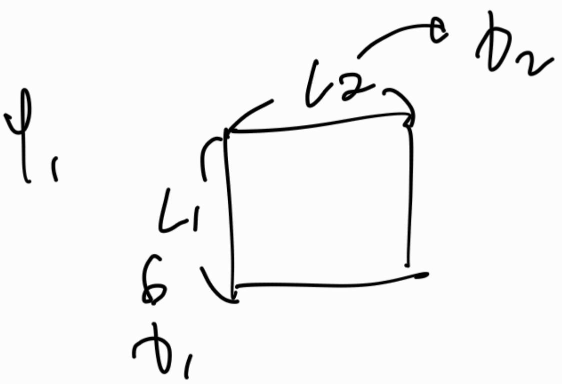
20190227 오형민



총 표면자유에너지

$$E = \sigma_1 L_1 + \sigma_2 L_2$$

때 $S = L_1 L_2$ = 일정

라그랑주 method에 의해

$$F(L_1, L_2, \alpha) = \sigma_1 L_1 + \sigma_2 L_2 + \alpha(L_1 L_2 - S)$$

$$\frac{\partial F}{\partial L_1} = \sigma_1 + \alpha L_2 = 0 \rightarrow L_2 = -\frac{\sigma_1}{\alpha} \cdots ①$$

$$\frac{\partial F}{\partial L_2} = \sigma_2 + \alpha L_1 = 0 \rightarrow L_1 = -\frac{\sigma_2}{\alpha} \cdots ②$$

$$\frac{\partial F}{\partial \alpha} = L_1 L_2 - S = 0 \cdots ③$$

①, ②를 ③에 넣으면, $\frac{\sigma_1 \sigma_2}{\alpha^2} = S$

$$\alpha^2 = \frac{\sigma_1 \sigma_2}{S}, \quad \alpha = \pm\sqrt{\frac{\sigma_1 \sigma_2}{S}}$$

이 때 $s = L_1 L_2$ (상수)

$$\alpha = \pm\sqrt{\frac{\sigma_1\sigma_2}{L_1L_2}}$$

$$L_2 = -\frac{\sigma_1}{\alpha} = \sqrt{\frac{\sigma_1 L_1 L_2}{\sigma_2}} \rightarrow L_2 = \frac{\sigma_1}{\sigma_2}L_1$$

$$L_1 = -\frac{\sigma_2}{\alpha} = \sqrt{\frac{\sigma_2 L_1 L_2}{\sigma_1}} \rightarrow L_1 = \frac{\sigma_2}{\sigma_1}L_2$$

즉, $\dfrac{L_1}{L_2} = \dfrac{\sigma_2}{\sigma_1}$

2.

먼저, 분배함수 $z = \sum e^{-\beta \varepsilon_k}$ 이고,

$E = \frac{n^2\hbar^2\pi^2}{2mL^2}$ 으로부터, 2차원 ε_k에 대해

$$\varepsilon_k = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right)$$ 을 구할 수 있다.

$$z = \sum e^{-\beta\varepsilon_k}$$

$$= \sum \exp\left(-\frac{h^2}{8mkT} \times \frac{n_x^2}{a^2}\right) \sum \exp\left(-\frac{h^2}{8mkT} \times \frac{n_y^2}{b^2}\right)$$

$$= \int_0^\infty \exp\left(-\frac{h^2}{8mkTa^2} \cdot n_x^2\right) dn_x$$

$$\int_0^\infty \exp\left(-\frac{h^2}{8mkTb^2} n_y^2\right) dn_y$$

$$= \frac{1}{2}\sqrt{\frac{8mkTa^2\pi}{h^2}} \times \frac{1}{2}\sqrt{\frac{8mkTb^2\pi}{h^2}}$$

$$= \frac{ab}{4}\left(\frac{8mkT\pi}{h^2}\right) = \frac{2AkT\pi}{h^2}$$

$$\ln Z = \ln A + \ln\frac{2k\pi}{h^2} + \ln T, \quad \left(\frac{\partial \ln Z}{\partial T}\right)_V = \frac{1}{T}$$

$$U = NkT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V \qquad \left(\frac{\partial \ln Z}{\partial A}\right)_T = \frac{1}{A}$$

$$= NkT^2 \times \frac{1}{T} = NkT$$

내부 에너지 $U = NkT$ 이고,

$P = NkT\left(\frac{\partial \ln Z}{\partial V}\right)_T$ 에서 2차원이면

$$P = NkT\left(\frac{\partial \ln Z}{\partial A}\right)_T$$

$= \frac{NkT}{A}$ 가 된다.

즉 $PA = NkT \Rightarrow PA = nRT$

3.

길이	에너지 E_k	방법 g_i	
a	$(N-1)\epsilon$	${}_{N-1}C_{N-1}$	×/- 1
$2a$	$(N-2)\epsilon$	${}_{N-1}C_{N-2}$	
$3a$	$(N-3)\epsilon$	${}_{N-1}C_{N-3}$	?
⋮	⋮	⋮	
Na	0	${}_{N-1}C_{0}$	0

$$Z = \sum g_i e^{-\beta E_k}$$

$$= \sum_{n=0}^{N-1} {}_{N-1}C_n \, e^{-\beta n \epsilon}$$

길이 L에 대해 평균 길이 $\langle L \rangle$은

$$\langle L \rangle = \frac{1}{Z} \sum_{n=0}^{N-1} (N-n) a \times {}_{N-1}C_n \, e^{-\beta n \epsilon}$$

$$= \frac{Na}{Z} \sum_{n=0}^{N-1} {}_{N-1}C_n \, e^{-\beta n \epsilon}$$

$$- \frac{a}{Z} \sum_{n=0}^{N-1} n \cdot {}_{N-1}C_n \, e^{-\beta n \epsilon}$$

$$= Na - \frac{a}{Z} \sum_{n=0}^{N-1} n \cdot {}_{N-1}C_n \, e^{-\beta n \epsilon}$$

가 된다.

4.

A 1mol	B 1mol
1.0atm	1.0atm

(a)

$$\Delta S_A = R\ln\frac{V_2}{V_1} = R\ln 2$$

$$\Delta S_B = R\ln\frac{V_2}{V_1} = R\ln 2$$

$$\Delta S = \Delta S_A + \Delta S_B = 2R\ln 2$$

(b)

A 2mol	B 1mol
0.5atm	1atm

$$\Delta S_A = 2R\ln\frac{V_2}{V_1} = 2R\ln 2$$

$$\Delta S_B = R\ln\frac{V_2}{V_1} = R\ln 2$$

$$\Delta S = \Delta S_A + \Delta S_B = 3R\ln 2$$

(c)-1

A 1mol 1atm	A 1mol 1atm

위 조건에선 P, T, n 모두 변하지 않고, 거시적인 관점에서 보면 아무런 변화가 없다. $\Delta S = 0$

(c)-2

A 2mol 2atm	A 1mol 1atm

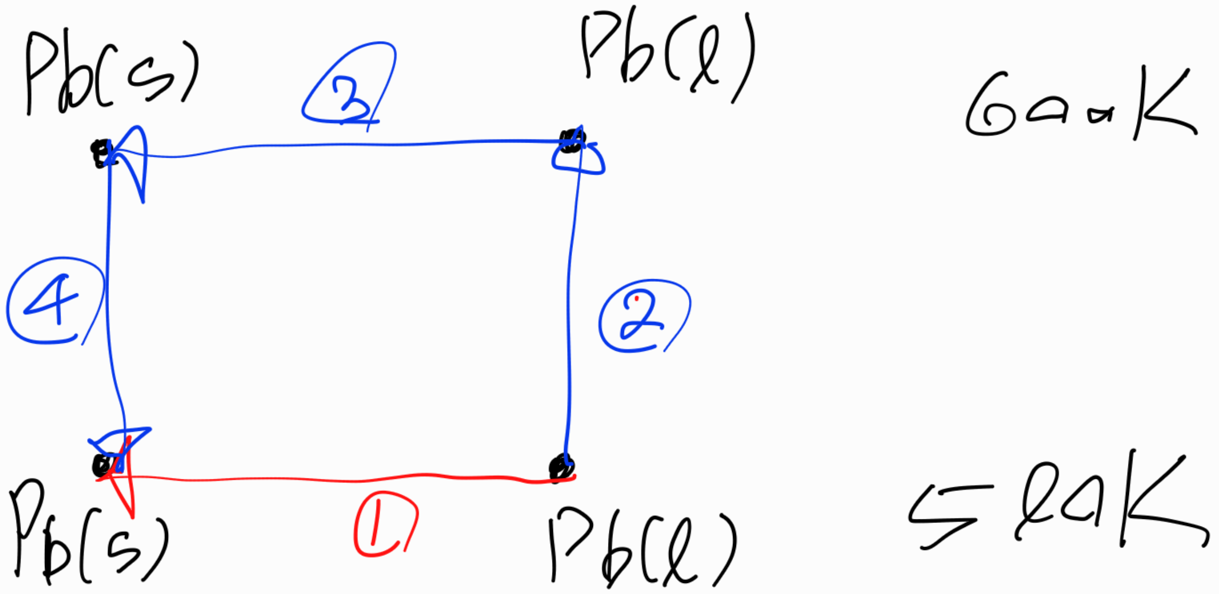
$$\Delta S_A = 2R\ln\frac{V_2}{V_1} = 2R\ln\frac{\frac{2}{3}}{\frac{1}{2}} = 2R\ln\frac{4}{3}$$

$$\Delta S_B = R\ln\frac{V_2}{V_1} = R\ln\frac{\frac{1}{3}}{\frac{1}{2}} = R\ln\frac{2}{3}$$

$$\Delta S = \Delta S_A + \Delta S_B = 2R\ln\frac{4}{3} + R\ln\frac{2}{3}$$

$$= R\ln\frac{16}{9}\times\frac{2}{3}$$

$$= R\ln\frac{32}{27}$$

5. 

(1) maximum-entropy criterion

entropy는 state function이므로,

$\Delta S_1 = \Delta S_2 + \Delta S_3 + \Delta S_4$

먼저 system에서,

$\Delta S_{1,sys} = \Delta S_{2,sys} + \Delta S_{3,sys} + \Delta S_{4,sys}$

$$= \int_{580}^{600} \frac{C_p(l)}{T} dT - \frac{\Delta H_{melting}}{600K} + \int_{600}^{580} \frac{C_p(s)}{T} dT$$

$$= \int_{580}^{600} \left(\frac{32.4}{T} - 3.1\times10^{-3}\right) dT - \frac{4810}{600} - \int_{580}^{600} 9.75\times10^{-3} dT$$

$$= 32.4 \ln\frac{600}{580} - 3.1\times10^{-3}\times10 - \frac{4810}{600} - 9.75\times10^{-3}\times10$$

$$= -7.65 J/K$$

surrounding 에서,

$$\Delta S_1 = -\frac{\Delta H_1}{T} = -\frac{\Delta H_2 + \Delta H_3 + \Delta H_4}{T} \quad (\because H는 \text{ state } f)$$

$\Delta H_2 \Rightarrow dH = C_p dT$ 에서

$$\Delta H_2 = \int_{590}^{600} C_p(l)\, dT$$

$$= \left[32.4T - \frac{3.1}{2} \times 10^{-3} T^2 \right]_{590}^{600}$$

$$= 305.6 \text{ J}$$

$$\Delta H_3 = -4810 \text{ J}$$

$$\Delta H_4 \Rightarrow \Delta H_4 = \int_{600}^{590} C_p(s)\, dT$$

$$= -\left[9.75 \times 10^{-3} \times \frac{1}{2} T^2 \right]_{590}^{600}$$

$$= -58 \text{ J}$$

$$\Delta H_2 + \Delta H_3 + \Delta H_4 = -4562.4 \text{ J}$$

$$= \Delta H_1$$

즉 $\Delta S_{1,surr} = -\frac{\Delta H_1}{T} = \frac{4562.4J}{590K}$

$= 7.73 J/K$

$\Delta S = \Delta S_{sys} + \Delta S_{surr} = -7.6 + 7.73$
$= 0.13 J/K > 0$

$\Delta S_{univ} > 0$ 이므로 반응은 자발적이다.

(2) Minimum Gibbs-Energy Criterion

$\Delta G = \Delta H - T\Delta S$

$\Delta H = -4562.4J$, $\Delta S = -7.6 J/K$ 이므로,

$\Delta G = -4562.4 - 590 \times (-7.6)$

$= -78.4 J < 0$

$\Delta G_{sys} < 0$ 이므로, 반응은 자발적이다.

(3) Adiabatic 이라면,

출입하는 $\Sigma q = 0$ 이므로, $\Delta H_{Total} = 0$ 이다.

590K 의 Pb(l) ⟶ 600 K의 Pb(l) 에서
(② 과정)

흡수한 열 중 전체는

600K의 $Pb(l) \to Pb(s)$ 에 사용된다. (뺏는다)

즉, 두 ΔH가 표값형이므로

$\Delta H_{l,590 \to l,600} = \Delta H_2 = 305.65$, 1mol 당

x mol 이 solid가 된다고 하면,

$305.6 = x \times 4810$

$x = 0.064$

즉, 전체 mol 수의

0.064 만큼은 solid

0.936 만큼은 liquid 상태로

두 상이 공존한다.

6. $g \to d$ means graphite $\to$ diamond

$$\Delta G_{g \to d} = \Delta H_{g \to d} - T \Delta S_{g \to d}$$

$$\Delta H_{g \to d} = 454 \text{ cal/mol}$$

$$\Delta S_{g \to d} = S_d - S_g = 0.58 - 1.37$$

$$= -0.79 \text{ cal/mol}$$

$$\Delta G_{g \to d} = 454 - 298 \times (-0.79)$$

$$= 689.42 \text{ cal/mol} \quad 1\text{cal} = 4.186\text{J}$$

$$= 2.89 \text{ kJ/mol}$$

$dG = -SdT + PdV$ 에서; T 일정이므로

$$\Delta G = \int dG = \int P dV$$

$$= P(V_d - V_g)$$

$\rho_g = 2.22\ g/cm^3$ 에서, 1mol 당 부피는

$M_c = 12$

$$\frac{M_c}{\rho_g} = \frac{12}{2.22} = 5.41\ cm^3 = V_g$$

$$= 5.41\times10^{-6}\ m^3$$

$\rho_d = 3.515\ g/cm^3$ 에서, 1mol당 부피는

$$\frac{M_c}{\rho_d} = \frac{12}{3.515} = 3.41\ cm^3 = V_d$$

$$= 3.41\times10^{-6}\ m^3$$

따라서

$$P = \frac{\Delta G}{V_d - V_g} = \frac{2.89\ kJ/mol}{5.41\times10^{-6}\ m^3 - 3.41\times10^{-6}\ m^3}$$

$$= 1.45\times10^{9}\ Pa$$

$= 1.45\ GPa$ 필요하다