1. Assuming a spherical nucleus, drive the following expression for the nucleation energy.

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

in here, $\frac{4}{3}\pi r^3 = nv \Rightarrow 4\pi r^3 = 3nv$

$$(4\pi r^3)^{\frac{2}{3}} = (4\pi r^2)\cdot(4\pi)^{\frac{1}{3}} = (3nv)^{\frac{2}{3}}$$

$$\therefore (4\pi r^2) = (3nv)^{\frac{2}{3}} \cdot (4\pi)^{\frac{1}{3}}$$

$$= 3^{\frac{2}{3}} \cdot 4^{\frac{1}{3}} \cdot \pi^{\frac{1}{3}} \cdot n^{\frac{2}{3}} \cdot v^{\frac{2}{3}}$$

$$= 9^{\frac{1}{3}} \cdot 4^{\frac{1}{3}} \cdot \pi^{\frac{1}{3}} \cdot n^{\frac{2}{3}} \cdot v^{\frac{2}{3}}$$

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

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

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2. Diamond is a less stable form of carbon than graphite, but it can be obtained by CVD under normal pressure and temperature.

a) For a spherical nucleus, express the energy change during nucleation as a function of number of atoms in cluster

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

b) using the results of (a), derive the expression for the critical number of atoms and energy barrier

→ * critical number of atoms → $\left(\frac{d\Delta G}{dn}\right)_{n=n^*} = 0$

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

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

$$\therefore n = \frac{\left(\frac{2}{3}\right)^3 36\pi \cdot v^2 \gamma^3}{(v\Delta G_v)^3} = \frac{32\pi}{3v}\left(\frac{\gamma}{\Delta G_v}\right)^3.$$

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

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

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

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

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b) 식은 →

$$\Delta G_1^* = -\frac{32\pi r^3}{3\Delta G_v^2} + 3(\frac{1}{4})^{\frac{1}{3}}\pi^{\frac{1}{3}}\cdot(\frac{32}{3})^{\frac{2}{3}}\cdot\pi^{\frac{2}{3}}\cdot\frac{1}{D^2}\cdot(\frac{r}{\Delta G_v})^2\cdot r^{\frac{2}{3}}\cdot r$$

$$+ \pi\sqrt[3]{\frac{1}{4}}\cdot\sqrt[3]{32^2}\cdot\sqrt[3]{\frac{1}{9}}$$

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

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

(c) Assuming isotropic and constant surface energy for both graphite and diamond, and using the data : $\gamma_{gr} = 3.1\ Jm^{-2}$, $\gamma_{dia} = 3.6$, 3.65 and $3.7\ Jm^{-2}$

$\ddagger$ $1\ J/m^2 = 1.29\times10^{-2}\ eV/Å^2$ $V_{gr} = 8\,Å^3/atom$, $V_{dia} = 6\,Å^3/atom$

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

compute the number of atoms in clusters where the stability of diamond becomes the same as that of graphite.

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

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

$$\Delta G_{gra} = -n({}^{\circ}G_v - {}^{\circ}G_{gra}) + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} V_{gra}^{\frac{2}{3}}\gamma_{gra}$$

$$n({}^{\circ}G_{dia} - {}^{\circ}G_{gra}) + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}}(V_{dia}^{\frac{2}{3}}\gamma_{dia} - V_{gra}^{\frac{2}{3}}\gamma_{gra}) = 0.$$

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

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

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i) $\gamma_{dia} = 3.6\ J/m^2$, $n = 36\pi \left(\frac{[(8Å^3/atom)^{\frac{2}{3}} \cdot 3.1 J/m^2 - (6Å^3/atom)^{\frac{2}{3}} \cdot 3.6 J/m^2]}{0.02\ eV/atom} \right)^3$

$= 36\pi \left(\frac{8^{\frac{2}{3}} \cdot 0.19344 - 6^{\frac{2}{3}} \cdot 0.22464}{0.02} \right)^3 = 464$

ii) $\gamma_{dia} = 3.15\ J/m^2$, $n = 36\pi \left(\frac{8^{\frac{2}{3}} \cdot 0.19344 - 6^{\frac{2}{3}} \cdot 0.22176}{0.02} \right)^3 = 145$

iii) $\gamma_{dia} = 3.7\ J/m^2$, $n = 36\pi \left(\frac{6^{\frac{2}{3}} \cdot 0.19344 - 6^{\frac{2}{3}} \cdot 0.23088}{0.02} \right)^3 = 21$.

(d) What is the necessary condition for a diamond cluster of any size to be more stable than graphite?

$\Rightarrow$ $\Delta G_{gra} > \Delta G_{dia}$ $\Leftarrow$ dia is more stable than graphite.

$\therefore$ $\Delta G_{gra} - \Delta G_{dia} > 0$

from (c), $n < 36\pi \left[\frac{(\gamma_{gra}^{\frac{2}{3}} d_{gra} - \gamma_{dia}^{\frac{2}{3}} d_{dia})}{({}^{\circ}G_{dia} - {}^{\circ}G_{gra})} \right]^3$

$\therefore$ i) $\gamma_{dia} = 3.6\ J/m^2$, $n < 464$

ii) $\gamma_{dia} = 3.15\ J/m^2$, $n < 145$

iii) $\gamma_{dia} = 3.7\ J/m^2$, $n < 21$

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(e) Assuming that the critical number of atoms for graphite nucleation is 100 estimate the diving force for graphite nucleation

> $n^*_{gra} = 100$

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

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

$$\therefore \Delta G_v = \frac{\gamma}{\left(\frac{3v}{32\pi} n^*\right)^{\frac{1}{3}}} = \frac{0.19344\ eV/\text{Å}^2}{\left(\frac{3 \times 8\text{Å}^3}{32\pi} \cdot 100\right)^{\frac{1}{3}}}$$

$$= 0.06718\ eV/\text{Å}^3$$

$$= 1.0766 \times 10^{10}\ J/m^3$$

(f) compute the ratio of nucleation rate between graphite and diamond, I_{gra}/I_{dia}.

$I = A \cdot \exp(-\Delta G^*/kT)$, A is same constant for both

> 1) $\gamma_{dia} = 3.6\ J/m^2$, $\frac{I_{gra}}{I_{dia}} = \frac{A \exp(-\Delta G^*_{gra}/kT)}{A \exp(-\Delta G^*_{dia}/kT)}$

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

$$\Delta G^*_{dia} - \Delta G^*_{gra} = \frac{16\pi}{3}\left[\frac{\gamma_{dia}^3}{\Delta G_v^{dia^2}} - \frac{\gamma_{gra}^3}{\Delta G_v^{gra^2}}\right]$$

$$v^{dia}\Delta G_v^{dia} = {}^\circ G_{gas} - {}^\circ G_{dia}$$

$$v^{gra}\Delta G_v^{gra} = {}^\circ G_{gas} - {}^\circ G_{gra}$$

$$v^{dia}\Delta G_v^{dia} - v^{gra}\Delta G_v^{gra} = {}^\circ G_{gra} - {}^\circ G_{dia}$$

$$\Delta G_v^{dia} = \frac{v^{gra}\Delta G_v^{gra}({}^\circ G_{gas} - {}^\circ G_{dia})}{v^{dia}}$$

$$= 0.08624\ eV/\text{Å}^3$$

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$$\therefore \frac{I_{gra}}{I_{dia}} = \exp\left(\frac{\Delta G^{*}_{gra} - \Delta G^{*}_{dia}}{kT}\right) = \exp\left[\frac{16\pi}{3kT}\left(\frac{\gamma_{dia}^{3}}{(\Delta G_V^{dia})^2} - \frac{\gamma_{gra}^{3}}{(\Delta G_V^{gra})^2}\right)\right]$$

i) $\gamma_{dia} = 3.6\ J/m^2$, $\Delta G_V^{gra} = \dfrac{V_{dia}\Delta G_V^{dia} - ({}^{\circ}G_{gra} - {}^{\circ}G_{dia})}{V^{gra}} = \dfrac{6\ \text{atom}/\text{Å}^3 \times 0.08624\ eV/\text{Å}^3 - (0.02\ eV/\text{atom})}{8\ \text{Å}^3/\text{atom}}$

$= \dfrac{0.5174\ eV/\text{atom} - 0.02\ eV/\text{atom}}{8\ \text{Å}^3/\text{atom}}$

$T = 1200\ k$, $k = 1.38\times10^{-23}\ J/k$ $= 0.06218\ eV/\text{Å}^3$

$$\therefore \frac{I_{gra}}{I_{dia}} = \exp\left[\frac{16\pi}{3\times8.62\times10^{-5}\times1200}\left(\frac{(0.22464)^3}{(0.08624)^2} - \frac{(0.19344)^3}{(0.06218)^2}\right)\right]$$

$= 3.47\times10^{-25}$

ii) $\gamma_{dia} = 3.15\ J/m^2$, $\dfrac{I_{gra}}{I_{dia}} = \exp\left[\dfrac{16\pi}{3\times8.62\times10^{-5}\times1200}\left(\dfrac{(0.22736)^3}{(0.08624)^2} - \dfrac{(0.19344)^3}{(0.06218)^2}\right)\right]$

$1.5886 \quad 1.0721$

-0.2834

$= 1.17\times10^{-20}$

iii) $\gamma_{dia} = 3.7\ J/m^2$ $\dfrac{I_{gra}}{I_{dia}} = \exp\left[\dfrac{16\pi}{3\times8.62\times10^{-5}\times1200}\left(\dfrac{(0.23088)^3}{(0.08624)^2} - \dfrac{(0.19344)^3}{(0.06218)^2}\right)\right]$

$1.6548 \quad 1.8721$

$0.2516 - 0.2173$

$= 5.28\times10^{-16}$

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(g) what is your conclusion on this problem?

→ nucleation rate ↑ diamond의 surface energy가 더 낮음을 알 수 있고 diamond의 경우 작아질수록 diamond가 graphite보다 안정해지며 nucleation rate가 graphite보다 더 커짐을 알 수 있다.

(h) suppose that the source of carbon in the CVD is the decomposition of CH_4 into C and H_2

$$CH_4 \rightarrow C + 2H_2$$

If C was ~~decompo~~ deposited as graphite, what would be physical meaning of driving force of graphite nucleation

→ 다음의 반응이 일어나면 C의 농도가 증가하게 되고 그러므로 Capillarity effect가 감소하여 graphite가 더 안정하게 된다. 따라서 graphite가 증착되게 높은 C의 농도 즉, Carbon pressure가 driving force이다.

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