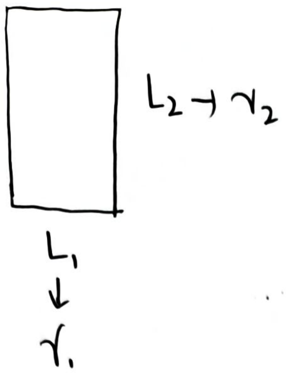
1.



Area $= L_1 L_2$: 일정 $\rightarrow L_1 L_2 = C$

표면 자유에너지 $(\Delta G) = (L_1\gamma_1 + L_2\gamma_2) \times 2$

$F(L_1, L_2) = (L_1\gamma_1 + L_2\gamma_2) \times 2$

표면 자유에너지가 최소 $\Rightarrow F'(L_1, L_2) = 0$

Lagrangian Undetermined Multiplier Method를 쓰면

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

$\frac{dF}{dL_1} = 2\gamma_1 + \lambda L_2 = 0 \rightarrow L_2 = -\frac{2\gamma_1}{\lambda} \Rightarrow \lambda = -\frac{2\gamma_1}{L_2}$

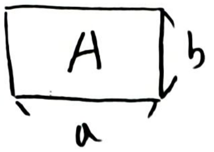
$\frac{dF}{dL_2} = 2\gamma_2 + \lambda L_1 = 0 \rightarrow L_1 = -\frac{2\gamma_2}{\lambda} \Rightarrow \lambda = -\frac{2\gamma_2}{L_1}$

$\frac{dF}{d\lambda} = L_1L_2 - C = 0 \rightarrow L_1L_2 = C$

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

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

2.



$ab = A$

$$Z = \sum_{\text{State}} e^{-\varepsilon_i/kT}$$

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

$$Z = \sum e^{-(h^2/8mkT)(n_x^2/a^2)} \sum e^{-(h^2/8mkT)(n_y^2/b^2)}$$

$$Z = \int_0^\infty e^{-(h^2/8mkT)(n_x^2/a^2)}\, dn_x \int_0^\infty e^{-(h^2/8mkT)(n_y^2/b^2)}\, dn_y$$

$$\int_0^\infty e^{-ax^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$$

$$Z = \frac{1}{2}\sqrt{\frac{8\pi mkTa^2}{h^2}} \times \frac{1}{2}\sqrt{\frac{8\pi mkTb^2}{h^2}} = \frac{8\pi ab\, mkT}{4h^2} = \frac{2\pi A mkT}{h^2}$$

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

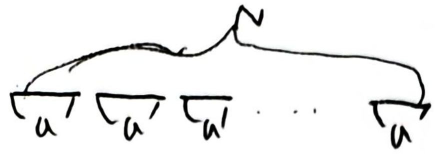
$$\ln Z = \ln A + \ln \frac{2\pi mkT}{h^2}$$

$$\frac{\partial \ln Z}{\partial A} = \frac{1}{A}$$

$$P = \frac{NkT}{A} \Rightarrow PA = nRT$$

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

3.



: 상호작용 $E=\pm\varepsilon$: 상호작용 $E=0$

전체 길이를 L이라 하자, 온도가 T일때 각각의 길이를 가질 확률

$$L=\begin{cases} a \to \varepsilon_1 = (N-1)\varepsilon \Rightarrow \text{존재할 확률}(P_1) = \dfrac{e^{-(N-1)\varepsilon/kT}}{\sum_{i=1}^{N} e^{-\varepsilon_i/kT}} \\ 2a \to \varepsilon_2 = (N-2)\varepsilon \Rightarrow P_2 = \dfrac{e^{-(N-2)\varepsilon/kT}}{\sum_{i=1}^{N} e^{-\varepsilon_i/kT}} \\ 3a \to \varepsilon_3 = (N-3)\varepsilon \Rightarrow P_3 = \dfrac{e^{-(N-3)\varepsilon/kT}}{\sum_{i=1}^{N} e^{-\varepsilon_i/kT}} \\ \vdots \\ Na \to \varepsilon_N = 0 \Rightarrow P_N = \dfrac{1}{\sum_{i=1}^{N} e^{-\varepsilon_i/kT}} \end{cases}$$

$$\text{평균길이} = a\times P_1 + 2a\times P_2 + \cdots\ Na\times P_N$$

$$= \frac{a}{\sum_{i=1}^{N} e^{-\varepsilon_i/kT}} \times \left(1\times e^{-(N-1)\varepsilon/kT} + 2\times e^{-(N-2)\varepsilon/kT} + 3\times e^{-(N-3)\varepsilon/kT} + \cdots\ N\times 1\right)$$

$$= \frac{a}{\sum_{i=1}^{N} e^{-\varepsilon_i/kT}} \times e^{-N\varepsilon/kT} \times \sum_{i=1}^{N} i e^{i\varepsilon/kT}$$

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

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

$$\sum_{i=1}^{N} i e^{i\varepsilon/kT} = S_N = 1\cdot e^{\varepsilon/kT} + 2\cdot e^{2\varepsilon/kT} + 3\cdot e^{3\varepsilon/kT} + \cdots + N e^{N\varepsilon/kT}$$

$$e^{\varepsilon/kT} S_N = e^{2\varepsilon/kT} + 2e^{3\varepsilon/kT} + \cdots + (N-1)e^{N\varepsilon/kT} + N e^{(N+1)\varepsilon/kT}$$

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

$$\text{평균길이} = a \times \frac{1-e^{-\varepsilon/kT}}{1-e^{-N\varepsilon/kT}} \times e^{-N\varepsilon/kT} \times \left\{\frac{e^{\varepsilon/kT}(1-e^{N\varepsilon/kT})}{(1-e^{\varepsilon/kT})^2} - \frac{N e^{(N+1)\varepsilon/kT}}{1-e^{\varepsilon/kT}}\right\}$$

$$\text{평균길이} = a \times \frac{-(1-e^{\varepsilon/kT})}{1-e^{-N\varepsilon/kT}} \times e^{-(N+1)\varepsilon/kT} \times \left\{ \frac{-e^{(N+1)\varepsilon/kT} \times (1-e^{-N\varepsilon/kT})}{(1-e^{\varepsilon/kT})^2} - \frac{Ne^{(N+1)\varepsilon/kT}}{1-e^{\varepsilon/kT}} \right\}$$

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

4.

A	B
1 mole	1 mole
1 atm	1 atm

(a) $\Delta S = k \ln \Omega$

$$= k \ln \frac{(n_A+n_B)!}{n_A!\, n_B!}$$

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

X_A X_B

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

$n_A + n_B = 2 \times N_a$

$$= -2R \left(X_A \ln X_A + X_B \ln X_B \right) \qquad X_A = \frac{1}{2} \quad X_B = \frac{1}{2}$$

$$= -2R \left(\frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2} \right) = 2R \ln 2$$

(b) A → 2mole

$$\Delta S_{config} = -3R \left(X_A \ln X_A + X_B \ln X_B \right)$$

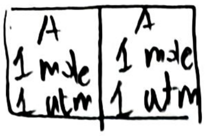
$$= -3R \left(2 \ln \frac{2}{3} + \ln \frac{1}{3} \right) = -R \ln \frac{4}{27} = R \ln \frac{27}{4}$$

$$\Delta S_{thermal,A} = nR \ln \frac{V_2}{V_1} = 2R \ln \frac{\frac{2}{3}}{\frac{1}{2}} = 2R \ln \frac{4}{3} = R \ln \frac{16}{9}$$

$$\Delta S_{thermal,B} = nR \ln \frac{V_2}{V_1} = nR \ln \frac{\frac{1}{3}}{\frac{1}{2}} = R \ln \frac{2}{3}$$

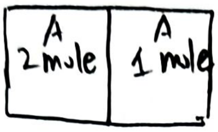
$$\Delta S_{total} = \Delta S_{config} + \Delta S_{thermal,A} + \Delta S_{thermal,B} = R \ln \frac{27}{4} + R \ln \frac{16}{9} + R \ln \frac{2}{3} = R \ln 8 = 3R \ln 2$$

(c)



같은물질이 동일한 P, V를 가지기 때문에

$\Delta S = 0$



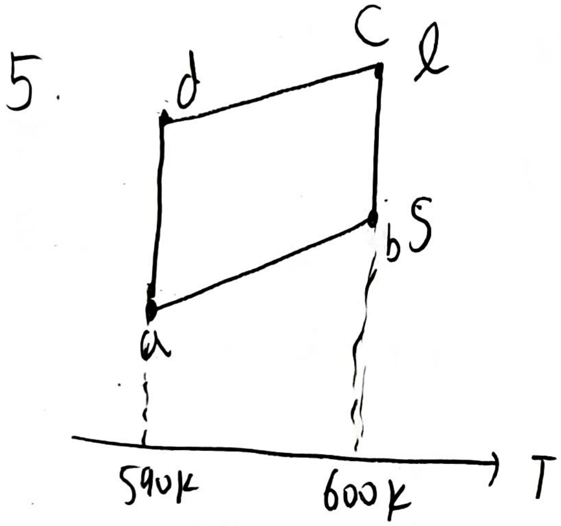
$\Delta S_{config} = 0$

$\Delta S_{thermal,A} = 2R\ln\frac{\frac{2}{3}}{\frac{1}{2}} = 2R\ln\frac{4}{3}$

$\Delta S_{thermal,B} = R\ln\frac{\frac{1}{3}}{\frac{1}{2}} = R\ln\frac{2}{3}$

$\Delta S = 2R\ln\frac{4}{3} + R\ln\frac{2}{3} = R\ln\frac{32}{27}$

5.



(1) $\Delta S_{d\to a} = \Delta S_{d\to c} + \Delta S_{c\to b} + \Delta S_{b\to a}$

$\Delta S_{d\to c} = \int_{590}^{600} \frac{C_p(l)}{T}\,dT = \int_{590}^{600} \frac{32.4}{T} - 3.1\times10^{-3}\,dT = 32.4\ln\frac{60}{59} - 3.1\times10^{-2} = 0.51\ \text{J/K}$

$\Delta S_{c\to b} = \frac{-\Delta H_{melting}}{T} = \frac{-4810}{600} = -8.017\ \text{J/mole K}$

$\Delta S_{b\to a} = \int_{600}^{590} \frac{C_p(S)}{T}\,dT = 9.75\times10^{-2} = 0.0975\ \text{J/K}$

$\Delta S_{d\to a} = -7.406\ \text{J/K}$

$\Delta S_{irr} = -\frac{\Delta H_{d\to a}}{T} = -\frac{\Delta H_{d\to c} + \Delta H_{c\to b} + \Delta H_{b\to a}}{T}$

$$\Delta H_{d\to c} = \int_{540}^{600} nC_p(l)\,dT = \int_{540}^{600} 32.4 - 3.1\times10^{-3}\,T\,dT \doteq 305.555\,J$$

$$\Delta H_{c\to b} = -4810\,J$$

$$\Delta H_{b\to a} = \int_{600}^{540} nC_p(s)\,dT = \int_{600}^{540} 9.75\times10^{-3}\,T\,dT = -58.013\,J$$

$$\Delta H_{d\to a} = -4562.46\,J$$

$$\Delta S_{irr} = +\frac{4562.46}{540} = +7.733\,J$$

$$\Delta S_{d\to a} + \Delta S_{irr} = \Delta S_{total} = -7.406 + 7.733 = 0.327\,J > 0$$

∴ 자발적 반응

(2) $G = \Delta H - T\Delta S_{sys}$

$$= -4562.46 - 590\times(-7.406) = -192.92\,J < 0$$

∴ 자발적반응이다.

Pb가 단열된 용기에 보관되어 있었다면 상변화에 의해 발생된 열이 빠져나가지 못하게 되어 모든 Pb가 다 상변화가 이뤄지지 못하고 일부만 상변화에 참여할 것이다. 상변화된 Pb의 몰수를 n이라고 하자.

단열 용기이기 때문에 $\Delta H = 0$ 이된다.

즉 $\Delta H_{d\to c} + \Delta H_{c\to b} = 0$

$$305.555 = 4810\times n$$

$$n = 0.064\,mol$$

고체 0.064 mol 액체 0.936mol 존재한다.

6. Graphite를 Diamond로 바꾸는데 필요한 P　C의 분자량은 12

$$\Delta G = \Delta H - T\Delta S + \int_1^P \Delta V_{graphite \to diamond}\, dp \le 0$$

$$454 - 298 \times (0.58 - 1.37) + \int_1^P \left(\frac{12}{3.515} - \frac{12}{2.22}\right) \times 10^{-6}\, dp \le 0$$

$$689.42\, cal/mol - 1.991 \times 10^{-6}(P-1)\ J/mol \le 0$$

$$1\, cal = 4.184\, J$$

$$P \ge \frac{689.42 \times 4.184}{1.991 \times 10^{-6}} + 1$$

$$P \ge 1.448 \times 10^{6}\ atm$$

∴ 압력은 최소 1.448×10^{6} atm 이상이어야 한다.