

AMSE205 Thermodynamics I

Nov. 30, 2023

Problem Set #3

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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

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.

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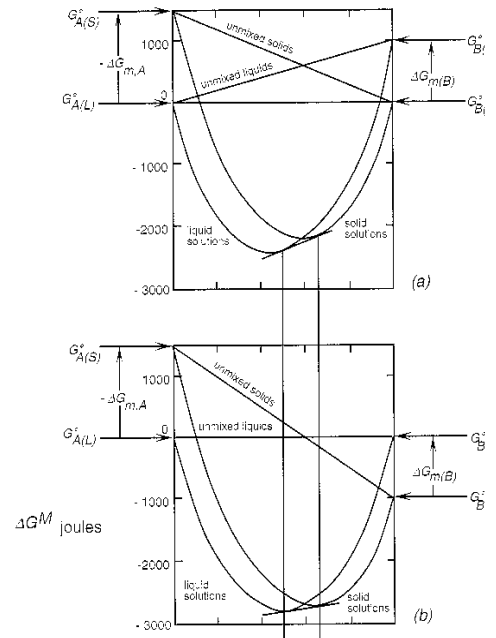
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3. 다음은 subregular solution model을 이용하여 A-B 2원 용액의 molar Gibbs energy를 표현한 것이다. (20)

$$G_m = x_A {}^oG_A + x_B {}^oG_B + RT \{x_A \ln x_A + x_B \ln x_B\} + x_A x_B \{L_o + (x_A - x_B)L_1\}$$

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

4. A-B 2 원계에서 α , β 두 solution phase 간의 평형 조성은 두 상의 Gibbs energy vs. composition curve 에 common tangent line (공통 접선)을 그어, 두 curve 와의 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)



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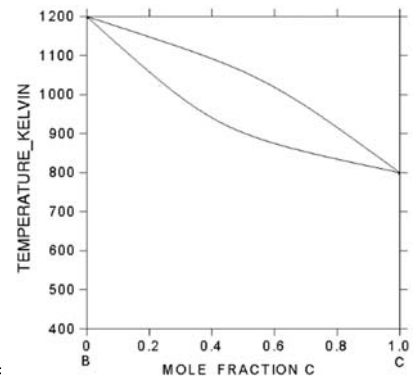
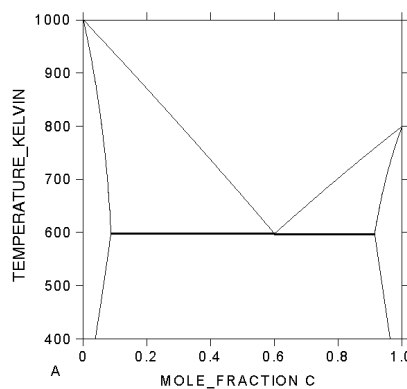
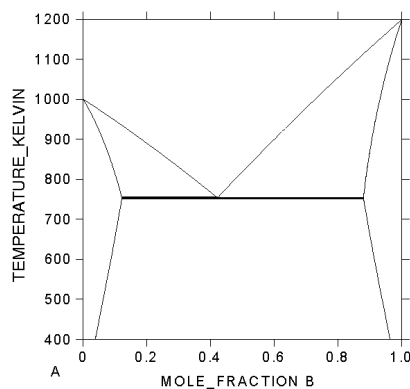
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5. 1273 K, A-B 2 원계 한 고용상에서 성분 B 의 조성에 따른 activity (wrt. solid B)가 다음과 같이 측정되었다. 이 고용상의 열역학 특성을 가장 잘 나타내는 모델을 찾고 (ideal, regular, sub-regular model), 성분 B 의 activity 와 molar Gibbs energy of mixing 을 analytic 한 수식으로 표현하시오. 또, 모델 수식으로 계산한 각 조성에서의 activity 값과 실험 측정된 activity 값을 비교하여 모델의 우수성을 보이시오. (20)

x_B	a_B
0.10	0.0320
0.20	0.0800
0.30	0.1498
0.40	0.2400
0.50	0.3510
0.60	0.4782
0.70	0.6162
0.80	0.7559
0.90	0.8874
1.00	1.0000

6. 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)



$$1. \ln P_{\text{sat}} = -\frac{34450}{T} - 2.10 \ln T + 33.74$$

$$\ln P_{\text{triple}} = -\frac{31090}{T} - 2.52 \ln T + 34.66$$

a) The normal boiling point of NaF

$$\because P_0 = 1 \text{ atm.} \quad \ln 1 = -\frac{31090}{T} - 2.52 \ln T + 34.66$$

$$\therefore T = 2006 \text{ K}$$

b) temperature & pressure at critical point

$\because P_c = P_c^{\text{sat}}$ at T_c .

$$\ln P_c = \ln 1. \quad -\frac{34450}{T} - 2.10 \ln T + 33.74 = -\frac{31090}{T} - 2.52 \ln T + 34.66$$

$$\Rightarrow T = 1291 \text{ K.} \quad \text{also calculated } P_c = 2.287 \times 10^4 \text{ atm.}$$

c) molecular heat of evaporation of NaF at its normal b.p.

$\because$ Clausius - Clapeyron eq.

$$\frac{1}{P} \frac{dP}{dT} \bigg|_q = \frac{\Delta H}{RT^2} = \frac{252}{\ln T} \quad R = 8.314 \text{ J/mol.K} \quad \text{is calculated}$$

$$\Delta H = R(31090 - 2.52T). \quad T = 2006 \text{ K is calculated } \Delta H = 216.4 \text{ kJ/mol.}$$

d) molar heat of melting of NaF at triple point

$$\because \Delta H_{\text{mel}} \Rightarrow \Delta H_{\text{sat}} - \Delta H_{\text{triple}}$$

$$\Delta H_{\text{triple}} = R(34450 - 2.10T). \rightarrow \text{value } 28500 \text{ at } +20.95T \text{ value}$$

$$\Rightarrow \Delta H_{\text{mel}} = 11700 + 4.24T \quad T = 1291 \text{ K}$$

$$\Rightarrow 33150 \text{ J} \quad \therefore \Delta H = 33150 \text{ J/mol}$$

$$e) \frac{d\Delta H}{dT} = C_p \Rightarrow \frac{d(11700 + 4.24T)}{dT} = 4.24 \text{ J/K.}$$

$$2. \quad dG = V dp - S dT.$$

$$dG_m = V_m dp - S_m dT, \quad \Delta G_m = 0, \quad T = T_m.$$

$$G_m = V_m \frac{2\gamma}{r} - S_m T_m.$$

$$\Delta G_m = \left(V_m \frac{2\gamma}{r} - S_m T_m \right) - \left(V_m - \frac{V_m}{r} - S_m \Delta T_m \right) = 0 = \Delta H_m - T_m \Delta S_m$$

$$\therefore \Delta T_m = \frac{2V_m(\gamma/r)}{\Delta S_m} \cdot T_m = \frac{\Delta H_m}{\Delta S_m}$$

$$\therefore \frac{\Delta T_m}{T} = \frac{2(\gamma/r)}{\Delta H_m} \cdot \frac{V_m}{r}$$

$$3. \quad G_m = x_A G_A + x_B G_B + RT [x_A \ln x_A + x_B \ln x_B] + x_A G_A^0 L_0 + (x_A - x_B) L_1?$$

$$a) \quad G_A = G_m + (1-x_A) \cdot \frac{dG_m}{dx_A} = G_m + (1-x_A) [G_A - G_B + RT (\ln x_A - \ln(1-x_A)) + (1-x_A)(L_0 + L_1(2x_A-1)) + x_A(-L_1)]$$

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

$$\bar{G}_B = RT \ln x_B + x_A^2 L_0 + x_A^2 (1-x_B) L_1 \text{ etc.}$$

$$b) \quad \lim_{x_A \rightarrow 1} \bar{G}_A^{RS} = \lim_{x_B \rightarrow 0} RT \ln x_A = L_0 - L_1, \quad x_A \neq 1 \rightarrow \text{Harrison's RS.}$$

$$\lim_{x_A \rightarrow 1} \bar{G}_A^{KS} = \lim_{x_B \rightarrow 0} RT \ln x_A = 0 \rightarrow x_A = 1. \quad \text{Rushkoff's RS.}$$

$$\lim_{x_B \rightarrow 0} \bar{G}_B^{RS} = \lim_{x_A \rightarrow 1} RT \ln x_B = L_0 + L_1 \cdot x_A \neq 1 \rightarrow \text{Harrison's RS.}$$

$$\lim_{x_B \rightarrow 0} \bar{G}_B^{KS} = \lim_{x_A \rightarrow 1} RT \ln x_B = 0 \rightarrow x_B = 1. \quad \text{Rushkoff's RS.}$$

$$c) \quad \sum_k \gamma_k d\bar{G}_k = 0, \quad \therefore \gamma_A d\bar{G}_A + \gamma_B d\bar{G}_B = 0.$$

$$\bar{G}_B = - \int_{x_B=0}^{x_B} \frac{\gamma_A}{\gamma_B} \frac{d\gamma_B}{d\gamma_A} d\gamma_A.$$

$$= - \int_{x_B=0}^{x_B} \frac{\gamma_A}{\gamma_B} \left(\frac{\gamma_A}{\gamma_B} - 2(1-x_B)L_0 - 2(1-x_B)(2x_B-1)L_1 + 4(1-x_B)L_1 \right) d\gamma_A$$

$$= \bar{G}_B + RT \ln x_B + \gamma_B^2 L_1 + \gamma_B^2 (1-x_B).$$

4. common tangent line.

$$\Delta G_{m, A} = G_A^L - G_A^S.$$

$$\Delta G_{m, B} = G_B^L - G_B^S.$$

by regular solution $\Rightarrow G_m = x_A G_A^L + x_B G_B^L + RT (x_A \ln x_A + x_B \ln x_B) + x_A x_B L_{AB}$

$$\Rightarrow \begin{cases} G_m^A = x_A G_A^L + x_B G_B^L + RT (x_A \ln x_A + x_B \ln x_B) + x_A x_B L_{AB} \\ G_m^B = x_A G_A^L + x_B G_B^L + RT (x_A \ln x_A + x_B \ln x_B) + x_A x_B L_{AB} \end{cases}$$

equilibrium $\rightarrow$ slope = 0.

$$\left. \frac{\partial G_m^A}{\partial x_B} \right|_{x_B=x_B^*} = \left. \frac{\partial G_m^B}{\partial x_B} \right|_{x_B=x_B^*} \rightarrow \mu_A + \mu_B = \mu_A^L + \mu_B^L$$

$$G_m^A = (1-x_B) G_A^L + x_B G_B^L + RT [(1-x_B) \ln(1-x_B) + x_B \ln x_B] + (1-x_B) x_B L_{AB}$$

$$G_m^B = (1-x_B) G_A^L + x_B G_B^L + RT [(1-x_B) \ln(1-x_B) + x_B \ln x_B] + (1-x_B) x_B L_{AB}$$

$$\text{or } \frac{\partial G_m^A}{\partial x_B} = \frac{\partial G_m^B}{\partial x_B}$$

$$G_A^L(x) - G_A^S(x) - G_B^L(x) + G_B^S(x) + RT \ln \frac{1-x_B^L(x)}{1-x_B^S(x)} + RT \ln \frac{x_B^L(x)}{x_B^S(x)} + (1-x_B^L(x)) L_{AB} - (1-x_B^S(x)) L_{AB} = 0$$

$$\begin{cases} \Delta G_m^{A, L} - \Delta G_m^{A, S} = \Delta G_m^{A, S} - \Delta G_m^{A, L} \\ \Delta G_m^{B, L} - \Delta G_m^{B, S} = \Delta G_m^{B, S} - \Delta G_m^{B, L} \end{cases}$$

$$\therefore -\Delta G_m^A + \Delta G_m^B + RT \left(\ln \frac{1-x_B^L}{1-x_B^S} + \ln \frac{x_B^L}{x_B^S} \right) + (1-x_B^L) L_{AB} - (1-x_B^S) L_{AB} = 0.$$

or $\mu_A = \mu_B$ in the common tangent.

5. <3 model of β_B >

γ_B	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
α_B	0.020	0.080	0.148	0.240	0.3510	0.4882	0.6462	0.8599	0.8884	1
γ_B	0.32	0.4	0.499	0.6	0.7	0.799	0.888	0.945	0.988	1

a) ex. "bad solution" $\Rightarrow \beta_B = \frac{\sum_{i=1}^n \alpha_i \gamma_i}{\sum_{i=1}^n \gamma_i}$ $\alpha_n = \gamma_n \Rightarrow \gamma_B \neq \alpha_B \neq 1 \Rightarrow$ not "bad solution" ($\gamma \neq 1$)

b) regular model is represented

$$G_m = \gamma_A \cdot G_A + \gamma_B \cdot G_B + RT (\gamma_A \ln \gamma_A + \gamma_B \ln \gamma_B)$$

$$= \gamma_A \epsilon_A^0 + \gamma_B \epsilon_B^0 + RT (\gamma_A \ln \gamma_A + \gamma_B \ln \gamma_B) \rightarrow \gamma_A \gamma_B \ln \gamma_B$$

$$\therefore \gamma_A \gamma_B \ln \gamma_B = RT (\gamma_A \ln \gamma_A + \gamma_B \ln \gamma_B)$$

(Unbekannt)

$$\gamma_A \gamma_B \ln \gamma_B = RT (\gamma_A \ln \gamma_A + \gamma_B \ln \gamma_B) \quad RT \ln \gamma_B = \ln \gamma_B \cdot \gamma_B^2$$

$$\rightarrow \gamma_A \gamma_B \ln \gamma_B = \gamma_A \gamma_B^2 \ln \gamma_B + RT \gamma_A \ln \gamma_B$$

$$\therefore \ln \gamma_B = \frac{RT \ln \gamma_B}{(1 - \gamma_B)^2}$$

$$\gamma_B = \frac{\alpha_B}{\gamma_B} \approx 1.572 \text{ } \gamma_B \text{ nicht}$$

01 γ_B nicht $\approx 1.5 \times 10^2$ konstant $\Rightarrow$ regular solution.

c) subregular of β_B . $\Rightarrow$ constant 112 X.

$$RT \ln \gamma_B = RT \ln \gamma_B + (1 - \gamma_B)^2 \ln \gamma_B + (1 - \gamma_B)^2 (1 - \gamma_B) \ln \gamma_B$$

Es ist ein Wert.

6.

