HW # 7 20222980 정대훈

1. (a) $G_m = X_A G_A^\circ + X_B G_B^\circ + RT(X_A \ln X_A + X_B \ln X_B) + \Omega X_A X_B$

$f(X_B)$: free energy density , V_m : molar volume of solutions

$f(X_B) = \dfrac{G_m}{V_m} = \dfrac{G_m}{V_A X_A + V_B X_B}$ (assumption : $V_m = V_A X_A + V_B X_B$)

$V_A = \dfrac{M_A}{\rho_A} = 9.07\ cm^3/mol$ $V_B = \dfrac{M_B}{\rho_B} = 10\ cm^3/mol$.

$$\frac{\partial^2 G_m}{\partial X_B^2} = RT\left(\frac{1}{X_A} + \frac{1}{X_B}\right) - 2\Omega$$

when $X_A = X_B = 0.5$, the system has the maximum unstability.

$\rightarrow V_m = \dfrac{9.07+10}{2} = 9.54 \times 10^{-6}\ m^3/mol$

at the critical temperature,

$f''(X_B) + \dfrac{2E\eta^2}{1-\nu} = 0$. where $X_B = 0.5$.

$$\rightarrow \frac{1}{9.54\times10^{-6}} \times \left[8.31 \times T_c\left(\frac{1}{0.5} + \frac{1}{0.5}\right) - 2\times 15\times10^3\right] + \frac{2\times10^{11}\times(0.06)^2}{1-0.3} = 0$$

(ii) $\therefore\ T_c = 606.8\ K$. ($\eta = 0.06$)

(i) $\eta = 0$ $8.31 \times T_c\left(\dfrac{1}{0.5} + \dfrac{1}{0.5}\right) - 2\times15\times10^3 = 0$.

$T_c = 902.5\ K$.

(b) ① $X_B = 0.75$.

At the temperature below which the system gets unstable,

$f''(X_B) + \frac{2E\eta^2}{1-\nu} = 0$, assuming V_m is constant during fluctuations,

$f''(X_B) = \frac{1}{V_m}\left[RT\left(\frac{1}{X_A}+\frac{1}{X_B}\right) - 2\Omega\right]$ $(V_m = V_A X_A + V_B X_B)$

(i) $\eta = 0$, $RT\left(\frac{1}{X_A}+\frac{1}{X_B}\right) - 2\Omega = 0$

$\rightarrow 8.31 \times T\left(\frac{1}{0.25}+\frac{1}{0.75}\right) - 2\times 15\times 10^3 = 0$.

$\therefore \underline{T = 676.9\,K}$

(ii) $\eta = 0.06$

$V_m = 9.07\times 0.25 + 10\times 0.75 = 9.77\ (cm^3/mol)$

$f''(X_B) + \frac{2E\eta^2}{1-\nu} = \frac{1}{9.77\times 10^{-6}}\left[8.31\times T\left(\frac{1}{0.25}+\frac{1}{0.75}\right) - 2\times 15\times 10^3\right] + 1.03\times 10^9 = 0$

$\therefore \underline{T = 450\,K}$.

② $X_B = 0.60$

(i) $\eta = 0$, $8.31\times T\left(\frac{1}{0.4}+\frac{1}{0.6}\right) - 2\times 15\times 10^3 = 0$

$\therefore \underline{T = 866.4\,K}$

(ii) $\eta = 0.06$, $V_m = 9.07\times 0.4 + 10\times 0.6 = 9.63\ (cm^3/mol)$

$f''(X_B) + \frac{2E\eta^2}{1-\nu} = \frac{1}{9.63\times 10^{-6}}\left[8.31\times T\left(\frac{1}{0.4}+\frac{1}{0.6}\right) - 2\times 15\times 10^3\right] + 1.03\times 10^9 = 0$

$\underline{T = 580\,K}$

(C)

$$\beta_c^2 = -\frac{1}{2k}\left[f''(X_B) + \frac{2E\eta^2}{1-\nu} \right]$$

① $X_B = 0.75$

Spinodal decomposition occurs below 676.9K, so there would be no spinodal fluctuation.

② $X_B = 0.60$

(i) $\eta = 0$, $\beta_c^2 = -\frac{1}{2k} \times f''(X_B)$

$$= -\frac{1}{2\times10^{-9}} \times \frac{1}{9.63\times10^{-6}} \times \left[8.31\times775\times\left(\frac{1}{0.4}+\frac{1}{0.6}\right) - 2\times15\times10^3 \right]$$

$$= 16.44\times10^{16} \ (m^{-2})$$

$\beta_c = 4.05\times10^8 \ m^{-1}$

$\lambda_c = \frac{2\pi}{\beta_c} = \underline{15.51\times10^{-9} \ m}$ //

(d) when $X_B = 0.5$, the system has the maximum unstability ($f''(X_B)$)

the amplitude R is proportional to the unstability.

(i) $\eta = 0$.

$$\beta_c^2 = -\frac{1}{2k}\times f''(X_B) = -\frac{1}{2\times10^{-9}} \times \frac{1}{9.54\times10^{-6}}\left[8.31\times775\times\left(\frac{1}{0.5}+\frac{1}{0.5}\right) - 2\times15\times10^3 \right]$$

$$= 22.22\times10^{16} \ (m^{-2})$$

$\lambda_c = \frac{2\pi}{\beta_c} = 13.34\times10^{-9} \ m$

$\lambda_m = \sqrt{2}\lambda_c = \underline{18.87 \ nm}$ is the fastest growing wavelength.

(ii) $\eta = 0.06$, $T_c = 606.8k$, any system is not in the unstable region.

(e) mobility $M = X_B X_A (X_A D_B^* + X_B D_A^*)$

$$D_A^* = D_B^* = 10^{-3} \exp\left(\frac{-100\times10^3}{8.31\times 775}\right) = 1.8\times10^{-10} (m^2/sec)$$

(i) $\eta = 0$

$$R(\beta) = -M f''(X_n)\beta^2 - 2KM\beta^4$$

when $X_n = 0.5$, $f''(X_n)$ is minimum and β is maximum.

from part (d), $\beta_m = \frac{2\pi}{\lambda_m} = 3.33\times10^8 \ (m^{-1})$

$$f''(X_n) = -4.44\times10^8 \ (J/m^3)$$

$$\rightarrow R(\beta) = 1.8\times10^{-10}\times4.44\times10^8\times3.33^2\times10^{16} - 2\times10^{-9}\times1.8\times10^{-10}\times3.33^4\times10^{32}$$

$$= 4.435\times10^{15} \ (J/m^3).$$

(ii) $\eta = 0.06$, No spinodal decomposition.

2. (a) $D_A = 10^{-4} \exp\left(\frac{-85000}{8.31 \times 298}\right) = 1.24 \times 10^{-19}\ m^2/s$

$C_{10} = C_0 \exp\left(\frac{-\pi^2 \times 1.24 \times 10^{-19} \times 10}{0.01^2 \times 10^{-12}}\right) = 0.885\, C_0$

$C_{100} = C_0 \exp\left(\frac{-\pi^2 \times 1.24 \times 10^{-19} \times 100}{0.01^2 \times 10^{-12}}\right) = 0.294\, C_0$

$\therefore \frac{C_{100}}{C_{10}} = 0.33$

(b) $C_{100}^{0.1\mu m} = C_0 \exp\left(\frac{-\pi^2 \times 1.24 \times 10^{-19} \times 100}{0.1^2 \times 10^{-12}}\right) = 0.988\, C_0$

$C_{100}^{0.01\mu m} = 0.294\, C_0$

$\therefore \frac{C_{100}^{0.01\mu m}}{C_{100}^{0.1\mu m}} = 0.30$

(c) $D_A' = 10^{-4} \exp\left(\frac{-85000}{8.31 \times 398}\right) = 6.90 \times 10^{-16}\ m^2/s$

$C_{100}^{398K} = C_0 \exp\left(\frac{-\pi^2 \times 6.9 \times 10^{-16} \times 100}{0.01^2 \times 10^{-12}}\right) \simeq 0$

$\therefore \frac{C_{100}^{398K}}{C_{100}^{298K}} = 0.$

(d) Temperature has the most sensitive effect on the transformation kinetics.