CHEMISTRY DEPARTMENT, PORTLAND STATE UNIVERSITY

CHEMISTRY 441/541, PHYSICAL CHEMISTRY

WINTER, 2005

Graded Assignment No. 1 (of 2)

This assignment is due in the professor’s office or mailbox by 4:30 PM Friday, February 4. Submission on Monday, February 7 will result in an automatic deduction of 50%. Submission on Tuesday will result in zero credit. Do your own work!!! While you may consult each other in your study groups, the submitted assignment should represent your own sole efforts.

Question 1 [40 points]
The following observations can easily be explained by invoking electrochemical principles. Rationalize these observations.

(a) Every big ocean-going liner (for example, the Titanic) has a big metallic chunk of aluminum welded to its hull. This chunk of aluminum has to be replaced every 7 to 10 years.

(b) A potential difference of between 70 - 85 mV is maintained across most biological cell walls. These cell walls are more permeable to K+ ions than to Na+ and Cl- ions. Generally, the concentration of K+ inside the cell wall is 23x that outside the cell wall.

(c) All corrugated iron sheets used for roofing are made up of a core of iron with a thin coat of zinc painted all around it.

(d) The standard potential of the simple water oxidation half reaction: \( \text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O}(l) \) is depressed by about 0.41 volts when it is run in the human body.

(e) Addition of 1.00 M Br\(^-\) ions to permanganate and acid (both at 1.00 M), shows a rapid formation of a yellowish-brown colored and evil-smelling liquid. Addition of Br\(^-\) ions, however, to the same mixture in a buffer that maintains a pH of 6.00 does not show anything as dramatic.

(f) Copper seems to have been universally chosen by most countries as a good metal to use for coins (money).

(g) Combining the standard hydrogen electrode (SHE) with the Hg\(_2^{2+}/2\text{Hg}(l)\) couple has the SHE as the anode. Is this correct? (Sketch the cell diagram). Evaluate the standard potential of this cell.

(a) After evaluating the standard electrode potential of the Fe\(^{2+}/Fe^{3+}\) couple combined with the Hg\(_2^{2+}/2\text{Hg}(l)\) couple, we are surprised by the direction of electron flow in a mixture that contains [Fe\(^{2+}\)] = 0.02 M; [Fe\(^{3+}\)] = 0.05 M and [Hg\(_2^{2+}\)] = 0.01 M

(b) A concentration cell can be created from two hydrogen electrodes. Make a crude sketch of this cell and give the cell reactions at both the anode and the cathode as well as the overall cell reaction. Is there any
difference between an electrolyte concentration cell or electrode concentration cell involving the SHE?
(c) Everyone agrees that the SHE is ungainly and clumsy. The new types of reference electrodes involve the insoluble-salt-type electrodes. Write the cell reactions for the silver-silver chloride electrode as well as the cell reactions for the calomel electrode.

Question 2 [40 points]
(a) The zero-current potential of the cell: Pt\(\text{H}_2(g)\text{HCl(aq)}\text{AgCl(s)}\text{Ag}\) is 0.368 V at 25 °C. What is the pH of the electrolyte solution?
(b) Calculate the solubility product and the solubility of AgBr at 298.15 K on the basis of the following standard electrode potentials:
\[
\begin{align*}
\text{AgBr(s)} + \text{e}^- & \rightarrow \text{Ag(s)} + \text{Br}^-(aq) & E^0 &= 0.0713 \text{ V} \\
\text{Ag}^+(aq) + \text{e}^- & \rightarrow \text{Ag(s)} & E^0 &= 0.7996 \text{ V}
\end{align*}
\]
(a) The emf of the cell
\[\text{Ag}^+\text{AgI(s)(aq)}\text{AgI(s)}\text{Ag}\]
is -0.9509 V at 25°C. Calculate the solubility and the solubility product of AgI at this temperature.
(a) An electrochemical cell \(\text{M(s)}\text{MCl(aq, 1.0 m)}\text{AgCl(s)}\text{Ag}\) where MCl is the chloride salt of the metal electrode, M, yields a cell potential of 0.2053 V at 298.15 K. What is the mean activity coefficient \(\gamma^\pm\) of the electrolyte MCl? [NB: \(E^0\) for the \(\text{M(s)}\text{M}^+\) electrode is 0.0254 V

Question 3 [20 points]
(a) The oxidation of lactate to pyruvate by the oxidized form of cytochrome-c (represented as c-(Fe\(^{3+}\)) is an important biological reaction. The following are relevant \(E^0\) values relating to pH 7 and 298.15 K.
\[
\begin{align*}
\text{pyruvate}^- + 2\text{H}^+ + 2\text{e}^- & \rightarrow 6 \text{lactate}^- & E^0 &= -0.19 \text{ V} \\
c-(\text{Fe}^{3+}) + \text{e}^- & \rightarrow 6 \text{c-(Fe}^{2+}) & E^0 &= + 0.254 \text{ V}
\end{align*}
\]
Calculate the equilibrium ratio: \([(c-(\text{Fe}^{2+}))^2[\text{pyruvate}^-])/(([c-(\text{Fe}^{3+}))^2[\text{lactate}^-])]\) at these conditions. Calculate, also, the ration at pH 6.
(a) The substance nicotinamide adenine dinucleotide (NAD\(^+\)) also plays an important role in biological systems. Under the action of certain enzymes it can react with a reducing agent and release a proton to the solution to form its reduced form, NADH. With pyruvate the reduced form NADH undergoes the reaction:
\[\text{NADH} + \text{pyruvate} + \text{H}^+ \rightarrow \text{NAD}^+ + \text{lactate}^-\]
The appropriate \(E^0\) values at 298.15 K and pH 7 are:
\[
\begin{align*}
\text{pyruvate} + 2\text{H}^+ + 2\text{e}^- & \rightarrow 6 \text{lactate}^- & E^0 &= -0.19\text{V} \\
\text{NAD}^+ + \text{H}^+ + 2\text{e}^- & \rightarrow 6 \text{NADH} & E^0 &= -0.34 \text{V}
\end{align*}
\]
Use these values to calculate \(\Delta G^0\) for the reaction and also the following equilibrium ratio at pH 7 and pH 8:
PostScript:
Some of the material in this assignment may not have been covered in class directly. The assignment requires the student to think and use his/her knowledge of the course to make the correct deductions. You may have to seek other text books for some of the solutions. As usual, I will be available and as cryptic as ever with my help up until after the assignment is due. I will then supply the class with the solutions.