October 7, 2003

Teacher: (reading from page on overhead)

Teacher: some of you took the kiersey test (Example on board.) for my class. Those letters tell me about your learning style. This time it is different from what my previous classes have done, meaning I have a lot more NTs, then SPs. I like the CSB, because it gives the feedback of doing a good job. (Reading from page relating to Kiersey) This just reminds us how different we are and I try to meet the needs of all my students. This helps me get a flavor of the class.

We are into chapter 16 and I hope that we can move on to chapter 17.
Mechanism is that series of steps, by which reactants turn into products. We are concerned in the steps in which bonds are broken. We were working on this (Example on board.) one and looked at the experiments. When the first step is the slow step, things are nice and oriented.

1. A bounces into B and forms AB (slow)
2. A into C and makes AC (fast)

You should get AB and AC… But in this, you should look at only the slow step, when it’s the first step. You look here and at the reactant. This says a molecule of A collides with B to make AB. When you increase the concentration of A or B, then you will have an increase of collisions. Now this cannot be because the rate law of expressions does not agree. Now, suppose we have them in equilibrium (Example on board.) like this:

\[
\begin{align*}
A + B & \rightleftharpoons AB \quad \text{fast equil.} \\
AB + C & \rightarrow ABC \quad \text{(called the intermediate) slow} \\
ABC + A & \rightarrow AC + AB \quad \text{fast}
\end{align*}
\]

Rate depends on slow step! Rate is as follows and you see that this (Example on board.) is not a reactant. Rate law expression must be a function of reactants (and maybe a catalyst)
We can look at chapter 17. This chapter is based on equilibrium (Example on board.) and looks like this. **Conventional** and **concentration** are two key terms that will be used in this chapter. In this chapter the rate depends on T.

Now, going back to our problem… From step 1, we can write (Example on board.). Solve for [AB] and substitute. [AB = Kc [A] [B]]. We see the little k, and then can use the k (prime) 1. K=constant… Our rate law expression is this (Example on board.) and we can write it this way. You see A B and C, so this is a possible mechanism; by proving the intermediate exists, and then we can know this is our mechanism. I will be giving you many mechanisms and you will need to be able to find tm.

We know the rate of reaction is controlled by:
1. Nature of reactants,
2. Concentration of reactants (not straightforward),
3. Temperature.

Consider 1-step reaction mechanism (Example on board.) and add heat, then the rate is k [And [But]]. When you add heat, they move faster and faster. The shape of the diagram will change.

_How does temperature affect the diagram?_ It does not! It does not affect the delE, but it goes faster. Why? As the temperature goes up, the molecules bounce around more.
At higher temperatures, more and more molecules have the necessary energy to make it over the hump. They have the necessary activation energy, $E_a$, to make and break bonds. The $E_a$ does not change with temperature, it changes only with the mechanism.

A man named Arrhenius developed this (Example on board.) theory as we can see. We know that $k$=rate constant and that equals $Ae$, $e$ is the base for $\ln$. As $T^\uparrow$, $k^\uparrow$ too. I want you to be able to do the math, but not to memorize. (Example on board.).

\[
\text{Natural log (ln) } \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{E_a}{R} \left( \frac{T_2-T_1}{T_1T_2} \right)
\]

*What is the activation energy, $E_a$, for this reaction?* (Example on board.).

We have $k_1$, $k_2$ and 5 different variables. I gave you $k_1$ and $k_2$. It works better putting the bigger number on top. Just make sure your $k_1$ and $T_1$ match up… this is written as degrees **Celsius**, but we have to work in **Kelvin**.

**Catalysts** speed up the rxn without being consumed.

*Do they participate in the reaction?*

Think about your lab. They always participate; they lower activation energy of the rate-determining step. There is a homework example using enzymes.
Here (Example on board.) we see the rxn coordinate and the potential energy. If we throw in a catalyst, the delE stays the same, but it lowers that. Meaning more molecules will have the necessary energy.

There are two kinds of catalysts **homogeneous**, like KI, and **heterogeneous**, which is solid. In this system, they absorb onto the solid, or stick onto it and then they desorb.

{Students chattering.} Break time.

Chapter 17: chemical equilibrium

Most rxns do not go to completion. Instead, they attain a state of dynamic equilibrium. This is a mixture of reactants and products. You have seen this before with an acid. What happens the acetate ion can go backward. If you just take a picture of it, you would be able to see the collisions. On the macro view, nothing is seen. Both the forward and reverse rxn occur at the same time and have rate constants associated with them.

A going to B. In this rxn (Example on board.) with **concentration** here. On this one, we do use **time**, as the rxn went to completion, then A would go to 0 and B moves upward.
In an equilibrium system you start with A (Example on board.) it decreases, but does not go to 0. We also see that B does not move all the way up either. The neat thing about equilibrium is that neither ever goes away and happens at the same time.

What if we change and have B in the container (Example on board.) like this. When a system is in equilibrium, you have some of each. In this, we lose B, but gain A. The system after equilibrium is the same here and here. It does not matter what you have. Using what I taught, (Example on board.), K=[B]/[A] point 8/point 2=4. In the other system the equilibrium constant will give you the same answer.

K is determined from equation the way it is written, not what is going on… We can derive the setup of K. Suppose we have (Example on board.) this 1-step rxn:

A+B \rightleftharpoons \text{kb} \ C+D

Kf is the rate constant for forward rxn and kb is the rate constant for reverse rxn. (Example on board.).

So, if I were to give you an equation (Example on board.) like this one, then you would need to have the Kc; c is the \textbf{conventional} or you can think of it as the \textbf{concentration}. 
The thermodynamic quantity depends only on T. All products and reactants (g) or (aq) are in units: M. You ignore solids and liquids.

So, say they have concentration equal to 1; really, solids and liquids have activity instead of concentration. K has no units, because we really are not plugging in concentrations, we are using activity.

If I told you that $K_c$, was 100 at a certain temperature, then what is the $K'_c$ (prime) for the (Example on board.) equation? How do they compare? It’s the inverse, so 1/100. What is the $K''_c$ (double prime) for this one (Example on board.)? Its not 50…

This one is then equal to the sq root of 100…