



## Lecture (1)

### An Introduction to Chemical Kinetics

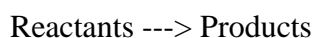
Kinetics is from the Greek, *kinein*, meaning "set in motion or move." Chemical kinetics studies two things:

- 1) the rate at which a chemical reaction takes place.
- 2) the factors which affect the speed of the reaction.

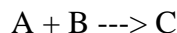
At the introductory level, most study is devoted to how fast a reactant is used up as opposed to how fast a product is formed.

#### Reminders!!

- 1) Chemical reactions are usually written in this form:



- 2) If there were two reactants and one product, it would be written like this:



- 3) Right now, we will keep all the coefficients at one. Later, we will change them.

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Kinetics studies the **rate** of a chemical reaction. That means it is a **time-based** study. In every case, we will ask **how fast** did something take place. Some time unit (seconds, minutes, etc) will always be involved and it will always be in the denominator. In kinetics, something will happen "per second" or "per minute."

That means we will see this often: (something in the numerator divided by a time unit in the denominator).

The most typical thing in the numerator is molarity. Remember that the symbol for molarity is M and the units are moles/liter. So there are three possible ways to discuss the above reaction:

- 1) a change in the molarity of A
- 2) a change in the molarity of B
- 3) a change in the molarity of C

In this introductory part of kinetics, we will only study reactions that go from left to right. Later on, it will get more complicated, but not right now.



Since A and B are reactants, their amounts will **go down** in amount. They are reactants being **used up** in order to make the product C.

Therefore:

- 1) as the reaction proceeds, the total molarity of A remaining unreacted will decrease.
- 2) as the reaction proceeds, the total molarity of B remaining unreacted will decrease.

Since C is a product, it is being made. Its amount will **go up**.

Therefore

- 3) as the reaction proceeds, the total molarity of C present will increase.

However, the above points 1, 2, 3 DO NOT have a time unit in them. In order to create a rate, we need time in the denominator:

- A - the rate of reaction for substance A will be the amount used up divided by the elapsed time.
- B - the rate of reaction for substance B will be the amount used up divided by the elapsed time.
- C - the rate of reaction for substance C will be the amount produced divided by the elapsed time.

The last point to make is that, since A and B are decreasing in amount, we will indicate that with a negative sign in front of the number.

### **Reaction Rates**

Chemical reactions require varying lengths of time for completion, depending upon the characteristics of the reactants and products and the conditions under which the reaction is taking place. *Chemical Kinetics* is the study of reaction rates, how reaction rates change under varying conditions and by which mechanism the reaction proceeds.

#### ***What factors affect the rate of a reaction?***

We've already said that the characteristics of the reactants affect the rate of the reaction, what we want to do here is see what physical factors affect the rate. We can list these;

1. The concentration of the reactants. The more concentrated the faster the rate (note in some cases the rate may be unaffected by the concentration of a particular reactant provided it is present at a minimum concentration). Remember for gasses, increasing the pressure simply increases the concentration so that's the same thing.
2. Temperature. Usually reactions speed up with increasing temperature ("10<sup>0</sup>C rise doubles rate").



3. Physical state of reactants. Powders react faster than blocks - greater surface area and since the reaction occurs at the surface we get a faster rate.
4. The presence (and concentration/physical form) of a catalyst (or inhibitor). A catalyst speeds up a reaction, an inhibitor slows it down. Check your class notes - there should be a graph with the effect of various catalysts upon the decomposition of hydrogen peroxide; draw it in below.
5. Light. Light of a particular wavelength may also speed up a reaction - refer to your organic chemistry notes for reaction of alkanes with halogens.

We've used the term *reaction rate*, so we should define what we mean by this; the reaction rate is the increase in molar concentration of product of a reaction per unit time or the decrease in molar concentration of reactant in unit time. The question is, how does reaction rate vary with time? Consider the decomposition of  $\text{N}_2\text{O}_5$ ;



The table shows the concentration of  $\text{N}_2\text{O}_5$  as a function of time (@45°C);

| Time / min | $[\text{N}_2\text{O}_5] / \text{mol dm}^{-3}$ |
|------------|---|
| 0          | 0.01756                                       |
| 20         | 0.00933                                       |
| 40         | 0.00531                                       |
| 60         | 0.00295                                       |
| 80         | 0.00167                                       |
| 100        | 0.00094                                       |
| 160        | 0.00014                                       |

Plot this data.

To find the rate we divide the change in concentration of  $\text{N}_2\text{O}_5$  by the time period over which this change occurred. Because  $\text{N}_2\text{O}_5$  is consumed in this reaction, this will be a negative figure, by convention, rate data are given as positive numbers:

If we calculate the rate over the first twenty minutes we get;

Rate =  $8.31 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}$ . That is the change in concentration from 0 to 20 minutes / 20 minutes. Now you try for the other times: (you should get  $2.01 \times 10^{-4}$ ,  $1.18 \times 10^{-4}$ ,  $0.64 \times 10^{-4}$  and  $0.37 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}$ ).

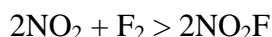
**REMEMBER THESE NOTES WILL ONLY HELP IF YOU TRY THESE CALCULATIONS/EXERCISES - SO DO THEM!!**



We can see that the rate is not constant - is this what you expected? Why should it slow down? - the rate slows down as the concentration of the reactant decreased.

### Rate Law and Reaction Order

If we examine the effect on the rate of a reaction by changing the initial concentration of reactants we may be able to derive the rate law and hence the reaction order. Consider the following reaction;



If the concentration of  $\text{NO}_2$  is doubled then the rate is doubled, likewise when the concentration of the fluorine is doubled the rate doubles and so we get the following rate law;

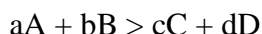
$$\text{Rate} = k [\text{NO}_2][\text{F}_2]$$

**The rate law is an equation that relates the rate of a reaction to the concentration of reactants raised to various powers.**

For the reaction above both reactant concentrations have an exponent of 1.

**The rate constant, k, is a proportionality constant in the relationship between rate and concentrations.** This has a fixed value at any given temperature but varies with temperature.

For a general reaction;



we would have a rate law;

$$\text{Rate} = k [\text{A}]^m [\text{B}]^n$$

Where m and n are determined experimentally (they are usually, but not always, integers). The values of m and n are the orders of reaction, hence the reaction is mth order with respect to A and nth order with respect to B giving a (m+n)th order overall. So if m = 1 and n = 2 the reaction would be first order with respect to A, second order with respect to B and third order overall. If we doubled the concentration of A for this reaction then we would double the rate but doubling the concentration of B would quadruple the rate. (Since 2nd order wrt to B.... work it out if you take  $2[ ]^2$  what do you get ? now take  $[4]^2$ )

### First Order Reactions

Consider a first order reaction;





The rate law is of the form;

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

If we set  $a$  = the initial concentration of A,  $x$  = loss of A with time then  $(a-x)$  is the concentration of A at any given time.

Integration of the equation gives;

$$kt = \ln [a/(a-x)]$$

Plots of  $\ln [a/(a-x)]$  against  $t$  should give a straight line with gradient  $k$

Plots of  $\log_{10} [a/(a-x)]$  against  $t$  should give a straight line with gradient  $k/2.303$

Plot  $\ln (a-x)$  against  $t$  give straight line with gradient  $-k$

(Units of  $k$  are  $\text{second}^{-1}$ )

For a first order reaction, the half life is dependant of the initial concentration and is the time for half of the initial concentration to have reacted. Since half has reacted then  $(a-x)$  must equal  $a/2$  (i.e. half the initial concentration).

Since  $(a-x) = a/2$ , we can rewrite the equation above to give;

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

Where  $t_{1/2}$  is the half life.

### Examples

The half - life for a first order reaction is 100 seconds. Calculate the rate constant and determine what fraction will have reacted after 250 seconds.

$$kt_{1/2} = 0.693 \quad k = 0.693 / t \quad k = 0.693 / 100$$

$$= 6.93 \times 10^{-3} \text{s}^{-1}$$

Asked then to calculate  $x$  - how much has reacted. Set  $a$ , the initial concentration to 1.00

$$kt = \ln [a/(a-x)] \quad \ln[a/(a-x)] = 6.93 \times 10^{-3} \times 250$$

$$= 1.7325$$

$$[a/(a-x)] = 5.6547 \quad = 0.1768$$



$$x = 1 - 0.1768 \quad x = 0.8232 \quad (82.32\% \text{ has reacted})$$

You try:

Half life of a first order reaction is 2 minutes. How much will have reacted after 3 minutes? (70.3%)

Half life of a first order reaction is 24 minutes. How much will have reacted after 33 minutes? (61.4%)

Carbon - 14 dating .... The half life for carbon - 14 is 5670 years. The value of  $a$ , the initial concentration is taken to be the same as for living material today. The value of  $(a-x)$  can be given as a percentage (e.g. 67% of that for living material) or as a fraction ( $\frac{3}{5}$ ths that of living material) or as a count 87cpm compared 100 cpm for living material)

Lets do an example.....

An item was carbon - 14 dated and found to have a carbon - 14 content  $\frac{4}{9}$ th that of living material.

Given the  $t = 5760$  years calculate the age of the item.

$$kt_{1/2} = \ln 2 = 0.693$$

$$k = 0.693 / 5760 = 1.20 \times 10^{-4} \text{ year}^{-1}$$

$$kt = \ln [a/(a-x)] = [\ln (1/(\frac{4}{9}))] = 0.810$$

$$t = 0.810 / 1.20 \times 10^{-4} = 6758 \text{ years}$$

Now try these:

An item was carbon -14 dated and found to have a carbon -14 content 73% that of living material. Given the  $t = 5760$  years calculate the age of the item. (2623 years).

An item was carbon -14 dated and found to have a carbon -14 content  $\frac{4}{5}$ th that of living material. Given the  $t = 5760$  years calculate the age of the item. (1860 years)



## The Integrated Form of a First-Order Kinetics Equation

Let us use the following chemical equation:  $A \rightarrow \text{products}$ .

The **decrease** in the concentration of A over time can be written as:  $-d[A] / dt = k [A]$

Rearrangement yields the following:  $d[A] / [A] = -k dt$

Integrate the equation, which yields:  $\ln [A] = -kt + C$

Evaluate the value of C (the constant of integration) by using boundary conditions. Specifically, when  $t = 0$ ,  $[A] = [A]_0$ .  $[A]_0$  is the original starting concentration of A.

Substituting into the equation, we obtain:  $\ln [A]_0 = -k(0) + C$ .

Therefore,  $C = \ln [A]_0$

We now can write the integrated form for first-order kinetics, as follows:

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

This last equation can be rearranged into several formats, such as:

$$\ln ([A] / [A]_0) = -kt$$

$$[A] / [A]_0 = \exp (-kt)$$

$$[A] = [A]_0 \exp (-kt)$$

Remember the exp notation means the natural constant e raised to the power of whatever follows. Usually what follows is enclosed in parenthesis, but not always.

### How do we determine the value of k for a given first-order reaction?

The integrated first-order equation is the equation of a straight line. (Remember the general equation of a straight line is  $y = mx + b$ .) In this case the y-value is  $\ln [A]$ , m equals negative k, the x-value is t, and the y-intercept is  $\ln [A]_0$ . A plot of  $\ln [A]$  versus t will yield a line with slope equal to negative k.



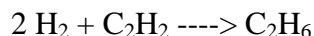


<http://www.gcsescience.com/rc.htm>

<http://www.ucdsb.on.ca/tiss/stretton/chem2/ratex.htm>

### [PROBLEM SETS]

1. Consider the reaction of  $\text{H}_2$  with ethyne to give ethane.

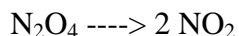


Determine the rate law and rate constant for the reaction from the following data

| initial concentration of $\text{H}_2$ | initial concentration of ethyne | rate of formation of ethane        |
|---------------------------------------|---------------------------------|------------------------------------|
| 0.10M                                 | 0.10M                           | $1.0 \times 10^{-4} \text{ M/min}$ |
| 0.20 M                                | 0.10 M                          | $2.0 \times 10^{-4} \text{ M/min}$ |
| 0.10 M                                | 0.20 M                          | $1.0 \times 10^{-4} \text{ M/min}$ |

2. Carefully explain the difference between the reaction of methyl iodide and t-butyl chloride with hydroxide ion. Give the rate law for each, a mechanism, and a reaction profile.

3. For the reaction:



the following data were collected:

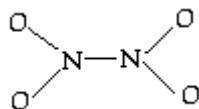
| $\text{N}_2\text{O}_4$ at start | amount of $\text{NO}_2$ after 1 min |
|---------------------------------|-------------------------------------|
| 1.0 M                           | 0.6 M                               |
| 0.5 M                           | 0.3 M                               |
| 0.25 M                          | 0.15 M                              |

- a. Give the rate law for this reaction.
- b. Calculate the rate constant.





- c. When the reaction is started with 1.0 mole of  $\text{N}_2\text{O}_4$  in a 1.0 L flask, how much  $\text{N}_2\text{O}_4$  remains after 1 min?
- d. Calculate  $\Delta H$  for this reaction.
- e. Postulate a mechanism for this reaction.
- f. Give a reaction profile for this mechanism and clearly label all parts of the profile.
- g.  $\text{N}_2\text{O}_4$  has the following structural formula



where the nitrogens are attached to each other and the oxygens are attached only to a nitrogen. Write an electron-dot formula for this molecule and put in the formal charges.

- h. Is the electron-dot formula for  $\text{N}_2\text{O}_4$  in g. above helpful in explaining your mechanism? Explain.
- i. Draw a picture showing the relative positions of all of the atoms in the transition state (if there are more than one in your mechanism, show each one).

### ***Chemical Kinetics***

You may be familiar with acid-base titrations that use phenolphthalein as the endpoint indicator. You might not have noticed, however, what happens when a solution that contains phenolphthalein in the presence of excess base is allowed to stand for a few minutes. Although the solution initially has a pink color, it gradually turns colorless as the phenolphthalein reacts with the  $\text{OH}^-$  ion in a strongly basic solution.

The table below shows what happens to the concentration of phenolphthalein in a solution that was initially 0.005 M in phenolphthalein and 0.61 M in  $\text{OH}^-$  ion. As you can see when these data are plotted in the graph below, the phenolphthalein concentration decreases by a factor of 10 over a period of about four minutes.



*Experimental Data for the Reaction Between Phenolphthalein and Excess Base*

| Concentration of Phenolphthalein (M) | Time (s) |
|--------------------------------------|----------|
| 0.0050                               | 0.0      |
| 0.0045                               | 10.5     |
| 0.0040                               | 22.3     |
| 0.0035                               | 35.7     |
| 0.0030                               | 51.1     |
| 0.0025                               | 69.3     |
| 0.0020                               | 91.6     |
| 0.0015                               | 120.4    |
| 0.0010                               | 160.9    |
| 0.00050                              | 230.3    |
| 0.00025                              | 299.6    |
| 0.00015                              | 350.7    |
| 0.00010                              | 391.2    |

Experiments such as the one that gave us the data in the above table are classified as measurements of **chemical kinetics** (from a Greek stem meaning "to move"). One of the goals of these experiments is to describe the **rate of reaction** — the rate at which the reactants are transformed into the products of the reaction.

The term *rate* is often used to describe the change in a quantity that occurs per unit of time. The rate of inflation, for example, is the change in the average cost of a collection of standard items per year. The rate at which an object travels through space is the distance traveled per unit of time, such as miles per hour or kilometers per second. In chemical kinetics, the distance traveled is the change in the concentration of one of the components of the reaction. The rate of a reaction is therefore the change in the concentration of one of the reactants —  $\Delta(X)$  — that occurs during a given period of time —  $\Delta t$ .

$$\text{Rate of reaction} = \frac{\Delta X}{\Delta t}$$

**Practice Problem 1:**

Use the data in the above table to calculate the rate at which phenolphthalein reacts with the  $\text{OH}^-$  ion during each of the following periods:



- (a) During the first time interval, when the phenolphthalein concentration falls from 0.0050 *M* to 0.0045 *M*.
- (b) During the second interval, when the concentration falls from 0.0045 *M* to 0.0040 *M*.
- (c) During the third interval, when the concentration falls from 0.0040 *M* to 0.0035 *M*.

[Click here to check your answer to Practice Problem 1.](#)

[Click here to see a solution to Practice Problem 1.](#)

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### ***Instantaneous Rates of Reaction and the Rate Law for a Reaction***

The rate of the reaction between phenolphthalein and the OH<sup>-</sup> ion isn't constant; it changes with time. Like most reactions, the rate of this reaction gradually decreases as the reactants are consumed. This means that the rate of reaction changes while it is being measured.

To minimize the error this introduces into our measurements, it seems advisable to measure the rate of reaction over periods of time that are short compared with the time it takes for the reaction to occur. We might try, for example, to measure the infinitesimally small change in concentration —  $d(X)$  — that occurs over an infinitesimally short period of time —  $dt$ . The ratio of these quantities is known as the **instantaneous rate of reaction**.

$$\text{Rate} = \frac{d(X)}{dt}$$

The instantaneous rate of reaction at any moment in time can be calculated from a graph of the concentration of the reactant (or product) versus time. The graph below shows how the rate of reaction for the decomposition of phenolphthalein can be calculated from a graph of concentration versus time. The rate of reaction at any moment in time is equal to the slope of a tangent drawn to this curve at that moment.

The instantaneous rate of reaction can be measured at any time between the moment at which the reactants are mixed and the reaction reaches equilibrium. Extrapolating these data back to the instant at which the reagents are mixed gives the *initial instantaneous rate of reaction*.



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### *Rate Laws and Rate Constants*

An interesting result is obtained when the instantaneous rate of reaction is calculated at various points along the curve in the [graph](#) in the previous section. The rate of reaction at every point on this curve is directly proportional to the concentration of phenolphthalein at that moment in time.

$$\text{Rate} = k(\text{phenolphthalein})$$

Because this equation is an experimental law that describes the rate of the reaction, it is called the **rate law** for the reaction. The proportionality constant,  $k$ , is known as the **rate constant**.

#### ***Practice Problem 2:***

Calculate the rate constant for the reaction between phenolphthalein and the  $\text{OH}^-$  ion if the instantaneous rate of reaction is  $2.5 \times 10^{-5}$  mole per liter per second when the concentration of phenolphthalein is 0.0025 M.

[Click here to check your answer to Practice Problem 2.](#)

[Click here to see a solution to Practice Problem 2.](#)

#### ***Practice Problem 3:***

Use the rate constant for the reaction between phenolphthalein and the  $\text{OH}^-$  ion to calculate the initial instantaneous rate of reaction for the experimental data listed in the preceding table.

[Click here to check your answer to Practice Problem 3.](#)

[Click here to see a solution to Practice Problem 3.](#)

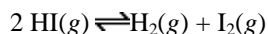
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### *Different Ways of Expressing the Rate of Reaction*

There is usually more than one way to measure the rate of a reaction. We can study the decomposition of hydrogen iodide, for example, by measuring the rate at which either  $H_2$  or  $I_2$  is formed in the following reaction or the rate at which HI is consumed.



Experimentally we find that the rate at which  $I_2$  is formed is proportional to the square of the HI concentration at any moment in time.

$$\frac{d(I_2)}{dt} = k (HI)^2$$

What would happen if we studied the rate at which  $H_2$  is formed? The balanced equation suggests that  $H_2$  and  $I_2$  must be formed at exactly the same rate.

$$\frac{d(H_2)}{dt} = \frac{d(I_2)}{dt}$$

What would happen, however, if we studied the rate at which HI is consumed in this reaction? Because HI is consumed, the change in its concentration must be a negative number. By convention, the rate of a reaction is always reported as a positive number. We therefore have to change the sign before reporting the rate of reaction for a reactant that is consumed in the reaction.

$$-\frac{d(HI)}{dt} = k' (HI)^2$$

The negative sign does two things. Mathematically, it converts a negative change in the concentration of HI into a positive rate. Physically, it reminds us that the concentration of the reactant decreases with time.

What is the relationship between the rate of reaction obtained by monitoring the formation of  $H_2$  or  $I_2$  and the rate obtained by watching HI disappear? The stoichiometry of the reaction says that two HI molecules are consumed for every molecule of  $H_2$  or  $I_2$  produced. This means that the rate of decomposition of HI is twice as fast as the rate at which  $H_2$  and  $I_2$  are formed. We can translate this relationship into a mathematical equation as follows.

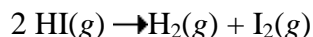
$$-\frac{d(HI)}{dt} = 2\left[\frac{d(H_2)}{dt}\right] = 2\left[\frac{d(I_2)}{dt}\right]$$



As a result, the rate constant obtained from studying the rate at which  $\text{H}_2$  and  $\text{I}_2$  are formed in this reaction ( $k$ ) is not the same as the rate constant obtained by monitoring the rate at which  $\text{HI}$  is consumed ( $k'$ )

***Practice Problem 4:***

Calculate the rate at which  $\text{HI}$  disappears in the following reaction at the moment when  $\text{I}_2$  is being formed at a rate of  $1.8 \times 10^{-6}$  moles per liter per second:



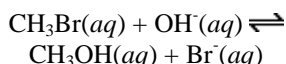
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[Click here to see a solution to Practice Problem 4.](#)

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### ***The Rate Law Versus the Stoichiometry of a Reaction***

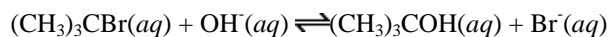
In the 1930s, Sir Christopher Ingold and coworkers at the University of London studied the kinetics of substitution reactions such as the following.



They found that the rate of this reaction is proportional to the concentrations of both reactants.

$$\text{Rate} = k(\text{CH}_3\text{Br})(\text{OH}^-)$$

When they ran a similar reaction on a slightly different starting material, they got similar products.



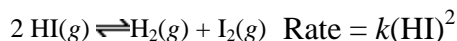
But now the rate of reaction was proportional to the concentration of only one of the reactants.

$$\text{Rate} = k((\text{CH}_3)_3\text{CBr})$$

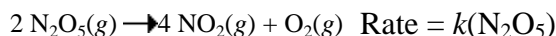
These results illustrate an important point: **The rate law for a reaction cannot be predicted from the stoichiometry of the reaction; it must be determined**



**experimentally.** Sometimes, the rate law is consistent with what we expect from the stoichiometry of the reaction.



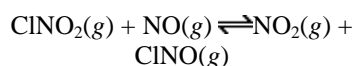
Often, however, it is not.



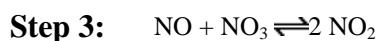
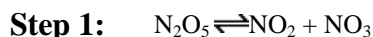
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### *Order of Molecularity*

Some reactions occur in a single step. The reaction in which a chlorine atom is transferred from  $\text{ClNO}_2$  to  $\text{NO}$  to form  $\text{NO}_2$  and  $\text{ClNO}$  is a good example of a one-step reaction.



Other reactions occur by a series of individual steps.  $\text{N}_2\text{O}_5$ , for example, decomposes to  $\text{NO}_2$  and  $\text{O}_2$  by a three-step mechanism.



The steps in a reaction are classified in terms of **molecularity**, which describes the number of molecules consumed. When a single molecule is consumed, the step is called **unimolecular**. When two molecules are consumed, it is **bimolecular**.

#### ***Practice Problem 5:***

Determine the molecularity of each step in the reaction by which  $\text{N}_2\text{O}_5$  decomposes to  $\text{NO}_2$  and  $\text{O}_2$ .

[Click here to check your answer to Practice Problem 5.](#)

[Click here to see a solution to Practice Problem 5.](#)





Reactions can also be classified in terms of their **order**. The decomposition of  $\text{N}_2\text{O}_5$  is a **first-order reaction** because the rate of reaction depends on the concentration of  $\text{N}_2\text{O}_5$  raised to the first power.

$$\text{Rate} = k(\text{N}_2\text{O}_5)$$

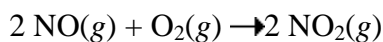
The decomposition of HI is a **second-order reaction** because the rate of reaction depends on the concentration of HI raised to the second power.

$$\text{Rate} = k(\text{HI})^2$$

When the rate of a reaction depends on more than one reagent, we classify the reaction in terms of the order of each reagent.

#### ***Practice Problem 6:***

Classify the order of the reaction between NO and  $\text{O}_2$  to form  $\text{NO}_2$ :



Assume the following rate law for this reaction:

$$\text{Rate} = k(\text{NO})^2(\text{O}_2)$$

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The difference between the molecularity and the order of a reaction is important. The molecularity of a reaction, or a step within a reaction, describes what happens on the molecular level. The order of a reaction describes what happens on the macroscopic scale. We determine the order of a reaction by watching the products of a reaction appear or the reactants disappear. The molecularity of the reaction is something we deduce to explain these experimental results.

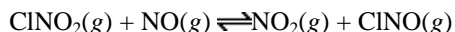
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### ***Collision Theory Model of Chemical Reactions***

The **collision theory model** of chemical reactions can be used to explain the observed rate laws for both one-step and multi-step reactions. This model assumes that the rate of any step in a reaction depends on the frequency of collisions between the particles involved in that step.



The figure below provides a basis for understanding the implications of the collision theory model for simple, one-step reactions, such as the following.

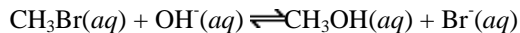


The kinetic molecular theory assumes that the number of collisions per second in a gas depends on the number of particles per liter. The rate at which  $\text{NO}_2$  and  $\text{ClNO}$  are formed in this reaction should therefore be directly proportional to the concentrations of both  $\text{ClNO}_2$  and  $\text{NO}$ .

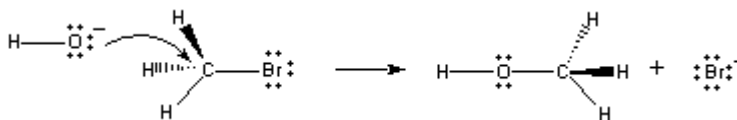
$$\text{Rate} = k(\text{ClNO}_2)(\text{NO})$$

The collision theory model suggests that the rate of any step in a reaction is proportional to the concentrations of the reagents consumed in that step. The rate law for a one-step reaction should therefore agree with the stoichiometry of the reaction.

The following reaction, for example, occurs in a single step.



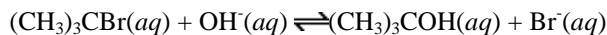
When these molecules collide in the proper orientation, a pair of nonbonding electrons on the  $\text{OH}^-$  ion can be donated to the carbon atom at the center of the  $\text{CH}_3\text{Br}$  molecule, as shown in the figure below.

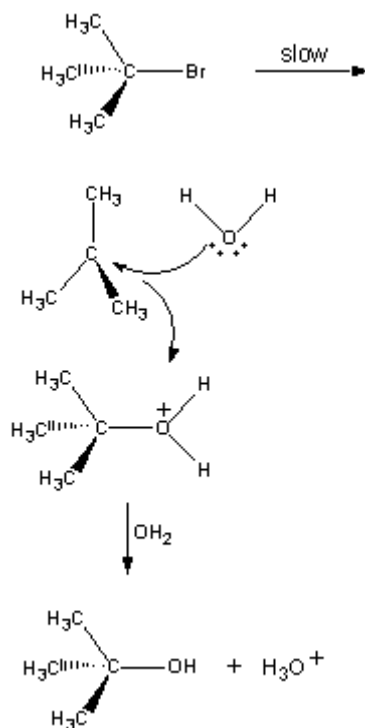


When this happens, a carbon-oxygen bond forms at the same time that the carbon-bromine bond is broken. The net result of this reaction is the substitution of an  $\text{OH}^-$  ion for a  $\text{Br}^-$  ion. Because the reaction occurs in a single step, which involves collisions between the two reactants, the rate of this reaction is proportional to the concentration of both reactants.

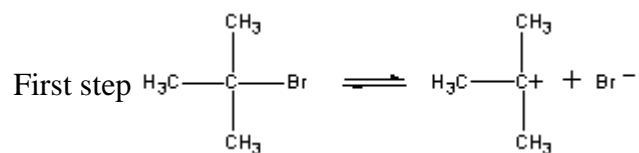
$$\text{Rate} = k(\text{CH}_3\text{Br})(\text{OH}^-)$$

Not all reactions occur in a single step. The following reaction occurs in three steps, as shown in the figure below.

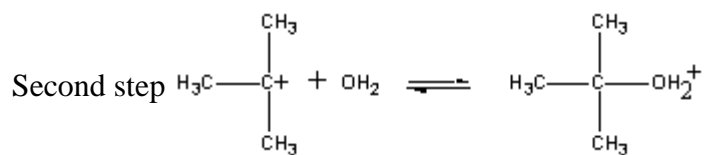




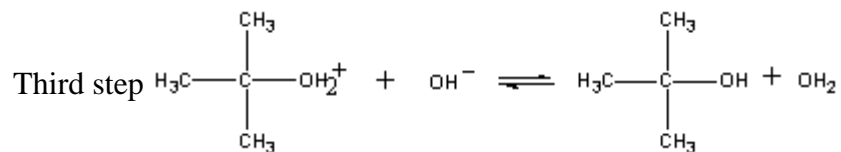
In the first step, the  $(\text{CH}_3)_3\text{CBr}$  molecule dissociates into a pair of ions.



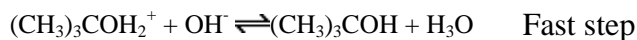
The positively charged  $(\text{CH}_3)_3\text{C}^+$  ion then reacts with water in a second step.



The product of this reaction then loses a proton to either the  $\text{OH}^-$  ion or water in the final step.



The second and third steps in this reaction are very much faster than first.



The overall rate of reaction is therefore more or less equal to the rate of the first step. The first step is therefore called the **rate-limiting step** in this reaction because it literally limits the rate at which the products of the reaction can be formed. Because only one reagent is involved in the rate-limiting step, the overall rate of reaction is proportional to the concentration of only this reagent.

$$\text{Rate} = k((\text{CH}_3)_3\text{CBr})$$

The rate law for this reaction therefore differs from what we would predict from the stoichiometry of the reaction. Although the reaction consumes both  $(\text{CH}_3)_3\text{CBr}$  and  $\text{OH}^-$ , the rate of the reaction is only proportional to the concentration of  $(\text{CH}_3)_3\text{CBr}$ .

The rate laws for chemical reactions can be explained by the following general rules.

- The rate of any step in a reaction is directly proportional to the concentrations of the reagents consumed in that step.
- The overall rate law for a reaction is determined by the sequence of steps, or the **mechanism**, by which the reactants are converted into the products of the reaction.
- The overall rate law for a reaction is dominated by the rate law for the slowest step in the reaction.