**Chem 664** **Problem Set #1** **Due: September 15, 2003**

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A. A polymer mixture with a termodal distribution consisting of 3 kg each of small, medium and large molecular weight samples, $M_{1=}$, $M_2$, and $M_3$, are to be characterized, where all three fractions are monodisperse. They are 10 kg/mol, 100 kg/mol and 1000 kg/mol, respectively. Compute $M_n$, $M_w$ and $M_z$ of the mixture.

B. Consider a polydisperse sample of a polymer whose weight fraction is given by the most probable distribution, i.e.

$$W(N) = \frac{N}{N_n} \cdot \exp\left(-\frac{N}{N_n}\right) \qquad (0 \le N \le \infty) \tag{1}$$

where W(N)dN is the weight fraction of polymer with a degree of polymerization in the range of N and N + dN.

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

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

Find $D_n$, $D_w$, and $D_z$ (number, weight and z-average) diffusion coefficients of the sample under the same conditions. Explain why $D_n > D_w > D_z$. The molecular weight of the repeating unit is 100. Also, note that

$$D_n = \int_0^\infty D(N) \cdot X(N) dN, \quad D_w = \int_0^\infty D(N) \cdot W(N) dN, \quad D_z = \int_0^\infty D(N) \cdot Z(N) dN, \tag{3}$$

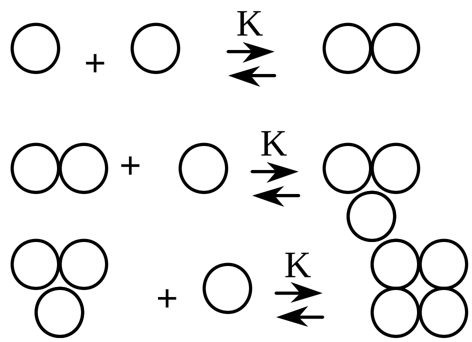
C. 1.9, 1.12, 1.14, 1.20, 1.21 of the text

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

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

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

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



$$\vdots$$

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

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 $4 \times 10^{-2}$ mol/L and $K = 9.5 \times 10^3$ (mole/L)$^{-1}$.

E. Another commonly used distribution for molecular weight is “log normal distribution”, expressed for the weight fraction of M as

$$W(M) = \frac{e^{-\beta^2/4}}{M^* \cdot \beta \cdot \sqrt{\pi}} \cdot \exp\left\{ -\frac{\left[\ln(M/M^*)\right]^2}{\beta^2} \right\} \qquad (4),$$

where M* and $\beta$ are two characteristic positive parameters of the distribution. Find the expressions for $M_n$, $M_v$, $M_w$ and $M_z$ of the distribution in terms of M* and $\beta$. $M_v$ is called the viscosity average molecular weight, defined as

$$M_v \equiv \left[ \int_0^{\infty} W(M) M^{\alpha} dM \right]^{1/\alpha}, \qquad (o < \alpha < 1) \qquad (5)$$

**Hints: Let $\ln(M/M^*)^{\circ}$ x such that $M=M^*\cdot e^{x}$ and $dM = M^* e^{x} \cdot dx$**