CHM 3514
Assignment #1
PAM 3/29/01

B&F 2.4 What are the cell reactions and their emf's in the following systems?

(a) $Ag/AgCl/K^+$, Cl^- (1 M)//Hg_2Cl_2/Hg
(b) Pt/Fe^{3+}(0.01 M), Fe^{2+} (0.1M), HCl (1 M)//Cu^{2+}(0.1 M), HCl (1 M)/Cu
(c) Pt/H_2 (1 atm)/H^+, Cl^- (0.1 M)//H^+, Cl^- (0.1 M)/O_2 (0.2 atm)/Pt
(d) Pt/H_2 (1 atm)/ Na^+, OH^- (0.1 M)// Na^+, OH^- (0.1 M)/O_2 (0.2 atm)/ Pt
(e) $Ag/AgCl/K^+$, Cl^- (1 M)//K^+, Cl^- (0.1 M)/AgCl/Ag
(f) Pt/Ce^{3+} (0.01 M), Ce^{4+} (0.1 M), H_2SO_4 (1 M)//Fe^{2+} (0.01 M), Fe^{3+} (0.1 M), HCl (1 M)/Pt

B&F 2.6 Devise a cell for evaluating the solubility product of $PbSO_4$. Calculate the solubility product from the appropriate E^0 values at 25^0C.

1. Oxidation-Reduction reactions play significant roles in biochemistry. The conditions corresponding to standard state that are usually used in electrochemistry are inappropriate when meaningful thermodynamic information is to be derived for biochemical processes. (Why?) Since most biochemical processes occur under physiological conditions, it is necessary to redefine standard state to be at pH 7. What is the standard oxidation-reduction potential of the hydrogen reference electrode at biochemical standard state?
ANS: -0.41 V

2. (a) Devise an electrochemical cell to measure the solubility product for cuprous iodide, (b) diagram the cell that you have designed and (c) then calculate the solubility product of cuprous iodide at 25^o C.
ANS: Cu(s)/ Cu^+ (aq, 1 M), I^- (aq, 1 M)// I^-(aq, 1 M), K^+(aq, 1 M)/ CuI(s)/Cu(s)
$K_{sp} = 10^{-12}$

3. An electrochemical cell is formed by placing gold electrodes in separate beakers, connected through a salt bridge. One beaker contains a solution of ferrous sulfate, ferric sulfate, and sulfuric acid. The second beaker contains potassium permanganate, manganese(II) sulfate, and sulfuric acid. The concentration of all reagents is 0.1 M.
(a) Write the cell diagram.(b) Write the cell reaction.(c) Determine the cell potential.
ANS: Au/Fe^{2+}(aq, 0.1 M), Fe^{3+}(aq, 0.1 M)//MnO_4^-(aq, 0.1 M), Mn^{2+}(aq, 0.1 M)/Au
$5Fe^{2+} + MnO_4^- + 8H^+ = 5Fe^{3+} + Mn^{2+} + 4H_2O$
E = +0.65 V

4. Calculate the cell potential for the Daniell cell for [$ZnSO_4$] = 1.2 M and [$CuSO_4$] = 1.2 x 10^{-3} M.
ANS: +1.02 V

5. Using the Nernst equation and the table of standard reduction potentials provided (B&F Table C.1), calculate K_w.
ANS: $K_w = 10^{-14}$

6. In freshman chemistry class, the **diagonal rule** is often taught as a method of determining whether a redox reaction is spontaneous. The diagonal rule states that, at standard state, any species on the left of a given half-reaction will react spontaneously with any species that appears on the right of any half-reaction that is listed above it in a table of standard reduction potentials ordered such that potent reducing agents are at the top and potent oxidizing agents appear at the bottom.
Suppose that:

$$A + ne^- = B \qquad E_1^o$$
$$C + ne^- = D \qquad E_2^o$$

represents a partial excerpt from a table of standard reduction potentials at standard state.
a) State clearly what the diagonal rule is in terms of species A, B, C, and D, the standard state reduction potentials E_1^o and E_2^o. Be sure to clearly identify the net reaction you are discussing, what species are being oxidized/reduced, what species are acting as the oxidizing/reducing agents, and any salient thermodynamic parameters. (b) Show that the diagonal rule works using the above information. Consider:
i) E_1^o and E_2^o both positive
ii) E_1^o and E_2^o both negative
iii) E_1^o negative and E_2^o positive

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