AMSE502 Phase Transformations 상변태론 HW #7

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1 (a) Criterion of unstability

$$f'' + \frac{2E\eta^2}{1-\nu} + 2K\beta^2 \le 0$$

$$\beta = \frac{2\pi}{\lambda}$$

at critical temp, $\lambda = \infty$

$$f'' + \frac{2E\eta^2}{1-\nu} = 0 \quad \cdots ①$$

$$f = \frac{G_m}{V_m}$$

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

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

$$\frac{\partial G_m}{\partial X_A} = {}^\circ G_A - {}^\circ G_B + RT\{\ln X_A + 1 - \frac{1}{1-X_A} - \ln(1-X_A) + \frac{X_A}{1-X_A}\} + \Omega - 2\Omega X_A$$

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

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

$$\therefore f'' = \frac{1}{V_m}\left\{\left(\frac{1}{X_A} + \frac{1}{1-X_A}\right)RT - 2\Omega\right\} \quad \cdots ②$$

②를 ①에 대입 후 정리

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

$$T^* = \left(\frac{1}{X_A} + \frac{1}{1-X_A}\right)^{-1} \cdot \frac{1}{R}\left\{-\frac{2E\eta^2 V_m}{1-\nu} + 2\Omega\right\} \quad \text{at critical temp.}$$

$X_A = 0.5$ 일 때 T^*가 최대가 됨.

$V_m = X_A V_A + X_B V_B$ 가정.

$$V_A = \frac{M_A}{\rho_A} = \frac{195\,g/mol}{21.5\,g/cm^3} = 9.07\,cm^3/mol$$

$$V_B = \frac{M_B}{\rho_B} = \frac{197\,g/mol}{19.7\,g/cm^3} = 10\,cm^3/mol$$

$$V_m = 0.5 \times 9.07 + 0.5 \times 10 = 9.535$$

i) $\eta = 0$ $\quad T^* = \frac{1}{4 \times 8.314}\left\{-\frac{2(10^{11})(0)^2(9.535\times10^{-6})}{1-0.3} + 2(15\times10^3)\right\} = 902.1K$

ii) $\eta = 0.06$ $\quad T^* = 607.2K$

(b) (i) $X_B = 0.75$, $\eta = 0$

$$V_m = 0.25 \times 9.07 + 0.75 \times 10$$

$$= 9.77\,cm^3/mol$$

$$= 9.77 \times 10^{-6}\,m^3/mol$$

$$T^* = \left(\frac{1}{0.25} + \frac{1}{0.75}\right)^{-1} \cdot \frac{1}{8.314}\left\{\frac{2(10^{11})(0)^2(9.77\times10^{-6})}{1-0.3} + 2(15\times10^3)\right\}$$

$$= 676.6K$$

같은 방식으로,

(ii) $X_B = 0.75$, $\eta = 0.06$

$T^* = 449.9K$

(iii) $X_B = 0.60$, $\eta = 0$

$T^* = 866.0K$

(iv) $X_B = 0.60$, $\eta = 0.06$

$T^* = 575.9K$

(c) $\lambda \geq \left[- \dfrac{8\pi^2 K}{f'' + \frac{2E\eta^2}{1-\nu}} \right]^{\frac{1}{2}}$

B 에서,
(i) $X_B = 0.75$, $\eta = 0$, $T \leq 676.6K$

(ii) $X_B = 0.75$, $\eta = 0.06$, $T \leq 449.9K$

(iii) $X_B = 0.60$, $\eta = 0$, $T \leq 866.0K$

(iv) $X_B = 0.60$, $\eta = 0.06$, $T \leq 575.9K$

$T = 775K$ 에서, (iii) 의 경우만 spinodal을 만족한다.

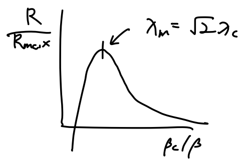
$\therefore$ (iii)의 $X_B = 0.60$, $\eta = 0$ 에서,

$$\lambda^* = \left[- \frac{8\pi^2 K}{\frac{1}{V_m}\left\{\left(\frac{1}{X_A} + \frac{1}{1-X_A}\right)RT - 2\Omega\right\} + \frac{2E\eta^2}{1-\nu}} \right]^{\frac{1}{2}}$$

$$= \left[- \frac{8\pi^2 (10^{-9})}{\frac{1}{9.77\times10^{-6}}\left\{\left(\frac{1}{0.40} + \frac{1}{0.60}\right)(8.314)(775) - 2(15\times10^3)\right\} + \frac{2(10^{11})(0)^2}{1-0.3}} \right]^{\frac{1}{2}}$$

$$= 1.56 \times 10^{-8}\ m$$

(d) $\dfrac{R}{R_{max}} = 4\left(\dfrac{\beta}{\beta_c}\right)^2 \left[1 - \left(\dfrac{\beta}{\beta_c}\right)^2\right]$



$\beta_c = \sqrt{2}\beta$ 일 때 $\dfrac{R}{R_{max}}$ 이 최대.

$\beta = \dfrac{2\pi}{\lambda}$

$\therefore$ $\lambda_m = \sqrt{2}\lambda_c$ 일 때 fastest growing

T^*가 가장 높은 $X_A = 0.5$ 에서 가장 먼저 growing 일어남.

(c) 에서 처럼 계산하면

(i) $\eta = 0$ $\quad \lambda_c = \lambda^* = 1.335 \times 10^{-8}\ m$

$\lambda_m = \sqrt{2}\lambda_c = 1.89 \times 10^{-8}\ m$

(ii) $\eta = 0.06$ spinodal X

$\because T > T^*$

(e) $R(\beta) = -M\left[f'' + \dfrac{2E\eta^2}{1-\nu}\right]\beta^2 - 2KM\beta^4$

$R_{max} = R(\beta = \beta_c) = \dfrac{1}{2}KM\beta_c^4$

$M = X_A X_B (X_A M_A + X_B M_B)$

$\dfrac{D_A}{kT} = M_A$, $\dfrac{D_B}{kT} = M_B$

$M = X_A X_B \left(\dfrac{D_A^*}{kT}X_A + \dfrac{D_B^*}{kT}X_B\right)$

앞 문제들에서와 마찬가지로 $X_A = 0.5$일 때 maximum.

$M = 0.5^2 \left\{ \dfrac{10^{-3}}{8.314} \exp\left(-\dfrac{100\times10^3}{(8.314)(775)}\right) \right\} = 4.249 \times 10^9\ m^2/J\cdot s$

(i) $\eta = 0$ $\quad R_{max} = \dfrac{1}{2}(10^{-9}\ J/m)(4.249\times10^9\ m^2/J\cdot s)\left(\dfrac{2\pi}{1.335\times10^{-8}\ m}\right)$

$= 1.00 \times 10^9\ s^{-1}$

(ii) $\eta = 0.06$ spinodal X

$\because T > T^*$

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

(a) $T = 300K$ $\quad \dfrac{C_A(x, 100s)}{C_A(x, 10s)} = ?$

$$D_A = 10^{-4}\exp\left\{-\frac{85000}{(8.314)(300)}\right\} = 1.584\times10^{-19}\ m^2/s$$

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

$$= \exp\left(\frac{-90\pi^2 D_A}{\lambda^2}\right)$$

$$= \exp\left\{-\frac{(90s)\pi^2(1.584\times10^{-19}\ m^2/s)}{(0.01\times10^{-6} m)^2}\right\}$$

$$\frac{C_A(x,100)}{C_A(x,10)} = 0.245$$

(b) $$\frac{C_{A,\lambda=0.01\mu m}(x,100)}{C_{A,\lambda=0.1\mu m}(x,100)} = \exp\left\{-\frac{\pi^2(1.584\times10^{-19} m^2/s)(100s)}{(0.01\times10^{-6} m)^2} + \frac{\pi^2(1.584\times10^{-19} m^2/s)(100s)}{(0.1\times10^{-6} m)^2}\right\}$$

$$= 0.213$$

(c) $$\frac{C_{A,T=400K}(x,100s)}{C_{A,T=300K}(x,100s)} = ?$$

$$D_A(T=400K) = 10^{-4}\exp\left\{-\frac{85000}{(8.314)(400)}\right\} = 7.938\times10^{-16} m^2/s$$

$$\therefore \frac{C_{A,T=400K}(x,100s)}{C_{A,T=300K}(x,100s)} = \exp\left\{-\frac{\pi^2(7.938\times10^{-16}\ m^2/s)(100s)}{(0.01\times10^{-6} m)^2} + \frac{\pi^2(1.584\times10^{-19} m^2/s)(100s)}{(0.01\times10^{-6} m)^2}\right\}$$

$$\simeq 0$$

(d) (a) ~ (c) 로부터, 온도 T 에 가장 sensitive 한 것을 알 수 있다.
(c) 로부터, T 가 클수록 A의 diffusivity 가 증가하고 A의 maximum concentration 이 감소하는 것을 알 수 있다.