20.110/2.772 Homework Set #9

Due Tuesday Nov 29, 2005 by 6 pm

<u>Note later due date & later due time</u>

1. A series of PEO polymers has been synthesized by living anionic polymerization, a process which results in a product with near-uniform molecular weight (in contrast to free-radical polymerization, which results in highly polydisperse polymer, as discussed on the last homework set). The molecular weight of the PEO repeat unit is 44 gm/mol. The polymers are characterized by osmotic pressure measurements and light scattering in a theta solvent, where it is known that chains assume an ideal conformation, at 300K. The following data are reported for the osmotic pressure determined under limiting dilution conditions (2.5 gm/L) and the radius of gyration (R_g) of each polymer in the series where $R_g = \langle r_0^2 \rangle^{1/2} / \sqrt{6}$.

Sample	π (atm)	R_g (nm)
P1	1.8×10^{-4}	0.7
P2	1×10^{-5}	2.0
P3	2×10^{-6}	6.8
P4	3.9×10^{-7}	15.2

(a) Determine the molecular weight of each sample P1-P4.

(b) What is the Kuhn segment length (b_k) for PEO, as determined by these data?

(c) A cell surface integrin receptor is capable of exerting a force of ~0.1 pN. Imagine that this receptor binds to one end of the PEO chains described above, and the other end is fixed. How far would the cell be able to move the ends apart, for each of the chains P1-P4? In reality, PEO is often used to "tether" adhesion molecules to solid surfaces to induce cell adhesion. Although the behavior of a chain with one end fixed to a solid plane is different than a random coil, these estimates are within the magnitude of what would be expected in that situation.

2. #32.7 from Dill and Bromberg (delayed from PS8). Figure 32-12 shows the stress-strain properties of a rubber band (presume the temperature is 25°C). Use the figure and the chain elasticity theory to

(a) Estimate the number of polymer chains in a cubic volume 10 nm on each side.

(b) If each monomer occupies 100Å^3, what is the length of each chain between the junction points?

3. A crosslinked hyaluronic acid gel strip weighing 1 gm is 4 cm long with a cross sectional area of 0.25 cm^2 and can be modeled as having a spring constant of 0.05 N/m.

(a) estimate the work required to stretch the gel 4 cm in the x-direction at a constant temperature of 300 K if the work is reversible

(b) As discussed in class, the internal energy change for stretching a polymer chain (or network of chains) is approximately zero. Show that when a chain (or the polymer gel) is stretched in an isothermal process, heat must be exchanged with the environment, and indicate whether the polymer gives off heat or adsorbs heat as it is stretched.

(c) Estimate the value of reversible heat adsorbed or released by the process in part (a). If the gel has a heat capacity of 4 J/K, how much would the temperature of the gel change if the heat associated with the process were used to change the temperature of the gel?

4. The simple dissociation of water is influenced by the presence of salts due to induced ordering of the H$^+$ and OH$^-$ ions by the salt ions. Thus while the chemical potential of H$^+$ and OH$^-$ ions in pure water can be described by the ideal solution equation

$\mu_{H+} = \mu_{H+}^0 + RT\ln x_{H+}$ (standard state chemical potential is based on x_{H+}=1)
or the more common form
$\mu_{H+} = \mu_{H+}^0 + RT\ln[H^+]$ (standard state chemical potential based on [H$^+$] = 1 M

In salt solutions the ions do not exhibit ideal behavior and the chemical potential is

$$\mu_{H+} = \mu_{H+}^0 + RT\ln[\gamma_{H+}H^+]$$

Statistical mechanics calculations along with experiment have yielded a simple expression for how the activity coefficient depends on ionic strength: $\gamma_{H+} = \dfrac{AI^{1/2}}{1+1.6I^{1/2}}$

I = ionic strength of the solution $I = \sum_{i=1}^{n} m_i z_i^2$ (m_i = molality = moles ion /kg solvent; z_i = charge on the ion)

A = Debye Constant; for aqueous solutions near 25C it has the value A = $\dfrac{2618}{T^{3/2}} kg^{1/2} mol^{-1/2}$

The enthalpy of water dissociation at 25C is 55.84 KJ/mol.

(a) Estimate the pH of an aqueous solution containing 0.1M $MgCl_2$ at 25°C.

(b) Estimate the pH of an aqueous solution containing 0.1M $MgCl_2$ at 37°C and explain an assumption implicit in using the Van't Hoff equation in this estimation.

5. (from Tinoco et al., 4.13) You want to make a pH 7.0 buffer using NaOH and phosphoric acid. The sum of the concentrations of all phosphoric acid species is 0.100M. The equilibrium constants at 25 C when the units of concentration are mol/L are as follows:

$HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-}$ $K_1 = 4.5 \times 10^{-13}$, $\Delta H^0 = 14.7$ kJ/mol
$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-}$ $K_2 = 6.2 \times 10^{-8}$, $\Delta H^0 = 4.15$ kJ/mol
$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^-$ $K_3 = 7.1 \times 10^{-3}$, $\Delta H^0 = -7.95$ kJ/mol

(a) Write the equation that specifies that the solution is electrically neutral.
(b) Calculate the concentrations of all species in the buffer at 25C
(c) Calculate the pH of the solution at 37°C.