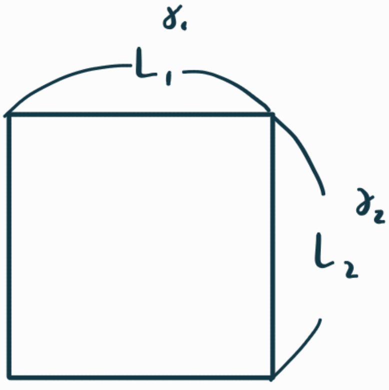
20220560 최원준

①



$L_1 L_2 = a$

$$E = \sum L \cdot \gamma = 2L_1\gamma_1 + 2L_2\gamma_2$$

using the Lagrangian undetermined multiplier method,

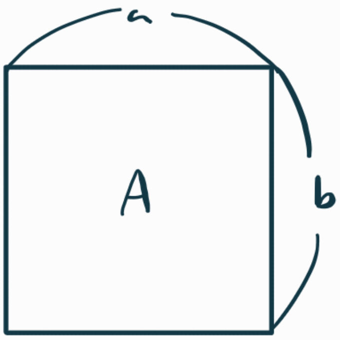
$$f(L_1, L_2) = E = 2L_1\gamma_1 + 2L_2\gamma_2 \quad \text{s.t. } L_1L_2 = a,\ L_1L_2 - a = 0$$

$$F(L_1, L_2, \lambda) = 2L_1\gamma_1 + 2L_2\gamma_2 + \lambda(L_1L_2 - a)$$

$$\frac{\partial F}{\partial L_1} = 2\gamma_1 + \lambda L_2 = 0 \quad \frac{\partial F}{\partial L_2} = 2\gamma_2 + \lambda L_1 = 0 \quad \frac{\partial F}{\lambda} = L_1L_2 - a = 0$$

$$\lambda = -\frac{2\gamma_1}{L_2} = -\frac{2\gamma_2}{L_1} \qquad \frac{\gamma_1}{L_2} = \frac{\gamma_2}{L_1} \rightsquigarrow \frac{L_1}{L_2} = \frac{\gamma_2}{\gamma_1}$$

②



$$U = NkT^2\left(\frac{\partial \ln z}{\partial T}\right)_v, \quad P = NkT\left(\frac{\partial \ln z}{\partial V}\right)_T, \quad \varepsilon = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right)$$

$$z = \sum e^{-\frac{\varepsilon}{kT}} = \sum e^{-\frac{h^2}{8mkT}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right)}$$

$$= \sum e^{-\frac{h^2}{8mkT}\cdot\frac{n_x^2}{a^2}} \cdot \sum e^{-\frac{h^2}{8mkT}\cdot\frac{n_y^2}{b^2}}$$

$$= \int_0^\infty e^{-\frac{h^2}{8mkT}\cdot\frac{n_x^2}{a^2}} dn_x \int_0^\infty e^{-\frac{h^2}{8mkT}\cdot\frac{n_y^2}{b^2}} dn_y$$

$$\left(\int_0^\infty e^{-ax^2}dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}\right) \qquad = \left(\frac{1}{2}\sqrt{\frac{\pi}{\frac{h^2}{8mkTa^2}}}\right)\left(\frac{1}{2}\sqrt{\frac{\pi}{\frac{h^2}{8mkTb^2}}}\right) = \frac{2mkT\pi}{h^2}\underbrace{ab}_{A}$$

$$\ln z = \ln\left(\frac{2A\pi mkT}{h^2}\right) = \ln C + \ln A + \ln T \qquad \left(C = \frac{2\pi mk}{h^2}\right)$$

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

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

n N-n

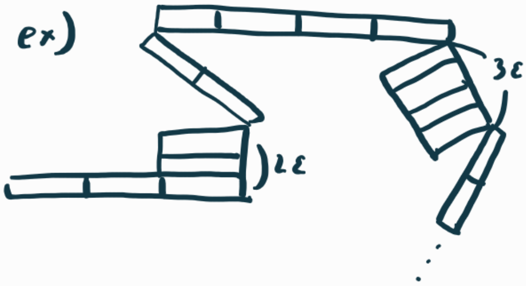
n-1 1 $_{N-n}C_2$

③ 

ε

0

length of singular $\begin{cases} 0 \\ a \end{cases}$

$\rightsquigarrow$ ex) 

selecting n out of k

$\binom{n+k-1}{k-1} = \binom{n+k-1}{n}$

$k = N-n$, $n = n$ $\rightsquigarrow \binom{N-1}{n}$

E	length	configurations
0	Na	$\binom{N-1}{0}$
ε	$(N-1)a$	$\binom{N-1}{1}$
2ε	$(N-2)a$	$\binom{N-1}{2}$
$\vdots$		$\vdots$
$(N-1)\varepsilon$	a	1

$$z = \sum_{n=0}^{N-1} \binom{N-1}{n} e^{-\frac{\varepsilon}{kT}}$$

$$= (\text{original } z)^n$$

$$= \left(1 + e^{-\frac{\varepsilon}{kT}}\right)^N$$

probability for length $0 = \dfrac{1}{1+e^{-\frac{\varepsilon}{kT}}}$

probability for length $a = \dfrac{e^{-\frac{\varepsilon}{kT}}}{1+e^{-\frac{\varepsilon}{kT}}}$

$$L_{av} = N\left(0 \cdot \frac{1}{1+e^{-\frac{\varepsilon}{kT}}} + a \cdot \frac{e^{-\frac{\varepsilon}{kT}}}{1+e^{-\frac{\varepsilon}{kT}}}\right) = \frac{Na\, e^{-\frac{\varepsilon}{kT}}}{1+e^{-\frac{\varepsilon}{kT}}}$$

4 (a) $\Delta S = k\ln W = k\ln \frac{(n_A+n_B)!}{n_A!\,n_B!} = k\ln\Big((n_A+n_B)\ln(n_A+n_B) - (n_A+n_B)$

$- n_A\ln n_A - n_B\ln n_B + (n_A+n_B)\Big)$

$= k\ln\Big((n_A+n_B)\ln(n_A+n_B) - n_A\ln n_A - n_B\ln n_B\Big)$

$= k\ln\Big(n_A\ln\left(\frac{n_A+n_B}{n_A}\right) + n_B\ln\left(\frac{n_A+n_B}{n_B}\right)\Big)$

$= -k(n_A+n_B)\ln\Big(\frac{n_A}{n_A+n_B}\ln\left(\frac{n_A}{n_A+n_B}\right) + \frac{n_B}{n_A+n_B}\ln\left(\frac{n_B}{n_A+n_B}\right)\Big)$

$= -k(n_A+n_B)\ln\Big(x_A\ln x_A + x_B\ln x_B\Big)$

$\Delta S = \Delta S_{config} + \Delta S_{therm} = \Delta S_{config}$

$= -k(2\,\mathrm{mol})\ln\left(\frac{1}{2}\ln\frac{1}{2} + \frac{1}{2}\ln\frac{1}{2}\right) = R\ln 4$

(b) $\Delta S_{config} = -k(3\,\mathrm{mol})\ln\left(\frac{2}{3}\ln\frac{2}{3} + \frac{1}{3}\ln\frac{1}{3}\right) = R\ln\frac{27}{4}$

$\Delta S_{therm} = n_A R\ln\left(\frac{V_2}{V_1}\right) + n_B R\ln\left(\frac{V_2}{V_1}\right)$

$= (2\,\mathrm{mol})R\ln\left(\frac{\frac{2}{3}}{\frac{1}{2}}\right) + (1\,\mathrm{mol})R\ln\left(\frac{\frac{1}{3}}{\frac{1}{2}}\right) = 2R\ln\frac{4}{3} + R\ln\frac{2}{3} = R\ln\frac{32}{27}$

$\Delta S = R\ln\frac{27}{4} + R\ln\frac{32}{27} = R\ln 8$

(c) for (a), $\Delta S = \Delta S_{config} = \Delta S_{therm} = 0$

for (b), $\Delta S_{config} = 0$

$\Delta S_{therm} = n_1 R\ln\left(\frac{V_2}{V_1}\right) + n_r R\ln\left(\frac{V_2}{V_1}\right)$

$= 2R\ln\left(\frac{\frac{2}{3}}{\frac{1}{2}}\right) + R\ln\left(\frac{\frac{1}{3}}{\frac{1}{2}}\right) = R\ln\frac{32}{27}$

⑤ (a) $\Delta S = \Delta S_{system} + \Delta S_{surr}$

path independent, so we can use $\Delta S_{system} = \Delta S_{AB} + \Delta S_{BC} + \Delta S_{CD}$

$$\underset{(A)}{590K\ Pb(l)} \rightarrow \underset{(B)}{600K\ Pb(l)} \rightarrow \underset{(C)}{600K\ Pb(s)} \rightarrow \underset{(D)}{590K\ Pb(s)}$$

$$\Delta S_{AB} = \int_{T_1}^{T_2} \frac{n\,c_p(l)}{T} dT = n\int_{590K}^{600K} \left(\frac{32.4}{T} - 3.1\times10^{-3}\right) dT = n(0.514)$$

$$\Delta S_{BC} = \frac{q}{T} = \frac{\Delta H}{T} = \frac{-4810\,J/mol}{600K} = -n(8.107)$$

$$\Delta S_{CD} = \int_{T_2}^{T_1} \frac{n\,c_p(s)}{T} dT = n\int_{600K}^{590K} 9.75\times10^{-3}\, dT = -n(0.0975)$$

$$\Delta S_{surr} = \frac{\Delta H_{AB} + \Delta H_{BC} + \Delta H_{CD}}{T}$$

$$\Delta H_{AB} = \int_{T_1}^{T_2} n\,c_p(l)\,dT = n\int_{590K}^{600K} (32.4 - 3.1\times10^{-3}T)\,dT = n(306)$$

$$\Delta H_{BC} = -n(4810)$$

$$\Delta H_{CD} = \int_{T_2}^{T_1} n\,c_p(s)\,dT = n\int_{600K}^{590K} 9.75\times10^{-3}\,T\,dT = -n(58.01)$$

$$\Delta S = n\left(0.514 - 8.107 - 0.0975 + \frac{306 - 4810 - 58.01}{590K}\right) = n(-15.423) < 0$$

(b) $\Delta G = \Delta H - T\Delta S$

$$= n\{-4810 - (590)(-7.6905)\} = -n(272) < 0$$

Pb가 단열 용기에 보관되어 있으면, 압력, 부피가 변하지 않는 한, 액체 상태로 유지될 것이다.

6 $\Delta G(P_0, T) = \Delta H - T\Delta S$ $\quad$ (C : 12,011 g/mol)

$$\left(\frac{\partial G}{\partial P}\right)_T = \Delta V$$

$$\Delta G(P, T) = \Delta G(P_0, T) + \int_{P_0}^{P} \left(\frac{\partial G}{\partial P}\right)_T dP$$

$$= \Delta G(P_0, T) + \int_{P_0}^{P} \Delta V \, dP$$

$$= \Delta G(P_0, T) + (P - P_0)\Delta V \quad = 0$$

$$P = P_0 - \frac{\Delta G(P_0 T)}{\Delta V} = P_0 - \frac{\Delta H - T\Delta S}{\Delta V}$$

$$= 1\,\text{atm} - \frac{454\,\text{cal/mol} - (298\,\text{K})(0.58\,\text{cal/mol/K} - 1.37\,\text{cal/mol/K})}{\left(\frac{12.011\,\text{g/mol}}{3.515\,\text{g/cm}^2} - \frac{12.011\,\text{g/mol}}{2.22\,\text{g/cm}^2}\right)}$$

$$= 1\,\text{atm} + 346\left(\frac{4.184}{0.1013}\right)\text{atm}$$

$$= 14300\,\text{atm}$$