1.

a) T_b에서 $P=1\ atm$.

$$\ln 1 = -\frac{31090}{T_b} - 2\ln T_b + 34.66$$, 공학용 계산기로 T_b를 계산하면 2006 K

b) 삼중점에서

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

마찬가지로 T_b를 계산하면 $T=1239K$, $P=2.29\times10^{-4}\ (atm)$

c) $$\frac{d\ln P}{dT} = \frac{\Delta H}{RT^2} = \frac{31090}{T^2} - \frac{2.52}{T}$$, $\Delta H_{(l\to v)} = 31,090R - 2.52RT$

↳ 2006K.

$\Delta H_{(l\to v)} = 216,500(J)$.

d) $$\frac{d\ln P}{dT} = \frac{\Delta H}{RT^2} = \frac{34450}{T^2} - \frac{2.01}{T}$$, $\Delta H_{(s\to v)} = 34450R - 2.01RT$.

$\Delta H_{(s\to v)} = 34450R - 2.01RT$.

$\Delta H_{(s\to l)} = \Delta H_{(s\to v)} - \Delta H_{(l\to v)} = 31,090R - 2.52RT - 34,450R + 2.01RT$, $T=1239K$.

$\Delta H_{(s\to l)} = 33,150\ KJ$.

e) $$\frac{d\Delta H_{(s\to l)}}{dT} = \Delta C_p = C_p^{\,l} - C_s^{\,S} = 4.24\ (J/K)$$

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

$\Delta G_0^\circ = \Delta H_m - T\Delta S_m$, T_m에서 $\Delta G_0 = 0$

$\Delta G = \Delta G_0^\circ + \int v\,dP = \Delta G_0^\circ + V_m\left(\frac{2\gamma_s}{r} - \frac{2\gamma_L}{r}\right)$

$= \Delta H_m - T\Delta S_m + V_m\left(\frac{2(\gamma_s - \gamma_L)}{r}\right)$

$T = T_m + \Delta T_m$ 일 때 $\Delta G = 0$.

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

$$\therefore -\Delta T_m \Delta S_m + \frac{2V_m(\gamma_s - \gamma_L)}{r} = 0$$

$$\Delta H_m - T_m \Delta S_m = 0.$$

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

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

partial molar Gibbs energy of A

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

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

마찬가지로 $G_m^B = G_B^\circ + RT \ln x_B + \underbrace{[L_0 + (x_A - x_B) L_1) x_A^2 - 2L_1 x_A^2 x_B}_{\overline{G_B}^{xs}}$

b) $RT \ln a_A = RT \ln x_A + (L_0 + (x_A - x_B) L_1) x_B^2 + 2L_1 x_A x_B^2$

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

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

dilute 조건
$\lim_{x_A \to 0} \overline{G_A}^{xs} = L_0 - L_1 \neq 0 \rightarrow$ Henritian
$\lim_{x_B \to 0} \overline{G_B}^{xs} = L_0 + L_1 \neq 0 \rightarrow$ Henritian

Rich 조건 $\lim_{x_A \to 1} \overline{G_A}^{xs} = \lim_{x_B \to 1} \overline{G_B}^{xs} = 0 \rightarrow$ Raoultian

c) Gibbs - Duhem equation $\sum_k x_k (d\overline{Q_k}) = 0$.

$\therefore x_A \frac{d\overline{G_A}}{dx_A} + x_B \frac{d\overline{G_B}}{dx_B} = 0$.

$\frac{d\overline{G_B}}{dx_B} = -\frac{x_A}{x_B} \frac{d\overline{G_A}}{dx_A}$, $\overline{G_B} = -\int_0^{x_A} \frac{x_A}{x_B} \frac{d\overline{G_A}}{dx_A} \cdot dx_A$

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

$$= -\int_0^{x_A} \frac{x_A}{x_B} \left(\frac{RT}{x_A} - 2(1-x_A)L_0 - 2(1-x_A)(4x_A-1)L_1 + 4(1-x_A)^2 L_1 \right) dx_A$$

$= G_B^\circ + RT\ln x_B + x_A^2 L_0 + x_A^2 (1-4x_B)$ 이고,

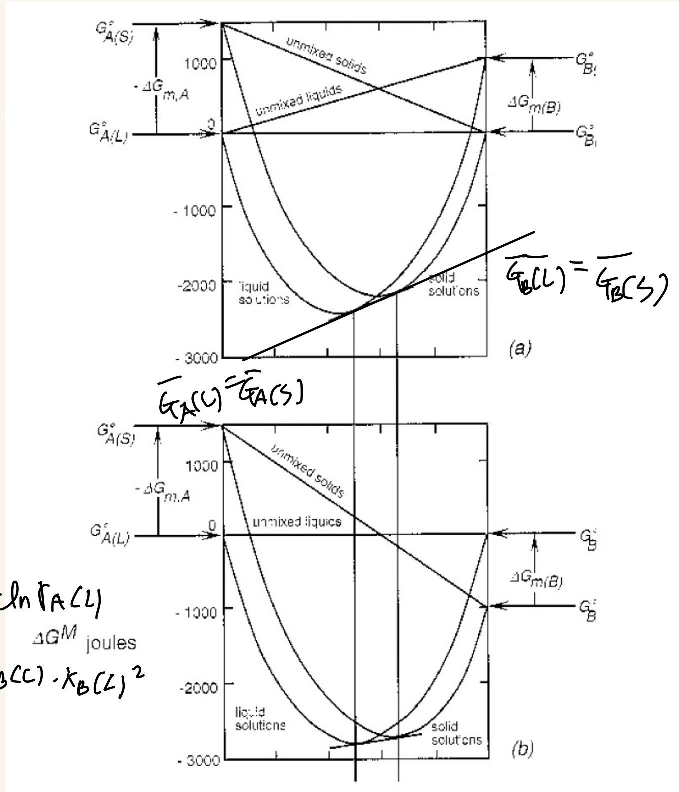
이전 결과와 같다.

4. $G_A^\circ(S) - G_A^\circ(L) = -\Delta G_m(A)$

$G_B^\circ(S) - G_B^\circ(L) = -\Delta G_m(B)$

$\Downarrow$

regular solution.



$\overline{G_B}(L) = \overline{G_B}(S)$

$\overline{G_A}(L) = \overline{G_A}(S)$

1. 두 그래프에서 y절편을 비교 하면

$\overline{G_A}(L) = \overline{G_A}(S)$

$\overline{G_B}(L) = \overline{G_B}(S)$

$\therefore \overline{G_A}(L) = G_A^\circ(L) + RT\ln a_A(L)$

$= G_A^\circ(L) + RT\ln X_A(L) + RT\ln \gamma_A(L)$

$= G_A^\circ(L) + RT\ln X_A(L) + L_{AB}(L)\cdot X_B(L)^2$

$\overline{G_A}(S) = G_A^\circ(S) + RT\ln a_A(S)$

$= G_A^\circ(S) + RT\ln X_A(S) + L_{AB}(S)\cdot X_B(S)^2$

$\overline{G_B}(L) = G_B^\circ(L) + RT\ln a_B(L) = G_B^\circ(L) + RT\ln X_B(L) + L_{AB}(L)\cdot X_A(L)^2$

$\overline{G_B}(S) = G_B^\circ(S) + RT\ln a_B(S) = G_B^\circ(S) + RT\ln X_B(S) + L_{AB}(S)\cdot X_A(S)^2$

$\overline{G_A}(S) = \overline{G_A}(L) \rightarrow \underbrace{G_A^\circ(S) - G_A^\circ(L)}_{-\Delta G_m(A)} + RT\ln\left(\frac{X_A(S)}{X_A(L)}\right) + L_{AB}(S)\cdot X_B(S)^2 - L_{AB}(L)\cdot X_B(L)^2 = 0.$

$\underbrace{G_B^\circ(S) - G_B^\circ(L)}_{-\Delta G_m(B)} + RT\ln\left(\frac{X_B(S)}{X_B(L)}\right) + L_{AB}(S)\cdot X_A(S)^2 - L_{AB}(L)\cdot X_A(L)^2 = 0$

2. 그리고 $X_A = 1 - X_B$

$G_m(L) = (1-X_B)G_A^\circ(L) + X_B G_B^\circ(L) + RT\{(1-X_B)\cdot\ln(1-X_B) + X_B\ln X_B\}$

$+ (1-X_B)\cdot X_B\cdot L_{AB}(L)$

$$G_m(S) = (1-X_B)\, G_A^\circ(S) + X_B\, G_B^\circ(S) + RT\{(1-X_B)\cdot \ln(1-X_B) + X_B \ln X_B)\}$$
$$+ (1-X_B)\cdot X_B\, L_{AB}(S)$$

$\underline{G_m(L),\ G_m(S)}$ 각각 X_B로 미분, $\dfrac{dG_m(L)}{dX_B} = \dfrac{dG_m(S)}{dX_B}$

$$\frac{dG_m(L)}{dX_B} = -G_A^\circ(L) + G_B^\circ(L) + RT(-\ln(1-X_B) + \ln X_B)) + (1-2X_B)\cdot L_{AB}(L)$$

$$\frac{G_m(S)}{dX_B} = -G_A^\circ(S) + G_B^\circ(S) + RT(-\ln(1-X_B) + \ln X_B) + (1-2X_B)\cdot L_{AB}(S)$$

$$(G_A^\circ(S) - G_A^\circ(L)) - (G_B^\circ(S) - G_B^\circ(L)) + RT\left(\ln\frac{1-X_B(S)}{1-X_B(L)} + \ln\frac{X_B(L)}{X_B(S)}\right)$$
$$+(1-2X_B(L))L_{AB}\cdot(L) - (1-2X_B(S))\cdot L_{AB}\cdot(S) = 0.$$

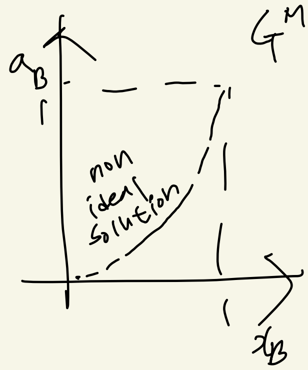
$\Rightarrow\ -\Delta G_m(A) + \Delta G_m(B) + F(X_B) = 0;$ $\qquad$ X_B에 의해 결정되는 함수 $F(X_B)$

1.의 결론은 $-G_m(A) + \Delta G_m(B) + RT\ln\left(\dfrac{X_A(S)\cdot X_B(L)}{X_A(L)\cdot X_B(S)}\right) = 0.$

$RT\ln\left(\dfrac{X_A(S)\cdot X_B(L)}{X_A(L)\cdot X_A(S)}\right) = F(X_B)$ 를 풀면 된다.

$\therefore X_B(S), X_B(L)$의 조성은 reference와 관계없이 일정한 값으로 나온다.

5.



$$G^M = x_A G_A^\circ + x_B G_B^\circ + x_A \ln a_A + x_B \ln a_B$$

$$= x_A G_A^\circ + x_B G_B^\circ + x_A \ln x_A + x_B \ln x_B \rightarrow \text{Ideal Sol}$$

$$= x_A G_A^\circ + x_B G_B^\circ + x_A \ln x_A + x_B \ln x_B + L_0 x_A x_B \text{ (Regular)}$$

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

$$\therefore x_A \ln a_A + x_B \ln a_B = x_A \ln X_A + X_B \ln X_B + \frac{X_A \cdot X_B}{RT} L_{AB}$$

$$\Leftrightarrow X_A \ln \gamma_A + X_B \ln \gamma_B = \frac{1}{RT} \cdot X_A \cdot X_B \cdot L_{AB}$$

$$\Leftrightarrow RT(x_A \ln \gamma_A + x_B \ln \gamma_B) = X_A \cdot X_B \cdot L_{AB} = X_A \cdot X_B \cdot \Omega_{AB}.$$

$$\rightarrow RT \ln \gamma_A = \Omega_{AB} \cdot X_B^2$$

$$X_A \cdot X_B \cdot \Omega_{AB} = RT x_B \ln \gamma_B + \Omega_{AB} \cdot X_B^2 \cdot X_A$$

$$\Leftrightarrow X_A \cdot \Omega_{AB} = RT \ln \gamma_B + \Omega_{AB} \cdot X_A \cdot X_B$$

$$(1 - x_B)\Omega_{AB} = (1 - x_B) x_B \Omega_{AB} + RT \ln \gamma_B$$

$$\rightarrow (1 - 2X_B + X_B^2)\Omega_{AB} = RT \ln \gamma_B$$

$$\rightarrow (1 - X_B)^2 \Omega_{AB} = RT \ln \gamma_B, \quad \Omega_{AB} = \frac{RT \ln \gamma_B}{(1 - x_B)^2}, \quad \gamma_B = \frac{a_B}{X_B}, \quad T = 1273K$$

x_B	a_B	Ω_{AB}
0.10	0.0320	−14888
0.20	0.0800	−15153
0.30	0.1498	−15000
0.40	0.2400	−15018
0.50	0.3510	−14979
0.60	0.4782	−15009
0.70	0.6162	−14995
0.80	0.7559	−15003
0.90	0.8874	−14922
1.00	1.0000	X

(−15000으로 근사)

$$RT \ln \gamma_B = \Omega_{AB} \cdot X_A^2$$

$$\rightarrow \gamma_B = \exp\left[\frac{1}{RT} \cdot \Omega_{AB} \cdot X_A^2\right]$$

$$X_A = 1 - X_B$$

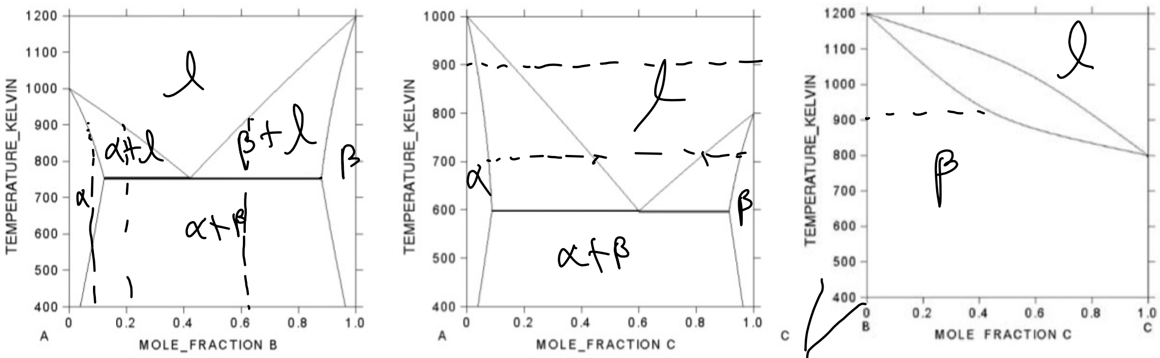
$$\gamma_B = e^{\frac{\Omega_{AB}}{RT}(1-X_B)^2}$$

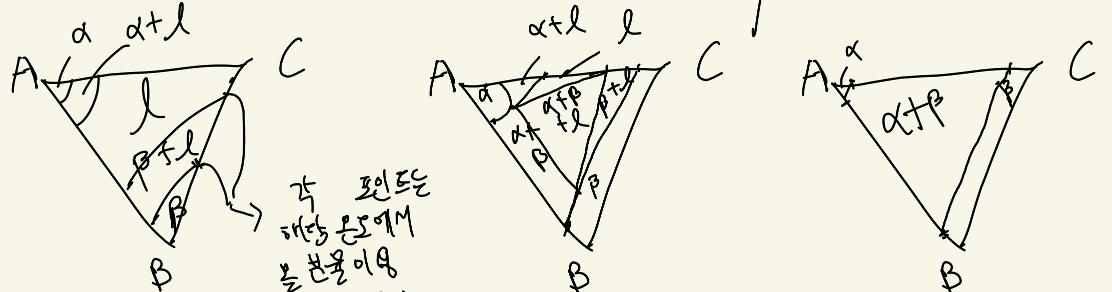
$$a_B = X_B \cdot \gamma_B = X_B\, e^{\frac{\Omega_{AB}}{RT}(1-X_B)^2}$$

x_B	a_B (이론)	a_B (측정)
0.1	0.0319	0.0320
0.2	0.0807	0.0800
0.3	0.1498	0.1498
0.4	0.2401	0.2400
0.5	0.3508	0.3510
0.6	0.4783	0.4782
0.7	0.6162	0.6162
0.8	0.7559	0.7559
0.9	0.8873	0.8874
1.0	1	1.0000

⇒ 오차가 매우 작은 우수한 model

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)



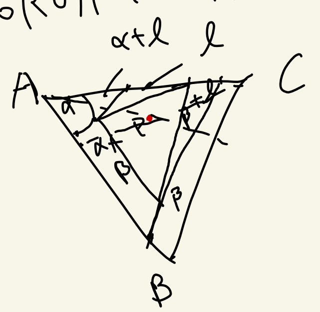


각 포인트는 해당 온도에서 본 분율이용 (포기생략)

900K 700K 400K

BC 조성을 통해 확인하면 B와 C모두 β상을 가짐을 알 수 있다. 따라서 예제 ppt와는 형태가 다름.

ex) [900K에서 α+β+l의 존재]



p의 조성.

p point에서 상 : ($x_A = x_C$, $x_A = 2x_B$)

$x_A = x_C = 0.4$, $x_B = 0.2$

AB diagram에서 α+β,
AC 〃 에서 l
BC 〃 에서 β

→ α+β+l