소재열역학 과제 3 20220381 김운찬

1. NaF(s) 증기압

$$\ln P(atm) = \frac{-34450}{T} - 2.01\ln T + 33.74$$

NaF(l) 증기압

$$\ln P(atm) = \frac{-31090}{T} - 2.52\ln T + 34.66.$$

(a) normal boiling temperature은?

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

$$\boxed{T = 2006.1K}.$$

(b) 삼중점의 T, P는?

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

$$\frac{-3360}{T} + 0.51\ln T - 0.92 = 0.$$

$$\boxed{T = 1238.9K}$$

이를 대입하면,

$$\boxed{P = 2.289 \times 10^{-4}\ atm.}$$

(c) normal boiling T 에서 molar 증발열은?

$$d\ln P = \frac{\Delta H}{RT^2}\, dT$$

$$\frac{d\ln P}{dT} = \frac{31090}{T^2} - \frac{2.52}{T} = \frac{\Delta H_{evap.}}{RT^2}$$

$$\Delta H_{evap.} = R(31090 - 2.52T)$$

normal boiling T 2006.1K, R = 8.31446 J/K·mol 에서,

$$\Delta H_{evap} = 216464\ J/mol$$

$$= \boxed{216.5\ kJ/mol}$$

(d) 삼중점에서 molar 융해열은?

$$\Delta H^{s\to l} = \Delta H^{s\to g} + \Delta H^{g\to l}$$
$$= \Delta H^{s\to g} - \Delta H^{l\to g}$$

$$= R(34450 - 2.01T) - R(31090 - 2.52T)$$

$T = 1238.9K$를 대입하면, (삼중점 T)

$$\Delta H^{s\to l} = 33190\ J/mol$$
$$= \boxed{33.19\ kJ/mol}$$

(e) NaF(l), NaF(s)의 C_p 차는?

$$\frac{dH}{dT} = C_p$$

$$\Delta C_p^{s\to l} = \frac{d\Delta H^{s\to l}}{dT} = \frac{dR(34450 - 31090 + 0.51T)}{dT}$$

$$= 0.51R$$
$$= \boxed{4.24\ J/mol\cdot K}$$

혹은, $\ln P = [\ * \ ]\frac{1}{T} + \frac{\Delta C_p}{R}\ln T + \text{constant}$ 에서,

$\frac{\Delta C_p^{s\to v}}{R} = -2.01$, $\frac{\Delta C_p^{l\to v}}{R} = -2.52$ 에서,

$$\Delta C_p^{s\to l} = 0.51R.$$

2. 반경 r 구형입자 $P = \frac{2\gamma}{r}$

$$dG^s = -S^s dT + V_m d\frac{2\gamma_s}{r}$$

$$dG^L = -S^L dT + V_m d\frac{2\gamma_L}{r}$$

$dG^s = dG^L$ 에서, (녹는점)

$$\Delta S_m dT = V_m\left(d\frac{2\gamma_L}{r} - d\frac{2\gamma_s}{r}\right)$$

$$-\frac{\Delta H_m}{T_m} dT = 2V_m(\gamma_s - \gamma_L)\, d\frac{1}{r}$$

$r \to \infty$ (bulk) 일 때 $T = T_m$, $r = r$ (nano) 일 때 $T = T_m'$

$$\int_{T_m}^{T_m'} -\frac{\Delta H_m}{T_m} dT = \int_{\infty}^{r} 2V_m(\gamma_s - \gamma_L)\, d\frac{1}{r}$$

$$\frac{\Delta H_m}{T_m}\Delta T_m = 2V_m(\gamma_s - \gamma_L)\frac{1}{r} \qquad (\Delta T_m = T_m - T_m')$$

$$\therefore \frac{\Delta T_m}{T_m} = \frac{\gamma_s - \gamma_L}{\Delta H_m}\cdot\frac{2}{r}V_m$$

3. subregular soln model, A-B 2원 soln.

(a) partial molar G_T는?

$$G_T = x_A\overline{G_{TA}} + x_B\overline{G_{TB}} \Rightarrow dG_T = \overline{G_{TA}}dx_A + \overline{G_{TB}}dx_B$$

$$\frac{dG_T}{dx_B} = -\overline{G_{TA}} + \overline{G_{TB}} \quad (\because x_A = 1-x_B)$$

$$(1-x_B)\frac{dG}{dx_B} = -\overline{G_{TA}}x_A + \overline{G_{TB}}x_A$$

$$+\underline{\left| G_T = x_A\overline{G_{TA}} + x_B\overline{G_{TB}} \right.}$$

$$G_T + (1-x_B)\frac{dG}{dx_B} = \overline{G_{TB}}.$$

$$\therefore \begin{cases} \overline{G_{TA}} = G_{Tm} + (1-x_A)\dfrac{dG_{Tm}}{dx_A} \\ \overline{G_{TB}} = G_{Tm} + (1-x_B)\dfrac{dG_{Tm}}{dx_B} \end{cases}$$

$$\overline{G_{TA}} = G_{Tm} + (1-x_A)\Big({}^\circ G_{TA} - {}^\circ G_{TB} + RT(\ln x_A + \cancel{1} - \ln x_B - \cancel{1})$$
$$+ 6L_1x_Ax_B - L_0(x_A - x_B) - L_1\Big)$$
$$= \cancel{x_A}{}^\circ G_{TA} + \cancel{x_B{}^\circ G_{TB}} + RT\{x_A\ln x_A + \cancel{x_B\ln x_B}\} + x_Ax_B\{L_0 + (x_A - x_B)L_1\}$$
$$+ (1-x_A){}^\circ G_{TA} - \cancel{x_B{}^\circ G_{TB}} + RT(\ln x_A - \cancel{\ln x_B})x_B$$
$$+ 6L_1x_Ax_B^2 - L_0x_B(x_A - x_B) - L_1x_B$$
$$= {}^\circ G_{TA} + RT\ln x_A + L_0x_B^2 + L_1x_B(x_A^2 + 5x_Ax_B - 1)$$
$$= \underline{{}^\circ G_{TA} + RT\ln x_A + L_0x_B^2 + L_1x_B^2(4x_A - 1)}$$

같은 방법으로,

$$\overline{G_{TB}} = \underline{{}^\circ G_{TB} + RT\ln x_B + L_0x_A^2 + L_1x_A^2(1 - 4x_B)}$$

(b) $\Delta G_A^{xs} = L_0 x_B^2 + L_1 x_B^2 (4x_A - 1)$

$= (1-x_A)^2 (L_0 + L_1(4x_A - 1))$

$= RT\ln\gamma_A.$

$\lim_{x_A\to 0} \Delta G_A^{xs} = \underbrace{L_0 - L_1}_{(constant)} = \lim_{x_A \to 0} RT\ln\gamma_A \neq 0.$

$\therefore x_A \to 0$ 에서 $\gamma_A = constant \neq 1 \Rightarrow$ Henrian 거동 만족

$\lim_{x_A\to 1} \Delta G_A^{xs} = 0 = \lim_{x_A \to 0} RT\ln\gamma_A$

$\therefore x_A \to 1$ 에서 $\gamma_A = 1 \Rightarrow$ Raoultian 거동 만족.

B 에서도 마찬가지로,

$\Delta G_B^{xs} = (1-x_B)^2 (L_0 + L_1(1-4x_B)) = RT\ln\gamma_B.$

$x_B \to 0$ 이면 $\Delta G_B^{xs} = L_0 + L_1 = constant = RT\ln\gamma_B \neq 0.$

$\therefore \gamma_B = constant \neq 1 \Rightarrow$ Henrian 거동 만족.

$x_B \to 1$ 이면 $\Delta G_B^{xs} = 0 = RT\ln\gamma_B$

$\therefore \gamma_B = 0 \Rightarrow$ Raoultian 거동 만족.

(c) $\overline{G}_A$, Gibbs-Duhem eqn $\left(\sum_{k=1}^{c} x_k d\overline{Q}_k = 0\right)$ 사용 → $\overline{G}_B$ 유도.

$$\begin{cases} \overline{G}_A = {}^{\circ}G_A + RT\ln x_A + L_0 x_B^2 + L_1 x_B^2(4x_A - 1) \\ x_A d\overline{G}_A + x_B d\overline{G}_B = 0. \Rightarrow x_A \frac{d\overline{G}_A}{dx_A} + x_B \frac{d\overline{G}_B}{dx_A} = 0. \end{cases}$$

$$\frac{dG_A}{dx_A} = \frac{RT}{x_A} + 2(x_A-1)L_0 + L_1 2(x_A-1)(4x_A-1) + L_1 4x_B^2$$

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

$$x_A \frac{dG_A}{dx_A} = RT - 2x_A x_B L_0 - 6L_1 x_A x_B (x_A - x_B)$$

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

$$x_B \frac{d\overline{G}_B}{dx_A} = -RT + 2x_A x_B L_0 + 6L_1 x_A x_B (x_A - x_B)$$

각 항을 나누어 보면, $\overline{G}_B$는,

① 첫째 항: $\int -\frac{RT}{x_B} dx_A = \int \frac{RT}{x_A - 1} dx_A = RT\ln|x_A - 1| + C$

$= RT\ln x_B. + C.$

② 둘째 항: $\int 2L_0 x_A dx_A = L_0 x_A^2 + C.$

③ 셋째 항: $\int 6L_1 x_A(x_A - x_B) dx_A = 6L_1\left(\frac{2}{3}x^3 - \frac{1}{2}x^2\right) + C$

$= L_1(4x_A^3 - 3x_A^2) + C.$

$= L_1 x_A^2(1 - 4x_B) + C.$

$$\therefore \overline{G}_B = RT\ln x_B + L_0 x_A^2 + L_1 x_A^2(1 - 4x_B) + C.$$

적분상수 C를 ${}^{\circ}G_B$라 하면,

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

5. 1273K

$$G_m = \begin{cases} x_A {}^{\circ}G_A + x_B {}^{\circ}G_B + RT(x_A \ln x_A + x_B \ln x_B) & \text{(ideal)} \\ \quad '' \qquad\qquad '' \qquad + x_A x_B L_0 & \text{(regular)} \\ \quad '' \qquad\qquad '' \qquad + x_A x_B (L_0 + (x_A - x_B) L_1) & \text{(subregular)} \end{cases}$$

i) ideal 이면, $x_B = a_B$.

ii) regular 이면,

$(x_B, a_B) = (0.10, 0.0320)$ 에서,

$$RT \ln a_B = RT \ln x_B + L_0 x_A^2$$

$$L_0 = \frac{RT(\ln a_B - \ln x_B)}{(1-x_B)^2} = -14889$$

$$\therefore a_B = \exp\left(\ln x_B - \frac{14889}{RT}(1-x_B)^2\right)$$

iii) subregular 이면,

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

$(x_B, a_B) = (0.10, 0.0320), (0.20, 0.0800)$ 에서,

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

$$L_0 + 0.6L_1 = -14889$$

$$L_0 + 0.2L_1 = -15154$$

$$0.4L_1 = 264$$

$$L_1 = 662.5, \quad L_0 = -15286.5.$$

$$\therefore a_B = \exp\left(\ln x_B - \frac{15286.5}{RT} x_A^2 + \frac{662.5}{RT} x_A^2 (1-4x_B)\right)$$

이를 그래프로 그리면 아래와 같으며, 따라서 regular 일 때 가장 정확했다.

(초록: ideal, 빨강: regular, 파랑: subregular)

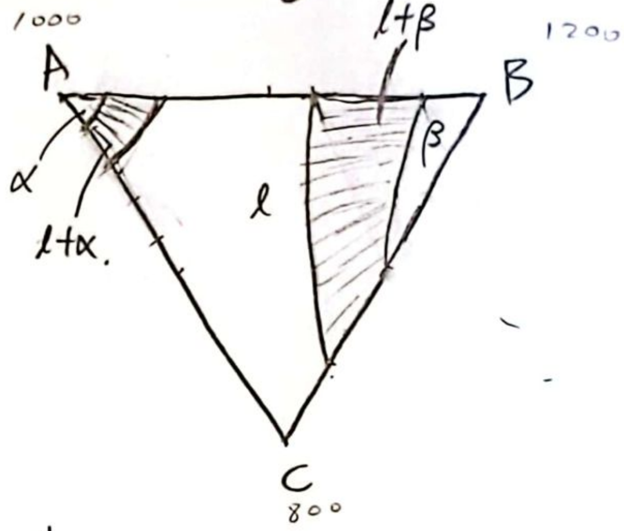
표로 나타내면 다음과 같다.

	ideal	regular	subregular	실험
0.10	0.1000	0.0320	0.0320	0.0320
0.20	0.2	0.8129	0.0800	0.0800
0.30	0.3	0.1506	0.1469	0.1498
0.40	0.4	0.2411	0.2346	0.2400
0.50	0.5	0.3518	0.3431	0.3510
0.60	0.6	0.4791	0.4696	0.4782
0.70	0.7	0.6168	0.6085	0.6162
0.80	0.8	0.7562	0.7509	0.7559
0.90	0.9	0.8874	0.8857	0.8874
1.00	1.0	1.0000	1.0000	1.0000

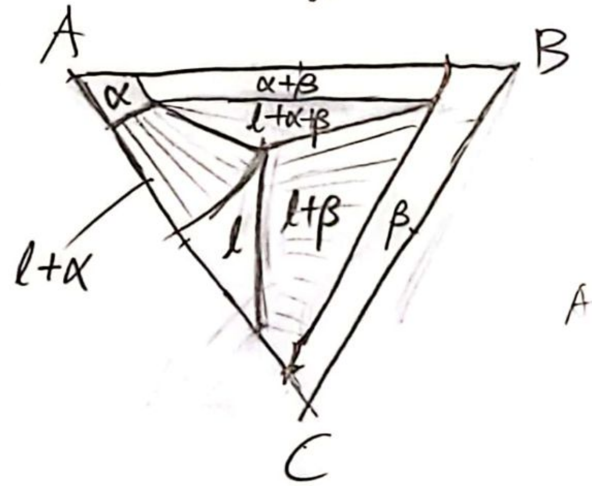
regular가 실험값과 가장 비슷하다.

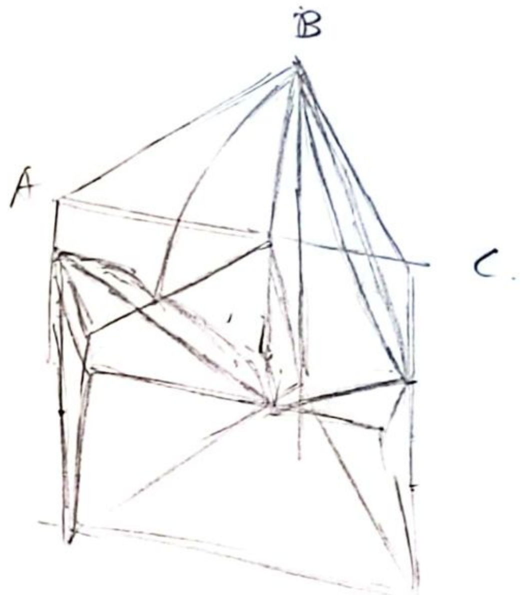
6. ternary phase diagram

900K.



700K





400K