**Ch 15 Chemical Kinetics Name:**

*15.1 Catching Lizards*  Read this section.

*15.2 The Rate of a Chemical Reaction*

The rate of a chemical reaction is measured as a \_\_\_\_\_\_\_\_\_\_\_\_ in the amount of \_\_\_\_\_\_\_\_\_\_\_\_\_ or \_\_\_\_\_\_\_\_\_\_\_\_\_

(usually in \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ units) divided by the change in \_\_\_\_\_\_\_. Note how a negative sign is used for the

reactants since the concentration \_\_\_\_\_\_\_\_\_\_\_\_\_\_ over time which makes the overall rate \_\_\_\_\_\_\_\_\_\_\_\_\_. Rates

with respect to the product are naturally \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ since concentrations \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_. Rates must

reflect \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ coefficients of the reaction. *Figure 15.2* shows for the reaction: H2(g) + I2(g) → 2HI(g)

the concentration of \_\_\_\_ increases at \_\_\_\_\_\_\_\_\_ the rate that the concentration of ­­H2 + I2 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_s.

The table in the middle of pg 634 shows that the average rate \_\_\_\_\_\_\_\_\_\_\_\_\_ (\_\_\_\_\_\_ down) as the reaction proceeds.

The \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ rate of the reaction is the rate at any \_\_\_\_\_ point in \_\_\_\_\_\_\_\_ and can be found by finding

the \_\_\_\_\_\_\_\_ of the tangent line *(see the slopes at 50s in Figure 15.2)* – notice the rate is the \_\_\_\_\_\_\_\_ whether using

one of the \_\_\_\_\_\_\_\_\_\_\_\_s or the \_\_\_\_\_\_\_\_\_\_\_\_\_\_. Equation [15.5] shows the relationship for a general reaction.

*Practice 15.1 CC 15.1 \_\_\_*

How was Ludwig Wilhelmy able to measure the rate of the conversion of sucrose (disaccharide) to glucose and fructose (monosaccharides)?

How can the reaction between ­­H2 and I2 be measured? *(Figure 15.3)*

How can a reaction such as the decomposition of nitrous oxide (N2O) be monitored?

For some slow reactions samples (\_\_\_\_\_\_\_\_\_\_\_\_s) may be taken over time. *What is most important is that reaction rates must be determined EXPERIMENTALLY – you can NOT determine them by looking at a reaction.*

*15.3 The Rate Law: The Effect of Concentration on Rate*

For the simple reaction A → products (as long as the reverse reaction does not occur) can be written as: Rate = \_\_\_\_\_\_

What is *k?* and what does it mean when n = 0 vs 1 vs 2?

What is an example of a simple zero order process?\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ *(15.7) Note in Figure 15.5 the plot of*

*concentration vs time is a \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ line for a zero order process while the lines for 1st order and 2nd order*

*processes are \_\_\_\_\_\_\_\_\_\_ed.* Rate =*k*[A]0 =\_\_\_ For a 1st order process Rate = \_\_\_\_\_\_\_\_\_\_. In *Figure 15.5* you can

see the curve for 1st order becomes less \_\_\_\_\_\_\_\_\_ (the rxn goes \_\_\_\_\_\_\_er) with time. In *Figure 13.6* rate is

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ proportional to the [A]. For a 2nd order process Rate = \_\_\_\_\_\_\_\_\_\_. In *Figure 15.5* you can see

the curve for 2nd order flattens out more \_\_\_\_\_\_\_\_\_\_\_ (the rxn rate slows faster than 1st order) with time. *Figure*

*15.6* shows a \_\_\_\_\_dratic relationship – rate is proportional to the \_\_\_\_\_\_\_\_\_\_\_\_ of the [A] (rate keeps ↑ with ↑ [A].

*The order of a reaction can be determined only by \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_.*

The table at the bottom of pg638 shows the method of \_\_\_\_\_\_\_\_\_\_\_\_\_ rates. How do we know the data is for a 1st order reaction?

Why are the units of the rate constant *(k)* for a 1st order reaction s−1?

Notice the table on the left of pg639 shows changing the \_\_\_\_\_\_\_\_\_\_ [A] does NOT affect rate for a \_\_\_\_\_ order rxn.

The table on the right shows that when [A] is \_\_\_\_\_\_\_\_\_\_ed the initial rate \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_s for a \_\_\_ order rxn.

Follow the “math” for determining the rate law in the center of the page – note how “log” is used to find the “power” (n) and hence the order of the reaction.

CC15.2 \_\_\_\_ *CC15.3 \_\_\_\_*

Note for the generic reaction at the top of pg640 the rate law can be written as Rate = \_\_\_\_\_\_\_\_\_\_\_\_\_. The overall

order of the reaction is the \_\_\_\_ of the exponents. The rate \_\_\_\_\_ must ALWAYS be determined by\_\_\_\_\_\_\_\_\_\_\_\_\_\_.

*Review Example 15.2 and complete Practice 15.2 (Note the order with respect to [CHCl3] can be determined via inspection of the data. The order for [Cl2] must be determined using the method on pg639. Hint: it is not a whole #)*

*CC 15.4 \_\_\_\_* Explain your choice*.*

*15.4 The Integrated Rate Law: Dependence of Concentration on Time*

*Table 15.1* shows the atmospheric \_\_\_\_\_\_\_\_\_\_\_\_\_\_s of several \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_carbons (\_\_\_\_\_s). CFC-12 or Freon

was the most common refrigerant used for years. *(The lifetime is a measure of how long it will last in the atmosphere.)*

The integrated or \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_al rate law is a relationship between concentration of reactants and \_\_\_\_\_\_\_.

For 1st order reactions the integrated rate law is: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ [15.12]

This is written in the form of y = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ so a plot of ln[A] vs \_\_\_\_\_\_\_ yields a \_\_\_\_\_\_\_\_\_\_\_\_\_\_ line

*(Figure 15.8) where the slope of the line is \_\_\_\_\_\_\_ and y-intercept = \_\_\_\_\_ (natural log of [A]0 at time = \_\_\_\_).*

or it can be written as \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ [15.13] (see natural log “ln” manipulation)

*Practice 15.3 (Use the equation of the line in Example 15.3 to calculate [SO2Cl2]. ln[SO2Cl2] = −0.00029t−2.30*

*Practice 53.4 ln[cyclopropane] = −3.36 x 10−5s−1 (t) + ln [0.0445M] Note ln of [ ] has no units for our purposes.*

For 2nd order reactions the integrated rate law is: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ [15.15] Again this is written in the

y = mx + b format so a plot of 1/\_\_\_\_\_ vs \_\_\_\_\_\_\_ yields a straight line with a slope = \_\_\_\_. *(Figure 15.9)*

*Note how the plot of ln[NO2] vs time in Example 15.5 does NOT produce a \_\_\_\_\_\_\_\_\_\_\_\_ line (so NOT \_\_\_\_ order).*

*Practice 15.5 (Use the eqn of the line in Example 15.5) 1/[NO2] = 0.255t + 100*

For 0 order reactions a plot of [A] vs \_\_\_\_\_\_\_ is a straight line. The integrated law is: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

*Note AP does not test the integrated rate law of a zero order reaction.*

The \_\_\_\_\_\_-life of a reaction is the \_\_\_\_\_\_\_ required for the concentration of a reactant to fall to \_\_\_\_\_\_\_\_\_\_ of its initial value. *Note the integrated rate law can be used to derive the expression for the half-life of a 1st order reaction:*

*t1/2 = \_\_\_\_\_\_\_\_\_\_\_\_\_* For 1st order reactions *t*1/2 is independent of \_\_\_\_\_\_\_\_\_\_\_ concentration. A \_\_\_\_\_\_\_\_\_\_\_\_\_

half-life is \_\_\_\_\_\_\_\_\_\_\_\_\_ to 1st order reactions *(*In *Figure 15.11* the half-life is \_\_\_\_\_\_\_s.)

*Review Example 15.6 and complete Practice 15.6 (complete the chart to show how to determine the answer)*

# of half-lives 0 1 \_\_\_\_\_\_ \_\_\_\_\_\_

Total time(s) 0 26.4 \_\_\_\_\_\_ \_\_\_\_\_\_

Fractional Amt.1/1 ½ \_\_\_\_\_\_ \_\_\_\_\_\_

The equation for *t*1/2 of a 2nd order reaction is: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ *Note that t*1/2 for 2nd order \_\_\_\_\_\_\_\_\_\_\_\_s on the

initial \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_. *AP does not test the t*1/2 *of 2nd order reactions or 0 order reactions.*

Zero order *t*1/2 = \_\_\_\_\_\_\_\_\_\_\_ *(again t*1/2 *depends on initial concentration in fact it is \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ proportional.*

*15.5 The Effect of Temperature on Reaction Rate*

*As a general rule the rate constant and, hence, the rate of a reaction increase rapidly with temperature, approximately doubling for each 10oC rise.* This section shows that the rate constant *(k)* is dependent on \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_.

*(k changes with temperature)* It also shows how the \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ energy *(Ea)* which is the energy that

must be \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ed for the reactants to be transformed into products by reaching the \_\_\_\_\_\_\_\_\_\_\_\_\_\_ed

complex can be calculated.

The higher the *Ea* the \_\_\_\_\_\_\_\_\_\_\_\_\_\_ the reaction \_\_\_\_\_\_\_ (at a given \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_). As temperature

increases the \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ of molecules that will surmount the *Ea* barrier also \_\_\_\_\_\_\_\_\_\_\_ *(Figure 15.14).*

We will use an Arrhenius Plot similar to *Example 13.7* to determine the *Ea* for reactions in lab. *CC15.8 \_\_\_\_*

slope = − *Ea*/*R where R is the gas law constant = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_*

In the \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ model a reaction occurs when reactants collide with sufficient energy *(Ea)* and in the correct

\_\_\_\_\_\_\_\_\_tion for an \_\_\_\_\_\_\_\_\_\_ive collision to form products.

*15.6 Reaction Mechanisms*

Why do you think reactions occur in a series of steps instead of a single step?

Look at the mechanism steps in the center of pg 657. What do elementary steps represent?

For a mechanism to be valid the elementary steps must add up to produce the \_\_\_\_\_\_\_\_\_\_\_\_\_ reaction. In the example mechanism why is HI an intermediate?

The most common molecularities (\_\_\_\_\_\_\_\_\_\_\_\_ of reactant particles in the step) are shown. Why are termolecular steps rare?

*CC15.11 \_\_\_\_*

*Table 15.3* shows that the \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ of the elementary step is \_\_\_\_\_\_\_\_\_ to the overall order of the step.

Reactions occur in steps, often one of the steps will be slower than the others and it will limit the overall reaction rate.

For the example reaction on pg658 the *experimentally determined* rate law is: \_\_\_\_\_\_\_\_\_\_\_\_\_\_

Notice this shows that the reaction must NOT occur a single step or the rate law would be :\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

*Figure 15.16* shows that the 1st step of the mechanism is \_\_\_\_\_\_\_\_\_er than the second step because the step has a

\_\_\_\_\_\_er *E*a. What are the 2 reasons why the mechanism is valid?

When a mechanism begins with a \_\_\_\_\_\_\_ initial step a subsequent step will be \_\_\_\_\_ -limiting. The rate law may

then contain \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_s (which generally are not included in the rate \_\_\_\_\_.) The concentration of the

intermediates can often be expressed in terms of the concentration of the \_\_\_\_\_\_\_\_\_\_\_\_\_\_s of the \_\_\_\_\_\_all reaction.

Why does the fast first step reach equilibrium?

How is this indicated? *(note k1 is for the forward step and k−1 is for the reverse step)*

Review the sample mechanism at the bottom of pg 660. Notice the 1st step is \_\_\_\_\_\_ and that the 2nd is \_\_\_\_\_\_\_\_.

Therefore the rate law would be: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ What intermediate is in both steps? \_\_\_\_\_\_\_\_

The key of this process is to set the Rate (\_\_\_\_\_\_\_\_\_\_\_\_) = Rate (\_\_\_\_\_\_\_\_\_\_\_\_) for the fast step. Review how the

expression is rearranged in order to solve for [N2O2] then substitution into the rate law for the slow step. What

happens to the 3 different rate law constants?

What is the overall rate law? \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ Is it consistent with the experimentally observed rate law?

*Review Example 15.9 and complete Practice 15.9*

*15.7 Catalysts*

Reaction rates can be \_\_\_\_\_\_\_\_\_\_\_\_ed by using \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_s (substance in NOT \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ by the

reaction) which work by providing an \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ mechanism for the reaction in which the \_\_\_\_\_-

determining step has a \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ *E*a. ***(NOTE catalysts do NOT lower the E*a *of the original mechanism.)***

How do Cl atoms from the photodissociation of CFCs act as a catalyst for ozone destruction?

How do we know Cl is the catalyst by looking at the mechanism?

What catalysts are used in vehicle catalytic converters? How do they reduce pollution?

Note that catalysts can be classified into: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ and \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

How is ozone destruction an example of both types? Identify the substance for each type.

Hydro\_\_\_\_\_\_\_\_\_\_\_\_ is another example of using \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ catalysts. This method is how margarine is produces from vegetable oil. Oils with double bond (unsaturated) are hydrogenated to produce saturated fats which are more solid at room temperature.

How does your body use catalysts?

Read *Chemistry and Medicine: Enzyme Catalysis and the Role of Chymotrypsin in Digestion*

*Exercises* (pgs 671-677) #27, 31a, 33a, 35-37, 39, 45, 47, 55, 63, 73, 77-80, 83, 95, 96