Phase transformation 20192742 손수정

Homework #5

1. 원형의 nuclei에 있는 atom의 수 n 일때

nuclei 의 부피 $V = n \cdot v$ 임

nuclei 의 표면적는 $A = 4\pi r^2$ (r은 nuclei의 반지름)

이때 $V = n \times v = \frac{4}{3}\pi r^3$ 이므로, $r = \left(\frac{3}{4\pi} n \times v\right)^{\frac{1}{3}}$

$$A = 4\pi r^2 = 4\pi \left(\frac{3}{4\pi} n \times v\right)^{\frac{2}{3}} = (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} v^{\frac{2}{3}}$$

즉 $\Delta G = -V \Delta G_v + A\gamma$

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

2.

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

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

n^*: critical number of atom

$$n^* = \left(\frac{3 \cdot v \cdot \Delta G_v}{2(36\pi)^{\frac{1}{3}} v^{\frac{2}{3}} \gamma}\right)^{-3} = \frac{8 \cdot 36\pi \cdot v^2 \gamma^3}{27 \cdot v^3 \cdot \Delta G_v^3} = \frac{32\pi\gamma^3}{3 v \Delta G_v^3}$$

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

$$= -\frac{32\pi}{3\Delta G_v^2}\gamma^3 + \left(36\pi \cdot \frac{(32)^2 \pi^2 \gamma^6}{9 v^2 \Delta G_v^6}\right)^{\frac{1}{3}} v^{\frac{2}{3}} \cdot \gamma$$

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

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

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

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

$$n^* = 36\pi \cdot \left(\frac{V_{dia}^{\frac{2}{3}} \gamma_{dia} - V_{gr}^{\frac{2}{3}} \gamma_{gr}}{{}^\circ G_{gr} - {}^\circ G_{dia}}\right)^3$$

$\gamma_{dia} = 3.6\ J/m^2$ $\quad n = 36\pi\left(\frac{6^{\frac{2}{3}} \cdot 0.2246 - 8^{\frac{2}{3}}\, 0.1934}{-0.02}\right)^3 = 462.69 \approx 463$개

$\gamma_{dia} = 3.65\ J/m^2$ $\quad n = 36\pi\left(\frac{6^{\frac{2}{3}} \cdot 0.2278 - 8^{\frac{2}{3}}\, 0.1934}{-0.02}\right)^3 = 138.96 \approx 139$개

$\gamma_{dia} = 3.7\ J/m^2$ $\quad n = 36\pi\left(\frac{(6)^{\frac{2}{3}} \cdot 0.2309 - 8^{\frac{2}{3}} \cdot 0.1934}{-0.02}\right)^3 = 19.78 \approx 20$개

(d) $\Delta G_{dia} < \Delta G_{gr}$

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

(e) $n^* = 100 = \frac{32\pi \, \gamma_{gr}^3}{3 V_{gr} \Delta G_v^3} = \frac{32\pi \, (3.1 J/m^2)^3}{3 \times 8 \times 10^{-30} m^3/atom \, \Delta G_v^3}$ $\quad \Delta G_v^{gr} = 1.077 \times 10^{10} J/m^3$

(f) $I = A \cdot \exp\left(-\frac{\Delta G^*}{kT}\right)$

$$\frac{I_{gr}}{I_{dia}} = \frac{A \exp\left(-\frac{\Delta G^*_{gr}}{kT}\right)}{A \exp\left(-\frac{\Delta G^*_{dia}}{kT}\right)} = \exp\left(\frac{\Delta G^*_{dia} - \Delta G^*_{gr}}{kT}\right) = 1.38 \times 10^{10} J/m^3$$

$\Delta G_{gr}^* = 4.3 \times 10^{-18} J$ / $\Delta G_{dia}^* = 4.10 \times 10^{-18} J$ (when $\gamma_{dia} = 3.6 J/m^2$)

$\Delta G_{dia}^* = 4.28 \times 10^{-18} J$ (when $\gamma_{dia} = 3.65 J/m^2$)

$\Delta G_{dia}^* = 4.46 \times 10^{-18} J$ (when $\gamma_{dia} = 3.7 J/m^2$)

상온임을 가정하면 $T = 300K$, $kT = 1.38 \times 10^{-23} \times 300 = 4.14 \times 10^{-21}$

$$\frac{I_{gr}}{I_{dia}} = \exp\left(\frac{\Delta G^*_{dia} - 4.3 \times 10^{-18} J}{4.14 \times 10^{-21} J}\right) = 3.42 \times 10^{-21} \quad (\gamma_{dia} = 3.6 J/m^2)$$

$= 5.29 \times 10^{-3}$ $(\gamma_{dia} = 3.65 J/m^2)$

$= 2.61 \times 10^{16}$ $(\gamma_{dia} = 3.7 J/m^2)$

(g) bulk일 때는 diamond가 불안정하다. 그러나 입자가 매우 작아지면 surface energy의 영향이 더욱 커진다.

(e)의 결과를 보면 n^*가 γ_{gr}의 영향을 받으며, 즉 diamond의 surface energy가 증가하면 nucleation에 더 많은 energy가 필요하고 nucleation이 감소한다

(h) graphite로 생성되었으므로 $\frac{I_{gr}}{I_{dia}} >> 1$임, 이는 ΔG_{gr}이 매우 커서 driving force로 작용했음을 의미하며 충분한 nuclei 크기로 ΔG_v가 γ보다 큰 영향을 끼침을 보여준다.