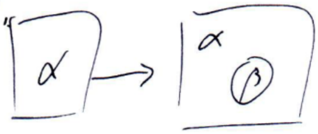
1.



$$dG = -SdT + VdP + \sum \mu_i dn_i + \sum \gamma_i dA_i$$

} const. T & P, for a "spherical" nucleus with radius of "r",

$$\Delta G = -\Delta G_v \delta V + \sum \gamma_i \Delta A_i$$

$$= -\Delta G_v \left(\frac{4}{3}\pi r^3\right) + \gamma \cdot 4\pi r^2$$

In a nucleus, $n = \frac{\left(\frac{4}{3}\pi r^3\right)}{V}$ where V is atomic volume,

n is number of atom in a nucleus

$$\rightarrow r = \left(\frac{3}{4\pi} \cdot nV\right)^{\frac{1}{3}}, \quad 4\pi r^2 = (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} V^{\frac{2}{3}}$$

$$\therefore \Delta G = -\Delta G_v \cdot n \cdot V + \gamma \cdot (36\pi)^{\frac{1}{3}} \cdot (nV)^{\frac{2}{3}}.$$

2. a) (w.l.o.g. problem 1) $\Delta G = -\Delta G_v nV + (36\pi)^{\frac{1}{3}} \gamma (Vn)^{\frac{2}{3}}$

b) when $n = n^*$,

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

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

$$\rightarrow \therefore n^* = \frac{32}{3}\pi \cdot \frac{1}{V} \cdot \frac{\gamma^3}{\Delta G_v^3}.$$

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

※ Note that ΔG_v is Gibbs energy change "per a unit volume".

$$\rightarrow \begin{cases} \Delta G_{gra} = - n_g V_g \dfrac{({}^\circ G_{gr} - {}^\circ G_{gra})}{V_g} + (36\pi)^{\frac{1}{3}} \gamma_g (n_g V_g)^{\frac{2}{3}} \\ \Delta G_{dia} = - n_d V_d \dfrac{({}^\circ G_{gr} - {}^\circ G_{dia})}{V_d} + (36\pi)^{\frac{1}{3}} \gamma_d (n_d V_d)^{\frac{2}{3}} \end{cases}$$

Let $\Delta G_{gra} = \Delta G_{dia}$ when $n_g = n_d = n^*$,

then. $\Delta G_{gra} - \Delta G_{dia} = 0$

$$= - n^* ({}^\circ G_{dia} - {}^\circ G_{gra}) + (36\pi)^{\frac{1}{3}} n^{*\frac{2}{3}} (\gamma_g V_g^{\frac{2}{3}} - \gamma_d V_d^{\frac{2}{3}})$$

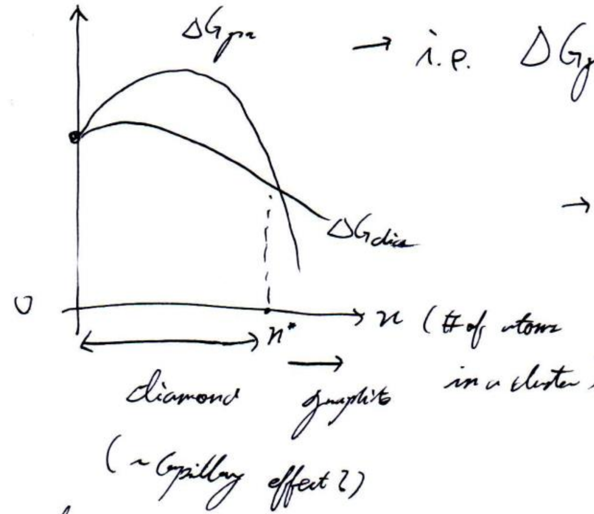
$$\therefore n^* = 36\pi \frac{(\gamma_g V_g^{\frac{2}{3}} - \gamma_d V_d^{\frac{2}{3}})}{({}^\circ G_{dia} - {}^\circ G_{gra})}$$

$\circ$ $1 \, J/m^2 = \frac{J}{m^2} \left(\frac{1m}{10^{10} Å}\right)^2 \cdot \left(\frac{1eV}{1.602\times10^{-19} J}\right)$

$\doteq 6.24 \times 10^{-2} \, eV/Å^2$

$$\Rightarrow \therefore n^* \doteq \begin{cases} 463.9 \ (\sim 440) \text{ when } \gamma_d = 3.6 \ J/m^2 \\ 144.7 \ (\sim 145) \text{ when } \gamma_d = 3.65 \ J/m^2 \\ 21.0 \ (\sim 21) \text{ when } \gamma_d = 3.7 \ J/m^2 \end{cases}$$

d) ΔG



→ i.e. $\Delta G_{gra} > \Delta G_{dia}$ ↔ diamond is more stable than graphite.

→ i.e. $\Delta G_{gra} - \Delta G_{dia} > 0$.

$$\therefore n < n^* \left(= 36\pi \frac{(\gamma_g V_g^{\frac{2}{3}} - \gamma_d V_d^{\frac{2}{3}})}{({}^{\circ}G_{dia} - {}^{\circ}G_{gra})} \right)$$

e) from problem 2.-(a), $n^* = \frac{32}{3}\pi\left(\frac{1}{V}\right)\left(\frac{\gamma}{\Delta G_v}\right)^3 = 100$

$$\rightarrow \Delta G_v = \gamma\left(\frac{32}{3}\pi \cdot \frac{1}{V n^*}\right)^{\frac{1}{3}} \doteq 1.08\times10^{10} J/m^3$$

← $n^* \sim 100$ atoms

$V_g = 8\ Å^3/\text{atom}$

$\gamma_g = 3.1\ J/m^2$

f)

$$\begin{cases} \Delta G^* = -n^* V \Delta G_v + (36\pi)^{\frac{1}{3}} \gamma (n^* V)^{\frac{2}{3}} \\ n^* = \frac{32}{3}\pi \frac{1}{V}\left(\frac{\gamma}{\Delta G_v}\right)^3 \end{cases}$$

$n^* V \Delta G_v \doteq 8.61\times10^{-18} J$

for spherical nucleus ; $\Delta G = -\left(\frac{4}{3}\pi r^3\right)\Delta G + 4\pi r^2 \gamma$

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

$$I_{gra}/I_{dia} = e^{-\frac{1}{kT}(\Delta G_{gra}^* - \Delta G_{dia}^*)}$$

$$= \exp\left[-\frac{1}{kT} \cdot \frac{16\pi}{3}\left(\frac{\gamma_{gra}^3}{\Delta G_{v,gra}^2} - \frac{\gamma_{dia}^3}{\Delta G_{v,dia}^2}\right)\right]$$

let $\gamma_{gra} = 3.1\ J/m^2$, $\Delta G_{v,gra} \approx 1.08\times10^{10} J/m^3$, while $\frac{{}^{\circ}G_{gra} - {}^{\circ}G_{gra}}{V_g} = \Delta G_{v,gra}$ & $\frac{{}^{\circ}G_{gra} - {}^{\circ}G_{dia}}{V_d} = \Delta G_{v,dia}$

$\Downarrow$

$\sim 1.08 \times 10^{-40}$ J/m²

$$\rightarrow V_g \Delta G_{v,gra} - V_d \Delta G_{v,dia} = -{}^{\circ}G_{gra} + {}^{\circ}G_{dia}$$

$$\therefore \Delta G_{v,dia} = \frac{V_g \Delta G_{v,gra} + ({}^{\circ}G_{gra} - {}^{\circ}G_{dia})}{V_d}$$

$({}^{\circ}G_{gra} - {}^{\circ}G_{dia}) = -0.02$ eV/atom

$$\doteq 1.39 \times 10^{10} \text{ J/m}^2$$

$$\therefore I_{gra}/I_{dia} = \exp\left[-\frac{1}{kT} \cdot \frac{16}{3}\pi\left(\frac{\gamma_{gra}^3}{\Delta G_{v,gra}^2} - \frac{\gamma_{dia}^3}{\Delta G_{v,dia}^2}\right)\right]$$ ← Let T = 298 K.

$$= \begin{cases} 1.39 \times 10^{-20} & \text{when } \gamma_{dia} = 3.6 \\ 2.53 \times 10^{-7} & \text{when } \gamma_{dia} = 3.65 \\ 8.88 \times 10^{11} & \text{when } \gamma_{dia} = 3.7 \end{cases} \quad (\text{J/m}^2)$$

g) Although "bulk" diamond is less stable than "bulk" graphite, nano-crystalline diamond can be more stable than nano-crystalline graphite and the nucleation rate (~ formation of diamond) is significantly sensitive to the surface energy.

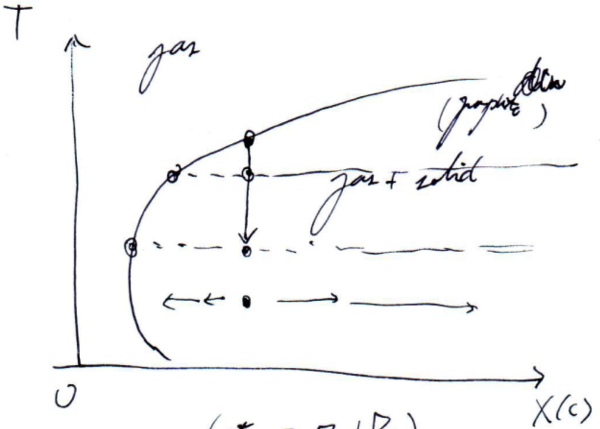
Consequently, control of the surface energy of nanocrystal can be an important key to yield the diamond more.

f)

$$CH_4(g) \rightarrow C(g) + 2H_2(g) \quad Q_1 \propto \frac{[C(g)]}{[CH_4]}$$

$$\rightarrow C(s)\downarrow + 2H_2(g) \quad Q_2 \propto \frac{[C(s)]}{[C(g)]}$$

$$CH_4(g) \rightarrow C\downarrow + 2H_2(g)$$



(at 2.7 kPa)

→ "Supersaturation" of carbon in the gas state.

(→ decomposition → P_c increases → ...)

↑ partial pressure of carbon