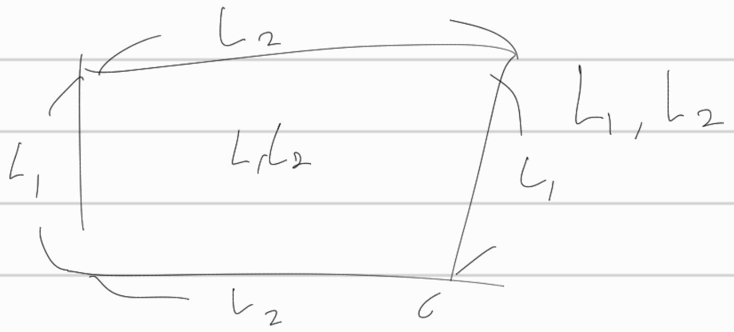
1.



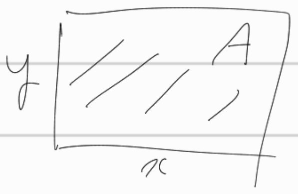
에너지 : $(\gamma_1 L_1 + \gamma_2 L_2) + (\gamma_1 L_1 + \gamma_2 L_2) = 2\gamma_1 L_1 + 2\gamma_2 L_2$

면적 : $L_1 L_2$

$$f = 2\gamma_1 L_1 + 2\gamma_2 L_2 - \lambda L_1 L_2$$

$$\left.\begin{aligned} \frac{\partial f}{\partial L_1} &= 2\gamma_1 - \lambda L_2 = 0 \\ \frac{\partial f}{\partial L_2} &= 2\gamma_2 - \lambda L_1 = 0 \end{aligned}\right\} \lambda = \frac{2\gamma_1}{L_2} = \frac{2\gamma_2}{L_1}, \quad \frac{L_1}{L_2} = \frac{\gamma_2}{\gamma_1}$$

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



$$Z = e^{-\varepsilon/kT}$$

$$= \int_0^\infty e^{-\frac{n_x^2 h^2}{8m_e x^2 \cdot kT}} dn_x \cdot \int_0^\infty e^{-\frac{n_y^2 h^2}{8m_e y^2 \cdot kT}} dy$$

$$= \frac{1}{2} \cdot \sqrt{\frac{8mx^2\pi \cdot kT}{h^2}} \cdot \frac{1}{2} \cdot \sqrt{\frac{8my^2\pi \cdot kT}{h^2}} = \frac{2m\pi kT}{h^2} xy = \frac{2m\pi}{h^2} A \cdot kT$$

$$\ln Z = \ln A + \ln T + C$$

$$\therefore P = \frac{\partial F}{\partial A} = NkT\left(\frac{\partial \ln Z}{\partial A}\right)_T = NkT \cdot \frac{1}{A}, \quad \therefore PA = nRT$$

$$U = NkT^2\left(\frac{\partial \ln Z}{\partial T}\right)_A = NkT = RT$$

3.

$$Z=\sum e^{-\varepsilon/kT},\quad \varepsilon \to 0 \sim (N-1)\varepsilon.$$

$$= 1+e^{-\varepsilon/kT}+e^{-2\varepsilon/kT}+\cdots+e^{-(N-1)\varepsilon/kT} = \frac{1-e^{-N\varepsilon/kT}}{1-e^{-\varepsilon/kT}}$$

평균길이 $\Rightarrow \dfrac{\left(1\times Na + e^{-\varepsilon/kT}\times(N-1)a+\cdots+e^{-(N-1)\varepsilon/kT}\cdot a\right)}{1+e^{-\varepsilon/kT}+\cdots+e^{-(N-1)\varepsilon/kT}}$

$$L = 1\times Na + e^{-\varepsilon/kT}\times(N-1)a+\cdots+e^{-(N-1)\varepsilon/kT}\cdot a$$

$$e^{-\varepsilon/kT}\cdot L = e^{-\varepsilon/kT}\times Na+\cdots+e^{-(N-1)\varepsilon/kT}\cdot 2a + e^{-N\varepsilon/kT}\cdot a$$

$-)$

$$\left(1-e^{-\varepsilon/kT}\right)L = Na - \left\{e^{-\varepsilon/kT}+e^{-2\varepsilon/kT}+\cdots+e^{-(N-1)\varepsilon/kT}+e^{-N\varepsilon/kT}\right\}a$$

$$= Na - \frac{e^{-\varepsilon/kT}-e^{-(N+1)\varepsilon/kT}}{1-e^{-\varepsilon/kT}}\cdot a$$

$$\therefore L = \frac{Na}{1-e^{-\varepsilon/kT}} - \frac{e^{-\varepsilon/kT}\left(1-e^{-N\varepsilon/kT}\right)}{\left(1-e^{-\varepsilon/kT}\right)^2}a$$

평균길이 $= \dfrac{L}{Z}$

$$= \frac{N - \dfrac{e^{-\varepsilon/kT}\left(1-e^{-N\varepsilon/kT}\right)}{\left(1-e^{-\varepsilon/kT}\right)}}{1-e^{-N\varepsilon/kT}}\, a$$

$$= \left\{\frac{N}{1-e^{-N\varepsilon/kT}} - \frac{e^{-\varepsilon/kT}}{1-e^{-\varepsilon/kT}}\right\}a$$

4.

1mol A	1mol B

a) $X_A = \frac{1}{2}, \quad X_B = \frac{1}{2}, \quad n_A + n_B = 2mol$

$$\Delta S = -k(N_A+N_B)\{X_A \ln X_A + X_B \ln X_B\}$$

$$= -2R\{\frac{1}{2}\ln\frac{1}{2} + \frac{1}{2}\ln\frac{1}{2}\} = 2R\ln 2$$

b) Boltzman entropy

$$S = k_B \ln \Omega$$

$$S_i = k_B \ln 1 = 0. \quad S_f = k_B\left(\ln 2^{2N} + \ln 2^{N}\right) = 3Nk_B \ln 2 = 3R\ln 2.$$

c)

①

A 1mol	A 1mol

$X_A = 1 \to X_A = 1$

- 같은 입자가 들어있고, 양쪽 압력 변화가 없어 거시적으로 두 상황의 차이를 구별할 수 없다. $\therefore \Delta S = 0$
- $\Delta S = kN[X_A \ln X_A + X_B \ln X_B]$ 에서, $X_A = X_B = 1$ 이므로 (둘다 A 이므로) $\therefore \Delta S = 0$

②

A 2mol	A 1mol
2P	P

- 압력이 변하면서 엔트로피의 변화가 생긴다. 그러나 혼합에 의한 $\Delta S = 0$ 이다.

각 압력을 $2P$, P라 하면 혼합 후 압력은 $\frac{3}{2}P$이다.
2mol의 분자는 공간 V를 차지하다 혼합 후 $\frac{2nRT}{\frac{3}{2}P} = \frac{4}{3}V$ 를 차지하게 되고,

1mol의 분자는 같은 방법으로 $V \to \frac{2}{3}V$를 차지하게 된다. 이때 ΔS는
$\Delta S_{left} = 2Nk \ln \frac{\frac{4}{3}V}{V} = 2R\ln\frac{4}{3}, \quad \Delta S_{right} = Nk\ln\frac{\frac{2}{3}V}{V} = R\ln\frac{2}{3}$ 이다.

$\Delta S_{config} = 0$ 이므로 $\Delta S_{tot} = \Delta S_{left} + \Delta S_{right} = 2R\ln\frac{4}{3} + R\ln\frac{2}{3} = R\ln\frac{32}{27}$

So state function 이므로 590K(l) → 600K(l) → 600K(s) → 590K(s) 과정을 거쳐 계산할 수 있다. 1mol이라 가정하면

(1) entropy (system)

· 590K (l) → 600K (l)

: $\int_{590}^{600} \frac{C_p(l)}{T} dT = \left[32.4 \ln T - 3.1 \times 10^{-3} T\right]_{590K}^{600K} = 0.51 J/K \cdot mol$

· 600K (l) → 600K (S)

: $\frac{-\Delta H_{melt}}{600K} = -8.01 J/K \cdot mol.$

· 600K (S) → 590K (S)

: $\int_{600K}^{590K} \frac{C_p(S)}{T} dT = \left[9.75 \times 10^{-3} T\right]_{600}^{590} = -9.75 \times 10^{-2} J/K \cdot mol$

· entropy (surround)

$\Delta S = \frac{\Delta H_{melt}}{600K} = 8.01 J/K \cdot mol$

$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{sur}$

$= 0.51 J/K mol + (-8.01 J/K \cdot mol) + (-9.75 \times 10^{-2} J/K mol)$

$+ 8.01 J/K \cdot mol.$

$= 0.4125 J/K mol > 0$, ∴ 자발적이다.

(2) Gibbs-Energy

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

(1)에서 $\Delta S = 0.51 - 8.01 - 9.75 \times 10^{-2} = -7.59 J \cdot K^{-1} \cdot mol^{-1}$

$\Delta G = -4810 J/mol - (590K)(-7.59 J \cdot K^{-1} \cdot mol^{-1})$

$= -331.9 J/mol < 0$, ∴ 자발적이다.

· 만일 adiabatic이면 용기 내부의 온도가 올라갈 것이고, 충분한 과냉각 Pb가 있다면 system의 온도를 올려 600K에서 고체와 액체가 평형을 이룰 것이다.

6. $\Delta G = \Delta H - T\Delta S + \int_1^P \Delta V_{G\to D}\, dP$ / let C 1mol, 12g

$\Delta H = +454$ calories/mol

$\Delta S = 0.58$ cal/mol·K $- 1.37$ cal/mol·K, $= -0.79$ cal/mol·K

$V_G = \frac{12g}{2.22g/cm^3} = 5.40\ cm^3/mol$

$V_D = \frac{12g}{3.515g/cm^3} = 3.41\ cm^3/mol$

$\Delta V = -1.99\ cm^3/mol,\ -1.99 \times 10^{-3}\ L/mol$

최소압력 = equilibrium $= \Delta G = 0$,

$\therefore \Delta G = 454cal/mol - (298K)(-0.79cal/mol\cdot K)$

$- (1.99 \times 10^{-3} L/mol)(P - 1\ atm)$

$= 689.42\ cal/mol - (1.99 \times 10^{-3}\ L/mol)(P-1\ atm)$

$= 2895\ J/mol - (101.325\ J/atm\cdot L)(1.99\times10^{-3}\ L\cdot mol^{-1})(P-1\ atm)$

$= 0$

$\therefore P = 1.4 \times 10^4$ atm.