

## Chapter 12 – Chemical Kinetics

Chemical kinetics is the study of the rates at which reactions proceed and of the pathways reactions follow to move from reactants to products. In this chapter, we will examine the factors that influence the rate and pathway a reaction takes.

Before we begin this chapter, we should briefly go over something that we'll see in much greater detail in a few days. When a reaction is written as  $A + 2 B \rightarrow C + D$ , what are we saying about the way the individual reactant molecules interact? Absolutely nothing. In fact, only a very small percentage of reactions involve a stoichiometric amount of each reactant interacting in a single step (in this example, exactly 1 molecule of **A** reacts with exactly 2 molecules of **B** in a single step). The book mentions this, but it's easy to forget as we move forward. **Always remember that almost all reactions require several steps to reach completion.**

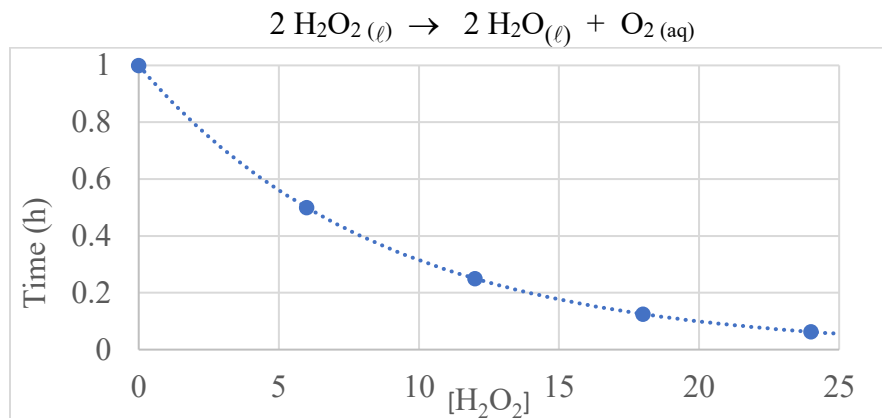
### 12.1 Chemical Reaction Rates

Reaction rate is the speed at which a reaction occurs. For liquid solutions or gas phase reactions (the most common types of reactions), the units are usually  $M s^{-1}$ .

There are four major factors that affect reaction rates: the physical states of the reactants, component concentrations, temperature, and catalysts (if present). Most reactions require at least two species to come together at some point in a reaction (decomposition reactions can be rare exception to this rule). The first two factors only address this requirement. The rate of reaction is also affected by the energy required to get the process started. Catalysts reduce this energy. Changes in temperature affect both factors. We'll go into each of these things in greater detail later in the chapter.

The simplest way of expressing a rate of reaction is to present how quickly a reactant is consumed or a product is generated. We do this by measuring the amount of the substance present at various times during the reaction.

We'll begin with the book's reaction, the decomposition of hydrogen peroxide.



A plot of  $[\text{H}_2\text{O}_2]$  vs. time shows a smooth drop in concentration.

The rate at which the hydrogen peroxide decomposes may be expressed mathematically by the following equation:

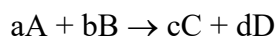
$$\text{Average rate} = -\frac{[\text{H}_2\text{O}_2]_f - [\text{H}_2\text{O}_2]_i}{t_f - t_i} = -\frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t}$$

So why does a negative sign precede the computed value? Rates are always positive quantities, while the loss of a substance is a negative change. Thus, a negative sign must be put in front of the quotient to indicate that the process results in the consumption of a reactant. This equation represents the rate of disappearance of hydrogen peroxide. Initially, it might strike you as odd that rates must be positive numbers, but the following analogy might help. A car moving in reverse gear is still traveling at a positive speed (velocity). It is only the direction that is reversed.

A major problem with using average rates is that the initial and final times are arbitrary, so the use of different times yields different rates. For example, if rates were calculated between successive pairs of points on the graph above, you would see the rate slow down between each of the pairs (e.g. Table 12.2). A standard set of conditions has been established to make sure that when a chemist reads rate data, s/he will know what is meant. Unless you are told otherwise, rates are initial rates. That is, the first point occurs at  $t = 0$ . This still leaves the problem of defining the final time. The rate will change as the final time changes. Unfortunately, a fixed final time can't

be chosen because some reactions occur very rapidly and others very slowly, so no common final time is practical. The only practical way to solve this problem is to use calculus. If the time interval  $\Delta t$  is infinitesimally small (approaches zero), then the average rate becomes the instantaneous rate, and the rate is the slope of the tangent to the curve. Thus, the expression “rate of reaction” almost always means the initial, instantaneous rate. You won’t need to know how to do the calculus for this course, but you should know where the expression comes from. We will derive instantaneous rate equations in Section 12.3. A second advantage to the use of initial, instantaneous rates is that it allows the convenient comparison of the rates of different reactions since an initial, instantaneous rate is common to all reactions.

Now that you’ve seen a specific example, we need to generalize. For any reaction:



$$\text{rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

For example, the reaction  $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$  has the following rates associated with it:

$$\text{rate} = -\frac{1}{2} \frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

Does this make sense? Imagine a bulb filled with 10 hydrogen molecules and 5 oxygen molecules. This is the correct stoichiometry for the reaction, so all of the hydrogen and oxygen will be used up to produce 10 water molecules. Now the hydrogen must be used up twice as quickly as the oxygen for this to occur. Hence, the rate of hydrogen loss must be divided by 2 to have it equal the rate of oxygen loss.

## 12.2 Factors Affecting Reaction Rates

There are four factors that influence the rates of chemical reactions. Three are things that you

might guess out of everyday experience.

- 1) Concentration – Usually the simplest way to follow the rate of reaction is to measure the concentration of one or more species in the reaction mixture at various times. Let's begin with the following question: What happens to the rate of a reaction when we change the concentration of one of the reactants? For example, what do you think would happen to the rate of a reaction if the concentration of one of the reactants was doubled?

You probably guessed that the rate doubled, or at least that it increased. You'd be correct much of the time, but far from always. Sometimes changing the concentration of a reactant has no effect on the reaction rate, sometimes the effect is surprisingly large. In some strange situations, the amount of product actually affects the rate of reaction! We'll see an example of this at the end of the chapter. The thing to remember from this is that there is no way to predict how changing concentrations will affect rate. The rate of reaction must be determined experimentally.

- 2) Temperature – For most reactions, increasing the temperature (adding energy), speeds up chemical reactions. Particles move more quickly, meaning there are more collisions between reactants and they strike each other more forcefully.
- 3) Physical State – This is similar to concentration in the way it works. Generally, for the same substances at the same temperature, if one of the reactants changes from solid to liquid, the reaction accelerates. The same acceleration occurs if a reactant changes from liquid to gas. The reason for this is mobility and accessibility. In a solid, the particles can't move and only the ones on the surface are accessible. In a liquid, the particles move, but again only the surface is available. In the gas, the particles move rapidly and all of them are accessible.

4) Catalysts - These change the reaction pathway and accelerate the reaction.

### 12.3 Rate Laws

Consider the general reaction:  $aA + bB \rightarrow cC + Dd$

Then the rate equation would be:  $\text{rate} = k[A]^x[B]^y$

where x & y may or may not equal a & b. This is a generic rate law. **In general, there is no direct connection between the stoichiometric coefficients in the chemical equation and the exponents in the rate law.** The exponents must be determined experimentally (empirically).

Since you've been told repeatedly the only way to determine a rate law is by experiments, how are rate laws determined? There are three methods employed. The first, less common method involves running an experiment several times at the same temperature but with different reaction concentrations. The second, also uncommon, method involves setting up ratios of whole equations. It is closely related to the first method. The third, usually employed method involves tracking the change in concentration of each species in a reaction over time.

We begin with method 1, which is illustrated in Example 12.4 (pp. 668-620). It provides rate

Trial	[NO] (mol/L)	[O <sub>3</sub> ] (mol/L)	$\Delta[\text{NO}_2]/\Delta t$ (mol•L <sup>-1</sup> s <sup>-1</sup> )
1	$1.00 \times 10^{-6}$	$3.00 \times 10^{-6}$	$6.60 \times 10^{-5}$
2	$1.00 \times 10^{-6}$	$6.00 \times 10^{-6}$	$1.32 \times 10^{-4}$
3	$1.00 \times 10^{-6}$	$9.00 \times 10^{-6}$	$1.98 \times 10^{-4}$
4	$2.00 \times 10^{-6}$	$9.00 \times 10^{-6}$	$3.96 \times 10^{-4}$
5	$3.00 \times 10^{-6}$	$9.00 \times 10^{-6}$	$5.94 \times 10^{-4}$

data for the reaction of nitric oxide with ozone. If you compare lines 1 & 2, you can see that when [O<sub>3</sub>] doubles (and [NO] remains constant), the reaction rate doubles. Mathematically, this is expressed as

$$\text{rate} \propto [\text{O}_3]$$

From lines 3 & 4, you can see that when [NO] doubles, the rate doubles again (here [O<sub>3</sub>] remains constant). Similarly, this is expressed mathematically as

$$\text{rate} \propto [\text{NO}]$$

These proportionalities combine to yield:

$$\text{rate} \propto [\text{NO}][\text{O}_3]$$

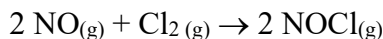
or

$$\text{rate} = k[\text{NO}][\text{O}_3]$$

where  $k$  is the rate constant. Since the rate and concentrations are known, the rate constant can be calculated. This formula is called the rate law. In this case, the reaction is second order, with the exponents equal to the coefficients.

#### Using Initial Rates to Determine Rate Laws

An example of the second method of determining a rate law is shown in Example 12.5 (pp. 670-672). We'll go over it here. For the reaction



we can write the general rate law

$$\text{rate} = k[\text{NO}]^x[\text{Cl}_2]^y$$

The book provides rate data for 3 experiments. Set up rate equations for the first two.

$$\text{rate}_1 = k(0.100 \text{ M})^x(0.100 \text{ M})^y = 3.00 \times 10^{-3} \text{ M/s}$$

$$\text{rate}_2 = k(0.100 \text{ M})^x(0.150 \text{ M})^y = 4.50 \times 10^{-3} \text{ M/s}$$

Now, generally in math if  $a = b$  and  $c = d$ , then  $a/c = b/d$

So, the pair of equations above can be converted to

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{k(0.100 \text{ M})^x(0.100 \text{ M})^y}{k(0.100 \text{ M})^x(0.150 \text{ M})^y} = \frac{3.00 \times 10^{-3} \text{ M/s}}{4.50 \times 10^{-3} \text{ M/s}}$$

$$\frac{(0.100 \text{ M})^y}{(0.150 \text{ M})^y} = 0.667$$

$$\left(\frac{0.100 \text{ M}}{0.150 \text{ M}}\right)^y = 0.667$$

$$\left(\frac{2}{3}\right)^y = 0.667$$

$$y = 1$$

Likewise, for experiments 1 & 3:

$$\frac{\text{rate}_1}{\text{rate}_3} = \frac{k(0.100 \text{ M})^x \cancel{(0.100 \text{ M})^y}}{k(0.150 \text{ M})^x \cancel{(0.100 \text{ M})^y}} = \frac{3.00 \times 10^{-3} \text{ M/s}}{6.75 \times 10^{-3} \text{ M/s}}$$

$$\frac{(0.100 \text{ M})^x}{(0.150 \text{ M})^x} = \left(\frac{0.100 \text{ M}}{0.150 \text{ M}}\right)^x = \left(\frac{3.00}{6.75}\right)^x$$

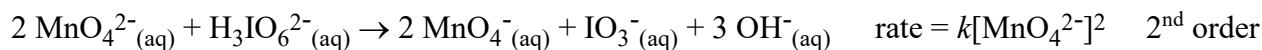
$$\left(\frac{2}{3}\right)^x = (0.444)^x$$

$$x = 2$$

Thus, the rate law for the reaction is:  $\text{rate} = k[\text{NO}]^2[\text{Cl}_2]^1$ .

The sum of the exponents ( $x + y$ ) in a rate law is called the reaction order. Reactions whose order totals one are called first-order reactions. Those equaling two are second-order reactions. These are the two most common reaction orders and we will examine them in detail shortly.

Examples of some reactions and their rate laws:



Remember that rate constants have units, but don't worry about memorizing Table 12.1.

## 12.4 Integrated Rate Laws

We now cover the third way of determining rate laws. While many reaction orders are possible, the vast majority of reactions proceed by either first- or second-order rate laws. Those

two cases will be examined in this section. Once the rate law has been determined, it is possible to make predictions about the time that it will take the reaction to reach completion. This is very important for industrial processes and for reactions that will take a long time to complete.

### First-Order Reactions

We will use the reaction “A → products” to simplify the math, but what follows is true of any standard first-order reaction.

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{d[A]}{dt} = k[A]$$

For those of you who have not yet taken calculus, the  $dA/dt$  term represents infinitesimally small changes in concentration and time, respectively. Therefore, it is very similar to the  $\Delta A/\Delta t$  term preceding it. Integrating the last two terms (via calculus), from  $t = 0$  (when the reaction starts) to some later time  $t$ , yields the following expression:

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

This rearranges to

$$\ln[A]_0 - \ln[A]_t = kt$$

or

$$\ln[A]_t = -kt + \ln[A]_0$$

which has the form of a straight line ( $y = mx + b$ )

This is the method usually used in chemical laboratories to test if a reaction is first-order in a particular reagent. The initial concentration is known and the concentration of each reactant is measured at several later times. **A plot of  $\ln(\text{concentration})$  vs. time is made and if the data form a straight line, the reaction is first-order in that reagent.** A nice feature of this method is that only one reaction per reactant is required to determine the exponent for that species. The methods

shown earlier require more experiments. It also allows you to easily calculate the concentration at any time in the future if you know the starting concentration or the time to stop a reaction if a certain final concentration is wanted.

### Second-Order Reactions

A second-order reaction is a reaction whose rate usually depends on either (i) the concentration of one reactant squared (rate =  $k[A]^2$ ) or (ii) two reactant concentrations, each raised to the first power (rate =  $k[A][B]$ ).

The second situation can be treated as a subset of 1<sup>st</sup> order reactions. To collect the data, if the concentration of reactant A is 100 times that of B, at the end of the reaction the concentration of A will hardly have changed, while that of B will be zero. A result is that the concentration of A is effectively constant so the reaction behaves as if it were first-order with respect to B. Running the reaction with a high concentration of B will then do the same thing. This is how such reactions are actually studied.

For a reaction dependent on only one reactant a new mathematical expression is required.

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{d[A]}{dt} = k[A]^2$$

If the last two terms are integrated, from  $t = 0$  to some later time  $t$ , the following expression is obtained:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

A plot of  $1/[A]$  vs. time yields a straight line for a second-order reaction.

When trying to determine the reaction order with respect to a particular reagent, the concentration of the reactant is measured as a function of time. Then the data are plugged into this equation and the equation for first-order reactions. The plot that yields the straight line indicates

the exponent for that component.

### Zero-Order Reactions – Skip

#### Half-Life

The half-life,  $t_{1/2}$ , of a reaction is the time required to reduce the initial concentration of a reactant by 50% ( $[A]_{t_{1/2}} = \frac{1}{2}[A]_0$ ). In the case of a first-order reaction, substituting this equality into the logarithmic equation on page 8 generates a short expression for the half-life of the reaction.

$$\ln \frac{[A]_{t_{1/2}}}{[A]_0} = -kt_{1/2}$$

$$\ln \frac{\frac{1}{2}[A]_0}{[A]_0} = -kt_{1/2}$$

$$\ln \frac{1}{2} = -kt_{1/2}$$

$$t_{1/2} = \frac{0.693}{k}$$

Hence, **the half-life of a first-order reaction is independent of the concentration of reactant!**

There are two nice aspects to using half-lives. First, it allows a convenient way of expressing how fast a reaction proceeds. Using rate constants accomplishes the same thing, but is less intuitive. Second, it can provide a convenient guide to when a reaction is completed. Since each half-life brings a reaction 50% closer to completion the following table can be constructed.

<u>half-life</u>	<u>% reaction</u>	<u>half-life</u>	<u>% reaction</u>
1	50	5	96.9
2	75	6	98.4
3	87.5	7	99.2
4	93.8	10	99.9

As you can see, reactions are essentially complete after 6 to 7 half-lives. For reactions with long half-lives, this table makes it easier to figure out when to stop the reaction and collect the

product.

The half-life equation of a second-order reaction can be derived as was done earlier for first-order reactions.

$$\frac{1}{[A]_{t_{1/2}}} = kt_{1/2} + \frac{1}{[A]_0}$$

$$\frac{1}{\frac{1}{2}[A]_0} = kt_{1/2} + \frac{1}{[A]_0}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

Here the half-life depends on the concentration of the reactant. Remember that it doesn't for first-order reactions. Is this reasonable? A first-order reaction you've heard of is radioactive decay. The nucleus spontaneously fragments with no outside interference. In any given time period, there is a certain probability the nucleus will fragment. Since neighbors don't interact with each other, it is reasonable that it should take the same period of time for half of a million nuclei to fragment as it does for half of a billion nuclei.

For a second-order process two molecules must collide. As time goes by, there are fewer molecules around, so it takes longer for two of them to find one another and collide. Thus, as concentration decreases, it is reasonable that the time for half of the molecules to react should increase.

## 12.5 Collision Theory

As you all know, reactions usually occur more rapidly at higher temperatures. For example, food cooks faster when you set the oven at a higher temperature and plants grow faster in warmer weather (other things being equal). Why is this so?

Increased reaction rate at higher temperatures is most easily illustrated using a reaction

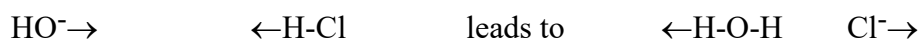
between **A** and **B**, where the reaction occurs in one step involving a single **A** molecule colliding with a single **B** molecule. (This also works for unimolecular reactions, but the explanation is more complicated.) In this situation, the reaction rate depends on how rapidly these species collide with one another. This is expressed mathematically as

$$\text{rate} \propto \frac{\text{no. of collisions}}{\text{time}}$$

and explains why rate depends on reactant concentration. As the concentration of a colliding reactant increases, the total number of collisions they undergo increases. So why does an increase in temperature increase reaction rate? There are two reasons: (i) molecules move faster at higher temperatures, so they collide more frequently in the same amount of time and (ii) since they are moving faster, they collide more forcefully. We'll discuss why more forceful collisions lead to faster reactions shortly.

In reality, not all collisions lead to reactions. For example, in the gas phase at STP there are about  $10^{30}$  collisions per second in a one-liter volume. This means, on average, each molecule undergoes about 10 billion collisions per second. If all collisions led to reaction, all gas phase reactions would be complete essentially instantaneously. Yet as you learned earlier, hydrogen and oxygen gases can be placed in a bulb at room temperature without reacting for a period of many years. Hence, not all collisions lead to reactions. Why not?

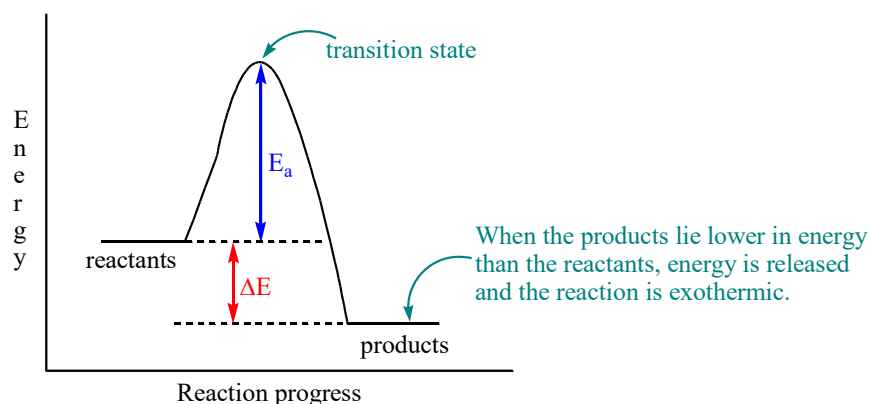
One reason is molecular orientation. Molecules usually have to be properly oriented for a reaction to take place. For example, consider the reaction between hydrogen chloride and hydroxide ion.



The point here is that for the hydroxide ion to abstract a hydrogen ion, it must strike the hydrogen

atom. If it hits the chlorine atom, nothing productive happens. For large molecules the orientation requirement can become significantly more severe because relatively small amounts of the molecule's surface participate in the reaction. Draw out the Lewis structure of acetic acid ( $\text{CH}_3\text{CO}_2\text{H}$ ) and look at its reaction with  $\text{OH}^-$  to illustrate how little of the molecule's surface is available for hydrogen ion abstraction (remember that the hydrogen atoms on the  $\text{CH}_3$  group are not acidic).

Still, at 10 billion collisions per second (per molecule) in the gas phase, this can't possibly be the only thing slowing reactions down. The second, more important, consideration is energy. When most reactions occur, existing bonds are broken and new bonds form. Initiating a reaction almost always requires energy to break one or more bonds in the reactants and that energy is supplied by collisions between molecules. The amount of energy required to initiate a reaction varies, depending on the strengths of the bonds to be broken. Weaker bonds require less energy to break, stronger bonds require more energy. This is represented pictorially as:



The activation energy,  $E_a$ , of a reaction is the minimum energy required for a reaction to proceed. When the collision of two molecules produces less than the activation energy, the two colliding reactant molecules simply fly apart unchanged. When the collision generates the activation energy and is properly oriented, a reaction occurs. As the reaction temperature

increases, the average speed of the colliding molecules increases. This results in more forceful collisions and a higher percentage of them exceeding the activation energy.

In conclusion, for a reaction to occur, molecules must collide in an acceptable orientation with at least the activation energy supplied.

### The Arrhenius Equation

As you may have already guessed, there is a mathematical relationship that quantifies the previous discussion. Earlier in this chapter you learned the general expression of a rate law

$$\text{rate} = k[\text{A}]^x[\text{B}]^y$$

We just went over the fact that rates generally increase with increasing temperature, but there is no temperature term in the rate law. Further, the concentration of a reactant will not change with temperature, so the change in reaction rate must result from a change in rate constant. The rate constant also takes molecular orientation into account.

In 1889, Svante Arrhenius proposed the concept of activation energy (*vide supra*) and an equation relating it to rate constants.

$$k = Ae^{-E_a/RT}$$

where  $A$  is the frequency factor. The frequency factor takes into account the probability that a particular collision will have the correct orientation for reaction and, to a lesser extent, the rate of collisions. If the natural logarithm of this equation is taken, a second, useful equation is produced.

$$\ln k = -\frac{E_a}{R} \left( \frac{1}{T} \right) + \ln A$$

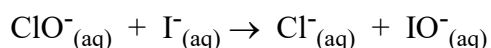
This equation is in the general form of a straight line and a plot of rate constants determined at several temperatures allows calculation of the activation energy of a reaction. If rate constants are provided at only two temperatures this equation simplifies to:

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

## 12.6 Reaction Mechanisms

As you heard and read earlier, reactions rarely occur in one step as is written in a balanced equation. **The large majority of reactions occur in two or more steps (reactions).** The sequence of steps is called the reaction mechanism. Each step in a mechanism is called an elementary reaction.

Consider the following reaction:



Although it looks at first glance like it might occur in a single step, it actually requires 3 steps. Just looking at the reaction, what about it would have allowed you to guess that the reaction might require more than one step? Both reactants are anions and would repel each other. Collisions are likely to be less energetic for this reason, so if the reaction moves at an appreciable rate some other pathway is required.

The following sequence of steps is now accepted for this reaction:



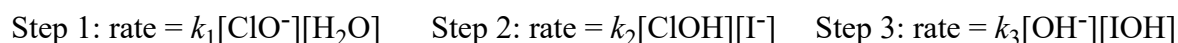
Notice how in this mechanism no anions are required to react with each other. Species that appear in the reaction mechanism, but not the overall reaction are called intermediates. In this mechanism, ClOH, OH<sup>-</sup>, and IOH are intermediates. Water is the solvent and is not considered an intermediate. Intermediates are always present in very small amounts. **The steps in any mechanism must add up to the net reaction with the correct stoichiometry.**

Molecularity refers to the number of molecules that participate in an elementary step. An

elementary reaction involving only 1 molecule is called unimolecular. Those involving 2 molecules are bimolecular and those involving 3 molecules are termolecular.

Earlier you learned there was no direct connection between the stoichiometry of an overall reaction and its rate law. However, as you might guess they are related,.

A rate law can be written for each elementary step in a reaction mechanism. Unlike for overall reactions, *the rate laws for elementary steps do follow reaction stoichiometry*. Thus, for the mechanism we just covered, the rate laws are:



We now examine the connection between the rate laws for the elementary reactions and the overall rate law. The first thing to remember is that the rates of the elementary steps are almost always very different from one another. Most important, the slowest step in the reaction is typically several orders of magnitude slower than the second slowest step. The overall reaction cannot proceed any faster than this slowest step, which has the special name: the rate-determining step.

Here is an analogy for how rate-determining steps work. Consider four pots of water, stacked on top of each other. Pots 1 (top) & 2 are connected by a 2" pipe, pots 2 & 3 by a 1" pipe, and 3 & 4 by a 2" pipe. If tank 1 is filled with water (the others start empty) what happens when the valve on tank 1 is opened. Water begins to flow into tank 2, but since tank two's drainpipe is much smaller than its fill pipe (1" vs. 2"), water begins to back up. Tank 3 has a wide pipe, so water that flows in immediately drains into tank 4. Thus, the "rate limiting" pipe is the narrow one. The slow step in a mechanism works much like the narrow pipe. Thus, *the rate of reaction equals the rate of the slowest step*.

There is a potential problem with the final two elementary rate laws in the  $\text{ClO}^- + \text{I}^-$  reaction.

Do you see it? Each of these rate laws uses the concentration of an intermediate. Unfortunately, you don't know what those concentrations are and it's rare that we can measure them. An unusual example is worked below to show you how to get from a mechanism to a final rate law and to show you how some of the 'weird' rate laws come into being. It is the reaction your book opens this section with.

Ozone exists in the upper atmosphere and slowly decomposes to molecular oxygen even in the absence of chlorofluorocarbons. It breaks down according to the following mechanism.



Since the rate of the overall reaction is controlled by the rate determining step, rate =  $k_2[\text{O}][\text{O}_3]$ . O is an intermediate and we do not know its concentration. But we know the following about intermediates, at the beginning and end of a reaction their concentration equals zero. As they form, the reactions that consume intermediates begin. Very quickly, the rates of production and consumption of each intermediate will become equal and the concentration of each intermediate will remain constant until the end of the reaction. This is the steady-state approximation and it is valid whenever a fast step precedes a slow one.

Since step 1 is faster than step two we can use the steady-state approximation here. Oxygen atoms are formed in the forward direction of step 1 and consumed in the reverse of step 1 and in step 2.

$$\text{rate (O formation)} = k_1[\text{O}_3]$$

$$\text{rate (O consumption)} = k_{-1}[\text{O}_2][\text{O}] + k_2[\text{O}][\text{O}_3]$$

Setting these rates equal to each other yields

$$k_1[\text{O}_3] = k_{-1}[\text{O}_2][\text{O}] + k_2[\text{O}][\text{O}_3]$$

But we know the second step is slow so the second term will be much smaller than the first and can be ignored ( $k_{-1}[\text{O}_2][\text{O}] \gg k_2[\text{O}][\text{O}_3]$ ). The equation then simplifies to

$$k_1[\text{O}_3] = k_{-1}[\text{O}_2][\text{O}]$$

Solve for [O]

$$[\text{O}] = \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]}$$

Now substitute back into the rate law for the overall reaction

$$\text{rate} = k_2 \left( \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]} \right) [\text{O}_3]$$

If the constants are combined, this simplifies to:

$$\text{rate} = k \frac{[\text{O}_3]^2}{[\text{O}_2]}$$

Technically, this is a first-order reaction! Note how the rate depends on the presence of a product too. Your book works a simpler example for you in Example 12.14 (pp. 693-694).

## 12.7 Catalysis

You've heard this word before, perhaps referring to the catalytic converter on your car. But what is a catalyst? A catalyst is a substance that increases the rate of a chemical reaction without itself undergoing a permanent change. Therefore, a typical catalyst molecule is reused many times. In fact, industrial catalysts may undergo millions of reactions before ultimately decomposing.

How does a catalyst accomplish this? First, remember there are three factors that affect the rate of a reaction: (i) collision rate, (ii) collision orientation, and (iii) activation energy. There is



no reason to believe an added third substance would cause molecules to collide more rapidly or cause them to orient properly more frequently when they collide. Hence, a catalyst must affect the activation energy of the process.

Catalysts work by lowering the activation energy of processes. They do so by altering the pathway of the reaction (that is, catalysts change the reaction mechanism). Typically, they interact with one or more of the reactant molecules and make them more susceptible to reaction. They can do this by weakening one or more bonds in the molecule or by moving electron density around.

Skip the discussion on heterogeneous catalysis.

Biological catalysts are called enzymes.

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