Exam #3 Chem 471 Fall 2001 Name:________________________

Work independently. Do not look at others' exams.
Do not allow your exam responses to be shared.

1. (25 points) Circle the correct answer or fill in the blank, as appropriate:

a. All other things being equal, the unhydrated form of a protein will show a (**higher / lower / the same**) diffusion coefficient compared with the hydrated form of the same protein.

$D = \frac{kT}{f} = \frac{kT}{6\pi\eta r}$ The unhydrated form of the protein has a smaller effective radius, so D will be **higher**.

b. A protein is spun in a centrifuge in two different centrifuge tubes, A and B. The medium in tube A is slightly more dense than that in tube B. For a 10 min centrifugation run at 20°C, the protein in tube A moves 2 cm away from the center of the centrifuge rotor. Under the same conditions, the protein in tube B moves (**greater than / less than / the same distance as**) the protein in tube A.

$s = \frac{m(1-\bar{v}_2\rho)}{f}$ Movement away from the rotor center tells us that $\bar{v}_2\rho < 1$ (see next question), so that if ρ increases, the protein moves **less than** the protein in the other tube.

c. A (different) lipoprotein is spun in a centrifuge in two centrifuge tubes, A and B. The medium in tube A is slightly more dense than that in tube B. For a 10 min centrifugation run at 20°C, the protein in tube A moves 2 cm inward towards the center of the centrifuge rotor. Under the same conditions, the protein in tube B moves (**greater than / less than / the same distance as**) the protein in tube A.

$s = \frac{m(1-\bar{v}_2\rho)}{f}$ **less than.**

d. For the system in part (c) above, $1/\bar{v}_2$ is (**greater than / less than / equal to**) ρ.

$s = \frac{m(1-\bar{v}_2\rho)}{f}$

To get negative movement, s<0, which means that $1-\bar{v}_2\rho < 0$**. Therefore** $\bar{v}_2\rho > 1$**, which leads to** $\frac{1}{\bar{v}_2} < \rho$ (less than)**.**

e. If the frictional coefficient of a protein doubles, but its molecular weight and partial specific volume remain the same, s (**doubles, is halved, quadruples, remains the same**).

$s = \frac{m(1-\bar{v}_2\rho)}{f}$ is halved**.**

2. (10 points) In question 1(e) above, it is suggested that two proteins with the same molecular weight can have very different frictional coefficients. Explain, in 20 words or less.

   Shape can have a dramatic effect on friction. A sphere presents much less resistive drag than an elongated shape, for example.

3. (15 points) For an unknown virus, the following sedimentation data, extrapolated to zero concentration, have been obtained.

$$s^{o}_{20,w} = 200\ S \qquad D^{o}_{20,w} = 6.03x10^{-8}\ \mathrm{cm}^2\ \mathrm{s}^{-1} \qquad \bar{\nu}_2 = 0.639\ cm^3\ g^{-1}$$

What is the molecular weight of the bacteriophage (1 S = 10^{-13} s)?

$$M = \frac{RTs}{D(1-\bar{v}_2\rho)} = \frac{(8.314\ J\,K^{-1}\,mole^{-1})(293K)(200x10^{-13}\,s)(kg\ m^2\ s^2\ J^{-1})(10^3\,g\ \mathrm{kg}^{-1})(10^2\,cm\ \mathrm{m}^{-1})^2}{(6.03x10^{-8}\mathrm{cm}^2\ \mathrm{s}^{-1})[1-(0.639\ cm^3 g)(0.998\ g\ cm^3)]}$$

$$M = 2.23x10^7\ \mathrm{g\ mol}^{-1}$$

4. (25 points) For the following kinetic mechanism:

$$\mathrm{A + B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{D} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{P}$$

write the expression for d[D]/dt in terms of [A], [B], [C], [D], and/or [P], and any or all of the rate constants.

$$\frac{d[D]}{dt} = k_2[C] - k_{-2}[D] - k_3[D] + k_{-3}[P]$$

5. (30 points) If A and B are mixed together in solution, it is found that the concentration of A decreases with time, but B remains constant. The stoichiometric equation is $A \to P$.

a. If the initial concentration of A is less than 0.01 M, it is found that the initial rate is

$$-\frac{d[A]}{dt} = k_1[A][B]$$

What is the order of the reaction with respect to A? First
What is the order of the reaction with respect to B? First

Write the integrated form of this equation (be careful).

Since [B] is constant, $-\frac{d[A]}{[A]} = k_1[B]dt = k_1^{'}dt$

Therefore, $\ln\frac{[A]}{[A]_0} = -k_1^{'}t = -k_1[B]t$ **(or a related form of the same)**

b. If the initial concentration of A is greater than 1 M, it is found that the initial rate is

$$-\frac{d[A]}{dt} = k_2[B]$$

What is the order of the reaction with respect to A? Zero
What is the order of the reaction with respect to B? First

Write the integrated form of this equation (again, be careful).

Since [B] is constant, $-d[A] = k_2[B]dt = k_2^{'}dt$

Therefore, $[A]_0 - [A] = k_2^{'}t = k_2[B]t$ **(or a related form of the same)**