Electrochemistry

- Topics Covered
  - Spontaneity of redox reactions
  - Effect of concentration on cell emf
- Homework
  - Read 20.7-20.8
  - Exercises 39, 43, 49, 51, 57

Spontaneity of Redox Reactions

- Any reaction that can occur in a voltaic cell to produce a positive emf must be spontaneous
- In general, we can write:
  - $E° = E°_{red}$(reduction process) - $E°_{red}$(oxidation process)
- A positive value of E indicates a spontaneous process and a negative value of E indicates a nonspontaneous one

Sample Problems

- Determine whether or not the following reactions are spontaneous under standard conditions
  - $Cu(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + H_2(g)$
    - Answer: Nonspontaneous
  - $Cl_2(g) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(s)$
    - Answer: Spontaneous

EMF and Free Energy Change

- Gibbs free energy and emf of a redox reaction are related in the following way:
  - $\Delta G = -nFE$ or $\Delta G^\circ = -nFE^\circ$ (at standard conditions)
  - n is a positive number that represents the number of electrons transferred in the reaction
  - F is called Faraday's constant and is the quantity of charge on 1 mol of electrons
    - 1 F = 96,500 C/mol = 96,500 J/V-mol
  - A positive value of E and a negative value of ΔG both indicate that a reaction is spontaneous

Sample Problems

- Calculate ΔG° for the following reactions using standard reduction potentials.
  - $4Ag(s) + O_2(g) + 4H^+(aq) \rightarrow 4Ag^+(aq) + 2H_2O(l)$
    - Answer: -170 kJ/mol
  - $3Ni^{2+} + 2Cr(OH)_3 + 10OH^- \rightarrow 3Ni + 2CrO_4^- + 8H_2O$
    - Answer: 87 kJ/mol

Effect of Concentration on Cell EMF

- As a voltaic cell discharges, reactants are consumed and products are generated, so the concentrations of these substances change
- The emf progressively drops until E = 0, at which point the cell is “dead”
- At that point the concentrations of reactants and products are in equilibrium

The Nernst Equation

- To find the emf of a cell under nonstandard conditions we can use the Nernst equation:

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF}\ln Q \quad or \quad E_{cell} = E^{\circ}_{cell} - \frac{0.0592}{n}\log Q \,@\, 298\ K$$

- Q is the reaction quotient

Sample Problems

- Given the following reaction:
  - $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^-(aq) \rightarrow 2Cr^{3+}(aq) + 3I_2(s) + 7H_2O(l)$
- Calculate the emf at 298 K when $[Cr_2O_7^{2-}]$ = 2.0 M, $[H^+]$ = 1.0 M, $[I^-]$ = 1.0 M, and $[Cr^{3+}]$ = 1.0 x 10^{-5} M.
  - Answer: 0.89 V
- If the voltage of a Zn-H^+ cell is 0.45 V at 25°C when $[Zn^{2+}]$ = 1.0 M and P_{H2} = 1.0 atm, what is the concentration of H^+?
  - Answer: 5.8 x 10^{-6} M

Sample Problems

- Using standard reduction potentials, calculate the equilibrium constant for the oxidation of Fe^{2+} by O_2 in acidic solution
  - Answer: 1×10^{31}
- Calculate the equilibrium constant for the following reaction:
  - $Br_2(l) + 2Cl^-(aq) \rightarrow Cl_2(g) + 2Br^-(aq)$
    - Answer: 1.2×10^{-10}