AMSE502 Phase Transformations 상변태론 HW #5

신소재공학과 20222244 조 우 택

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

sol) $dG = -SdT + VdP + \Sigma \mu_i dn_i + \gamma dA$

at const T, P

$dG = \mu_{vap} dn_{vap} + \mu_{liq} dn_{liq} + \gamma dA$

$= -(\mu_{vap} - \mu_{liq}) dn_{liq} + \gamma dA$

set driving force $\Delta G_v = -(\mu_{liq} - \mu_{vap}) = \Delta G_{vaporization}$ (per volume of liq)

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

for spherical nucleus of atoms n, $n \cdot v = \frac{4}{3}\pi r^3$

$r = \left(\frac{3vn}{4\pi}\right)^{\frac{1}{3}}$

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

$= -nv\Delta G_v + (4\pi)^{\frac{1}{3}} \cdot (3vn)^{\frac{2}{3}} \cdot \gamma$

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

set, $v \cdot \Delta G_v = \Delta G_a$

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

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

(i) n^*

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

$\Delta G_a^3 = 36\pi \cdot \frac{8}{27} \cdot n^{*-1} \cdot v^2 \cdot \gamma^3$

$\underline{n^* = \frac{32\pi}{3} \cdot \frac{v^2 \cdot \gamma^3}{(\Delta G_a)^3}}$

(ii) ΔG^*

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

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

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

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

c) $n = ?$

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

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

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

stability of diamond becomes the same as that of gr, $\Delta G_{gr} = \Delta G_{dia}$

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

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

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

$\gamma_{gr} = 3.1\ J/m^2$ $\quad \gamma_{dia} = 3.6,\ 3.65,\ 3.7\ J/m^2$ $\quad V_{gr} = 8\ \mathring{A}^3/atom$, $\quad V_{dia} = 6\ \mathring{A}^3/atom$ $\quad {}^\circ G_{dia} - {}^\circ G_{gr} = 0.02eV/atom$

(i) $\gamma_{dia} = 3.6\ J/m^2$

$$n = 36\pi \frac{\{(6\times10^{-30} m^3/atom)^{\frac{2}{3}}(3.6 J/m^2) - (8\times10^{-30} m^3/atom)^{\frac{2}{3}}(3.1 J/m^2)\}^3}{(-0.02\times1.602\times10^{-19} J/atom)^3} = 464 \text{ atoms}$$

(ii) $\gamma_{dia} = 3.65\ J/m^2$

$n = 145$ atoms

(iii) $\gamma_{dia} = 3.7\ J/m^2$

$n = 21$ atoms

d) $\Delta G_{gr} > \Delta G_{dia}$ 일 때 diamond가 graphite보다 더 안정하다.

$$-n({}^{\circ}G_v - {}^{\circ}G_{gr}) + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} v_{gr}^{\frac{2}{3}} \gamma_{gr} > -n({}^{\circ}G_v - {}^{\circ}G_{dia}) + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} v_{dia}^{\frac{2}{3}} \gamma_{dia}$$

$$n({}^{\circ}G_{dia} - {}^{\circ}G_{gr}) < (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} (v_{gr}^{\frac{2}{3}} \gamma_{gr} - v_{dia}^{\frac{2}{3}} \gamma_{dia})$$

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

(i) $\gamma_{dia} = 3.6 J/m^2 \rightarrow n < 464$ atoms

(ii) $\gamma_{dia} = 3.65 J/m^2 \rightarrow n < 145$ atoms

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

e) Given, $n^* = 100$, $\Delta G_v = ?$

$$n^* = \frac{32\pi}{3} \cdot \frac{v_{gr}^2 \cdot \gamma_{gr}^3}{(\Delta G_a)^3}$$

$$\Delta G_{a,gra} = \left(\frac{32\pi}{3} \frac{v_{gr}^2 \gamma_{gr}^3}{n^*} \right)^{\frac{1}{3}}$$

$$= \left\{ \frac{32\pi}{3} \cdot \frac{(8 \times 10^{-30} m^3/atom)^2 (3.1 J/m^2)^3}{100\ atom} \right\}^{\frac{1}{3}}$$

$$= 8.61 \times 10^{-20} J/atom$$

$$\Delta G_{v,gra} = \frac{\Delta G_{a,gra}}{v_{gra}} = 1.08 \times 10^{10} J/m^3$$

f) $I = A \cdot \exp(-\Delta G^*/kT)$, $T = 300K$

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

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

$$\Delta G^*_{dia} = \frac{16\pi}{3} \frac{v_{dia}^2 \cdot \gamma_{dia}^3}{(\Delta G_{a,dia})^2} = \frac{16\pi}{3} \frac{\gamma_{dia}^3}{(\Delta G_{v,dia})^2}$$

$$\Delta G^*_{gra} = \frac{16\pi}{3} \frac{v_{gr}^2 \cdot \gamma_{gr}^3}{(\Delta G_{a,gra})^2} = \frac{16\pi}{3} \frac{\gamma_{gra}^3}{(\Delta G_{v,gra})^2}$$

- (e) 에서, $\Delta G_{v,gra} = 1.08 \times 10^{10} J/m^3$
- ${}^{\circ}G_{dia} - {}^{\circ}G_{gr} = v_{gr} \Delta G_{v,gr} - v_{dia} \Delta G_{v,dia} = 0.02 eV/atom$

$$\Delta G_{v,dia} = \frac{-0.02 \times 1.602 \times 10^{-19} J/atom + (8 \times 10^{-30} m^3/atom)(1.08 \times 10^{10} J/m^3)}{6 \times 10^{-30} m^3/atom}$$

$$\Delta G_{v,dia} = 1.387 \times 10^{10} J/m^3$$

- $$\Delta G^*_{gra} = \frac{16\pi}{3} \frac{(3.1 J/m^2)^3}{(1.08 \times 10^{10} J/m^3)^2} = 4.28 \times 10^{-18} J$$

(i) $\gamma_{dia} = 3.6 J/m^2$

$$\Delta G^*_{dia} = \frac{16\pi}{3} \frac{(3.6 J/m^2)^3}{(1.387 \times 10^{10} J/m^3)^2} = 4.06 \times 10^{-18} J$$

$$I_{gra}/I_{dia} = \exp\left\{ \frac{(4.06 - 4.28) \times 10^{-18} J}{(1.381 \times 10^{-23} J/K)(300K)} \right\}$$

$$= 8.67 \times 10^{-24}$$

(ii) $\gamma_{dia} = 3.65 J/m^2$

$$\Delta G^*_{dia} = 4.24 \times 10^{-18} J$$

$$I_{gra}/I_{dia} = 6.41 \times 10^{-5}$$

(iii) $\gamma_{dia} = 3.7 J/m^2$

$$\Delta G^*_{dia} = 4.41 \times 10^{-18} J$$

$$I_{gra}/I_{dia} = 4.24 \times 10^{13}$$

g) Bulk 상태에서는 graphite 상태가 더 안정하지만 cluster size가 작아지면 diamond 상이 graphite상보다 안정할 수 있다.
γ_{dia}가 작을수록 I_{dia}가 I_{gra} 보다 빨라지기 때문에 surface energy를 조절한다면 CVD로 diamond를 만들 수 있을 것이다.