#4-4

2.

$$\Delta\mu_1 = RT[\ln(1-\phi_2) + \phi_2 + \chi_1\phi_2^2]$$

$$\approx RT[(-\phi_2 - \tfrac{1}{2}\phi_2^2 - \tfrac{1}{3}\phi_2^3 - \cdots) + \phi_2 - \frac{\phi_2}{x} + \chi_1\phi_2^2]$$

$\phi_2 << 1$

$$= -RT\left[\frac{\phi_2}{x} + \left(\tfrac{1}{2} - \chi_1\right)\phi_2^2 + \cdots\right]$$

$$\phi_2/x = \frac{n_2}{n_1 + x n_2} = \frac{v N_2}{v(N_1 + x N_2)} = \frac{v N_{av} \cdot n_2}{V_{total}} = \frac{\bar{V}^\circ \cdot n_2}{V_{tot}}$$

$$= \bar{V}_1^\circ \frac{n_2}{V_{tot}} = \bar{V}_1^\circ \frac{c}{M}$$, where v = unit cell volume of the lattice

$v \cdot N_{av}$ = molar volume of solvent $\bar{V}_1$

N_1 = # of solvent molecules

N_2 = # of solute molecules

$$\phi_2 = x\,\bar{V}_1^\circ \frac{c}{M} = \frac{\bar{V}_2^\circ}{\bar{V}_1^\circ}\bar{V}_1^\circ \frac{c}{M}$$

$$= \frac{c}{(M/\bar{V}_2^\circ)} = c/\rho$$

$$\therefore \Delta\mu_1 = -RT\left[\bar{V}_1^\circ \frac{c}{M} + \left(\frac{1}{2} - \chi_1\right)\left(\frac{c}{\rho}\right)^2 + \cdots\right] = RT\ln a_1$$

$$\Pi = -\frac{\Delta\mu_1}{\bar{V}_1^\circ} = RT\left[\frac{c}{M} + \left(\frac{1}{2} - \chi_1\right)\frac{c^2}{\bar{V}_1^\circ\rho^2} + \cdots\right]$$

Finally, $$\frac{\Pi}{c} = RT\left[\frac{1}{M} + \left(\frac{1}{2} - \chi_1\right)\frac{1}{\bar{V}_1^\circ\rho^2}\,c + \cdots\right]$$

$$= RT\left[\frac{1}{M} + A_2 c + \cdots\right]$$

3. a) For polydisperse systems, $\Pi_i = RT \frac{c_i}{M_i}$ in the infinite dilution of all species

$$\sum_i \Pi_i = \Pi, \quad \sum_i c_i = c$$

$$\frac{\sum \Pi_i}{\sum c_i} = RT \frac{\sum c_i/M_i}{\sum c_i}, \quad \underline{\underline{\frac{\Pi}{c} = RT \frac{1}{M_n}}}$$

since $M_n = \frac{\sum X_i M_i}{\sum X_i} = \frac{\sum \left(\frac{n_i}{\sum n_i}\right) M_i}{\sum \frac{n_i}{\sum n_i}} = \frac{\sum \left(\frac{c_i}{M_i}\right) \cdot M_i}{\sum \left(\frac{c_i}{M_i}\right)}$

$$= \frac{\sum c_i}{\sum (c_i/M_i)}$$

$$\therefore M_n^{-1} = \frac{\sum (c_i/M_i)}{\sum c_i}$$

b) Sample 1 $\left[\left(\frac{\Pi}{c}\right)^{1/2}_{c \to 0}\right]^2 = 0.019 \cdot 10^{-2} \cdot 8.653 \cdot 10^2 \cdot 980$

$m \cdot kg^{-1} \cdot m^3 \cdot kg/m^3 \cdot m/s^2$

$= 1.59\ m^2/s^2 = 1.59\ J/kg$

$M_n = \frac{8.314 \cdot 303.15}{1.59} = 1.59 \cdot 10^3\ kg/mol = 1.59 \cdot 10^6\ g/mol$

$A_2 = \frac{2 \cdot slope}{\left(\frac{\Pi}{c}\right)^{1/2}_{c \to 0} \cdot M_n}$ $\quad A_2 = 2 \cdot 0.230 / 1.38 \cdot 15.9 \cdot 10^2 = 2.10 \cdot 10^{-4}\ kg^{-2} m^3 \cdot mol$

Sample 2 $\left[\left(\frac{\Pi}{c}\right)^{1/2}_{c \to 0}\right]^2 = 0.046 \cdot 10^{-2} \cdot 8.653 \cdot 10^2 \cdot 9.80$

$= 3.86\ J/kg$

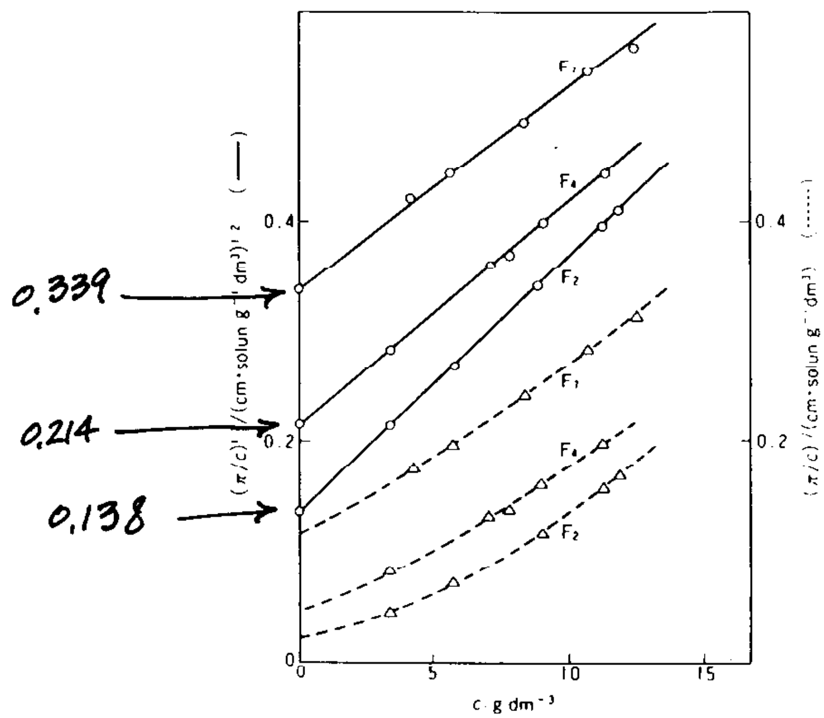
$M_n = 6.53 \cdot 10^5\ g/mol$

$A_2 = \frac{2 \cdot 0.0202}{0.214 \cdot 6.53 \cdot 10^2} = 2.89 \cdot 10^{-4}\ kg^{-2} \cdot m^3 \cdot mol$

Sample 3 $\left[\left(\frac{\Pi}{c}\right)^{1/2}_{c \to 0}\right]^2 = 9.65\ J/kg$

$M_n = 2.61 \cdot 10^5\ g/mol$

$A_2 = \frac{2 \cdot 0.0186}{0.339 \cdot 2.61 \cdot 10^2} = 4.20 \cdot 10^{-4}\ kg^{-2} m^3 mol$



Sample 1 : $\left\{\left(\frac{\pi}{c}\right)^{1/2}_{c\to 0}\right\}^2 = (0.0190\times10^{-2}) \times (8.653\times10^2) \times 9.80$

$(\mathrm{m\ kg^{-1}\ m^3 \cdot kg\ m^{-3} \cdot m\ s^{-2}})$

$= 1.59(\mathrm{m^2\ s^{-2}}) = 1.59\ (\mathrm{J\ kg^{-1}})$

" 2 : $\left\{\left(\frac{\pi}{c}\right)^{1/2}_{c\to 0}\right\}^2 = (0.046\times10^{-2}) \times (8.563\times10^2) \times 9.80$

$= 3.86\ (\mathrm{J\ kg^{-1}})$

" 3 : $\left\{\left(\frac{\pi}{c}\right)^{1/2}_{c\to 0}\right\}^2 = (0.115\times10^2) \times (8.563\times10^2) \times 9.80$

$= 9.65\ (\mathrm{J\ kg^{-1}})$