

Rates of Reaction Notes

Why study Rates of Reaction?

There are good economic reasons for studying rates of reaction. In an industrial setting, you want to be able to manufacture a desired compound as quickly as possible ("time is money"). On the other hand, some reactions may proceed more quickly than you want them to. For example, a reaction may occur exothermically, and so fast that the system becomes dangerously hot. You may need to slow it down for safety reasons. Also, a material that you wish to make or keep may break down over time. This is a reaction that you would wish to slow down.

Collision Theory for Reactions

This is an extension of the Kinetic Molecular Theory. The Kinetic Molecular Theory states that all particles in a system are in rapid, **random** motion. The temperature of the system is a measure of the average kinetic energy of the particles in the system. As a result, if temperature rises, the particles in a system move more rapidly on average. Collision theory states that reactions occur due to random collisions between reactant molecules. The collisions must be hard enough to break old bonds. This would allow new bonds to form. Due to the randomness of the collisions, the reaction is governed by the laws of probability.

Factors Affecting Rates of Reaction

1. Concentration of reactants (in a homogeneous reaction)
Surface area of reactants (in a heterogeneous reaction)
2. Temperature of the system
3. Presence of a catalyst
4. Nature of the reactants

Effects of Concentration/Surface Area

Consider what would happen if you had a reaction $A + B \rightarrow C$

If you introduced a small amount of A into a container already containing some B, what would happen? **Collisions**. What type of collision would be most common if the concentration of A is low and concentration of B is relatively high? B molecules colliding with B molecules would be most common. But this collision is not terribly interesting to us. The less common type of collision: A molecules

colliding with B molecules is of more interest. The least common type of collision, A colliding with A is also of little interest. As was said before, these random collisions are governed by the laws of probability. If we gradually add more A to the container, so its concentration increases, what would happen to the likelihood of A—B collisions? The rate of collision between A and B molecules will increase as you add A. If the molecules are colliding faster, bonds will break faster. This will allow new bonds to form faster, hence the rate of reaction increases.

In a heterogeneous reaction case, what happens to the rate of collision if you increase the surface area of a reactant? (Remind students of dust explosion). Rate of collision, hence rate of reaction increases when you increase surface area for a heterogeneous reaction case.

Rate Laws

You can describe a reaction as fast or slow, but those are relative terms. Chemists like to use numbers to describe rates. Chemists have decided that rates of reaction should be measured as the rate of appearance of a product or rate of disappearance of a reactant. Of course, the rate of appearance of a product is related to the disappearance of a reactant. The faster that a reactant is disappearing, the faster the product will appear. For a given reaction, chemists use whichever is easier to measure for that given reaction: rate of disappearance or rate of appearance. The units chosen were moles per litre per second. In other words, we are measuring the rate of change of concentration of either a product or reactant. This numerical approach leads us to a formulaic description of the rate of a reaction. Chemists have discovered that there is a mathematical relationship between the rate of a reaction and the concentration of one or more of the reactants. We call them rate laws. What types of mathematical relationships have you studied in math? The earliest one that you learned about was linear relationships. In other words, $y=mx$. Since then, you have learned that other types of relationships exist, such as $y=mx^2$. Here are two data tables:

x	y
1	3
2	6
3	9
4	12
5	15

x	y
1	3
2	12
3	18
4	32
5	50

What is the equation for the function for the first table? How about the second one? For the first one, what happens to y when you double x? For the second one, what happens to the value of y when you double x? The rate law for a reaction can be of that form: Rate = $k[\text{reactant}]$ where the square brackets mean the concentration of whatever is in the brackets, or Rate = $k[\text{reactant}]^2$.

Generally, it will be of the form $\text{Rate} = k[\text{reactant}]^m$. m can be 0, 1, 2. Theoretically it could be higher, but is unlikely.

Consider the following “experimental” data for a hypothetical reaction $A + B \rightarrow C$:

Trial	$[A]_0$	$[B]_0$	Initial Rate (M/s)
1.	0.100	0.100	0.012
2.	0.200	0.100	0.024
3.	0.200	0.200	0.048

What happens to the rate of the reaction when you double the concentration of A? It doubles. Does that suggest that $\text{Rate} = k[A]$ or $\text{Rate} = k[A]^2$? Examine how the concentration of B affects the rate.

It appears that two relationships are true:

$$\text{Rate} = k_1[A]$$

and

$$\text{Rate} = k_2[B]$$

We can actually combine those two relationships into a single function:

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

Do some additional problems to reinforce the idea. Introduce second order and zero order examples. Then discuss the term “order”

Show the ratio method of doing Rate Law Problems.

Differential Rate Law Problems

1. Determine the rate law and the specific rate constant for the hypothetical reaction: $A + B \rightarrow C$ given the following data

Trial	Initial Conc of A	Initial Conc of B	Initial Rate (mol/L/S)
1.	0.100	0.100	2.4×10^{-3}
2.	0.100	0.200	4.8×10^{-3}
3.	0.200	0.200	9.6×10^{-3}

2. Determine the rate law and the specific rate constant for the hypothetical reaction: $X + Y \rightarrow Z$ given the following data

Trial	Initial Conc of X	Initial Conc of Y	Initial Rate (mol/L/S)
1.	0.100	0.100	0.003
2.	0.200	0.100	0.003
3.	0.200	0.200	0.006

3. Determine the rate law and the specific rate constant for the hypothetical reaction: $X + Y \rightarrow A$ given the following data

Trial	Initial Conc of X	Initial Conc of X	Initial Rate (mol/L/S)
1.	0.100	0.100	0.0002
2.	0.200	0.100	0.0008
3.	0.200	0.200	0.0016

4. Determine the rate law and the specific rate constant for the hypothetical reaction: $S + P \rightarrow Q$ given the following data

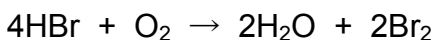
Trial	Initial Conc of S	Initial Conc of P	Initial Rate (mol/L/S)
1.	0.100	0.100	1.2×10^{-2}
2.	0.100	0.200	2.4×10^{-2}
3.	0.200	0.100	2.4×10^{-2}

5. Determine the rate law and the specific rate constant for the hypothetical reaction: $A + B \rightarrow X$ given the following data

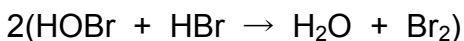
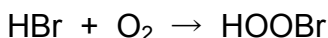
Trial	Initial Conc of	Initial Conc of	Initial Rate (mol/L/S)
1.	0.100	0.100	0.002
2.	0.100	0.200	0.004
3.	0.200	0.400	0.016

Reaction Mechanism

Consider the reaction:



If we picture this reaction happening as described in the equation, it would require 4 HBr's colliding with an O₂ molecule. The collisions would have to be simultaneous, and all with enough energy and at an appropriate angle to break existing bonds and allow new ones to form. This is highly unlikely. As a result, although it will happen, it will happen so slowly that the overall reaction would be extremely slow. But in fact, this reaction occurs fairly rapidly. Scientists have theorized that the reaction happens in a series of relatively simple steps instead of by one large, complicated multi-molecular collision. Instrumental analysis suggests this set of steps:



(The last reaction is doubled in order to maintain consistency with the first two steps. The second reaction produces two HOBr's so the third reaction would happen twice for every occurrence of the first and second reactions)

These three steps add up to give us the equation for the overall reaction. This set of steps is known as a **Reaction Mechanism**. Each step in it is known as an **Elementary Step**.

But what about these two materials, HOBr and HOBr? They do not appear in the overall reaction. That is because they are produced in an early step of the mechanism and consumed in a subsequent step. They are referred to as **Reaction Intermediates**. Reaction Intermediates are generally relatively unstable materials, so they are often present only fleetingly.

In every mechanism, there is one step that is slower than all of the rest. This one acts as a bottleneck for the overall reaction. The reaction mechanism cannot occur faster than its slowest step. Such a step is known as the **Rate Determining Step**.

Think of the reaction mechanism as a path or route for the reaction to take. There may be several routes to take from point A to point B. Some routes will be faster than others. A reaction may actually proceed by several routes, but the fastest one will be the most important.

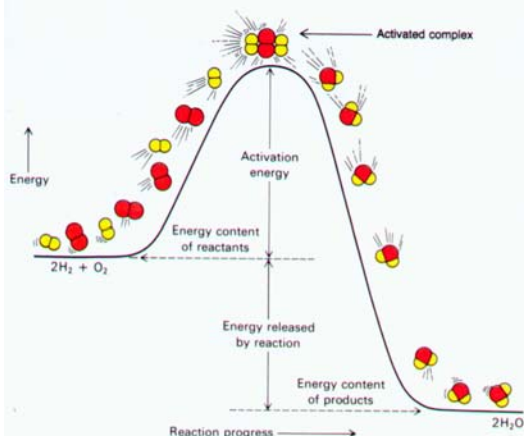
Transition State/Activated Complex Theory

According to the Collision theory, molecules must collide in order to react. The collisions must be hard enough to break bonds. But not all collisions are hard enough to break bonds. Studies show that due to the random collisions between molecules, there is a whole range of kinetic energy values in any given sample.

For most typical reactions, there is a “threshold energy”, that is, a minimum amount of kinetic energy that molecules must have in order to collide hard enough to cause reaction. For most typical reactions, the threshold energy is out in the “tail” of the distribution curve. In other words, at any given time, only a small fraction of the molecules are capable of reacting. The other, slower molecules will eventually have enough energy to react, but do not have enough at that moment. Very fast reactions would have lower threshold energies. Slow reactions would have higher threshold energies.

A 10°C temperature increase is relatively small, yet it can often double a reaction rate. That is due to the fact that the energy distribution curve changes shape, flattening out. Although the average KE increases only slightly, the portion to the right of the threshold energy barrier doubles in size.

Sometimes, it is useful to study the reaction in terms of its potential energy. As molecules collide, their electron clouds interact, deforming as they bend and stretch bonds. As the bonds deform, their potential energy rises. It reaches a maximum when the bonds deform enough to break. As this happens, one of two things can happen: the old bonds can re-form or new ones can form. If you graph potential energy as the reaction proceeds, you get a potential energy curve that looks like this:

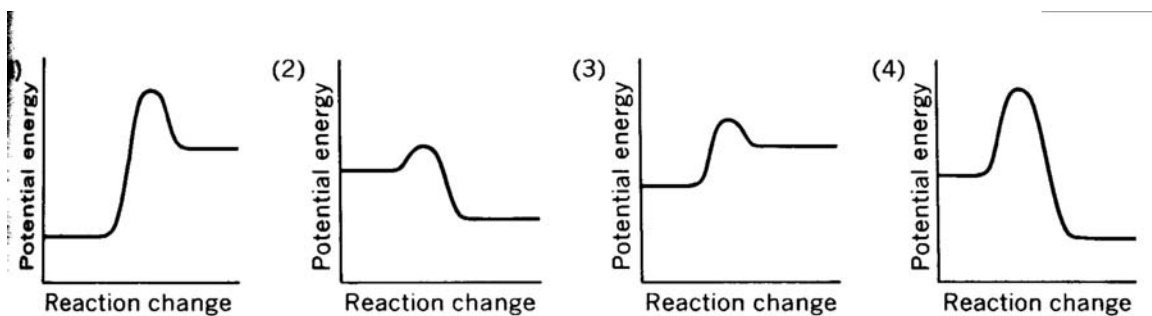


The state of maximum potential energy, in transition between reactants and products is known as the Activated Complex. The minimum potential energy increase required to reach the Activated Complex is known as the Activation Energy. The higher the activation energy barrier, the fewer molecules at any time would have sufficient energy to reach the activated complex, and the slower the reaction would be. Think of the reaction mechanism as an obstacle course, and the activation energy as a wall on the

obstacle course. Everyone will get over a one-foot wall quickly. But if the wall is higher, people may need a few “runs” at the wall to get over it. The higher the wall, the slower the group will get through the course.

Note that there is a net decrease in potential energy for the products as compared to the reactants. That means that heat is released to the surroundings. In other words, an exothermic reaction.

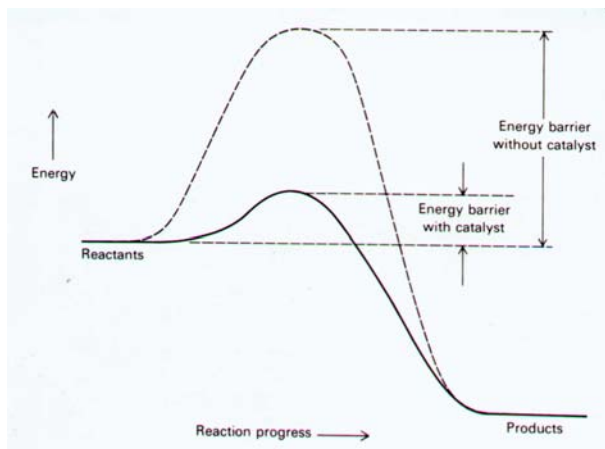
Consider the potential energy diagrams for four reactions. What do the different shapes of the curves represent?



Curve 1 represents an endothermic reaction. So does Curve 3? What is different about them? The activation energy barrier is smaller in 3, so it is faster. 2 and 4 are exothermic. 2 is a faster reaction because its activation energy is smaller.

Catalysis

A catalyst is a substance which speeds up a reaction without being consumed in the reaction. How does it work?



There are two general types of catalysts: Heterogeneous Catalysts and Homogeneous Catalysts. Both work by creating a new mechanism or route that has a lower activation energy than the fastest uncatalysed mechanism.

Homogeneous catalysts are in the same phase as the reactants. They work by providing a new mechanism in which they react in an early step and are re-created in a later step,

thus there is no net loss of catalyst. Heterogeneous catalysts are in a different phase than the reactants. Typically, heterogeneous catalysts are solids and the reactants flow over their surface. Reactant molecules are adsorbed onto the catalyst surface. The molecules' bonds are weakened as they stick to the surface. In addition, the molecules are held in a position so that when other molecules collide with them, chances are better of having an effective collision. Think of it as being the difference between teeing a golf ball up to get a better shot at it compared to trying to hit it out of the rough or a sand trap. The Catalytic Converter in your car's exhaust system is a prime example of a heterogeneous catalyst.

Outline for Rates of Reaction

- I) Need for studying Rates of Reaction
- II) Factors Affecting Rates of Reaction
 - A) Concentration/Surface Area
 - B) Temperature
 - C) Presence of a Catalyst
 - D) Nature of the Reactants
- III) How rates are measured: mol/L/s
- IV) Effects of Concentration
 - A) Using Collision Theory: Explain how concentration affects reaction rate
 - B) Rate Laws
 - 1) By inspection
 - 2) Ratio Method
- V) Reaction Mechanism
 - A) Elementary Steps
 - B) Reaction Intermediates
 - C) Rate Determining Step
- VI) Activated Complex/Transition State Theory
 - A) Energy Distribution Curves
 - B) Threshold Energy
 - C) 10°C increase can double reaction rate
 - D) Potential Energy Diagrams
 - E) Activated Complex
 - F) Activation Energy
 - G) Classifying reactions as fast/slow/endothermic or exothermic based upon their potential energy graphs
- VII) Catalysts
 - A) Provide a new reaction mechanism
 - B) Lower Activation Energy
 - C) Homogeneous catalysts: same state as reactants
 - D) Heterogeneous catalysts: Different state than reactants, provide a surface for the reaction to occur on.