1.

(a) $P_l = 1$ $\quad \therefore 0 = -\frac{31090}{T} - 2.52\ln T + 34.66 \quad \therefore T_b = 2006K$

(b) $P_s = P_l = P_g \qquad P_s = P_l$

$\Rightarrow -\frac{34450}{T} - 2.01\ln T + 33.74 = -\frac{31090}{T} - 2.52\ln T + 34.66 \Rightarrow T = 1239K$

(c) $d(\ln P)/dT = \Delta H/RT^2 \Rightarrow 31090 \cdot \frac{1}{T^2} - \frac{2.52}{T} = \frac{\Delta H}{RT^2} \Rightarrow \Delta H = 216.5kJ/mol$

$(T = 2006K)$

(d) $\Delta H_{s\to l} = \Delta H_{s\to g} - \Delta H_{l\to g}$, $\Rightarrow \Delta H_{s\to g} = R(34450 - 2.01T)$, $\Delta H_{l\to g} = R(31090 - 2.52R)$, $T = 1239K$

$\Rightarrow \Delta H_{s\to g} = 265.7\,kJ/mol$, $\Delta H_{l\to g} = 232.5kJ/mol$

$\therefore \Delta H_{s\to l} = 33.2kJ/mol$

(e) $\Delta C_p = d(\Delta H_{s\to l})/dT = d(\Delta H_{s\to g})/dT - d(\Delta H_{l\to g})/dT = -2.01R + 2.52R = 4.24J/K$

2,

$l \to s \qquad \Delta P = \frac{2}{r}(\gamma_s - \gamma_l) \qquad \frac{dP}{dT} = \frac{\Delta H_m}{T\Delta V_m} \Rightarrow \frac{\Delta T_m}{T_m} = \frac{\Delta V_m}{\Delta H_m} \cdot P = \frac{2}{r}(\gamma_s - \gamma_l) \cdot \frac{\Delta V_m}{\Delta H_m}$

3.

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

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

$\bar{G}_B = G_m + (1 - x_B)\frac{\partial G_m}{\partial x_B} = {}^{\circ}G_B + RT\ln x_B + (1 - x_B)^2\{L_0 + (1 - 4x_B)L_1\}$

$\bar{G}_A = G_m + (1 - x_A)\frac{\partial G_m}{\partial x_A} = {}^{\circ}G_A + RT\ln x_A + (1 - x_A)^2\{L_0 + (4x_A - 1)L_1\}$

(b)

i) $x_A \gg x_B \qquad \bar{G}_A = {}^{\circ}G_A + RT\ln x_A = G_A^{\circ} + RT\ln a_A \qquad \therefore \lim_{x_A\to 1} a_A = x_A$

$\bar{G}_B = {}^{\circ}G_B + RT\ln x_B + (L_0 + L_1) = {}^{\circ}G_B + RT\ln a_B \qquad \therefore \lim_{x_B\to 0} a_B = \exp\left(\frac{L_0 + L_1}{RT}\right)x_B = \gamma_B^{\circ} x_B$

ii) $x_A \ll x_B \qquad \bar{G}_A = {}^{\circ}G_A + RT\ln x_A + (L_0 - L_1) = G_A^{\circ} + RT\ln a_A \qquad \therefore \lim_{x_A\to 0} a_A = \exp\left(\frac{L_0 - L_1}{RT}\right)x_A = \gamma_A^{\circ} x_A$

$\bar{G}_B = {}^{\circ}G_B + RT\ln x_B = G_B^{\circ} + RT\ln a_B \qquad \therefore \lim_{x_B\to 1} a_B = x_B$

(c) $x_A d\bar{G}_A + x_B d\bar{G}_B = 0 \Rightarrow d\bar{G}_B = -\frac{x_A}{x_B} d\bar{G}_A = -\frac{x_A}{x_B}\cdot\left(\frac{RT}{x_A} - 2(1 - x_A)\{L_0 + (4x_A - 1)L_1\} + 4(1 - x_A)^2 L_1\right)$

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

$\therefore \bar{G}_B = \int d\bar{G}_B = RT\ln x_B + x_A^2 L_0 + 4x_A^3 L_1 - 3x_A^2 L_1$

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

4.

(a) : liquid A, solid B

(b) : liquid A, liquid B

i) (a) $\Delta G_l^M = RT(x_A \ln x_A + x_B \ln x_B) + L_{AB}(l) x_A x_B + (G_B^\circ(l) - G_B^\circ(s)) x_B$

$\Delta G_s^M = RT(x_A \ln x_A + x_B \ln x_B) + L_{AB}(s) x_A x_B + (G_A^\circ(s) - G_A^\circ(l)) x_A$

$\partial(\Delta G_l^M)/\partial x_B = \partial(\Delta G_s^M)/\partial x_B \Rightarrow \partial(\Delta G_l^M - \Delta G_s^M)/\partial x_B = 0$

$\Rightarrow \{(G_B^\circ(l) - G_B^\circ(s)) + L_{AB}(l) x_A\} - \{(G_A^\circ(l) - G_A^\circ(s)) + L_{AB}(s) x_A\} = 0$

ii) (b) $\Delta G_l^M = RT(x_A \ln x_A + x_B \ln x_B) + L_{AB}(l) x_A x_B$

$\Delta G_s^M = RT(x_A \ln x_A + x_B \ln x_B) + L_{AB}(s) x_A x_B + (G_A^\circ(s) - G_A^\circ(l)) x_A + (G_B^\circ(s) - G_B^\circ(l)) x_B$

$\Rightarrow \partial(\Delta G_l^M - \Delta G_s^M)/\partial x_B = 0$

$\Rightarrow (L_{AB}(l) x_A) - \{L_{AB}(s) x_A + (G_A^\circ(l) - G_A^\circ(s)) + (G_B^\circ(s) - G_B^\circ(l))\} = 0$

(a) 와 (b) 에서의 평형이 되기 위해 만족해야 하는 식이 같다.

따라서 상평형 조건은 reference state에 상관없이 unique 하다.

5.

i) ideal solution : $x_B \neq a_B$ 이므로 ideal 하지 않다.

ii) regular solution ; $\Delta G^m = RT(x_A \ln a_A + x_B \ln a_B) = RT(x_A \ln x_A + x_B \ln x_B) + x_A x_B \Omega_{AB}$

$$x_A x_B \Omega_{AB} = RT(x_A \ln \gamma_A + x_B \ln \gamma_B)$$

$$x_A x_B \Omega_{AB} = x_A x_B^2 \Omega_{AB} + RT x_B \ln \gamma_B$$

$$x_A \Omega_{AB} = x_A x_B \Omega_{AB} + RT \ln \gamma_B$$

$\Omega_{AB} = RT \ln \gamma_B / (1-x_B)^2$ => regular model 에서 상수

x_B	a_B	γ_B	Ω_{AB}
0.1	0.032	0.32	-14888.2
0.2	0.08	0.4	-15152.8
0.3	0.1498	0.499333	-15000.4
0.4	0.24	0.6	-15017.9
0.5	0.351	0.702	-14979
0.6	0.4782	0.797	-15009.1
0.7	0.6162	0.880286	-14994.6
0.8	0.7559	0.944875	-15003.1
0.9	0.8874	0.986	-14921.9
1	1	1	

=> Ω_{AB}가 -15000으로 거의 일정

∴ regular solution model이 가장 적합

iii) sub regular solution model : Ω_{AB}가 x_B에 따라 달라지지만, 실험 데이터에서 Ω는 거의 일정하다. 따라서 부적합

$$\Rightarrow \Delta G^M = RT(x_A \ln x_A + x_B \ln x_B) + x_A x_B \Omega_{AB}$$

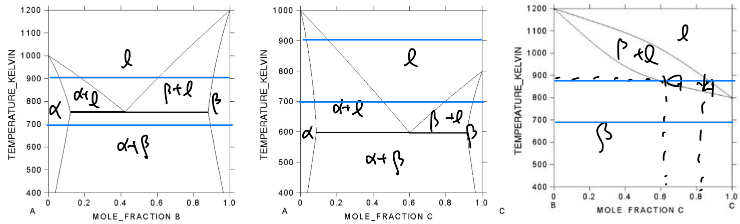
$$= RT\{(1-x_B)\ln(1-x_B) + x_B \ln x_B\} + (1-x_B)x_B \cdot \frac{RT \ln \gamma_B}{(1-x_B)^2}$$

$RT \ln \gamma_B = \Omega_{AB}(1-x_B)^2 = \Omega_{AB} x_A^2 \Rightarrow \gamma_B = \exp(\Omega_{AB} \cdot x_A^2 / RT)$

$\Rightarrow a_B = x_B \exp(\Omega_{AB} x_A^2 / RT)$, Ω_{AB}는 평균값인 -14951.9 사용

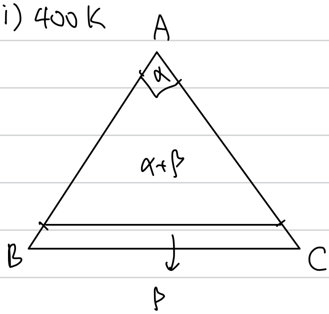
x_B	x_A	a_B	Ω_{AB}	a_B(이론)	오차율
0.1	0.9	0.032	-14488.2	0.031844	0.486198
0.2	0.8	0.08	-15152.8	0.080978	-1.22201
0.3	0.7	0.1498	-15000.4	0.150137	-0.22482
0.4	0.6	0.24	-15017.9	0.240539	-0.22468
0.5	0.5	0.351	-14979	0.351225	-0.06406
0.6	0.4	0.4782	-15009.1	0.478614	-0.08648
0.7	0.3	0.6162	-14994.6	0.616424	-0.03635
0.8	0.2	0.7559	-15003.1	0.756046	-0.01936
0.9	0.1	0.8874	-14921.9	0.887375	0.002834
1	0	1	**-14951.9**		

6.

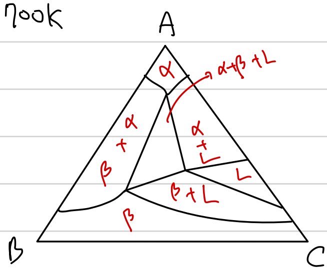


A + B   A + C   B + C

i) 400 K



ii) 700K



iii) 900K