17.19: Problems

1. Balance the following chemical equations assuming that they occur in aqueous solution.

(a) $Cu^0 + Ag^+ \rightarrow Cu^{2+} + Ag^0$

(b) $Fe^{2+} + Cr_2O_7^{2-} \rightarrow Fe^{3+} + Cr^{3+}$

(c) $Cr^{2+} + Cr_2O_7^{2-} \rightarrow Cr^{3+}$

(d) $Cl_2 + Br^- \rightarrow Cl^- + Br_2$

(e) $ClO_3 \rightarrow Cl^- + ClO_4^-$

(f) $I^- + IO_3^- \rightarrow I_2$

(g) $I^- + O_2 \rightarrow I_2 + OH^-$ (basic solution)

(h) $H_2C_2O_4^{2-} + MnO_4^- \rightarrow CO_2 + Mn^{2+}$

(i) $Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$

(j) $H_2O_2 + MnO_4^- \rightarrow Mn^{2+} + O_2$

(k) $PbO_2 + Pb^0 + H_2SO_4 \rightarrow PbSO_4$

(l) $Fe^{2+} \rightarrow Fe^0 + Fe^{3+}$

(m) $Cu^{2+} + Fe^0 \rightarrow Cu^0 + Fe^{3+}$

(n) $Al^0 + OH^- \rightarrow H_2 + Al(OH)_4^-$ (basic solution)

(o) $Au^0 + CN^- + O_2 \rightarrow Au(CN)_4^-$ (basic solution)

(p) $Cu^0 + HNO_3 \rightarrow Cu^{2+} + NO_2$

(q) $Al^0 + Fe_2O_3 \rightarrow Al_2O_3 + Fe^0$

(r) $I^- + H_2O_2 \rightarrow I_2 + OH^-$ (basic solution)

(s) $HFeO_4^- + Mn^{2+} \rightarrow Fe^{3+} + MnO_2$

(t) $Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-}$

(u) $Cu^+ + O_2 \rightarrow Cu^{2+} + OH^-$ (basic solution)

2. Calculate the equilibrium constant, K_a, for the reaction $Cu^0 + 2Ag^+ \rightarrow Cu^{2+} + 2Ag^0$. An excess of clean copper wire is placed in a 10^{-1} $\underline{\text{M}}$ silver nitrate solution. Assuming that molarities adequately approximate the activities of the ions, find the equilibrium concentrations of Ag^+ and Cu^{2+}.

3. The standard potentials for reduction of Fe^{2+} and Fe^{3+} to Fe^0 are

$$Fe^{2+} + 2e^- \rightarrow Fe^0 \mathcal{E}^o = -0.447 \text{ v}$$

$$Fe^{3+} + 3e^- \rightarrow Fe^0 \mathcal{E}^o = -0.037 \text{ v}$$

(a) Find the standard potential for the disproportionation of Fe^{2+} to Fe^{3+} and Fe^0: $Fe^{2+} \rightarrow Fe^0 + Fe^{3+}$.

(b) Find the standard half-cell potential for the reduction of Fe^{3+} to Fe^{2+}: $Fe^{3+} + e^- \rightarrow Fe^{2+}$.

4. The standard potential for reduction of tris-ethylenediamineruthenium (III) to tris-ethylenediamineruthenium (II) is

$$[Ru(en)_3]^{3+} + e^- \rightarrow [Ru(en)_3]^{2+} \mathcal{E}^o = +0.210 \text{ v}$$

Half-cell potential data are given below for several oxidants. Which of them can oxidize $[Ru(en)_3]^{2+}$ to $[Ru(en)_3]^{3+}$ in acidic ($[H^+] \approx \tilde{a}_{H^+} = 10^{-1}$) aqueous solution?

(a) $UO_2^{2+} + e^- \rightarrow UO_2^+$ $\mathcal{E}^o = +0.062 \text{ v}$

(b) $[Ru(NH_3)_6]^{3+} + e^- \rightarrow [Ru(NH_3)_6]^{2+}$

$$\mathcal{E}^o = +0.10 \text{ v}$$

(c) $Cu^{2+} + e^- \rightarrow Cu^+ \ \ \mathcal{E}^o = +0.153 \text{ v}$

(d) $AgCl + e^- \rightarrow Ag^0 + Cl^- \ \ \mathcal{E}^o = +0.222 \text{ v}$

(e) $Hg_2Cl_2 + 2e^- \rightarrow 2Hg^0 + 2Cl^-$

$$\mathcal{E}^o = +0.268 \text{ v}$$

(f) $AgCN + e^- \rightarrow Ag^0 + CN^- \ \ \mathcal{E}^o = -0.017 \text{ v}$

(g) $SnO_2 + 4H^+ + 4e^- \rightarrow Sn^0 + 2H_2O$

$$\mathcal{E}^o = -0.117 \text{ v}$$

5. An electrochemical cell is constructed in which one half cell is a standard hydrogen electrode and the other is a hydrogen electrode immersed in a solution of $pH = 7 \ \left([H^+] \approx \tilde{a}_{H^+} = 10^{-7}\right)$. What is the potential difference between the terminals of the cell? What chemical change occurs in this cell?

6. The standard half-cell potential for the reduction of oxygen gas at an inert electrode (like platinum metal) is

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O\mathcal{E}^o = +1.229 \text{ v}$$

An electrochemical cell is constructed in which one half cell is a standard hydrogen electrode and the other cell is a piece of platinum metal, immersed in a 1 $\underline{M}$ solution of $HClO_4$, which is continuously in contact with bubbles of oxygen gas at a pressure of 1 bar.

(a) What is the potential difference between the terminals of the cell? What chemical change occurs in this cell?

(b) The 1 $\underline{M}$ $HClO_4$ solution in part (a) is replaced with pure water $\left([H^+] \approx \tilde{a}_{H^+} = 10^{-7}\right)$. What is the potential difference between the terminals of this cell?

(c) The 1 $\underline{M}$ $HClO_4$ solution in part (a) is replaced with 1 $\underline{M}$ $NaOH$ $\left([H^+] \approx \tilde{a}_{H^+} = 10^{-14}\right)$. What is the potential difference between the terminals of this cell?

7. A variable electrical potential source is introduced into the external circuit of the cell in part (a) of problem

6. The negative terminal of the potential source is connected to the oxygen electrode and the positive terminal of the potential source is connected to the standard hydrogen electrode. If the applied electrical potential is 1.3 v, what chemical change occurs? What is the minimum electrical potential that must be applied to electrolyze water if the oxygen electrode contains a 1 $\underline{M}$ $HClO_4$ solution? A neutral ($pH = 7$) solution? A 1 $\underline{M}$ $NaOH$ solution?

8. Two platinum electrodes are immersed in 1 $\underline{M}$ $HClO_4$. What potential difference must be applied between these electrodes in order to electrolyze water? (Assume that $P_{O_2} = 1 \text{ bar}$ and $P_{H_2} = 1 \text{ bar}$ at their respective electrodes, as will be the case as soon as a few bubbles of gas have accumulated at each electrode.) What potential difference is required if the electrodes are immersed in pure water? In 1 $\underline{M}$ $NaOH$?