HW2 20220318 윤정현

1 $L_1 L_2 = k$ (일정) $\Rightarrow L_2 = \frac{A}{L_1}$

$U$가 최소가 되는 지점 $\Rightarrow \frac{\partial U}{\partial L_1} = 0$ 이 되는 지점

$$U = \int r\,dl = 2\int_0^{L_1} r_1\,dl + 2\int_0^{L_2} r_2\,dl = 2(r_1 L_1 + r_2 L_2) = 2(r_1 L_1 + r_2 \frac{A}{L_1})$$

$\frac{\partial U}{\partial L_1} = 0$ 일때 $U$가 최소, $\frac{dU}{dL_1} = 2(r_1 - \frac{r_2 A}{L_1^2}) = 0$

$\therefore L_1 = \sqrt{\frac{r_2 A}{r_1}}$ , $L_2 = \frac{A}{L_1} = \sqrt{\frac{r_1 A}{r_2}}$ $\quad \therefore \frac{L_1}{L_2} = \sqrt{\frac{r_2 A}{r_1}} \cdot \sqrt{\frac{r_2}{r_1 A}} = \frac{r_2}{r_1}$

$\therefore \frac{L_1}{L_2} = \frac{r_2}{r_1}$

2 $Z = \sum e^{-\varepsilon_i / kT}$

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

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

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

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

$$Z = \frac{a}{2}\sqrt{\frac{8\pi mkT}{h}}\ \frac{b}{2}\sqrt{\frac{8\pi mkT}{h^2}} = \frac{ab}{4}\ \frac{8\pi mkT}{h^2} = \frac{A}{4}\ \frac{8\pi mkT}{h^2} = \frac{2A\pi mkT}{h^2}$$

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

$$p \Rightarrow -\left(\frac{\partial F}{\partial V}\right)_T = NkT\left(\frac{\partial \ln Z}{\partial V}\right)_T$$

$$\Rightarrow NkT\left(\frac{\partial \ln Z}{\partial A}\right)_T = NkT\frac{1}{A} = \frac{nkT}{A} \qquad PA = nRT$$

2-b

$-\left(\frac{\partial F}{\partial A}\right)_T$

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

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| 에너지 | 길이 | 경우의 수 |
| --- | --- | --- |
| $0$ | $Na$ | $1$ |
| $\varepsilon$ | $(N-1)a$ | ${}_{N-1}C_1$ |
| $\vdots$ | $\vdots$ | $\vdots$ |
| $n\varepsilon$ | $(N-n)a$ | ${}_{N-1}C_n$ |
| $\vdots$ | $\vdots$ | $\vdots$ |
| $(N-1)\varepsilon$ | $a$ | $1$ |

$$Z = \sum g_i e^{-\varepsilon_i/kT} = \sum_{n=0}^{N-1} {}_{N-1}C_n\, e^{-n\varepsilon/kT}$$

$$= {}_{N-1}C_0 e^{-0} + {}_{N-1}C_1 e^{-\varepsilon/kT} + \cdots + {}_{N-1}C_{N-1} e^{-(N-1)\varepsilon/kT} = [1+e^{-\varepsilon/kT}]^{N-1}$$

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

$$= Na - \frac{a}{Z}\sum_{n=0}^{N-1} n\,{}_{N-1}C_n\, e^{-n\varepsilon/kT} = Na + akT\frac{\partial}{\partial\varepsilon}(\ln Z)$$

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

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

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

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

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

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

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

$\Delta S = \Delta S_{con} + \Delta S_{the} = \Delta S_{con}$

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

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

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

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

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

(c) (a)에 따라 $\Delta S = \Delta S_{con} = \Delta S_{the} = 0$

(b)에 따라, $\Delta S_{con} = 0$

$\Delta S_{the} = n_1 R \ln\left(\frac{V_2}{V_1}\right) + n_2 R \ln\left(\frac{V_2}{V_1}\right)$

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

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

path indepent $\Rightarrow \Delta S_{sys} = \Delta S_{AB} + \Delta S_{BC} + \Delta S_{CD}$

590K Pb(l) $\rightarrow$ 600K Pb(l) $\rightarrow$ 600K Pb(s) $\rightarrow$ 590K Pb(s)

(A) (B) (C) (D)

$\Delta S_{AB} = \int_{T_1}^{T_2} \frac{nC_p(l)}{T} dT = n \int_{590K}^{600K} \left(\frac{32.4}{T} - 3.1(\times 10^{-3})\right) dT = n(0.514)$

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

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

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

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

$\Delta H_{BC} = -n(4810)$ $\quad \Delta H_{CD} = \int_{T_2}^{T_1} nC_p(s)\, dT = n \int_{600K}^{590K} 9.75\times10^{-3}T\, dT = -n(58.01)$

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

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

$= n\left(-4810 - (580)(-7.690J)\right) = -n(272) < 0$

(c) Pb가 단일 용기 보관시 액체 상태로 유지될 것 (압력, 부피 안변할 시)

6 graphite $\rightarrow$ diamond

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

$V_{gra} = \dfrac{12\ g/mol}{2.22\ g/cm^3} = 5.405\ (cm^3/mol)$

$V_{dia} = \dfrac{12\ g/mol}{3.515\ g/cm^3} = 3.415\ (cm^3/mol)$

$\rightarrow \Delta V = -1.99\ cm^3/mol$

이때 $\left(\dfrac{\partial G}{\partial P}\right)_T = \Delta V$ 이므로 $\Delta G(P, T=298K) = \Delta G(P=1, T=298K) + \int_1^P \Delta V\, dP$

$1\,cm^3 \cdot atm \times \dfrac{1\,L}{1000\,cm^3} \times \dfrac{101.325\,J}{1\,atm \cdot L} = 0.1013\,J$

$\therefore \Delta G(P, T=298K) = 2896 + (-1.99 \times 0.1013)(P-1) = 0$ 일 때

$P - 1 = \dfrac{2896}{1.99 \times 0.1013} = 14.366 \quad \therefore P = 14.367\ (atm)$

$\therefore\ 14.367\ atm$