

6. RATE, ENERGY AND EQUILIBRIUM IN CHEMICAL REACTION

6.1 Introduction

We have studied in Chapter 5 how a chemist calculates the amounts of reactants to mix, and the amount of product to expect. He may also need to know how fast a reaction proceeds in order to take a decision about what method to follow in making a compound. How do chemists determine the rates of chemical reactions? What factors affect the rates? What do chemists do to control a reaction if the reaction is reversible, endothermic or exothermic? We shall answer these and other questions in this chapter.

6.2 Types of Chemical Reactions

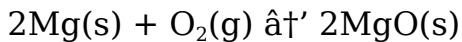
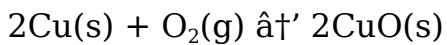
We can classify chemical reactions into the following broad groups according to some phenomena observed during the reactions:

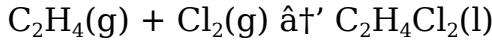
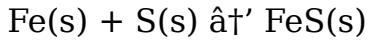
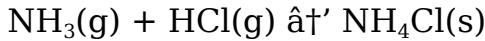
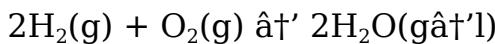
- (1) Simple combination,
- (2) Thermal decomposition,
- (3) Neutralization,
- (4) Double decomposition,
- (5) Reduction-oxidation (Redox) reactions,
- (6) Hydrolysis,
- (7) Reversible reactions,
- (8) Displacement reaction.

We have already encountered examples of most of these groups. They are reproduced below for clarity. Some reactions may fall into two or more of these groups.

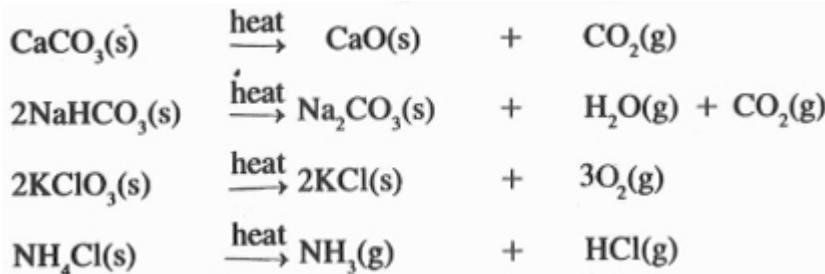
- (1) **Simple combination reactions are those in which two or more elements or simple compounds combine to form a compound.**

Examples include the following:



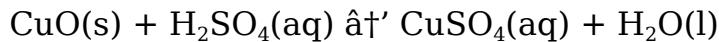
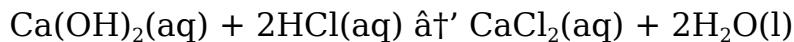
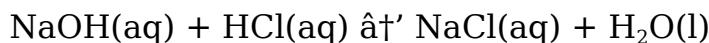


- (2) **Thermal decomposition involves a breakdown of a compound by heat into two or more components.** Examples include:

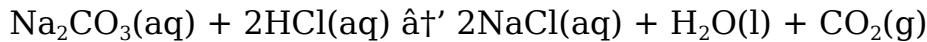


- (3) **Neutralization is the reaction between an acid and a base to form salt and water only.**

Examples:



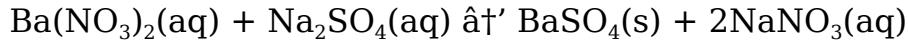
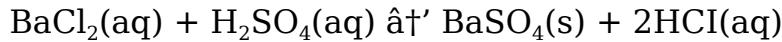
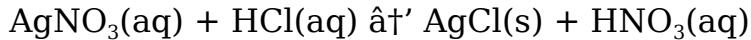
The use of sodium trioxocarbonate(IV) in volumetric analysis does not make the reaction



a neutralization reaction. Rather, sodium trioxocarbonate(VI) is hydrolysed by water to form sodium hydroxide which is then neutralised by the acid. (See hydrolysis below).

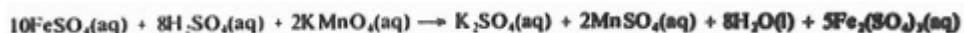
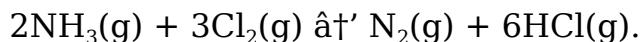
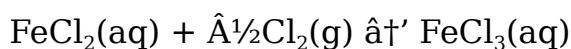
- (4) **Double decomposition is a reaction between the aqueous solutions of two soluble compounds in which an insoluble compound precipitates out.**

Examples:



- (5) **Oxidation is defined as increase in the oxidation number of an element, and reduction as decrease in the oxidation number of an element.**

Examples of redox reactions include the following:





- (6) **Hydrolysis:** We noted earlier that sodium trioxocarbonate(IV) undergoes hydrolysis in water to give an alkaline solution. It is not alone in this behaviour. What type of salts behave similarly? Does every hydrolysis produce an alkaline solution? Let us find out.

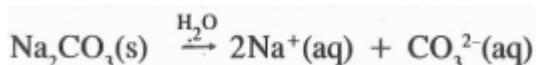
Experiment 6.1: Investigating Hydrolysis of Salts.

Dissolve about 1g of each of the salts listed in Table 6.1 in about 5 cm³ of water. Test the resulting solutions with litmus paper (blue and red). Table 6.1 shows the results that should be obtained.

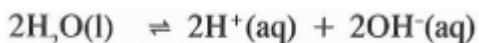
TABLE 6.1 HYDROLYSIS OF SOME SALTS

| Salt | Effect of solution on litmus |
|---------------------------------|------------------------------|
| Na ₂ CO ₃ | Red litmus turns blue |
| CH ₃ COONa | Red litmus turns blue |
| AlCl ₃ | Blue litmus turns red |
| FeCl ₃ | Blue litmus turns red |

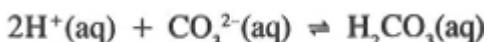
Each of the salts dissociates into free ions in water, e.g,



Water also ionises, though to a small extent.



Since trioxocarbonate(IV) acid is a weak acid, something similar to a double decomposition occurs: union of 2H⁺ and CO₃²⁻ to form weakly dissociated trioxocarbonate(IV) acid.



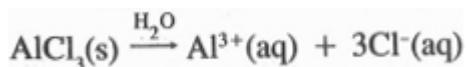
The withdrawal of H⁺ from the solution causes the ionisation of more water. Hydroxide and sodium ions therefore accumulate and the solution becomes alkaline.

Salts of strong bases and weak acids hydrolyse in water to yield alkaline solutions.

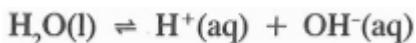
TABLE 6.2 SALTS OF STRONG BASE AND WEAK ACIDS

| Strong base | Weak acid | Derived salt |
|-------------|--------------------------------|---------------------------------|
| NaOH | H ₂ CO ₃ | Na ₂ CO ₃ |
| NaOH | CH ₃ COOH | CH ₃ COONa |

With aluminium chloride in water the reactions occurring are



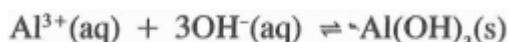
i.e. dissociation to mobile ions of AlCl₃



i.e. partial ionisation of water.

H⁺ and Cl⁻ remain in solution because hydrogen chloride acid (hydrochloric acid) is a strong acid.

Al³⁺ and 3OH⁻ combine to form poorly ionised aluminium hydroxide since aluminium hydroxide is a weak base.



The withdrawal of OH⁻ causes ionisation of more water resulting in excess of H⁺, hence the solution becomes acidic.

Salts of strong acids and weak bases hydrolyse in water to yield acidic solutions.

TABLE 6.3 SALTS OF STRONG ACID AND WEAK BASE

| Strong acid | Weak base | Derived salt |
|--------------------|---------------------|---------------------|
| HCl | Al(OH) ₃ | AlCl ₃ |
| HCl | Fe(OH) ₃ | FeCl ₃ |

EXERCISE 6A

What type of aqueous solution:-, neutral, acidic or basic, will the following salts yield? Explain.

- (a) Copper(II) chloride
- (b) Sodium chloride
- (c) Potassium ethanoate.

Note: Salts of strong acids and strong bases or weak acids and weak bases are not hydrolysed in aqueous solution, hence they give neutral solutions.

(7) **Reversible reactions:** These are reactions in which the reactants form products which can themselves react to give back the reactants.

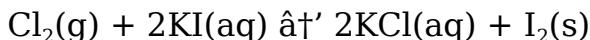
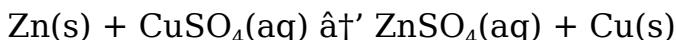
Ammonium chloride is decomposed by heat to ammonia and hydrogen chloride, while ammonia and hydrogen chloride can combine to form ammonium chloride under certain conditions. This is an example of a reversible reaction.



More examples and further information about reversible reactions will be discussed later.

- (8) **Displacement reaction** is one in which an element that is more active replaces another element that is less active from a solution of its compound.

For example:



6.3 Factors which affect the Rate of Chemical Reactions

Consider the general reaction,



The rate of production of either C or D, or the rate at which either A or B is used up is a measure of the rate of the reaction. We know from everyday experience that changes in certain factors such as temperature, changes the rate of chemical reactions. Also, we know that the more we dilute a sample of an acid such as hydrochloric acid, the less vigorous it will react with zinc or magnesium. Beside temperature and concentration, there are other factors which affect the rate of chemical reactions.

The effects of all these factors will now be investigated.

Experiment 6.2: Investigating the effect of concentration on reaction rate.

Wash and dry five conical flasks thoroughly. Label the flasks 1 – 5. Mix the amounts of distilled water and hydrogen peroxide (20 volume) as indicated in Table 6.4 inside the flasks.

TABLE 6.4

| Flasks | 1 | 2 | 3 | 4 | 5 |
|--|----|----|----|----|----|
| Volume of water (cm ³) | 20 | 15 | 10 | 5 | 0 |
| Volume of 20 volume H ₂ O ₂ (cm ³) | 5 | 10 | 15 | 20 | 25 |

If only 10 volumes H₂O₂ is available, use the mixtures in Table 6.5.

TABLE 6.5

| Flasks | 1 | 2 | 3 | 4 | 5 |
|--|----|----|----|----|----|
| Volume of water (cm ³) | 40 | 30 | 20 | 10 | 0 |
| Volume of 10 volume H ₂ O ₂ (cm ³) | 10 | 20 | 30 | 40 | 50 |

Set up the apparatus shown in Figure 6.1. To each flask in turns, add 1g of manganese(IV) oxide, and immediately start a stop-clock. Determine the time it takes to collect 10 cm³ of oxygen in the gas syringe.

SPECIMEN RESULTS AND CALCULATION

| | | | | | |
|--|---------|---------|---------|---------|--------|
| Relative fractional concentration of H ₂ O ₂ . | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 |
| Time (sec) | 396 | 231 | 156 | 120 | 91.8 |
| $\frac{1}{\text{time}}$ | 0.00253 | 0.00433 | 0.00641 | 0.00833 | 0.0109 |

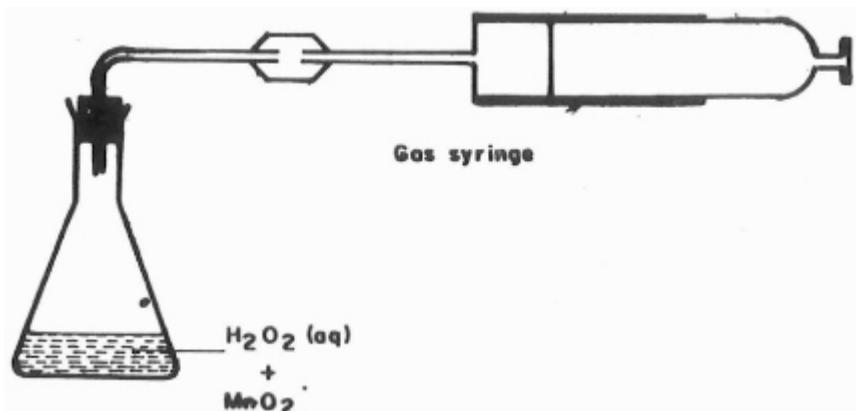


Figure 6.1 Studying the effect of concentration on the rate of chemical reaction.

Notice that as the concentration of H₂O₂ increases, the time taken to produce 10 cm³ of oxygen decreases. The shorter the time to produce 10 cm³ of oxygen, the faster the reaction. Calculate the reciprocal of

the time, $\frac{1}{t}$. This is a measure of the rate. A plot of $\frac{1}{t}$ against concentration hydrogen peroxide thus gives the variation of rate with concentration (Figure 6.2). It is a straight line graph passing through the origin. This indicates that the rate of reaction is directly proportional to the concentration of the reactant.

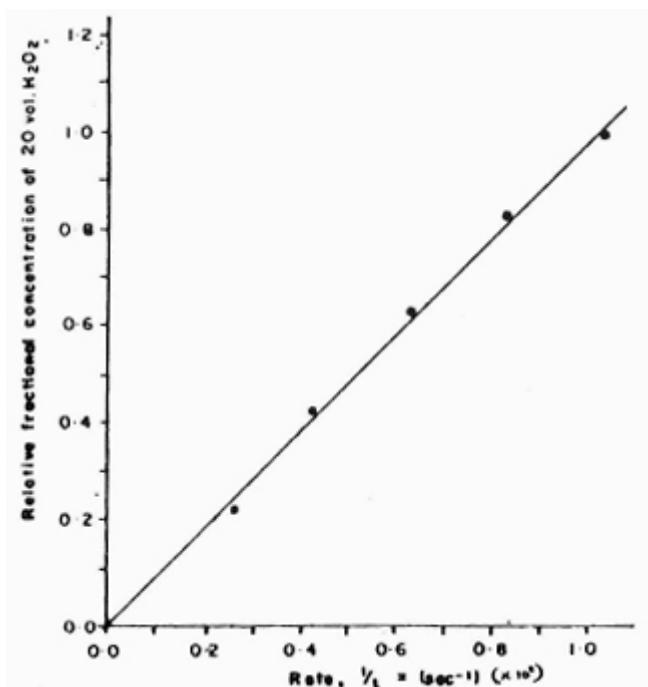


Figure 6.2 Graph of relative fractional concentration of H_2O_2 vs.

$$\frac{1}{t}$$

Experiment 6.3: Investigating the effect of concentration on the rate of precipitation of sulphur from sodium thiosulphate, $Na_2S_2O_3$.

Prepare approximately 2 mol dm^{-3} solution of sodium thiosulphate, $Na_2S_2O_3$ by dissolving 50g of the crystals in 100 cm^3 of water. Transfer 30 cm^3 of the solution into a clean 100 cm^3 beaker and add 5 cm^3 of water to it. Place the beaker on a piece of white paper on which a cross is marked (Figure 6.3). Add 5 cm^3 of bench 2 mol dm^{-3} hydrogen chloride acid (hydrochloric acid) and simultaneously start a stop-clock. Stop the stop-clock when the cross becomes just invisible while viewing it from above the beaker. Record the time taken for the precipitation of enough sulphur to cover the mark.

Repeat with the other concentrations of the mixture of sodium thiosulphate solution as shown in the Table 6.6. Calculate $\frac{1}{t}$ and plot a graph of the relative concentration of $Na_2S_2O_3$ against $\frac{1}{t}$ (Figure 6.4).

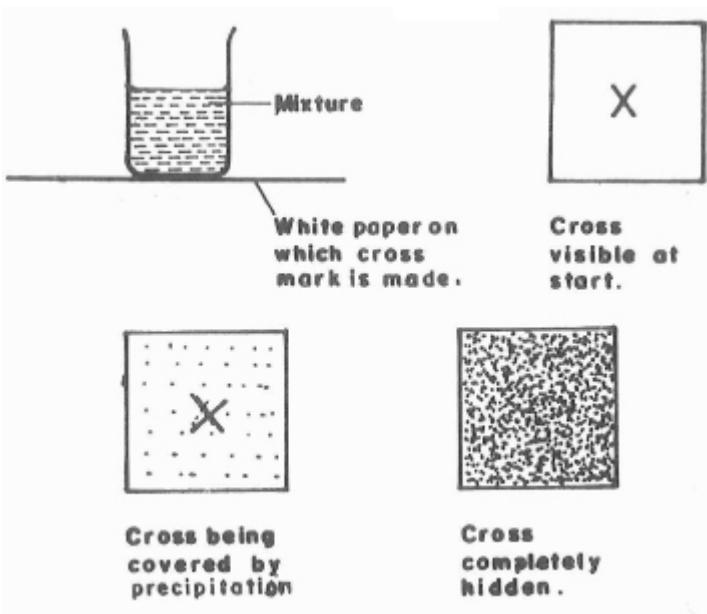
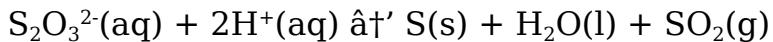


Figure 6.3 Effect of concentration on the rate of reactions

TABLE 6.6

| | | | | | | |
|---|--------|-------|-------|-------|-------|-------|
| Na ₂ S ₂ O ₃ solution (cm ³) | 30 | 25 | 20 | 15 | 10 | 5 |
| Water (cm ³) | 5 | 10 | 15 | 20 | 25 | 30 |
| HCl (cm ³) | 5 | 5 | 5 | 5 | 5 | 5 |
| Time (seconds) | 11.6 | 15 | 17 | 24 | 36 | 90 |
| Reciprocal of time ($\frac{1}{t}$) | 0.0867 | 0.067 | 0.059 | 0.042 | 0.028 | 0.011 |

It will be observed from the results that the higher the concentration of the sodium thiosulphate in the solution, the faster the rate of the reaction. The equation for the reaction is:



The explanation for the general observation that the higher the concentration of reactants the faster the reaction, is that reactions result from the collision between reactant molecules. The higher the concentration, the more the number of collisions per unit time, and hence the faster the rate of the reaction.

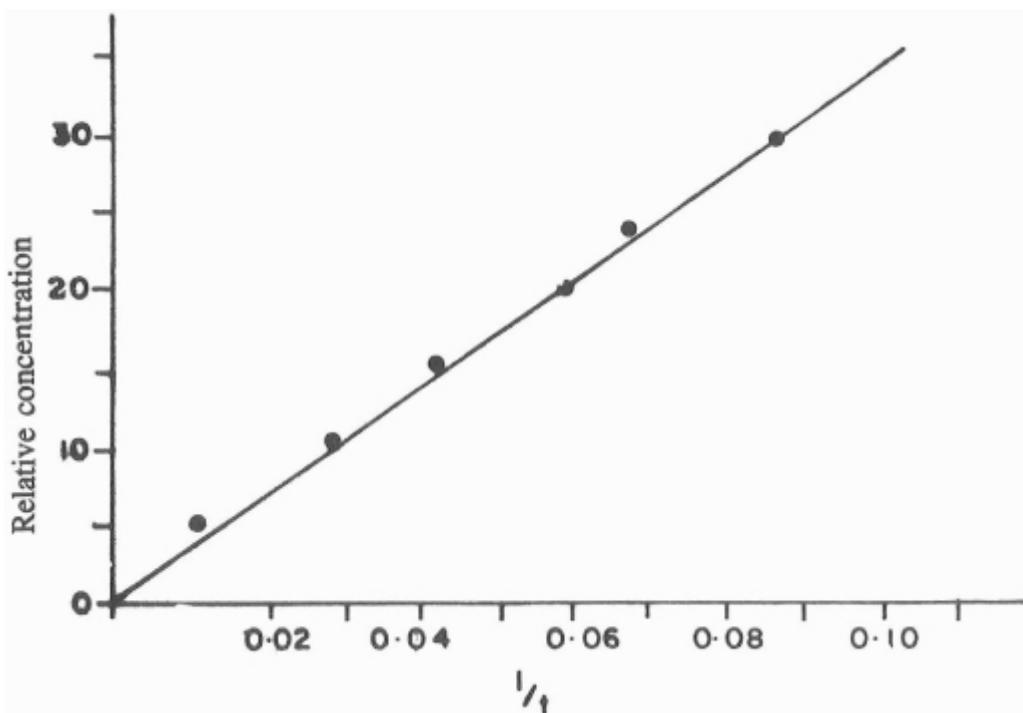


Figure 6.4 Graph of concentration of $\text{Na}_2\text{S}_2\text{O}_3$ vs $\frac{1}{t}$

Experiment 6.4: Investigating the effect of concentration on the rates of chemical reactions: the iodine-clock experiment.

Prepare the following solutions:

- (1) A solution containing 2 g of sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$, crystals plus 5 cm^3 bench tetraoxosulphate(VI) acid, made up to 100 cm^3 .
- (2) A solution containing 4.5 g potassium trioxoiodate(V), KIO_3 , made up to 1 dm^3 .
- (3) Starch solution, made by adding boiling water to a paste of starch in a little cold water.

Pour 10 cm^3 of the acidified solution of sodium thiosulphate into a small beaker (100 cm^3 beaker will do). To this, add 1 cm^3 of the starch solution and 10 cm^3 of the potassium trioxoiodate(V) solution. Start a stop-clock immediately. Swirl the beaker to mix the reactants, then place it on a white paper with a cross marked on it. Note the time it takes for the mark to become completely covered by the blue solution that is formed.

Repeat the experiment with different dilutions of the potassium trioxoiodate(V) solution made by mixing the solution prepared above with water as in Table 6.7.

TABLE 6.7

| | | | | | | |
|---|----|---|---|---|---|---|
| Volume of KIO_3 solution (cm^3) | 10 | 8 | 6 | 5 | 4 | 2 |
| Volume of water (cm^3) | 0 | 2 | 4 | 5 | 6 | 8 |

Tabulate your results as follows:

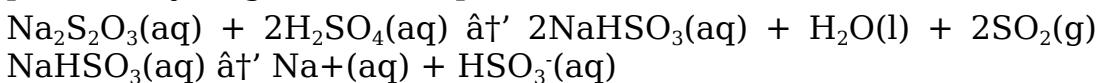
TABLE 6.8

| | | | | | | |
|--|----|---|---|---|---|---|
| Relative concentration of KIO_3 | 10 | 8 | 6 | 5 | 4 | 2 |
| Time taken (seconds) | | | | | | |
| Reciprocal of time, $\frac{1}{t}$ | | | | | | |

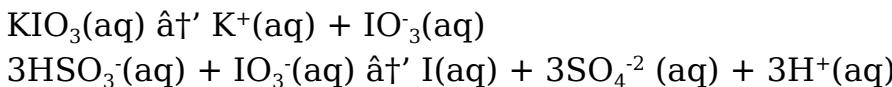
Treat the results as in Experiments 6.2 and 6.3.

The reactions that take place are as follows:

1. Sodium thiosulphate and tetraoxosulphate(VI) acid react to produce hydrogen trioxosulphate(IV) ions.

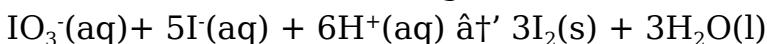


2. The hydrogen trioxosulphate (IV) ion reacts with trioxoiodate(V) ion from the ionisation of potassium trioxoiodate(V) forming iodide ion.



Reactions (2) continue until all the hydrogen trioxosulphate(IV) from reaction (1) is used up.

- (3) The excess trioxoiodate(V) ions then react with the iodide ion from reaction (2), liberating free iodine molecules.



The iodine liberated then forms a complex blue colour with starch.

The experiment illustrates that the higher the concentration of trioxoiodate(V) ions, the shorter the time to produce iodine. That is, the faster the reaction.

From these experiments we conclude that the rates of chemical reactions increase with increase in the concentrations of the reactants. This is because at high concentration the reacting particles are crowded and collision between them is more frequent, resulting in increased rate of reaction.

Effect of temperature on the rate of chemical reaction

Experiment 6.5: Investigating the effect of temperature on the rate of

chemical reactions.

Experiments 6.2, 6.3 and 6.4 can be repeated at different temperatures, keeping the concentrations of the reactants constant.

Repeat Experiment 6.2 at room temperature using 30 cm³ of 10 volume hydrogen peroxide and 1g of manganese(IV) oxide.

Immerse the flask containing the reaction mixture in a larger beaker of ice (Figure 6.5). Note the temperature of the experiment and the time it takes to produce 10 cm³ of oxygen. Again immerse the beaker in a water bath maintained at a fairly constant temperature. Note the temperature and time it takes to produce 10 cm³ of oxygen. Raise the temperature of the

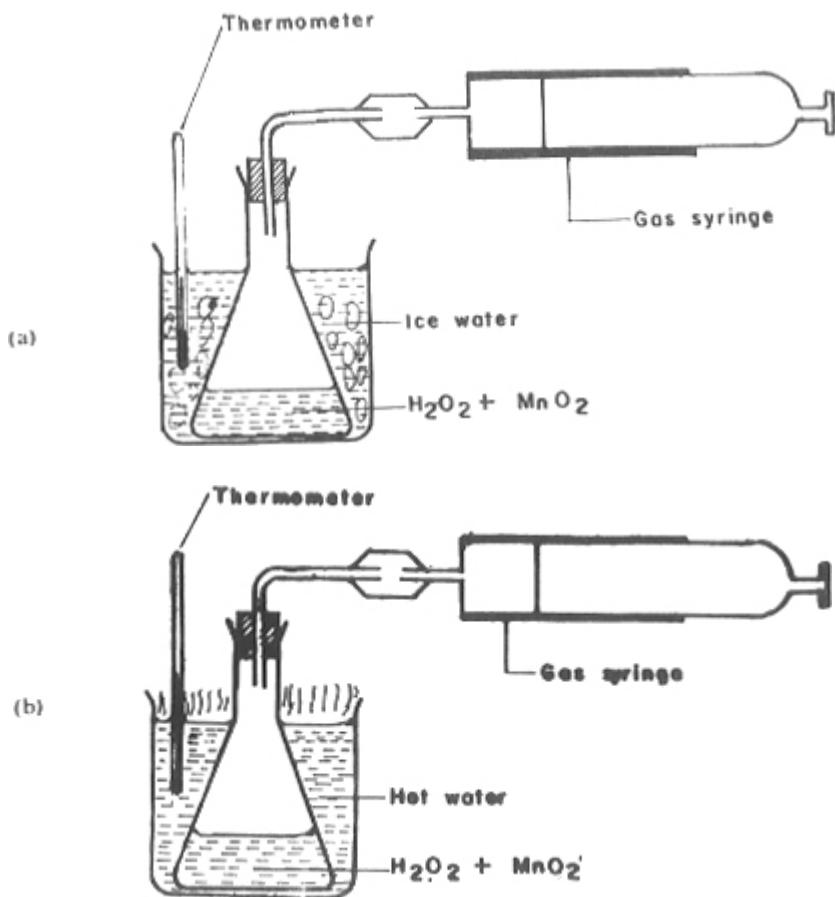


Figure 6.5: Studying the effect of temperature on reaction rate.

water bath and repeat. In the absence of a water bath, water heated by a low bunsen flame in a large beaker can be used. If the temperature tends to rise above a desired temperature, the flame is removed, and replaced when the temperature begins to fall.

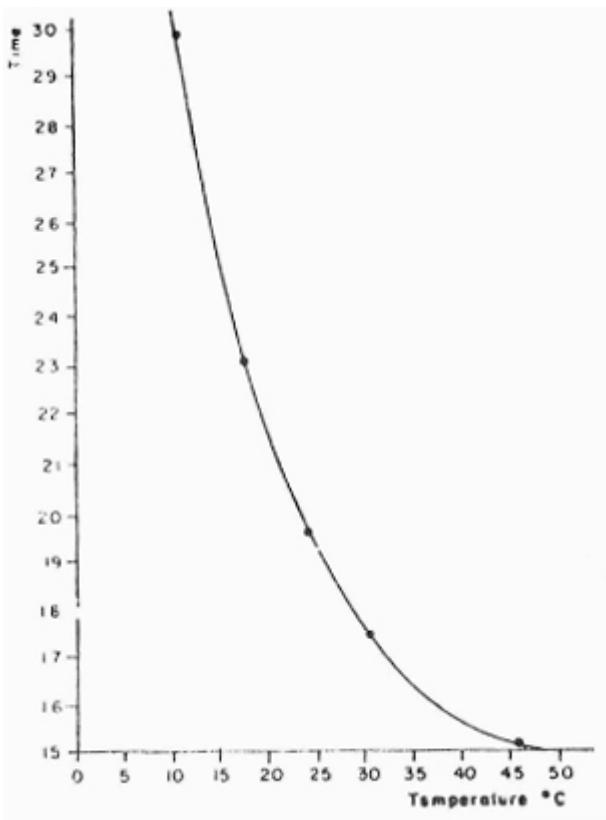


Figure 6.6 Graph of time vs temperature

SPECIMEN RESULT

TABLE 6. 9

| | | | | | |
|-------------------|------|------|------|------|------|
| Temperature (°C) | 12 | 20 | 26 | 32 | 46 |
| Time taken (secs) | 29.5 | 22.8 | 19.6 | 17.6 | 15.2 |

Plot a graph of time against temperature. Figure 6.6 represents the graph. It shows at a glance that it takes progressively shorter time to produce 10 cm^3 of oxygen as the temperature increases. That is, the rate of the reaction increases with temperature. Similar results will be obtained if Experiments 6.3 and 6.4 are similarly repeated.

Chemical reactions occur as a result of the collision of the reactant molecules. Molecules of every substance are at constant motion at temperatures above the absolute zero (-273°C or 0K). They acquire higher kinetic energy (energy of motion) at higher temperatures and collide more often than at lower temperatures. The increased rate of collision at higher temperature results in increased rate of chemical reaction.

Effect of catalysis on the rate of chemical reaction

Experiment 6.6: Effect of catalyst on the rate of a chemical reaction.

Put about 3 g of potassium trioxochlorate(V) into each of two dry test-tubes, labelled I and II. To test-tube I, also add 1 g of manganese(IV) oxide. Put 4 g of manganese(IV) oxide into a third dry test-tube labelled III. Stand the three test-tubes in a sand bath and heat the bath (Figure 6.7). Test for oxygen periodically in the three test-tubes by lowering a glowing splint into each tube.

The tube containing potassium trioxochlorate(V) and manganese(IV) oxide, test-tube I, is observed to rekindle a glowing splint within a short time, showing that oxygen is first liberated in it. It takes a longer time for oxygen to be liberated from test-tube II, while it is not liberated at all from tube III.

Stop heating after about 20 minutes. Allow the tubes to cool slightly. Dissolve the residue in test-tubes I and II in water, then filter to recover the insoluble manganese(IV) oxide from test-tube I. Dry and weigh it. It is observed that there is no loss in the mass of the manganese(IV) oxide. That is, the mass of the dry residue is still 1 g. The other product in the residue, potassium chloride, dissolves in water.

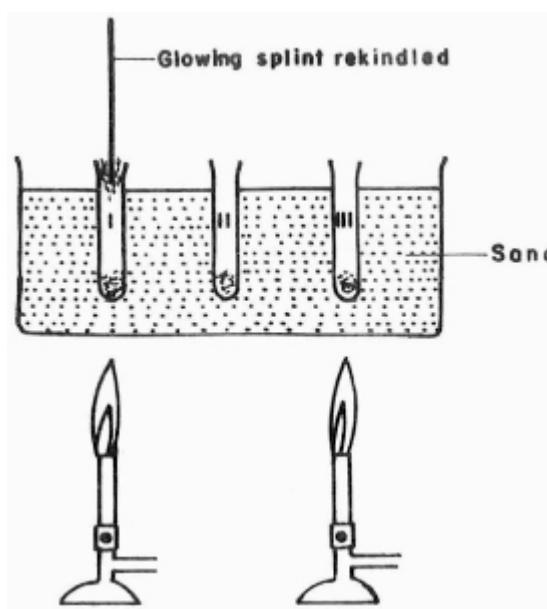
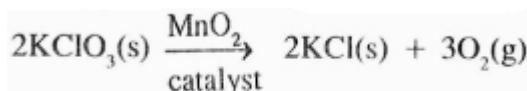


Figure 6.7 Effect of catalyst in chemical reaction

A catalyst is a substance which alters the rate of a chemical reaction but remains chemically unchanged at the end of the reaction.

Catalysts are specific in their actions, that is, each catalyst affects the rate of a particular reaction, but not all reactions. Manganese(IV) oxide speeds up the rate of the thermal decomposition of potassium trioxochlorate(V) but remains unchanged.

Some common catalysts and the specific reactions catalysed are shown in Table 6.10

TABLE 6.10 COMMON CATALYSTS

Experiment 6.7: Effect of the nature of reactants on the rate of a chemical reaction (A)

| Catalyst | Reactions catalysed |
|-------------------------------------|---|
| MnO ₂ | i) 2KClO ₃ (s) → 2KCl(s) + 3O ₂ (g) ii) 2H ₂ O ₂ (aq) → 2H ₂ O(l) + O ₂ (g) |
| Fe | N ₂ (g) + 3H ₂ (g) → 2NH ₃ (g) |
| V ₂ O ₅ or Pt | 2SO ₂ (g) + O ₂ (g) → 2SO ₃ (g) |
| Pt, Pd or Ni | -C = C- + H ₂ (g) → - $\begin{matrix} \text{C} \\ \\ \text{H} \end{matrix}$ - $\begin{matrix} \text{C} \\ \\ \text{H} \end{matrix}$ - |
| (CH ₃) ₄ Pb | C _n H _{2n+2} (l) + $\frac{n+1}{2}$ O ₂ (g) → nCO ₂ (g) + (n+1) H ₂ O(g) (slows down the rate) |
| Enzymes | Biological activities in living organisms. |

Repeat Experiment 6.2 using calcium trioxocarbonate(IV) and 2 mol dm⁻³ hydrogen chloride acid (hydrochloric acid) as reactants. Put equal masses (10 g say) of lumps of marble and fine particles of marble in two separate flasks (Figure 6.8). Add an equal volume of 2 mol dm⁻³ hydrogen chloride acid (hydrochloric acid) in each case and determine the volume of carbon(IV) oxide evolved at regular intervals.

Alternatively, weigh the flasks occasionally to find the rate of change of mass of the flask and contents. Plot a graph of either volume of carbon(IV) oxide against time from start of experiment, or of mass of flask and content, against time from start.

It is observed that more carbon(IV) oxide is produced at any given time, in the flask containing the fine particles. Consequently, it takes a shorter time for the mass of this flask to become constant than for the flask with lumps of marble. These show that the reaction is faster with the fine particles than with the lumps of marble.

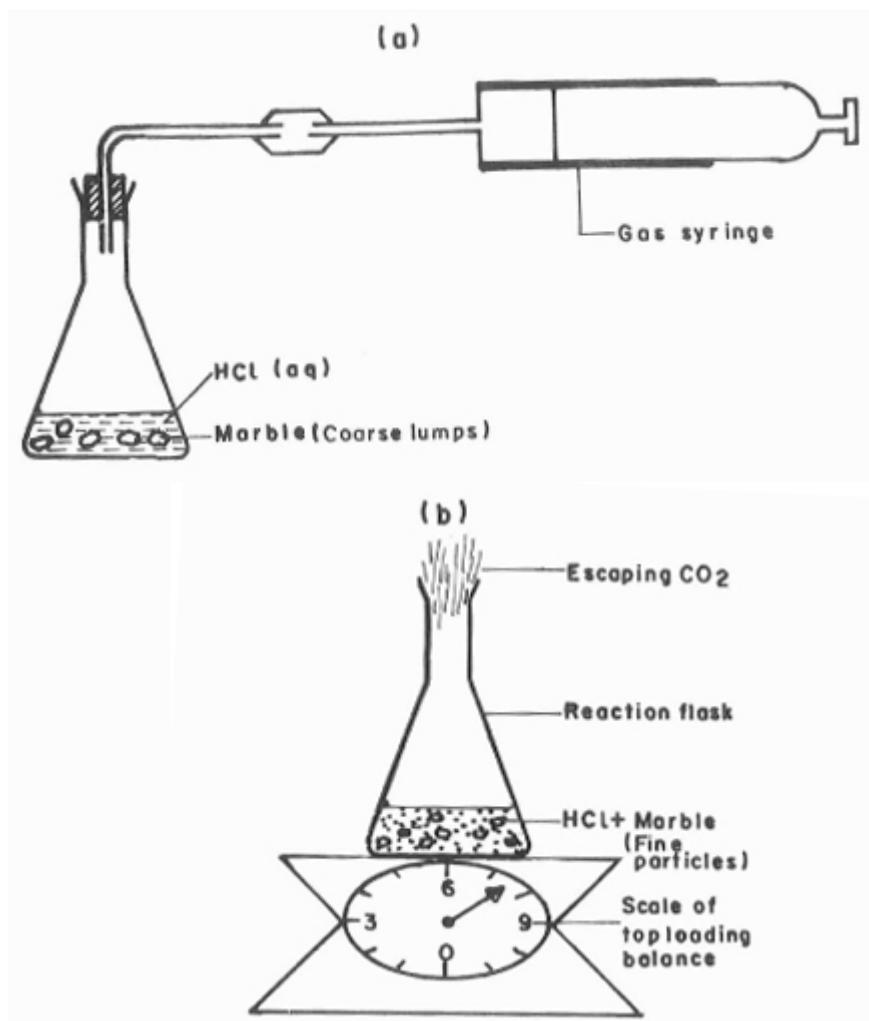


Figure 6.8 Effect of surface area on rate of chemical reaction

TABLE OF RESULTS

| Time (secs) | 10 | 20 | 30 | 40 | 50 | 60 |
|-------------------------------|----|----|----|----|----|----|
| (a) Volume of CO ₂ | | | | | | |
| (b) Mass of flask and content | | | | | | |

Graphs of volume of carbon(IV) oxide and mass of flask with content versus time are shown in Figure 6.9.

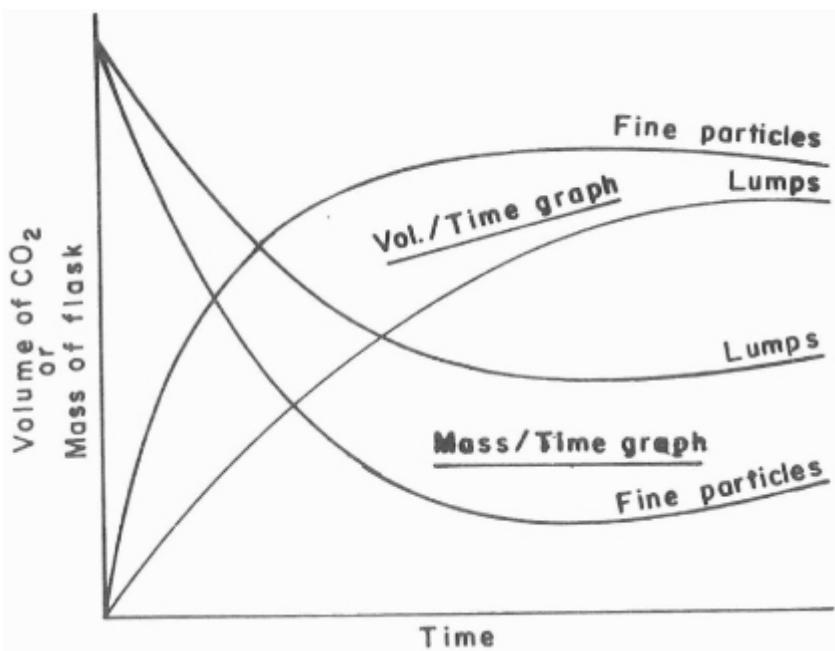


Figure 6.9 Graphs of volume of CO_2 and mass of flask against time

Reactions involving solids are surface phenomena. A larger surface area is exposed if the solid is in fine particle than if it is in lumps. The reaction is consequently faster with the fine particles.

Experiment 6.8: Effect of nature of reactants on the rate of chemical reaction (B).

Prepare the following solutions:

- (1) 0.1 M 2-methyl-2-chloropropane, $(\text{CH}_3)_3\text{CCl}$, solution in acetone;
- (2) 0.1 M sodium hydroxide solution in water;
- (3) Water-ethanol solution of bromophenol blue indicator.

Using a small measuring cylinder, transfer 10 cm^3 of the 0.1 M 2-methyl-2-chloropropane solution into a small conical flask. Pipette 1 cm^3 of the 0.1 M sodium hydroxide solution (use a micropipette) into another small beaker. Add 9 cm^3 of distilled water to it, then 3 drops of the bromophenol blue indicator. Place the flask on a white tile. Pour the 10 cm^3 2-methyl-2-chloropropane solution in acetone into it, and simultaneously start a stop-clock. Swirl the flask to mix the components. The reaction begins as soon as the two solutions are mixed. The mixture remains blue as long as there are excess hydroxide ions from the sodium hydroxide, but as soon as the base is completely neutralized, the indicator turns yellow (Figure 6.10). Stop the stop-clock then, and note the time taken for the reaction.

Prepare 0.1 M solution of 2-chloropropane (iso propylchloride), $(\text{CH}_3)_2\text{CHCl}$, in acetone. Repeat the experiment with this solution instead of the 2-methyl-2-chloropropane solution. After 5 minutes, heat the reaction mixture on a steam bath.

Notice that whereas the reaction occurs within seconds with 2-methyl-2-chloropropane at room temperature, no change is noticed when 2-chloropropane is used until the mixture is heated.

The reaction occurring is the hydrolysis of the halogenoalkanes.

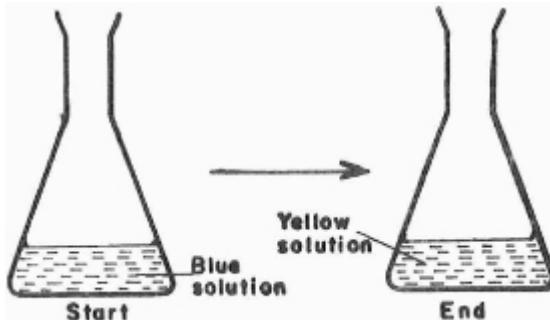
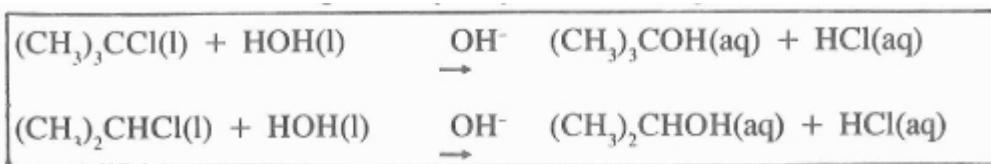
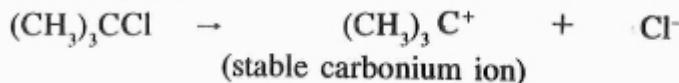


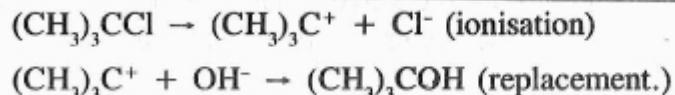
Figure 6.10: Effect of nature of reactant on reaction rate.

The rate of hydrolysis is faster with the tertiary halogenoalkane because it can ionize readily (due to the stable carbonium ion formed by its ionization).

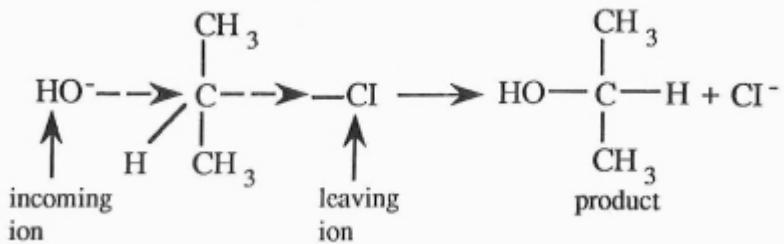


The secondary halogenoalkane does not form a carbonium ion readily, so its reaction is slow. This shows the effect of the nature of a reactant on the rate of a chemical reaction.

The same experiment demonstrates the effect of reaction mechanism on the rate of a chemical reaction. With 2-methyl-2-chloropropane, a tertiary halogenoalkane, ionization precedes the replacement of the Cl^- by OH^- . The mechanism is by **unimolecular nucleophilic substitution**.



With 2-chloropropane, a secondary halogenoalkane, ionization and replacement occur simultaneously. That is, as the Cl^- ion is leaving, the OH^- is coming in to take its place, from the opposite end of the molecule.



This mechanism is known as a **bimolecular nucleophilic substitution** mechanism.

This experiment can be modified to show the effect of temperature on reaction rate. This is done by carrying out the experiment at various temperatures, using an ice bath and a hot water bath. It can also be modified to demonstrate the effect of concentration on the rate of a chemical reaction by using various dilutions of the halogenoalkane - acetone solution and/or sodium hydroxide-water solution. It is observed that the reaction rate is independent of the concentration of sodium hydroxide, but dependent only on the concentration of the halogenoalkane.

The effect of light on the rate of chemical reaction

Experiment 6.9: Effect of light on reactions

Mix equal volumes of bench silver trioxonitrate(V) solution and 1 M potassium bromide solution in bright daylight, and again in a dark cupboard. Filter off the yellow precipitates of silver bromide that form, under the conditions in which the precipitates were formed. Allow the solids to stand for some time, then examine them.

While the silver bromide left in the dark cupboard remains yellow, the one formed in bright daylight turns grey (Figure 6.11). This is because light initiates the reduction of silver halides to metallic silver. The solid in the dark remains yellow because it is not reduced in the absence of light. Light initiates some chemical reactions by providing energy for the formation of reactive species.

The effect of light on the rate of a chemical reaction is similar to that of a catalyst hence it is called a photocatalytic reaction. It may be classified as a catalytic reaction.

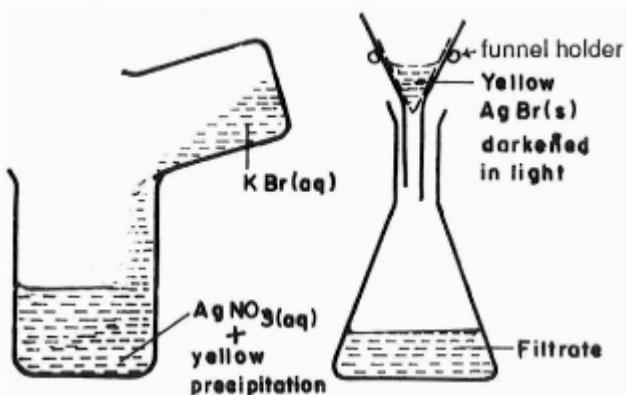


Figure 6.11 Action of light on silver bromide

Collision theory

Chemical reactions result from the rearrangement of particles of matter by the breaking and making of bonds between molecules, ions or atoms. For a chemical reaction to occur the molecules must collide or come together.

The rate of the reaction depends on the nature of the collision. In general, for a reaction to occur the molecules must acquire the necessary **activation energy**. According to the kinetic theory of matter, particles of matter are in constant random motion at temperatures above absolute zero. The higher the temperature, the higher is the rate of motion. Therefore when molecules are enclosed in a vessel, the higher the temperature the faster the rate of collision between them. Also, if the particles of matter or molecules are in high concentration, they become crowded and this results in more frequent collisions.

It therefore follows that the greater the rate of collision between reacting particles, the faster the rate of reaction. This is the collision theory. However, not all collisions result in chemical reaction. Reaction is most likely to occur if the collision between the particles is head-on.

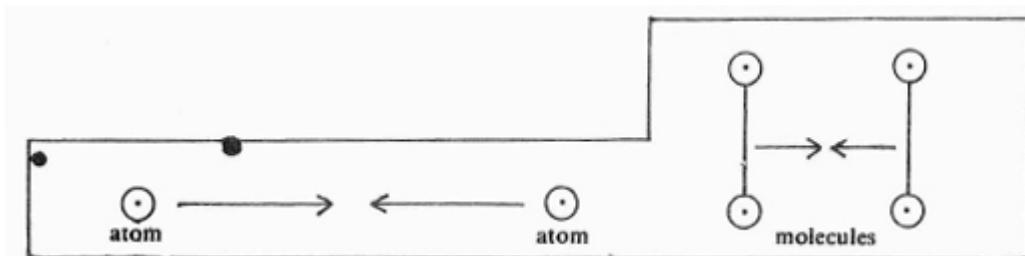


Figure 6.12(a) Collision of particles

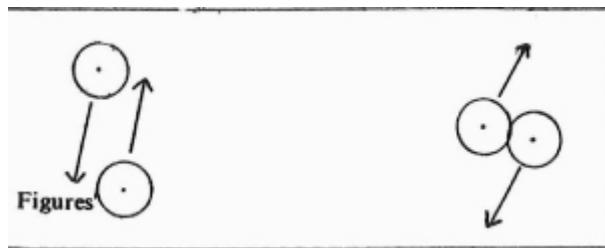


Figure 6.12(b) Particles brush the sides of each other.

If they just brush the side of each other, reaction is not likely to occur.

Secondly, the energy of collision must be high enough for the reaction to occur.

The following factors can increase the rate of chemical reactions because they increase the rate of collision:

- (a) increase in temperature,
- (b) increase in concentration (pressure for gases),
- (c) increase in surface area. This is because the larger the surface area of the reactants that is exposed, the greater is the number of particles exposed for collision. This is why powdered reactants react faster than solid ones.
- (d) Use of catalyst in reactions. Catalysts provide additional surfaces where reactants can be concentrated thereby enhancing the rate of reaction. When the collisions between the molecules become more frequent, the reaction will become faster because the fraction of the total number of particles with the required activation energy for reaction will be higher.

From the results of Experiments 6.2 to 6.9, we conclude that in a chemical reaction;

- (a) Increase in temperature increases the rate of chemical reaction.
- (b) Increase in concentration of the reactants or pressure of the reactants, if they are gases, increases the rate of chemical reaction.
- (c) Increase in the surface area of the reactants increases the rate of chemical reaction.
- (d) Catalysts can alter the rate of chemical reaction. Depending on the type of catalyst it can increase or decrease the rate of chemical reaction. Light also acts as catalyst. It can initiate a chemical reaction.
- (e) The type of reaction mechanism can alter the rate of a chemical reaction.

WORKED EXAMPLES:

1. At what time is the reaction between solid sodium

trioxocarbonate(IV) and dilute hydrogen chloride acid (hydrochloric acid) fastest, and why?

SOLUTION

The concentration of the hydrochloric acid solution and the surface area of the solid sodium trioxocarbonate(IV) are highest at the start of the experiment. Since the higher the concentration of a reactant, the faster the reaction, it follows that the reaction will be fastest at the start of the reaction. This is because the surface area of the solid and the concentrations of the reactants are all highest at the start of the reaction.

2. 0.01 mole of magnesium ribbon was added to 50 cm^3 of a 0.50 mol dm^{-3} solution of tetraoxosulphate(VI) acid and the time taken for all the magnesium to react was recorded. The experiment was repeated with the same amount of magnesium ribbon added to 50 cm^3 of $0.250 \text{ mol dm}^{-3}$ solution of the acid. Similar experiments were carried out with magnesium powder.

The Table below summarizes the results obtained.

| Experiment | Type of magnesium | Amount of magnesium | Molar concentration of acid | Volume of acid | Time taken for reaction |
|------------|-------------------|----------------------------|-----------------------------|-------------------|-------------------------|
| I | Ribbon | 0.01 mol dm^{-3} | $0.500 \text{ mol dm}^{-3}$ | 50 cm^3 | 280 s. |
| II | Ribbon | 0.01 mol dm^{-3} | $0.250 \text{ mol dm}^{-3}$ | 50 cm^3 | 1480 s. |
| III | Powder | 0.01 mol dm^{-3} | $0.500 \text{ mol dm}^{-3}$ | 50 cm^3 | 80 s. |
| IV | Powder | 0.01 mol dm^{-3} | $0.250 \text{ mol dm}^{-3}$ | 50 cm^3 | 140 s. |

What information do the results give about the conditions which affect the rate of a chemical reaction? Explain your answer.

(WAEC)

SOLUTION

Compare experiments I and II; and experiments III and IV.

The increase in time taken for magnesium to react completely in II and IV is because of the dilution of the acid from $0.500 \text{ mol dm}^{-3}$ to $0.250 \text{ mol dm}^{-3}$, since all other factors are constant. Therefore decrease in concentration of a reactant results in the reaction taking a longer time (or lowers the rate of the reaction).

Compare experiments I and III; and experiments II and IV. The concentration of the acid solution is the same for each pair. The mass of magnesium is the same too. The only difference is the exposed surface area for the magnesium. Experiments III and IV take shorter time because magnesium is in the powder form which exposes a larger surface area of reaction. Therefore increase in the surface area of a solid reactant reduces the time it takes to react completely, i.e.

increases its rate of reaction.

EXERCISE 6A

2 cm³ of 2 mol dm⁻³ hydrogen chloride acid (hydrochloric acid) is added to each of the following:

- 1 g of sodium hydroxide pellets.
- 10 cm³ of sodium hydroxide solution containing 1 g of the solid.
- powdered sodium hydroxide.

In which case is the reaction fastest and in which case is it slowest? Explain your answer.

6.4 Energy and Chemical Reaction

Experiment 6.10: Investigating Heat changes during Chemical Reactions.

- Add 1 cm³ of concentrated tetraoxosulphate(VI) acid to 5 cm³ of water in a test-tube. Feel the test-tube on the back of your hand. Note that the test-tube feels quite hot, showing that the dissolution of this acid in water produces heat.
- Add about 0.5 g of calcium oxide to 5 cm³ of water in a beaker. Note the hissing sound associated with the dissolution as steam is given off. Note too, that the beaker feels quite hot.
- Sodium hydroxide pellets also dissolve in water with evolution of heat. Add 1 g of sodium thiosulphate, Na₂S₂O₃ to 5 cm³ of water in a test-tube. Feel the test-tube on the back of your hand. Note that the test-tube feels quite cold. The dissolution of that compound in water absorbs heat, lowering the temperature of the reactants and vessel.

Many chemical reactions give out heat to the surroundings. Others absorb heat and cool their surroundings. Those reactions that give out heat, causing a rise in the temperature of the surroundings, are said to be **exothermic**. The ones that absorb heat are described as **endothermic**.

We used the collision theory to explain the effect of concentration and temperature on reaction rates. By proposing that with solids, reactions occur on the surfaces, we explained the effect of surface area on reaction rates. But why do catalysts change the rates of chemical reactions and why does light initiate some reactions? The activated complex can be regarded as an intermediate compound containing partially broken old bonds between the reactants and partially formed new bonds of the products. It is not a true compound and so cannot be isolated. Why is heat evolved in some reactions but absorbed in some others?

To explain these and other experimental observations, Arrhenius proposed that not all collisions between reactant molecules result in a reaction. He demonstrated that even at the same temperature, all

molecules of a substance do not have equal energy. He proposed further that there is an energy barrier which reacting molecules must scale, if their collision is to result in a reaction. Molecules which possess sufficient energy, form an **activated complex** when they collide. The energy of the activated complex is higher than that of the reactants. **The difference between the energy of the activated complex and the average energy of the reactants is the energy barrier that must be scaled and is called the activation energy.** That amount of energy must be possessed by reacting molecules for their collision to result in a reaction.

Experiment 6.11: Demonstrating activation energy.

Arrange the apparatus in Figure 6.13(a). Gradually increase the potential difference across the electrodes. No current passes until an appreciable potential difference has been applied. A plot of current against potential difference is represented in Figure 6.13(b).

The potential difference at which an appreciable current begins to flow is called the **decomposition potential**. It is the potential difference at which electrolysis begins. It represents the activation energy that must be scaled before the reactions involved in the electrolysis can take place.

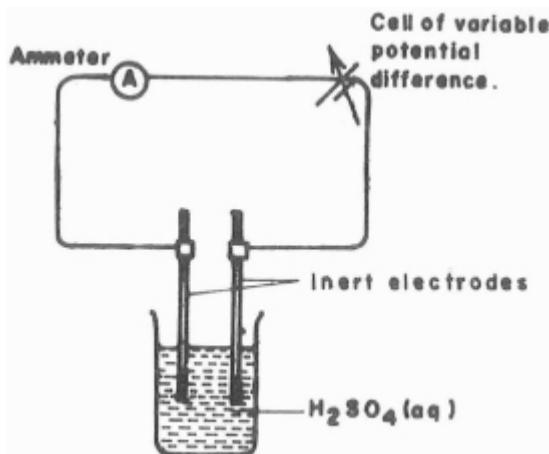


Figure 6.13(a) Determination of decomposition potential.

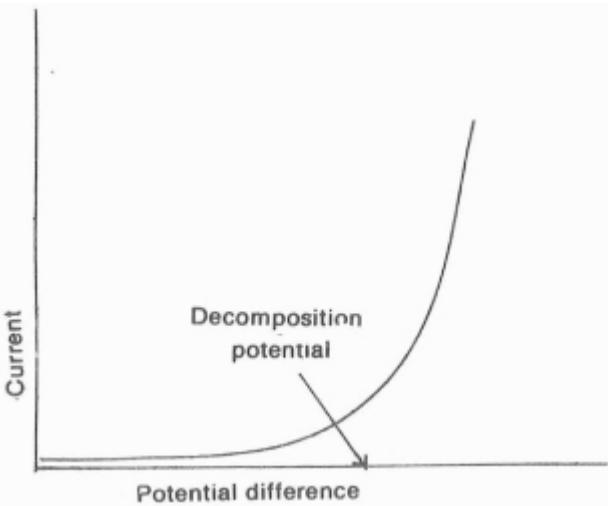


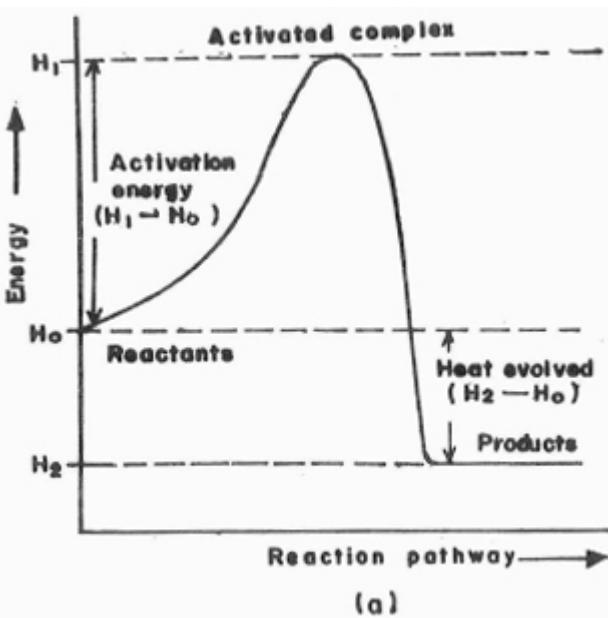
Figure 6.13(b) Graph of current vs potential difference.

6.5 Reaction Profile Diagrams

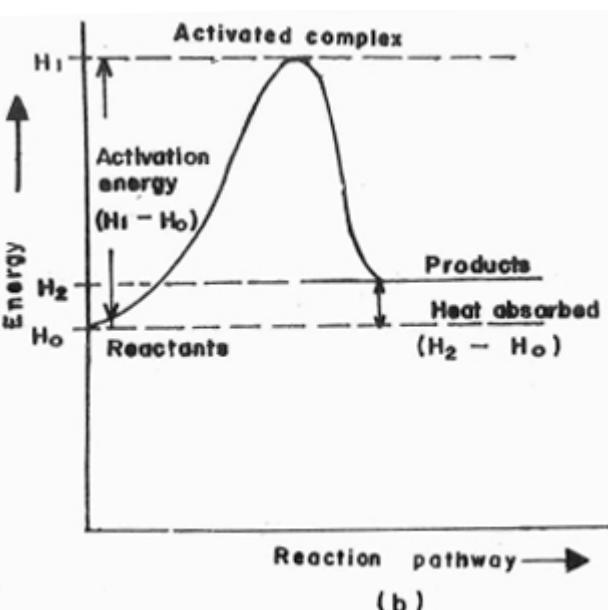
The activated complex is unstable. It quickly gives off the excess energy it possesses to form stable compounds (products). But from where does the energy to scale the energy barrier come?

It can come from the surrounding environment, including the reaction vessel. It can also come from externally applied heat or light energy. When it comes from an applied heat energy, the reaction will not occur until heated. For those reactions that are initiated by light, the reaction will not occur, or occurs very slowly in the absence of light.

If the activated complex gives out more heat to form the product, than the reactants absorb to form it, the reaction will be exothermic. The excess heat is given to the surroundings. If however, the activated complex gives out less heat energy to form the product than the reacting molecules absorb, the reaction will be endothermic. These conditions are represented by the reaction profile diagrams in Figure 6.14.



(a)



(b)

Figure 6.14: Reaction profiles (a) Exothermic reaction (b) Endothermic reaction.

\hat{H} Notation: Chemical energy often appears as heat, H . The symbol \hat{H} denotes a change in heat energy. Using the notations in Figure 6.14,

H_0 is the energy possessed by the reactants.

H_1 is the energy of the activated complex.

H_2 is the energy of the products.

$$\hat{H} = H_2 - H_0$$

For exothermic reactions, is H_2 greater than H_0

$$\hat{H} = H_2 - H_0$$

For endothermic reactions, H_2 is greater than H_0

$$\Delta H = H_2 - H_0 \text{ is positive.}$$

Catalysis: We can use the concept of activation energy to explain the part played by catalysts in chemical reactions. Since solid catalysts act better when in powder form than when in lumps, and since reaction rates of solid reactants increase with increase in surface area, it is proposed that catalysed reactions occur on the surface of the catalysts. The reactant molecules and the catalyst together form a new activated complex which has a lower activation energy than the activated complex formed in the absence of the catalyst. What this means is that **catalysts lower the activation energy**. Many more molecules can thus scale the energy barrier and react, than would be the case without the catalyst. This situation is illustrated by Figure 6.15.

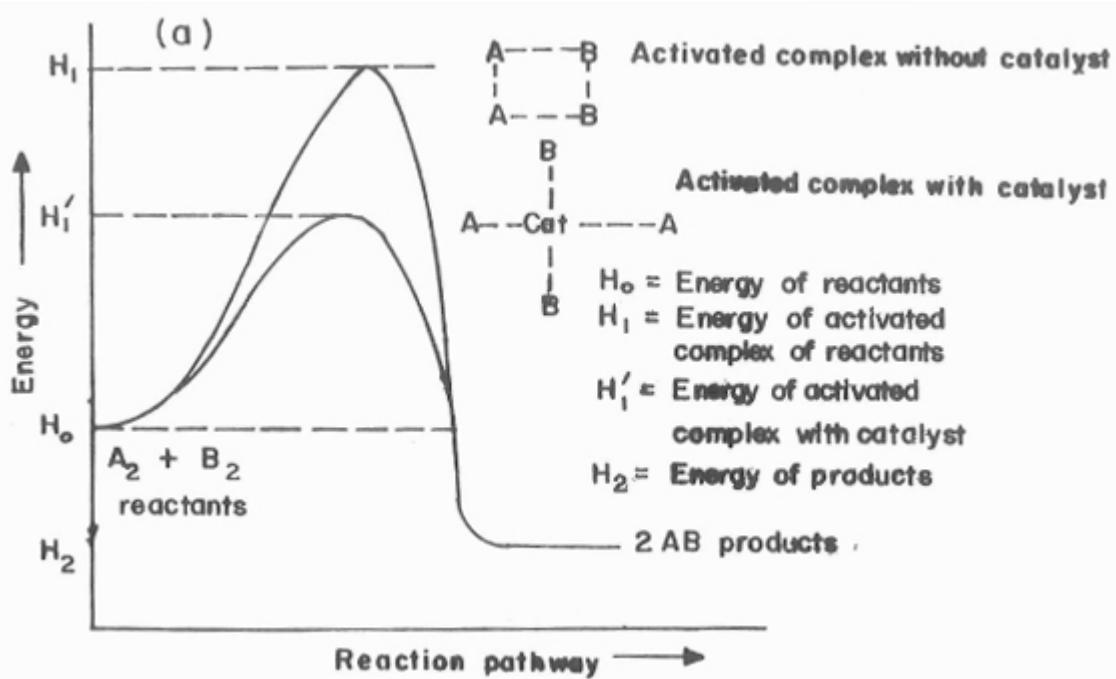


Figure 6.15: The effect of catalyst (a) Exothermic reaction

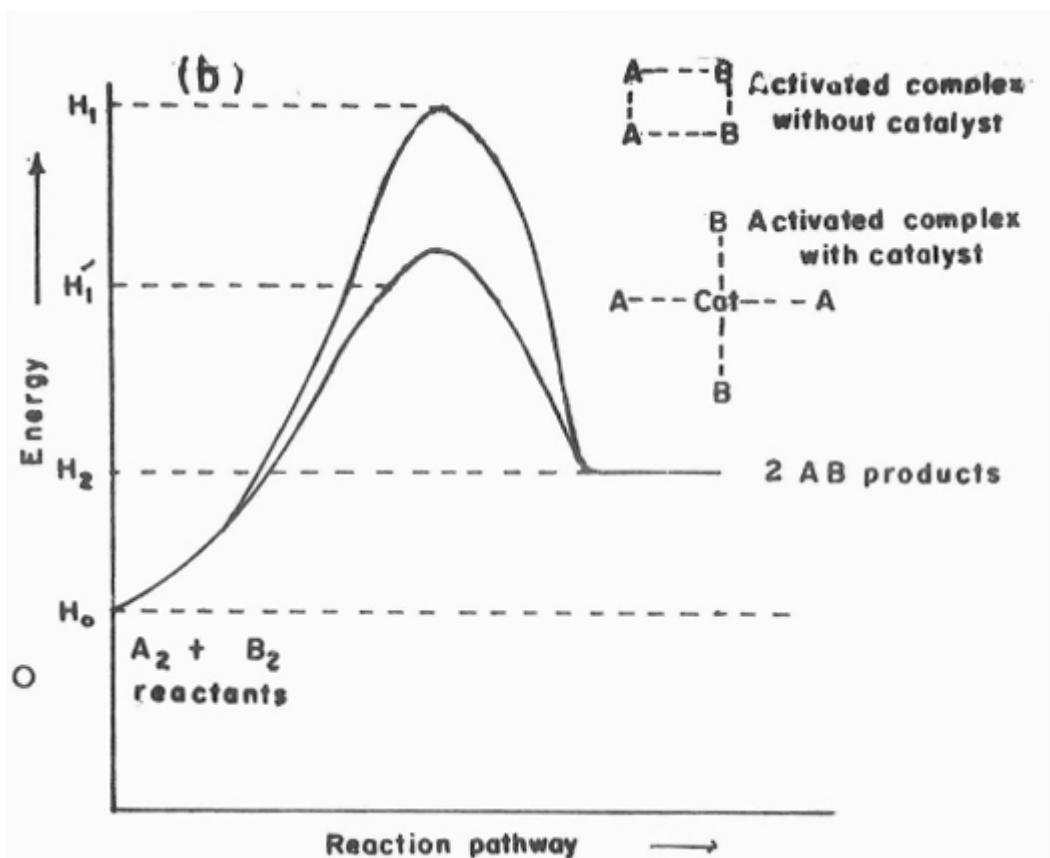


Figure 6.15 (b) Endothermic reaction.

Consider the diagram in Figure 6.16.

EXERCISE 6B

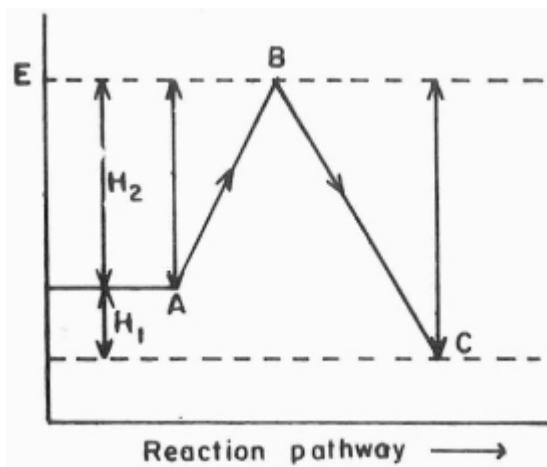


Figure 6.16 Reaction profile

What do the letters A, B, and C represent?

What are H_1 and H_2 ?

6.6 Heats of Reaction

The heat of neutralization of a strong acid by a strong base was determined in Chapter 5.

Heat of Solution: In Experiment 6.10 tetraoxosulphate(VI) acid, calcium oxide, sodium hydroxide and sodium thiosulphate were dissolved in water and the heat changes noted. If a thermometer were inserted into the reacting vessels the rise or fall in temperature could have been determined, and hence the heat changes calculated. The molar heat of solution is **the heat change which occurs when one mole of a substance is dissolved in so much solvent that further dilution does not lead to any further heat change.**

Experiment 6.12: To determine the heat of solution of sodium chloride in water.

Measure 100 cm³ of water into a clean dry 250 cm³ beaker. Put the beaker into a larger one lined with cotton wool inside it (Figure 6.17). Measure the temperature of the water. Weigh out accurately about 30 g of sodium chloride. Dissolve the sodium chloride in the water, stirring with the thermometer. Take the lowest temperature reached during the dissolution process.

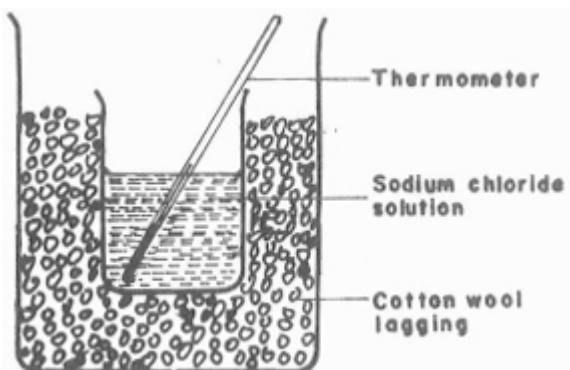


Figure 6.17 Heat of solution of sodium chloride

SPECIMEN RESULTS AND CALCULATIONS

Volume of water = 100 cm³

Mass of water = 100 g (since density of water is about 1 g cm⁻³).

Initial temperature of water = 27°C.

Lowest temperature of solution = 22.2°C.

Fall in temperature = 4.8°C.

Assuming that the density of the solution is equal to the density of water, Heat absorbed by the solution = 100 J – 4.8 J = 4.2 joules.

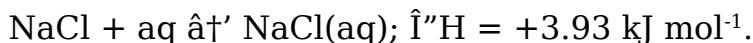
1 mole of NaCl = 58.5 g.

30 g causes absorption of 100 J – 4.8 J = 4.2 joules

∴ 58.5g will cause absorption of

$$\begin{aligned} & \frac{100 \times 4.8 \times 4.2 \times 58.5}{30} \quad \text{joules} \\ & = \frac{100 \times 4.8 \times 4.2 \times 58.5}{30 \times 1000} \quad \text{kJ} \\ & = 3.93 \text{ kJ} \end{aligned}$$

∴ Heat of solution of sodium chloride, ΔH solution = +3.93 kJ mol⁻¹
The positive sign signifies heat absorbed since there was a fall in temperature. We therefore write



The heats of solution of some other substances are given in Table 6.11.

TABLE 6.11: HEATS OF SOLUTION OF SOME SUBSTANCES

| Compound | Heat of solution (kJ mol ⁻¹) |
|-----------------------------------|--|
| KCl | + 17.2 |
| K ₂ SO ₄ | + 23.8 |
| NH ₄ Cl | + 15.2 |
| NH ₄ NO ₃ | + 25.8 |
| CaCl ₂ | - 82.9 |
| Ca(OH) ₂ | - 16.2 |
| NaOH | - 42.7 |
| Na ₂ CO ₃ | - 24.6 |
| CuSO ₄ | - 73.3 |
| Cu(NO ₃) ₂ | - 41.8 |

Heat of combustion.

The heat of combustion of a substance is the heat liberated when one mole of the substance is completely burnt in oxygen.

It is a measure of the fuel value of combustible substances. It can be determined accurately with a bomb calorimeter (joulemeter) (Figure 6.18). The rise in temperature of the water in which the calorimeter is immersed is determined, and hence the heat evolved calculated.

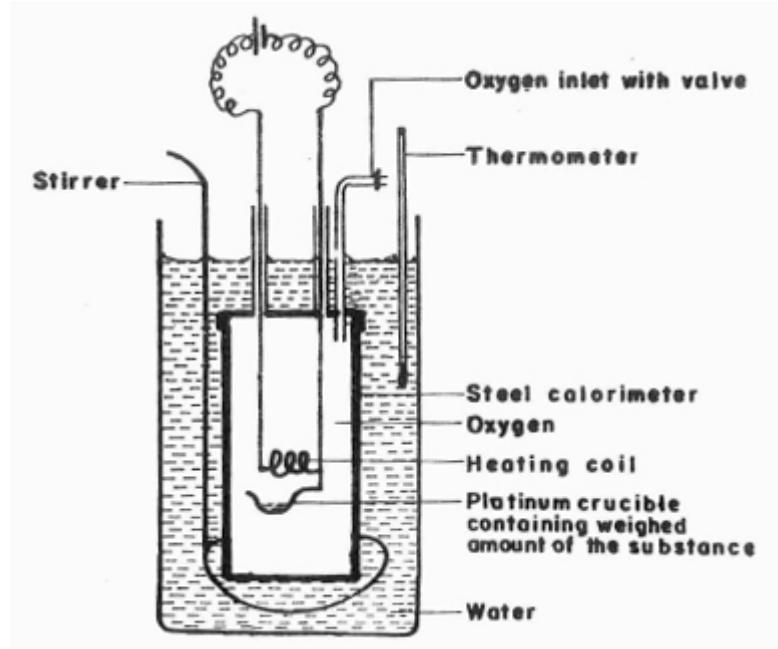


Figure 6.18 Bomb calorimeter

The heats of combustion of some compounds are given in Table 6.12.

TABLE 6.12 HEATS OF COMBUSTION OF SOME SUBSTANCES

| Substance | Heat of combustion (kJ mol ⁻¹) |
|------------------------------------|---|
| H ₂ | - 285.5 |
| C (graphite) | - 393.5 |
| C (diamond) | - 395.4 |
| S (rhombic) | - 296.9 |
| S (monoclinic) | - 297.2 |
| CH ₄ (g) | - 890.4 |
| C ₂ H ₆ (g) | - 1560 |
| C ₃ H ₈ (g) | - 2220 |
| C ₄ H ₁₀ (g) | - 2877 |
| C ₆ H ₁₂ (l) | - 3509 |
| C ₆ H ₁₄ (l) | - 4194 |
| C ₈ H ₁₈ (l) | - 5512 |
| C ₂ H ₅ OH | - 1371 |
| CH ₃ OH | - 715 |

6.7 Reversible Reactions

Experiment 6.13: Investigating Reversible Reactions (A)

Pass carbon(IV) oxide into water in a test-tube using the device in Figure 6.19(a). Test the resulting solution with blue litmus paper. The

litmus paper turns scarlet, showing that the solution is weakly acidic. Transfer a little of the solution with a dropper pipette into a test-tube, and add a few drops of barium chloride solution to it. A white precipitate of barium trioxocarbonate(IV) results. Fit a cork carrying a delivery tube to the test-tube containing the rest of the acidic solution, then heat it. Pass the gas evolved into lime water. The lime water turns milky showing that the gas is carbon(IV) oxide.

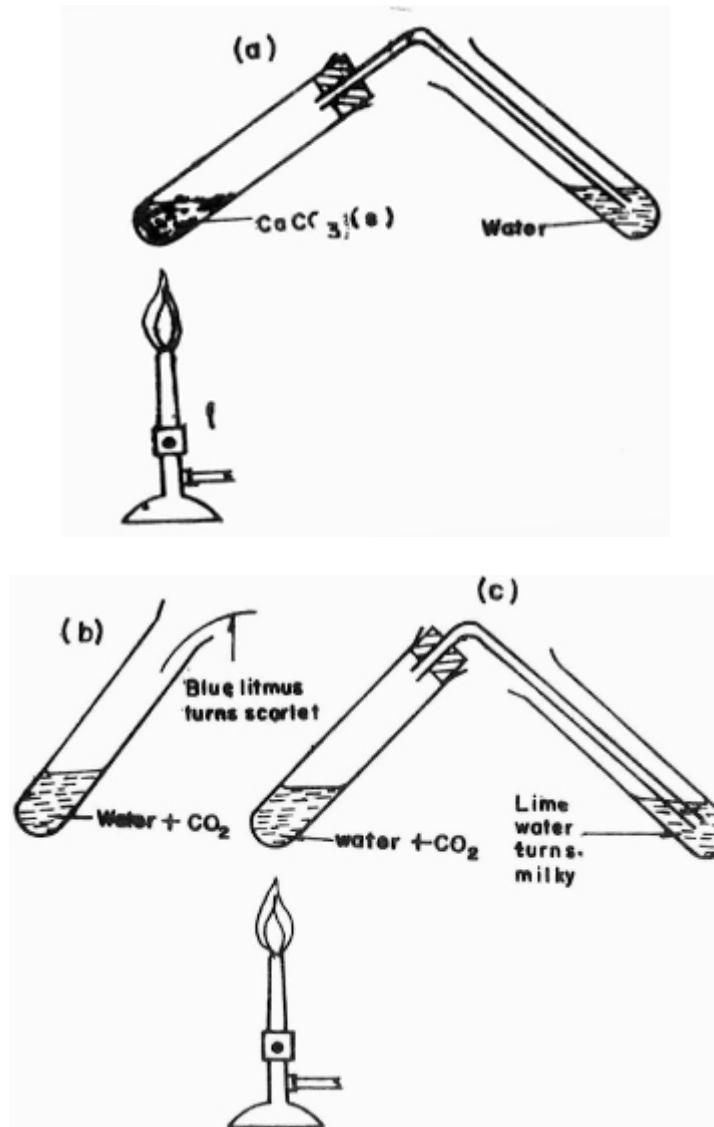
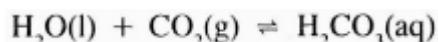


Figure 6.19 Reversible action of carbon(IV) oxide on water

Thus, carbon(IV) oxide dissolves in water forming trioxocarbonate(IV) acid, a weak acid. On heating, this acid gives off carbon(IV) oxide. Both reactions can be represented by a single equation, thus:



The sign \rightleftharpoons indicates that the reactants on the left hand side form product(s) on the right hand side, which, if conditions change,

undergo reaction to produce the original starting materials.

Experiment 6.14; Investigating Reversible Reactions (B).

Fill two round-bottomed flasks with nitrogen(IV) oxide using the apparatus in Figure 6.20(a). Cork the flasks tightly with rubber bungs. Immerse one of them in ice water contained in a beaker, and the other in hot water. The colour of the gas immersed in ice water becomes lighter, whereas the colour of the gas immersed in hot water deepens.

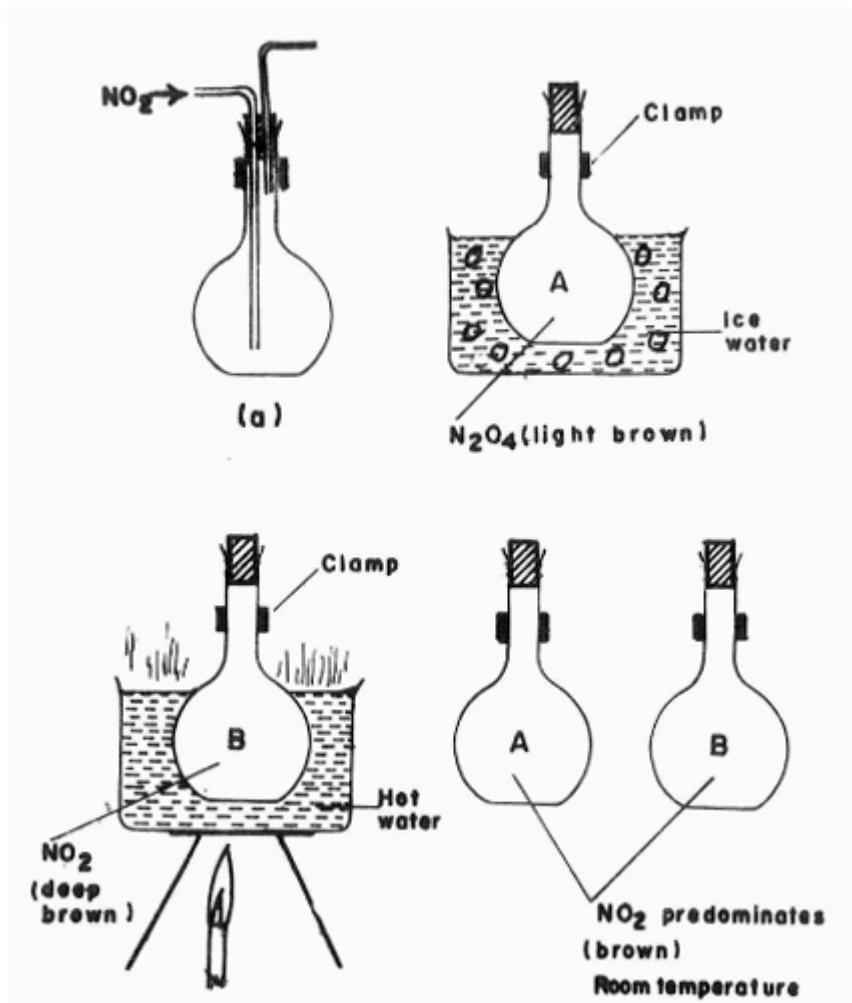
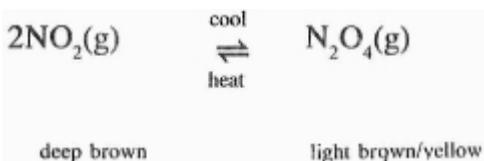


Figure 6.20 Equilibrium between NO₂ and N₂O₄

Now withdraw both flasks from the cold and hot water and allow them to warm up/cool down to room temperature respectively. The original colour is restored in both flasks. The deep-brown gas is nitrogen(IV) oxide. The light-brown gas is dinitrogen tetroxide.

At low temperature nitrogen(IV) oxide **dimerises** to dinitrogen tetraoxide. On heating, the dimer dissociates to nitrogen(IV) oxide.



Below 22°C all the molecules exist as dinitrogen tetraoxide. Above 150°C all the molecules exist as nitrogen(IV) oxide. At temperatures between 22°C and 150°C a mixture of both molecules exist.

Experiment 6.15: Investigating Reversible Reactions (C).

Put a little ammonium chloride into a test-tube. Keep the test-tube in a slanting position, then insert moist blue and red litmus papers, and glass wool as shown in Figure 6.21. Heat the bottom of the test-tube.

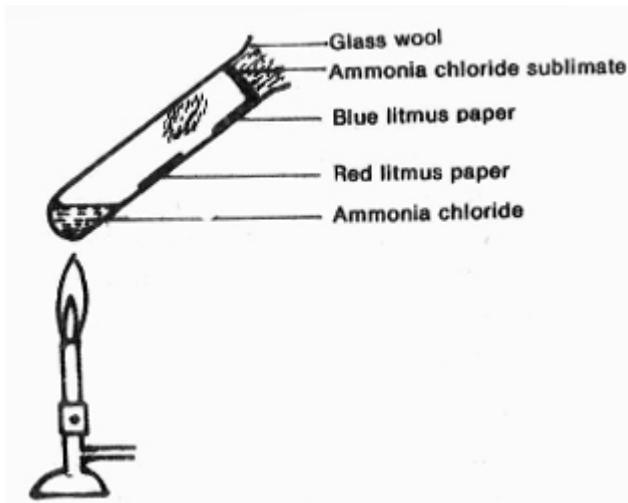
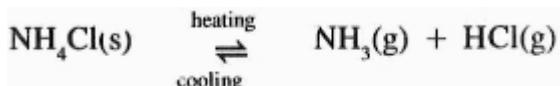


Figure 6.21: Reversible decomposition of ammonium chloride

The red litmus paper turns blue as ammonia gas reaches its position. The blue litmus paper also turns red, indicating the arrival of hydrogen chloride to that position. Later, white sublimate of ammonium chloride are observed near the mouth of the test tube. These results show that ammonium chloride is decomposed by heat to ammonia gas and hydrogen chloride gas which recombine at the colder part of the test-tube to reform solid ammonium chloride. The reaction is written as



The reactions in Experiments 6.13, 6.14 and 6.15 are all reversible, reactions. Under a set of conditions the reactants form products which at other conditions react to reform the original reactants.

6.7 Chemical Equilibrium

If a reversible reaction is carried out in a closed vessel, initially, only reactants are present in the vessel. Then, at any given time after the start of the reaction, the vessel contains both reactants and products. Soon, a situation is reached when the concentrations of reactants and products no longer change with time. **A state of dynamic**

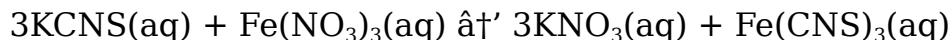
equilibrium is said to have been established. The rate of the forward reaction is equal to the rate of the backward reaction at that stage.

Experiment 6.16: Investigating a system in equilibrium.

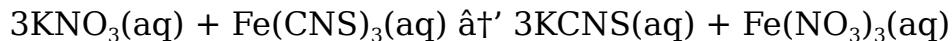
Prepare the following solutions:

- (1) 0.1 mol dm⁻³ potassium thiocyanate(II), KCNS,
- (2) 0.1 mol dm⁻³ iron(III) trioxonitrate(V),
- (3) 0.1 mol dm⁻³ potassium trioxonitrate(V).

Add 2 cm³ of 0.1 mol dm⁻³ potassium thiocyanate(II) solution and 2cm³ of the 0.1 mol dm⁻³ iron(III) trioxonitrate(V) to 100 cm³ of water in a conical flask (Figure 6.22). The solution is red in colour due to the formation of iron(III) thiocyanate.



Put 5 cm³ of this solution into each of two test-tubes labelled A and B. To test-tube A, add a further 5 cm³ of iron(III) trioxonitrate(V) solution. The red colour deepens due to the formation of more iron(III) thiocyanate. To test-tube B, add 5 cm³ of the 0.1 mol dm⁻³ potassium trioxonitrate(V) solution. The red colour clears and the solution becomes almost colourless. The disappearance of the red colour is due to the reaction.



Thus the reaction is reversible. The formation of more iron(III) thiocyanate on addition of iron(III) trioxonitrate(V) to the initial reaction at equilibrium, shows that there were still some CNS⁻ ions in the mixture at equilibrium. Similarly the disappearance of the red colour on addition of potassium trioxonitrate(V) to the equilibrium mixture, indicates that Fe³⁺ ions were equally present in the equilibrium mixture. Therefore at equilibrium both reactants and products exist together.

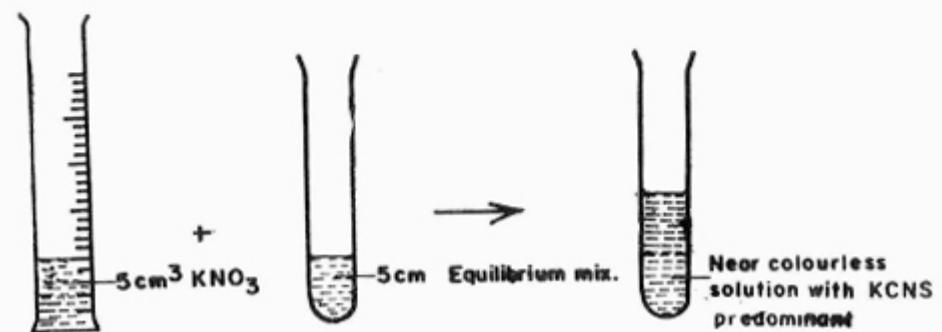
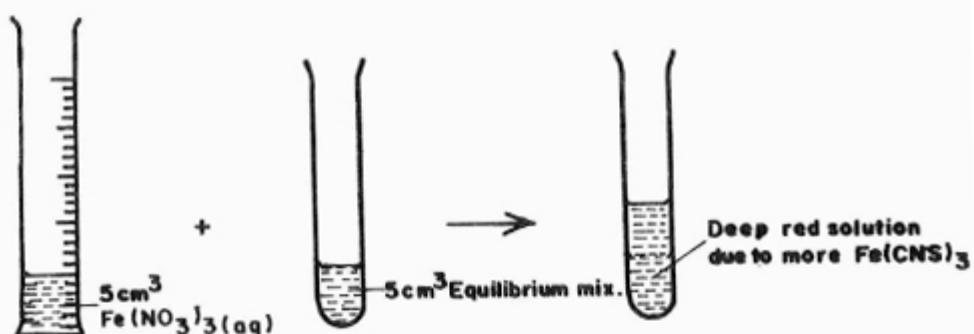
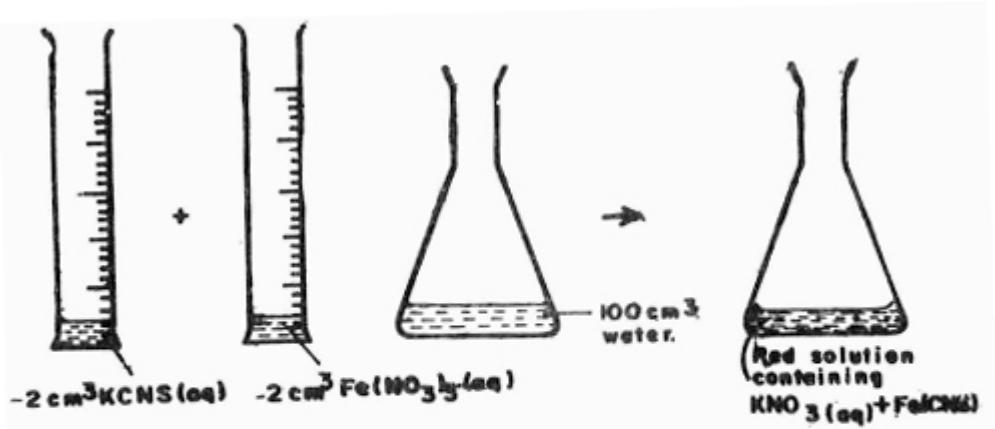


Figure 6.22 The $3\text{KCNS(aq)} + \text{Fe}(\text{NO}_3)_3\text{(aq)} \rightleftharpoons 3\text{KNO}_3\text{aq} + \text{Fe(CNS)}_3\text{(aq)}$ equilibrium.

Effect of concentration on equilibrium

The deepening of the red colour on addition of iron(III) trioxonitrate(V) to the iron(III) thiocyanate equilibrium, and the clearing of the red colour on addition of potassium trioxonitrate(V) to the equilibrium mixture, also illustrate the effect of concentration on the position of equilibrium. These changes indicate that increase in the concentration of reactant(s) enhances the forward reaction (shifts the equilibrium to the right) while increase in the concentration of the

product(s) enhances the backward reaction (shifts the equilibrium to the left.) This behaviour is true of all reversible reactions.

Effect of pressure on equilibrium

Pressure is to reactants and products in the gaseous phase, what concentration is to reactants and products in solution. But the effect of the total pressure in the reaction vessel on the equilibrium position of reversible gaseous reactions is not straightforward. It depends on whether the forward reaction leads to a decrease, or an increase in the total volume.

Consider the dimerisation of nitrogen(IV) oxide.



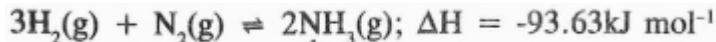
Two volumes of a gaseous reactant yield one volume of a gaseous product. That is, the volume decreases. The forward reaction is favoured by increase in pressure. The reverse reaction which leads to increase in volume is favoured by a decrease in pressure. Table 6.13 is a summary of the effects of pressure on gaseous systems in equilibrium.

TABLE 6.13: EFFECT OF PRESSURE ON GASEOUS REACTIONS IN EQUILIBRIUM

| Change in volume from left → right | Effect of high pressure. | Effect of low pressure | Examples |
|------------------------------------|------------------------------|------------------------------|--|
| Decrease | Equilibrium shifts to right. | Equilibrium shifts to left. | i) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ ii) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ |
| Increase | Equilibrium shifts to left | Equilibrium shifts to right. | i) $2\text{O}_3(\text{g}) \rightleftharpoons 3\text{O}_2(\text{g})$ ii) $\text{PCl}_3(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ |
| No change | No effect | No effect | $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ |

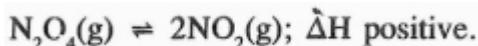
Effect of temperature on equilibrium

A rise in temperature generally increases the rate of a reaction. For a reaction in equilibrium the rates of both the forward and the backward reactions are increased equally. The reaction therefore remains in equilibrium. But if the forward reaction is exothermic, then a rise in temperature is like increasing the concentration of one of the products of the reaction. The backward reaction is thus favoured, as the equilibrium shifts to the left. For example, in the Haber process,



raising the temperature favours the decomposition of ammonia to nitrogen and hydrogen. A low temperature would be expected to favour the formation of ammonia. But the rate of the reaction is normally slow at low temperatures. A favourable balance is reached for this reaction at 200 atmosphere pressure and 450 $^{\circ}\text{C}$ to 500 $^{\circ}\text{C}$, in the presence of finely divided iron catalyst.

If the forward reaction is endothermic, then raising the temperature favours the forward reaction since this implies the supply of the activation energy needed. Thus the decomposition of dinitrogen tetraoxide is favoured by high temperature.



All these factors which affect the equilibrium position of reversible reactions are summed up by the Le Chatelier principle.

Le Chatelier's principle states that if a chemical system in equilibrium is disturbed by a change in one of the factors involved, the equilibrium readjusts itself in such a way as to eliminate the effect of the change.

6.8 Equilibrium Constant

We have noted that at equilibrium the concentrations of reactants and products no longer change with time.

Thus in the equilibrium reaction



$$\frac{\text{Concentration of product(C)} \times \text{Concentration of product(D)}}{\text{Concentration of reactant(A)} \times \text{Concentration of reactant(B)}} = \text{Constant}$$

$$\frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} = (k).$$

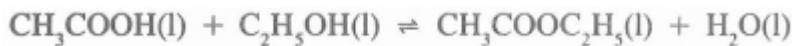
i.e.

[A] = molar concentration of reactant A at equilibrium
(k) = equilibrium constant.

WORKED EXAMPLE

- One mole of ethanoic acid is mixed with one mole of ethanol, and a sample of the mixture withdrawn and analysed. Suppose 0.67 mole of ethyl ethanoate is found to be present in the equilibrium mixture, calculate the equilibrium constant of the reaction.

SOLUTION



1 mole of acid reacts with one mole of alkanol to form one mole of ester and one mole of water.

Since 0.67 mole of ester is present at equilibrium, 0.67 mole of water must also have formed, and 0.67 mole of both ethanol and ethanoic acid must have reacted.

∴ (1 – 0.67) mole of ethanoic acid and
(1 – 0.67) mole of ethanol must be left.

That is,

$$\begin{aligned}\text{Amount of ester} &= \text{amount of water} = 0.67 \text{ mole} \\ \text{Amount of ethanol} &= \text{amount of ethanoic acid} \\ &= (1 - 0.67) \text{ mole} = 0.33 \text{ mole.}\end{aligned}$$

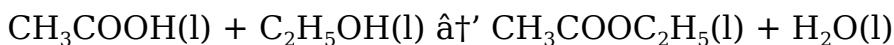
$$\therefore \text{Equilibrium constant, } k = \frac{0.67 \times 0.67}{0.33 \times 0.33} = 4.12$$

Equilibrium constant has no units.

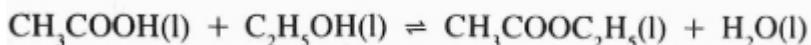
2. (a) Explain what happens initially, and after a day, if one mole of ethanol and one mole of ethanoic acid are mixed in the presence of a little concentrated tetraoxosulphate(VI) acid as catalyst, and
(b) If one mole of ethanol and one mole of ethanoic acid are mixed with a large quantity of water.
(c) How can you arrange to collect the ester formed in the reaction?

SOLUTION:

- (a) On mixing the two, a sweet-smelling compound, ethyl ethanoate, is formed. The initial concentration of the ester is small and its formation reaction goes on at a reasonably fast rate.



After a day, however, equilibrium must have been established. The ester is hydrolysed by water to ethanol and ethanoic acid at the same rate as it is formed from these compounds. The concentrations of the reactants and products remain constant.



- (b) In the presence of a large amount of water the initial production of ester is extremely slow. The pleasant odour is not perceived for quite a long time. Even if eventually it is perceivable say after a day, only a negligible amount of ester is produced, as the reaction lies far to the left because the concentration of one of the products is very large.

- (c) If the ester is distilled off as it is formed, the reaction can be made to yield an appreciable amount of ester.

EXERCISE 6C

What is the effect of

- (i) temperature,
- (ii) pressure, on the following reactions?



6.9 Concept of Free Energy

One would think that reactions which liberate heat energy should occur readily because the reactants possess excess energy which they liberate to form stable compounds. Similarly, reactions which absorb heat would be expected to occur only when heat is supplied to them. But the result of Experiment 6.10 shows that the dissolution of sodium thiosulphate in water which absorbs heat, occurs readily. Therefore, there are possibly other factors which also determine whether a reaction will proceed spontaneously or otherwise.

The natural universal tendency to disorderliness is extended to chemical reactions. This tendency is termed **entropy**. It is suggested that **a reaction will occur freely if it leads to an increase in entropy**. Consider the thermal decomposition of ammonium chloride to ammonia and hydrogen chloride.



The orderly arranged solid particles in ammonium chloride give rise to randomly moving ammonia and hydrogen chloride molecules. This is a clear case of orderliness giving way to disorder. The dissolution of sodium thiosulphate also occurs because it leads to disorder. The orderly arranged sodium and thiosulphate ions in the solid become freely moving ions, in solution.

We shall, however, not dismiss heat change during reactions as playing a part in determining whether a reaction will occur readily or not. After all, if heat is given out the molecules move faster and become more random, while if heat is absorbed their motion is slowed down or even stopped and they become orderly. So both the heat of reaction (enthalpy, symbol H), and disorder (entropy, symbol S) determine whether a reaction will occur readily or not. The net effect of the two factors is termed the **free energy, G**.

The actual value of entropy cannot be measured and we are usually not interested in its actual value. What concerns us is the change in

entropy, AS. We already know how to measure change in enthalpy, $\hat{\Delta}H$. The relationship between the two is

$$\hat{\Delta}G = \hat{\Delta}H - T\hat{\Delta}S.$$

Where T is the temperature in Kelvin;

$\hat{\Delta}H$ is total energy change accompanying the reaction;

$T\hat{\Delta}S$ is part of the total energy change that is due to the reorganisation of the atoms.

$\hat{\Delta}G$ is the part of the total energy change (free energy change), that can be used to do useful work.

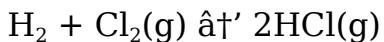
We are aware of the fact that if $\hat{\Delta}H$ is negative, the reaction is exothermic and heat is given out. If it is positive, the reaction is endothermic. We must also note that:

1. **If $\hat{\Delta}G$ is negative, a reaction will occur spontaneously.**
2. **If $\hat{\Delta}G$ is positive, a reaction will not occur spontaneously.**
3. **If $\hat{\Delta}G = 0$, i.e. if $\hat{\Delta}H = T\hat{\Delta}S$, the reaction is reversible and at equilibrium.**

WORKED EXAMPLE

Given that the heat of formation of hydrogen chloride gas from hydrogen and chlorine is -92.3 kJ and the entropy change accompanying the reaction is $187 \text{ J K}^{-1} \text{ mol}^{-1}$ at 25°C , calculate the change in free energy of the reaction. Is the reaction spontaneous in the forward or in the backward direction?

SOLUTION



$\hat{\Delta}H = -(2 \times -92.3) \text{ kJ}$ since two mole of HCl are formed.

$$\hat{\Delta}S = 2 \times 187 \text{ J K}^{-1}$$

$$= 0.374 \text{ kJ K}^{-1}$$

$$\hat{\Delta}T = 25^\circ\text{C} = 298 \text{ K}$$

$$\hat{\Delta}G = \hat{\Delta}H - T\hat{\Delta}S$$

$$= [-184.6 \text{ kJ} - (298 \text{ K} \times 0.374)]$$

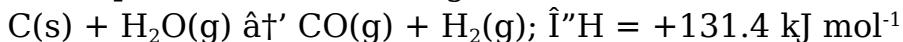
$$= (-184.6 \text{ kJ} - 111.4)$$

$$= -296 \text{ kJ}$$

$\hat{\Delta}G$ is negative. Therefore, the forward reaction (i.e. formation of hydrogen chloride) is spontaneous.

EXERCISE 6D

In the production of water gas,



if AS at $25^\circ\text{C} = 0.317 \text{ J K}^{-1} \text{ mol}^{-1}$ calculate $\hat{\Delta}G$, and thus state whether the reaction is spontaneous or not.

Answer: $\hat{\Delta}G = + 36.9 \text{ kJ mol}^{-1}$

Chapter Summary

- 1 The rate of a chemical reaction is proportional to the rate of change of the concentrations of the reactants or products.

$$\text{Rate} = \frac{\text{Concentration at time (2)} - \text{Concentration at time (1)}}{\text{Time interval.}}$$

2. Factors that affect the rate of chemical reactions are
- temperature,
 - concentration of reactants (or pressure of reactants, if they are gaseous),
 - the presence of a catalyst
 - the nature of the reactants (including the surface area of solid reactants), and
 - the mechanism of the reaction.
- Light may initiate a reaction, it does not affect the rate of reaction.
3. Activation energy is the energy required to break old bonds to form an activated complex. Reactant molecules must possess the activation energy for a reaction, in order to form products.
4. Exothermic reactions give out heat to the surroundings.
5. Endothermic reactions absorb heat from the surroundings.
6. At equilibrium, the rate of a forward reaction is equal to the rate of the backward reaction.

For the reaction $A + B \rightleftharpoons C + D$

$$\frac{\text{Molar concentration of } C \times \text{Molar concentration of } D}{\text{Molar concentration of } A \times \text{Molar concentration of } B} = \text{Constant.}$$

$$\text{i.e. } \frac{[C][D]}{[A][B]} = k, \text{ the equilibrium constant.}$$

7. (a) For a system at equilibrium:



Increase in the concentration of A or B shifts the equilibrium to the right.

Increase in the concentration of C or D shifts the equilibrium to the left.

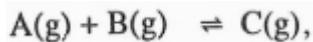
- (b) For the system $A + B \rightleftharpoons C; \Delta H = -ve$,

rise in temperature after equilibrium has been reached shifts the equilibrium to the left.

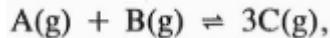
For $A + B \rightleftharpoons C; \Delta H = +ve$,

rise in temperature shifts equilibrium to the right.

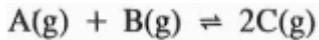
- (c) For a gaseous system at equilibrium such as,



increase in pressure shifts the equilibrium to the right; whereas for the system



increase in pressure shifts the equilibrium to the left. The system



is not affected by pressure changes.

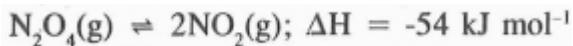
8. $\hat{\Delta}G = \hat{\Delta}H - T\hat{\Delta}S$

If $\hat{\Delta}G$ is negative, the reaction is spontaneous.

If $\hat{\Delta}G$ is positive, the reaction is not spontaneous.

Assessment

1. Study the information in the equation



What conditions of reaction will increase

- (i) the yield of nitrogen(IV) oxide?
- (ii) the yield of dinitrogen tetraoxide?

2. Flasks A, B, C are connected to gas syringes.

Flask A contains 10g lumps of sodium trioxocarbonate(IV), flask B 10g of the powdered salt, and flask C a solution of 10g of the salt in 100 cm³ of water. The volume of carbon(IV) oxide produced in each flask is recorded every minute. Match the following plots (Figure 6.23) against the flasks.

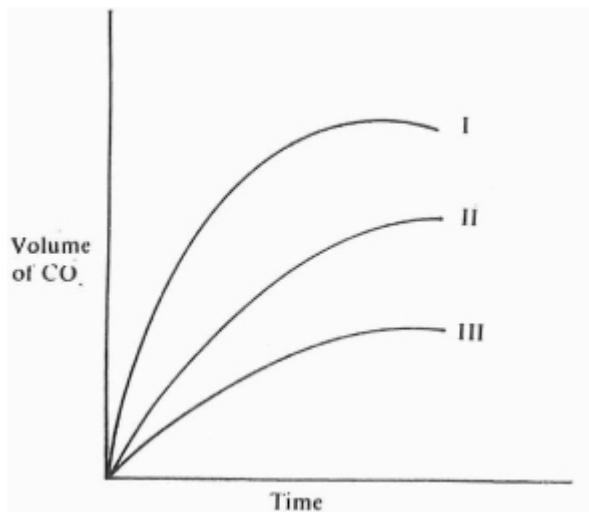


Figure 6.23

3. What factors affect the rates of chemical reactions?

Describe an experiment to illustrate the dependence of the rate of a named chemical reaction on one of these factors.

4. State Le Chatelierâ€™s principle. Using this principle, predict the conditions necessary for converting graphite to diamond, given that
- $C(\text{graphite}) \rightleftharpoons C(\text{diamond}); \Delta H = 1.88 \text{ kJ mol}^{-1}$
 - density of graphite = 2.26 g cm^{-3}
 - density of diamond = 3.51 g cm^{-3}
5. (a) List three factors that may affect the rate of a chemical reaction.

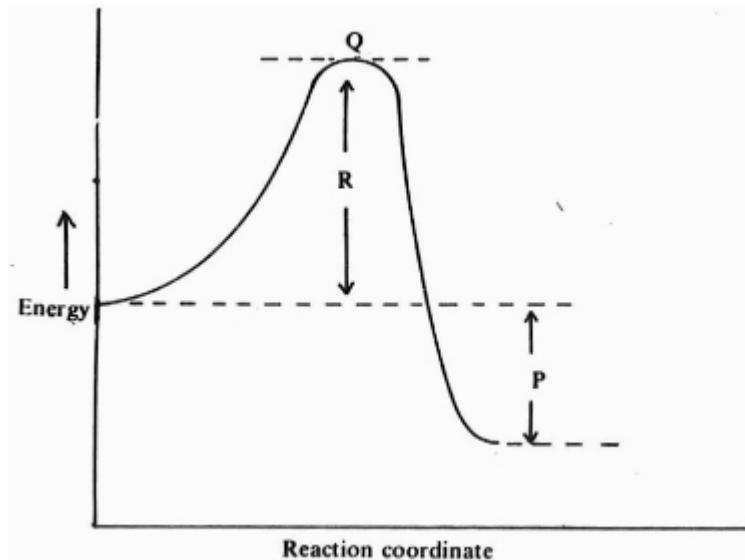


Figure 6.24

In the above diagram (Figure 6.24) what do P, Q and R represent? (WAEC)

6. (a) From the equation
- $$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \Delta H = -50 \text{ kJ mol}^{-1}$$
- List two conditions that favour a good yield of ammonia.
- (b) What principle governs the choice of the conditions listed in (a) above? (WAEC)
7. When 4.9g of concentrated tetraoxosuphate(VI) acid is dissolved in 100 cm^3 of water, a rise in temperature of $0.5 \text{ }^\circ\text{C}$ is recorded. Calculate the heat of solution of the acid.