열역학 HW#3

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1. ① solid NaF $\ln P(atm) = -\dfrac{34450}{T} - 2.01 \ln T + 33.74$

② liquid NaF $\ln P(atm) = -\dfrac{31090}{T} - 2.52 \ln T + 34.66$

a) normal boiling temperature T_b

② 에 $P=1$ 넣으면,

$$0 = -\frac{31090}{T} - 2.01 \ln T + 33.74.$$

$T_b = 2006K$

b) Triple point 에선, P, T 일치하므로,

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

$$\frac{3560}{T} - 0.51 \ln T + 0.92 = 0$$

$T_{tp} = 1239K,$

$$\ln P_{tp} = -\frac{31090}{1239} - 2.52 \ln 1239 + 34.66$$

$P_{tp} = 2.29 \times 10^{-4}$ atm

c) $\frac{d\ln P}{dT} = \frac{\Delta H}{RT^2}$ 에서, l-eg. at T_b 이므로,

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

$$\frac{d\ln P}{dT} = \frac{31090}{T^2} - \frac{2.52}{T} = \frac{\Delta H_i}{RT^2}$$

$$\Delta H_i = 31090R - 2.52RT_b$$

$$= R(31090 - 2.52T_b)$$

$$= 2.16\times10^5\ J/mol$$

d) $\frac{d\ln P}{dT} = \frac{\Delta H}{RT^2}$ 에서, s-eg at T_{ep} 이므로,

$$\ln P = -\frac{34450}{T} - 2.01\ln T + 33.74$$

$$s\text{-}eg\ \frac{d\ln P}{dT_{ep}} = \frac{34450}{T_{ep}^2} - \frac{2.01}{T_{ep}} = \frac{\Delta H_{s\text{-}eg}}{RT_{ep}^2}$$

$$\Delta H_{seg} = R(34450 - 2.01T_{ep})$$

$$= 2.66\times10^5\ J/mol$$

$$l\text{-}g \quad \ln P = -\frac{31080}{T} - 2.52\ln T + 34.66$$

$$\frac{d\ln P}{dT} = \frac{31080}{T_{tp}^2} - \frac{2.52}{T_{tp}} = \frac{\Delta H_{l\text{-}g}}{RT_{tp}^2}$$

$$\Delta H_{l\text{-}g} = R(31080 - 2.52T_{tp})$$

$$= 2.33\times 10^5\ J/mol$$

$$\Delta H_{s\text{-}l} = \Delta H_{s\text{-}g} - \Delta H_{l\text{-}g}$$

$$= 3.3\times 10^4\ J/mol$$

(e) $C_p = \frac{dH}{dT}$

$$\Delta C_p = \frac{d\Delta H}{dT} = \frac{\Delta H_{s\text{-}g} - \Delta H_{l\text{-}g}}{dT}$$

$$= \frac{R(3960 + 0.51T)}{dT} = 0.51R$$

$$= 4.24\ J/mol\cdot K$$

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

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

먼저, $dG = -SdT + VdP$ 에서,

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

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

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

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

$$= 0$$

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

이 때, $\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T \Delta V}$ 에서, $\Delta S_m = \frac{\Delta H_m}{T_m}$

$$\frac{\Delta H_m}{T_m} = 2(\sigma^L - \sigma^S) V_m \cdot \frac{d\left(\frac{1}{r}\right)}{dT}$$

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

$$\int_{T_m'}^{T_m} \frac{\Delta H_m}{T_m} dT = \int_r^{\infty} 2(\gamma^L - \gamma^S) V_m \, d\left(\frac{1}{r}\right)$$

$T_m - T_m' = \Delta T_m$ 이고,

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

따라서, 정리하면

$$\frac{\Delta T_m}{T_m} = \frac{\gamma^S - \gamma^L}{\Delta H_m} \times \frac{2}{r} V_m$$ 이다.

3,

$$(1-x_A)\ln(1-x_A) \qquad x_1$$

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

a) $\bar{G}_A = G + (1-x_A)\dfrac{dG_m}{dx_A}$ 이므로,

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

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

$$\bar{G}_A = x_A {}^\circ G_A + (1-x_A){}^\circ G_B + RT(x_A \ln x_A + (1-x_A)\ln(1-x_A))$$
$$+ x_A(1-x_A)L_0 + x_A(1-x_A)(2x_A-1)L_1$$
$$+ (1-x_A){}^\circ G_A - (1-x_A){}^\circ G_B + (1-x_A)RT(\ln x_A - \ln(1-x_A))$$
$$+ (1-x_A)(1-2x_A)\{L_0 + (2x_A-1)L_1\} + (1-x_A)(x_A - x_A^2)\times 2L_1$$

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

$$+ x_A(1-x_A)(2x_A-1)L_1 +$$
$$+ (2x_A-1)(1-x_A)(1-2x_A)L_1$$
$$+ 2x_A(1-x_A)(1-x_A)L_1$$

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

$+ (1-x_A)^2(2x_A-1)L_1 + 2x_A(1-x_A)^2 L_1$

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

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

$\overline{G_B}$는 $\overline{G_A}$와 L_1항을 제외한 대칭이므로,

$\overline{G_B} = {}^\circ G_B + RT\ln x_B + x_A^2 L_0 + \alpha L_1$

αL_1에서, $(1-x_B)x_B(1-2x_B)$ x_B

$\overline{G_B} = G_m + (1-x_B)\cdot\frac{dG_m}{dx_B}$에서 L_1항만 찾으면

$\big((1-x_B)x_B(1-2x_B) - (1-x_B)x_B(1-2x_B) + (1-x_B)^2(1-2x_B)$

$-2(1-x_B)^2 x_B\big)L_1$

$= (1-x_B)^2(1-4x_B)L_1 = x_A^2(1-4x_B)L_1$

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

b)

DIM $\overline{G_A}$, $\overline{G_B}$에서 각각

$$G_A^{xs} = x_B^2 L_0 + x_B^2(4x_A - 1)L_1 = x_B^2\left(L_0 + (4x_A - 1)L_1\right)$$
$$= RT\ln\gamma_A$$

$$G_B^{xs} = x_A^2 L_0 + x_A^2(1 - 4x_B)L_1 = x_A^2\left(L_0 + (1 - 4x_B)L_1\right)$$
$$= RT\ln\gamma_B$$

dilute 영역에서,

$$\lim_{x_A \to 0} G_A^{xs} = \lim_{x_A \to 0} (1 - x_A)^2\left(L_0 + (4x_A - 1)L_1\right)$$
$= L_0 - L_1 \neq 0$, 즉 $\gamma_A \neq 1$이므로,

Henrian 거동이다.

$$\lim_{x_B \to 0} G_B^{xs} = \lim_{x_B \to 0} (1 - x_B)^2\left(L_0 + (1 - 4x_B)L_1\right)$$
$= L_0 + L_1 \neq 0$, 즉 $\gamma_B \neq 1$이므로

Henrian 거동을 보인다.

rich 영역에서,

$$\lim_{x_A \to 1} \overline{G}_A^{XS} = \lim_{x_A \to 1} (1-x_A)^2 (L_0 + (4x_A - 1)L_1)$$

$$= 0, \text{ 즉 } \gamma_A = 1$$

Raoultian 거동을 보인다

$$\lim_{x_B \to 1} \overline{G}_B^{XS} = \lim_{x_B \to 1} (1-x_B)^2 (L_0 + (1-4x_B)L_1)$$

$$= 0, \text{ 즉 } \gamma_B = 1$$

Raoultian 거동을 보인다.

(c)

Gibbs-Duhem equation

$$x_A d\overline{G_A} + x_B d\overline{G_B} = 0$$

즉, $x_A \dfrac{\partial \overline{G_A}}{\partial x_A} + x_B \cdot \dfrac{\partial \overline{G_B}}{\partial x_A} = 0$

$$\frac{\partial \overline{G_B}}{\partial x_A} = -\frac{x_A}{x_B} \times \frac{\partial \overline{G_A}}{\partial x_A}$$

$$= -\frac{x_A}{x_B} \times \left(\frac{RT}{x_A} - 2x_A L_0 + (-4x_A^2 - 6x_A + 4) \right)$$

$(1-x_A)^2(4x_A-1)$

$-2x_A(4x_A-1)$

$+4(1-x_A)^2$

$= -8x_A^2 + 2x_A$

$+4x_A^2 - 8x_A$

$+4$

$2x_A^2 + 3x - 2$ $(2x+1)(x+2$

$2x_A($

$$= -\frac{RT}{x_B} + \frac{2x_A^2}{x_B}L_0 + \frac{4x_A^3 + 6x_A^2 - 4x_A}{x_B}$$

4.

regular solution model에서,

$$G_m = x_A\,{}^\circ G_A + x_B\,{}^\circ G_B + RT(x_A \ln x_A + x_B \ln x_B) + x_A x_B L$$

$$= x_A \Delta G_A^{ref=0} + x_B \Delta G_B^{ref=0} + RT(x_A \ln x_A + x_B \ln x_B) + x_A x_B L$$

즉,

$$G_m^{\alpha} = x_A\,{}^\circ G_A(\alpha) + x_B\,{}^\circ G_B(\alpha) + RT(x_A \ln x_A + x_B \ln x_B) + x_A x_B L^{\alpha}$$

$$G_m^{\beta} = x_A\,{}^\circ G_A(\beta) + x_B\,{}^\circ G_B(\beta) + RT(x_A \ln x_A + x_B \ln x_B) + x_A x_B L^{\beta}$$

상호접촉일 때, 공통접선을 가지고 있으므로,