Chem 664 **Problem Set #1** **Due: September 16, 2002**

A. The component polymer fractions of a bimodal distribution consisting of 3 kg each of smaller and larger molecular weight samples, M_1 and M_2, are to be characterized. The two fractions are known to be monodisperse and the following averages are determined experimentally;

$$M_n = 2.67 \times 10^5 \;, \quad M_w = 3.00 \times 10^5 \;, \quad M_z = 3.33 \times 10^5$$

Calculate M_1 , M_2 and M_{z+1}.

B. Consider a well defined polydisperse sample of a polymer whose weight fraction has a triangular profile, i.e.

$$W(x) = 10^{-4}\, x - 2\cdot 10^{-2} \quad \text{for } 200 = x < 300$$
$$W(x) = 4\cdot 10^{-2} - 10^{-4}x \quad \text{for } 300 = x = 400$$

where W(x)dx is the weight fraction of polymers with d.p. in the range of x and x + dx.

The translation diffusion coefficient (in units of cm^2/s) of any monodisperse fraction of this polymer with a molecular weight M (in g/mol) in cyclohexane at 37°C is given by

$$D_M = 1.21 \cdot \frac{10^{-4}}{M^{1/2}}$$

Find D_n, D_w, and D_z (number, weight and z-average) diffusion coefficients of the sample. Molecular weight of monomer is 100. Note that

$$D_n = \int_0^\infty D(x)X(x)dx, \; D_w = \int_0^\infty D(x)W(x)dx, \; \text{and } D_z = \int_0^\infty D(x)Z(x)dx$$

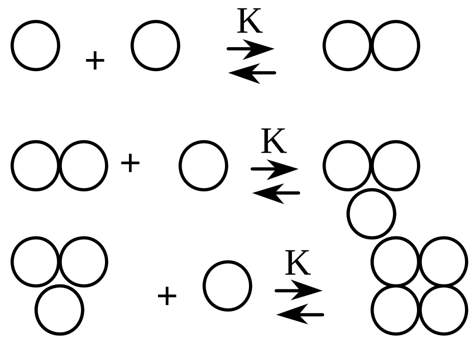
C. 1.9, 1.12, 1.14, 1.20, 1.21 of the text

D. Consider the self-association phenomenon of a globular protein where the equilibrium constant is the same for each step such that the multiple equilibria hold

$$M + M \overset{K}{\rightleftarrows} M_2 ;$$

$$M_2 + M \overset{K}{\rightleftarrows} M_3 ;$$

$$M_3 + M \overset{K}{\rightleftarrows} M_4 ;$$



$$\vdots$$

$$M_x + M \overset{K}{\rightleftarrows} M_{x+1} ;$$

assuming the solution to be ideal, i.e., activity coefficient is unity for all species. Find the distribution function expression for x-mer in terms of K and the equilibrium monomer concentration. Assuming that the density of monomeric protein does not change upon association, calculate the number average and weight average molecular weight of the equilibrium mixture if the monomer molecular weight is 10^4, the unimer concentration at the beginning was 4×10^{-2} mol/L and $K = 9.5 \times 10^3$ (mole/L)$^{-1}$.

E. The most probable distribution in the continuous limit is written as

$$P(x) = \left(\frac{1}{x_n}\right) \exp\left(-\frac{x}{x_n}\right)$$

where x_n is the number average degree of polymerization. From the above equation, derive the expressions for X(M) and W(M) and Z(M), where X(M)dM denotes the mole fraction of polymeric species having a molecular weight range M and M+dM, and W(M)dM and Z(M)dM have the corresponding meanings for the weight fraction and the z-fraction, respectively. Hence,

$$\int_0^\infty X(M)dM = 1, \quad \int_0^\infty M\cdot X(M)dM = M_n$$

$$\int_0^\infty W(M)dM = 1, \quad \int_0^\infty M\cdot W(M)dM = M_w$$

$$\int_0^\infty Z(M)dM = 1, \quad \int_0^\infty M\cdot Z(M)dM = M_z$$