

$$1. \quad \Delta G = -V \Delta G_v + A \cdot \gamma$$

Spherical nucleus ; $V = \frac{4}{3} \pi r^3$

$$A = 4\pi r^2$$

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

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

$$\begin{aligned} \Delta G &= -nV \cdot \Delta G_v + 4\pi \left(\frac{3}{4\pi} nV \right)^{2/3} \cdot \gamma \\ &= -nV \cdot \Delta G_v + (36\pi)^{1/3} \cdot n^{2/3} \cdot V^{2/3} \cdot \gamma \end{aligned}$$

2.

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

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

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

$$\begin{aligned} \Delta G^* &= -n^* \cdot V \cdot \Delta G_v + (36\pi)^{1/3} \cdot n^{*2/3} \cdot V^{2/3} \cdot \gamma \\ &= -\frac{32\pi}{3} \frac{\gamma^3}{(\Delta G_v)^2} + (4 \times 32^2)^{1/3} \pi \cdot \frac{r^3}{(\Delta G_v)^2} \\ &= \frac{16\pi}{3} \cdot \frac{r^3}{(\Delta G_v)^2} \end{aligned}$$

$$(c) \quad \Delta G_{gr} = -n(\Delta G_v - \Delta G_{gr}) + (36\pi)^{1/3} n^{2/3} V_{gr}^{2/3} \gamma_{gr}$$

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

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

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

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

$$i) \gamma_{dia} = 9.6 \text{ J/m}^2, n = 465$$

$$ii) \gamma_{dia} = 3.65 \text{ J/m}^2, n = 145$$

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

(d) diamond

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

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

$$(e) \quad n^* = \frac{32\pi}{3V} \left(\frac{\gamma}{\Delta G_v} \right)^3 = 100$$

$$\Delta G_{vgr} = 1.08 \times 10^{10} \text{ J/m}^3 \quad (\text{driving force for graphite nucleation})$$

$$\text{f)} \quad \frac{I_{gr}}{I_{dra}} = \frac{A \exp(-\Delta G_{gr}^*/kT)}{A \exp(-\Delta G_{dra}^*/kT)} = \exp \left[- \frac{(\Delta G_{gr}^* - \Delta G_{dra}^*)}{kT} \right]$$

$$\Delta G_{gr}^* = \frac{16}{3} \pi \frac{\gamma_{gr}^3}{(\Delta G_{v,gr})^2} = 4.3 \times 10^{-18} \text{ J}$$

$$\Delta G_{dra}^* = \frac{16}{3} \pi \frac{\gamma_{dra}^3}{(\Delta G_{v,dra})^2}$$

$$\text{① } \gamma_{dra} = 3.6 \text{ J/m}^2 \rightarrow \Delta G_{dra}^* = 4.10 \times 10^{-18} \text{ J}$$

$$\text{② } \gamma_{dra} = 3.65 \text{ J/m}^2 \rightarrow \Delta G_{dra}^* = 4.28 \times 10^{-18} \text{ J}$$

$$\text{③ } \gamma_{dra} = 3.7 \text{ J/m}^2 \rightarrow \Delta G_{dra}^* = 4.46 \times 10^{-18} \text{ J}$$

$$T = 300 \text{ K}, \quad \frac{I_{gr}}{I_{dra}} = \exp \left[\frac{\Delta G_{dra}^* - \Delta G_{gr}^*}{4.14 \times 10^{-21} \text{ J}} \right]$$

$$\text{① } 3.42 \times 10^{21}$$

$$\text{② } 5.29 \times 10^{23}$$

$$\text{③ } 2.61 \times 10^{16}$$

(g) Diamond is unstable than graphite in case of bulk. However, in case of small nanoscale size, we have to consider surface and surface energy as effect of surface energy increase. When surface energy of diamond increase, nucleation rate of diamond decrease.

(h) $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$ is decomposition.

As CH_4 is decomposed, concentration of C increase. If concentration of C increases, capillary effect is not applied, and therefore eq. ($\Delta G_{v,gr} > \Delta G_{v,dia}$) cannot be established.

eq. ($\Delta G_{v,gr} > \Delta G_{v,dia}$) is defined in nanometer as capillary effect is applied.