Chapter 15: Rates of Reactions

As we know, chemical reactions occur when one or more reactants react to form new substances, called products.

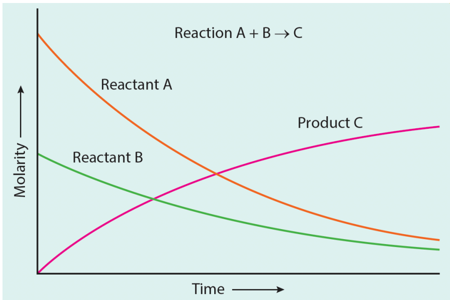
The rate of reaction is the change in concentration of a reactant or product per unit time.

Rate of reaction = $\dfrac{\text{change in concentration of a reactant or product}}{\text{time}}$

We can measure the change in concentration of either:

1. A reactant – (which will react and whose concentration will decrease).

2. The product - (which will form and whose concentration will increase).



Graphs

- The steeper the gradient (slope), the faster the rate.
- The gradient is steepest at the beginning, indicating that the reaction is fastest at that point.
- Reactions are usually fastest at the beginning because the concentration of reactants is at its highest.
- As the reaction progresses and the reactants are used up (i.e. their concentration decreases), the rate of reaction slows down, shown by the slope of the curve becoming less and less steep.
- The slope levels off (flattens) when the reaction stops.

Average rate of reaction

To measure the average reaction rate, we use the formula:

$$\frac{\text{Total change in reactant or product}}{\text{Total time}}$$

For example, let's imagine that it took ten seconds to make 1,000cm^3 of oxygen.
The average rate of the reaction would be: $\dfrac{1000\text{cm}^3}{10}$ = 100 cm^3/ second

Instantaneous rate of reaction

The instantaneous rate of reaction is the rate of reaction at a specific moment in time during the reaction.

To find the instantaneous rate of a reaction, we must use a graph. Choose the time you are finding the instantaneous rate for – e.g. three minutes (180 seconds).

Draw a tangent at that specific point on the graph. To draw a tangent, draw a straight line that just touches the graph at that specific point without crossing the curve.

Choose two easily identifiable points on the tangent ((x1, y1) and (x2, y2)), and use the formula $\frac{y_2-y_1}{x_2-x_1}$ to calculate the slope of the tangent.

Initial rate of reaction

To calculate initial rate, a tangent is drawn at t = 0 and the slope of the tangent calculated using the same formula.

Rate (1/ time)

Time and rate are inversely proportional – as time increases, rate decreases (i.e. if time increases, the reaction takes longer and the reaction rate slows), and vice versa.

$$\textbf{rate} = \frac{1}{\textbf{time}}\ (s^{-1})$$

Collision theory

Collision theory states that particles must collide with one another in order to react. However, not all collisions lead to a reaction – the particles must collide with sufficient energy.

The activation energy of a chemical reaction is the minimum energy that colliding particles must have for effective collisions to occur.

An effective collision is a collision that results in a product being formed

If the colliding particles have less energy than the activation energy, they'll still collide but no bonds will be broken or formed and no product will be made. These are ineffective collisions.

Particles must also collide in a specific orientation. Particles need to collide with the correct orientation so that the atoms that will form new bonds line up correctly with one another. When they do this, bonds in the reactant(s) are broken and new ones formed to make the product(s).

Since only effective collisions result in the formation of products, the **rate of a reaction is dependent on the number of effective collisions per unit time.**

Therefore, to speed up the rate of a reaction, the number of effective collisions per unit time would have to increase.

Either:

1. The total collisions could increase – this also leads to an increase of effective collisions.

or

2. The proportion of particles that have energy equal to or above the activation energy could increase – and therefore the proportion of effective collisions increases.

Factors affecting the rate of a chemical reaction

1. Temperature

Experiment 8: Investigate the effect of temperature on the rate of a reaction (EI) *Since this is an experimental investigation rather than an experiment, different students may have carried out different experiments. Make some brief notes on the investigation **you** carried out & the conclusion you drew from this investigation.*

When a reaction mixture is heated, the particles gain energy = greater number of effective collisions per unit time.

1. Since particles have gained energy, **a larger proportion of them can now reach or exceed the activation energy**, meaning that more of the collisions already occurring are effective.

2. An increase in temperature = increase in energy = increased kinetic energy of the particles. Since particles are moving faster, there are **more collisions**. **If the total number of collisions per unit time increases, the number of effective collisions per unit time also increases.**

A small increase in temperature can lead to a large increase in the rate. A general rule of thumb is that an increase of 10K/10ºC doubles the rate of a reaction.

Exception: Enzymes (which are biological catalysts) work best at a temperature of 37ºC. Above that, the rate may slow or stop entirely.

2. Surface area

Experiment 9: Investigate the effect of surface area on the rate of a reaction (EI)

Since this is an experimental investigation rather than an experiment, different students may have carried out different experiments. Make some brief notes on the investigation ***you*** *carried out & the conclusion you drew from this investigation.*

When a solid reacts in solution – e.g. calcium carbonate in hydrochloric acid – the size of the solid pieces will affect the rate of the reaction. This is because **the size of the pieces determines the surface area of the solid** available to react.

The smaller the particle size = the greater the surface area. This leads to a greater number of effective collisions per unit time, and therefore an increased rate of reaction.

3. Concentration

Experiment 10: Investigate the effect of concentration on the rate of a reaction (EI)

Since this is an experimental investigation rather than an experiment, different students may have carried out different experiments. Make some brief notes on the investigation ***you*** *carried out & the conclusion you drew from this investigation.*

If the concentration of a reactant is increased, it means there are now more particles of the reactant per unit volume = increased number of collisions (per unit time) = increased number of effective collisions (per unit time).

Generally, increase in concentration = increase in rate. There are exceptions to this – see pg 8).

4. Pressure

For reactions happening between gases – i.e. **all-gaseous reactions – increasing the pressure has the same effect as increasing the concentration.**

Note: To identify if a reaction is all-gaseous, we must look carefully at the symbols beside each chemical formula that indicate the state of matter: (s) for solid, (l) for liquid, (g) for gas, and (aq) for aqueous (the substance is dissolved in water*).*

5. Catalysts

Experiment 7: Investigate the effect of a catalyst on the rate of a reaction (EI)

Since this is an experimental investigation rather than an experiment, different students may have carried out different experiments. Make some brief notes on the investigation ***you*** *carried out & the conclusion you drew from this investigation.*

A catalyst is a substance that alters the rate of a reaction without being consumed (used up of chemically changed) in the reaction.

Catalysts are used to speed up chemical reactions. They do this by providing **an alternative reaction mechanism with a lower activation energy**. If the activation energy is lower, more particles will have enough energy to equal or exceed the activation energy. Therefore, a greater number of effective collisions per unit time will occur and the rate will increase.

(Negative catalysts or inhibitors have the opposite effect – they slow down the rate of a reaction).

Enzymes: Enzymes are biological catalysts – i.e. proteins that act as catalysts in living things (organisms). Examples: amylase aids digestion by speeding up the breakdown of starch, lactase aids the breakdown of lactose.

Advantages of using a catalyst

- Allows lower temperatures and/or pressures to be used, which reduces cost.
- Environmental benefit of using catalysts since fossil fuels are often burnt to create the high temperatures needed for industrial reactions. Using a catalyst reduces the use of fossil fuels for this purpose, preventing more CO_2 from entering the atmosphere.
- Catalysts can be reused.

Factor	To increase the rate	What happens?	To decrease the rate	What happens?
Temperature	Increase the temperature (hotplate, Bunsen burner)	Particles gain energy so: 1. More particles reach the activation energy & 2. Particles move faster = the number of collisions increases. Overall = an increase in the number of effective collisions per unit time.	Decrease the temperature (place in fridge or in an ice bath)	Particles lose energy so: 1. Fewer particles reach the activation energy & 2. Particles move more slowly = fewer collisions. Overall = a decrease in the number of effective collisions per unit time.
Surface area	Use reactants with large surface area (e.g. crushed/ powdered $CaCO_3$)	A greater surface area = more collisions per unit time = more effective collisions per unit time	Use reactants with a small surface area (e.g. chips of $CaCO_3$)	A smaller surface area = fewer collisions per unit time = fewer effective collisions per unit time
Concentration	Increase concentration of one or more reactants	Increased concentration = increased number of particles = increased number of collisions per unit time = increased number of effective collisions per unit time	Decrease concentration of one or more reactants	Decreased concentration = decreased number of particles = decreased number of collisions per unit time = decreased number of effective collisions per unit time
Pressure (for all-gaseous reactions)	Increase pressure	Increased pressure = decreased volume = increased number of collisions per unit time = increased number of effective collisions per unit time	Decrease pressure	Decreased pressure = increased volume = decreased number of collisions per unit time = decreased number of effective collisions per unit time
Catalysts	Use a catalyst	Provides an alternative pathway with a lower activation energy	Use a negative catalyst (inhibitor)	It increases the activation energy or interferes with the reaction mechanism

Catalytic mechanisms

1. Surface adsorption theory &
2. The intermediate formation theory

Surface adsorption theory describes heterogeneous catalysis.

Heterogeneous catalysis occurs when the reactants and catalyst are in different phases.

There are three main steps in surface adsorption theory:
1. Adsorption
2. Reactants form product(s)
3. Desorption: product(s) desorb from catalyst

1. Adsorption

The first stage in the surface adsorption mechanism occurs when reactants adsorb onto the surface of the catalyst.

This adsorption is due to temporary bonds formed between the reactants and catalyst.

The formation of these weak bonds between the reactants and the catalyst weakens the bonds of the reactants, reducing the energy required to break them (i .e. lowering the activation energy of the reaction in step 2).

The adsorption of reactants to the surface of the catalyst also brings the reactants close together, resulting in higher concentrations (and therefore more frequent collisions and more effective collisions).

In addition, the catalyst also helps to position the reactants in the correct orientation for the reaction.

Transition metals – e.g. nickel, platinum and iron – are commonly used as catalysts. These catalysts are often used in powdered form or as thin metal coatings in order to maximise their surface area to make them as efficient as possible. Increased surface area = increased adsorption ability.

2. Reactants from product(s)

The adsorbed reactants react to form product(s). Since the reactants are only weakly bound to the catalyst, they can still move, collide and react to form product(s).

3. Desorption

Once the product is formed, it desorbs from the catalyst. More reactants can now adsorb onto the catalyst (which has remained unchanged) and the cycle continues.

Intermediate formation theory

Intermediate formation theory is usually used to describe the mechanism of homogenous catalysis.

Homogeneous catalysis occurs when the reactants and catalyst are both in the same phase.

This mechanism involves the formation of an intermediate. An intermediate is a temporary substance formed during a reaction that's no longer present at the end of the reaction, as it's consumed to form the final product(s).

1. Formation of intermediate
A reactant reacts with the catalyst to form an intermediate compound – e.g. A + C → AC.

2. The intermediate reacts with other reactant(s) to form the product(s)
e.g. AC + B → AB + C.

The activation energy for these two steps is lower than the activation energy needed for the reaction without a catalyst. Since the activation energy is lower, the reaction between AC + B will result in more effective collisions per unit time than the reaction between A + B. Therefore, the rate of reaction will be faster with the catalyst than in the uncatalysed reaction.

Reaction without a catalyst: A+ B → AB (slow)
Reaction with a catalyst (C): A + C → AC
AC + B → AB + C (fast)

Limitations of collision theory

1. Orientation

As we know, collision theory states that particles must collide in the correct orientation for a reaction to occur. However, collision theory treats particles as fairly simple shapes and doesn't sufficiently explain the collisions of molecules with more complex shapes.

2. Catalysts

Catalysts will alter the rate of a chemical reaction only as long as they are not (a) saturated or (b) poisoned.

a) Saturation of catalysts
If the surface of the catalysts is saturated (i.e. fully occupied by reactant molecules), increasing the concentration of the reactants will have no effect on the rate of reaction. Products must desorb from the surface of the catalyst before more reactants can adsorb.

b) Poisoned catalysts
Although catalysts can be reused, they are often poisoned by catalyst poisons. A catalyst poison poisons the catalyst by permanently adsorbing onto its surface. The poison accumulates on the surface of the catalyst over time and causes it to be less effective or stops it from working entirely.

3. Concentration

Collision theory states that an increase in concentration increases the rate of reaction. Generally this is true. However, there are some exceptions to this:

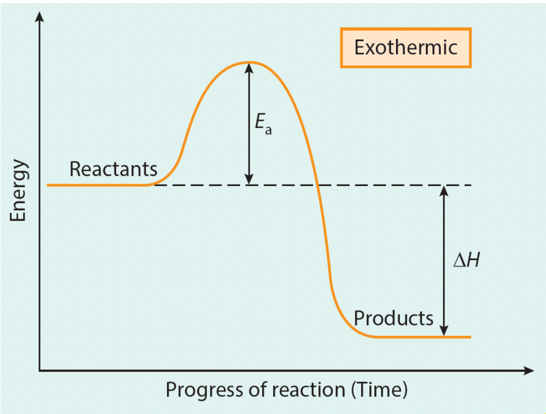
Saturated catalyst: As we have just seen, if the catalyst is saturated, an increase in concentration of the reactants doesn't lead to an increase in the rate of reaction.

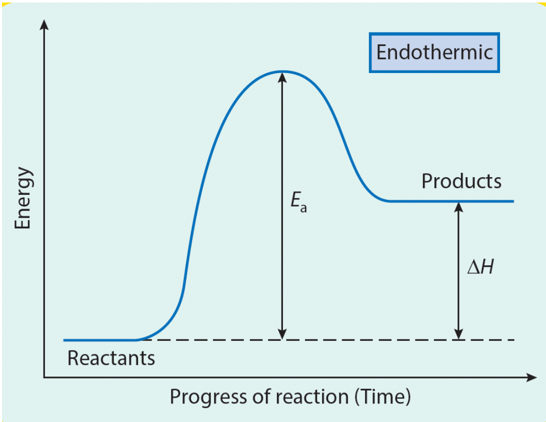
Limiting reagents: When a reaction involves multiple reactants, an increase in the concentration of one reactant may not alter the rate of reaction unless there is a sufficient amount of the other reactants also.

If a change in concentration does not affect the rate determining step: Some complex reactions happen in several steps. The slowest step in a reaction mechanism is the one that controls the overall rate at which the reaction proceeds and is called the rate-determining step. It usually has the highest activation energy. An increase in concentration may not change the overall speed of the reaction if it doesn't alter the rate determining step.

<u>Energy profile diagram</u>

Exothermic reactions are chemical reactions that release energy (typically in the form of heat. The products of an exothermic reaction have less energy than the reactants, with the excess energy released as heat. As a result, the temperature increases and the reaction vessel warms up.





Endothermic reactions are chemical reactions that absorb energy (typically in the form of heat). The reactants in an endothermic reaction take in energy in the form of heat, which is used as chemical energy to break bonds and enable the reaction to proceed. Since heat is absorbed, the products have more energy than the reactants. Since heat energy is taken from the surroundings (and converted into chemical energy), the temperature falls and the reaction vessel cools down.

<u>Catalysed reaction profile diagrams</u>

Include…
1. A **lower activation energy**
2. **Colour coding** or a **key** to distinguish between the catalysed and uncatalysed reactions.