2016 2530

장효선

상변태론 hw 3

1\. i) Vapor 가 liquid 로 바뀔 때 free energy 변화는,

$$dG = -SdT + VdP + \sum \mu_i dn_i + \gamma dA$$

constant T, P 일 때,

$$dG = \sum \mu_i dn_i + \gamma dA$$

이때 system 내에 vapor 와 liquid 만 존재한다고 하면

$$dG = \mu_v dn_v + \mu_l dn_l + \gamma dA$$

$$= \mu_v(-dn_l) + \mu_l dn_l + \gamma dA$$

$$= -(\mu_v - \mu_l) dn_l + \gamma dA$$

$$= -\Delta G_v dV + \gamma dA$$

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

이때 liquid nucleus 이 spherical 이라고 가정하고,

$$V = \frac{4}{3}\pi r^3. \qquad A = 4\pi r^2$$

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

ii) $v \equiv$ molecular (atomic) volume.

$n \equiv$ number of molecules (atoms) in cluster

라고 정의하면,

$$nv \doteq V = \frac{4}{3}\pi r^3.$$

이것을 r에 관하여 풀면,

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

$$4\pi r^2 = 4\pi \cdot \left(\frac{3nv}{4\pi}\right)^{2/3} = (4\pi)^{1/3} \cdot (3nv)^{2/3} = (36\pi)^{1/3} (nv)^{2/3}$$

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

2 (a) 1 의 결과를 인용하면,

$$\Delta G = n\Delta\mu^{gas\to solid} + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} \Omega^{\frac{2}{3}} \sigma$$
$$= n\Delta\mu + 4\pi\left(\frac{3\Omega}{4\pi}\right)^{\frac{2}{3}} n^{\frac{2}{3}}\sigma$$

(b)
$$\left.\frac{\partial\Delta G}{\partial n}\right|_{n=n^*} = \Delta\mu + 4\pi\cdot\frac{2}{3}\left(\frac{3\Omega}{4\pi}\right)^{\frac{2}{3}} n^{*-\frac{1}{3}}\sigma = 0$$

$$n^* = \left(-\frac{\frac{8}{3}\pi\left(\frac{3\Omega}{4\pi}\right)^{\frac{2}{3}}\sigma}{\Delta\mu}\right)^3$$
$$= -\frac{8^3\pi^3}{27}\cdot\frac{9\Omega^2}{16\pi^2}\cdot\left(\frac{\sigma}{\Delta\mu}\right)^3$$
$$= -\frac{32}{3}\pi\Omega^2\left(\frac{\sigma}{\Delta\mu}\right)^3$$

$$\Delta G^* = n^*\Delta\mu + 4\pi\left(\frac{3\Omega}{4\pi}\right)^{\frac{2}{3}}\cdot(n^*)^{\frac{2}{3}}\sigma$$
$$= -\frac{32}{3}\pi\Omega^2\left(\frac{\sigma}{\Delta\mu}\right)^3\Delta\mu + 4\pi\left(\frac{3\Omega}{4\pi}\right)^{\frac{2}{3}}\cdot\left(\frac{32\pi}{3}\right)^{\frac{2}{3}}\Omega^{\frac{4}{3}}\left(\frac{\sigma}{\Delta\mu}\right)^2\sigma$$
$$= -\frac{32\pi\Omega^2\sigma^3}{3(\Delta\mu)^2} + \frac{16\pi\Omega^2\sigma^3}{\Delta\mu^2}$$
$$= \frac{16\pi\Omega^2\sigma^3}{3(\Delta\mu)^2}$$

(c) 2-(b)의 결과는 gas → solid 로 nucleation 될 때 이다.
이 식을 graphite 와 diamond 에 대해서 적용하면

$$\Delta G_{gr} - \Delta G_{dia} = n\left(\Delta\mu^{gas\to gra} - \Delta\mu^{gas\to dia}\right) + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}}\left(\Omega_{gra}^{2/3}\cdot\sigma_{gra} - \Omega_{dia}^{2/3}\sigma_{dia}\right) = 0$$
$$\therefore n = (36\pi)\left(\Omega_{gra}^{2/3}\sigma_{gra} - \Omega_{dia}^{2/3}\sigma_{dia}\right) / \left({}^{\circ}G_{dia} - {}^{\circ}G_{gra}\right)$$

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

$$n = 32\pi\left[\frac{3.4\ J/m^2\cdot(8\times10^{-30}\ m^3/atom)^{2/3} - 3.6\ J/m^2\,(6\times10^{-30}\ m^3/atom)^{2/3}}{40.02\times1.6022\times10^{-19}\ J/atom}\right]^3$$
$$= 464\ atom$$

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

$n = 147\ atom$

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

$n = 21\ atom$

2 (d) size에 상관없이 diamond cluster가 graphite보다 안정하기 위해서는
$\Delta\mu^{dia \to gra} > 0$ 이어야 한다.

(e) $n^* = 100$.

$$\Delta\mu^{gas \to gra} = -\frac{4\pi}{3}\left(\frac{3\Omega}{4\pi}\right)^{\frac{2}{3}}(n^*)^{-\frac{1}{3}}\sigma$$

$$= -\left(\frac{32\pi^3}{3}\cdot\frac{9}{16\pi^2}\right)^{\frac{1}{3}}\cdot\Omega^{\frac{2}{3}}(n^*)^{-\frac{1}{3}}\sigma$$

$$= -\left(\frac{32}{3}\pi\right)^{\frac{1}{3}}(8\times10^{-30}\,m^3/atom)^{\frac{2}{3}}(100\,atom)^{-\frac{1}{3}}(3.1\,J/m^2)/1.6022\,J/eV$$

$$= -0.53756\ eV/atom.$$

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

$$\Delta G^{*,dia} - \Delta G^{*,gra} = \frac{16\pi(\Omega^{dia})^2(\sigma^{dia})^3}{3(\Delta\mu^{gas\to dia})^2} - \frac{16\pi(\Omega^{gra})^2(\sigma^{gra})^3}{3(\Delta\mu^{gas\to gra})^2}$$

$\Delta\mu^{gas \to gra} = -0.53756\ eV/atom.$

$\Delta\mu^{gas \to dia}$

$T = 1200K$ 에서, $k = 1.38\times10^{-23}\ J/K$

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

$\Delta\mu^{gas\to dia} = -0.5153\ eV/atom$

$\Delta G^{*,dia} - \Delta G^{*,gra} = -1.782\times10^{-19}\ J/atom.$

$I^{gra}/I^{dia} = 2.12\times10^{-5}$

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

$\Delta\mu^{gas\to dia} = -0.5225\ eV/atom.$

$\Delta G^{*,dia} - \Delta G^{*,gra} = -1.2088\times10^{-19}\ J/atom.$

$I^{gra}/I^{dia} = 6.77\times10^{-4}$

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

$\Delta\mu^{gas\to dia} = -0.5296\ eV/atom$

$\Delta G^{*,dia} - \Delta G^{*,gra} = -6.35\times10^{-20}\ J/atom.$

$I^{gra}/I^{dia} = 2.16\times10^{-2}$

(g) ① $\Delta \mu_{dia \to gra} > 0$ 일때는 size 에 관계없이, diamond가 더 stable 하고,
② $\Delta \mu_{dia \to gra} < 0$ 일때는 diamond의 surface energy가 작을수록 diamond가 graphite 보다 dominant nucleation 된다.

(h) $CH_4 \to C + 2H_2$ 가 발생하게되면, C의 농도가 증가하여 cluster size가 증가하게 된다 그 결과 capillarity effect가 감소하여 bulk 상태에 비슷하게 graphite 가 더 안정해진다. 그 결과 graphite가 diamond보다 잘 생성되게 된다. 즉, 여기서의 driving force 는 높은 carbon pressure 이다.