Reaction Kinetics

Chemistry 30

Chemical Reactions

- A **chemical reaction** is the process in which chemical species react to form new substances.
- Reacting molecules are changing into product molecules.
- For reactions to successfully occur, a specific set of criteria must be met. These criteria are easier to meet for some reactions than others, meaning not all reactions will occur at the same rate.

Reaction Rate

- The **rate** of a reaction is a measure of how frequently molecules are changing from reactants to products.
- It is measured as a **decrease in concentration of reactants per unit time** or an **increased in concentration of products per unit time**.
- Units are generally mol/L·s (moles per litre per second) but other units can be used if properties other than concentration are measured

Example Reaction Rates

The reaction rate for the following reaction can be measured in a few different ways:

$CaCO_3 (s) + 2HCl (aq) \rightarrow CaCl_2 (aq) + H_2O (l) + CO_2 (g)$

- Volume change (since a gas is produced):

$$rate = \frac{\Delta V}{t}$$

- Mass change (as solid $CaCO_3$ reacts):

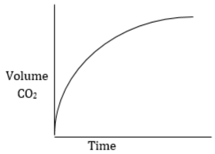
$$rate = \frac{\Delta m}{t}$$

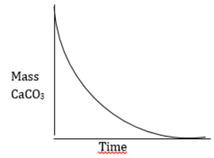
- Concentration change (of HCl or $CaCl_2$):

$$rate = \frac{\Delta[HCl]}{t} \text{ or } rate = \frac{\Delta[CaCl_2]}{t}$$

Sample Reaction Rates

- Each of these changes could be graphed, and would look like this:





Reaction Rates

- All reactions will begin rapidly, then slow down as time progresses. The slope of the line in a rate graph will always start steep and decrease in steepness as the reaction continues.
- This has to do with the number of reactant and product molecules in the system.
- To determine the **instantaneous reaction rate** at any point in time, find the slope of the tangent to the curve at that point.

Review: Particle Theory

- All matter is made of particles (atoms, molecules and ions).
- Particles have empty space between them and are constantly in motion.
- As energy is added to particles, they move faster and spread further apart.

Also remember that breaking chemical bonds (the ones in molecules) requires energy to be put into the system. When new bonds are formed, some energy is released.

Collision Theory

What needs to happen for reactant molecules to start reacting?

This is explained by collision theory. Reactant molecules need:

- To collide (hit each other)
- To be in the correct orientation (collide in the correct way)
- To have enough energy for the bonds to break (this is kinetic energy – basically, they need to be going fast enough)

Collision Theory

What happens when reactant molecules successfully collide?

- The molecules bond together in a very unstable (high potential energy) transition state called the activated complex.
- The molecules in the AC are very weakly bonded, which makes it extremely easy to break apart.

Collision Theory

How are the products formed?

- The AC breaks apart into either the products molecules, or back into the reactant molecules.
- Each of these options is equally likely to occur, which is why it is considered a transition state.

Collision Theory Diagram

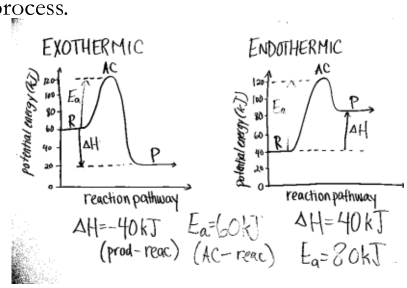
$$A_2 + B_2 \rightarrow 2\ AB$$

Activation Energy

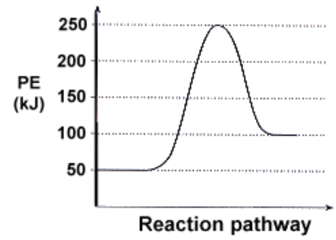
- Activation energy is the minimum amount of energy needed for reactant particles to form the activated complex.
- Even though bonds are being formed, energy is put into the reaction because the AC is so unstable – it takes energy to keep it that way.
- Reactions with a high AE will have fewer successful collisions, which may mean it will be very slow or that it will not produce many product molecules.

Energy Diagrams

- Energy diagrams can be used to model the energy level in the system for a chemical process.



Example: Energy Diagram

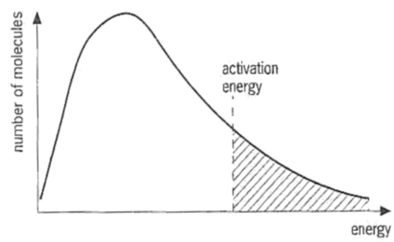


Maxwell-Boltzmann Distribution Curve

- This graph classifies the **number of molecules** in a system based on the **kinetic energy** they have.
- Since temperature is an <u>average</u> of the kinetic energy of the molecules, it means that some will have low energy and some with have very high energy, all averaging around a central value.
- While the shape of the curve is often the same, factors in the system can be changed to alter its shape.

Maxwell-Boltzmann Distribution Curve

- Note that the energy value <u>never</u> touches the y-axis; molecules cannot have zero energy!



Rate-Determining Factors

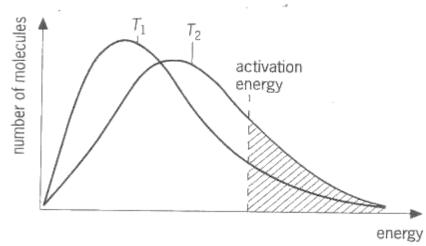
<u>Temperature</u>

Higher temperatures increase the reaction rate.

- It increases the average kinetic energy of the particles in the system, so more particles have enough energy to react.
- The molecules are moving more, so there will be more collisions.

Rate-Determining Factors

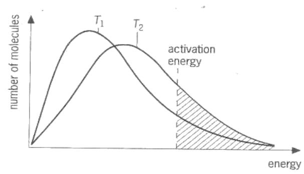
<u>Temperature</u>



Example: Rate-Determining Factors

What would happen to the reaction rate if the temperature was:

- Increased to a higher temperature than T_2?
- Decreased to a lower temperature than T_1?

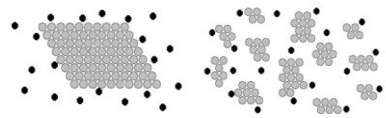


Rate-Determining Factors

Surface Area

More surface area increases reaction rate.

- Reactant molecules can access each other more easily, increasing the number of collisions.



Rate-Determining Factors

Concentration

Increasing the concentration will increase the reaction rate.

- More reactant molecules are present in the system, so there will be more collisions.
- Although the reaction may take longer, since there are more reactants, the average rate will increase.

Rate-Determining Factors

Concentration

Rate-Determining Factors

Catalysts

- A catalyst is a substance that increases the rate of a reaction without being consumed by the reaction.
- An inhibitor acts as the opposite of a catalyst, and slows down the reaction rate without being consumed. An example of this is a food preservative.

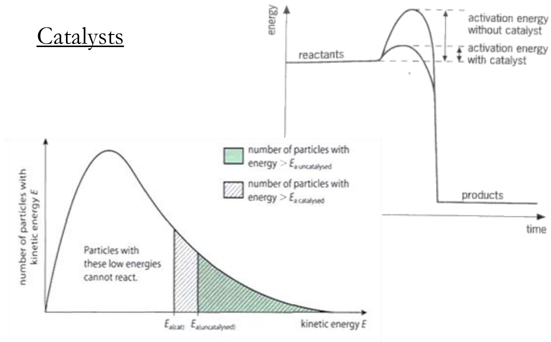
Rate-Determining Factors

Catalysts

- The catalyst lowers the activation energy of the reaction, meaning that more reactant molecules will have enough energy to react.

Rate-Determining Factors

Catalysts



Rate-Determining Factors

In General

- Anything that increases the number of collisions will increase the rate of the reaction.
- By increasing the number of collisions between reactant molecules, there is more chance of having successful collisions that result in the formation of the products.

Reaction Mechanisms

Consider the following reaction:

$$2\ C_2H_2 + 5\ O_2 \rightarrow 4\ CO_2 + 2\ H_2O$$

It seems pretty unlikely that all seven reactant molecules will collide successfully enough times for this reaction to occur at all.

However, this reaction actually occurs very quickly – it is a combustion reaction.

Reaction Mechanisms

- More complex reactions actually undergo a series of simple reactions, simultaneously.
- Different molecules that are not products or reactants are in existence for a brief period of time – these are called **reaction intermediates**.

Reaction Mechanisms

- Each step is called an **elementary step**, because it is a simple reaction. The steps will all add together to make the original reaction (just like in Hess' Law).
- Reaction mechanisms are sometimes "best guesses" of the steps a reaction undergoes, since it is very difficult to measure the presence of reaction intermediates, which are only present for brief periods of time.

Reaction Mechanisms

- Each reaction step will have a different reaction rate, depending on the complexity of the molecules and how much energy they have.
- The slowest step is called the **rate-determining step**, because it sets the pace of the whole reaction.

Example 1: Reaction Mechanism

The reaction between nitrogen monoxide and hydrogen gas occurs in a series of steps.

The reaction mechanism is:

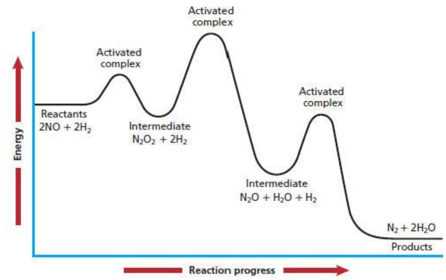
(1) $2\ NO \rightarrow N_2O_2$

(2) $N_2O_2 + H_2 \rightarrow N_2O + H_2O$

(3) $N_2O + H_2 \rightarrow N_2 + H_2O$

- What is the overall reaction?
- What are the reaction intermediates?
- Is there a catalyst? If so, what?

Example 2: Reaction Mechanism



Example 2: Reaction Mechanism

- Which is the slowest step?
- Which is the fastest?
- Which is the rate-determining step? How do you determine which this is?