1.

(a)

System A, B가 regular solution behavior를 보이므로, G_m을 다음과 같이 정의할 수 있다.

$$G_m = X_A G_A^\circ + X_B G_B^\circ + RT\left(X_A \ln X_A + X_B \ln X_B\right) + X_A X_B \Omega$$

V_m : molar volume of solutions ($V_m = V_A X_A + V_B X_B$), free energy density $f = \frac{G_m}{V_m}$ 라 정의하자.

Solid miscibility의 critical temperature 에서는 다음식이 성립한다.

$$f''(X_B) + \frac{2E\eta^2}{1-\nu} = 0$$

이때,

$$f''(X_B) = \frac{1}{V_m} G_m'' \quad \text{에서} \quad G_m' = \frac{d}{dX_B}\left[X_A G_A^\circ + X_B G_B^\circ + RT\left(X_A \ln X_A + X_B \ln X_B\right) + X_A X_B \Omega\right]$$

$$= \frac{d}{dX_B}\left[(1-X_B)G_A^\circ + X_B G_B^\circ + RT\{(1-X_B)\ln(1-X_B) + X_B \ln X_B\} + (1-X_B)X_B\Omega\right]$$

$$= -G_A + G_B + RT\left[-\ln(1-X_B) + \cancel{(1-X_B)\frac{-1}{(1-X_B)}} + \ln X_B \cancel{+1}\right\} + (1-2X_B)\Omega,$$

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

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

$$\therefore f''(X_B) + \frac{2E\eta^2}{1-\nu} = \frac{1}{V_m}\left[RT\left(\frac{1}{X_A} + \frac{1}{X_B}\right) - 2\Omega\right] + \frac{2E\eta^2}{1-\nu} = 0$$

$\therefore$ critical temperature T_c 는

$$T_c = \frac{\frac{2E\eta^2}{\nu-1}\cdot V_m + 2\Omega}{R\left(\frac{1}{X_A} + \frac{1}{X_B}\right)} \quad \cdots\cdots ①$$

주어진 조건에서

$E = 10^{11}\,Pa = 10^{11}\,J/m^3$, $\nu = 0.3$, $\Omega = 15\times10^3\,J/mol$,

$$V_m = V_A X_A + V_B X_B = \frac{M_A}{\rho_A}X_A + \frac{M_B}{\rho_B}X_B = \frac{195\,g/mol}{21.5\,g/cm^3}X_A + \frac{197\,g/mol}{19.7\,g/cm^3}X_B = 9.07X_A + 10X_B \quad cm^3/mol$$

이를 ①에 대입하여 정리하면

① $\eta = 0$ 일때 : $T_c = \dfrac{2\Omega}{R\left(\frac{1}{X_A}+\frac{1}{X_B}\right)} = \dfrac{30\times10^3}{R\left(\frac{1}{X_A}+\frac{1}{X_B}\right)}$

② $\eta = 0.06$ 일때 : $T_c = \dfrac{\frac{2\times10^{11}}{0.3-1}(0.06)^2\cdot(9.07X_A+10X_B)\times10^{-6} + 30\times10^3}{R\left(\frac{1}{X_A}+\frac{1}{X_B}\right)} = \dfrac{30\times10^3 - 1028.57(9.07X_A+10X_B)}{R\left(\frac{1}{X_A}+\frac{1}{X_B}\right)}$

$$\boxed{\begin{aligned} \therefore\ \eta = 0 &\rightarrow T_c = \frac{3\times10^4}{R\left(\frac{1}{X_A}+\frac{1}{X_B}\right)} \\ \eta = 0.06 &\rightarrow T_c = \frac{30\times10^3 - 1028.57(9.07X_A+10X_B)}{R\left(\frac{1}{X_A}+\frac{1}{X_B}\right)} \end{aligned}}$$

(b)

① $x_B = 0.75$ 일 때, $x_A = 0.25$

i) $\eta = 0$ 일 때 : $T_c = \dfrac{30\times10^3}{8.314\times\left(\frac{1}{0.75}+\frac{1}{0.25}\right)} = 676.57K$

ii) $\eta = 0.06$ 일 때 . $T_c = \dfrac{30\times10^3 - 1028.57\,(9.07\times0.25+10\times0.75)}{8.314\times\left(\frac{1}{0.75}+\frac{1}{0.25}\right)} = 449.996K$

② $x_B = 0.60$ 일 때 , $x_A = 0.4$

i) $\eta = 0$ 일 때 : $T_c = \dfrac{30\times10^3}{8.314\times\left(\frac{1}{0.6}+\frac{1}{0.4}\right)} = 866.01\ k$

ii) $\eta = 0.06$ 일 때 . $T_c = \dfrac{30\times10^3 - 1028.57\,(9.07\times0.4+10\times0.6)}{8.314\times\left(\frac{1}{0.6}+\frac{1}{0.4}\right)} = 580.14K$

$\therefore$ $x_B = 0.75$ $\begin{cases} \eta = 0 \rightarrow T_c = 676.57K \\ \eta = 0.06 \rightarrow T_c = 449.996\ k \end{cases}$

$x_B = 0.6$ $\begin{cases} \eta = 0 \rightarrow T_c = 866.01K \\ \eta = 0.06 \rightarrow T_c = 580.14K \end{cases}$

(c)

Critical wavelength β_c는 다음과 같이 정의된다.

$$\beta_c^2 = -\frac{1}{2k}\left[f''(C_0) + \frac{2E\eta^2}{1-\nu}\right]$$

$$= -\frac{1}{2k}\left[\left(RT\left(\frac{1}{X_A}+\frac{1}{X_B}\right) - 2\Omega\right)\frac{1}{(9.07x_A+10x_B)\times10^{-6}} + \frac{2\times10^{11}\eta^2}{1-0.3}\right]$$

$T = 775K$ 일 때, ($K = 10^{-9}J/m$)

① $x_B = 0.75$ 일 때, $x_A = 0.25$,

i) $\eta = 0 \rightarrow \beta_c^2 = -\dfrac{1}{2\times10^{-9}}\left[\left(8.314\times775\times\left(\frac{1}{0.75}+\frac{1}{0.25}\right) - 2\times15\times10^3\right)\times\dfrac{10^6}{9.07\times0.25+10\times0.75}\right] = -2.23\times10^{17} < 0$

ii) $\eta = 0.06 \rightarrow \beta_c^2 = -\dfrac{1}{2\times10^{-9}}\left[\left(8.314\times775\times\left(\frac{1}{0.75}+\frac{1}{0.25}\right) - 2\times15\times10^3\right)\times\dfrac{10^6}{9.07\times0.25+10\times0.75} + \dfrac{2\times10^{11}\times0.06^2}{0.7}\right]$

$= -7.38\times10^{17} < 0$

$\therefore$ $x_B = 0.75$ 일 때는 spinodal decomposition이 발생하지 않는다

② $x_B = 0.6$ 일 때, $x_A = 0.4$,

i) $\eta = 0 \rightarrow \beta_c^2 = -\dfrac{1}{2\times10^{-9}}\left[\left(8.314\times775\times\left(\frac{1}{0.6}+\frac{1}{0.4}\right) - 2\times15\times10^3\right)\times\dfrac{10^6}{9.07\times0.4+10\times0.6}\right] = 1.64\times10^{17}\ m$

$\therefore$ $\beta_c = 4.05\times10^8$, $\lambda_c = \dfrac{2\pi}{\beta_c} = 1.55\times10^{-8}\ m$

ii) $\eta = 0.06 \rightarrow \beta_c^2 = -\dfrac{1}{2\times10^{-9}}\left[\left(8.314\times775\times\left(\dfrac{1}{0.6}+\dfrac{1}{0.4}\right)-2\times15\times10^3\right)\times\dfrac{10^6}{9.07\times0.4+10\times0.6}+\dfrac{2\times10^{11}\times0.06^2}{0.7}\right]$

$= -3.51\times10^{17} < 0$

→ Spinodal decomposition이 발생하지 않는다.

∴ $x_B = 0.75 \rightarrow \eta=0,\ \eta=0.06$ 모두 spinodal decomposition이 발생하지 않는다.

$x_B = 0.6 \rightarrow \eta = 0 : \lambda_c = 1.55\times10^{-8}m$

$\rightarrow \eta = 0.06$: spinodal decomposition이 발생하지 않는다.

(d)

$$\beta_c^2 = -\frac{1}{2K}\left[\left(RT\left(\frac{1}{X_A}+\frac{1}{X_B}\right)-2\Omega\right)\frac{1}{(9.07X_A+10X_B)\times10^{-6}}+\frac{2\times10^{11}\eta^2}{1-0.3}\right]$$

에서 $T=775K$로 고정되어 있으므로, β_c^2은 X_B에 대한 함수이다.

spinodal decomposition의 maximum unstability는 $X_B=0.5$일 때 나타나므로, 이 때의 growing wavelength는

① $\eta = 0$ 일 때 $\rightarrow \beta_c^2 = -\dfrac{1}{2\times10^{-9}}\left[\left(8.314\times775\times\left(\dfrac{1}{0.5}+\dfrac{1}{0.5}\right)-2\times15\times10^3\right)\times\dfrac{10^6}{9.07\times0.5+10\times0.5}\right]$

$= 2.226\times10^{17}\,(m^{-2})$

$\therefore \lambda_c = 1.334\times10^{-8}m \rightarrow$ fastest growing wavelength $\lambda_m = \sqrt{2}\lambda_c = 1.887\times10^{-8}m$

② $\eta = 0.06$일 때 $\rightarrow \beta_c^2 = -\dfrac{1}{2\times10^{-9}}\left[\left(8.314\times775\times\left(\dfrac{1}{0.5}+\dfrac{1}{0.5}\right)-2\times15\times10^3\right)\times\dfrac{10^6}{9.07\times0.5+10\times0.5}+\dfrac{2\times10^{11}\times0.06^2}{0.7}\right]$

$= -2.926\times10^{17} < 0 \rightarrow$ no spinodal decomposition

∴ fastest growing wavelength $\lambda_m = 1.887\times10^{-8}m$

(e)

$$R(\beta) = -M\beta^2\left[f'' + \frac{2E\eta^2}{1-\nu} + 2K\beta^2\right]$$

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

문제의 주어진 조건에서 mobility M을 계산하면

$M = X_A X_B \{X_A D_B^* + X_B D_A^*)$

$= X_A X_B \{X_A + X_B\} \times 10^{-3}\exp(-100000/RT)$

$X_B = 0.5$일 때, β가 maximum 이고, $R(\beta)$도 maximum 이므로,

① $\eta = 0$ 일 때,

(d) 에서 $\lambda_m = 1.887\times10^{-8}m$ 이므로, $\beta_m = \dfrac{2\pi}{\lambda_c} = 3.330\times10^8\,(m^{-1})$,

$R_{max} = R(\beta_m) = -0.5^2\times10^{-3}\times\exp\left(-\dfrac{100000}{8.314\times775}\right)\times(3.33\times10^8)^2\times\left[\dfrac{1}{9.07\times0.5+10\times0.5}\times\left(8.314\times775\times\left(\dfrac{1}{0.5}+\dfrac{1}{0.5}\right)-30\times10^3\right)\right.$

$\left. + 2\times10^{-9}\times(3.33\times10^8)^2\right]$

$= 1.12\times10^{15}$

② $\eta = 0.06$: 775K에서 spinodal decomposition이 일어나지 않으므로, 고려X

$$\boxed{\therefore R_{max} = 1.12 \times 10^{15}}$$

2.

at room temperature (298K) 에서의 $C_A(x,t)$를 나타내면

$$D_A = 10^{-4}\exp\left(-85000J/_{8.314\times 298K}\right) = 1.2599\times10^{-19}\ m^2/s$$ 에서

(a)

$$C_A(x,t) = C_A(x,0)\exp\left[-\frac{\pi^2 t\cdot 1.2599\times10^{-19}}{\lambda^2}\right] = C_t$$

$\lambda = 0.01\mu m = 10^{-8}m$

① $t = 10s$ 일 때,

$$C_{10} = C_A(x,10) = C_A(x,0)\exp\left[-\frac{\pi^2\times10s\times1.2599\times10^{-19}m^2/s}{(10^{-8}m)^2}\right] = 0.8831\,C_A(x,0)$$

② $t = 100s$ 일 때,

$$C_{100} = C_A(x,100) = C_A(x,0)\exp\left[-\frac{\pi^2\times100\times1.2599\times10^{-19}m^2/s}{(10^{-8}m)^2}\right] = 0.2884\,C_A(x,0)$$

①, ② 에서 $\frac{C_{100}}{C_{10}} = \frac{C_A(x,100)}{C_A(x,10)} = \frac{0.2884}{0.8831} = 0.3266$

∴ 시간 t가 증가하면, maximum concentration은 감소한다.

(b) $t = 100s$, $\lambda_1 = 0.1\mu m$, $\lambda_2 = 0.01\mu m$

① $\lambda_1 = 0.1\mu m = 10^{-7}m$ 일 때

$$C_1 = C_A'(x,100) = C_A(x,0)\exp\left[-\frac{\pi^2\times100\times1.2599\times10^{-19}}{(10^{-7})^2}\right] = 0.9876\,C_A(x,0)$$

② $\lambda_2 = 0.01\mu m = 10^{-8}m$ 일 때 → (a)에서 $C_2 = 0.2884\,C_A(x,0)$

⇒ ①, ② 에서 $\frac{C_1}{C_2} = \frac{0.9876}{0.2884} = 3.42$

∴ fluctuation wavelength λ가 증가하면, maximum concentration은 증가한다.

(c) $\lambda = 0.01\mu m$, $t = 100s$,
$T = 398K$ 일 때,

$$D_A = 10^{-4}\exp\left(-85000J/_{8.314\times398}\right) = 6.982\times10^{-16}m^2/s$$

이 때, $C_A(x,100)$을 계산하면

$$C_{398K} = C_A(x,0)\exp\left[-\frac{\pi^2\times100\times6.982\times10^{-16}}{(10^{-8})^2}\right) \simeq 0$$

∴ 온도 T가 증가하면, maximum concentration은 0에 가까워지며 0에 수렴한다.

(d)

(a) ~ (c) 에서의 결과를 비교했을 때, 온도 T의 변화가 가장 sensitive 하다.