HW5 20222571 최찬식

1. a). for a spherical nucleus, the energy change during nucleation as a function of radius of nucleus.

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

for a spherical nucleus which have volume of $\frac{4}{3}\pi r^3$ there are n number of atoms.

ΔG_v is expressed as energy per unit volume. and ΔG_a is expressed as energy per atom.

$\Delta G_v = \frac{1}{v}\Delta G_a$. and $\underline{\frac{4}{3}\pi r^3 / v = n}$ ① so that $\frac{4}{3}\pi r^3 \Delta G_v$ is converted to $n\Delta G_a$.

from ①. $r = \left(\frac{3nv}{4\pi}\right)^{\frac{1}{3}} = \left(\frac{3}{4\pi}\right)^{\frac{1}{3}} \cdot n^{\frac{1}{3}} \cdot v^{\frac{1}{3}}$

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

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

b). $\frac{d}{dn}\Delta G = -\Delta G_a + \frac{2}{3}(36\pi)^{\frac{1}{3}} n^{-\frac{1}{3}} \cdot v^{\frac{2}{3}} \cdot \gamma$. for $n = n^*$. $\frac{d}{dn}\Delta G\big|_{n^*} = 0$. n^* is critical number of atoms.

$\Delta G_a = \left(\frac{32}{3}\pi\right)^{\frac{1}{3}} n^{-\frac{1}{3}} \cdot v^{\frac{2}{3}} \cdot \gamma$. $\qquad n^* = \left(\frac{32}{3}\pi\right) \cdot v^2 \cdot \left(\frac{\gamma}{\Delta G_a}\right)^3$

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

$$= \frac{v^2 \gamma^3}{\Delta G_a^2}\left(-\frac{32}{3}\pi + 16\pi\right)$$

$$\therefore \Delta G^* = \frac{16}{3}\pi \frac{v^2 \gamma^3}{\Delta G_a^2}$$

c). for graphite. $\Delta G_a = {}^\circ G_a - {}^\circ G_{gr}$.

$$\Delta G_{gr} = -n_{gr}({}^\circ G_a - {}^\circ G_{gr}) + (36\pi)^{\frac{1}{3}} n_{gr}^{\frac{2}{3}} \cdot v_{gr}^{\frac{2}{3}} \cdot \gamma_{gr}$$

for diamond. $\Delta G_a = {}^\circ G_a - {}^\circ G_{dia}$.

$$\Delta G_{dia} = -n_{dia}({}^\circ G_a - {}^\circ G_{dia}) + (36\pi)^{\frac{1}{3}} n_{dia}^{\frac{2}{3}} \cdot v_{dia}^{\frac{2}{3}} \gamma_{dia}$$

same stability.

$\Delta G_{gr} = \Delta G_{dia}$ and $n_{dia} = n_{gr}$.

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

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

$$\therefore n = \frac{(36\pi)\left(v_{gr}^{\frac{2}{3}} \gamma_{gr} - v_{dia}^{\frac{2}{3}} \gamma_{dia}\right)^3 \cdot (J/atom)^3}{(0.02\ eV/atom)^3}$$

① $\gamma_{dia} = 3.6.$ $n = 464$

②. $\gamma_{dia} = 3.65.$ $n = 145.$

③. $\gamma_{dia} = 3.7$ $n = 21$

d). $\Delta G_{gr} > \Delta G_{dia}$. for any given n value.

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

$$n < \frac{36\pi\left[v_{gr}^{\frac{2}{3}}\gamma_{gr} - v_{dia}^{\frac{2}{3}}\gamma_{dia}\right]^3}{(0.02\,eV/atom)^3}$$

and the right component should diverge. $\gamma_{dia} \ll \gamma_{gr}$.

e) $n^* = 100.$

formula for critical number of atoms in a cluster.

$$n^* = \left(\frac{32}{3}\pi\right)v^2\left(\frac{\gamma}{\Delta G_a}\right)^3 = 100$$

$$\Delta G_{v,g} = \frac{1}{v}\Delta G_a = \frac{atom}{8A^3}\cdot 0.538\,eV/atom$$

$$= 6.725\times10^{28}\,eV/m^3.$$

$$\Delta G_a = \left(\frac{32\pi}{3}\cdot\frac{v^2}{n}\right)^{\frac{1}{3}}\cdot\gamma = 0.538\,eV/atom$$

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

$$\Delta G^*_{gr} - \Delta G^*_{dia} = n^*({}^{\circ}G_{gr} - {}^{\circ}G_{dia}) - (36\pi)^{\frac{1}{3}}\left(v_{dia}^{\frac{2}{3}}\gamma_{dia} - v_{gr}^{\frac{2}{3}}\gamma_{gr}\right)n^{*\frac{2}{3}}$$

$$= -0.02\times n^* - (36\pi)^{\frac{1}{3}}\left(v_{dia}^{\frac{2}{3}}\gamma_{dia} - v_{gr}^{\frac{2}{3}}\gamma_{gr}\right)n^{*\frac{2}{3}}$$

assume. $n^* = 100.$

① $\gamma_{dia} = 3.6\,J/m^2$

$$\Delta G^*_{gr} - \Delta G^*_{dia} = -0.02\times100 + 3.34\,eV = 1.34\,eV.$$

$$I_{gr}/I_{dia} = A\cdot\exp\left[-\frac{1.34\,eV}{k_B\cdot300}\right] = A\cdot3.08\times10^{-23}.$$

② $\gamma_{dia} = 3.65\,J/m^2$

$$\Delta G^*_{gr} - \Delta G^*_{dia} = -2eV + 2.26eV = 0.26eV$$

$$I_{gr}/I_{dia} = A\exp\left[-\frac{0.26eV}{k_B\cdot300}\right] = A\cdot4.29\times10^{-5}.$$

③ $\gamma_{dia} = 3.7\,J/m^2$

$\Delta G^*_{gr} - \Delta G^*_{dia} = -2eV + 1.19eV = -0.81eV.$ $I_{gr}/I_{dia} = A\cdot4.05\times10^{13}.$

9). Even small difference in surface energy of diamond, the critical size of nucleus is significantly affected.
this means, if a condition where surface energy of diamond increased is made, the diamond nucleus dominates the whole ratio.

However, as nucleation rate is affected by surface energy, even if the critical nucleus size is small, the nucleation rate is sluggish. After all, the nucleus is desolved.

In this problem, it is a good opportunity to consider both the nucleation thermodynamics and kinetics.