## Textbook Chapters for Exam 4

Chapter 11, sections 1-5 and 7 (no sections 6 and 8). Chapter 15 (except section 7). 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 so you need to know them**. Values for equilibrium constants and any standard potentials are given where needed.

## Chapter 11 - Electrochemistry

I'm repeating this information from the exam 3 review sheet because it is still relevant.

Remember your redox chemistry - Chapter 4. Know the basic concepts that were presented on homework 12 (Redox Rxn Review).

Know how to assign oxidation numbers to all the elements in a given formula.

Know how to balance a redox equation in acid.

What is the difference in oxidation and reduction. KNOW your definitions here!

Know what a redox reaction is. What is being oxidized 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. $\quad E^0_{\text{cell}} = E^0_{\text{red}} + E^0_{\text{ox}}$

    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 $\Delta G$, $E$, and $K$.
$$\Delta G^0 = -nFE^0 \qquad\qquad \Delta G^0 = -RT \ln K$$

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

"$n$" 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:

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

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

## 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. Know how to solve for any of those variables (*I, t, n*, and *mol*) in that equation above. Remember, sometimes we work backwards from the amount to time, current, or even number of electrons.

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:   $MX(s) \rightleftharpoons M^+ + X^-$

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 and from my lecture - 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 all the formulas you need to know. 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 $NO_2$ 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. 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. (hint: use stoichiometry! the amounts LOST as reactants must relate to the amounts GAINED in products.)

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

## Collision Theory

Know the two criteria for an effective collision. (p 736 and notes). Part of this theory involves the graphical depiction of the energy criteria (aka, the activation energy). This is shown as $E$a on a potential energy diagram (Figure 15.11 on page 737) or on a distribution diagram (Figure 15.12, p 737).

## Reaction Mechanisms

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. This means that absolutely nothing will be on the exam about that subject.

How do you get the kinetic version of an equilibrium constant? Zumdahl comes close to showing this but he stops a little 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...
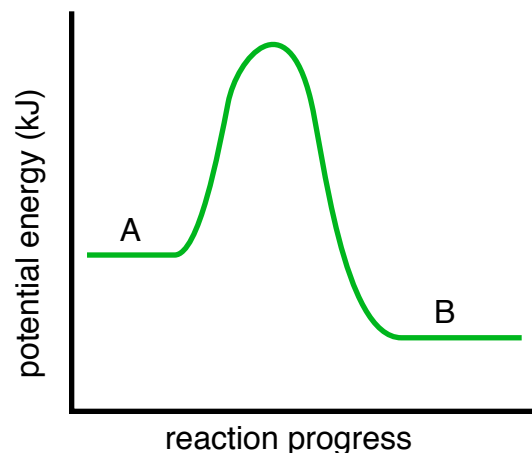
for   $A \rightleftharpoons B$        $k_f[A] = k_r[B]$

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

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

## Potential Energy Diagrams

These are the plots that show potential energy of the reactants and products and the transition state in between the two. See Figure 15.11 in Zumdahl for a good example, plus I did go over this in class. Here's a A goes to B example as a single step:



Know HOW to interpret the diagram. How to get $\Delta E$ and $E_{a,f}$ and $E_{a,r}$. Know transition state theory (activated complex) and how it relates to a potential energy diagram - where does it occur?

Sometimes the "potential energy" is different thermodynamic state functions, so you could be dealing with $\Delta H$, $\Delta E$, or $\Delta G$ on this diagram (the energy difference between A and B in the diagram above).

Also know how a multistep reaction would look on a diagram. I showed this in class. Zumdahl only shows an example of a 2 step reaction scheme in Exercise 75(d) at the end of the chapter - there is a picture there. Notice the 2 humps in the middle. Those "humps" are the 2 transition states for the 2 steps in the mechanism.

## Temperature Dependence of *k*

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

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?). And, let's remember that half-life is inversely proportional to $k$ so that we can also use half-life ratios in place of the $k_2/k_1$ ratio...

$$\ln\left(\frac{t_1}{t_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Note the "flipping" of the positions for $t_1$ and $t_2$ which are the half-lives at $T_1$ and $T_2$. One more thing... those times don't have to be half-life times. Any kind of time will work: quarter-life, third-life, 3/7th's-life... any convenient stopping point. Think of it like running a race. You can put the finish line anywhere you want and time the runners. As long as the reference points are the same, you can use ratios of times ($t_1/t_2$) in place of the rate constant ratios ($k_2/k_1$). Just make sure you remember to put them in the correct positions. Remember, the FASTEST reaction will have the SMALLEST time and vice-versa. No matter what your "finishing line" is, rate is always inversely proportional to time which means $k$ is proportional to $1/t$.

## 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? There is a whole 2 page spread on this in your book called "Chemical Insights" (in section 15.9).

How does catalysis effect the distribution plot? Take a look at Figure 15.16 in this section. Note how the activation energy is smaller when catalyzed. This means that more of the molecules have sufficient energies to react.

**Remember to take a look a the Echem and Kinetics Formula sheet that I have on our web page under help sheets.**