HW#7 신소재공학과 20222571 최찬식

1. Regular solution satisfies expression below.

$$G_m = x_A {}^\circ G_A + x_B {}^\circ G_B + RT(x_A \ln x_A + x_B \ln x_B) + x_A x_B \Omega.$$

$$x_B = 1 - x_A.$$

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

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

$$= {}^\circ G_A - {}^\circ G_B + RT(\ln x_A - \ln(1-x_A)) - (2x_A - 1)\Omega.$$

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

considering criterion for unstability.

$$f''(c_0) + \frac{2E\eta^2}{1-\nu} + 2K\beta^2 \le 0.$$

at critical temperature. $\lambda = \infty$, $\beta = \frac{2\pi}{\lambda} = 0.$, $x_A = x_B = 0.5.$

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

and. $f = \frac{G_m}{V_m}$. $f'' = \dfrac{\frac{\partial^2 G_m}{\partial x_A^2}}{V_m} = \frac{1}{V_m}\left[RT\left(\frac{1}{x_A} + \frac{1}{1-x_A}\right) - 2\Omega\right] = -\frac{2E\eta^2}{1-\nu}.$

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

$$\boxed{T = \frac{2}{R}\left[\Omega - V_m\left(\frac{E\eta^2}{1-\nu}\right)\right] \Big/ \left(\frac{1}{x_A} + \frac{1}{1-x_A}\right).}$$

$x_A = 0.5.$ $T = \frac{1}{2R}\left[\Omega - V_m\left(\frac{E\eta^2}{1-\nu}\right)\right]$

$$V_m = x_A \cdot \frac{M_A}{\rho_A} + x_B \cdot \frac{M_B}{\rho_B} = 9.54\ cm^3/mol = 9.54 \times 10^{-6}\ m^3/mol$$

(a). $\eta = 0$, $T = \frac{1}{2R}[\Omega] = 902K.$

$$\eta = 0.06 \quad T = 902K - \frac{9.54 \times 10^{-6}}{2R}\left(\frac{10^{11} \cdot (0.06)^2}{1 - 0.3}\right)$$

$$= 902K - 295K$$

$$= 607K.$$

(b) ① $\eta = 0.$

$x_B = 0.75$, $x_A = 0.25.$ $V_m = 0.25 \cdot 9.07 + 0.75 \times 10 = 9.77 \times 10^{-6}\ m^3/mol.$ $\frac{1}{x_A} + \frac{1}{1-x_A} = 5.33.$

$$T = \frac{2 \times 15 \times 10^3}{5.33 \times 8.3145} = 677K.$$

$x_B = 0.6$. $x_A = 0.4$. $V_m = 0.4 \times 9.07 + 0.6 \times 10 = 9.63 \times 10^{-6}\, m^3/mol$. $\frac{1}{x_A} + \frac{1}{1-x_A} = 4.17$.

$$T = \frac{2 \times 15 \times 10^3}{4.17 \times 8.3145} = 866\,K.$$

② $\eta = 0.06$.

$x_B = 0.75$.

$$T = 677 - \frac{2 \times 9.77 \times 10^{-6} \cdot 10^{11} (0.06)^2}{8.3145 \times 5.33 \times 0.7} = 450\,K.$$

$x_B = 0.6$.

$$T = 866 - \frac{2 \times 9.63 \times 10^{-6} \cdot 10^{11} (0.06)^2}{8.3145 \times 4.17 \times 0.7} = 580\,K$$

(c). Critical wavelength.

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

for the calculated temperatures at (b), only $x_B = 0.6$, $\eta = 0$. case is higher than 775K.
Therefore, critical wavelength can be calculated.

$$f'' = \frac{1}{9.63 \times 10^{-6}} \left[8.3145 \times 775 \times 4.17 - 2 \times 15 \times 10^3 \right] = -3.25 \times 10^8.$$

$$\lambda = \left[- \frac{8\pi^2 K}{f''} \right]^{\frac{1}{2}} = 1.56 \times 10^{-8}\, m.$$

(d). Temperature difference from critical temperature is largest at $x_A = 0$, $\eta = 0$. ($T = 902\,K$).
which means the highest driving force, therefore shows the fastest growth.
however the expected wavelength at that condition is not the fastest growth wavelength

$\lambda = \sqrt{2}\lambda_c$.

$$\lambda_c = \left[\frac{8 \times \pi^2 \cdot 10^{-9}}{\frac{1}{9.54 \times 10^{-6}} \left[8.3145 \times 775K \times 4 - 2 \times 15 \times 10^3 \right]} \right]^{\frac{1}{2}} = 1.34 \times 10^{-8}\, m.$$

$\lambda = 1.89 \times 10^{-8}\, m$.

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

$R_{max} = \frac{1}{2} KM\beta_c^4$. $\beta_c = \frac{2\pi}{\lambda_c}$

$M = x_A x_B (x_A \cdot D_B^* + x_B D_A^*)$. $x_A = x_B = 0.5$. for maximum R.
$\eta = 0$.

$= 4.55 \times 10^{-11}\, m^2/s$.

$R_{max} = 4.48 \times 10^{12}$

2. (a). D_A at RT. $x = 10^{-8}m$.

$D_A = 10^{-4}\exp(-85000J/(8.3145\times298)) = 1.26\times10^{-19}\,m^2/s$.

$C_A(x,10) = C_A(x,0)\exp(-\pi^2\cdot D_A\cdot 10/10^{-16}) = C_A(x,0)\cdot 0.883$.

$C_A(x,100) = C_A(x,0)\exp(-\pi^2 D_A\cdot 100/10^{-16}) = C_A(x,0)\cdot 0.288$.

$\frac{C_A(x,100)}{C_A(x,10)} = 0.326$. decrease in maximum concentration.

(b). $x = 0.1\mu m = 10^{-7}m$.

$C_A(x,100) = C_A(x,0)\exp(-\pi^2\cdot D_A\cdot 100/10^{-14}) = C_A(x,0)\cdot 0.988$.

$\frac{C_A(x,100)|_{x=0.01\mu m}}{C_A(x,100)|_{x=0.1\mu m}} = 0.291$

(c). at 398K. $D_A = 10^{-4}\exp(-85000J/(8.3145\times398K)) = 6.99\times10^{-16}$.

$C_A(x,100)|_{T=398K} = C_A(x,0)\exp(-\pi^2\cdot 6.99\times10^{-16}\cdot 100/10^{-16}) = 0$. $\sim 10^{-300}$

(d). Temperature is the most crucial factor.