Problem set #3 20220735 김주영

1.

a) liquid NaF의 증기압력이 1 atm이 될 때의 온도를 구해보자.

(0=) $\ln 1 = -\frac{31090}{T} - 2.52\ln T + 34.66$, $T = 2006K$

b) Triple point의 온도를 T_T, 압력을 P_T 라고 하면

$\ln P_T = -\frac{34450}{T_T} - 2.01\ln T_T + 33.74$

$\ln P_T = -\frac{31090}{T_T} - 2.52\ln T_T + 34.66$

위의 연립 방정식을 풀면, $T_T = 1239K$, $P_T = e^{-\frac{34450}{1239} - 2.01\ln 1239 + 33.74} = 2.287\times10^{-4}\,atm$

c) Clausius-Clapeyron equation.

$\left(\frac{dP}{dT}\right)_{eq} = \frac{P\Delta H}{RT^2} \Rightarrow \frac{1}{P}\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{RT^2} \rightarrow \frac{d}{dT}\ln P = \frac{\Delta H}{RT^2}$

$\frac{d}{dT}\ln P = \frac{d}{dT}\left(\frac{-31090}{T} - 2.52\ln T + 34.66\right) = \frac{31090}{T^2} - \frac{2.52}{T} = \frac{\Delta H}{RT^2}$

$\rightarrow \Delta H = 31090R - 2.52RT = R(31090 - 2.52T)$

T에 위에서 구한 normal boiling temperature를 대입하면,

$\Delta H = 8.3145(31090 - 2.52\times2006) = 216.5\,kJ/mol$.

d) melting ΔH을 구해야하는데 주어진 식이 없으므로

$\Delta H_{s\to l} = \Delta H_{s\to g} + \Delta H_{g\to l} = \Delta H_{s\to g} - \Delta H_{l\to g}$ 로 구한다.

$\Delta H_{l\to g} = R(31090 - 2.52T)$ (c) 에서 구함) --- ①

c)의 방법으로 $\Delta H_{s\to g}$를 구해보면, $\frac{d}{dT}\ln P = \frac{34450}{T^2} - \frac{2.01}{T} = \frac{\Delta H_{s\to g}}{RT^2}$

$\Delta H_{s\to g} = R(34450 - 2.01T)$ --- ②

$\Delta H_{s\to l} = ② - ① = R(3360 + 0.51T)$, $T = T_T = 1239K$ 대입하면

$\Delta H_{s\to l} = 33.19\,kJ/mol$

e) solid, T_0 ⟶ solid, $T_{melting\ point}$ ⟶ liquid, $T_{melting\ point}$ ⟶ liquid, T_0 ($T_{melting\ point}$ // T_m)

$\Delta H_{s\to l} = C_{p,solid}(T_m - T_0) + \Delta H_{melting} + C_{p,liquid}(T_0 - T_m)$

$=$ (same polynomial) $+ (C_{p,liquid} - C_{p,solid})T$

$\Delta H_{s\to l} = R(3360 + 0.51T)$ 에서 $R(0.51) = C_{p,liquid} - C_{p,solid}$ 라고 할 수 있고 그 값은 $4.24\,J/mol\cdot K$ 이다.

2.

bulk 상태의 $\Delta G_{bulk} = \Delta H - T\Delta S$

nano particle 상태의 $\Delta G_{n.p} = \Delta H - T\Delta S + V_m\left(\frac{2\gamma_\ell}{r} - \frac{2\gamma_s}{r}\right)$

각상태의 melting point를 $T_{m,b}$, $T_{m,n}$ 으로 두면

$$\Delta G_{bulk,m} = \Delta H_m - T_{m,b}\Delta S_m = 0$$

$$\Delta G_{n.p,m} = \Delta H_m - T_{m,n}\Delta S_m + V_m\left(\frac{2\gamma_\ell}{r} - \frac{2\gamma_s}{r}\right) = 0$$

$$\Delta G_{bulk,m} = \Delta G_{np,m}$$

$$\cancel{\Delta H_m} - T_{m,b}\Delta S_m = \cancel{\Delta H_m} - T_{m,n}\Delta S_m + V_m\left(\frac{2\gamma_\ell}{r} - \frac{2\gamma_s}{r}\right)$$

$$(T_{m,n} - T_{m,b})\Delta S_m = V_m\left(\frac{2\gamma_\ell}{r} - \frac{2\gamma_s}{r}\right)$$

melting point 강하정도 $= \frac{2}{r}V_m \cdot \frac{\gamma_s - \gamma_\ell}{\Delta S_m}$

$$\frac{\Delta T_m}{T} = \frac{2}{r}V_m\frac{\gamma_s - \gamma_\ell}{T_m\Delta S_m}$$

$$= \frac{2}{r}V_m\frac{\gamma_s - \gamma_\ell}{\Delta H_m}$$

3.

a) $\overline{Q}_2 = Q + (1-X_2)\frac{dQ}{dX_2}$ 이므로

$\overline{G}_A = G_m + (1-X_A)\frac{dG_m}{dX_A} = G_m + (1-X_A)\left[{}^\circ G_A - {}^\circ G_B + RT\{\ln X_A - \ln(1-X_A)\} + (1-2X_A)\{L_0 + L_1(2X_A-1)\} + X_A(1-X_A)2L_1\right]$

$= X_A{}^\circ G_A + X_B{}^\circ G_B + RT\{X_A\ln X_A + X_B\ln X_B\} + X_AX_B\{L_0 + (X_A - X_B)L_1\} +$

$= {}^\circ G_A + RT\ln X_A + X_B^2L_0 + X_B^2(4X_A-1)L_1$

$\overline{G}_B = G_m + (1-X_B)\frac{dG_m}{dX_B} = {}^\circ G_B + RT\ln X_B + X_A^2L_0 + X_A^2(1-4X_B)L_1$

b) $RT\ln a_A = \overline{G}_A - {}^\circ G_A = RT\ln X_A + X_B^2L_0 + X_B^2(4X_A-1)L_1$

i) $X_A \to 1$, $RT\ln a_A \to 0$, $a_A \to 1$

a_A가 1에 근사한다는 것은 ideal 한 model이 된다. $\boxed{\text{Rault's law}}$

ii) $X_A \to 0$, $RT\ln a_A = RT\ln X_A + L_0 - L_1$,

$a_A = e^{X_A + \frac{L_0-L_1}{RT}} \longrightarrow e^{\frac{L_0-L_1}{RT}}$ (constant) $\boxed{\text{Henry's law}}$

c) $G^m = \sum X_i\overline{G}_i = X_A\overline{G}_A + X_B\overline{G}_B$

$X_B\overline{G}_B = \cancel{X_A{}^\circ G_A} + X_B{}^\circ G_B + RT\{\cancel{X_A\ln X_A} + X_B\ln X_B\} + X_AX_B\{L_0 + (X_A-X_B)L_1\}$

$- \cancel{X_A{}^\circ G_A} - \cancel{X_ART\ln X_A} - X_AX_B^2L_0 + X_AX_B^2(4X_A-1)L_1$

$= X_B{}^\circ G_B + RTX_B\ln X_B + X_AX_B(1-X_B)L_0 + X_AX_B(X_A - X_B - 4X_AX_B + X_B)L_1$

$= X_B{}^\circ G_B + RTX_B\ln X_B + X_AX_B(1-X_B)L_0 + X_A^2X_B(1-4X_B)L_1$

$\overline{G}_B = {}^\circ G_B + RT\ln X_B + X_A(1-X_B)L_0 + X_A^2(1-4X_B)L_1$

4.

Regular Solution

$$G_m = X_A G_A^\circ + X_B G_B^\circ + RT(X_A \ln X_A + X_B \ln X_B) + X_A X_B L_{AB}$$

liquid에 대하여, $X_A G_A^{ref\to l} + X_B G_B^{ref\to l} + RT(X_A \ln X_A + X_B \ln X_B) + X_A X_B L_{AB}(l) =: G_m(l)$

solid에 대하여, $X_A G_A^{ref\to s} + X_B G_B^{ref\to s} + RT(X_A \ln X_A + X_B \ln X_B) + X_A X_B L_{AB}(s) =: G_m(s)$

$X_A = 1 - X_B$ 대입

$$G_m(l) = (1-X_B) G_A^{ref\to l} + X_B G_B^{ref\to l} + RT((1-X_B)\ln(1-X_B) + X_B \ln X_B) + (1-X_B) X_B L_{AB}(l)$$

$$G_m(s) = (1-X_B) G_A^{ref\to s} + X_B G_B^{ref\to s} + RT((1-X_B)\ln(1-X_B) + X_B \ln X_B) + (1-X_B) X_B L_{AB}(s)$$

X_B에 대해 미분

$$\frac{\partial G_{m(l)}}{\partial X_B} = -G_A^{ref\to l} + G_B^{ref\to l} + RT(-\ln(1-X_B) + \ln X_B) + (1-2X_B) L_{AB}(L)$$

$$\frac{\partial G_{m(s)}}{\partial X_B} = -G_A^{ref\to s} + G_B^{ref\to s} + RT(-\ln(1-X_B) + \ln X_B) + (1-2X_B) L_{AB}(s)$$

X_B에 $X_{B(s)}$를 대입한 값 = $X_{B(l)}$을 대입한 값.

$$-G_A^{ref\to l} + G_B^{ref\to l} + G_A^{ref\to s} - G_B^{ref\to s} + \underbrace{RT\left(\ln\frac{1-X_{B(s)}}{1-X_{B(l)}} + \ln\frac{X_{B(l)}}{X_{B(s)}}\right) + (1-2X_{B(l)}) L_{AB}(l) - (1-2X_{B(s)}) L_{AB(s)}}_{=:\ \text{remainder}} = 0$$

그러면서, $\Delta G_{m(A)} = G_A^{ref\to l} - G_A^{ref\to s}$, $\Delta G_{m(B)} = G_B^{ref\to L} - G_B^{ref\to s}$ 이므로 위의 식을 다시 쓰면

$-\Delta G_{m(A)} + \Delta G_{m(B)} + \text{remainder} = 0$. 이때 $\Delta G_{m(A)}$, $\Delta G_{m(B)}$는 constant이고

remainder에는 reference term이 없으므로 unique 함을 증명할 수 있다.

5.

$a_B \neq X_B$ 이므로 ideal model이 아니다

regular solution model에서

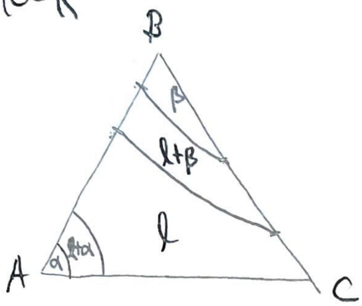
$$G_m = X_A G_A^\circ + X_B G_B^\circ + RT(X_A \ln a_A + X_B \ln a_B) = X_A G_A^\circ + X_B G_B^\circ + RT(X_A \ln X_A + X_B \ln X_B) + RT(X_A \ln \gamma_A + X_B \ln \gamma_B)$$

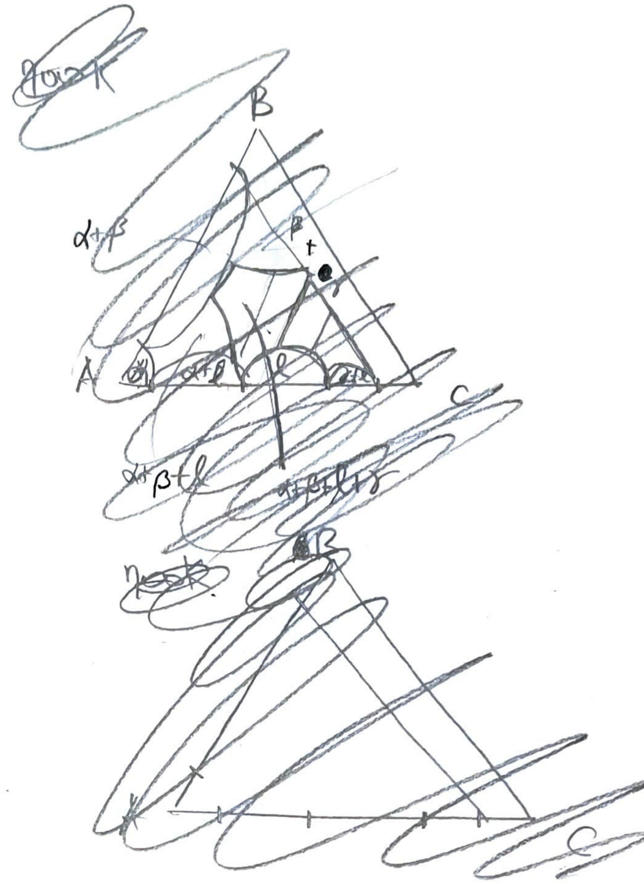
이므로 $X_A X_B L_{AB} = RT(X_A \ln \gamma_A + X_B \ln \gamma_B)$ $\left(\gamma_A = \frac{a_A}{X_A},\ \gamma_B = \frac{a_B}{X_B}\right)$

$RT \ln \gamma_A = L_{AB}$

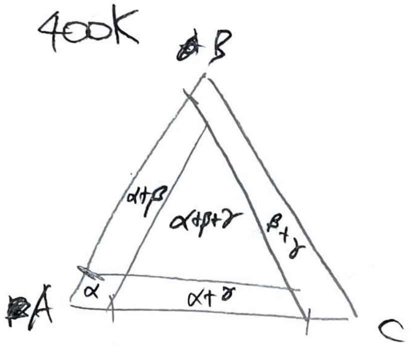
6.

900K





400K



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