Worksheet 9

Some things to note that are often misunderstood:

- Anions flow through the salt bridge into the anode compartment while cations flow into the cathode compartment to maintain electroneutrality.
- The anode of a voltaic cell is negative (like an anion), and the cathode is positive (like a cation). Electrons move from the negative anode through an external circuit to the positive cathode.
- When a chemical equation is balanced by the half-reaction method, the number of electrons that occur on both sides of the balanced equation (before canceling) is equal to the value of *n*.
- For a spontaneous reaction ΔG is negative but *E* is positive.
- Standard conditions for E° , the standard cell potential, are identical with standard conditions for the ΔG° , ΔH° , and ΔS° .
- Every reduction half-cell reaction has a corresponding standard reduction potential, E°_{red} . If the reaction is reversed, it becomes an oxidation half-cell reaction with a corresponding standard oxidation half-cell potential, E°_{ox} . For any given half-cell reaction, $E^{\circ}_{ox} = -E^{\circ}_{red}$.
- Half-cell potentials are *never* multiplied by a coefficient when used in the equation $E^{\circ}_{cell} = E^{\circ}_{ox} + E^{\circ}_{red}$.
- The general form of the Nernst equation is used to correct the standard cell potential for concentrations other than 1 M, partial pressures other than 1 atm, or a temperature other than 25°C. This form of the Nernst equation applies only to reactions occurring at 25°C.
- The Nernst equation relates the concentrations of any chemical species, including H⁺, to cell potential.

1. Describe voltaic cells that use the following reactions. In each case, write the anode and cathode half-reactions, and sketch the experiment setup. Label the anode and cathode, identify the sign of each electrode, and indicate the direction of electron and ion flow.

(a)
$$\operatorname{Cd}(s) + \operatorname{Sn}^{2+}(aq) \longrightarrow \operatorname{Cd}^{2+}(aq) + \operatorname{Sn}(s)$$

(b) 2 Al(s) + 3 Cd²⁺(aq)
$$\rightarrow$$
 2 Al³⁺(aq) + 3 Cd(s)

(c)
$$\operatorname{Cr}_2 \operatorname{O}_7^{2-}(aq) + 6 \operatorname{Fe}^{2+}(aq) + 14 \operatorname{H}^+(aq) \longrightarrow 2 \operatorname{Cr}^{3+}(aq) + 6 \operatorname{Fe}^{3+}(aq) + 7 \operatorname{H}_2 O(l)$$

2. Write the shorthand notation for each cell in Problem 1.

3. Write balanced equations for the electrode and overall cell reactions in the following voltaic cells.

(a)
$$Co(s) | Co^{2+}(aq) || Cu^{2+}(aq) | Cu(s)$$

(b) $\operatorname{Fe}(s) | \operatorname{Fe}^{2^+}(aq) || \operatorname{O}_2(g) | \operatorname{H}^+(aq), \operatorname{H}_2\operatorname{O}(l) | \operatorname{Pt}(s)$

4. The silver oxide-zinc battery used in hearing aids delivers a voltage of 1.60 V. Calculate the free-energy change (in kilojoules) for the cell reaction:

$$Zn(s) + Ag_2O(s) \rightarrow ZnO(s) + 2 Ag(s)$$

5. Calculate E° for each of the following reactions, and tell which are spontaneous under standard-state conditions.

(a) 2 Fe²⁺(aq) + Pb²⁺(aq)
$$\rightarrow$$
 2 Fe³⁺(aq) + Pb(s)

(b)
$$Mg(s) + Ni^{2+}(aq) \rightarrow Mg^{2+}(aq) + Ni(s)$$

6. The Nernst equation applies to both cell reactions and half-reactions. For the conditions specified, calculate the potential for the following half-reactions at 25°.

(a)
$$I_2(s) + 2 e^- \rightarrow 2 I^-(aq); [I^-] = 0.020 M$$

(b)
$$\operatorname{Fe}^{3+}(aq) + e^{-} \longrightarrow \operatorname{Fe}^{2+}(aq); [\operatorname{Fe}^{3+}] = [\operatorname{Fe}^{2+}] = 0.10 \text{ M}$$

(c)
$$\operatorname{Sn}^{2+}(aq) \to \operatorname{Sn}^{4+}(aq) + 2 \text{ e}^{-}; [\operatorname{Sn}^{2+}] = 1.0 \times 10^{-3} \text{ M}, [\operatorname{Sn}^{4+}] = 0.40 \text{ M}$$

(d) 2 $\operatorname{Cr}^{3+}(aq) + 7 \operatorname{H}_2O(l) \longrightarrow \operatorname{Cr}_2O_7^{2-}(aq) + 14 \operatorname{H}^+(aq) + 6 \operatorname{e}^-; [\operatorname{Cr}^{3+}] = [\operatorname{Cr}_2O_7^{2-}] = 1.0 \operatorname{M}, [\operatorname{H}^+] = 0.010 \operatorname{M}$

7. The following cell has a potential of 0.27 V at 25° C:

$$Pt(s) | H_2(1 \text{ atm}) | H^+(? M) || Ni^{2+}(1 M) | Ni(s)$$

What is the pH of the solution in the anode compartment?

8. Calculate the equilibrium constant at 25°C for the disproportionation of Hg_2^{2+} :

$$\operatorname{Hg_2}^{2^+}(aq) \longrightarrow \operatorname{Hg}(l) + \operatorname{Hg}^{2^+}(aq)$$