Kinetics

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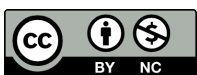
CHAPTER **1**

Kinetics

CHAPTER OUTLINE

The cars roar around the oval track at speeds up to 200 miles/hour. The victor is determined by who crosses the finish line first after a pre-determined number of laps have been driven. Speed is a major factor in winning, but there is also a heavy dose of strategy, driving skill, and some luck in avoiding crashes.

Drag racing involves one basic issue: who can get to the finish line the fastest. The strip is a quarter-mile in length and is straight. Driving skill is important and luck always plays a role. In drag racing the car with the fastest acceleration has an advantage, but top speed is also important. The Top Fuel category (running on nitromethane) record is over 330 miles per hour at the finish line (that's from a standing start and a quarter-mile distance).

Speed is important both on the track and in the chemistry lab. We want to know how fast a reaction occurs for several reasons. The reaction rate can give us useful information about how the reaction occurs. In a manufacturing plant, if the speed of a reaction can be increased, the chemical product can be made in less time, which often means a lower manufacturing cost.

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1.1 Rates of Reactions

Lesson Objectives

- Define "rate."
- Describe collision theory as it relates to chemical reactions.
- List and describe factors that affect the rate of a chemical reaction.

Lesson Vocabulary

- **reaction rate**: The change in concentration of a reactant or product with time.
- **collision theory**: Molecules need to collide in order for a reaction to take place.
- **activation energy**: The energy that is needed to get reactants close enough together for a reaction to occur.
- **activated complex**: The highest energy state that must be passed through in order for reactants to convert into products.
- **catalyst**: A substance that speeds up the rate of reaction by providing a lower energy pathway but does not undergo any change itself.

Check Your Understanding

What do energy versus reaction progress graphs look like for exothermic and endothermic reactions?

Introduction

In our discussion of car racing, we talked about the speed of the vehicles. Car speed is measured in miles/hour (or kilometers/hour in countries using the metric system). A race car traveling at a speed of 200 miles/hour could go a distance of 200 miles in one hour. A rate indicates the extent of some change in relation to the amount of time that has passed. The rate of travel for a car or other object tells us what distance is traversed in a given unit of time. If we know the total distance traveled and the total time taken, we can calculate the rate as follows:

$$Rate = \frac{\Delta distance}{\Delta time}$$

Rates can also be expressed for changes in variables other than physical location. In this lesson, you will learn how to use rates to describe chemical reactions.

What is a Rate?

When studying chemical reactions, we are interested in how quickly the amount or concentration of a given reactant or product changes over time. This is known as the **reaction rate**. Mathematically, the reaction rate can be expressed by either of the following equations:

$$Rate = -\frac{\Delta[reactant]}{\Delta time}$$
$$Rate = \frac{\Delta[product]}{\Delta time}$$

Because the concentrations of the reactants decrease over time, the negative sign in the first equation above means that the reaction rate will be a positive value.

Example 18.1

The initial concentration of a given reactant is 0.45 M. After two minutes, its concentration is measured and found to be 0.35 M. What is the rate of this reaction?

Answer:

Use the appropriate rate equation and fill in the given values:

$$Rate = -\frac{\Delta[reactant]}{\Delta time}$$
$$Rate = -\frac{c(final) - c(initial)}{t(final) - t(initial)}$$
$$Rate = -\frac{0.35\text{ M} - 0.45\text{ M}}{2\text{ min} - 0\text{ min}}$$
$$Rate = -\frac{-0.10\text{ M}}{2\text{ min}}$$
$$Rate = 0.05\text{ M/min}$$

The concentrations of reactants and products are always measured in moles/liter (M) when discussing reaction rates.

For real reactions, we also need to consider the coefficients from the balanced equation. For example, in the reaction $2A \rightarrow B$, the rate of disappearance of A is twice the rate of formation of B, as can be inferred from the stoichiometric coefficients. The rate of product formation can be expressed as follows:

$Rate = \frac{\Delta[B]}{\Delta t}$

However, the rate of disappearance of reactant A is twice the rate of formation of product B. We want to end up with the same reaction rate value regardless of which reaction component is being considered. In order to achieve this, we need to write each rate with respect to the coefficient on the corresponding reaction component.

In the basic reaction formula above, we have determined that the rate of disappearance of reactant A is twice the rate of formation of product B. This means that the rate expression above for the product B is equivalent to the following in terms of the reactant A:

$Rate = -\frac{1}{2}\frac{\Delta[A]}{\Delta t}$

By accounting for the coefficients in the balanced chemical equation, these two rates are equal and we can also say the following:

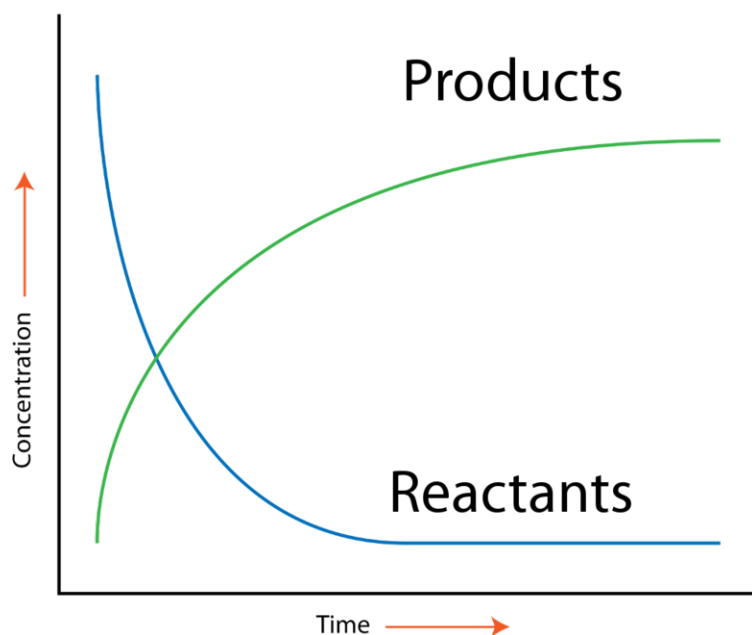$\frac{\Delta[B]}{\Delta t} = -\frac{1}{2}\frac{\Delta[A]}{\Delta t}$

FIGURE 1.1

Collision Theory

Collision theory states that chemical reactions occur when atoms, ions, or molecules collide. In other words, these species need to make contact with one another in order for a reaction to take place. Based on this concept, along with a couple of other key points, collision theory helps to explain why certain factors will influence the rate of a chemical reaction.

We discussed earlier some basic principles about the behavior of gases called the kinetic-molecular theory. Among other things, this theory suggests that gas molecules are in constant motion, and the average speed of the individual gas particles is dependent upon temperature –the higher the temperature, the faster the molecules move. It is not just gas particles that are in constant motion. The molecules and ions that make up liquids and solutions are also continually moving in nearly random directions. As a result, molecules and ions in a solution will collide with one another fairly frequently. As with gases, a temperature increase will produce an increase in the average particle speed.

However, not all collisions between reactant molecules will result in the formation of a product. The colliding particles must possess a minimum amount of energy in order for the reactant-product transition to occur. In the *Thermochemistry* chapter, we saw that simple exothermic reactions have an energy diagram that looks something like **Figure** 1.2.

Although the overall process involves a release of energy (the products are lower energy than the reactants), a certain initial amount of energy needs to be present before the reaction can occur. The amount of energy required to get over the "hump" in the reaction diagram is referred to as the **activation energy** of the reaction. At the top of the peak, the reactants form what is known as an activated complex. The **activated complex** is the highest energy state that must be achieved in order for reactants to convert into products.

In the **Figure** 1.3, the starred compound in the center represents the activated complex. For the indicated transformation, the reactant molecules must come into contact with enough energy to partially break the A-B and C-D bonds that are initially present. If the molecules are simultaneously able to partially form the A-C and B-D bonds in the product, the energetic barrier will not be quite as high, but breaking any chemical bonds requires at least an initial
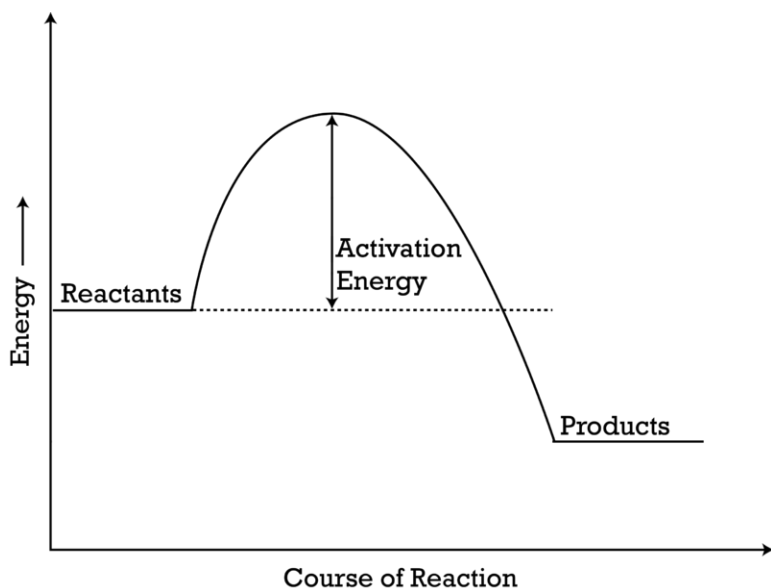
FIGURE 1.2
Activation energy for an exothermic reaction.
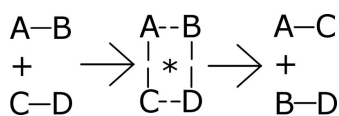
FIGURE 1.3
Formation of activated complex with subsequent release of products.

input of energy.

Factors Affecting Reaction Rate

Several factors influence the rate at which a reaction proceeds. Many of these effects can be predicted and rationalized using the basic concepts of collision theory.

Concentration

FIGURE 1.4

Collision theory tells us that molecules need to collide in order for a reaction to take place. All else being equal, anything that increases the frequency of collisions would also increase the rate of reaction. One way to do this is to increase the concentrations of one or more of the reactants. Using a real world example, a busy freeway will

experience much more frequent car collisions than a fairly empty neighborhood street. Similarly, forcing more randomly moving molecules into the same amount of space will cause an increased number of collisions over a given length of time, providing the reactants with more opportunities to transform into products.

Low concentration = Few collisions   High concentration = More collisions
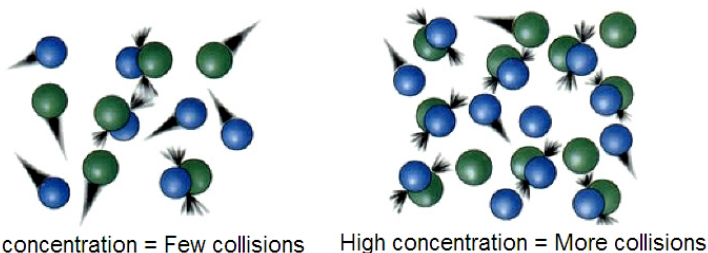
FIGURE 1.5

Pressure

If the pressure of a gaseous mixture is increased by decreasing the available volume, we are effectively pushing the same amount of material into a smaller overall volume. In other words, we are increasing the concentration of the gaseous materials. As we just discussed, an increase in concentration leads to more frequent collisions, thus increasing the rate of reaction.

Note that increasing the external pressure on liquids and solids, which are relatively incompressible, has very little effect on the reaction rate. The volume will be decreased very little, if any, so no significant increase in concentration will result from the pressure change.

Temperature

As the temperature of a system increases, the average speed of its particles also increases. If particles are moving faster, they cover more distance in a shorter amount of time, which increases the frequency of collisions. As a result, the rate of any potential reaction is increased.

FIGURE 1.6

Effect of temperature on reaction rate.

Additionally, there is another way in which increasing the temperature will increase the rate of a reaction. Funda-

mentally, the temperature of a substance is a measure of the average kinetic energy of its individual particles. Recall that a collision will only lead to a reaction if the colliding reactants have enough energy to overcome the activation barrier. Increasing the average kinetic energy of the reactants makes it more likely that any given collision will result in a transformation from reactants to products.
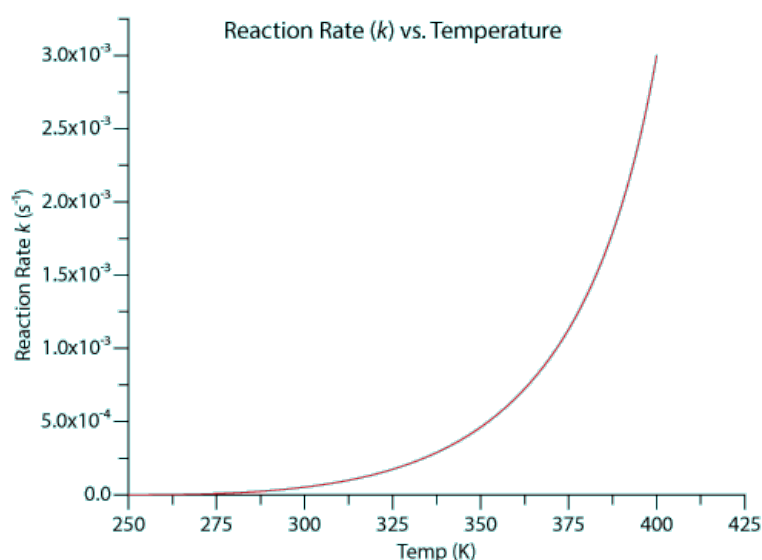
For example, the reaction of wood with oxygen to produce carbon dioxide and water is a very exothermic reaction. The excess energy is released as heat and light, which we experience as fire. However, wood can be stored in the air almost indefinitely without bursting into flames. In order for wood to burn, enough energy needs to be added to overcome the initial activation energy barrier. This can be accomplished by increasing the temperature of a small amount of the wood, often by exposing it to another source of flame or the focused rays of the sun. Once the reaction begins, the energy given off by the exothermic combustion process heats the surrounding wood, thus providing the necessary activation energy for continued burning.

Surface Area

Many reactions take place in solution or in the gas phase, where the reactants are evenly dispersed throughout a homogeneous mixture. However, for reactions in which one of the reactants is a pure solid or liquid (meaning that this reactant is not already mixed together with any other reactants), reactivity only occurs at the surface, where particles of the solid or liquid reactant come into contact with particles of the other reactants. All of the molecules or ions in the interior of the pure substance will not be colliding with the other necessary reactants, so they are not really contributing to the overall rate of the reaction. However, increasing the surface area will increase the frequency of potentially reactive collisions, because more reactant particles will be in contact with the other necessary reactants.

For example, if a solid pellet of NaOH is placed into a chamber of HCl gas, a relatively slow acid-base reaction will occur between gaseous HCl molecules and hydroxide ions on the surface of the pellet. If we were to grind the pellet into smaller pieces, it would greatly increase the total surface area, and therefore the overall reaction rate. Once ground up, many hydroxide ions that were on the interior of the pellet, where they were not exposed to any HCl molecules, will now be on the surface, where the necessary collisions can occur.

Catalysts

A **catalyst** is a material that speeds up the rate of a reaction without being consumed by the reaction. For example, the following reaction is very slow, even when heated:

$2KClO_3 \rightarrow 2KCl + 3O_2$
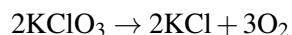
However, adding a tiny amount of manganese dioxide (MnO_2) to a solution of potassium chlorate ($KClO_3$) results in a dramatic increase in the rate at which oxygen gas is produced. At the end of the reaction, the manganese dioxide can be recovered. This is because it is not actually used up in the reaction, but merely facilitates the reaction.

A catalyst works by providing a lower energy pathway from reactants to products. The use of a catalyst involves intermediate reactions which have lower activation complexes than the original reaction. On a simplified reaction energy diagram, this can be thought of as lowering the activation energy for a given transformation. If the activation energy of a reaction is decreased, more collisions will have enough energy to overcome this lower barrier, so the reactant-to-product transformation will occur more frequently. As a result, the overall reaction rate will be higher than for an identical reaction with a larger activation energy barrier.

Another example of a catalytic process is the reaction between an alkene (a carbon-carbon double bond) and hydrogen gas. Due to the details of how covalent bonds are broken and formed, a simple collision between these two molecules will not result in the formation of a product. In the absence of a catalyst, very high energy intermediates, which involve the complete breakage of an H-H single bond, would be required for this process to occur. Because of the very large activation energy required, this uncatalyzed reaction would only occur in extremely high temperatures.

However, the addition of a metal catalyst, such as platinum, provides a lower energy pathway. The energy require-
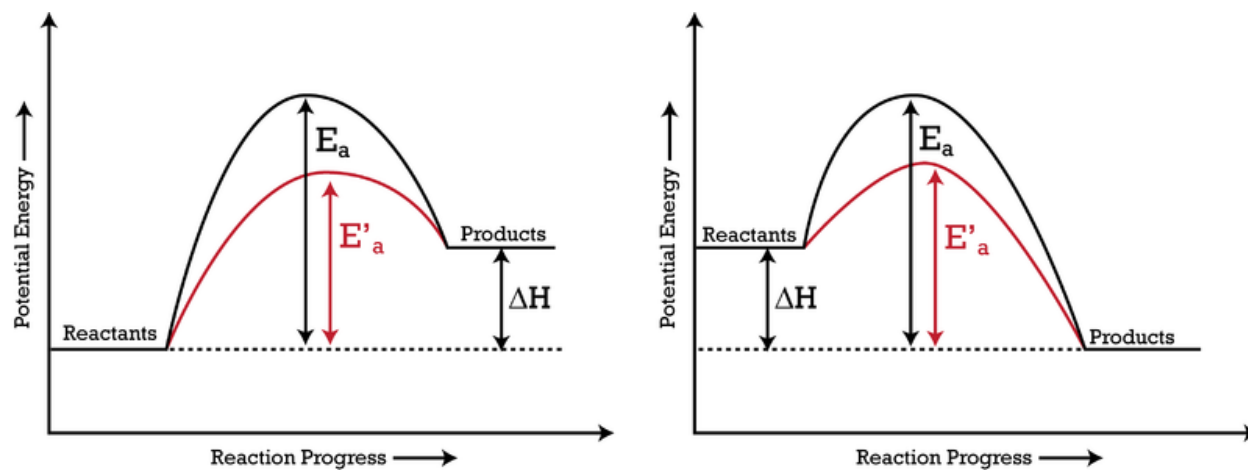
FIGURE 1.7

ments for breaking the H-H bond are offset somewhat if each hydrogen atom can form a new bond with the metal surface. Then, collisions between the alkene and the metal-hydrogen complex result in the formation of a product. The metal surface is regenerated after the hydrogen atoms are removed, so it is not used up by the reaction, but it increases the rate by stabilizing the high energy hydrogen atoms.
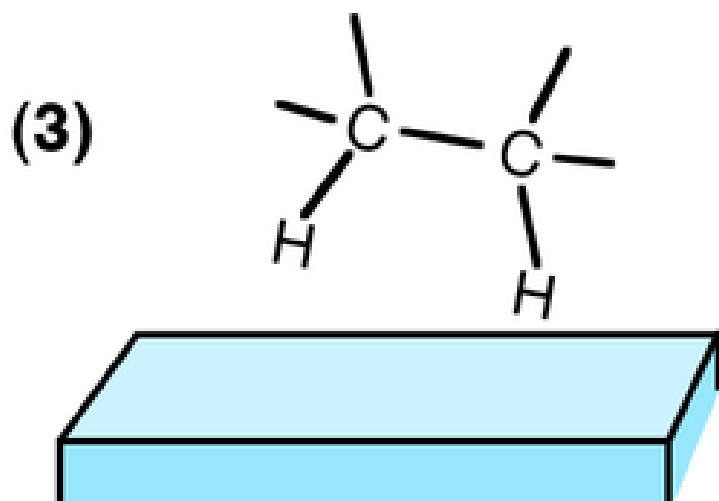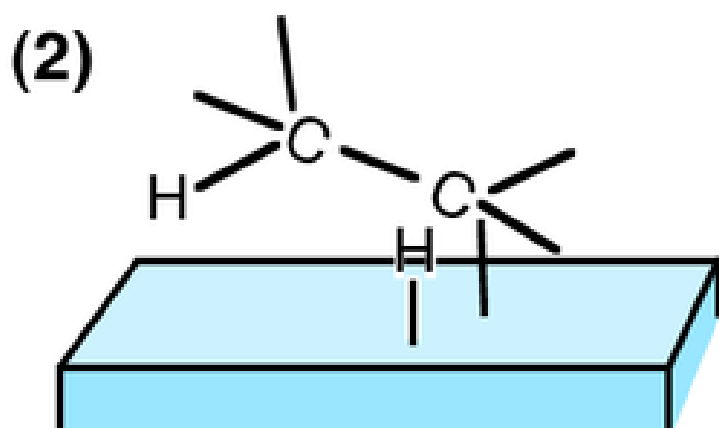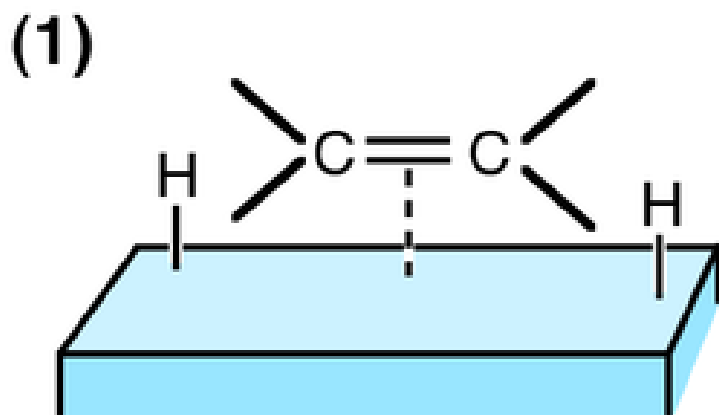
(1)

(2)

FIGURE 1.8

(3)

Catalytic converters in cars increase the rates of several important reactions. Unburned hydrocarbons can more easily be converted to carbon dioxide and water in the presence of a catalyst. Additionally, carbon monoxide (a harmful gas produced by incomplete combustion of fuel) is further oxidized to carbon dioxide, and nitrous oxide compounds (which contribute to smog and acid rain) are transformed back into nitrogen and oxygen gases. By passing car exhaust over these catalysts before their release into the air, the emissions from a combustion engine are made into much less harmful substances, resulting in a much cleaner atmosphere.

Because these catalysts contain expensive metals (rhodium costs about $70.00/gram, platinum about $50.00/gram, and palladium about $15.00/gram), the theft of catalytic converters is a growing problem. A stolen catalytic converter can be sold for over $100.00 at a junk yard.

Lesson Summary

- The rate of a reaction tells us how quickly the reactants are transformed into products. It can be expressed as the change in the concentration of a given reactant or product over a certain length of time.
- Collision theory states that chemical reactions occur when reactants collide with enough energy to overcome the activation energy barrier.
- The activated complex is the highest energy state that must be passed through in order for reactants to be transformed into products.
- The activation energy of a reaction is the amount of energy necessary to form the activated complex from the initial reactants.
- Several factors affect the rate of a chemical reaction, including concentration, pressure (for gases), temperature, surface area (for solids and liquids), and the presence of a catalyst. All of these factors can be rationalized by the basic ideas of collision theory.
- A catalyst increases the rate of a reaction without being consumed. It accomplishes this by providing a lower energy pathway from reactants to products, thus decreasing the activation energy barrier.

Lesson Review Questions

Reviewing Concepts

1. How is the rate of a reaction typically described?
2. Explain the reaction energy graph for an exothermic reaction in terms of collision theory.
3. What is activation energy?
4. For each of the following situations, tell whether the rate of the reaction would increase or decrease, and explain your answer in terms of collision theory.

    a. The concentration of a reactant is doubled.
    b. The reaction is moved from a lab bench at room temperature into an ice bath.
    c. A solid crystalline reactant is broken into smaller pieces with a hammer.

Problems

1. In the reaction A + B → C, the initial concentration of A is 0.054 M. After 1.5 minutes, [A] = 0.032 M. Calculate the rate of the reaction in M/sec.
2. If the above reaction is run under different conditions, it might take 0.8 minutes for the concentration of product C to reach 0.029 M. Assuming that no C was present initially, calculate the rate of formation of C in M/sec.

3. Consider the following reaction: $N_2 + 3H_2 \rightarrow 2NH_3$. At a certain point in the reaction, hydrogen gas is being consumed at a rate of 0.096 M/sec. What is the rate at which ammonia is being formed at this point?
4. The decomposition of dinitrogen pentoxide is described by the reaction: $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$. If O_2 is being formed at a rate of 2.40 mol/min, what is the rate at which N_2O_5 is being used up?

Further Reading/Supplementary Links

- Reaction rates: http://www.chm.davidson.edu/vce/kinetics/ReactionRates.html
- Reaction rate simulation: http://phet.colorado.edu/en/simulation/reactions-and-rates
- Activation energy: http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch22/activate.html
- How a catalytic converter works: http://www.howstuffworks.com/catalytic-converter.htm

Points to Consider

- How do we calculate the rate of a reaction?

1.2 Rate Laws

Lesson Objectives

- Explain why reaction rates are often measured only at the very beginning of a reaction.
- Derive rate laws based on initial rates of reaction.
- Explain what it means for a reaction to be zero-order, first-order, or second-order with respect to a given reactant. Show how this information can be obtained from an experimental rate law.

Lesson Vocabulary

- **initial rate of reaction**: The rate of product formation (or reactant disappearance) that occurs directly after the reactants have been mixed.
- **rate constant**: The proportionality constant "k".
- **second-order**: Indicates an exponent of two; the rate increases twice as fast as the corresponding concentration.
- **first-order**: Indicates an exponent of one; the rate increases directly with the corresponding concentration.
- **zero-order**: Indicates an exponent of zero; the rate does not depend on the corresponding reactant concentration.

Check Your Understanding

Recalling Prior Knowledge

- What do we mean by the "rate" of a reaction?
- How does the concentration of a reactant affect the rate of a reaction?

Introduction

Imagine when you are hungry at the beginning of a meal. A large plate of food is set in front of you, and you start eating quickly. As you become full, you start eating more slowly. Or, maybe you start off eating slowly and the food is so delicious that you start eating more rapidly. The rate at which you eat may be changing throughout the meal based on your level of satisfaction. The rate of chemical reactions can be thought of in a similar way, as these rates do not necessarily stay constant over time. In this lesson, you will learn how to use initial rates and experimental data to determine rate laws.

Initial Rate of Reaction

If we were to graph the concentration of a reactant over time in a given reaction, we might get a plot that looked something like **Figure** 1.9. For a given portion of the curve, the rate of disappearance is equal to the slope at that point. Because the curve is not linear, it has different slopes at different points. This means that the rate of reaction changes over the course of the reaction. As the reactant is used up, its concentration decreases, resulting in a slower rate for any subsequent reactivity.
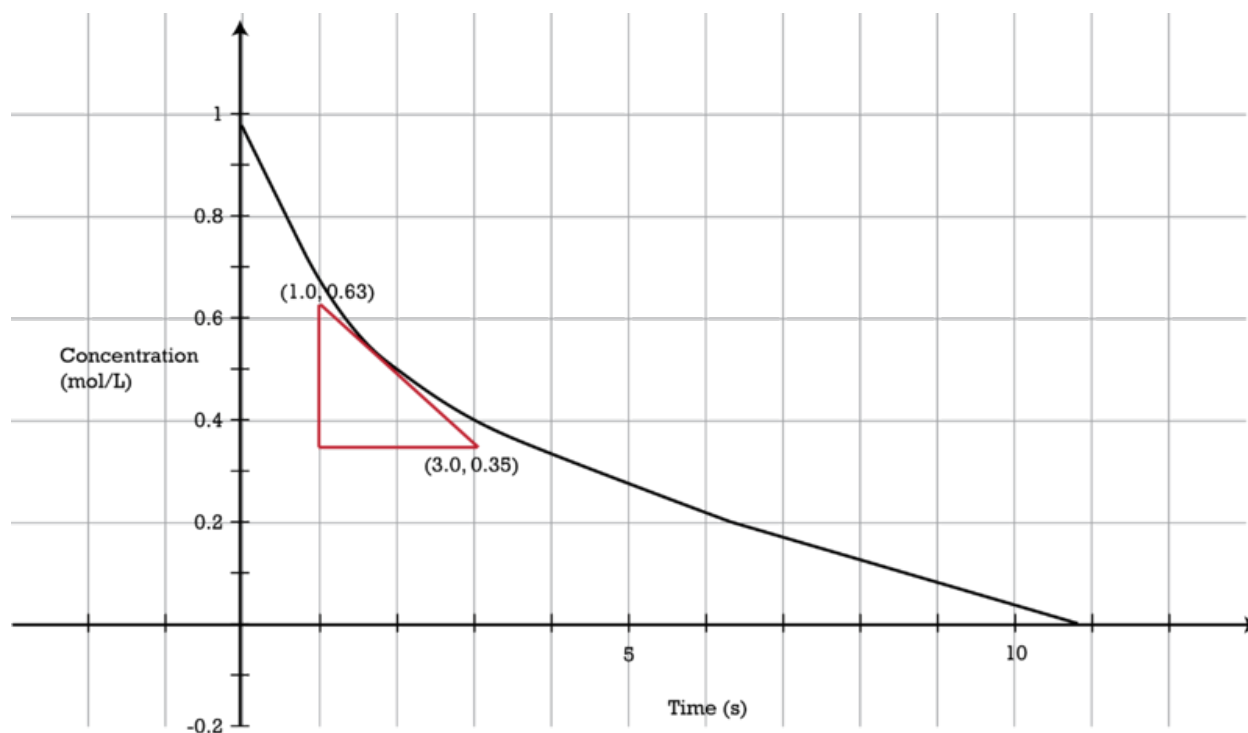
FIGURE 1.9

It is often difficult to monitor the exact concentrations of each reactant in the middle of an ongoing reaction. However, much more precise measurements can be made regarding the concentration of each reactant before they are mixed and the reaction is allowed to proceed. To record more reliable data about the extent to which the rate of a given reaction depends on the concentration of a specific reactant, we often look at the **initial rate of reaction**, which is the rate of product formation (or reactant disappearance) that occurs directly after the reactants have been mixed. In those first few seconds, we can assume that the concentrations of each reactant are essentially equivalent to the amounts that were originally added to the reaction mixture. Additionally, if the presence of the product alters the rate of reaction, this effect is minimized when there is little to no product in the mixture, further simplifying our analysis of the data.

When studying the kinetics of a reaction, what do we measure? The easiest parameter to look at is product formation. If we start at a concentration of zero, we can measure the amount of product present after a short period of time, and the concentration of product divided by the time elapsed gives us the initial rate of reaction. Measuring the disappearance of a reactant is also possible. However, the change in the concentration of the product is often easier

to measure, because it is a much larger change based on percentage.

For example, in the generic reaction A $\rightarrow$ B, let's say we start with 1.000 M A and 0 M B. If we allow the reaction to proceed for a very short period of time, we might have 0.998 M A and 0.002 M B. The difference between 0 M and 0.002 M is generally easier to measure accurately than the difference between 1.000 M and 0.998 M.

Rate Laws

So far, we have been assuming that most reactions occur by a very simple process, in which all the necessary reactants collide, and products are formed if the collision is sufficiently energetic. However, most reactions are much more complicated than that. Except for the most basic reactions, several simpler steps, each of which involves a single collision, are required to get from reactants to products. This sequence of steps, known as the reaction mechanism, will be covered in the next lesson.

We have also assumed that increasing the concentration of any reactant will increase the overall rate of reaction. However, the extent to which this is true, and whether it is true for all reactants, depends on the reaction mechanism. What we can say is that the rate of reaction is proportional to the concentration of each reactant raised to some exponent. Mathematically, this can be expressed as follows for the generic reaction A + B $\rightarrow$ C.

$Rate \propto [A]^x[B]^y$

Alternatively, we can express this as an equation:

$Rate = k[A]^x[B]^y$

where k is a proportionality constant known as the **rate constant**. In general, a larger rate constant is indicative of a faster reaction.

The exponents for an unknown reaction cannot be predicted simply by looking at the chemical equation. Instead, they must be determined experimentally by comparing initial rate data for multiple sets of initial concentrations.

Determining Rate Laws Experimentally

Consider the reaction between nitrogen monoxide gas and hydrogen gas to form nitrogen gas and water vapor.

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$
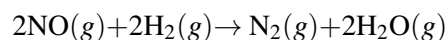
The rate law for this reaction will have the following form:

$$Rate = k[NO]^x[H_2]^y$$

In order to determine the exponents in this equation, the following data were collected at a set temperature and pressure:

TABLE 1.1: Rate Law example

Experiment	[NO] (M)	[H$_2$] (M)	Initial Rate (M/s)
1	0.0050	0.0020	1.25×10^{-5}
2	0.010	0.0020	5.00×10^{-5}
3	0.010	0.0040	1.00×10^{-4}

Notice that the starting concentrations of NO and H_2 were varied in a specific way. In order to compare the rates of reaction and determine the exponent associated with each reactant, the initial concentration of each reactant must be changed while the other is held constant.

Comparing experiments 1 and 2: the concentration of NO was doubled, while the concentration of H_2 was held constant. Doubling the concentration of NO quadrupled the initial reaction rate ($5.00 \times 10^{-5}/1.25 \times 10^{-5} = 4$). Therefore, the exponent associated with the concentration of NO must be 2. In other words, Rate $\propto [NO]^2$. Because $2^2 = 4$, doubling the value of [NO] increases the rate by a factor of four.

Comparing experiments 2 and 3: the concentration of H_2 was doubled while the concentration of NO was held constant. Doubling the concentration of H_2 doubled the initial rate of the reaction ($1.00 \times 10^{-4}/5.00 \times 10^{-5} = 2$). Therefore, the exponent associated with the concentration of H_2 is 1 (Rate $\propto [H_2]^1$). Because $2^1 = 2$, doubling the value of $[H_2]$ also doubles the reaction rate.

The overall rate law incorporates both of these results into a single equation:

$$Rate = k[NO]^2[H_2]$$

Note that exponents of 1 are generally not included, since $[A]^1 = [A]$. Based on the exponents associated with each concentration, we would say that this reaction is **second-order** with respect to NO and **first-order** with respect to H_2. The overall reaction order is the sum of the individual reaction orders, or the sum of all exponents in the rate law. You can see that this would be a third-order reaction overall.

Additionally, now that we know the form of the rate law, we can plug in data from any of the experiments to determine the value of k for this reaction under the conditions (temperature, pressure, etc.) at which the data was measured. Using the data from experiment 1:

$$Rate = k[NO]^2[H_2]$$
$$1.25 \times 10^{-5}\ \frac{M}{s} = k[0.0050\ M]^2[0.0020\ M]$$
$$k = 250\ \frac{1}{M^2 \cdot s}$$

Let's consider another hypothetical reaction of the form A + B $\rightarrow$ C + D. Under a certain set of conditions, the following data were collected:

TABLE 1.2:

Experiment	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.015	0.025	0.112
2	0.030	0.025	0.224
3	0.030	0.050	0.224

Comparing experiments 1 and 2, we see that doubling the concentration of A while holding [B] constant doubles the rate. Therefore, this reaction is first-order with respect to A (Rate $\propto [A]^1$). Plugging this into our generic rate law, we get the following:

$$Rate = k[A]^x[B]^y$$
$$Rate = k[A]^1[B]^y$$
$$Rate = k[A][B]^y$$

Next, we can compare experiments 2 and 3, in which [A] is constant but [B] is doubled. This change *does not affect* the overall reaction rate. We can conclude that the rate of the reaction is independent of the concentration of reactant B. How can we express this in terms of the exponents of the rate law? Recall that any value raised to the 0th power is equal to 1 ($x^0 = 1$). To completely remove a concentration from the rate law, we could set its exponent equal to zero:

$$Rate = k[A][B]^0$$
$$Rate = k[A] \times 1$$
$$Rate = k[A]$$

We say that this reaction is **zero-order** with respect to reactant B. Overall, this is a first-order reaction.

Although other exponents are possible, most reactions are zero-, first-, or second-order with respect to each reactant. Again, the values of the exponents generally cannot be predicted and must be determined experimentally.

Lesson Summary

- The initial rate of reaction is the rate at which the reaction proceeds directly after mixing the reactants. At this point, the concentrations of the reactants have not changed appreciably and the concentrations of the products are negligible.
- The rate law for a given reaction expresses the reaction rate as the product of a rate constant and the concentration of each reactant raised to some exponent.
- The exponents in a rate law, referred to as the order of each reactant, must be determined experimentally, usually by comparing initial rates for multiple combinations of starting concentrations.

Lesson Review Questions

Reviewing Concepts

1. What is the advantage of measuring the initial rate of reaction?
2. What does it mean if a reaction is second-order with respect to a given reactant?
3. What does it mean if a reaction is first-order with respect to a given reactant?
4. What does it mean if a reaction is zero-order with respect to a given reactant?

Problems

1. A generic reaction is found to have the following experimental rate law: $Rate = k[A][B]$. What will happen to the rate of reaction if the concentration of A is tripled?
2. Another reaction has the following rate law: $Rate = k[A][B]^2$. What will happen to the rate of reaction if the concentration of B is doubled?
3. Consider the generic reaction A + B → products. For each set of data given below, determine the reaction order with respect to each reactant and write the experimental rate law.

TABLE 1.3: Table for 3A

Experiment	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.023	0.014	0.011
2	0.046	0.014	0.044
3	0.023	0.028	0.011

1.

TABLE 1.4: Table for 3B

Experiment	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.017	0.021	0.023
2	0.034	0.021	0.023
3	0.017	0.042	0.046

2.

TABLE 1.5: Table for 3C

Experiment	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.023	0.017	0.023
2	0.046	0.017	0.046
3	0.023	0.034	0.092

3.

4. For one reaction of the type A + B → products, the reaction is first-order with respect to A and zero-order with respect to B. Fill in the missing values in the following **Table** 1.6.

TABLE 1.6: Table for 4

Experiment	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.106	0.012	0.355
2	?	0.012	0.710
3	0.212	0.036	?

5. For another reaction of the type A + B → products, the reaction is second-order with respect to both A and B. Fill in the missing values in the following **Table** 1.7.

TABLE 1.7: Table for 5

Experiment	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.106	0.012	0.355
2	0.212	0.012	?
3	0.212	0.036	?

Further Reading/Supplementary Links

- Reaction order: http://www.files.chem.vt.edu/RVGS/ACT/notes/rxn_order.html
- Reaction order graphing: http://chem.usm.my/LECTURER/KFT%20131%20sitimariam/Topic_8.pdf

Points to Consider

How would the rate of reaction be calculated for a multiple step process?

1.3 Reaction Mechanisms

Lesson Objectives

- Define and give examples of elementary steps, and be able to identify the molecularity of each step.
- Define and give examples of reaction mechanisms.
- Predict the rate law for a given elementary step.
- Evaluate validity of reaction mechanisms based on rate law data.

Lesson Vocabulary

- **elementary step**: One step in a series of simple reactions that show the progress of a reaction at the molecular level.
- **reaction mechanism**: The sequence of elementary steps that together comprise an entire chemical reaction.
- **intermediate**: A species that appears in the mechanism of a reaction but not in the overall balanced equation.
- **molecularity**: The total number of reactant molecules in an elementary step.
- **bimolecular reaction**: A reaction in which two reacting molecules are present as reactants in an elementary step.
- **unimolecular reaction**: A reaction in which one molecule is present as a reactant in an elementary step.
- **termolecular reaction**: A reaction in which three reacting molecules in an elementary step.
- **rate-determining step**: The slowest elementary step in the reaction mechanism.

Check Your Understanding

Recalling Prior Knowledge

- How do we measure reaction rate?
- What does the order of a reaction tell us?

Elementary Steps

The overall balanced equation for a chemical reaction does not always tell us how a reaction actually proceeds. In many cases, the overall reaction takes place in a series of small steps. An **elementary step** (or elementary reaction) is one step in a series of simple reactions that show the progress of a reaction at the molecular level. In terms of collision theory, each elementary step corresponds to a single collision. A **reaction mechanism** is the sequence of elementary steps that together comprise an entire chemical reaction. As an analogy, consider the route that you might take while driving to the grocery store. That route may consist of several turns, similar to the elementary steps. The overall reaction specifies only the beginning point (your house) and the final destination (the store), with no information about the specifics in between.

Understanding the mechanism of a reaction can be very useful, because this knowledge often gives us insights into how to improve the reaction, get better yields, or make the reaction proceed more rapidly. Additionally, many seemingly different reactions often have very similar reaction mechanisms. Understanding the types of elementary steps that are common to many different chemical species allows us to make predictions about the reactivity patterns of unknown compounds.

The reaction mechanism concept can be illustrated by the reaction between nitrogen monoxide and oxygen to form nitrogen dioxide:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$
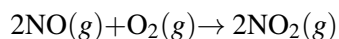
It may seem as though this reaction would occur as the result of a collision between two NO molecules and one O_2 molecule. However, a careful analysis of the reaction has detected the presence of N_2O_2 during the reaction. A proposed mechanism for this reaction consists of two elementary steps:

Step 1: $2NO(g) \rightarrow N_2O_2(g)$
Step 2: $N_2O_2(g) + O_2(g) \rightarrow 2NO_2(g)$
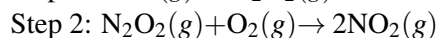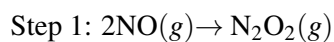
In the first step, two molecules of NO collide to form a molecule of N_2O_2. In the second step, that molecule of N_2O_2 collides with a molecule of O_2 to produce two molecules of NO_2. The overall chemical reaction is the sum of the two elementary steps:

$$2NO(g) \rightarrow \cancel{N_2O_2(g)}$$
$$\underline{\cancel{N_2O_2(g)} + O_2(g) \rightarrow 2NO_2(g)}$$
$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

The N_2O_2 molecule is not part of the overall reaction. It was produced in the first elementary step, then reacts in the second elementary step. An **intermediate** is a species that appears in the mechanism of a reaction but not in the overall balanced equation. An intermediate is always formed in an earlier step of the mechanism and then consumed in a later step.
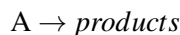
Molecularity

The **molecularity** of an elementary step is the total number of reactant molecules in that step. In both steps of the reaction mechanism shown above, two reactant molecules collide with one another. These are both **bimolecular reactions**. Notice that the colliding molecules may be the same (as in step 1 above) or different (as in step 2 above).

A **unimolecular reaction** is one in which only one molecule is present as a reactant. If we think about this in terms of collision theory, we would expect a unimolecular reaction to take place when the reactant molecule collides with either the wall of the container or molecules of solvent. The substance with which the reactant collides does not participate in the reaction, but it provides the necessary energy to cause whatever rearrangement or bond breakage is required for the given step.

A **termolecular reaction** involves three reacting molecules in one elementary step. Termolecular steps are relatively rare, because they require the simultaneous collision of three molecules with sufficient energy and the correct orientation to form an activated complex, which is an extremely unlikely event. When termolecular reactions do occur, they tend to be very slow. The vast majority of elementary steps are either unimolecular or bimolecular.

Rate Laws and Mechanisms

In general, we cannot predict the rate law for a chemical reaction by looking at its balanced equation, because the rate law for a multi-step reaction depends on the reaction mechanism. In contrast, we *can* predict the rate law for an elementary step. Consider the following unimolecular step:

A $\rightarrow$ *products*

Because it occurs in a single elementary step, the rate of product formation will increase linearly with the concentration of A, making the rate of this reaction first-order with respect to A.

$Rate = k[\text{A}]$

A bimolecular elementary step could be one of two types. Either a molecule of A could react with a molecule of B or two molecules of A could react with each other. In either case, the rate of reaction depends on how frequently the collisions between reactant molecules occur.

$$\text{A} + \text{B} \rightarrow \text{products} \qquad\qquad \text{rate} = \text{k}[\text{A}][\text{B}]$$
$$2\text{A} \rightarrow \text{products} \qquad\qquad \text{rate} = \text{k}[\text{A}]^2$$

The reaction order for each reactant in an elementary step is equal to its stoichiometric coefficient in the equation for that step. In the first equation above, each coefficient is a 1, and so the reaction is first-order with respect to A and first-order with respect to B. In the second equation, the coefficient of 2 means the reaction is second-order with respect to A.

Rate-Determining Steps

The determination of a reaction mechanism can only be made in the laboratory. When a reaction occurs in a sequence of elementary steps, the overall reaction rate is governed by whichever one of those steps is the slowest. The **rate-determining step** is the slowest step in the reaction mechanism. To get an idea of how one step is rate-determining, imagine driving on a one-lane road where it is not possible to pass another vehicle. The rate of flow of traffic on such a road would be dictated by whatever car is traveling at the lowest speed.

Consider the reaction mechanism presented in the previous section:

Step 1: $2\text{NO}(g) \rightarrow \text{N}_2\text{O}_2(g)$
Step 2: $\text{N}_2\text{O}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$
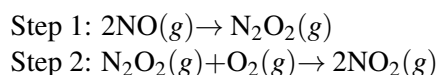
Let's say that the first step is much slower than the second step. If this is true, the rate of the overall reaction would be completely determined by the speed at which the first elementary step proceeds. As soon as it is formed, the N_2O_2 intermediate would immediately be consumed by the (much faster) second step.

What is the rate of the first step? Because it is an elementary step, we can predict its rate law based on the balanced equation. An elementary step in which the reactants consist of two molecules of NO(g) would have the following rate law:

$Rate = k[\text{NO}]^2$

If we have correctly identified the mechanism of this reaction and chosen the correct rate-determining step, this will also be the rate of the overall reaction:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$
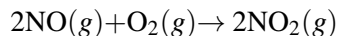
If the experimentally determined rate law for this reaction does not match the one predicted by the proposed mechanism, then the mechanism (or the choice of rate-determining step) is incorrect. However, if the two rate laws do match, we cannot necessarily say that we have found the correct mechanism, because there is always more than one mechanism that can be proposed for any given rate law. Thus, the experimentally determined rate law can invalidate or provide support for a proposed mechanism, but it cannot prove that the mechanism is correct.

In general, the rate law for a mechanism can be predicted based on the form of the rate-determining step. However, the analysis gets more complicated when a step other than the first step is rate-determining. This is due to the fact that intermediates in a reaction are not directly included in the rate law. For the purposes of this book, you will not be required to predict the rate law for any multi-step reactions unless the first step is the rate-determining step.

Lesson Summary

- A reaction mechanism describes the series of elementary steps by which the reactants are transformed into the products.
- The number of reactant molecules in an elementary step is referred to as its molecularity. The vast majority of elementary steps are unimolecular or bimolecular.
- Unlike the rate law for a multi-step reaction, the rate law of an elementary step can be predicted from its balanced equation.
- The rate-limiting step is the slowest step in a mechanism. The rate of the overall reaction is directly dependent on the speed of the rate-determining step.
- The experimentally determined rate law can rule out incorrect mechanisms but cannot prove that a mechanism is correct.

Lesson Review Questions

1. Describe an elementary step as it relates to collision theory.
2. How can the molecularity of an elementary step be determined?
3. Why must all reactions contain a rate-determining step?
4. Which of the following elementary steps is bimolecular?

    1. A → C + D
    2. A + B → 2C + D
    3. 2A + B → 2C

5. The rate law for the reaction 2A + B → Products is: $Rate = k[A][B]$. Which reaction mechanism is consistent with this information?
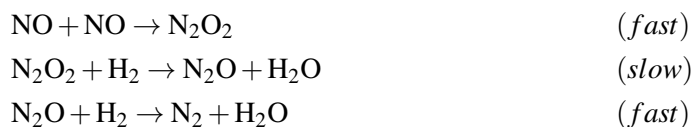
    1.

$$A + B \rightarrow AB \qquad\qquad (slow)$$
$$AB + A \rightarrow Products \qquad (fast)$$

    2.

$$A + A \rightarrow A_2 \qquad\qquad (slow)$$
$$A_2 + B \rightarrow Products \qquad (fast)$$

3.

$$A + B \rightarrow AB \qquad\qquad (fast)$$
$$AB + A \rightarrow Products \qquad\qquad (slow)$$

4.

$$A + A \rightarrow A_2 \qquad\qquad (fast)$$
$$A_2 + B \rightarrow Products \qquad\qquad (slow)$$

6. The following three-step mechanism is proposed for the reaction between NO and H_2:

$$NO + NO \rightarrow N_2O_2 \qquad\qquad (fast)$$
$$N_2O_2 + H_2 \rightarrow N_2O + H_2O \qquad\qquad (slow)$$
$$N_2O + H_2 \rightarrow N_2 + H_2O \qquad\qquad (fast)$$

1. What is the rate determining step?
2. Write the balanced equation for the overall reaction.
3. Are there any intermediates? if so, state what they are.

Further Reading/Supplementary Links

- Reaction mechanisms: http://www.sparknotes.com/chemistry/kinetics/mechanisms/section1.html
- More reaction mechanisms: http://chemwiki.ucdavis.edu/Physical_Chemistry/Kinetics/Rate_Laws/Reactions/Reaction_Mechanisms
- Reaction mechanism video: http://chemwiki.ucdavis.edu/Physical_Chemistry/Kinetics/Rate_Laws/Reactions/Reaction_Mechanisms

Points to Consider

Do reactions only go in one direction? Can reverse reactions occur?

1.4 References

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