

1. The vapor pressure of solid NaF varies with temperature as

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

and the vapor pressure of liquid NaF varies with temperature as

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

Calculate: (20)

- The normal boiling temperature of NaF
- The temperature and pressure at the triple point
- The molar heat of evaporation of NaF at its normal boiling temperature
- The molar heat of melting of NaF at the triple point
- The difference between the C_p of liquid and solid NaF

$$a) p=1, \text{ liquid} \rightarrow 0 = \frac{-31090}{T} - 2.52 \ln T + 34.66 \quad T_b = 2006 \text{ K}$$

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

$$\frac{-3360}{T} + 0.51 \ln T - 0.92 = 0 \quad T = 1239 \text{ K}, \rightarrow P_{\text{triple}} = 2.28 \times 10^{-4} \text{ atm}$$

$$c) \text{ Clausius-Clapeyron} \rightarrow \ln P = \left(-\frac{\Delta H_{\text{vap}}}{R} \right) \frac{1}{T} + C, \text{ T in Kelvin}$$

$$\frac{1}{P} \frac{dP}{dT} = \frac{\Delta H}{RT^2} = \frac{d}{dT} \ln P = \frac{d}{dT} \left(-\frac{31090}{T} - 2.52 \ln T + 34.66 \right) = \frac{31090}{T^2} - \frac{2.52}{T} = \frac{\Delta H}{RT^2}$$

$$\Delta H = 31090R - 2.52RT \quad T_b = 2006 \text{ K} \rightarrow \Delta H^{\text{evap}} = 216.5 \text{ kJ/mol}$$

$$d) \text{ solid}$$

$$\frac{d}{dT} \ln P = \frac{d}{dT} \left(\frac{-34450}{T} - 2.01 \ln T + 33.74 \right) = \frac{34450}{T^2} - \frac{2.01}{T} = \frac{\Delta H}{RT^2}$$

$$\Delta H^{\text{sub}} = 34450R - 2.01RT$$

$$\Delta H^{\text{evap}} = 31090R - 2.52RT + 182$$

$$\Delta H^{\text{melt}} = \Delta H^{\text{sub}} - \Delta H^{\text{evap}} = 3360R + 0.51RT$$

$$\underbrace{1239 \text{ K}}_{T=T_c} \quad T=T_c \therefore \Delta H^{\text{melt}} = 33140(T)$$

$$e) \Delta C_p = \frac{d\Delta H}{dT} = 0.51R = 4.24 \text{ J/mol} \cdot \text{K}$$

2. 반경이 r 인 spherical particle 은 표면 효과로 인해 다음 식만큼 압력을 받게 된다.
(capillary pressure)

$$P = \frac{2\gamma}{r}$$

여기서 γ 는 표면에너지를 의미한다.

Nano particle이나 wire는 위 효과로 인해 melting point 등 thermodynamic property가 bulk 상태일 때와는 달라지게 되는데, spherical nano particle의 melting point 강하 정도가 다음의 식으로 표현될 수 있음을 유도하시오. (10)

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

T_m 은 bulk 상태에서의 melting point임.

ΔT_m 은 melting point가 낮아진 정도이며, 낮아졌을 때 (+)값을 가짐.

γ_s, γ_L 는 각각 solid와 liquid의 표면에너지,

ΔH_m 은 enthalpy of melting을 나타냄.

ΔH_m 와 ΔS_m 은 melting point 근처에서 constant라고 가정하며,

Solid 와 liquid 의 molar volume은 V_m 으로 동일하다고 가정함.

$$G = H - TS$$

$$dG = -VdP - SdT = 0 \quad T \text{ 변화 가정}$$

$$\begin{aligned} dG &= -VdP \\ &= -V_m(P_L - P_S) \\ &= V_m(P_S - P_L) = V_m \frac{2(\gamma_S - \gamma_L)}{r} = 0 \end{aligned}$$

$$\Delta G_{\text{particle}} = \Delta G_{\text{bulk}} + \Delta G_{\text{capillary}}$$

$$\Delta G_{\text{bulk}} = \Delta H_m - T\Delta S_m = \Delta H_m - T \cdot \frac{\Delta H_m}{T_m} = \frac{\Delta H_m}{T_m} (T_m - T)$$

$$\Delta G_{\text{capillary}} = \frac{2}{r} V_m (\gamma_L - \gamma_S)$$

$$\text{but } \Delta G_{\text{particle}} = 0 \quad \therefore \Delta G_{\text{bulk}} = -\Delta G_{\text{capillary}}$$

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

$$\frac{\Delta T}{T_m} = \frac{(\gamma_S - \gamma_L)}{\Delta H_m} \cdot \frac{2}{r} \cdot V_m$$

3. 다음은 subregular solution model을 이용하여 A-B 2원 용액의 molal Gibbs energy를 표현한 것이다. (20)

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

- a) 이 식으로부터 A, B 성분의 partial molar Gibbs energy 식을 유도하시오.
 b) 위 subregular 용액 모델이, A, B 각 성분이 dilute 영역에서는 Henrian 거동을, rich 영역에서는 Raoultian 거동을 나타낸다는 실험적 사실을 재현해 낼 수 보이시오.
 c) 위 a)에서 유도한 A 성분의 partial molar Gibbs energy로부터 Gibbs-Duhem equation을 이용하여 B 성분의 partial molar Gibbs energy를 유도하시오.

a) A의 partial molar Gibbs energy

$$x_A + x_B = 1$$

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

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

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

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

$$+ \{ x_A x_B (2x_A-1) + (2x_A-1) - 4x_A^2 + 2x_A + 2x_A - 2x_A^2 - 2x_A^2 + x_A + 2x_A^2(2x_A-1) - 2x_A^2(1-x_A) \} L_1$$

$$\begin{aligned} & \underbrace{(x_A - x_A^2 + 1 - 2x_A + 2x_A^2 - x_A)}_{1} L_0 \\ & (x_A^2 - 2x_A + 1) L_0 \\ & \underbrace{(x_A - 1)^2}_{1} L_0 \\ & x_B^2 L_0 \end{aligned}$$

$$\begin{aligned} & (x_A - x_A^2)(2x_A-1) + (2x_A-1) - 4x_A^2 + 5x_A - 4x_A^2 \\ & + 4x_A^3 - 2x_A^2 - 2x_A^2 + 2x_A^3 \\ & = 2x_A^2 - x_A - 2x_A^3 + x_A^2 + 2x_A - 1 - 8x_A^2 + 5x_A \\ & + x_A^3 - 4x_A^2 \\ & = 4x_A^3 - 9x_A^2 + 6x_A - 1 \\ & = \end{aligned}$$

$$(4\lambda_A - 1)(1 - \lambda_A)^2$$

$$\begin{array}{c|ccc|c} 1 & 4 & -9 & 6 & -1 \\ & & 4 & -5 & 1 \\ \hline 1 & 4 & -5 & 1 & 0 \\ & & 4 & -1 & \\ \hline & 4 & -1 & 0 & \end{array}$$

$$\therefore (4\lambda_A - 1)(\lambda_B^2) = (3\lambda_A - \lambda_B)(\lambda_B^2)$$

$$\therefore G_A + RT \ln \lambda_A + \lambda_B^2 (L_0 + (3\lambda_A - \lambda_B)L_1)$$

$$= G_A + RT \ln \lambda_A + (L_0 + (3\lambda_A - \lambda_B)L_1)\lambda_B^2 + 2L_1\lambda_A\lambda_B^2$$

Def 2.2.3 Def. partial molar Gibbs energy $\bar{G}$

$$G_m + (1 - \lambda_B) \frac{dG_m}{d\lambda_B} \quad \text{of 1}$$

$$G_B + RT \ln \lambda_B + (L_0 + (\lambda_A - \lambda_B)L_1)\lambda_A^2 + 2L_1\lambda_A\lambda_B \quad \text{of 1}$$

b) $\lim_{\lambda_A \rightarrow 0} RT \ln a_A = 0 \quad \therefore a_A = 1 \rightarrow \text{Raoultian H.S.}$

$$\lim_{\lambda_A \rightarrow 1} RT \ln a_A = \lim_{\lambda_A \rightarrow 1} RT \ln \lambda_A + L_0 + L_1$$

$$a_A \neq 1 \rightarrow \text{Henrician H.S.}$$

c) Gibbs-Duhem $\rightarrow \lambda_A G_m^A + \lambda_B G_m^B = G_m$

$$\lambda_B G_m^B = G_m - \lambda_A G_m^A$$

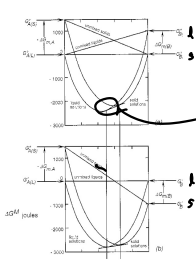
$$- \cancel{\gamma_A} \cancel{G_A} \cancel{\gamma_A} \ln \gamma_A - \cancel{\gamma_A} (L_0 + (\gamma_A - \gamma_B) h) \gamma_B^2 - 2 L_1 \gamma_A \gamma_B^2$$

$$= \gamma_B^0 G_B + R T \chi_B \ln \chi_B + (1 - \chi_B) \chi_A \chi_B L_0 + (\chi_A - \chi_B) (\chi_A \chi_B - \gamma_A \gamma_B^2) \chi_1 - 2 \chi_A^2 \chi_B^2 L_1$$

$$= \quad // \quad + (\chi_A - \chi_B) \chi_A^2 \chi_B L_1 - 2\gamma(A^2 \gamma(B^2 L_1$$

:- H_2O

4. A-B 2 원계에서 α, β 두 solution phase 간의 평형 조성은 두 상의 Gibbs energy vs. composition curve에 common tangent line (공중 접선)을 그려, 두 curve 외의 접점을 찾음으로써 결정할 수 있다. 그런데, Gibbs energy curve 는 그림에서처럼 각 원소의 reference state 에 따라 달리 그려질 수 있다. 정규 용액 모델을 사용하여 α, β 두 상 간의 상평형을 나타내는 조건 식을 작성하고, 각 원소에 대해 일관된 reference state 를 사용하는 한 상평형 조성은 reference state 에 관계없이 unique 하게 결정된다는 것을 보이시오. (10)



slope가 같음

$$\text{정규 용액 모델} \rightarrow \Delta G^M = RT(x_A \ln x_A + x_B \ln x_B) + \alpha x_A x_B$$

$$\Delta G_{m(\alpha\beta)} = G_{\alpha(\alpha\beta)}^0 - G_{\beta(\alpha\beta)}^0 = G_0^{S-\gamma_L}$$

$$- \Delta G_{m(\alpha\beta)} = -G_{\alpha(\alpha\beta)}^0 + G_{\beta(\alpha\beta)}^0 = G_0^{S-\gamma_L}$$

$$G_m^{\alpha} = x_A G_A^0(\alpha) + x_B G_B^0(\alpha) + RT(x_A \ln x_A + x_B \ln x_B) + x_A x_B L_{AB}^0$$

$$G_m^{\beta} = x_A G_A^0(\beta) + x_B G_B^0(\beta) + RT(x_A \ln x_A + x_B \ln x_B) + x_A x_B L_{AB}^0$$

$$\therefore \frac{\partial G_m^{\alpha}}{\partial x_B^{\alpha}} = \frac{\partial G_m^{\beta}}{\partial x_B^{\beta}}$$

$$G_m^{\alpha} = (1-x_B) G_A^0(\alpha) + x_B G_B^0(\alpha) + RT((1-x_B) \ln(1-x_B) + x_B \ln x_B) + (1-x_B)x_B L_{AB}^0$$

$$\frac{\partial G_m^{\alpha}}{\partial x_B^{\alpha}} = -G_A^0(\alpha) + G_B^0(\alpha) + RT(-\ln(1-x_B^{\alpha}) + \ln x_B^{\alpha}) + (1-2x_B^{\alpha}) L_{AB}^0 \quad \dots (1)$$

$$G_m^{\beta} = (1-x_B) G_A^0(\beta) + x_B G_B^0(\beta) + RT((1-x_B) \ln(1-x_B) + x_B \ln x_B) + (1-x_B)x_B L_{AB}^0$$

$$\frac{\partial G_m^{\beta}}{\partial x_B^{\beta}} = -G_A^0(\beta) + G_B^0(\beta) + RT(-\ln(1-x_B^{\beta}) + \ln x_B^{\beta}) + (1-2x_B^{\beta}) L_{AB}^0 \quad \dots (2)$$

$$\therefore (1) = (2) \Rightarrow \underbrace{G_A^0(\alpha) - G_A^0(\beta)}_{G_m^{\uparrow}} - \underbrace{(G_B^0(\alpha) - G_B^0(\beta))}_{G_m^0} + RT \left(\ln \frac{1-x_B^{\alpha}}{1-x_B^{\beta}} - \ln \frac{x_B^{\alpha}}{x_B^{\beta}} \right) + (1-2x_B^{\alpha}) L_{AB}^0 - (1-2x_B^{\beta}) L_{AB}^0 = 0$$

5. 이 Y-값이 0일

$$\therefore \bar{G}_A^{\alpha} = \bar{G}_A^{\beta} \quad \left(\bar{G}_B^{\alpha} = \bar{G}_B^{\beta} \right) \rightarrow \Delta G_m^B + RT \ln \left(\frac{x_B^{\alpha}}{x_B^{\beta}} \right) + L_{AB}^0 x_A^{\alpha^2} - L_{AB}^0 x_A^{\beta^2} = 0$$

$$G \quad \bar{G}_A^{\alpha} = G_A^0(\alpha) + RT \ln a_A^{\alpha} \quad \bar{G}_A^{\beta} = G_A^0(\beta) + RT \ln a_A^{\beta}$$

$$\therefore \underbrace{G_A^0(\alpha) - G_A^0(\beta)}_{G_m^A} + RT \ln \frac{a_A^{\alpha}}{a_A^{\beta}} = 0 = G_m^A + RT \ln \frac{x_A^{\alpha}}{x_A^{\beta}} + L_{AB}^0 x_B^{\alpha^2} - L_{AB}^0 x_B^{\beta^2} = 0$$

$$\therefore \left(G_m^A + RT \ln \frac{\chi_A}{\chi_B} \right) - \left(G_m^B + RT \ln \frac{\chi_B}{\chi_A} \right) + (1-2\chi_A) L_{AB}^B - (1-2\chi_B) L_{AB}^A$$

$\overset{L_{AB}^B \chi_B^{\beta^2} - L_{AB}^A \chi_B^{\alpha^2}}{\parallel}$
 $\overset{L_{AB}^B \chi_A^{\beta^2} - L_{AB}^A \chi_A^{\alpha^2}}{\parallel}$

$$= L_{AB}^B (\chi_B^{\beta^2} + \chi_A^{\beta^2} + 1 - 2\chi_B^B) - L_{AB}^A (\chi_B^{\alpha^2} + \chi_A^{\alpha^2} + 1 - 2\chi_B^A) = 0$$

but $L_{AB}^B, L_{AB}^A \neq \text{constant}$ 이니

위 식은 만족시키지 못함 $\therefore$ 이 경우 reference 와 관련됨

unique 이기 때문.

1273 K, A-B 2 원계 한 고용상에서 성분 B 의	x_B	a_B
조성에 따른 activity (wrt. solid B)가 다음과 같이	0.10	0.0320
측정되었다. 이 고용상의 열역학 특성을 가장	0.20	0.0800
잘 나타내는 모델을 찾고 (ideal, regular, sub-	0.30	0.1498
regular model), 성분 B 의 activity 와 molar Gibbs	0.40	0.2400
energy of mixing 을 analytic 한 수식으로	0.50	0.3510
표현하시오. 또, 모델 수식으로 계산한 각	0.60	0.4782
조성에서의 activity 값과 실험 측정된 activity	0.70	0.6162
값을 비교하여 모델의 우수성을 보이시오. (20)	0.80	0.7559
	0.90	0.8874
	1.00	1.0000

$$G_m = x_A^0 G_A + x_B^0 G_B + RT(x_A \ln a_A + x_B \ln a_B)$$

$$\text{ideal} \rightarrow a_A = x_A \quad a_B = x_B$$

$$G_m = x_A^0 G_A + x_B^0 G_B + RT(x_A \ln x_A + x_B \ln x_B) + x_A x_B L_{AB} \quad (\text{regular})$$

$$\rightarrow \mu = \mu^0 + RT \ln a, \quad x_A = a_B \quad (\text{ideal})$$

$$RT \ln a_B = RT \ln x_B + \frac{(x_B)^2}{L_0} \quad (\text{regular})$$

$$a_B = x_B e^{\frac{(x_B)^2}{RT} L_0}$$

$$x_B = 0.1 \quad a_B = 0.032 \quad RT \ln \frac{a_B}{x_B} = L_0$$

$$L_0 = -14886$$

Subregular

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

$$a_B = x_B e^{\frac{(x_A^2 [L_0 + (x_A - x_B) L_1] + 2x_A x_B x_A^2)}{RT}}$$

$$a_B = 0.0320 \quad x_B = 0.1 \quad a_B = 0.08 \quad x_B = 0.2 \quad \text{대입하여 연립 방정식}$$

$$\rightarrow L_0 = -16663, \quad L_1 = 2159$$

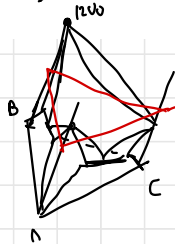
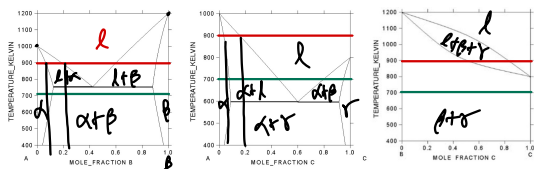
예제로 계산하니

x_B	ideal	regular	subregula
0.1	0.032	0.032000531	0.032001
0.2	0.08	0.081291115	0.080005
0.3	0.1498	0.150581597	0.148118
0.1	0.21	0.032000531	0.032001
0.5	0.351	0.351755374	0.35496
0.6	0.4782	0.479076118	0.491395
0.7	0.6162	0.616759014	0.64035
0.8	0.7559	0.75622896	0.787578
0.9	0.8874	0.887428432	0.914215
1	1	1	1

다음과 같이 하고

regular 모델이 가장 정확

The followings are binary phase diagrams among three elements A, B, C, with melting point of 1000, 1200 and 800K, respectively. Based on binary phase diagrams, sketch isothermal sections of the A-B-C ternary phase diagram at 900, 700 and 400K. (20)



900K

