20220560 최원준

① (a) $\ln P = \frac{-31090}{T} - 2.52 \ln T + 34.66 \qquad P = 1\text{atm}$

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

$T = 2006\text{K}$

(b) $\ln P_\ell = \ln P_s$ at triple point 음

$\ln P_\ell = \frac{-31090}{T} - 2.52 \ln T + 34.66 = \ln P_s = \frac{-34450}{T} - 2.01 \ln T + 33.24$

$\frac{3360}{T} - 0.51 \ln T + 0.92 = 0$

$T = 1239\text{K}$

$\ln P = -\frac{31090}{1239} - 2.52 \ln 1239 + 34.66 = -8.380$

$P = 2.293 \times 10^{-4}$ atm

(c) By the Clausius-Clapeyron equation, $\frac{d\ln P_\ell}{dT} = \frac{\Delta H}{RT^2}$ for the vapor pressure of a liquid

$\frac{d\ln P}{dT} = \frac{\Delta H}{RT^2} = \frac{31090}{T^2} - 2.52 \cdot \frac{1}{T}$

$\Delta H_{(\ell \to v)} = R \cdot 31090 - 2.52 \cdot R \cdot T = R \cdot 31090 - 2.52 \cdot R \cdot (2006\text{K})$

$= 216500\text{J}$

(d) Similarly, for $s \to v$, $\frac{d\ln P_s}{dT} = \frac{\Delta H_{(s\to v)}}{RT^2} = \frac{34450}{T^2} - 2.01 \cdot \frac{1}{T}$

$\Delta H_{(s \to v)} = R \cdot 34450 - 2.01 \cdot R \cdot (1239\text{K})$

$\Delta H_{(s\to \ell)} + \Delta H_{(\ell \to v)} = \Delta H_{(s \to v)}$

$\Delta H_{(s \to \ell)} = \Delta H_{(s \to v)} - \Delta H_{(\ell \to v)}$

$= R \cdot (34450 - 31090) - R(2.01T - 2.52T) = R \cdot 3360 - R \cdot 0.51 \cdot T$

$= R \cdot 3360 - R \cdot 0.51 \cdot 1239\text{K}$

$= 33190\text{J}$

(e) $d\Delta H_{(s\to\ell)} = \Delta C_p \, dT$

$\Delta C_p = \frac{d\Delta H_{(s\to \ell)}}{dT} = \frac{d}{dT}(R \cdot 3360 - R \cdot 0.51 \cdot T) = R \cdot 0.51 = 4.240 \text{ J/K}$

② At equilibrium, $\Delta G_{np}^{s\to l} = \Delta G_{bulk}^{s\to l} + \Delta G_{capillary}^{s\to l} = 0$ (they have different T_m: T_{bulk}, T_{np})

$$\Delta G_{bulk}^{s\to l} = \Delta H_m - T_{bulk}\Delta S_m = 0$$

$$\Delta G_{capillary}^{s\to l} = -S\Delta T + V_m\Delta P = V_m\Delta P = V_m\frac{2\Delta\gamma}{r} = \frac{2V_m}{r}(\gamma_s-\gamma_L)$$

$$\Delta G_{np}^{s\to l} = \Delta H_m - T_{np}\Delta S_m + \frac{2V_m}{r}(\gamma_s-\gamma_L) = 0$$

$$\Delta G_{bulk}^{s\to l} = \Delta G_{np}^{s\to l} = \Delta H_m - T_{bulk}\Delta S_m = \Delta H_m - T_{np}\Delta S_m + \frac{2V_m}{r}(\gamma_s-\gamma_L) = 0$$

$$(T_{np}-T_{bulk})\Delta S_m = \frac{2V_m(\gamma^l-\gamma^s)}{r}, \quad \Delta T_m\Delta S_m = \frac{2V_m(\gamma_s-\gamma_L)}{r}$$

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

$$\frac{\Delta T_m}{T_{bulk}} = \frac{2V_m(\gamma_s-\gamma_L)}{r\Delta H_m}$$ change T_{bulk} to T_m and we get

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

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

(a) $\mu_A = \left(\frac{\partial G'}{\partial n_A}\right) = \frac{\partial}{\partial n_A}\left\{n_A{}^{\circ}G_A + n_B{}^{\circ}G_B + RT(n_A \ln x_A + n_B \ln x_B) + RT(n_A \ln \gamma_A + n_B \ln \gamma_B)\right\}$

$$= \frac{\partial}{\partial n_A}\left\{n_A{}^{\circ}G_A + n_B{}^{\circ}G_B + RT(n_A \ln x_A + n_B \ln x_B) + (n_A + n_B)x_A x_B (L_0 + (x_A - x_B)L_1)\right\}$$

$$= \frac{\partial}{\partial n_A}\left\{n_A{}^{\circ}G_A + n_B{}^{\circ}G_B + RT(n_A \ln x_A + n_B \ln x_B) + \frac{n_A n_B}{n_A + n_B}(L_0 + (x_A - x_B)L_1)\right\}$$

$$= \frac{\partial}{\partial n_A}\left\{n_A{}^{\circ}G_A + n_B{}^{\circ}G_B + RT\left(n_A \ln n_A + n_B \ln n_B - (n_A + n_B)\ln(n_A + n_B)\right) + \frac{n_A n_B}{n_A + n_B}\left(L_0 + \left(\frac{n_A - n_B}{n_A + n_B}\right)L_1\right)\right\}$$

$$= {}^{\circ}G_A + RT\left(\ln n_A + 1 - \ln(n_A + n_B) - 1\right) + \frac{n_A n_B + n_B^2 - n_A n_B}{(n_A + n_B)^2}\left(L_0 + \left(\frac{n_A - n_B}{n_A + n_B}\right)L_1\right)$$

$$+ \frac{n_A n_B}{n_A + n_B} \cdot \frac{n_A + n_B - n_A + n_B}{(n_A + n_B)^2} L_1$$

$$= {}^{\circ}G_A + RT \ln x_A + x_B^2(L_0 + (x_A - x_B)L_1) + 2x_A x_B^2 L_1 = {}^{\circ}G_A + RT \ln x_A + x_B^2(L_0 + (3x_A - x_B)L_1)$$

Similarly, $\mu_B = \left(\frac{\partial G'}{\partial n_B}\right) = {}^{\circ}G_B + RT \ln x_B + x_A^2(L_0 + (x_A - 3x_B)L_1)$

(b) $a = x\gamma$

$RT n_A \ln \gamma_A = n_A \cdot x_B^2(L_0 + (3x_A - x_B)L_1)$, $RT n_B \ln \gamma_B = n_B \cdot x_A^2(L_0 + (x_A - 3x_B)L_1)$

$\ln \gamma_A = \frac{x_B^2}{RT}(L_0 + (3x_A - x_B)L_1)$, $\gamma_A = e^{\frac{x_B^2}{RT}(L_0 + (3x_A - x_B)L_1)}$

$\ln \gamma_B = \frac{x_A^2}{RT}(L_0 + (x_A - 3x_B)L_1)$, $\gamma_B = e^{\frac{x_A^2}{RT}(L_0 + (x_A - 3x_B)L_1)}$

$a_A = x_A e^{\frac{x_B^2}{RT}(L_0 + (3x_A - x_B)L_1)}$, $a_B = x_B e^{\frac{x_A^2}{RT}(L_0 + (x_A - 3x_B)L_1)}$

For solution of B in A

↳ dilute ($x_B \to 0$): $\gamma_B \to e^{\frac{1}{RT}(L_0 + L_1)}$, which means slope = constant ≠ 1, so Henrian

↳ rich ($x_B \to 1$): $\gamma_B \to 1$, which means slope = 1, so it is Raoultian

For solution of A in B

↳ dilute ($x_A \to 0$): $\gamma_A \to e^{\frac{1}{RT}(L_0 - L_1)}$, which means slope = constant ≠ 1, so Henrian

↳ rich ($x_B \to 1$): $\gamma_A \to 1$, which means slope = 1, so it is Raoultian.

(d) $\frac{\partial \mu_A}{\partial x_B} x_A + \frac{\partial \mu_B}{\partial x_B} x_B = 0$

$$\frac{\partial \mu_B}{\partial x_B} = -\frac{x_A}{x_B}\frac{\partial \mu_A}{\partial x_B} = -\frac{x_A}{x_B}\frac{\partial}{\partial x_B}\left({}^{\circ}G_A + RT\ln x_A + (1-x_A)^2\left(L_0 + (4x_A-1)L_1\right)\right)$$

$$= -\frac{x_A}{x_B}\frac{\partial}{\partial x_B}\left({}^{\circ}G_A + RT\ln(1-x_B) + x_B^2\left(L_0 + (3-4x_B)L_1\right)\right)$$

$$= -\frac{x_A}{x_B}\left(-\frac{RT}{1-x_B} + 2x_B\left(L_0 + (3-4x_B)L_1\right) - 4x_B^2L_1\right)$$

$$= \left(\frac{RT}{x_B} - 2x_A\left(L_0 + (3-4x_B)L_1\right) - 4x_Ax_BL_1\right)$$

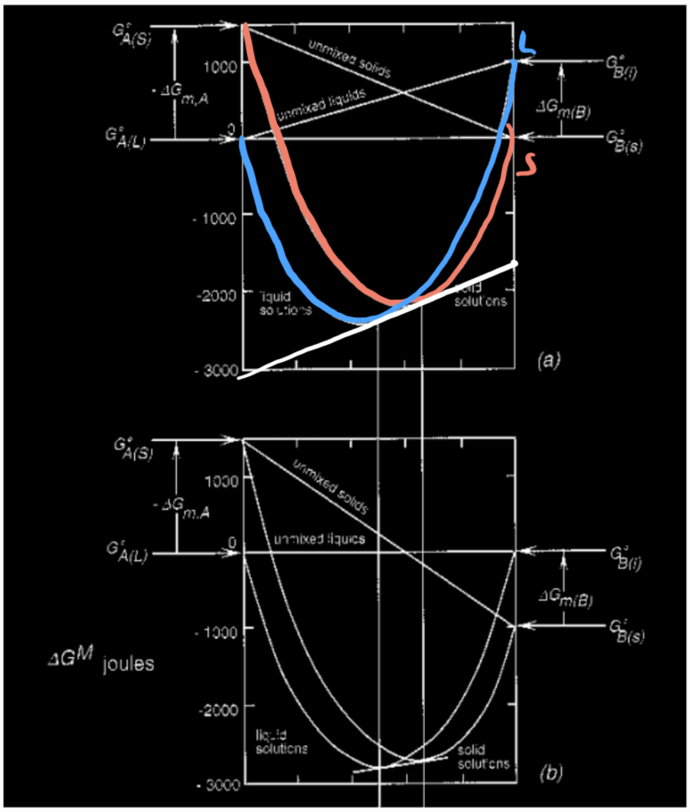
$$= \left(\frac{RT}{x_B} - 2(1-x_B)\left(L_0 + (3-4x_B)L_1\right) - 4(1-x_B)x_BL_1\right)$$

$$\mu_B = \int \frac{RT}{x_B} - 2(1-x_B)\left(L_0 + (3-4x_B)L_1\right) - 4(1-x_B)x_BL_1 \, dx_B$$

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

$$= {}^{\circ}G_B + RT\ln x_B + x_A^2\left(L_0 + (3x_B - x_A)L_1\right)$$

4



$$\overline{G_A}(l) = \overline{G_A}(s), \quad \overline{G_B}(l) = \overline{G_B}(s)$$

$$\begin{cases} \overline{G_A}(l) = G_A^\circ(l) + RT\ln a_A(l) \\ \qquad = G_A^\circ(l) + RT\ln x_A(l) + L_{AB}(l)\, x_B^2(l) \\ \overline{G_A}(s) = G_A^\circ(s) + RT\ln a_A(s) \\ \qquad = G_A^\circ(s) + RT\ln x_A(s) + L_{AB}(s)\, x_B^2(s) \end{cases}$$

$$\begin{cases} \overline{G_B}(l) = G_B^\circ(l) + RT\ln x_B(l) + L_{AB}(l)\, x_A^2(l) \\ \overline{G_B}(s) = G_B^\circ(s) + RT\ln x_B(s) + L_{AB}(s)\, x_A^2(s) \end{cases}$$

$$\overline{G_A}(s) - \overline{G_A}(l) = G_A^\circ(s) - G_A^\circ(l) + RT\ln\left(\frac{x_A(s)}{x_A(l)}\right) + L_{AB}(s)\cdot x_B^2(s) - L_{AB}(l)\cdot x_B^2(l)$$

$$= -\Delta G_m(A) + RT\ln\left(\frac{x_A(s)}{x_A(l)}\right) + L_{AB}(s)\cdot x_B^2(s) - L_{AB}(l)\cdot x_B^2(l) = 0 \quad \cdots (a)$$

$$\overline{G_B}(s) - \overline{G_B}(l) = G_B^\circ(s) - G_B^\circ(l) + RT\ln\left(\frac{x_B(s)}{x_B(l)}\right) + L_{AB}(s)\cdot x_A^2(s) - L_{AB}(l)\cdot x_A^2(l)$$

$$= -\Delta G_m(B) + RT\ln\left(\frac{x_B(s)}{x_B(l)}\right) + L_{AB}(s)\cdot x_A^2(s) - L_{AB}(l)\cdot x_A^2(l) = 0 \quad \cdots (b)$$

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

$$= (1-x_B)G_A^\circ(l) + x_B G_B^\circ(l) + RT\,((1-x_B)\ln(1-x_B) + x_B\ln x_B) + (1-x_B)x_B L_{AB}(l)$$

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

$$= (1-x_B)G_A^\circ(s) + x_B G_B^\circ(s) + RT\,((1-x_B)\ln(1-x_B) + x_B\ln x_B) + (1-x_B)x_B L_{AB}(s)$$

$$\frac{dG_m(l)}{dx_B} = -G_A^\circ(l) + G_B^\circ(l) + RT\,(-\ln(1-x_B) + \ln x_B) + (1-2x_B)\cdot L_{AB}(l)$$

$$\frac{dG_m(s)}{dx_B} = -G_A^\circ(s) + G_B^\circ(s) + RT\,(-\ln(1-x_B) + \ln x_B) + (1-2x_B)\cdot L_{AB}(s)$$

$$\frac{dG_m(l)}{dx_B} - \frac{dG_m(s)}{dx_B} = \left(G_A^\circ(s) - G_A^\circ(l)\right) - \left(G_B^\circ(s) - G_B^\circ(l)\right) + RT\left(\ln\left(\frac{1-x_B(s)}{1-x_B(l)}\right) + \ln\left(\frac{x_B(l)}{x_B(s)}\right)\right)$$

$$+ (1-2x_B(l))L_{AB}(l) - (1-2x_B(s))L_{AB}(s)$$

$$= -\Delta G_m(A) + \Delta G_m(B) + RT\left(\ln\left(\frac{x_A(s)}{x_A(l)}\right) + \ln\left(\frac{x_B(l)}{x_B(s)}\right)\right) \quad \cdots (c)$$

$$+ (x_A^2(l) - x_B^2(l))L_{AB}(l) - (x_A^2(s) - x_B^2(s))L_{AB}(s) = 0$$

Insert (2), (3) into (1). We get

$$RT\ln\left(\frac{x_B(s)\left(1-x_B(l)\right)}{\left(1-x_B(s)\right)x_B(l)}\right)+\left(1-2x_B(s)\right)L_{AB}(s)-\left(1-2x_B(l)\right)L_{AB}(l)+RT\ln\left(\frac{x_A(s)}{x_A(l)}\right)+L_{AB}(s)\,x_B^2(s)$$

$$-L_{AB}(l)x_B^2(l)-RT\ln\left(\frac{x_B(s)}{x_B(l)}\right)-x_A^2(s)L_{AB}(s)+x_A^2(l)L_{AB}(l)$$

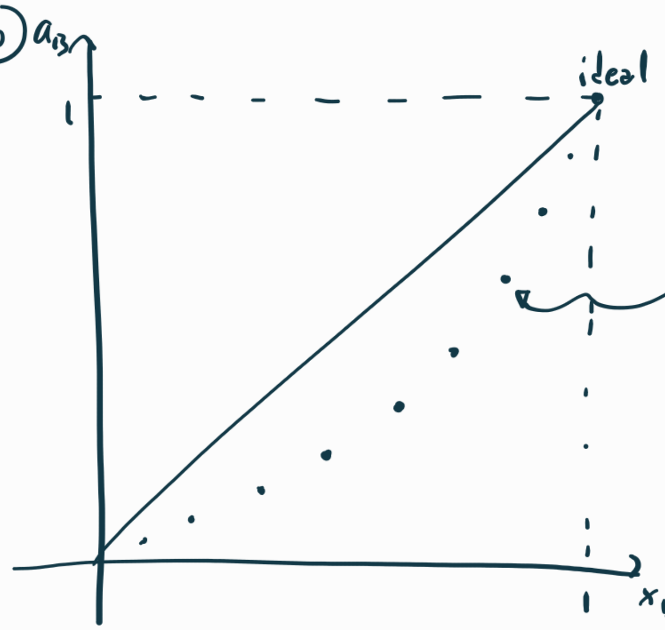
$$=RT\ln\left(\frac{x_B(s)x_A(l)}{x_A(s)x_B(l)}\right)-RT\ln\left(\frac{x_B(s)\,x_A(s)}{x_B(l)x_A(l)}\right)+\left(x_B(s)-1\right)^2L_{AB}(s)-\left(x_A(l)-1\right)^2L_{AB}(l)+x_A^2(l)L_{AB}(l)-x_A^2(s)L_{AB}(s)$$

$$=\left(x_B(s)-1\right)^2L_{AB}(s)-\left(x_A(l)-1\right)^2L_{AB}(l)+x_A^2(l)L_{AB}(l)-x_B^2(s)L_{AB}(s)$$

$$=x_A^2(s)\cancel{L_{AB}(s)}-x_B^2(l)\cancel{L_{AB}(l)}+x_B^2(l)\cancel{L_{AB}(l)}-\cancel{x_A^2(s)}L_{AB}(s)=0$$

Thus, it always holds regardless of reference. (As long as same reference is used)

5



data given → lower activity than ideal solution
→ large stability when together

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

$$= x_A G_A^\circ + x_B G_B^\circ + RT(x_A \ln x_A + x_B \ln x_B) + RT(x_A \ln \gamma_A + x_B \ln \gamma_B)$$

$$= x_A G_A^\circ + x_B G_B^\circ + RT(x_A \ln x_A + x_B \ln x_B) + x_A x_B L_0 \quad (\text{if regular})$$

If regular, $RT \ln \gamma_A = L_0 x_B^2$, so

$$x_A x_B L_0 = RT(x_A \ln \gamma_A + x_B \ln \gamma_B) = RT x_B \ln \gamma_B + L_0 x_B^2 x_A$$

$$x_A L_0 = (1-x_B) L_0 = RT \ln \gamma_B + L_0 x_B x_A = RT \ln \gamma_B + (1-x_B) x_B L_0$$

$$(x_B^2 - 2x_B + 1) L_0 = RT \ln \gamma_B \quad \rightsquigarrow \quad L_0 = \frac{RT \ln \gamma_B}{(1-x_B)^2} = \frac{RT \ln\left(\frac{a_B}{x_B}\right)}{(1-x_B)^2} \qquad (T = 1273K)$$

Using this, we get the following: -14884.1, -15153.7, -15001.3, -15018.8, -14979.9, -15010,
-14995.5, -15004, -14922.8

This is very consistant, indicating that L_0 is approximately constant, about -14997.2 J/mol
Thus, we can assume that the model fits well, and it is a regular solution

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

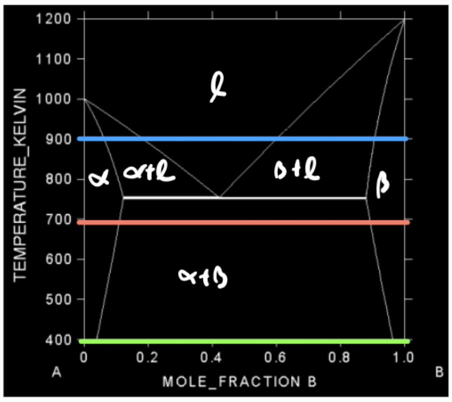
$$= x_A G_A^\circ + x_B G_B^\circ + RT(x_A \ln x_A + x_B \ln x_B) - (14997.2) x_A x_B$$

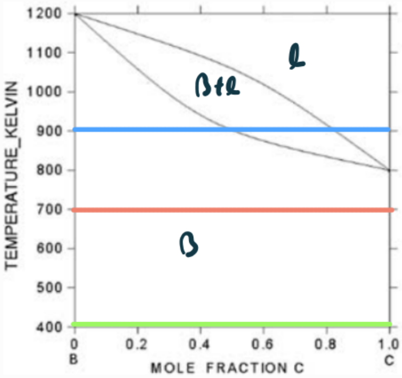
$RT \ln \gamma_B = L_0 x_A^2$, $\gamma_B = e^{\frac{L_0}{RT}(1-x_B)^2}$, $a_B = x_B \gamma_B$, and when using $L_0 = -14997.2$,

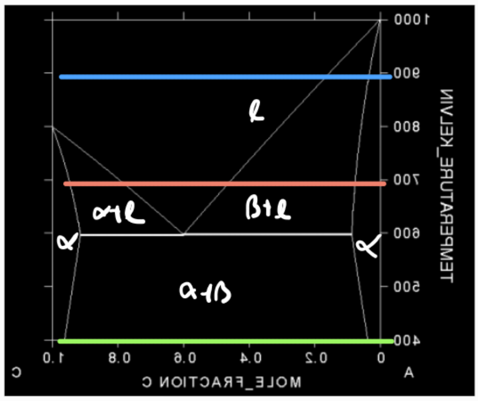
we get the following: 0.030987, 0.079251, 0.147679, 0.23764, 0.348279, 0.476041, 0.614558,
0.755028, 0.887076

These values have less than ≈ 0.001 error, so the model is sufficiently accurate.

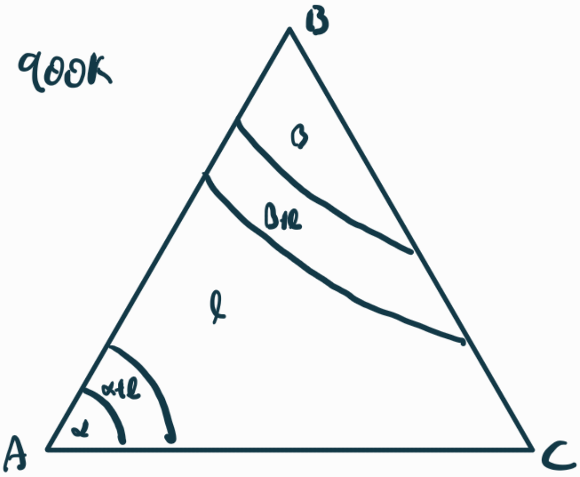
6







900K



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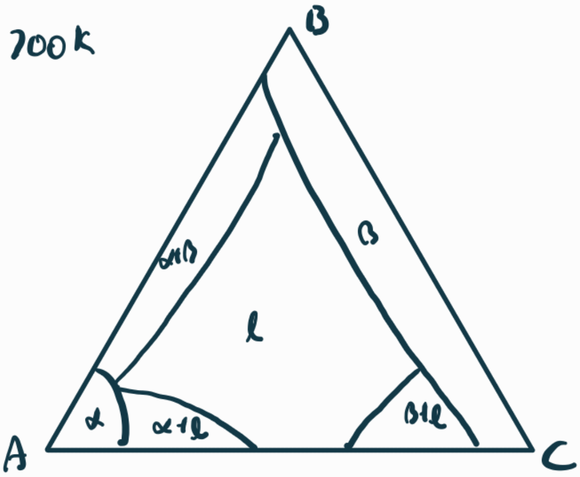

400K