1. vapor pressure of solid: $\ln p = -\frac{34450}{T} - 2.01\ln T + 33.74$

vapor pressure of liquid: $\ln p = -\frac{31090}{T} - 2.52\ln T + 34.66$

a) boiling T: Vapor pressure = 1 atm 일때의 온도.

$\ln 1 = 0 = -\frac{31090}{T} - 2.52\ln T + 34.66$

$T_b = 2006K$

b) T, P at the triple point

$-\frac{34450}{T} - 2.01\ln T + 33.74 = -\frac{31090}{T} - 2.52\ln T + 34.66$

$\frac{3360}{T} - 0.51\ln T + 0.88 = 0$

$T_{triple} = 1239K$

(C) Molar heat of evaporation at boiling T.

$\ln p = -\frac{31090}{T} - 2.52\ln T + 34.66$

$\frac{d\ln p}{dT} = \frac{\Delta H}{RT^2} = \frac{31090}{T^2} - \frac{2.52}{T}$

$\Delta H = 31090R - 2.52RT$

$T = 2006K$

$\Delta H_{l \to v} = 31090 \times 8.314 - 2.52 \times 8.314 \times 2006 = 216454J$

d) Molar heat of melting at triple point

$$\ln p = -\frac{34450}{T} - 2.01\ln T + 33.74$$

$$\frac{d\ln p}{dT} = \frac{\Delta H}{RT^2} = \frac{34450}{T^2} - 2.01 \times \frac{1}{T}$$

$$\Delta H_{s\to v} = 34450 \times R - 2.01 \times RT \Big|_{T=1239}$$

$$\Delta H_{s\to v} = 34450 \times 8.314 - 2.01 \times 8.314 \times 1239 = 265712\,J$$

$$\Delta H_{s\to l} = \Delta H_{s\to v} - \Delta H_{l\to v}$$

$$\Delta H_{l\to v} = 31090R - 2.52RT \Big|_{T=1239}$$

$$= 232524\,J$$

$$\Delta H_{s\to l} = 265712 - 232524 = 33188\,J$$

e) $\Delta C_p = \frac{d\Delta H}{dT}$

$$\Delta H_{s\to l} = \Delta H_{s\to v} - \Delta H_{l\to v} = 3360R + 0.51RT$$

$$\frac{d\Delta H}{dT} = 0.51R = 4.24\,J/K$$

$$\Delta C_p = 4.24\,J/K$$

2. $$\begin{array}{l} dG^S = -S^S dT + V dp^S \\ - \ dG^L = -S^L dT + V dp^L \\ \hline \end{array}$$

$$dG^{S\to L} = dG_m = (S^L - S^S)\, dT + V(dp^S - dp^L)$$

$$dG_m = 0, \Rightarrow (S^L - S^S)\, dT + V_m(dp^S - dp^L) = 0$$

$$\Delta G \quad \Delta S = \frac{\Delta H}{T} \Rightarrow S^L - S^S = \frac{\Delta H_m}{T_m}$$

$$\frac{\Delta H_m}{T_m} \Delta T_m + V_m(dp^S - dp^L) = 0$$

$$dp^S - dp^L = \frac{2\gamma_L}{r} - \frac{2\gamma_S}{r}$$

$$\frac{\Delta T_m}{T_m} \times \Delta H_m + V_m \times \frac{2(\gamma_L - \gamma_S)}{r} = 0$$

$$\frac{\Delta T_m}{T_m} = \frac{\gamma_S - \gamma_L}{\Delta H_m} \times \frac{2}{r} V_m$$

3. $G_m = x_A {}^\circ G_A + x_B {}^\circ G_B + RT\{x_A \ln x_A + x_B \ln x_B\} + x_A x_B\{L_0 + (x_A - x_B)L_1\}$

(a) $G_m = x_A \overline{G_A} + x_B \overline{G_B}$

$dG_m = \overline{G_A}\, dx_A + \overline{G_B}\, dx_B$

$x_A + x_B = 1 \rightarrow dx_A = -dx_B$

$dG = (\overline{G_B} - \overline{G_A})\, dx_B$

$x_A \frac{dG}{dx_B} = x_A \overline{G_B} - x_A \overline{G_A}$

$x_A \frac{dG}{dx_B} = x_A \overline{G_B} - G_m + x_B \overline{G_B}$

$\overline{G_B} = G_m + x_A \frac{dG_m}{dx_B} = G_m - x_A \frac{dG_m}{dx_A}$

$\overline{G_A} = G_m + x_B \frac{dG_m}{dx_A} = G_m + (1-x_A)\frac{dG_m}{dx_A}$

$G_m = x_A {}^\circ G_A + (1-x_A){}^\circ G_B + RT\{x_A \ln x_A + (1-x_A)\ln(1-x_A)\} + x_A(1-x_A)\{L_0 + (2x_A-1)L_1\}$

$\frac{dG_m}{dx_A} = {}^\circ G_A - {}^\circ G_B + RT\{\ln x_A - \ln(1-x_A)\} + (1-2x_A)\{L_0 + (2x_A-1)L_1\} + 2L_1 x_A(1-x_A)$

$\overline{G_A} = G_m + (1-x_A)\frac{dG_m}{dx_A} = {}^\circ G_A + RT\ln x_A + (1-x_A)(1-x_A)L_0 + (1-x_A)(1-x_A)(4x_A-1)L_1$

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

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

$\overline{G_B} = G_m - x_A \frac{dG_m}{dx_A} = {}^\circ G_B + RT\ln(1-x_A) + x_A^2 L_0 + x_A^2(4x_A-3)L_1$

$\doteq {}^\circ G_B + RT\ln x_B + x_A^2 L_0 + x_A^2(-4x_B+1)L_1$

$= {}^\circ G_B + RT\ln x_B + (1-x_B^2)L_0 + (1-x_B^2)(-4x_B+1)L_1$

(b) $\overline{G_A^{xs}}$: dilute 영역 $x_A \to 0 \Rightarrow (1-x_A^2)L_0 + (1-x_A^2)(4x_A-1)L_1 \big|_{x_A=0} = L_0 - L_1$: Henrian 거동

rich 영역 $x_A \to 1 \Rightarrow (1-x_A^2)L_0 + (1-x_A^2)(4x_A-1)L_1 \big|_{x_A=1} = 0$: Raoultian 거동

$\overline{G_B}$ dilute 영역 $x_B \to 0 \Rightarrow (1-x_B^2)L_0 + (1-x_B^2)(-4x_B+1)L_1 \big|_{x_B=0} = L_0 + L_1$: Henrian 거동

rich 영역 $x_B \to 1 \Rightarrow (1-x_B^2)L_0 + (1-x_B^2)(-4x_B+1)L_1 \big|_{x_B=1} = 0$: Raoultian 거동

(1) $\sum_i x_i \, d\bar{G}_i = 0$

$$x_A \, d\bar{G}_A + x_B \, d\bar{G}_B = 0$$

$$d\bar{G}_B = -\frac{x_A}{x_B} \, d\bar{G}_A$$

$$\int d\bar{G}_B = \bar{G}_B = -\int \frac{x_A}{x_B} \, d\bar{G}_A$$

$$\bar{G}_A = {}^0G_A + RT\ln x_A + (1-x_A)^2 L_0 + (1-x_A)(1-x_A)(4x_A-1)L_1$$

$$d\bar{G}_A = \left(\frac{1}{x_A}RT - 2(1-x_A)L_0 - 2(1-x_A)(4x_A-1)L_1 + 4(1-x_A)^2 L_1\right)dx_A$$

$$\bar{G}_B = -\int \frac{x_A}{1-x_A}\left[\frac{1}{x_A}RT - 2(1-x_A)L_0 - 2(1-x_A)(4x_A-1)L_1 + 4(1-x_A)^2 L_1\right]dx_A$$

$$= -\int \frac{RT}{1-x_A} - 2x_A L_0 - 2x_A(4x_A-1)L_1 + 4x_A(1-x_A)L_1 \, dx_A$$

$$= RT\ln(1-x_A) + x_A^2 L_0 + (4x_A^3 - 3x_A^2)L_1 + \overset{G_B^0}{\overset{\parallel}{C}}$$

$$= RT\ln x_B + (1-x_B)^2 L_0 + (1-x_B)^2(-4x_B+1)L_1 + G_B^0$$

4.

(a) $\Delta G^M_{(l)} = RT(X_A \ln X_A + X_B \ln X_B) + X_B \Delta G^0_m(B)$

$\Delta G^M_{(s)} = RT(X_A \ln X_A + X_B \ln X_B) - X_A \Delta G^0_m(A)$

(b) $\Delta G^M_{(l)} = RT(X_A \ln X_A + X_B \ln X_B)$

$\Delta G^M_{(s)} = RT(X_A \ln X_A + X_B \ln X_B) - X_B \Delta G^0_{m(B)} - X_A \Delta G^0_{m(A)}$

(a)에서의 공통접선

$\Delta G^M_{(l)} = RT(X_A \ln X_A + (1-X_A)\ln X_A) + (1-X_A)\Delta G^0_m(B)$

$\Delta G^M_{(s)} = RT(X_A \ln X_A + (1-X_A)\ln(1-X_A)) - X_A \Delta G^0_m(A)$

$\frac{dG^M_{(l)}}{dX_A} = RT\ln\frac{X_A}{1-X_A} - \Delta G^0_m(B)$

$\frac{dG^M_{(s)}}{dX_A} = RT\ln\frac{X_A}{1-X_A} - \Delta G^0_m(A)$

$G^M_{(l)}$의 $X_A = X_{A,l}$에서의 접선: $\{RT\ln\frac{X_{A,l}}{1-X_{A,l}} - \Delta G^0_m(B)\}(X_A - X_{A,l}) + \Delta G^M_{(l)}\big|_{X_A = X_{A,l}}$

$G^M_{(s)}$의 $X_A = X_{A,s}$에서의 접선: $\{RT\ln\frac{X_{A,s}}{1-X_{A,s}} - \Delta G^0_m(A)\}(X_A - X_{A,s}) + \Delta G^M_{(s)}\big|_{X_A = X_{A,s}}$

→ 두 접선이 같기 위해서는 접선의 기울기와 y절편이 같아야 한다

$RT\ln\frac{X_{A,l}}{1-X_{A,l}} - \Delta G^0_m(B) = RT\ln\frac{X_{A,s}}{1-X_{A,s}} - \Delta G^0_m(A)$ — ①

$-X_{A,l} RT\ln\frac{X_{A,l}}{1-X_{A,l}} + \Delta G^0_m(B)\cdot X_{A,l} + \Delta G^M_{(l)}\big|_{X_A = X_{A,l}} = -X_{A,s} RT\ln\frac{X_{A,s}}{1-X_{A,s}} + X_{A,s}\cdot\Delta G^0_{m(A)} + \Delta G^M_{(s)}\big|_{X_A = X_{A,s}}$

→ $2X_{A,l} RT\ln(1-X_{A,l}) + \Delta G^0_{m(B)} = 2X_{A,s} RT\ln(1-X_{A,s})$ — ②

(b)에서의 공통접선

$\Delta G^M_{(l)}$의 $X_A = X_{A,l2}$에서의 접선: $\left(RT\ln\frac{X_{A,l2}}{1-X_{A,l2}}\right)(X_A - X_{A,l2}) + \Delta G^M_{(l)}\big|_{X_A = X_{A,l2}}$

$\Delta G^M_{(s)}$의 $X_A = X_{A,s2}$에서의 접선: $\left(RT\ln\frac{X_{A,s2}}{1-X_{A,s2}} + \Delta G^0_m(B) - \Delta G^0_{m(A)}\right)(X_A - X_{A,s2}) + \Delta G^M_{(s)}\big|_{X_A = X_{A,s2}}$

$RT\ln\frac{X_{A,l2}}{1-X_{A,l2}} = RT\ln\frac{X_{A,s2}}{1-X_{A,s2}} + \Delta G^0_m(B) - \Delta G^0_{m(A)}$ — ③

$$-X_{A,l_2} RT \ln \frac{X_{A,l2}}{1-X_{A,l2}} + \Delta G^{M}_{(l)}\Big|_{X_A = X_{A,l2}} = -X_{A,S2} RT \ln \frac{X_{A,S2}}{1-X_{A,S2}} - X_{A,S2}\Delta G^{\circ}_{m(A)} + X_{A,S2}\Delta G^{\circ}_{m(B)} + \Delta G^{M}_{(S)}\Big|_{X_A = X_{A,l2}}$$

$$2X_{A,l2} RT \ln (1-X_{A,l2}) = 2X_{A,S2} RT \ln (1-X_{A,S2}) - \Delta G^{\circ}_{m}(B) \quad - ④$$

①식과 ③번식이, ②식과 ④식이 같다.

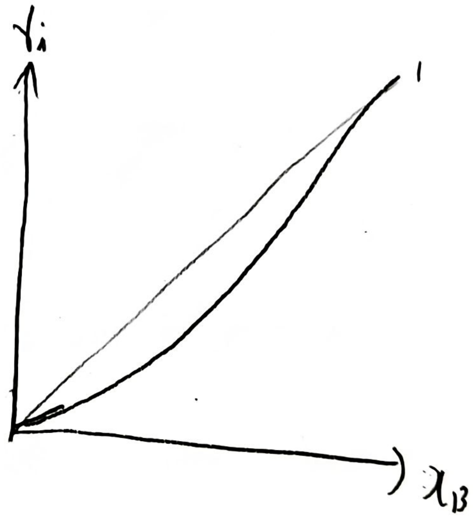
따라서 ~~[illegible]~~ $X_{A,l} = X_{A,l2}$ & $X_{A,S} = X_{A,S2}$

∴ 상평형 조성은 둘이 같다.

5.

$$\gamma_i = \frac{a_B}{X_B}$$

x_B	a_B	γ_i
0.1	0.0320	0.3200
0.2	0.0800	0.4000
0.3	0.1498	0.4993
0.4	0.2400	0.6000
0.5	0.3510	0.7020
0.6	0.4782	0.7970
0.7	0.6162	0.8803
0.8	0.7559	0.9449
0.9	0.8874	0.9860
1.0	1.000	1.000



ideal 한 경우 $\gamma_i = 1$ 이어야 하는데 그렇지 않다.

regular model 인 경우 $\frac{\ln \gamma_i}{(1-X_i)^2}$ 가 일정해야 한다.

x_B	γ_i	$\frac{\ln \gamma_i}{(1-x_B)^2}$
0.1	0.3200	-1.4067
0.2	0.4000	-1.4317
0.3	0.4993	-1.4173
0.4	0.6000	-1.4190
0.5	0.7020	-1.4153
0.6	0.7970	-1.4181
0.7	0.8803	-1.4168
0.8	0.9449	-1.4176
0.9	0.9860	-1.4099
1	1	

$\frac{\ln \gamma_i}{(1-x_B)^2} = \alpha_i$ 는 거의 일정하다

∴ 성분 B는 regular 모델을 따른다.

Molar Gibbs energy of mixing $\bar{G}_B = RT\, x_B \ln a_B$

$$\frac{\ln \gamma_i}{(1-x_B)^2} = \alpha \simeq -1.4164$$

$$\ln \frac{a_i}{x_B} = \alpha(1-x_B)^2$$

$$a_i = x_B\, e^{\alpha(1-x_B)^2} = x_B\, e^{-1.4164(1-x_B)^2}$$

x_B	a_i 수식
0.1	0.0317
0.2	0.0808
0.3	0.1498
0.4	0.2402
0.5	0.3509
0.6	0.4783
0.7	0.6162
0.8	0.7559
0.9	0.8873
1	1

수식으로 계산한 것과 실험 데이터 와의 차이가 거의 없다.

Sub regular model은 3번 문제에서 구한 식을 이용한다.

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

$$RT\ln a_B = RT\ln x_B + (1-x_B^2)L_0 + (1-x_B^2)(1-4x_B)L_1$$

L_0, L_1을 구하기 위해 $\left(\begin{array}{ll} x_B=0.1 & a_B=0.032 \\ x_B=0.2 & a_B=0.08 \end{array} \right)$ 대입

$$8.314\times1273\times\ln0.032 = 8.314\times1273\times\ln0.1 + (1-0.1^2)L_0 + (1-0.1^2)(1-4\times0.1)L_1$$

$$-36429 = -24370 + 0.99L_0 + 0.594L_1$$

$$0.99L_0 + 0.594L_1 = -12059$$

$$\cancel{8.3}\ 8.314\times1273\times\ln0.08 = 8.314\times1273\times\ln0.2 + (1-0.2^2)L_0 + (1-0.2^2)(1-4\times0.2)L_1$$

$$-26732 = -17034 + 0.84L_0 + 0.192L_1$$

$$0.84L_0 + 0.192L_1 = -9698$$

$L_0 = -11154$ $\quad L_1 = -1711$

이를 통해 a_B 값을 구해보면

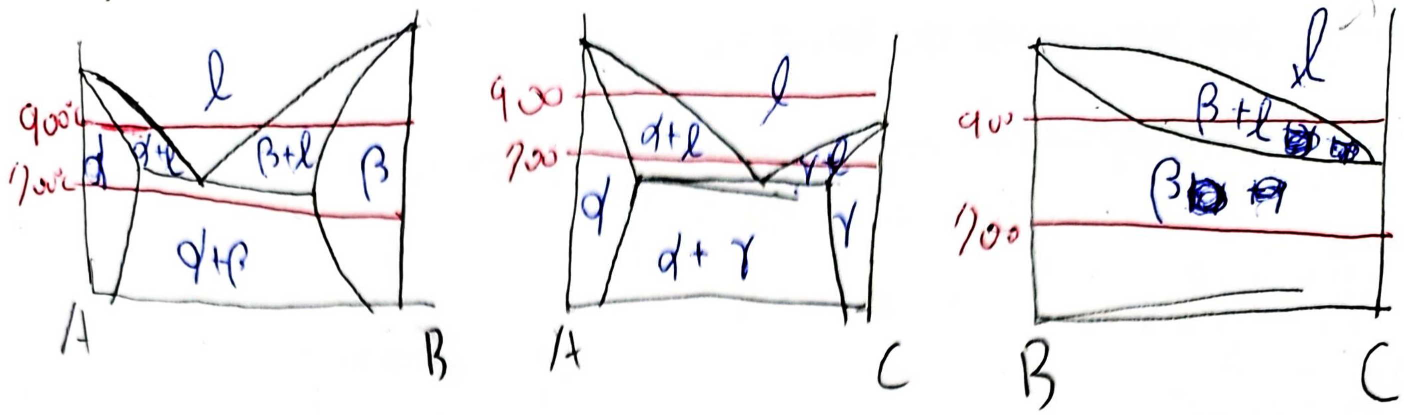
$$a_B = \exp\left\{ \ln x_B + \frac{-(1-x_B^2)\times11154-(1-x_B^2)(1-4x_B)\times1711}{RT} \right\}$$

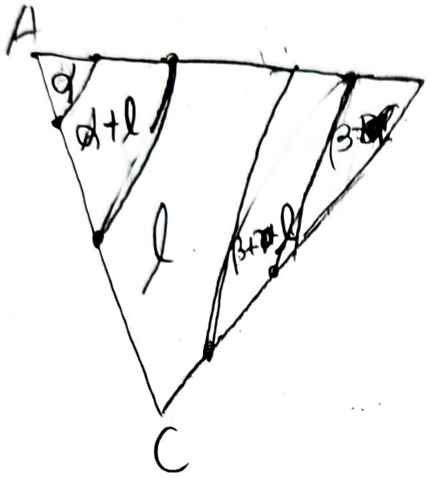
x_B	a_B
0.1	0.032
0.2	0.08
0.3	0.1184
0.4	0.1791
0.5	0.2561
0.6	0.3533
0.7	0.4744
0.8	0.6222
0.9	0.7979
1.0	1

수식으로 계산한 것과 실험데이터와의 차이가 크다.

∴ regular 모델을 따른다고 볼수있다.

6.





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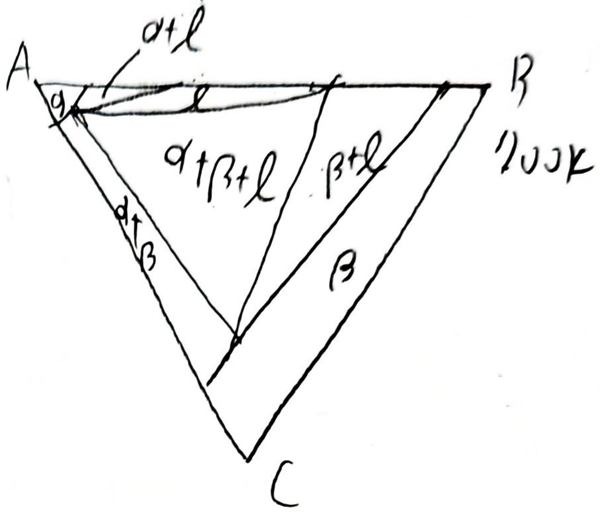

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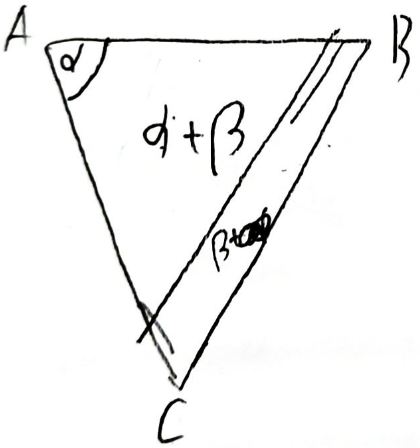

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