

1.

a) liquid 의 Vapor pressure 가 1 atm 일 때 이므로

$$\ln P(\text{atm}) = \frac{-31090}{T} - 2.52 \ln T + 34.66 \quad \text{or } P=1 \text{ atm 일 때,}$$

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

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

b) 두 곡선의 교점 이므로

$$\ln P = \frac{-34450}{T} - 2.01 \ln T + 33.14 = \frac{-31090}{T} - 2.52 \ln T + 34.66,$$

$$T = 1238 \text{ K}, \quad P = 2.28 \times 10^{-4} \text{ atm} \quad \frac{-3360}{T} + 0.51 \ln T - 0.92 = 0.$$

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

evaporation, vapor pressure of liquid at 1M

$$\frac{d(\ln P)}{dT} = \frac{31090}{T^2} - \frac{2.52}{T} = \frac{\Delta H}{RT^2}, \quad T = 2006 \text{ K} \text{ 때,}$$

$$\Delta H = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (2006 \text{ K})^2 \cdot \left\{ \frac{31090}{(2006 \text{ K})^2} - \frac{2.52}{(2006 \text{ K})} \right\}$$

$$= 216.4 \text{ kJ} \cdot \text{mol}^{-1}$$

d) same way,

$$\frac{d \ln P}{dT} = \frac{34450}{T^2} - \frac{2.01}{T} = \frac{\Delta H}{RT^2}, \quad T = 1238 \text{ K} \text{ 때}$$

$$\Delta H = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \left[34450 - 2.01 \times 1238 \text{ K} \right] = 265 \text{ kJ} \cdot \text{mol}^{-1}$$

e) let $\Delta H = \Delta H_{298} + \Delta C_p(T - 298)$, Then.

$$\ln P = \frac{[298 \Delta C_p - \Delta H_{298}]}{R} \cdot \frac{1}{T^2} + \frac{\Delta C_p}{R} \ln T + \text{constant}$$

$$\text{Solid NaF: } \frac{\Delta C_p}{R} = -2.01, \quad \Delta C_p = C_{p \text{ gas}} - C_{p \text{ solid}} = -16.71 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\text{liquid NaF: } \frac{\Delta C_p}{R} = -2.52, \quad \Delta C_p = C_{p \text{ gas}} - C_{p \text{ liquid}} = -20.95 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\therefore C_{p \text{ solid}} - C_{p \text{ liquid}} = -4.24 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

2. 반응에서

$$dG^S = -S^S dT + V_m dP = -S^S dT + V_m d\left(\frac{2\gamma^S}{r}\right) = -S^S dT + 2V_m \gamma^S d\left(\frac{1}{r}\right)$$

$$dG^L = -S^L dT + V_m dP = -S^L dT + 2V_m \gamma^L d\left(\frac{1}{r}\right)$$

$$\Delta S_m dT = 2V_m (\gamma^L - \gamma^S) d\left(\frac{1}{r}\right)$$

$$\frac{\Delta H_m}{T_m} dT = 2V_m (\gamma^L - \gamma^S) d\left(\frac{1}{r}\right) \quad / \quad r \rightarrow \infty \text{ 이면 } \Delta T_m \rightarrow 0$$

적분 구간

$$\int_{T_{mf}}^{T_m} \frac{\Delta H_m}{T_m} dT = \int_{R=r}^{R=\infty} 2V_m (\gamma^L - \gamma^S) d\frac{1}{r}$$

$$\therefore \frac{\Delta H_m}{T_m} (T_m - T_{mf}) = 2V_m (\gamma^L - \gamma^S) \left(-\frac{1}{r}\right),$$

$T_m - T_{mf} = \Delta T_m$ / 이러면 낮아지면 ΔT_m 이 (+) 값.

$$\therefore \frac{\Delta H_m}{T_m} \cdot \Delta T_m = \frac{2V_m (\gamma^S - \gamma^L)}{r} \quad , \quad \frac{\Delta T_m}{T_m} = \frac{(\gamma^S - \gamma^L)}{\Delta H_m} \cdot \frac{2}{r} V_m$$

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

$$a) \quad \overline{Q}_2 = Q + (1-x_2) \frac{dQ}{dx_2}$$

$$\overline{Q}_1 = Q + (1-x_1) \frac{dQ}{dx_1}$$

partial molar Gibbs energy of A

$$: G_m + (1-x_A) \frac{dG_m}{dx_A} =$$

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

$$+ (1-x_A) \left[G_A - G_B + RT \{ \ln x_A - \ln(1-x_A) \} + (1-2x_A) \{ L_0 + (2x_A-1) L_1 \} + 2L_1 x_A (1-x_A) \right]$$

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

partial molar Gibbs energy of B

$$: G_m + (1-x_B) \frac{dG_m}{dx_B} =$$

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

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

$$- 2L_1 x_A^2 x_B$$

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

check) $x_A G_m^A + x_B G_m^B = G_m$ (Gibbs-Duhem equation) ; 성립.

$$b) \quad RT \ln a_A = \overline{G}^m - {}^\circ G = RT \ln x_A + x_B^2 \{ L_0 + (x_A - x_B) L_1 \} + 2L_1 x_A x_B^2$$

$$① \lim_{x_A \rightarrow 1} : RT \ln a_A \rightarrow 0, \quad a_A \rightarrow 1,$$

ideal behavior $\approx$ $\approx$ Raoult's law 성립.

$$② \lim_{x_A \rightarrow 0} : RT \ln a_A = RT \ln x_A + (L_0 - L_1)$$

$a_A = \gamma x_A = x_A \cdot e^{(L_0 - L_1)/RT}$, activity constant γ 가 1이
아닌 상황에서 $\approx$ Henry's law 성립.

3 - (c)

$$\begin{aligned}
 G^m &= \sum x_i \bar{G}_i = x_A \bar{G}_A + x_B \bar{G}_B, \quad x_B \bar{G}_B = G^m - x_A \bar{G}_A \\
 &= x_A^\circ G_A + x_B^\circ G_B + RT \{ x_A \ln x_A + x_B \ln x_B \} + x_A x_B \{ L_0 + (x_A - x_B) L_1 \} \\
 &\quad - \left[x_A^\circ G_A + RT x_A \ln x_A + x_A x_B^2 \{ L_0 + (x_A - x_B) L_1 \} + 2L_1 x_A^2 x_B^2 \right] \\
 &= x_B^\circ G_B + RT x_B \ln x_B + x_A x_B (1 - x_B) \{ L_0 + (x_A - x_B) L_1 \} - 2L_1 x_A^2 x_B^2 \\
 \therefore \bar{G}_B &=^\circ G_B + RT \ln x_B + x_A^2 \{ L_0 + (x_A - x_B) L_1 \} - 2L_1 x_A^2 x_B
 \end{aligned}$$

4.

$$G_m = x_A^\circ G_A + x_B^\circ G_B + RT (x_A \ln x_A + x_B \ln x_B) + a x_A x_B$$

liquid에서 $x_A G_A^{\text{ref} \rightarrow l} + x_B G_B^{\text{ref} \rightarrow l} + RT (x_A \ln x_A + x_B \ln x_B) + a x_A x_B$,

solid에서 activity 는 ideal 하므로 $G_m = x_A G_A^{\text{ref} \rightarrow s} + x_B G_B^{\text{ref} \rightarrow s} + RT (x_A \ln x_A + x_B \ln x_B)$

solid의 $(x_A, x_B) = (x, 1-x)$ 에서 공통 접선이 생길 때

기울기는 $\frac{dG_m}{dx} = G_A^{\text{ref} \rightarrow s} - G_B^{\text{ref} \rightarrow s} + RT \ln \frac{x}{1-x}$

liquid에서 $(x_A, x_B) = (y, 1-y)$ 에서 접한 지 할 때

$$\frac{dG_m}{dy} = G_A^{\text{ref} \rightarrow l} - G_B^{\text{ref} \rightarrow l} + RT \ln \frac{y}{1-y} + a(1-2y)$$

두 기울기가 같으므로

$$G_A^{\text{ref} \rightarrow s} - G_B^{\text{ref} \rightarrow s} + RT \ln \frac{x}{1-x} = G_A^{\text{ref} \rightarrow l} - G_B^{\text{ref} \rightarrow l} + RT \ln \frac{y}{1-y} + a(1-2y)$$

$$G_A, G_B \text{ 항에서 } G_A^{\text{ref} \rightarrow s} - G_A^{\text{ref} \rightarrow l} = G_A^{l \rightarrow s}, \quad G_B^{\text{ref} \rightarrow s} - G_B^{\text{ref} \rightarrow l} = G_B^{l \rightarrow s}$$

이므로 각 원소에 대해 동일한 ref 를 사용하면 ref에 관계없이 쓴 것이다.

상-액평형 조건식: $\bar{G}_A(\text{solid}) = \bar{G}_A(\text{liquid}), \quad \bar{G}_B(\text{solid}) = \bar{G}_B(\text{liquid})$

$$G_A^{\text{ref} \rightarrow \text{solid}} + RT \ln x = G_A^{\text{ref} \rightarrow \text{liquid}} + RT \ln y + a(1-y)^2$$

$$G_B^{\text{ref} \rightarrow \text{solid}} + RT \ln x = G_B^{\text{ref} \rightarrow \text{liquid}} + RT \ln y + a(1-y)^2$$

5.

ideal model: $\mu = {}^\circ G + RT \ln x$, $a_B = x_B$

regular model: $\Delta G_m^{xs} = x_A x_B$

Sub-regular model: $\Delta G_m^{xs} = x_A x_B [L_0 + (x_B - x_A) L_1]$

$$\mu = {}^\circ G + RT \ln a$$

ideal model: $x_B = a_B$

regular model: $RT \ln a_B = RT \ln x_B + \alpha x_A^2$,

$$a_B = x_B \exp\left(\frac{\alpha x_A^2}{RT}\right)$$

$$x_B = 0.1 \text{ 일 때 } a_B = 0.0320 \frac{\text{g}}{\text{g}} \text{ 대입하면}$$

$$8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 1273 \text{ K} \ln 0.0320 = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 1273 \text{ K} \ln 0.1 + \alpha (0.9)^2,$$

$$RT \ln \gamma_k = \alpha (0.9)^2, \alpha = -14888.0 \frac{\text{J}}{\text{mol}} \text{ 이므로 이 결과를 아래 } \frac{\text{J}}{\text{mol}} \text{ 과 같게}$$

Subregular model:

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

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

$$RT \ln \frac{a_B}{x_B} = (1 - x_B)^2 [L_0 + (x_A - x_B) L_1] + 2 L_1 (1 - x_B) x_B^2 \alpha$$

$$x_B = 0.1, a = 0.0320 \frac{\text{g}}{\text{g}} \text{ 대입하면}$$

$$RT \ln 0.320 = (0.9)^2 [L_0 + 0.8 L_1] + 2 L_1 (0.9) (0.1)^2,$$

$$x_B = 0.2, a = 0.0800 \frac{\text{g}}{\text{g}} \text{ 대입하면}$$

$$RT \ln 0.4 = (0.8)^2 [L_0 + 0.6 L_1] + 2 L_1 (0.8) (0.2)^2$$

$$-12059 = 0.81 L_0 + 0.648 L_1 + 0.018 L_1$$

$$= 0.81 L_0 + 0.666 L_1,$$

$$-9691 = 0.64 L_0 + 0.384 L_1 + 0.064 L_1$$

$$= 0.64 L_0 + 0.448 L_1$$

$$L_0 = -16663, L_1 = 2159$$

이제 계산한 결과에 각각

ideal model

```
In [1]: import math
import numpy as np
```

```
In [20]: xb=float(0)
a=float(xb)

for data in range(1,11):
    xb+=0.1
    a=xb
    print('activity:',round(a,2))
```

```
activity: 0.1
activity: 0.2
activity: 0.3
activity: 0.4
activity: 0.5
activity: 0.6
activity: 0.7
activity: 0.8
activity: 0.9
activity: 1.0
```

regular model

```
In [3]: xb=float(0)
a=float(xb)
r=8.314
t=1273
alpha=-14888

for data in range(1,11):
    xb+=0.1
    a=xb*np.exp(alpha*(1-xb)**2/(r*t))
    print('activity:',round(a,4))
```

```
activity: 0.032
activity: 0.0813
activity: 0.1506
activity: 0.2411
activity: 0.3518
activity: 0.4791
activity: 0.6168
activity: 0.7562
activity: 0.8874
activity: 1.0
```

subregular model

```
In [7]: xb=0
L0=-16663
L1=2159
for data in range(1,11):
    xb+=0.1
    a=xb*np.exp(((L0*(1-2*xb)*L1)*(1-xb)**2+2*L1*(1-xb)*xb**2)/(r*t))
    print('activity:',round(a,4))
```

```
activity: 0.032
activity: 0.08
activity: 0.1481
activity: 0.2395
activity: 0.355
activity: 0.4914
activity: 0.6403
activity: 0.7876
activity: 0.9142
activity: 1.0
```

이므로 regular 일 때 가장 우수했다.

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)

