Textbook Chapters for Exam 4

All of Chapter 11 and Chapter 15 (except section 7). Sections 1-3 in Chapter 11 were covered on Exam 3 but you still need to know that material - especially how to get standard potential and how to interpret the shorthand notation for an electrochemical cell. You're responsible for any material covered in class whether it was on the homework or not. This review sheet covers most everything we have done. Also remember that no equations are given on the exams. Values for equilibrium constants and any standard potentials are given where needed.

Chapter 11 - Electrochemistry

The majority of questions will come from sections 4-8 but you still need to know the basics out of sections 1-3. I'm repeating some of that material here (from review 3).

Know what a redox reaction is. What is being oxidizing and what is being reduced? What is the oxidizing agent and what is the reducing agent?

What is a half-reaction? Why is it so useful? Know how to write half-reactions for both oxidations and reductions.

Know how to combine 2 half-reactions to give an overall cell reaction. (electron balance?) This is essentially the same as what was stated above except that in electrochemical cells we run the 2 half-reactions in 2 different locations - that is we have them physically separated.

Know the difference in voltaic vs electrolytic cells

Know how to write half-reactions for both oxidations and reductions.

Know how to combine 2 half-reactions to give an overall cell reaction. (electron balance?)

Know how to draw a picture of both a voltaic and an electrolytic cell if given the shorthand notation.

anode | anodic solution || cathodic solution | cathode

where the "|" are phase changes and "||" is a salt bridge.

What's the sign convention used for the cathode and anode?

What's the significance of the SHE?

What's an inert electrode? Used for what? Pt in the SHE, graphite in a dry cell

Know what standard conditions are and how it is symbolized (same as always).

Calculations, how to get:

- E^0 for any half-reaction (look it up in a table if it is not given in the question itself).
- E^0 for any overall cell reaction. $E^0_{cell} = E^0_{red} + E^0_{ox}$

remember that Zumdahl uses cathode potential minus the anode potential which is the same as above. My oxidizing potential is the "minus the anode potential". Bottom line is that you always leave the reduction reaction as is off the table but you must FLIP the table value for an oxidation and when you FLIP, you must change the sign.

How to convert between ΔG, E, and K.

$$\Delta G^0 = -nFE^0 \qquad \Delta G^0 = -RT\ln K$$

$$nFE^0 = RT\ln K$$

"n" here is the # of total e^- cancelled out in the whole rxn.

Non-Standard Conditions : Nernst Eq.

Know how to use the Nernst Equation to get cell potentials at non standard conditions. Also know how to calculate an unknown concentration from a given non-standard potential. Here are 3 forms of the Nernst Equation:

$$E = E^0 - \frac{RT}{nF}\ln Q \qquad E = E^0 - \frac{0.0257}{n}\ln Q$$

$$E = E^0 - \frac{0.05916}{n}\log Q$$

Electrolysis

When you pass current through an electrolytic cell you are pushing and pulling electrons. You use your power source to PULL electrons out of the anodic solution via the anode (oxidation) and then PUSH electrons into the cathodic solution via the cathode (reduction). Here, the charge on the electrode is positive (+) for the anode and negative (-) for the cathode. This is the opposite sign convention as for voltaic cells.

You can count moles of electrons via a calculation using current (I), time (t), and the faraday constant (F). Unit analysis will get you there although the following equation works well also.

$$\frac{I \cdot t}{F \cdot n} = mol\ of\ rxn$$

From here you can easily calculate the number of grams of metal that are electroplated during the process. You should also be able to calculate the number of liters of gas formed during the process if there is a gas forming reaction. Remember, you'll get your moles of gas from the previous equation and then you'll plug that answer into the Ideal Gas Law for your answer.

How to calculate K (or K_{sp}) for a reaction using electrochemical data. The key is to find the 2 half-reactions that add up to equal the overall K_{sp} reaction. Remember, all K_{sp} reactions are just dissociations: $MX(s) \rightleftharpoons M^+ + X^-$

What is corrosion? What are some methods of protecting against corrosion?

Know the general concepts of how batteries work. Read book and refer to class notes. What's the difference in a primary, secondary, and fuel cell? Know examples of each type as mentioned in the textbook - names only here. However, you DO need to know the specific reactions that drive a lead storage battery. Know how the reactions work during discharge and during recharge.

What would make one battery capable of delivering more current than another if they have the same potential (voltage)?

Chapter 15 - Kinetics

Refer to equation sheet that is available on our web site for formulas. We also are skipping section 7 in Chapter 15.

Know how to express (show) the rate of a reaction in terms of ANY of the reactants or products.
This also means being able to calculate one rate from another. Zumdahl goes through all this for the decomposition of NO2 in section 15.1

What FOUR factors affect reaction rates? I gave these in class.

Know how to obtain the rate law and value of k by the method of initial rates (p 712). This is where you analyze those tables of data.

Know how reaction order relates to concentration for 0, 1st, and 2nd order reactions.

Know how to calculate for any of the different variables in the integrated rate law equations. Here are a few cases:

Know how to calculate the concentration of a reactant (or product) at a particular time (t).

Know how to calculate the value of the rate constant (k) using the proper integrated rate equation.

Know how to calculate the time (t) required to reach a particular final concentration.

Know how to calculate the half-life (what is it?) for a particular reactant.

Can you calculate the concentration of a PRODUCT after a given amount of time? You should be able to.

What should you PLOT to get a straight line for 0, 1st, and 2nd order kinetics?

Know the two criteria for an effective collision. (p 736 and notes)

Know how to interpret and write a plausible Reaction Mechanism for a chemical reaction. What are elementary steps? What is the molecularity of a reaction (uni- or bimolecular?). What is the rate-determining step and how does that affect your version of the rate law. What is a pre-equilibrium condition when looking at a multistep mechanism? This is a fast reaction preceding a slow reaction and is in Zumdahl starting on page 729. Know how to use these fast equilibrium steps to "get rid of" your intermediate in your rate equation.

DON'T worry about section 15.7 - the Steady State Approximation.

How do you get the kinetic version of an equilibrium constant? Zumdahl comes close to showin this on page 730 but he stops short. The bottom line is that you set the forward and reverse rate equations equal to each other and then collect concentration terms on the right and the rate constants on the left. You get the following...

for $A \rightleftharpoons B$ $\qquad k_f[A] = k_r[B]$

$k_f/k_r = [B]/[A]$

and therefore the equilibrium constant $K = k_f/k_r$

Temperature Dependence of *k*

Arrhenius Equation: $k = Ae^{-E_a/RT}$

This shows the temperature dependence and the activation energy dependence of k. And, there's that special pre-exponential factor A in it. This will be different for every reaction - of course E_a is different too. We know that for relatively small temperature changes that A and E_a do not change much witch allows us to algebraically get rid of the A and write:

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

This is another form of the Arrhenius equation - one in which you should now be very familiar with (remember the Claussius-Clapeyron and the van't Hoft eqations?). Anyway, Know it!

Know transition state theory (activated complex) and how it relates to a potential energy diagram - where does it occur?

Be able to interpret information from a potential energy diagram: values for ΔH, (or ΔE or ΔG) and $E_{a,f}$ and $E_{a,r}$, this is also know as a "reaction profile".

Catalysis

How do catalysts affect reaction rates? How is this represented on a potential energy diagram? What is the difference in a homogeneous and a heterogeneous catalyst? How does a catalyst affect the thermodynamics of a reaction ? What are catalysts in living systems called? (see p 744-745)