Solutions to Problem Set #1 - Chem 664
due 09/16/02

A. Bimodal 1, 2 species $= i$

	1	2	
w_i	$1/2$	$1/2$	$M_w = \frac{1}{2}M_1 + \frac{1}{2}M_2 = \frac{1}{2}(M_1+M_2) = 3\cdot 10^5$
n_i	$\frac{w_1/M_1}{w_1/M_1 + w_2/M_2} = \frac{1/M_1}{1/M_1 + 1/M_2}$	$\frac{w_2/M_2}{w_2/M_2 + w_1/M_1} = \frac{1/M_2}{1/M_1 + 1/M_2}$	$M_n = \frac{M_1/M_1}{1/M_1 + 1/M_2} + \frac{M_2/M_2}{1/M_1 + 1/M_2} = \frac{2M_1M_2}{M_1+M_2} = 2.67\cdot 10^5$
M_i	M_1	M_2	
z_i	$\frac{w_1\cdot M_1}{w_1\cdot M_1 + w_1\cdot M_2}$	$\frac{w_2\cdot M_2}{w_1\cdot M_1 + w_2\cdot M_2}$	$M_z = \frac{M_1^2 + M_2^2}{(M_1+M_2)} = \underline{\underline{3.33\cdot 10^5}}$

$$M_1 + M_2 = 6\cdot 10^5, \quad 3\cdot 2.67\cdot 10^5 = M_1 M_2$$

$$M_2 = 3\cdot 2.67\cdot 10^5 / M_1$$

$$M_1^2 - 6\cdot 10^5 M_1 + 8.01\cdot 10 = 0$$

$$M_1 = \frac{6\cdot 10^5 \pm \sqrt{36\cdot 10^{10} - 8.01\cdot 10^{10}\cdot 4}}{2} = \frac{(6\pm 2)\cdot 10^5}{2} = 4\cdot 10^5 \text{ or } 2\cdot 10^5$$

Since $M_1 < M_2$ & $M_1 + M_2 = 6\cdot 10^5$, $M_1 = \underline{\underline{2\cdot 10^5}}$, $M_2 = \underline{\underline{4\cdot 10^5}}$

Then $M_z = \frac{(4+16)\cdot 10^{10}}{6\cdot 10^5} = \underline{\underline{3.33\cdot 10^5}}$ which agrees with the value given in the problem

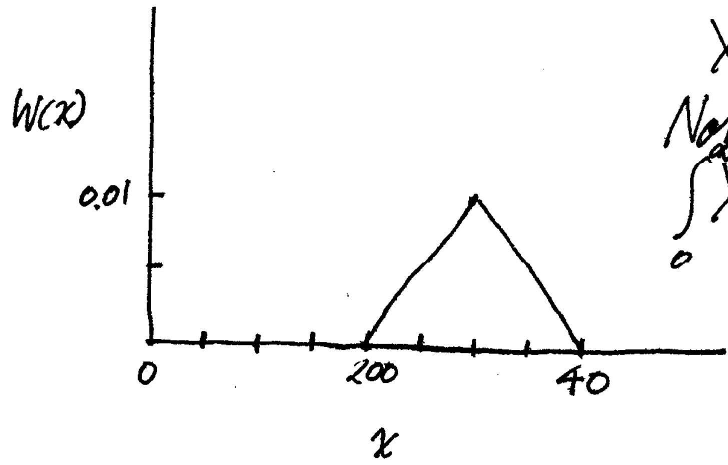
$$M_{z+1} = \frac{M_1^3 + M_2^3}{M_1^2 + M_2^2} = \frac{(8+64)\cdot 10^{16}}{(4+16)\cdot 10^{10}} = \underline{\underline{3.6\cdot 10^5}}$$

B. Notation difference

$X(x)$ - mole fraction of x-mer
$W(x)$ - weight " "
$Z(x)$ - z-fraction of "

$$W(x) = 10^{-4}x - 2\cdot 10^{-2} \qquad 200 \le x \le 300$$

$$= 4\cdot 10^{-2} - 10^{-4}x \qquad 300 \le x \le 400$$



$$X(x) = A\,\frac{W(x)}{x}$$

Normalization

$$\int_0^\infty X(x)\,dx = 1 = A\int_0^\infty \frac{W(x)}{x}\,dx$$

$$= A\left\{\int_{200}^{300}\left(\frac{10^{-4}x - 2\cdot 10^{-2}}{x}\right)dx + \int_{300}^{400}\left(\frac{4\cdot 10^{-2} - 10^{-4}x}{x}\right)dx\right\}$$

$$= A\cdot 2\cdot 10^{-2}(0.170)$$

Thus

$$A = 2.94\cdot 10^{2}$$

$$X(x) = 2.94\left(10^{-2} - \frac{2}{x}\right),\quad 200 \le x \le 300$$

$$= 2.94\left(\frac{4}{x} - 10^{-2}\right),\quad 300 \le x \le 400$$

Similarly, $Z(x) = B\,x\,W(x)$, $1 = \int_0^\infty Z(x)dx = B\underbrace{\int_0^\infty x\,W(x)\,dx}_{300}$

$$B = 1/300 = 3.33\cdot 10^{-3}$$

Thus

$$Z(x) = 3.33\cdot 10^{-5}(10^{-2}x^2 - 2x),\quad 200 \le x \le 300$$

$$= 3.33\cdot 10^{-5}(4x - 10^{-2}x^2),\quad 300 \le x \le 400$$

$$D(x) = 1.21\cdot 10^{-4}/(M_0 x)^{1/2} = 1.21\cdot 10^{-5}/x^{1/2} \quad \text{since } M_0 = 100$$

$$D_n = \int_0^\infty D(x)\,X(x)\,dx = \int_{200}^{300}\frac{1.21\cdot 10^{-5}}{x^{1/2}}\cdot 2.94\left(10^{-2} - \frac{2}{x}\right)dx + \int_{300}^{400}\frac{1.21\cdot 10^{-5}}{x^{1/2}}\,2.94\left(\frac{4}{x} - 10^{-2}\right)dx$$

$$= 7.34\cdot 10^{-7}\ (\mathrm{cm^2/s})$$

$$D_w = 1.21\cdot 10^{-7}\left\{\int_{200}^{300}\left(10^{-2}x^{1/2} - \frac{2}{x^{1/2}}\right)dx + \int_{300}^{400}\left(\frac{4}{x^{1/2}} - 10^{-2}x^{1/2}\right)dx\right.$$

$$= 7.04\cdot 10^{-7}\ (\mathrm{cm^2/s})$$

$$D_z = 1.21\cdot 10^{-5}\cdot 3.33\cdot 10^{-5}\left\{\int_{200}^{300}\left(10^{-2}x^{3/2} - 2x^{1/2}\right)dx + \int_{300}^{400}\left(4\cdot 10^{1/2} - 10^{-2}x^{3/2}\right)dx\right\}$$

$$= 6.96\cdot 10^{-7}\ (\mathrm{cm^2/s})$$

Note that $x_n = 294$, $x_w = 300$, $x_z = 305$, $D_n \ne 1.21\cdot 10^{-5}/x_n^{1/2} = 7.06\cdot 10^{-7}$

C. Problem 1.9 of the Textbook

$N \sim \langle R^2 \rangle \sim R^2$ where $R \equiv \langle R^2 \rangle^{1/2}$ the root-mean-square end-to-end distance of a chain

$N \sim R^D$ with $D = 2$

$$\frac{N_1}{N_2} = \left(\frac{R_1}{R_2}\right)^D, \quad \frac{R_1}{R_2} = \left(\frac{N_1}{N_2}\right)^{1/D} \underset{D=2}{=} \left(\frac{1000}{250}\right)^{1/2} = \underline{\underline{2}}$$

1.12. $M \sim R^D$ where $D = 4/3$ is given

$$\frac{R_1}{R_2} = \left(\frac{M_1}{M_2}\right)^{1/D} = \left(\frac{M_1}{M_2}\right)^{3/4} = 16^{3/4} = (2^4)^{3/4} = 2^3 = \underline{\underline{8}}$$

1.14. $\rho_{298} = 0.895\ g/cm^3$ for 1,4-polybutadiene

$M_0 = 54\ g/mol$ for the repeating unit

$-(CH_2-CH=CH-CH_2)-$

$C_4H_6 = 4 \cdot 12 + 6 = 54$

$$v_{mon} = v_0\ (R.U.\ vol) = \frac{M_0}{\rho N_{AV}} = \frac{54}{0.895 \cdot 6.02 \cdot 10^{23}}\ cm^3$$

$$= 92.8 \cdot 10^{-24}\ cm^3$$

$$= 92.8\ \mathring{A}^3 \cong \underline{\underline{100 \mathring{A}^3}}$$

1.20. $V_{total} = V_1 + V_2 = \frac{m_1}{\rho_1} + \frac{m_2}{\rho_2}$ if no volume of mixing, subscripts 1 & 2 stand for solvent & solute, respectively

ϕ_2 (vol fraction of solute)

$$= \frac{m_2/\rho_2}{V_{total}} = \frac{(0.020/0.8)\ mL}{10\ mL} = \underline{\underline{2.5 \cdot 10^{-3}}}$$

1.21 $c^* \approx \frac{M}{V N_{AV}}$, c^* = overlap conc., V = pervaded vol per polymer molec

$$V \quad \frac{10^5}{1.67 \cdot 10^{-2} \cdot 6.02 \cdot 10^{23}} \cong 10 \cdot 10^{-18}\ cm^3 = 10^4\ nm^3$$

$$\cong (215\ \mathring{A})^3$$

D. At equilibrium, conc of each species is SPS 1/4

$$(M_2) = K(M)^2,\quad (M_3) = K(M_2)(M) = K^2(M)^3, \cdots$$

$$(M_x) = K^{x-1}(M)^x$$

$$\sum_{x=1}^{\infty}(M_x) = \sum_{x=1}^{\infty} K^{x-1}(M)^x = (M)\sum_{x=1}^{\infty}[K(M)]^{x-1}$$

$$= \frac{(M)}{1-K(M)} \quad \text{if } K^2(M)^2<1$$

n_x (mole fraction of x-mer)

$$= \frac{(M_x)}{\sum(M_x)} = \frac{K^{x-1}(M)^{x-1}\cancel{(M)}}{\frac{\cancel{(M)}}{1-K(M)}} = \underbrace{[K(M)]^{x-1}[1-K(M)]}_{p^{x-1}(1-p)}$$

where $p \equiv K(M)<1$

Another $\underline{\underline{MPD}}$!

$$(M)_0 = \sum x(M_x) = (M)\left[\sum x K^{x-1}(M)^{x-1}\right]$$

$$= (M)/[1-K(M)]^2$$

$$\because \frac{1}{(1-p)^2} = 1+2p+3p^2+\cdots$$

$$K^2(M)_0(M)^2 - [2K(M)_0+1](M) + (M)_0 = 0$$

$$K^2(M)_0 = (9.5\cdot10^3)^2(4\cdot10^{-2}) = 3.61\cdot10^6$$

$$2K(M)_0+1 = 7.61\cdot10^2$$

$$\therefore (M) = \frac{7.61\cdot10^2 \pm 0.39\cdot10^2}{7.22\cdot10^6} = \begin{cases} 10^{-4}, & K(M)=0.95<1 \\ 1.11\cdot10^{-4}, & K(M)=1.05>1 \end{cases}$$

Hence $(M)=10^{-4}$ is the right root of the quadratic equ.

$$x_n = \frac{1}{1-K(M)} = \frac{1}{0.05} = 20, \quad M_n = 2\cdot10^5$$

$$x_w = \frac{1+K(M)}{1-K(M)} = \frac{1.95}{0.05} = 39, \quad M_w = 3.9\cdot10^5$$

$$M_w/M_n \simeq 2$$

E. Notation comparison

Problem Set	Textbook
$\boxed{\text{discrete}}$	$\boxed{\text{discrete}}$
mole fraction of x-mer	mole fraction of N-mer
$X_x = p^{x-1}(1-p)$	$n_N = p^{N-1}(1-p)$
$1 \leq x \leq \infty$	$1 \leq N \leq \infty$
$0 \leq p < 1$	$0 \leq p < 1$
$\boxed{\text{continuous}}$	$\boxed{\text{Continuous}}$
$\mathbb{P}(x) = X(x) = \frac{1}{x_n} e^{-x/x_n}$	$n_N(p) \cong \frac{1}{N_n} e^{-N/N_n}$
$0 \leq x \leq \infty$	$0 \leq N \leq \infty$
$p \lessapprox 1$	$p \lessapprox 1$
$x = M/M_0$	$N = M/M_0$

$$X(x) = \frac{1}{M_0} X(M), \quad X(M) = M_0 X(x) = M_0 \frac{1}{\frac{M_n}{M_0}} e^{-M_0 M / M_0 M_n}$$

$$\underline{\underline{X(M) = \frac{1}{M_n} e^{-M/M_n}}}, \quad \text{Note that } \int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \quad n = \text{integer}$$

Normalization

$$\int_0^\infty X(M) dM = \frac{1}{M_n} \int_0^\infty e^{-M/M_n} dM = \frac{1}{M_n} \frac{0!}{\left(\frac{1}{M_n}\right)} = 1$$

$$W(M) = \frac{M X(M)}{\int_0^\infty M X(M) dM}, \quad \int_0^\infty M X(M) dM = M_n, \quad \underline{\underline{W(M) = \frac{M}{M_n^2} e^{-M/M_n}}}$$

$$\int_0^\infty W(M) dM = \frac{1}{M_n^2} \int_0^\infty M e^{-M/M_n} dM = \frac{1}{M_n^2} \cdot \frac{1!}{\left(\frac{1}{M_n}\right)^2} = 1$$

$$Z(M) = \frac{M W(M)}{\int_0^\infty M W(M) dM} = \frac{M W(M)}{M_w} = \frac{M^2}{M_w M_n^2} e^{-M/M_n} = \underline{\underline{\frac{M^2}{2M_n^3} e^{-M/M_n}}}$$

$$M_w = \int_0^\infty M W(M) dM = \frac{1}{M_n^2} \int_0^\infty M^2 e^{-M/M_n} dM = \frac{1}{M_n^2} \frac{2!}{\left(\frac{1}{M_n}\right)^3} = 2M_n$$

$$\int_0^\infty Z(M) dM = \frac{1}{2M_n^3} \int_0^M M^2 e^{-M/M_n} dM = \frac{1}{2M_n^3} \frac{2!}{\left(\frac{1}{M_n}\right)^3} = 1$$