phase Transformations Problem Set #7 20222102 이마태

1.

a) $$G = \int_V \left[f(x_B) + \frac{E\eta^2}{1-\nu}(x_B - x_{B_0})^2 + K(\nabla x_B)^2 \right] dV$$

Critical temperature 에서는 조성 변화가 없으므로

$$\Rightarrow G = \int_V \left[f(x_B) + \frac{E\eta^2}{1-\nu}(x_B - x_{B_0})^2 \right] dV$$

$$\frac{\partial^2 G}{\partial x_B^2} = f''(x_B) + \frac{2E\eta^2}{1-\nu}$$

Critical point는 entropy가 최대가 되는 $x_A = x_B = 0.5$ 에서 형성.

$\therefore$ $x_B = 0.5$ 라 했을 때 $\frac{\partial^2 G}{\partial x_B^2} = 0$ 에서 critical point

f''를 구해보자

$$f = \frac{G_m}{V_m}, \quad G_m = x_A G_A^\circ + x_B G_B^\circ + RT(x_A \ln x_A + x_B \ln x_B) + \Omega x_A x_B$$

$\frac{\partial V_m}{\partial x_B} = 0$ 이라 하면 (작기 때문에)

$$f'' = \frac{\frac{\partial^2 G_m}{\partial x_B^2}}{V_m} = \frac{1}{V_m}\left[RT\left(\frac{1}{1-x_B} + \frac{1}{x_B} \right) - 2\Omega \right]$$

$\frac{\partial^2 G}{\partial x_B^2} = 0$ 에 대입

$$\Rightarrow \frac{1}{V_m}\left[RT\left(\frac{1}{1-x_B} + \frac{1}{x_B} \right) - 2\Omega \right] + \frac{2E\eta^2}{1-\nu} = 0$$

$$\Rightarrow T = \left(-\frac{2E\eta^2}{1-\nu} \times V_m + 2\Omega \right) \Big/ R\left(\frac{1}{1-x_B} + \frac{1}{x_B} \right)$$

i) $\eta = 0$ $\Rightarrow$ $T = \dfrac{2 \times 15 \times 10^3}{8.3145 \times 4} = 902 \text{ K}$

ii) $\eta = 0.06$

$$V_m = 0.5(V_A + V_B) = 0.5 \times 10^{-6}\left(\frac{M_A}{\rho_A} + \frac{M_B}{\rho_B} \right)$$

$$\therefore T = \frac{\left(- \frac{2 \times 10^{11} \times 0.06^2}{1 - 0.3} \times 0.5 \times 10^{-6} \left(\frac{195}{21.5} + \frac{197}{197} \right) + 2 \times 15 \times 10^3 \right)}{8.3145 \times 4}$$

$$= 607 \text{ K}$$

b)

i) $x_B = 0.75$, $\eta = 0$

$$T = \frac{2 \times 15 \times 10^3}{8.3145 \times 5.33} = 678 \text{ K}$$

ii) $x_B = 0.75$, $\eta = 0.06$

$$T = \frac{\left(- \frac{2 \times 10^{11} \times 0.06^2}{1 - 0.3} \times 10^{-6} \left(\frac{195}{21.5} \times 0.25 + \frac{197}{19.7} \times 0.75 \right) + 2 \times 15 \times 10^3 \right)}{8.3145 \times 5.33}$$

$$= 450 \text{ K}$$

iii) $x_B = 0.6$ $\eta = 0$

$$T = \frac{2 \times 15 \times 10^3}{8.3145 \times 4.17} = 865 \text{ K}$$

iv) $x_B = 0.6$ $\eta = 0.06$

$$T = 580 \text{ K}$$

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

i) $x_B = 0.75$, $\eta = 0$

ii) $x_B = 0.75$, $\eta = 0.06$

두 경우 모두 775K보다 b)에서 구한 spinodal 온도가

작아서 spinodal 발생 X $\Rightarrow$ critical wave length X

iii) $x_B = 0.6$, $\eta = 0$

$$\lambda \geq \left[\frac{8\pi^2 \times 10^{-9}}{\frac{1}{9.68\times10^{-6}}\left[8.3145 \times 775 \times 4.17 - 2 \times 15 \times 10^3\right]} \right]^{\frac{1}{2}}$$

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

iv) $x_B = 0.6$, $\eta = 0.06$

이 경우도 775K보다 b)에서 구한 spinodal 온도가

작아서 critical wave length X

d) $x_B = 0.5$ 일 때 구동력이 가장 커져 fastest growing wave length 가 존재한다.

$x_B = 0.5$, $\eta = 0$ 일 때

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

$$= \left[- \frac{8 \times \pi^2 \times 10^{-9}}{\frac{1}{9.54\times10^{-6}}\left[8.3145 \times 775 \times 4 - 2 \times 15\times10^3\right]} \right]^{\frac{1}{2}}$$

$$= 1.34 \times 10^{-8}\ m$$

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

$\eta = 0.06$ 일 때는 775 K에서 Spinodal 일어나지 않음.

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

$$M = (1-x_B)x_B \left[(1-x_B) D_B^* + x_B D_A^* \right]$$

$$= 0.5^2 \times 10^{-3} \exp\left(\frac{-100\times10^3}{8.3145 \times 775} \right)$$

$$= 4.55 \times 10^{-11}$$

$$\beta = \frac{2\pi}{\lambda_m} = 3.324 \times 10^8$$

$$\therefore R(\beta) = -4.55\times10^{-11} \times (3.324\times10^8)^2 \times \left(-4.429\times10^8 + 2\times10^{-9} \times (3.324\times10^8)^2\right)$$

$$= 1.12 \times 10^{15}$$

$\eta = 0.06$ 일 때는 spinodal decomposition X

2.

a) $C_A(x, 10) = C_A(x, 0)\ \exp(-\pi^2 D \times 10 / \lambda^2)$

$C_A(x, 100) = C_A(x, 0)\ \exp(-\pi^2 D \times 100 / \lambda^2)$

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

$$= \exp\left(\frac{-\pi^2 \times 10^{-4} \exp\left(\frac{-85000}{8.3145 \times 298}\right) \times 90}{(0.01)^2 \times 10^{-12}}\right)$$

$$= 0.326$$

시간을 증가시키면 maximum concentration 감소

b) $\lambda_1 = 0.1 \times 10^{-6}$ $\lambda_2 = 0.01 \times 10^{-6}$

$$\frac{C_A(x, 100, \lambda_2)}{C_A(x, 100, \lambda_1)} = \exp\left(\frac{-\pi^2 Dt}{(0.01)^2 \times 10^{-12}} \times 99\right)$$

$$= 0.291$$

fluctuation wave length를 줄이면 농도 감소.

c) $T_1 = 298\,K$ $T_2 = 398\,K$

$$\frac{C_A(x, 100, T_2)}{C_A(x, 100, T_1)} = \exp\left(\frac{-\pi^2 \times 100}{(0.01)^2 \times 10^{-12}} \times 10^{-4} \times \left(\exp\left(-\frac{85000}{8.3145 \times 398}\right) - \exp\left(-\frac{85000}{8.3145 \times 298}\right)\right)\right)$$

$$= 0$$

온도를 늘리면 농도 크게 감소

d) 온도를 변화시키는 것에 가장 sensitive 하다.