^{1/3}\pi\cdot\frac{\gamma^3}{(\Delta G_v)^2}$

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

(c)

$\Delta G_{gr} = -n\cdot({}^\circ G_v - {}^\circ G_{gr}) + (36\pi)^{1/3} n^{2/3}\upsilon_{gr}^{2/3}\gamma_{gr}$

$\Delta G_{dia} = -n\cdot({}^\circ G_v - {}^\circ G_{dia}) + (36\pi)^{1/3} n^{2/3}\upsilon_{dia}^{2/3}\gamma_{dia}$

Same stability ; $\Delta G_{gr} = \Delta G_{dia}$

$n({}^\circ G_{dia} - {}^\circ G_{gr}) + (36\pi)^{1/3} n^{2/3}(\upsilon_{dia}^{2/3}\gamma_{dia} - \upsilon_{gr}^{2/3}\cdot\gamma_{gr}) = 0$

$\therefore n = \frac{36\pi(\upsilon_{gr}^{2/3}\gamma_{gr} - \upsilon_{dia}^{2/3}\gamma_{dia})^3}{({}^\circ G_{dia} - {}^\circ G_{gr})^3}$

$\gamma = 3.1\ J/m^2$
$\upsilon_{gr} = 8\ \text{Å}^3/\text{atom}$
$\upsilon_{dia} = 6\ \text{Å}^3/\text{atom}$
${}^\circ G_{dia} - {}^\circ G_{gr} = 0.02\ eV/\text{atom}$

$\therefore$ ① $\gamma_{dia} = 3.6\ J/m^2 \rightarrow n = 465$

② $\gamma_{dia} = 3.65\ J/m^2 \rightarrow n = 145$

③ $\gamma_{dia} = 3.7\ J/m^2 \rightarrow n = 21$

(d) diamond is more stable than graphite

$\Rightarrow \Delta G_{dia} < \Delta G_{gr}$

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

$8\times10^{-30}\,m^3/atom$ $\quad$ $3.1\,J/m^2$

(e) $$n^* = \frac{32\pi}{3V}\left(\frac{\gamma}{\Delta G_V}\right)^3 \quad \text{(from 2-(b))}$$

$= 100$

$$\therefore \Delta G_{v\,gr} = 1.08\times10^{10}\,J/m^3$$

(driving force for graphite nucleation)

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

$$\Delta G^*_{gr} = \frac{16\pi}{3}\cdot\frac{\gamma_{gr}^3}{(\Delta G_{v\,gr})^2} = 4.3\times10^{-18}\,J$$

$$\Delta G^*_{dia} = \frac{16\pi}{3}\cdot\frac{\gamma_{dia}^3}{(\Delta G_{v,dia})^2} = \begin{cases} ① \ \gamma_{dia} = 3.6\,J/m^2 \rightarrow \Delta G^*_{dia} = 4.10\times10^{-18}\,J \\ ② \ \gamma_{dia} = 3.65\,J/m^2 \rightarrow \Delta G^*_{dia} = 4.28\times10^{-18}\,J \\ ③ \ \gamma_{dia} = 3.7\,J/m^2 \rightarrow \Delta G^*_{dia} = 4.46\times10^{-18}\,J \end{cases}$$

$T = 300K$

$$\therefore \frac{I_{gr}}{I_{dia}} = \exp\left[\frac{\Delta G^*_{dia} - \Delta G^*_{gr}}{4.14\times10^{-21}\,J}\right] = \begin{cases} ① \ 3.42\times10^{-21} \\ ② \ 5.20\times10^{-3} \\ ③ \ 2.61\times10^{16} \end{cases}$$

(g) In case of bulk, diamond is more unstable than graphite.
However, if the size of particle becomes very small (like nanoscale), we have to consider the surface because the effect of surface energy is increasing. From (e), we know that nucleation rate is greatly influenced by surface energy. Therefore, as the surface energy of diamond increases, nucleation rate of diamond decrease.

(h) $CH_4 \rightarrow C + 2H_2$ is decomposition.

So, as CH_4 is decomposed, concentration of C increase.

From above, $\Delta G_{v,gr} > \Delta G_{v,dia}$

However, if the concentration of C increases and the capillary effect is not applied, the above eqn. will not be established. Therefore, the above eqn. is defined in nanometers to which the capillary effect is applied