Electrochemistry

Assign oxidation numbers to all elements in the following compounds:

$KMnO_4$	Fe_2O_3	H_2O_2
$NiCl_2$	Fe_3O_4	Cu_2O
FeO	$Na_2C_2O_4$	BeH_2

Identify the oxidizing agent, the reducing agent, the substance being oxidized, and the substance being reduced in the following reaction:

$$SiCl_4(l) + 2Mg(s) \leftrightarrows 2MgCl_2(s) + Si(s)$$

Balance the following reaction in acid

$$As_2O_3(s) + NO_3^-(aq) \leftrightarrows H_3AsO_4(aq) + NO(g)$$

Balance the following reaction in base

$$CN^-(aq) + MnO_4^-(aq) \leftrightarrows CNO^-(aq) + MnO_2(s)$$

Electrochemical Cells

Any device in which a redox reaction occurs is an Electrochemical Cell

What is the difference between an Electrolytic Cell and a Galvanic (Voltaic) Cell?

The Daniell Cell

	Left side	Right side
Half Reaction		
Change		
Electrode		
Charge on electrode		
Ion Flow from Salt Bridge		

What is the purpose of the salt bridge?

Standard Reduction Potentials

Who is SHE? (The Standard Hydrogen Electrode)

Copper and Zinc Cells

Calculate the cell potential for electrochemical cells based on the following reactions:

1) $Ag^{+}(aq) + Cu(s) \leftrightarrows Cu^{2+}(aq) + Ag(s)$

2) $Zn^{2+}(aq) + Ni(s) \leftrightarrows Zn(s) + Ni^{2+}(aq)$

3) $F_2(aq) + Br^{-}(aq) \leftrightarrows F^{-}(aq) + Br_2(aq)$

4) $Zn(s) + 2H^{+}(aq) \leftrightarrows Zn^{2+}(aq) + H_2(g)$

5)$Cu(s) + 2H^{+}(aq) \leftrightarrows Cu^{2+}(aq) + H_2(g)$

Line Notation

Consider the Daniell Cell

In shorthand notation we write this:

How about a reaction involving a gas?

Let's get a little complicated:

Summing it all up

	Keq	ΔG°	E°
Spontaneous Reaction			
Non-Spontaneous Reaction			

Electrolysis

Michael Faraday

Faraday = F = 96, 485 coulombs/mole electrons

Let's learn some units from Physics

Name	Unit of?	Basis	Derived From

Electrolysis problems are much the same as stoichiometry problems. Watch the units!

1) What mass of zinc (II) ion will be reduced by one mole of electrons?

2) How many moles of electrons would be required to reduce 0.100 g of Eu^{3+} to the metal?

3) What mass of molten sodium would be produced by electrolyzing molten NaBr with 1.5 amps for 3.0 hours?

4) What mass of copper can be produced by the electrolysis of a copper(II) sulfate solution for 1.00 hours at a current of 100.0 amps?

5) Calculate the amount of current necessary to deposit 0.50 g of platinum from a solution of $PtCl_6^{2-}$ in 5.0 hours?

6) The same quantity of charge that deposited 0.583 g of silver was passed through a solution of a gold salt and 0.355 g of gold was formed. What is the oxidation state on gold in this solution?

7) A solution containing a 3+ ion is electrolyzed by a 5.0 A current for 10.0 minutes. If 1.18 g of the metal is plated out what is the molar mass of the metal?

8) It took 74.6 seconds for a 2.50 A current to plate out 0.1086 g of a metal from a solution of M^{2+}. What is the metal?

9) What volume of F_2 gas at 25°C and 1.00 atmospheres is collected when molten KF is electrolyzed for 2.00 hours at 10.0 amps?

10) What volumes of hydrogen and oxygen are collected at STP by electrolyzing water for 15.0 minutes with a current of 2.50 amps?

EMF and Free Energy

What determines if a reaction happens?

How can we relate EMF and Free Energy?

Who is this Nernst guy anyway?

Equilibrium Constants

Units can be a problem

Calculate ΔG^o and the Equilibrium constant for the following reactions:

$Ag^+(aq) + Cu(s) \leftrightarrows Cu^{2+}(aq) + Ag(s)$

$Zn^{2+}(aq) + Ni(s) \leftrightarrows Zn(s) + Ni^{2+}(aq)$

Consider the following reaction at 25°C:

$$Fe\ (s) + Cd^{2+}\ (aq) \leftrightarrows Fe^{2+}\ (aq) + Cd\ (s)$$

a) What is the standard EMF for the reaction?

b) What is the value of $\Delta G°$ for this reaction?

c) What is the equilibrium constant expression for the reaction?

d) What is the value of the equilibrium constant for this reaction at 25°C?

e) What is the EMF when the concentration of iron (II) is 0.010 M and cadmium (II) is 1.0 M?

f) What is the EMF when the concentration of iron (II) is 1.0 M and cadmium (II) is 0.010 M?

g) What is the value of ΔG for this reaction when the concentration of iron (II) is 1.0 M and cadmium (II) is 0.010 M?

Electrolysis of Water

What happens when you run electricity through water?

There are three reactions that we are concerned with here:

$2H_2O(l) \leftrightarrows O_2(g) + 4H^+(aq) + 4e^-$ E°= —1.23V

$2H_2O(l) + 2e^- \leftrightarrows H_2(g) + 2OH^-(aq)$ E°= —0.83V

$H_2(g) \leftrightarrows 2H^+(aq) + 2e^-$ E°= 0.00 V

To make this work we must add some electrolyte (usually H_2SO_4). Why?

What does SHE have to say about this?

The EMF for this is negative is that cool? Think about the driving forces.

What if it were a solution of NaCl instead of water? What species are really present?

What are the **four** possible reactions?

Anode (oxidation)

Cathode (reduction)

Which two actually happen? Why?

Overvoltage

Imagine you had a mixture of three ions:

$Ag^{+}(aq)$ $Cu^{2+}(aq)$ $Zn^{2+}(aq)$

$Ag^{+}(aq) + e^{-} \leftrightarrows Ag$ $E° = 0.80$ V

$Cu^{2+}(aq) + 2e^{-} \leftrightarrows Cu$ $E° = 0.34$ V

$Zn^{2+}(aq) + 2e^{-} \leftrightarrows Zn$ $E° =- — 0.76$ V

If you run a current through a solution containing all three ions which one would plate out first?

REDOX Titration

The Purple Juice!

Standardization

Hydrogen Peroxide

Consider the standardization of some $KMnO_4$ with $Na_2C_2O_4$.

	Sample 1	Sample 2	Sample 3
Mass of $Na_2C_2O_4$ Used	5.5736 g	5.7285 g	5.7955 g
Initial Buret Reading	1.23 mL	1.26 mL	1.32 mL
Final Buret Reading	58.48 mL	58.26 mL	59.02 mL
Volume of $KMnO_4$ used			
Moles of $Na_2C_2O_4$ Used			
Moles $KMnO_4$ Present			
Molarity of $KMnO_4$			
Average Molarity of $KMnO_4$			

Calculations:

Consider the titration of some hydrogen peroxide with some permanganate ion.

	Sample 1	Sample 2	Sample 3
Mass of Solution Used	10.00 mL	10.00 mL	10.00 mL
Initial Buret Reading	7.83 mL	13.71 mL	19.20 mL
Final Buret Reading	13.71 mL	19.20 mL	24.30 mL
Volume of $KMnO_4$ used			
Moles of $KMnO_4$			
Moles H_2O_2 Present			
Mass of H_2O_2			
Percentage of H_2O_2			
Average Percentage of H_2O_2			

Calculations: