상변태론 HW#7 20222399 김창윤

1.(a) spinodal decomposition 의 한계 온도 및 조성

$$-\frac{d^2G}{dx^2} > \frac{2K}{\lambda^2} + 2\eta^2 E' \cdot V_m \xrightarrow{\lambda \to \infty} \frac{d^2G}{dx^2} = -2\eta^2 \cdot E' \cdot V_m \quad (E' = E/(1-\nu))$$

$$G = X_A \cdot G_A^\circ + X_B \cdot G_B^\circ + RT(X_A \ln X_A + X_B \ln X_B) + \Omega X_A \cdot X_B \quad ; \text{ Regular solution}$$

$$G = X_A \cdot G_A^\circ + (1-X_A) \cdot G_B^\circ + RT(X_A \ln X_A + (1-X_A)\ln(1-X_A)) + \Omega X_A(1-X_A)$$

$$\frac{dG}{dX_A} = G_A^\circ - G_B^\circ + RT(\ln X_A + 1 - \ln(1-X_A) - 1) + \Omega(1-X_A) - \Omega X_A$$

$$\frac{d^2G}{dX_A^2} = RT\left(\frac{1}{X_A} + \frac{1}{(1-X_A)}\right) - 2\Omega$$

$$\Rightarrow RT\left(\frac{1}{X_A(1-X_A)}\right) - 2\Omega = -2\eta^2 \cdot E \cdot V_m/(1-\nu)$$

Regular solution 에서 $X_A = X_B = 0.5$ 일때 최댓값을 가짐

$$\left(\begin{array}{ll} V_m = V_A \cdot X_A + V_B \cdot X_B & V_A = \frac{M_A}{\rho_A} = 9.069\ cm^3/mol,\ V_B = 10\ cm^3/mol \\ V_m = 9.535\ cm^3/mol & \end{array} \right) ; V_m \text{ 계산}$$

$(Pa \cdot m^3 = J)$

$$\Rightarrow \boxed{T = \left(\frac{-2\eta^2 \cdot E \cdot V_m}{(1-\nu)} + 2\Omega\right) \times \frac{1}{4R}} = \left(\left(\frac{-2}{0.7}\right) \cdot \eta^2 \cdot 10^{11} \cdot Pa \cdot \underbrace{9.535\ cm^3/mol}_{9.535 \times 10^{-6}\ m^3} + 30kJ/mol\right) \times \frac{1}{4R}$$

$$= (-27.243 \cdot \eta^2 \cdot 10^5 + 30000) \cdot \frac{1}{8.314 \times 4}$$

$\therefore$ (I) $\eta = 0 \rightarrow T = 902.09\ K$

(II) $\eta = 0.06 \rightarrow T = 607.18\ K$

(b)

$$T = \frac{X_A \cdot (1-X_A)}{R}\left(V_m \cdot \left(\frac{-2}{0.7}\right) \cdot \eta^2 \cdot 10^5 + 30000\right) / \ V_A = 9.069\ cm^3/mol,\ V_B = 10\ cm^3/mol$$

위 식 전개를 X_A로 해서 T에대해 변경 하였습니다.

(I) $X_A = 0.25$ $\rightarrow V_m = 0.25 \cdot V_A + 0.75 \cdot V_B = 9.76\ cm^3/mol$

$\rightarrow \eta = 0,\ T = \frac{30000}{8.314} \cdot 0.25 \cdot 0.75 = 676.57\ K$

$\rightarrow \eta = 0.06,\ T = 450.17\ K$

(II) $X_A = 0.40$ $\rightarrow V_m = 0.4 V_A + 0.6 V_B = 9.63\ cm^3/mol$

$\rightarrow \eta = 0,\ T = 866.01\ K$

$\rightarrow \eta = 0.06,\ T = 580.08\ K$

(c) critical wavelength at 775K (i) $x_A=0.25$, ii) $x_A=0.4$)

i) $x_A=0.25$ 일때

앞서 구한 최대 온도가 676.57 K므로 775K에서는 spinodal decomposition 발생 X

따라서, wavelength λ는 구하지 않음

ii) $x_A=0.4$

① $\eta=0$

$$\beta^2 = -\frac{1}{2K}\cdot\left(\frac{d^2G}{dx^2}\cdot\frac{1}{V_m} + 2\eta^2\cdot E/(1-\nu)\right)$$

$$\hookrightarrow \left(\underset{J/mol\cdot K}{8.314} \times \frac{1}{0.4}\times\frac{1}{0.6}\times 775K - 30000\,J/mol\right) = -3152.708 \cdot \frac{1}{V_m} = -327.38$$

$$\therefore \beta^2 = -\frac{1}{2}\times 10^9 \times 327.38\times 10^6 = 1.637\times 10^{17}$$

$$\therefore \beta_c = 4.037\times 10^{8} m \rightarrow \lambda_c = \frac{2\pi}{\beta_c} = 1.56\times 10^{-8} m = 15.6\ nm$$

② $\eta=0.06 \rightarrow T=580.08K$로 775K 보다 낮은 온도에서 critical

따라서, spinodal X

(d) $$R/R_{max} = 4\left(\frac{\beta}{\beta_c}\right)^2\left[1-\left(\frac{\beta}{\beta_c}\right)^2\right] \rightarrow \frac{\beta_c}{\beta}가\ \sqrt{2}\ 일때\ \frac{R}{R_{max}}\ 최대.$$

$$\rightarrow \beta_c = \sqrt{2}\beta \Longleftrightarrow \lambda_m = \sqrt{2}\lambda_c \quad \left(\because \beta = \frac{2\pi}{\lambda}\right)$$

Regular solution 이므로 $x_A=x_B=0.5$ 일때 가장 불안정하여 fast growing이 일어난다.

↳ 해당 조건에 수반되는 parameter들은 (a)에서 계산했음

i) $\eta=0$, $\beta_c^2 = 2.216\times 10^{17}$, $\beta_c = 4.707\times 10^{8} \rightarrow \lambda_c = 1.334\times 10^{-8} m$

$= 13.34\ nm$

$\Rightarrow \lambda_m = \sqrt{2}\lambda_c = 18.86\ nm$

ii) $\eta=0.06$ 일때 $\beta_c^2<0$ 이어서 성립하지 않음

(e) $$R(\beta) = -M\cdot\beta^2\cdot\left[\frac{d^2G}{dx^2}\cdot\frac{1}{V_m} + \frac{2E\cdot\eta^2}{1-\nu} + 2K\cdot\beta^2\right]$$

$\beta_m = \beta_c/\sqrt{2}$, $M = x_A\cdot x_B\cdot\{x_A\cdot D_B^* + x_B\cdot D_A^*\}$

$= (0.5)^2\cdot\{10^{-3}\times\exp(-100\,kJ/RT)\}$

i) $\eta=0$ $$\rightarrow R(\beta) = -\frac{1}{2}\times(4.707\times 10^{8})^2\cdot\frac{1}{4}\cdot\frac{1}{1000}\times\exp\left(\frac{-10^5}{8.314\times 775}\right)\times\left(8.314\times 775\times 4 - 30000\right)\cdot\times\frac{1}{9.535\times 10^{6}}$$

$= 4.74\times 10^{15}$

ii) $\eta=0.06$ spinodal 발생 X (d) 동일.

2

$$C_A(x,t) = C_A(x,0)\exp(-\pi^2 Dt/\lambda^2)$$

(a)

$$\frac{C_A(x,100)}{C_A(x,10)} = \frac{\exp(-\pi^2\cdot D\cdot 100/\lambda^2)}{\exp(-\pi^2\cdot D\cdot 10/\lambda^2)} = \exp\left(-\pi^2\cdot D\cdot \frac{1}{\lambda^2}\cdot 90\right)$$

$$D = 10^{-4}\cdot\exp(-85000/8.314\cdot 300) = 1.584\times10^{-19}\ m^2/s \quad /(\lambda = 1\times10^{-8}\ m)$$

$$\therefore \frac{C_A(x,100)}{C_A(x,10)} = \exp(-1.407) = 0.24$$

(b) $t=100$ 유지하고 $\lambda_1 = 0.1\ \mu m$ to $\lambda_2 = 0.01\ \mu m$

$= 10^{-7} m \qquad = 10^{-8} m$

$$\frac{C_A(x,100,\lambda_2)}{C_A(x,100,\lambda_1)} = \exp\Big(-100\cdot D\cdot\pi^2\cdot\underbrace{\big((\tfrac{1}{\lambda_2})^2-(\tfrac{1}{\lambda_1})^2\big)}_{10^{16}-10^{14}=0.99\times10^{16}}\Big) = \exp(-1.547) = 0.21$$

(C) $T_1 = 300K,\ T_2 = 400K$

$$\frac{C_A(x,100,T_2)}{C_A(x,100,T_1)} = \exp(-100\pi\cdot10^{16}\cdot(D_2-D_1)) \simeq 0$$

$$D_1 = 1.584\times10^{-19}\ m^2/s$$
$$D_2 = 7.938\times10^{-12}\ m^2/s$$

(d) t 와 λ가 각각 10배 차이일때, 비율이 0.24, 0.21로 거의 비슷함

그러나 T가 100K 증가했을때 비율이 거의 0으로

온도에 가장 영향을 받는다고 볼수 있다