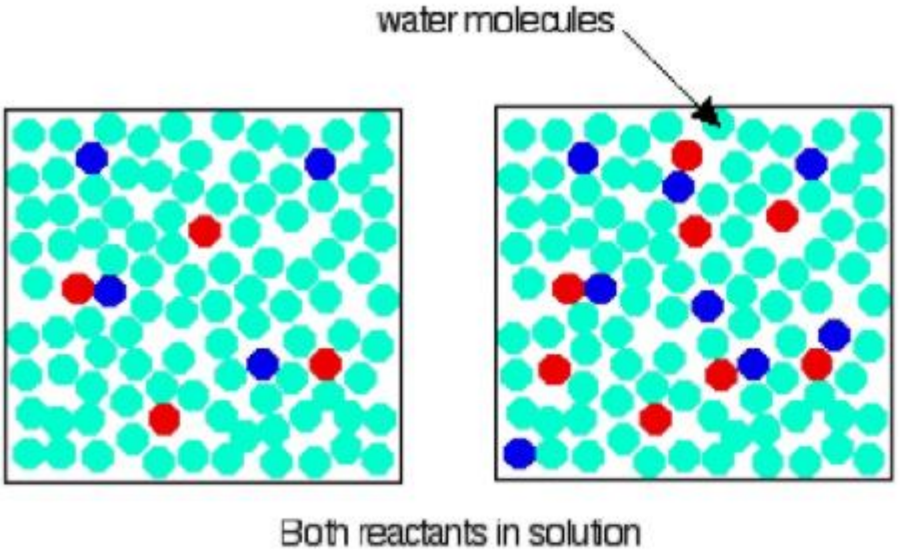
UNIT 4

INTRODUCTION TO PHYSICAL CHEMISTRY

PART 2 – RATES OF REACTION



Contents

Key words: collision, effective collision, collision frequency, collision energy, activation energy, catalyst, surface area, concentration-time graph, gradient, tangent.

Units which must be completed before this unit can be attempted:
Unit 1 – Atomic Structure and the Periodic Table
Unit 2 – Particles, Structure and Bonding
Unit 3 – Amount of Substance

1. Simple collision theory

Substances in the liquid, aqueous and gaseous phase consist of particles in rapid and constant motion, which are constantly colliding with each other. According to simple collision theory, there are two requirements for a reaction to take place between two particles:

- They must first collide
- The colliding particles must have enough energy to react together

(a) collision frequency

If a chemical reaction is to take place between two particles, they must first collide. The number of collisions between particles per unit time in a system is known as the **collision frequency** of the system.

The greater the collision frequency, the faster a chemical reaction.

(b) collision energy

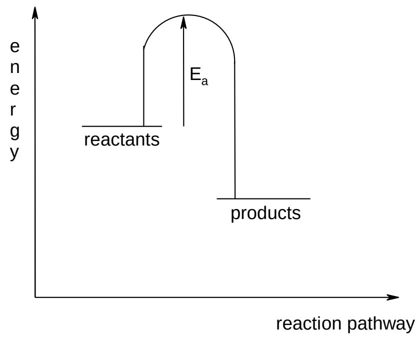
Not all collisions, however, result in a chemical reaction. This is because the reacting particles contain chemical bonds which must be broken before the particles can react. Energy is required to break these bonds, and the colliding particles often do not have enough energy to do this. Most collisions, therefore, just result in the colliding particles bouncing off each other. Collisions which do not result in a reaction are known as **unsuccessful (or ineffective) collisions**.

The combined energy of the colliding particles is called the **collision energy**. If the collision energy is sufficient to break the bonds in the reacting particles, a reaction will take place.

Collisions which result in a chemical reaction are known as **successful (or effective) collisions**.

(c) activation energy

Most reacting particles contain chemical bonds which must be broken for a chemical reaction to take place. The minimum energy required to do this is known as the **activation energy**. The activation energy can be shown in an enthalpy level diagram:



This enthalpy diagram shows a simple exothermic reaction. The activation energy E_a is the energy needed to break the bonds in the colliding particles. The potential energy of the substance increases as the bonds are broken. Once the bonds have been broken, new bonds can be formed and the potential energy will decrease. In exothermic reactions, more heat energy is released when new bonds are made than is absorbed when the old bonds are broken. So overall, heat energy is released.

If the collision energy of the colliding particles is less than the activation energy, the collision will be ineffective. If the collision energy is equal to or greater than the activation energy, the collision will be effective and a reaction will take place.

2. Factors Affecting Rate of Reaction

The rate of a chemical reaction can be changed in a number of ways:
- by changing the concentration of the reacting particles
- by changing the pressure of the system (if some of the reacting particles are in the gas phase)
- by changing the temperature of the system
- by adding a catalyst

Each of these factors can be considered in turn:

a) concentration

The greater the concentration of the species in a liquid or gaseous mixture, the greater the number of species per unit volume and the greater the frequency with which they will collide. Hence **an increase in concentration causes the rate of reaction to increase by increasing the collision frequency**.

The collision energy and activation energy are unaffected by a change in concentration.

An increase in concentration increases the rate of reaction because
- **the number of particles per unit volume increases**
- **so the collision frequency increases**

Practical: investigate the effect of the concentration of sodium thiosulphate ($Na_2S_2O_3$) on the rate of its reaction with hydrochloric acid (HCl)

1) Take a piece of paper and use a thick pen to draw the letter X on it
2) Measure out 20 cm of 0.2 moldm^{-3} HCl into a measuring cylinder labelled "HCl" and then pour the HCl into a conical flask
3) Measure out 20 cm of 0.2 moldm^{-3} $Na_2S_2O_3$ into a measuring cylinder labelled "$Na_2S_2O_3$"
4) Pour the $Na_2S_2O_3$ into the same conical flask, starting the stopwatch immediately.
5) Record the time taken for the X to stop being visible through the conical flask.
6) Repeat steps 2 to 5, but using different concentrations of $Na_2S_2O_3$ in step 3, prepared as follows:

Concentration of $Na_2S_2O_3$moldm^{-3}	Volume of 0.2 moldm^{-3} $Na_2S_2O_3$/cm^3	Volume of distilled water/cm^3
0.15	16	4
0.10	12	8
0.05	8	12

7) Compare the times taken for the X to disappear in the four reactions. How does the rate of reaction change as you change the concentration of $Na_2S_2O_3$?
www.youtube.com/watch?v=FSwd7X_c_Qs

b) pressure

A change in pressure has exactly the same effect as a change in concentration.

The greater the pressure in a gaseous mixture, the greater the number of species per unit volume and the greater the frequency with which they will collide. Hence **an increase in pressure causes the rate of reaction to increase by increasing the collision frequency**. The pressure of a system is generally increased by reducing its volume (compressing it).

The collision energy and activation energy are unaffected by a change in pressure.

An increase in pressure increases the rate of reaction because

- **the number of particles per unit volume increases**
- **so the collision frequency increases**

c) temperature

An increase in temperature increases the rate of a reaction for two reasons:

As the temperature is increased, the average kinetic energy of the particles increases, and so the **collision energy** increases. As the collision energy increases, there is a greater chance that the collision energy will be sufficient to overcome the activation energy, and the collision is more likely to be effective. So **an increase in temperature increases the rate of reaction by increasing the collision energy.**

In addition, at a higher temperature, the molecules have more kinetic energy and are thus moving faster. Thus they collide more often, and the **collision frequency** increases. So **an increase in temperature increases the rate of reaction by increasing the frequency.**

The rate of reaction increases when the temperature is increased because the collision frequency and the collision energy both increase. Of these two reasons, the increase in collision energy is the most important and accounts for about 95% of the increase in rate for a given reaction. The activation energy is unchanged.

An increase in temperature increases the rate of reaction because

- **the mean collision energy of the particles increases**
- **so more of the particles have a collision energy greater than the activation energy**
- **so the collisions are more likely to be effective**
- **and the particles are moving faster**
- **so the collision frequency increases**

On average, a 10^{o}C temperature rise approximately doubles the rate of reaction.

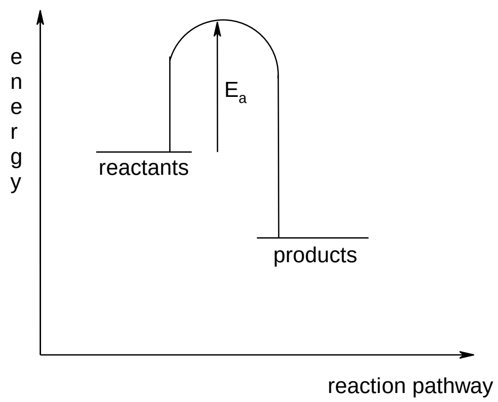
Practical: investigate the effect of temperature on the rate of reaction between sodium thiosulphate ($Na_2S_2O_3$) and hydrochloric acid (HCl)

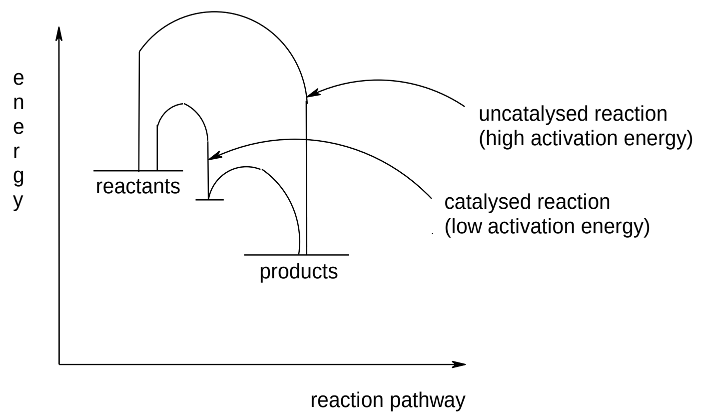
1) Set up three water baths at 30 ^{O}C, 40 ^{O}C and 50 ^{O}C and place stock solutions of 0.2 moldm^{-3} HCl and 0.2 moldm^{-3} $Na_2S_2O_3$ in each water bath until they have reached the desired temperature. Keep a sample of both solutions at room temperature.
2) Take a piece of paper and use a thick pen to draw the letter X on it
3) Using the room temperature solutions, measure out 20 cm of 0.2 moldm^{-3} HCl into a measuring cylinder labelled "HCl", then measure out 20 cm of 0.2 moldm^{-3} $Na_2S_2O_3$ into a measuring cylinder labelled "$Na_2S_2O_3$"
4) Pour both solutions into the same conical flask, starting the stopwatch immediately. Record the initial temperature of the mixture.
5) Record the time taken for the X to stop being visible through the conical flask.
6) Repeat steps 3 to 5, but using the solutions at 30 ^{O}C, then at 40 ^{O}C and then at 50 ^{O}C.
7) Compare the times taken for the X to disappear in the four reactions. How does the rate of reaction change as you change the temperature?
   www.youtube.com/watch?v=L9nVcKYVjjA

d) catalysts

A **catalyst is a substance which changes the rate of a chemical reaction without itself being chemically altered at the end of the reaction**.

Catalysts provide an alternative pathway for the reaction, usually by introducing an extra step into the reaction, which has a lower activation energy than the uncatalysed reaction. This effect can be illustrated with an enthalpy level diagram:





The enthalpy level diagram on the left shows a reaction without a catalyst. The diagram on the right shows the effect of adding a catalyst. The reaction pathway changes and the activation energy is lowered.

Catalysts increase the rate of a reaction by lowering the activation energy. The collision frequency and collision energy are unchanged.

A catalyst increases the rate of reaction because
- **the activation energy of the particles decreases**
- **so more of the particles have a collision energy greater than the activation energy**

Practical: investigate the effect of a catalyst on the rate of reaction between potassium peroxodisulphate ($K_2S_2O_8$) and potassium iodide (KI)

1) Mix together 25 cm^3 of 0.3 $moldm^{-3}$ KI, 5 cm^3 of 0.02 $moldm^{-3}$ sodium thiosulphate, 1 cm of 1% starch solution and 10 cm^3 of distilled water.
2) Add 10 cm^3 of 0.1 $moldm^{-3}$ $K_2S_2O_8$ and immediately start the stopwatch. Note the time taken for the mixture to turn a dark blue colour.
3) Repeat steps 1 and 2, but this time using 9 cm^3 of distilled water and 1 cm^3 of iron (III) sulphate solution.
4) Compare the reaction times in both reactions. Why is the second reaction faster?
www.youtube.com/watch?v=5da9e-rrjxQ

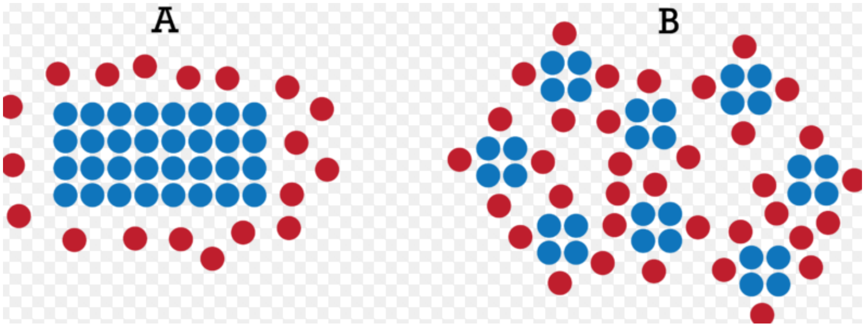
e) physical states of reactants

If reactants are gaseous, or well mixed in liquid or aqueous form, then all of the particles in the sample are able to react.

Particles in the solid state, however, are not free to move. Therefore only the particles at the **surface** of the solid are able to collide with other particles. This reduces the collision frequency and will reduce the rate of reaction.

Reactants in the solid state react more slowly than reactants in the liquid, gaseous or aqueous states because the particles not at the surface of the solid are unable to take part in collisions with other reactants, reducing the collision frequency.

The rate of reaction in solids can be increased by reducing the particle size, and hence increasing the **surface area** exposed to collisions:



A – large particle size, fewer of the blue solid particles can collide with the red particles, slower reaction.
B – small particle size, more of the blue solid particles can collide with the red particles, faster reaction.

Practical: investigate the effect of particle size on the rate of reaction between calcium carbonate and hydrochloric acid

1) Pour 40 cm^3 of 2 $moldm^{-3}$ HCl into a conical flask.
2) Weigh out 2.5 g of marble chips (large particle size).
3) Add the marble chips to the conical flask containing the HCl, start the stopwatch and weigh the conical flask with all its contents.
4) Weigh the conical flask again after 2 minutes and record the loss in mass.
5) Repeat steps 1 – 4 but using 2.5 g of marble chips (small particle size).
6) Why does the mass of the conical flask decrease? In which experiment is there a larger decrease in mass? Why is this?
www.youtube.com/watch?v=p6Kq4YqztQM

f) the reaction medium (the solvent)

If reactions are taking place in solution, the nature of the solvent can influence the rate of reaction. This is because different solvents can interact with the reacting particles in different ways, making them more likely, or less likely, to react with each other.

Eg magnesium reacts rapidly with HCl dissolved in water, but very slowly with HCl dissolved in methylbenzene.

g) Summary of factors affecting rate of reaction

Effect:	On collision frequency	On collision energy	On activation energy	On rate of reaction
Increase concentration	Increases	No effect	No effect	Increases
Increase pressure	Increases	No effect	No effect	Increases
Increase temperature	Increases	Increases	No effect	Increases
Add a catalyst	No effect	No effect	Decreases	Increases
Using solid state reactants	Decreases	No effect	No effect	Decreases
Using different solvents	No effect	No effect	Changes	Changes

3. Measuring rates of reaction

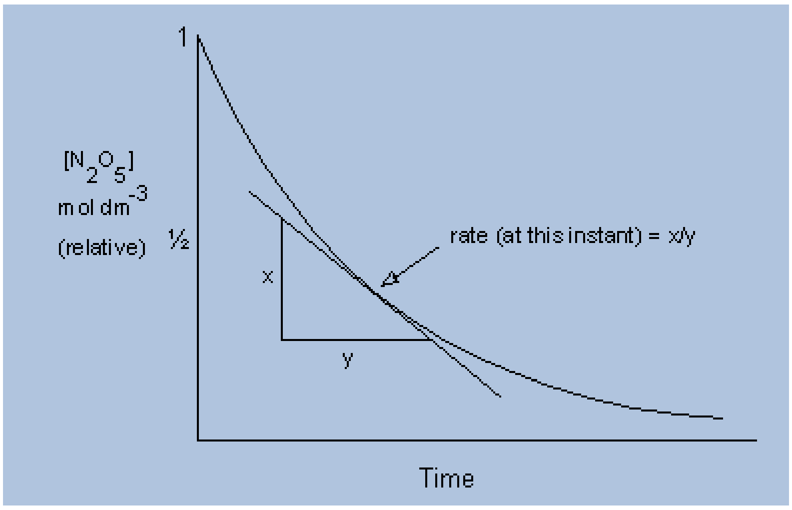
The rate of reaction can be defined as the **change in concentration of reactants or products per unit time**. It has the units $moldm^{-3}s^{-1}$.

It is possible to determine the rate of a reaction by monitoring how the concentration of a reaction changes over time in a single reaction, and then plotting a graph of concentration against time (a **concentration-time graph**).

As reactions proceed, the concentration of reactants decreases, making collisions between the remaining particles less frequent. As a result, the rate of reaction usually decreases with time.

The rate of reaction is the change in concentration per unit time and can therefore be calculated from the gradient of the line at a particular time.

As the graph is a curve (its gradient is steadily decreasing with time), the gradient of the line at a particular point must be calculated by drawing a tangent to that line at a particular point and calculating the gradient of that tangent.



The initial rate of reaction is the gradient of the tangent to the curve at t = 0.

The rate of reaction at a particular time is the gradient of the tangent to the curve at that particular time.

Test Your Progress: Topic 4 Part 2 Exercise 1

Hydrogen peroxide, H_2O_2, decomposes according to the equation:

$$2H_2O_2(g) \rightarrow 2H_2O(g) + O_2(g)$$

In an experiment, the concentration of the reactant H_2O_2 was measured over a period of time. The results are shown below:

Time/s	0	15	30	60	100	180
$[H_2O_2]$/moldm^{-3}	0.40	0.28	0.19	0.07	0.03	0.01

Plot a graph to show how concentration varies with time and use your graph to calculate the rate of reaction:

a) Initially
b) When $[H_2O_2]$= 0.20 moldm^{-3}
c) After 50 s

Practical: measuring the rate of the reaction between magnesium and hydrochloric acid (HCl) from a concentration-time graph

1. Clamp a gas syringe into a horizontal position so that the bung attached to it can be easily attached to a measuring cylinder.
2. Pour 25 cm^3 of 0.2 moldm^{-3} HCl into a 100 cm^3 conical flask.
3. Weigh out 1 g of magnesium on a weighing boat.
4. Add the magnesium to the conical flask, attaching the bung and starting the stopclock immediately.
5. Record the volume of gas produced every 10 seconds until the reaction stops or the volume of gas reaches 100 cm^3. Record your data in the table below:

Time/s	Volume of H_2 produced (V_t) /cm^3	(V_f – V_t)/cm^3
0		
10		
20		
30		
40		
50		
60		
70		
80		
90		
100		
final		

(V_f – V_t) gives you a value proportional to [HCl]

6. Plot a graph of (V_f – V_t) (on the y-axis) against time (on the x-axis)
7. Use your graph to determine the initial rate of reaction.