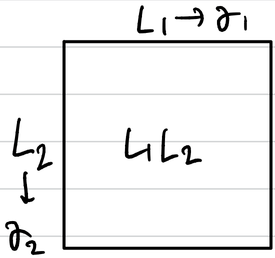
20220018 임진성 소재열역학 HW2.

1.



$$\Delta G = \int \gamma \, dl$$
$$= 2 \times \int_0^{L_1} \gamma_1 \, dl + 2 \times \int_0^{L_2} \gamma_2 \, dl$$
$$= 2\gamma_1 L_1 + 2\gamma_2 L_2$$

라그랑주 방법이용 $f(L_1, L_2) = 2\gamma_1 L_1 + 2\gamma_2 L_2$

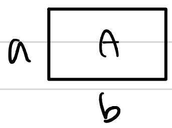
$$F(L_1, L_2, \lambda) = 2\gamma_1 L_1 + 2\gamma_2 L_2 + \lambda(\overset{L_1L_2}{A} - L_1L_2)$$

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

$$\boxed{\therefore \frac{L_1}{L_2} = \frac{\gamma_2}{\gamma_1}}$$

$$\boxed{G = 2(\gamma_1 L_1 + \gamma_2 L_2)}$$

2.



$$A = ab$$

$$\varepsilon_i = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right)$$

$$Z = \sum e^{\frac{-h^2 n_x^2}{8mkTa^2}} \cdot \sum e^{-\frac{h^2 n_y^2}{8mkTb^2}}$$

$$= \int_0^\infty e^{\frac{-h^2 n_x^2}{8mkTa^2}} \, dn_x \cdot \int_0^\infty e^{-\frac{h^2 n_y^2}{8mkTb^2}} \, dn_y \qquad \left(\int_0^\infty e^{-ax^2} dx\right) = \frac{1}{2}\sqrt{\frac{\pi}{a}}$$

$$= \frac{a}{2}\sqrt{\frac{8\pi mkT}{h^2}} \times \frac{b}{2}\sqrt{\frac{8\pi mkT}{h^2}} = \frac{ab\,8\pi mkT}{\cancel{4}h^2} = \frac{2ab\pi mkT}{h^2}$$

$$= \frac{2A\pi mkT}{h^2}$$

$$\ln Z = \ln A + \ln T + \ln\left(\frac{2\pi mk}{h^2}\right)$$

$$P = -\left(\frac{\partial F}{\partial A}\right)_T = NkT\left(\frac{\partial \ln Z}{\partial A}\right)_T = \frac{NkT}{A} \qquad \frac{1}{A}$$

$$PA = NRT$$

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

3. 가장 짧을때 길이 $a \rightarrow (N-1)\varepsilon$.

n개가 펼친다 하면 길이가 $(N-n)a$ 일때 E는 $n\varepsilon$.

이때 경우의 수는 ${}_{N-1}C_n$개이다.

$$\therefore Z = \sum g_i e^{-\frac{\varepsilon_i}{kT}}$$

$$\sum_{n=0}^{N-1} {}_{N-1}C_n e^{-\frac{n\varepsilon}{kT}} \Rightarrow \text{by } \sum_{r=0}^{n} {}_nC_r x^r = (1+x)^n$$

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

$$\therefore \text{average length} = \frac{\sum_{n=0}^{N-1} (N-n)a\, {}_{N-1}C_n e^{-\frac{n\varepsilon}{kT}}}{Z}$$

$$= \frac{1}{Z}\left(Na\left(\underbrace{\sum_{n=0}^{N-1} {}_{N-1}C_n e^{-\frac{n\varepsilon}{kT}}}_{Z}\right) - a\left(\sum_{n=0}^{N-1} n\, {}_{N-1}C_n e^{-\frac{n\varepsilon}{kT}}\right)\right)$$

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

$$= Na + akT\frac{\partial}{\partial \varepsilon}\ln Z = Na - a\left(\frac{N-1}{1+e^{\frac{\varepsilon}{kT}}}\right)$$

4.

(a) $S_{처음} = S_A + S_B = k\ln 1 + k\ln 1 = 0$

$S_{나중} = S_{A+B} = k\ln \frac{(n_A+n_B)!}{n_A!\,n_B!}$

by $\ln x! = x\ln x - x$

$k\left((n_A+n_B)\ln(n_A+n_B) - (n_A+n_B) - n_A\ln n_A - n_B\ln n_B + n_A + n_B\right)$

$n_A = 1 \quad n_B = 1 \qquad 2k = 2R, \quad \therefore k = R$

$\therefore \quad k(2\ln 2) = k\ln 4 = R\ln 4.$

$\therefore \Delta S = S_{나중} - S_{처음} = R\ln 4.$

(b) $\Delta S_{tot} = \Delta S_C + \Delta S_A + \Delta S_B.$

$\hookrightarrow \quad k\ln \frac{3n!}{2n!\,n!} = k\left(3n\ln 3n - 3n - (2n\ln 2n - 2n) - (n\ln n - n)\right)$

$= R\ln \frac{27}{4}$

$\Delta S_A = 2R\ln \frac{\frac{4}{3}V}{V} = 2R\ln\frac{4}{3}$

$\Delta S_B = R\ln \frac{\frac{2}{3}V}{V} = R\ln \frac{2}{3}$

$\rightarrow R\ln 8$

(c) 같은 기체 A에 대해서

(a) 상황의 경우 온도 / 부피 / 압력 변화 X

$\therefore \Delta S_C = \Delta S_T = 0 \qquad \therefore \Delta S = 0$

(b) 상황의 경우 온도는 없음.

$\therefore \Delta S_1 = 2R\ln\frac{2}{3}$

$\Delta S_2 = R\ln\frac{4}{3}$

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

5.

(1) Maximum-entropy criterion. ΔS는 state func. $\Delta S = \Delta S_{계} + \Delta S_{주위}$

$$\text{liq } 590K \xrightarrow{\text{I}} \text{liq } 600K \xrightarrow{\text{II}} \text{solid } 600K \xrightarrow{\text{III}} \text{solid } 590K.$$

$$\Delta S_{\text{I}} = \int \frac{1}{T} dq_p = \int \frac{1}{T} nC_p dT = \int_{590K}^{600K} \frac{nC_p}{T} dT$$

$$\Delta S_{\text{II}} = \frac{\Delta q}{T} = -\frac{\Delta H}{T} n.$$

$$\Delta S_{\text{III}} = \int \frac{1}{T} nC_p dT = \int_{600K}^{590K} \frac{nC_p}{T} dT$$

$\Delta S_{계} = -1.6\ J/K.$

$$\Delta S_{주위} = -\frac{q}{T} = -\frac{\Sigma \Delta H}{T} = -\frac{1}{T}\left(\int_{590}^{600} nC_p dT + \Delta H n + \int_{600}^{590} nC_p dT\right)$$

$= 1.72\ J/K.$

$0.13\ J/K > 0$

$\therefore \Delta S > 0$, $\therefore$ 자발적.

(2) minimum Gibbs E criterion.

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

$$= -4562 + 590 \times 1.6 = -18.xx < 0 \rightarrow \therefore \text{자발적.}$$

단열된 용기에 보관되어있을 경우 $\Delta H = 0$ 이다. $\rightarrow$ $\therefore$ 고체+액체 공존

$$\Delta H = \Delta H_{\text{I}} + \Delta H_{\text{II}} = 0$$

$\Delta H_{\text{II}} \rightarrow -4810 n x$

$\Delta H_{\text{I}} \rightarrow \int_{590K}^{600K} nC_p dT = 306 n.$

$$x = \frac{306}{4810} = 0.064 \text{ (solid)}$$

6.

Graphite → Diamond

$\Delta G = \Delta H - T\Delta S = 454 \times 4.2 - 298 \times (0.58 - 1.37) \times 4.2 = 2896\ J.$

$\left(\frac{\partial G}{\partial p}\right)_T = \Delta V \rightarrow \Delta G = 2896 + \int_1^P \Delta V\, dp. = 0$

$\Delta V = 12\left(\frac{1}{3.515} - \frac{1}{2.22}\right) = -1.99\ cm^3/mol.$

$(-1.99 \times 0.1013)(P-1)$

$P = 14.4\ atm$