Phase transformation HW3

2015200 3
김용민

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

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

$4\pi r^2 = 4\pi \cdot \left(\frac{3nV}{4\pi}\right)^{2/3} = \frac{4\pi}{(4\pi)^{2/3}} \cdot 3^{2/3} \cdot n^{2/3} V^{2/3} = (4\pi)^{1/3} \cdot 9^{1/3} \cdot n^{2/3} V^{2/3}$

$= (36\pi)^{1/3} n^{2/3} V^{2/3}$

$\therefore \Delta G = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma = -nV\Delta G_v + (36\pi)^{1/3} n^{2/3} V^{2/3} \gamma$

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

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

$\therefore n^{-\frac{1}{3}} = \frac{V\Delta G_v}{(36\pi)^{1/3} \cdot \frac{2}{3} \cdot V^{2/3} \gamma} \Rightarrow n = \frac{36\pi \cdot \left(\frac{2}{3}\right)^3 \cdot V^2 \cdot \gamma^3}{(V\Delta G_v)^3} = \frac{32\pi}{3V} \left(\frac{\gamma}{\Delta G_v}\right)^3$

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

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

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

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

c) $1\,J/m^2 = 6.24 \times 10^{-2}\,eV/Å^2 \Rightarrow \gamma_{gr} = 3.1\,J/m^2 = 0.19344\,eV/Å^2$

$\gamma_{dia} = \begin{cases} 3.6\,J/m^2 = 0.22464\,eV/Å^2 \\ 3.65\,J/m^2 = 0.22776\,eV/Å^2 \\ 3.75\,J/m^2 = 0.23088\,eV/Å^2 \end{cases}$

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

Diamond 의 Stability 가 graphite 와 같다. $\Leftrightarrow \Delta G^{dia} = \Delta G^{gra}$

$\therefore -nV_{dia}\left(G_V^{gas}-G_V^{o\,dia}\right)+(36\pi)^{1/3}n^{2/3}V_{dia}^{2/3}\gamma_{dia}=-nV_{gra}\left(G_V^{gas}-G_V^{o\,gra}\right)+(36\pi)^{1/3}n^{2/3}V_{gra}^{2/3}\gamma_{gra}$

$\Rightarrow (36\pi)^{1/3}n^{2/3}\left(V_{dia}^{2/3}\gamma_{dia}-V_{gra}^{2/3}\gamma_{gra}\right)=n\left(G^o_{gra}-G^o_{dia}\right)$ (이때의 G는 molar value이다)

$$\therefore n=36\pi\cdot\left(\frac{V_{gra}^{2/3}\gamma_{gra}-V_{dia}^{2/3}\gamma_{dia}}{G^o_{dia}-G^o_{gra}}\right)^3$$

i) $\gamma_{dia}=3.6\,J/m^2$ 일때 $n=36\pi\left(\frac{8^{2/3}\cdot 0.19344-6^{2/3}\cdot 0.22464}{0.02}\right)^3=464$

ii) $\gamma_{dia}=3.65\,J/m^2$ 일때 $n=36\pi\left(\frac{8^{2/3}\cdot 0.19344-6^{2/3}\cdot 0.22776}{0.02}\right)^3=145$

iii) $\gamma_{dia}=3.7\,J/m^2$ 일때 $n=36\pi\left(\frac{8^{2/3}\cdot 0.19344-6^{2/3}\cdot 0.23088}{0.02}\right)^3=21$

(d) diamond cluster가 graphite 보다 안정하기 위해서는 $\Delta G^{dia}<\Delta G^{gra}$ 이어야 한다.

$\therefore \Delta G^{dia}-\Delta G^{gra}=n\left(G^o_{dia}-G^o_{gra}\right)+(36\pi)^{1/3}n^{2/3}\left(V_{dia}^{2/3}\gamma_{dia}-V_{gra}^{2/3}\gamma_{gra}\right)<0$

$=0.02n^{1/3}+(36\pi)^{1/3}\cdot\left(V_{dia}^{2/3}\gamma_{dia}-V_{gra}^{2/3}\gamma_{gra}\right)<0$

$$\therefore n<36\pi\cdot\left(\frac{V_{gra}^{2/3}\gamma_{gra}-V_{dia}^{2/3}\gamma_{dia}}{0.02}\right)^3$$

e) $n^*=\frac{32\pi}{3V_{gra}}\left(\frac{\gamma_{gra}}{\Delta G_V^{gra}}\right)^3=100 \Rightarrow \Delta G_V^{gra}=\left(\frac{32\pi}{3V_{gra}\cdot 100}\right)^{1/3}\cdot\gamma_{gra}$

$=\left(\frac{32\pi}{3\cdot 8\cdot 100}\right)^{1/3}\cdot 0.19344$

$=0.06718\ eV/Å^3$

$=1.076\times10^{10}\ J/m^3$

f) $A_{gra}=A_{dia}=A$, $\Delta G^*=\frac{16\pi}{3}\frac{\gamma^3}{\Delta G_V^2}$

$$\frac{I_{gra}}{I_{dia}}=\frac{Ae^{-\frac{\Delta G^*_{gra}}{kT}}}{Ae^{-\frac{\Delta G^*_{dia}}{kT}}}=e^{\frac{\Delta G^*_{dia}-\Delta G^*_{gra}}{kT}}=\mathrm{Exp}\left[\frac{16\pi}{3kT}\cdot\left(\frac{\gamma_{dia}^3}{\Delta G_V^{dia\,2}}-\frac{\gamma_{gra}^3}{\Delta G_V^{gra\,2}}\right)\right]$$

이때 $V^{dia}\Delta G_V^{dia}={}^oG^{gas}-{}^oG^{dia}$

$-\ \left| V^{gra}\Delta G_V^{gra}={}^oG^{gas}-{}^oG^{gra}\right.$

$V^{dia}\Delta G_V^{dia}-V^{gra}\Delta G_V^{gra}={}^oG^{gra}-{}^oG^{dia}$

$\Rightarrow \Delta G_V^{dia}=\frac{V^{gra}\Delta G_V^{gra}-\left({}^oG^{dia}-{}^oG^{gra}\right)}{V^{dia}}$

$=\frac{8\cdot 0.06718-0.02}{6}$

$=0.086241\ eV/Å^3=1.38\times10^{10}\ J/m^3$

$$\therefore \frac{I_{gra}}{I_{dia}} = Exp\left[\frac{16\pi}{3\cdot 8.62\times10^{-5}\cdot 300}\left(\frac{\gamma_{dia}^3}{0.086241^2} - \frac{0.19344^3}{0.06718^2}\right)\right] \quad (300K 가정)$$

i) $\gamma = 3.6 J/m^2$, $\frac{I_{gra}}{I_{dia}} = 3.93\times10^{-23}$

ii) $\gamma = 3.65 J/m^2$, $\frac{I_{gra}}{I_{dia}} = 5.18\times10^{-5}$

iii) $\gamma = 3.7 J/m^2$, $\frac{I_{gra}}{I_{dia}} = 2.17\times10^{14}$

g) Bulk 상태에서는 graphite의 Gibbs energy of formation이 더 낮아 diamond 보다 더 안정하게 존재한다. 하지만 bulk가 아닌 작은 size 에서는 capilliary effect 로 인해 diamond가 graphite 보다 더 안정하게 nucleation이 일어날 수 있다. f 에서 보다시피 두 상간의 nucleation rate 의 비율은 diamond의 surface energy에 민감하며, diamond 의 surface energy가 더 커질수록 diamond nuclei의 비율은 감소함을 알 수있다.

h) $CH_4 \leftrightarrow C + 2H_2$ 는 흡열 반응이다. CH_4의 분해가 활발하려면 높은 열이 필요하며, 이경우 CVD 내의 C gas의 농도가 커지게 된다. 이때 C gas가 더 많은 atom 으로 이루어진 nuclei를 형성할 확률이 증가한다. 이 경우 에너지 순위에 역전이 일어나 이 영역에서는 graphite nuclei가 diamond보다 더 안정하다 (capilliary effect 감소) 따라서 graphite가 증착이 된다.