RATE OF REACTION AND EQUILIBRIUM

Rate of reaction

Some reactions proceed very fast. For example, when aqueous ammonia is added to a solution of lead(II) salts, a white precipitate forms immediately. Some reactions proceed at moderate speed. For example, it takes some time for the reaction between calcium carbonate and dilute hydrochloric acid to come to completion. Other reactions are slow. For example, it takes iron a few days to rust in moist air. The above mentioned reactions proceed at different rates.

The rate of a chemical reaction is the progress of the reaction in unit time. In other words, the rate of a chemical reaction is the rate at which products are formed or the rate at which reactants are used up in the reaction.

$$\text{Rate of reaction} = \frac{\text{concentration in moles per litre}}{\text{time in seconds}}$$

Units for the rate of reaction are moles/litre/second i.e mol/l/s.

Determination of rate of reaction

Let us consider the reaction between magnesium and dilute hydrochloric acid.

$Mg(s) + 2HCl\ (aq) \rightarrow MgCl_2\ (aq) + H_2(g)$

The determination of the rate of this reaction can be done by either measuring the volume of hydrogen evolved with time or by measuring the time a given length of magnesium ribbon takes to dissolve in varying concentrations of the acid.

Determination of rates of reaction by measuring the volume of the gas evolved with time

A known mass of magnesium and a known volume of dilute hydrochloric acid in a test-tube tied with a thread, are placed in a conical flask and the experiment is set up as shown in figure 11.1. The stopper is opened for a moment so that thread is free. The test-tube drops pouring hydrochloric acid into the conical flask. At the same time, the clock is started. The volume of hydrogen in the syringe is recorded at regular intervals until the reaction is complete.

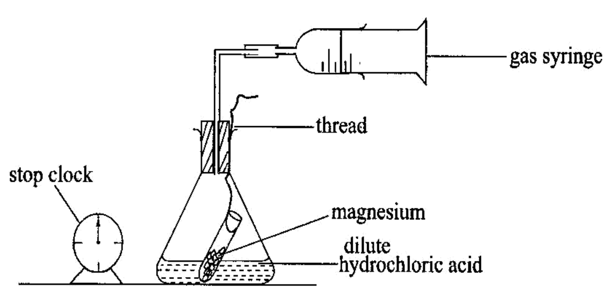

Fig 11.1 Determination of rate of reaction

A graph of volume of hydrogen evolved against time is plotted. A typical graph has the form of figure 11.2.

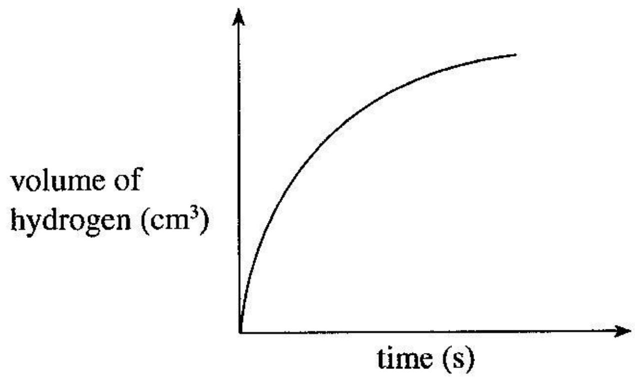

Fig 11.2 Graph of volume of hydrogen evolved against time

To determine the rate of reaction at a given time, say t_1, the tangent to the curve is drawn at that time as shown in figure 11.3. The gradient of the tangent is the rate of reaction at that time, that is y/x. the units are cm^3/s.

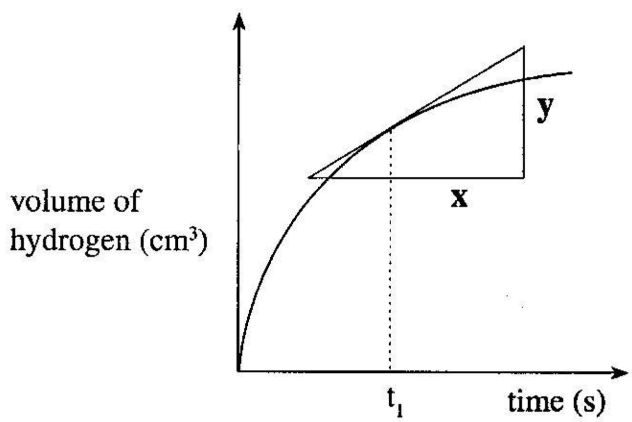

Fig 11.3 Determination of rate of reaction

Exercise

In determination of the rate of reaction, 10 g of calcium carbonate were reacted with dilute hydrochloric acid. The mass of the flask and its contents was weighed with time.

Write the equation for the reaction that took place.
Sketch a graph of mass of flask and its contents against time.

Factors affecting the rate of chemical reactions

Factors which affect the rate of a chemical reaction are concentration, temperature, surface are (particle size), pressure, catalyst and light. You are required to perform various experiments to investigate the effect of these factors on the rate of chemical reactions.

Effect of concentration of reactants on the rate of reaction

The rate of the reaction depends on the frequency with which reacting particles collide, which frequency depends on the concentration of the reactants. The higher the concentration, the higher the frequency of collision and therefore the higher the rate of the chemical reaction.

Experiment:

Investigation of the effect of concentration on the rate of the reaction

Make a mark with blue or black ink on a piece of paper. Place 50 cm^3 of 0.05 M sodium thiosulphate solution into a beaker. Add 10 cm^3 of 1 M hydrochloric acid to the sodium thiosulphate and at the same time start the stop clock. Gently shake the mixture to mix the solution well and place the beaker on the paper over the mark. Watch the mark through the solution from above the beaker. Stop the clock when the mark just disappears.
Vary the concentration of the thiosulphate solution by taking 40, 30, 20 and 10 cm^3 each time by adding distilled water. Tabulate your results including 1/time. Plot graphs of volume of sodium thiosulphate solution against 1/time ($time^{-1}$) and against time. The rate of reaction is proportional to the reciprocal of time ($time^{-1}$). Your graphs should appear as shown in figure 11.4a and 11.4b.

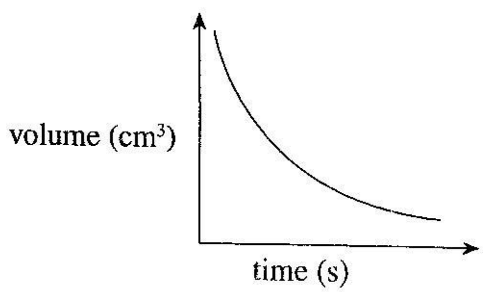

Fig 11.4a Graph of volume of sodium thiosulphate against time

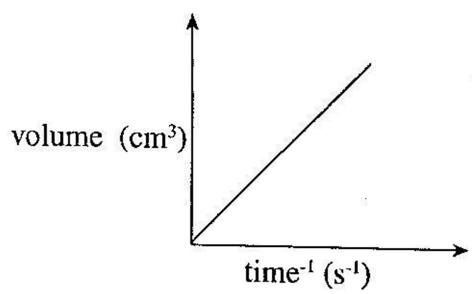

Fig 11.4b Graph of volume of sodium thiosulphate agaist time $^{-1}$

The mark disappears because the reaction between hydrochloric acid and sodium thiosulphate forms a precipitate of sulphur which renders the mixture opaque.

$NaS_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + S(s) + H_2O(l) + SO_2(g)$

Figure 11.4a shows that the higher the volume of the sodium thiosulphate, the less the time taken to form a precipitate. Figure 11.4b shows that the rate of the reaction increases with increase in volume of sodium thiosulphate solution.

Exercise

Magnesium was reacted with excess dilute sulphuric acid.

Write an equation for the reaction that took place.

On the same axis, sketch a graph of volume of hydrogen evolved against time when equal volumes of the following are reacted with the same mass of magnesium

0.5 M sulphuric acid.

2 M sulphuric acid.

On the same axis, sketch a graph of volume of hydrogen evolved against time when the following are reacted with the same concentration and volume of sulphuric acid.
10 g of magnesium.
50 g of magnesium.

Effects of temperature on the rate of reaction

When the temperature is increased, the reacting particles gain more kinetic energy and move at a greater speed. The frequency at which the reacting particles collide increases and thus the rate of the reaction increases. Therefore, the higher the temperature, the higher the rate of reaction.

Investigation of the effect of temperature on the rate of reaction

The previous experiment can be repeated by reacting sodium thiosulphate solution and hydrochloric acid at varying temperatures, using the same concentration of the thiosulphate. Put a test-tube containing 1 M hydrochloric acid into a beaker of water maintained at 30 ^{O}C. After sometime, add at the same time start of 0.05 M sodium thiosulphate solution in a beaker and at the same time start mark. Note the time taken for the mark to disappear. The experiment is repeated using different temperatures. Tabulate your results including 1/time. Plot graphs of temperature against 1/time. The shapes of typical graphs are shown in figure 11.5a and 11.5b.

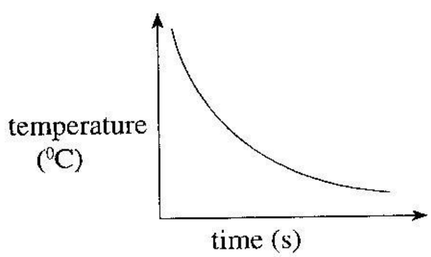

Fig 11.5a
Graph of temperature against time

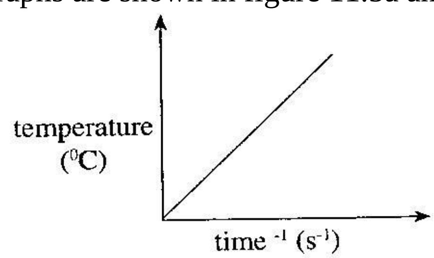

Fig 11.5b
Graph of temperature against time $^{-1}$

Figure 11.5a shows that the higher the temperature the less the time taken to form a precipitate. Figure 11.5b shows that the rate of the reaction increases with increase in temperature.

Exercise
Sodium sulphite solution was added to dilute sulphuric acid.

Write an equation for the reaction that took place.
On the same axis, sketch a graph of volume of sulphur dioxide against time when the reaction was carried out at
24 ^{O}C.

40 ^{O}C.

Effect of a catalyst on the rate of reaction

A catalyst is a substance which alters the rate of chemical reactions without undergoing any overall chemical change itself. Most catalysts speed up the rate of reaction. The greater the amount of the catalyst but within the limits, the higher the rate of reaction. Powdered catalysts offer a larger surface area over which the reaction takes place and therefore are more effective than one in lump form. Catalysts remain unchanged chemically after a reaction has taken place.

Catalysts are very specific to a particular chemical reaction. A catalyst which slows down a reaction is called a negative catalyst.

Investigation of the effect of catalyst on the rate of reaction

Place 100 cm^3 of 0.1 M hydrogen peroxide in a conical flask. Add 0.5 g of manganese(IV) oxide to the hydrogen peroxide in conical flask. Then set up the experiment as shown in figure 11.1. record the volume of oxygen in the syringe at regular intervals until the reaction is complete. Repeat the experiment using 1 g of manganese(IV) oxide. When the graphs of volume of oxygen against time are plotted using the same axes, they appear as shown in figure 11.6.

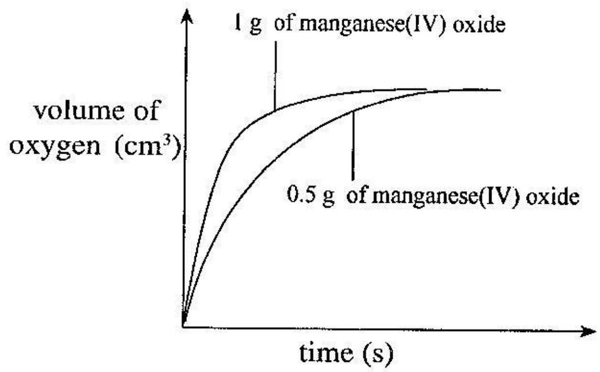

Fig 11.6 Graphs of volume of oxygen against time

Exercise

a) Name the catalysts used in the following processes/reactions.

The contact process.

The Haber process.

The decomposition of hydrogen peroxide.

Hydrogenation of oils to form fats.

b) Potassium chlorate decomposes according to the following equation.
$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$

(a) Name the catalyst that may be used in this reaction.

(b) On the same axis, sketch a graph of volume of oxygen evolved against time when

The catalyst is not used.

0.5 g of the catalyst are used.

Effect of surface area on the rate of reaction

Solid react much more rapidly when powdered than when in large lumps. This is because reactions with solids take place at the surface. Powdered solids present a large surface area over which the reaction occurs than solids in lump form.

Investigation of the effect of surface area on the rate of reaction

Pour 20 cm^3 of 1 M hydrochloric acid in a test-tube. To the conical flask add 10 g of calcium carbonate lumps and then set up the experiment as shown in figure 11.1. Record the volume of carbon dioxide in the syringe at regular intervals until the reaction is complete. Repeat the experiment using the same mass of powdered calcium carbonate. When the graphs of volume of carbon dioxide against time for both powdered calcium carbonate and calcium carbonate lumps, are plotted using the same axes, they appear as shown in figure 11.7.

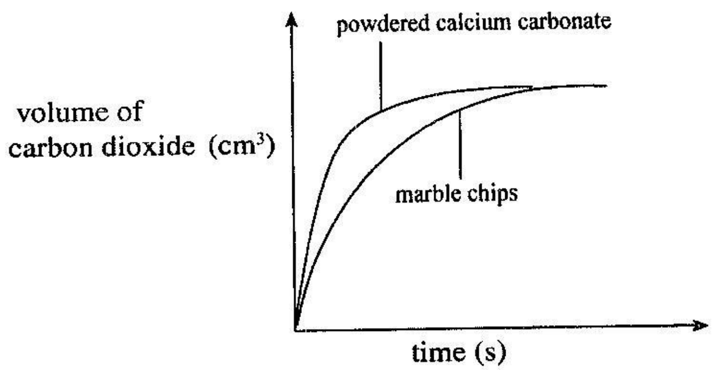

Fig 11.7 Graphs of volume of carbon dioxide against time

Exercise

Calcium carbonate lumps were mixed with dilute nitric acid in a conical flask. The mass of the flask and its contents was weighed with time.
Write the equation for the reaction that took place.
(i) Sketch a graph of mass of flask and its contents against time. Label the graph A.

On the same axis, sketch the graph that would be obtained when powdered calcium carbonate is used instead of calcium carbonate lumps. Label the graph B.

(a) Which one of the following reaction mixtures will produce hydrogen more quickly at room temperature?
Magnesium ribbon + dilute sulphuric acid.

Magnesium powder + dilute sulphuric acid.

Give a reason for your answer in (a).

Suggest two other methods by which the rate of this reaction can be altered.

Effect of light on the rate of reaction

Some reactions are photosensitive, that is, their rates are affected by light.

Investigation of the effect of light on the rate of reaction

Add 1 cm^3 of sodium chloride solution to two test-tubes. To each test-tube add a few drops of silver nitrate solution. Immediately, a white precipitate forms. Put one test-tube in a dark cup board and the other in sunlight for about 4 minutes. Record your observations.
Sodium chloride solution forms a white precipitate with silver nitrate solution according to the equation.

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

In presence of light, the precipitate darkens because of the decomposition of silver chloride to solver and chlorine. In absence of light, the precipitate remains white.

$$2AgCl(s) \rightarrow 2Ag(s) + Cl_2(g)$$

The effects of light on hydrogen peroxide and concentrated nitric acid explain why they are stored in dark-glass bottles.

Effect of pressure on the rate of reaction

A change in pressure only affects reactions which occur in the gas phase. When pressure of a gaseous mixture is increased, the gases are compressed. This brings the reacting particles together and thus increases the frequency at which the reacting particles together and thus increases the frequency at which the reacting particles collide hence increased rate of reaction.

EQUILIBRIUM

Equilibrium is the point in a reversible reaction when the rate at which the reactants are forming the products is equal to the rate at which the products are dissociating to the reactants. Therefore, at equilibrium, both the products and the reactants are present. A reversible reaction is one which proceeds in both directions, that is, forward and backward.

Factors affecting equilibrium

The factors that affect equilibrium are temperature, pressure, concentration and catalyst. The effect of these factors on equilibrium was first investigated by Louise Le Chatelier who came up with a principle known as **Le chatelier's principle.** The principle states that when a chemical equilibrium reaction is distributed externally by a change in one of the factors upon which it depends, the equilibrium shifts in a direction so as to reduce the effects of the change.

Temperature

Consider the Haber process where the reaction is exothermic.

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = 93.63 \text{ kJ mol}^{-1}$$

The forward reaction is exothermic and therefore the backward reaction is endothermic. If heat is supplied, the equilibrium shifts in the direction which requires more heat, that is, the backward reaction which uses up the excess heat occurs. However, if the equilibrium vessel is cooled, the equilibrium shifts to the right, producing more ammonia.

Pressure

In a gaseous system, an increase in pressure leads to a decrease in the volume of the gases involved and the reverse is true. Let us again consider the Haber process.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

One volume of nitrogen combines with three volumes of hydrogen to produce two volumes of ammonia. The forward reaction occurs with a decrease in volume from four to two volumes. If additional pressure is applied to the system, the equilibrium shifts in the direction of a reduction in volume, that is, the forward reaction is favoured and more ammonia is produced. If pressure of the system is decreased, the equilibrium shifts in the direction of an increase in volume, that is, the backward reaction occurs and more of the reactants are produced. Gaseous equilibrium reactions which are not accompanied by a change in volume, are not affected by pressure changes e.g

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

Exercise

Consider the following reaction equations:

$H_2(g) + I2(g) \rightarrow 2HI(g) \qquad \Delta H = +52\ kJ\ mol^{-1}$

$3H_2(g) + N_2(g) \rightarrow 2NH_3(g) \qquad \Delta H = 93.63\ kJ\ mol^{-1}$

What will be the effect on the concentration of hydrogen iodide and ammonia in the equilibrium mixture of

Increasing the temperature?

Decreasing the temperature?

Increasing the pressure?

Decreasing the pressure?

Concentration

If the concentration of one of the substances present in an equilibrium reaction is changed, the equilibrium shifts in the direction of a decrease in the concentration of the added substance. Consider the following reaction.

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

If extra oxygen is pumped into the reaction vessel, the equilibrium shifts in the direction that results in a decrease in oxygen concentration, that is, the forward reaction occurs and more nitrogen monoxide is produced. If the concentration of one of the reactants decreases instead of increasing, the equilibrium will shift to cancel this decrease and the backward reaction will occur to restore the balance. If more of nitrogen monoxide is added to the equilibrium mixture, the backward reaction will occur producing more reactants, that is, the equilibrium shifts to the left in order to offset the effect of the increase in concentration of nitrogen monoxide. If there is a decrease in the concentration of nitrogen monoxide, the forward reaction is favoured and the equilibrium shifts to the right producing more nitrogen monoxide.

Catalyst

Catalysts do not have any effect on the position of the equilibrium. In an equilibrium reaction, a catalyst increases the rate of both the forward and backward reactions, that is, a catalyst enables an equilibrium to be attained much more quickly than when there is no catalyst.

Industrial applications of chemical equilibrium

This idea of equilibrium is applied in some industrial process. In the Haber process, ammonia is synthesized from nitrogen and hydrogen according to the equation.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -93.63 \text{ kJ mol}^{-1}$$

Ammonia is produced with a decrease in volume and therefore high pressure will increase the yield of ammonia. The reaction is exothermic therefore low temperature will favour the production of ammonia. However, by lowering the temperature, the rate of the reaction is reduced. The presence of a catalyst will give a sufficient reaction rate despite the relatively low temperature. In general, a maximum yield of ammonia is obtained by using the following conditions.

Very high temperature of 250 to 500 atmospheres.
Temperature of about 450 ^{o}C.
Catalyst of finely divided iron.
Aluminium oxide is added to make the catalyst more porous hence promoting its effectiveness.

Exercise

1. A certain mass of zinc powder was reacted with dilute hydrochloric acid at room temperature.
   (i) Write an equation for the reaction.
   (ii) Draw a graph to show how the volume of the gaseous product varied with time.
   (b) What would be the effect of
   - (i) Adding copper(II) sulphate solution to the reaction mixture at room temperature?
   - (ii) Using the same mass of zinc granules instead of the zinc powder?

   Give a reason for your answer in (b) (ii).

2. 12.0 g of clean magnesium ribbon were added to 50 cm^3 of 1 M sulphuric acid. The volume of the gas evolved was measured at fixed time interval until the reaction stopped.
   a. Write the equation of the reaction that took place.
   b. (i) sketch a graph of volume of the gas (on y-axis) against time (on-axis). Label the graph G_1.
   (ii)On the same axis sketch the graph that would be obtained if 12.0 g of magnesium powder were used instead of magnesium ribbon. Label this graph G_2.

   (iii) Give a brief explanation of the cause of difference in the graphs G_1 and G_2. (ii) Name one other factor that can cause similar results as in b(i) above
3. a. 12 g of large pieces of calcium carbonate were reacted with 50 cm^3 of 2 M hydrochloric acid at room temperature. The decrease in mass was measured at regular intervals.
   i. Write an equation for the reaction.

ii. Sketch a graph to show variations of decrease in mass with time.

b. State what would be observed if the same mass of calcium carbonate powder was used instead of the large pieces. Give a reason for your answer.

c. State what would be observed if the same mass of large pieces of calcium carbonate was used at 40 ^{O}C. Give a reason for your answer.

d. Which of the two reactants was in excess?

4. The figure 11.11 shows the setup of the experiment used to study the rate of evolution of a gas when 1.0g of powdered calcium carbonate was reacted with 50cm^3 of 2 M hydrochloric acid at 25 ^{O}C.

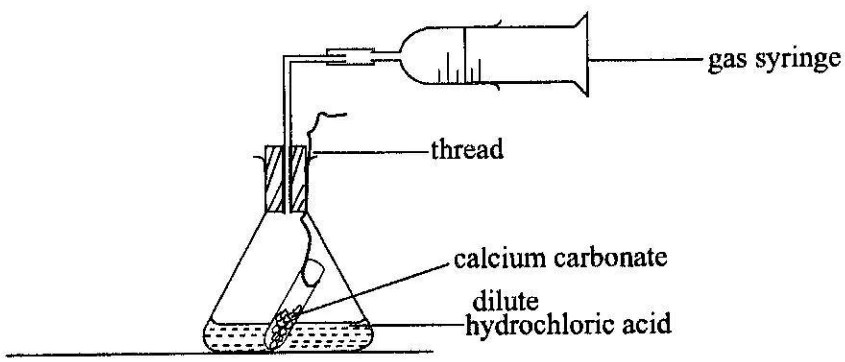

Fig. 11.11

a) Sketch a graph to show the variation of the volume of the gas evolved in the reaction with time. Describe the shape of the graph.
b) On the same diagram in (a) above sketch a graph to show the results obtained when 1.0 g of powdered calcium carbonate was reacted with 100 cm^3 of 1M hydrochloric acid at 25 ^{O}C.
c) 1.0 g of powdered calcium carbonate was reacted with 50 cm^3 of 2 M hydrochloric acid at 25 ^{O}C.

   i. Explain the shapes of the graphs you have sketched in (b) (i) and (ii) above.
   ii. 1.0 g of powdered calcium carbonate was reacted with 20 cm^3 of 2 M hydrochloric acid. Which one of the reactants was in excess?

d) When a certain volume of 0.1 M hydrochloric acid was reacted at room temperature with excess of iron filings, a gas was produced.
   i. Draw a labeled diagram to show how the rate of reaction was determined.
   ii. Write equation for the reaction that took place.
   iii. Draw a sketch graph of the volume of the gas evolved against time.
   iv. State how the rate of reaction would change if the reactions was carried out at a temperature above room temperature.