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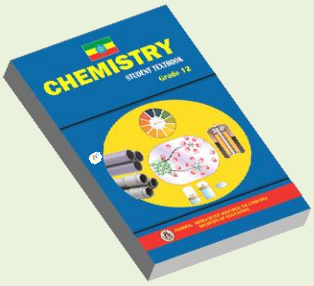

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CHEMISTRY

STUDENT TEXTBOOK

GRADE 12

Authors, Editors and Reviewers:

JL Sharma (Ph.D.)
Nell Angelo (M.A.)
Gashaw Melkamu (M.Sc.)
Tolessa Mergo (M.Ed. prospective)
Teketel Yohannes (Prof.)

Evaluators:

Nega Gichile
Mahtot Abera
Solomon Haileyesus

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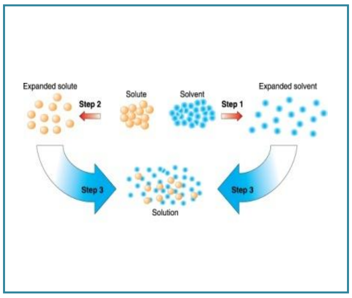

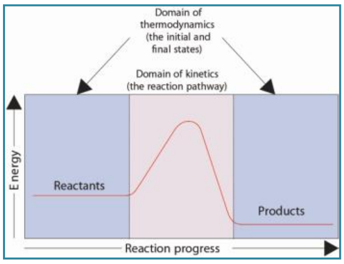

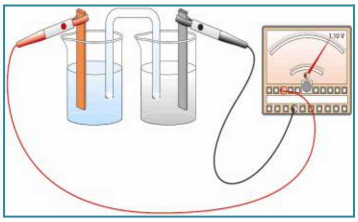
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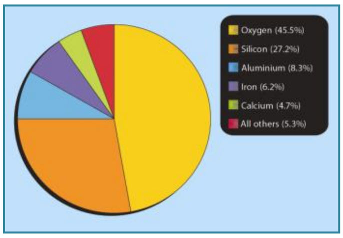
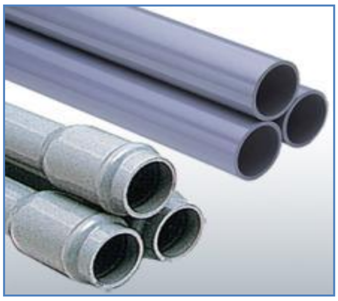
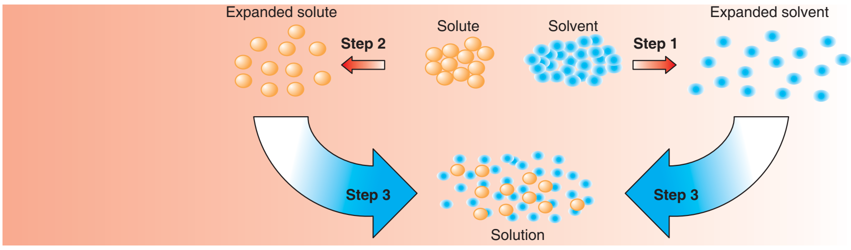

Oxygen (45.5%)
Silicon (27.2%)
Aluminium (8.3%)
Iron (6.2%)
Calcium (4.7%)
All others (5.3%)



UNIT 1



Solutions

Unit Outcomes

At the end of this unit, you should be able to:

- *know the types of solutions;*
- *understand the process of solution formation, the rate of solution, the heat of solution and solubility;*
- *describe the dependence of solubility on the temperature and pressure of the solution;*
- *know how to solve problems involving the concentration of solutions and to express the result in various units;*
- *describe, the behaviour of ionic solute in unsaturated, saturated and supersaturated solutions using the concept of equilibrium;*
- *prepare solutions of a required concentration by dissolving a solute or diluting a concentrated solution;*
- *understand the relationship between the colligative properties of solutions and know how to solve problems involving colligative properties of solutions;*
- *describe scientific inquiry skills along this unit: observing, classifying, comparing and contrasting, measuring, asking questions, drawing conclusion, applying concept and problem solving.*

MAIN CONTENTS

Most of the materials around us are mixtures. In this unit, we shall be concerned with properties and types of mixtures, and with the relationships of their properties to those of the individual components.

A homogeneous mixture, also known as solution, is a mixture that is uniform in its properties throughout a given sample. When sodium chloride is dissolved in water, you obtain a homogeneous mixture, or solution. Air is a gaseous solution, principally of two elementary substances, nitrogen and oxygen, which are physically mixed but not chemically combined.

There are various practical reasons for preparing solutions. For instance, most chemical reactions are run in solution. Solutions have specific useful properties. For example, when gold is used for making jewellery, it is mixed, or alloyed with a small amount of silver. Gold-silver alloys are not only harder than pure gold, but they also melt at lower temperatures and are therefore easier to cast.

In this unit, you will study the dependence of solubility (*the amount of substance that dissolves in another*) on temperature and (in some cases) on pressure; the ways of expressing the concentration of a solution. You will also study about the colligative properties of solutions.

1.1 HOMOGENEOUS AND HETEROGENEOUS MIXTURES

At the end of this section, you should be able to:

- define the terms mixture, homogeneous and heterogeneous mixture, solute, solvent, solution;

- distinguish between homogeneous and heterogeneous mixtures;
- describe suspensions and colloids.

1.1.1 Some Basic Definitions

How do you distinguish homogeneous and heterogeneous mixtures?

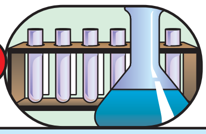
Mixtures are combinations of two or more substances in which each substance retains its own chemical identity and hence its own properties. A sample of clean air, for example, consists of many elements and compounds physically mixed together, including oxygen (O_2), nitrogen (N_2), carbon dioxide (CO_2), noble gases, and water vapour (H_2O). *Can you give more examples of mixtures?* There are two broad classes of mixtures, homogeneous and heterogeneous mixtures.

A **homogeneous mixture** is a mixture in which the composition of the mixture is the same throughout. i.e., it has no visible boundaries because the components are mixed as individual atoms, ions and molecules. For example, when a spoonful of sugar dissolves in water you obtain a homogeneous mixture.

A **heterogeneous mixture** has one or more visible boundaries between the components. Thus, its composition is not uniform. In this type of mixture, each component's particles can be detected by the naked eye or with a magnifying glass. If sand is mixed with iron filings, the sand grains and the iron filings remain separate. This is an example of a heterogeneous mixture.

A typical solution consists of at least two substances; a substance in smaller amount called the solute, dissolved in a larger amount of another substance, known as the solvent. The solvent is often but not always present in excess. For example, the physical state of a solution containing 40 g of table sugar and 30 g of water is liquid. In this case, though water is present in small amount, it is present as solvent.

Experiment 1.1



Distinction between homogeneous and heterogeneous mixtures

Objective: To distinguish between homogeneous and heterogeneous mixtures.

Apparatus: Beakers, test tubes, watch glass, stirrer.

Chemicals: Table salt, water, iron filings, sulphur powder, oil, alcohol.

Procedure:

Prepare mixtures of the following pairs in suitable apparatus.

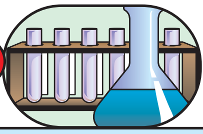
a Table salt and water

- b Iron filings and sulphur powder
- c Oil and water
- d Water and alcohol

Use either naked eye or hand lens to observe each mixture. Classify the mixtures you prepared as homogeneous and heterogeneous. Give reason for your classification.

1.1.2 Suspension and Colloids

Experiment 1.2



Investigating properties of some mixtures

Objective: To see the difference between suspensions, solutions and colloids.

Apparatus: Three 100 mL beakers.

Chemicals: Sand, gentian violet and bile.

Procedure:

1. Label the beakers as A, B, and C; add sand to beaker A, gentian violet to beaker B, and bile to beaker C.
2. Add about 50 mL water to each beaker and stir the contents.
3. Leave the beakers undisturbed for about 30 minutes and see if they become clear on standing.
4. Pass a beam of light through each beaker.

Observations and analysis:

- a In which beaker the contents separate in two layers on standing?
- b Which beaker scatters light without separating the contents on standing?
- c Which beaker contains a solution and which beaker contains a colloid?
- d What do you conclude from this experiment?

Exercise 1.1

Define each of the following terms and give examples for each.

- a homogeneous mixture
- b heterogeneous mixture
- c solute
- d solvent
- e colloid
- f suspension

What is the difference between suspensions and solutions?

We are all familiar with suspensions such as a mixture of mud and water or flour and water. Sometimes we prepare and use a suspension of paint in water. These suspensions are heterogeneous mixtures composed of particles that are visible *to the naked eye or that can be seen with a magnifying glass*. The suspended particles appear cloudy, and settle down in due course of time. When $Mg(OH)_2$ (called milk of magnesia) is shaken with water, it forms a suspension. In contrast, when we make a solution, we prepare a homogeneous mixture in which the dissolved species are molecules or ions. A solution may be coloured, but it is transparent; the dissolved molecules or ions are invisible, and they do not settle out on standing. Figure 1.1a and Figure 1.1b show a solution and a suspension, respectively.

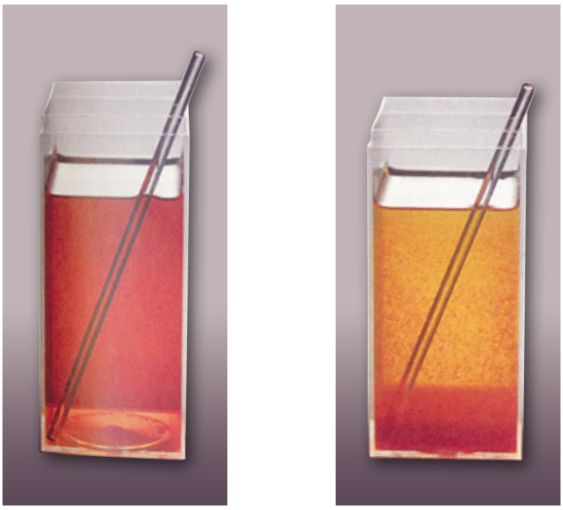


Figure 1.1 a) Solution b) Suspension

There is another group, called colloids that exhibit properties intermediate between those of suspensions and solutions. The particles in a colloid are larger than most simple molecules. However, colloidal particles are small enough and do not settle down. Although colloid particles may be so small that the dispersion appears uniform, even under a microscope, they are large enough to scatter light very effectively (see Figure 1.2). Consequently, most colloids appear cloudy or opaque unless they are very dilute. Like solutions, colloids can be gaseous, liquid or solid. Clouds are colloidal mixtures composed of air and water droplets that are small enough that they do not settle out.

Figure 1.2 The light beam is not visible as it passes through a true solution (left), but it is clearly visible as it passes through colloidal mixture (right).

1.2 TYPES OF SOLUTIONS

At the end of this section, you should be able to:

- explain different types of solutions;
- give examples for each type of solution;
- after a visit to nearby gold smith, present a report to class on how jewellery gold is made.

Solutions may exist in any of the three states of matter.

Activity 1.1

Form groups and discuss the following points. Report the result of your discussion in tabular form.

1. Mention the types of solutions.
2. What are the possible physical states of solutes and solvents in each type of solution?
3. Give at least one example to each type of solution.
4. Explain briefly how solid solutions are formed?
5. Copy the given table in your note book and write your answers in it:

State of solute	State of solvent	State of solution	Type of solution	Examples

PROJECT

Do you know how jewellery gold is made?

Your teacher will arrange a visit to the nearby goldsmith. Ask the following questions during your visit to the goldsmith:

How is jewellery made from gold? What are the possible components, other than gold present in the jewellery? Which component is present in large quantity? What is the advantage of mixing gold with other materials? Can you separate the components present in the jewellery? How is purity of gold assessed and what is the unit of measuring the purity? Write a report about what you have observed during your visit and present it to the class.

Exercise 1.2

1. Give two examples of
   - a gas-gas solution
   - b gas-liquid solution
   - c liquid-liquid solution
   - d solid-liquid solution
   - e solid-solid solution
2. What are the possible physical states of solutes and solvents in
   - a gaseous solutions?
   - b liquid solutions?
   - c solid solutions?

1.3 THE SOLUTION PROCESS

At the end of this section, you should be able to:

- explain how the “like dissolves like” rule depends on inter-particle forces of interactions and predict relative solubility;
- define rate of dissolution;

- define heat of solution, solvation energy and hydration energy;
- apply the concept of heat of solution to a solution of ammonium nitrate and sodium hydroxide crystals;
- explain how heat of solution is influenced by the inter-particle interaction forces.

Activity 1.2

Try to mix the following substances with water.

a oil b benzene c ethanol

What did you observe? Which of the substances is completely miscible with water and which of them is immiscible? Discuss your observations with your classmates, and report your possible reasons to the class.

1.3.1 Liquid Solutions and Interparticle Forces of Attractions

What are the major factors that affect the solubility of substances in liquid solvents?

When a solute dissolves in a solvent, particles of the solute disperse throughout the solvent. The solute particles occupy positions that are normally taken by solvent molecules i.e., particles of the solute mix with particles of the solvent. The tendency to mix is affected by the relative strengths of three types of interaction. These are

* *Solvent-solvent interaction*

* *Solute-solute interaction*

* *Solvent-solute interaction*

Strong forces of attraction between solute particles (*solute-solute interactions*) or between solvent particles (*solvent-solvent interactions*) tend to keep like particles close together and reduce the solubility of solute in the solvent. On the other hand, strong attraction forces between solute and solvent particles (*solute-solvent interactions)* makes dissolving easier and helps to keep particles in solution. For simplicity, we can imagine the solution process taking place in three distinct steps (Figure 1.3).

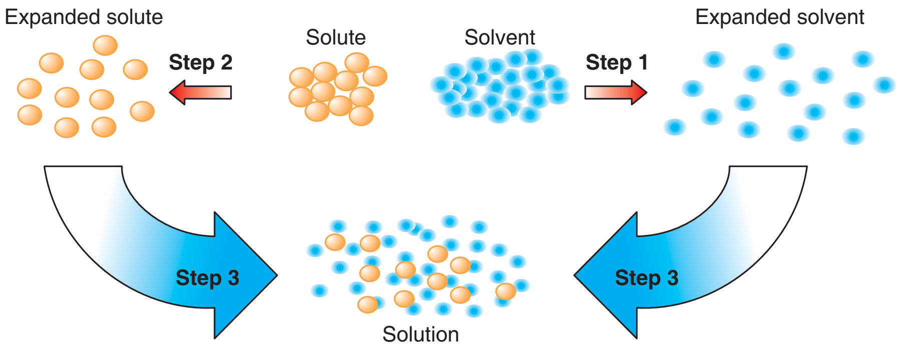


Figure 1.3 A molecular view of the solution process, portrayed as taking place in three steps.

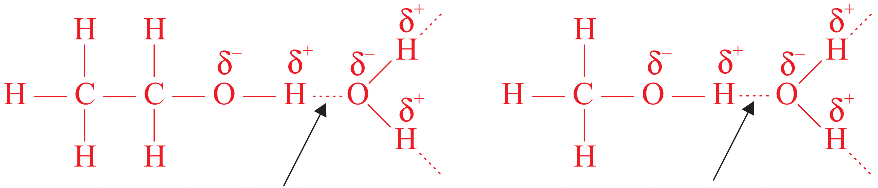
Step 1 – is the separation of solvent molecules from each other to "make room" for the incoming solute particles and **step 2** – is the separation of solute molecules. These two steps require energy input to break attractive intermolecular forces. Therefore, they are endothermic. In **step 3** – the solvent and solute molecules mix. This process can be exothermic or endothermic.

Solution of liquids in liquids

Ethanol mixes with water but oil does not. Why? Solubility is a measure of how much solute will dissolve in a solvent at a specific temperature. Do you know the principle "like dissolves like"? The "like dissolves like" principle is helpful in predicting the solubility of a substance in a given solvent. What this expression means is that two substances with intermolecular forces of similar type and magnitude are likely to be soluble in each other.

For example, in a solution formed between benzene (C_6H_6) and carbon tetrachloride (CCl_4), both species are non-polar and experience only relatively weak London forces. When these two liquids are mixed, they readily dissolve in each other because the attraction between CCl_4 and C_6H_6 molecules is comparable in magnitude to the forces between CCl_4 molecules and between C_6H_6 molecules. Two liquids are said to be miscible if they are completely soluble in each other in all proportions. *What can you say about the solubility of* C_6H_6 *and* CCl_4*?*

Water is the most prominent solvent because it is so common and dissolves so many ionic and polar substances. Water molecules are strongly associated with each other through hydrogen bonding. Compounds that form hydrogen bonding tend to be soluble in water. For example, alcohols such as methanol, ethanol and 1, 2-ethylene glycol are miscible in water because they can form hydrogen bonding with water molecules.



Hydrogen bonding between ethanol and water

Hydrogen bonding between methanol and water

Figure 1.4 Solubility of ethanol and methanol in water through hydrogen bonding.

What happens if octane, a typical hydrocarbon, is added to water? Water molecules are held in contact by hydrogen bonding, while octane molecules are held in contact by London or dispersion forces. When the two liquids are mixed, the attraction between the octane molecules and the water molecules is not strong enough to overcome the hydrogen bonding between the water molecules. The relatively strong hydrogen bonding keep the water molecules clustered together, and no mixing occurs.

Solutions of Solids in Liquids

Activity 1.3

Take two containers and add water to both. Put table salt in the first container and table sugar in the second container and stir. What did you observe? Did both solids dissolve in water? Repeat the same procedure using oil instead of water.

What did you observe? Did both solids dissolve in oil? Discuss your observations with your classmates. Can you make generalization from your observation?

Solids composed of polar molecules or ions, are insoluble in non-polar solvents. The weak solute-solvent interaction, compared with the strong attractions within the crystal, is not sufficient to tear apart the lattice. This is why sugar, which consists of molecules lightly bound to each other by hydrogen bonding, is insoluble in solvents like oil. However, sugar is soluble in water, because this solvent attracts sugar molecules in the same way that sugar molecules attract each other.

Solids whose crystals are held together by London forces are able to dissolve to appreciable extents in non-polar solvents. However, they are not soluble to any great degree in polar solvents, for the same reason that non-polar liquids are insoluble in polar solvents.

Can you give an example of a solid non-polar compound that dissolves in benzene but not in water? Water and other polar molecules are attracted to ions. The electrostatic attraction between an ion and a molecule with a dipole is called an ion-dipole attraction. These attractions play an important role in the dissolution of ionic compounds in water (Figure 1.5).

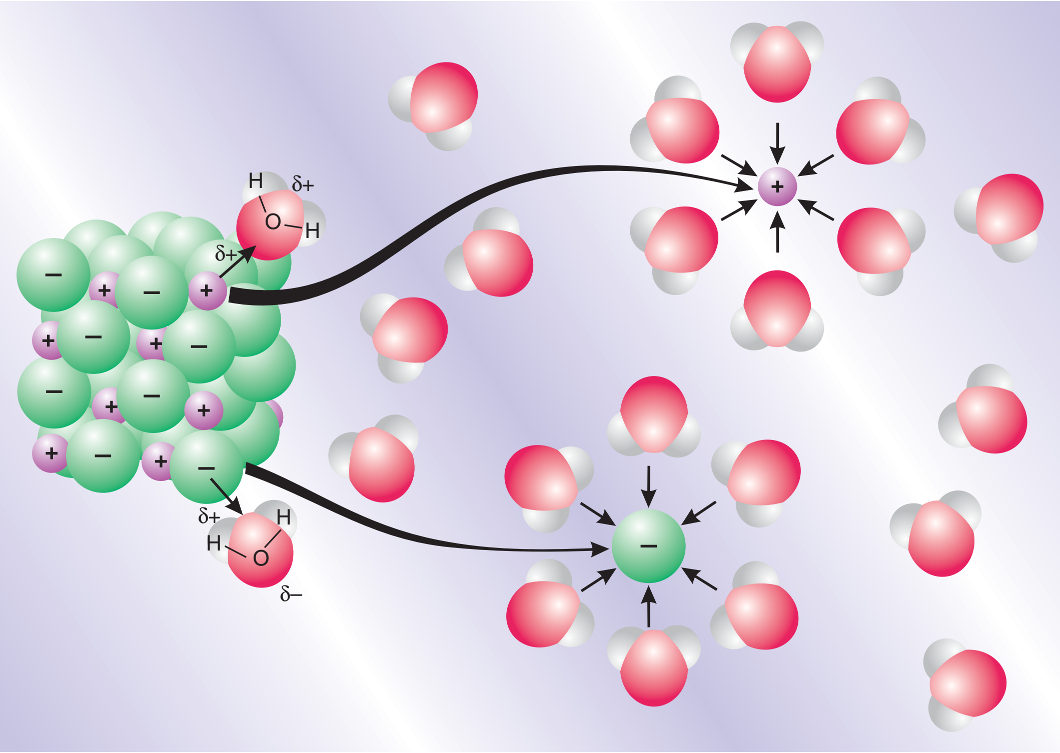


Figure 1.5 Ion-dipole force in dissolving an ionic crystal.

What happens when ionic compounds dissolve in water?

When ionic compounds, such as KCl, dissolve in water, (Figure 1.6), the ions in the solid separate because water molecules surround and solvate the ions. When potassium chloride is added to water, the ion-dipole forces attract the positive (*hydrogen*) end of the polar water molecules to the negative chloride ion at the surface of the solid, and they attract the negative (*oxygen*) end to the positive potassium ions. The water molecules penetrate between individual K^+ and Cl^- ions and surround them, reducing the strong inter-ionic forces that bind the ions together. This reduction allows them to move off into solution as hydrated ions. In general, when a solute particle becomes surrounded by solvent molecules, we say that it is solvated. When the solvent is water the process is called hydration.

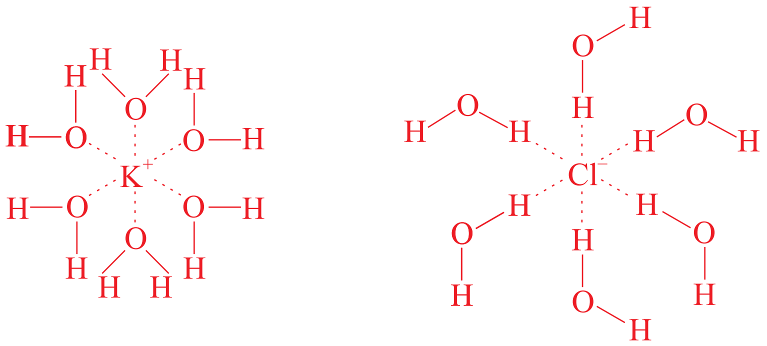


Figure 1.6 K^+ and Cl^- surrounded by H_2O molecules.

In Grade 11 Chemistry, you learned about the cleansing action of soap, which work on the principle of "like dissolves like". Non-polar tails of soap dissolve in oil and grease globules. The polar heads keep the particle suspended in water in which they can be washed away.

1.3.2 The Rate of Dissolution

What are the major factors that affect the rate of dissolution?

The rate of dissolution is the speed with which a solute goes into solution. This largely depends upon the inter-particle forces and, to a lesser extent, on conditions such as the surface area of the solid solute, and the temperature and the pressure of the system.

Inter-particle force is the extent to which solvent molecules interact with particles of the solute. When the solvent-solute interactions are stronger than those between solute-solute and solvent-solvent particles, the dissolution process becomes easier.

Increasing surface area will increase the rate of dissolution because it increases the number of solute particles in contact with the solvent.

1.3.3 Energy Changes in the Solution Process

Heat of Solution

Experiment 1.3

Investigation of Heat of Solution

Objective: To investigate the heat of solution of sodium hydroxide and ammonium nitrate.

Apparatus: Erlenmeyer flask, thermometer, cork.

Chemicals: Sodium hydroxide, ammonium nitrate and water.

Procedure:

1. Pour 50 ml of water into Erlenmeyer flask and place a thermometer as shown in Figure 1.7.

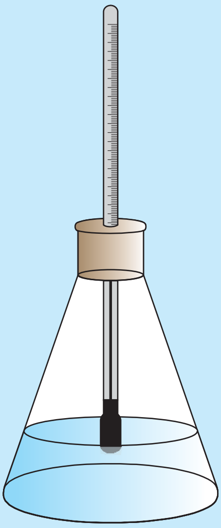


Figure 1.7 Apparatus to measure the heat of solution of sodium hydroxide.

2. Record the initial temperature of the water.
3. Remove the cork, along with the thermometer, and add 4 g of sodium hydroxide pellets.
4. Replace the cork gently, stir the contents, and note the highest temperature reading.
5. Determine the heat of the solution of sodium hydroxide.

6. Repeat the experiment, using 4 g of ammonium nitrate.
7. Copy and complete the following table.

Chemical	Initial temperature of the solvent	Maximum temperature of the solution	Heat of solution
NaOH			
NH_4NO_3			

8. Write down your conclusion.
9. Present your findings.

What are the three major interactions that are observed in the solution process?

You have learned that the solution process has three steps. The amount of energy that is absorbed or released when one mole of a substance enters solution is called *the heat of solution* and is given the symbol ΔH°_{Sol}, which is the sum of the enthalpies associated with the three steps in the solution process (Figure 1.3).

- The separation of solute particles is endothermic because energy is required to overcome the forces holding the solute particles together. For gases, this step is ignored because their molecules are already widely separated.
- The separation of solvent particles is also endothermic because energy is required to overcome the forces holding the solvent molecules together.
- Each solute particle is surrounded by a layer or "cage" of solvent molecules that is attracted to it by *intermolecular forces*. This step can be endothermic or exothermic, and is referred to as solvation.

The heat of solution ΔH°_{Sol}

$$\Delta H^\circ_{Sol} = \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3 = \Delta H^\circ_{Hydration} + \Delta H^\circ_{Latice\ energy}$$

where ΔH°_1 and ΔH°_2 are enthalpies required to separate solute particles and solvent molecules, respectively, and ΔH°_3 is the enthalpy of solvation. If the solute-solvent attraction is stronger than both the solvent-solvent attraction and the solute-solute attraction, the solution process is favourable, or exothermic ($\Delta H^\circ_{Sol} < 0$). If the solute-solvent interaction is weaker than the solvent-solvent and solute-solute interactions, then the solution process is endothermic ($\Delta H^o_{Sol} > 0$).

Hydration of Ionic Solids in Water

What is lattice energy? How can it affect the solubility of ionic solids?

Hydration of ions favours the dissolution of an ionic solid in water. The ions in an ionic crystal are very strongly attracted to one another. Therefore, the solubility of an ionic solid depends not only on the energy of the hydration of ions, but also on lattice energy, which are the energy holding ions together in the crystal lattice. Lattice energy works against the solution process, so an ionic solid with relatively large lattice energy is usually insoluble.

Lattice energies depend on the charge on the ions and also the distance between the centres of the neighbouring positive and negative ions. As the magnitude of the charge on the ions increases the lattice energy also increases. For this reason, you can expect substances with single charged ions to be more comparatively soluble, and those with multiple charged ions to be less soluble in water.

Activity 1.4

Take 1 g of KNO_3, NH_4Cl, and Na_2CO_3 each and dissolve them in water in different test tubes. What did you observe? Which of these chemicals dissolves faster? Is there any change in temperature before and after mixing? Which solution becomes hot and which becomes cold, when solute and solvents are mixed? Discuss your observations with your classmates.

Activity 1.5

Discuss the following questions and write a report. Present your report to the class.

1. How do you compare the hydration of the ions of Group I metals with that of Group II metals? Give reasons.
2. Compare the solubility of $Mg(OH)_2$ with $Ba(OH)_2$, $MgSO_4$ with $BaSO_4$. Justify your answers in terms of lattice energy and hydration energy.

Exercise 1.3

1. Define each of the following.
    - a rate of dissolution
    - b heat of solution
    - c solvation
    - d hydration energy
    - e lattice energy
    - f ideal solution
2. Indicate the type of solute-solvent interaction that should be most important in each of the following solutions:
    - a KBr in water
    - b Toluene, C_7H_8, in cyclohexane, C_6H_{12}
    - c NaOH in water
3. Sodium carbonate is soluble in water, while calcium carbonate is insoluble. Why?

1.4 SOLUBILITY AS AN EQUILIBRIUM PROCESS

At the end of this section, you should be able to:

- describe the distinctions among unsaturated, saturated and supersaturated solutions;
- prepare a supersaturated solution of sodium phosphate;
- explain the equilibrium nature of a saturated solutions;
- define solubility and describe the factors that affect the solubility of substances;
- investigate the effect of temperature on the solubility of sodium sulphate in water;
- conduct an experiment to determine the solubility of table salt and sugar in water;
- state Henry's law;
- use Henry's law to calculate the concentration of gaseous solute in a solution.

Activity 1.6

Form a group and perform the following activity.

1. Pour 50 mL water in a beaker.
2. Add some crystal of Na_2SO_4 into the water using spatula and stir until it dissolves.
    - a What do you call this type of solution?
3. Continue adding more and more Na_2SO_4 stirring to dissolve.
    - b What do you observe after addition of large amount of solute?
4. Filter the undissolved solute. Collect the filtrate or the solution.
    - c Why does the solute remains undissolved?
    - d What is the name of such a solution?
5. Add some more solute to the filtrate and stir.
    - e Does the additional solute dissolve?

Discuss your findings with rest of the class.

Experiment 1.4

Investigating the solubility of NaCl

Objective: To determine the solubility of sodium chloride in water.

Apparatus: Beaker, evaporating dish, measuring cylinder, glass rod, filter paper, analytical balance, and Bunsen burner.

Chemicals: Sodium chloride and water.

Figure 1.8 Experimental set-up for the determination of the solubility.

Procedure:

1. Take an evaporating dish and weigh it.
2. Take 100 mL of water in a beaker and add sodium chloride to it. Stirr the solution vigorously with a glass rod, until undissolved sodium chloride is left in the beaker.
3. Take 50 mL of the supernatant saturated solution (assume that 50 mL of solution is equal to 50 mL of the solvent) and transfer it to an evaporating dish.
4. Heat the solution in the evaporating dish as shown in the Figure 1.8, till all the water has evaporated and dry sodium chloride is left in the evaporating dish.
5. Cool the evaporating dish containing dry sodium chloride to room temperature and weigh it again.

Observations and analysis:

1. Volume of the NaCl solution ……………………..
2. Weight of the empty evaporating dish ……………………..
3. Weight of the evaporating dish + NaCl collected after evaporating the solvent ....
4. Calculate the solubility of NaCl in water and express the results in grams of NaCl/ 100 g of water.

When an ionic solid dissolves, ions leave the solid and become dispersed in the solvent. Occasionally some dissolved ions collide with the undissolved solute and crystallize. As long as the rate of dissolution is greater than the rate of crystallization, the concentration of ions in the solution rises. Eventually, ions from the solid are dissolved at the same rate as the ions in the solution are crystallized. At this point, even though dissolution and crystallization continue, there is no further change in the concentration over time. The system has reached equilibrium. That is, excess undissolved solute is in equilibrium with the dissolved solute.

$$\text{Solid (solute)} \underset{\text{Crystallization}}{\overset{\text{Dissolution}}{\rightleftarrows}} \text{Dissolved ions}$$

After equilibrium is established, no more solid dissolves. *Why?* Such a solution is said to be saturated. A saturated solution is a solution in which the dissolved and undissolved solutes are in dynamic equilibrium see Figure 1.9.

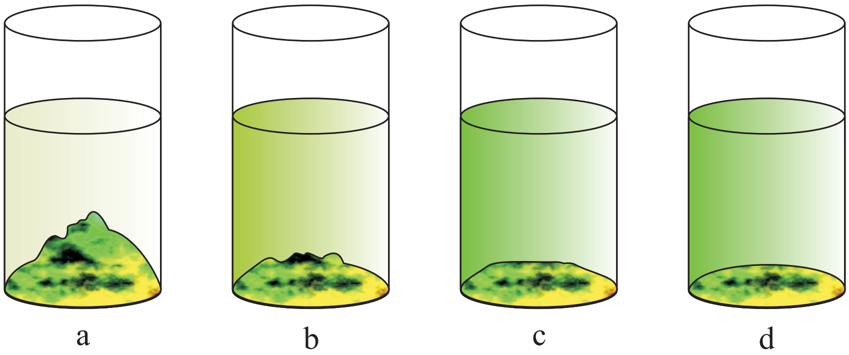


Figure 1.9 Formation of a saturated solution.

a A coloured solid solute is added to water.

b After a few minutes, the solution is coloured, due to the dissolved solute, and there is less undissolved solute than in (a).

c After more time passes, the solution's colour has intensified and there is less undissolved solute. Therefore, the solution in (b) must have been unsaturated.

d Still later, the solution colour and the quantity of undissolved solute appear to be the same as that in (c). Dynamic equilibrium must have been attained in (c) and persists in (d). The solution is saturated.

Before equilibrium is reached, the solution is said to be unsaturated. An unsaturated solution is a solution that can dissolve more solute at a given temperature.

Activity 1.7

Prepare a saturated solution of sodium thiosulphate ($Na_2S_2O_3$) in beaker containing 50 mL water. Heat the solution so that extra amount of solute dissolves.

Filter and divide the solution into two parts in two different beakers. Keep both the solutions to cool slowly undisturbed. After cooling stir one of the solutions and observe what happens.

Drop a small grain of crystal in the second one and observe the result.

a What is the name of such a solution that is made by cooling concentrated solution?

b What happens when the solution was stirred?

c What about the solution to which a crystal grain is dropped? Why?

d What did you understand from the activity?

The solubility of many ionic solids in water increases as temperature increases. They form supersaturated solutions, which actually contain larger amounts of solute than in saturated solutions. Supersaturated solutions can sometimes be prepared by saturating a solution at a high temperature. Honey is an example of naturally occurring supersaturated solution. It contains glucose, as a solute, and water, as a solvent. If honey is left to stand, the glucose eventually crystallizes.

Supersaturated solutions are unstable, and addition of a “seed” crystal of solute will generally cause all of the excess solute to suddenly crystallize see Figure 1.10.

A Hot supersaturated solution before seeding.

B Cold and undisturbed supersaturated solution without seeding.

C Cold supersaturated solution after seeding.

Figure 1.10 Seeding a supersaturated solution.

1.4.1 Effect of Temperature on Solubility of Solute

Activity 1.8

1. Prepare a saturated solution of Na_2SO_4 at room temperature.
2. Heat the solution on a tripod with wire gauze and add some crystal of Na_2SO_4.
3. What happens to the solute?
4. If the solute dissolves add more and continue heating.
5. What is the effect of temperature on solubility of this solute?
6. After all the additional solute dissolves remove the beaker from the tripod and add cold water on the side of the beaker.
7. What do you observe?
8. What is the effect of cooling the solution?
9. Why do we always mention temperature when we report solubility of substances?

Temperature affects the solubility of most substances. When a solid dissolves in a liquid, the solute particles must separate, so energy must be added. Thus, for a solid, $\Delta H^\circ_{\text{Solute}} > 0$. In contrast, gas particles are already separated, so $\Delta H^\circ_{\text{Solute}} \approx 0$. Because the hydration step is exothermic ($\Delta H^\circ_{\text{Hydra}} < 0$), the sum of these two terms must be negative. Thus, for all gases in water, $\Delta H^\circ_{\text{Sol}} < 0$.

$$\text{Solute(g)} + \text{Water(l)} \rightarrow \text{Saturated solution(aq)} + \text{Heat}$$

This equation means that solubility of gases in water decreases with rising temperature. In most (*but certainly not all*) cases, the solubility of a solid substance increases with increase in temperature. The magnitude of the increase in solubility varies from one substance to another. The solubility of sodium chloride in water increases by only about 10% from 35.7 g/100 g to 39.8 g/100 g, when the temperature is raised from 0 °C to 100 °C. The solubility of silver nitrate, however, increases by over 700% from 122 g /100 g to 951 g/100 g, over the same temperature range.

A few solids such as sodium sulphate have unusual solubility characteristics in water. The solubility of sodium sulphate rises between 0 °C to 32.4 °C, where it reaches a maximum of 49.7 g Na_2SO_4 per 100 g water. Further, the solubility of sodium sulphate, decreases by about 19.23%, changing from 49.7 g/100 g at 32.4 °C, to 42 g/100 g at 100 °C. Thus some ionic compounds show mixed solubility behaviour. Figure 1.11 shows the solubility of some ionic compounds in water, as a function of temperature.

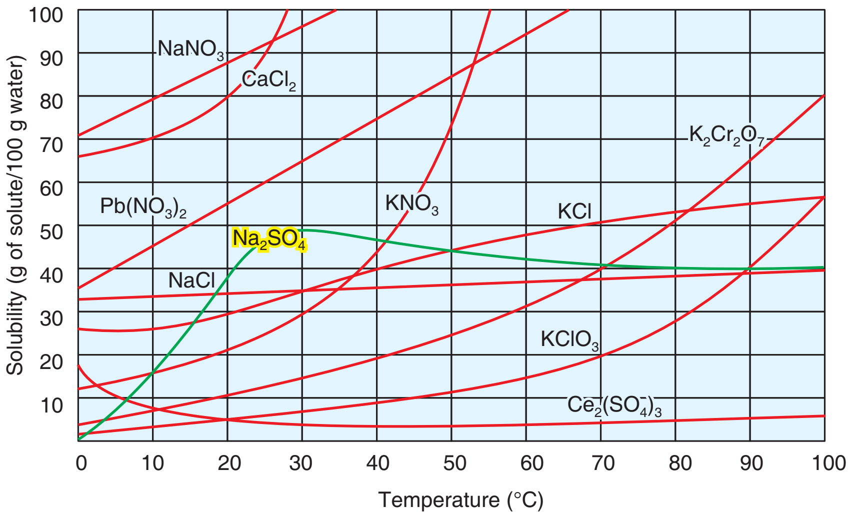


Figure 1.11 Approximate variation of solubility with temperature for some ionic salts in water.

1.4.2 The Effect of Pressure on Solubility

Why pressure significantly affect only the solubility of gases? Since liquids and solids are almost incompressible, pressure has little effect on their solubility, but it has a major effect on gas solubility. The solubility of gases always increases with increasing pressure. The effect of increased pressure on solubility has long been used in the beverage industry, where carbonated beverages such as champagne, beer and many soft drinks are bottled under CO_2 pressure, up to 4 Pa.

The solubility of a gas in a liquid is directly proportional to the partial pressure of the gas over the solution.

The quantitative relationship between gas solubility and pressure is given by Henry's law, which states that

"at a given temperature the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas over the solution".

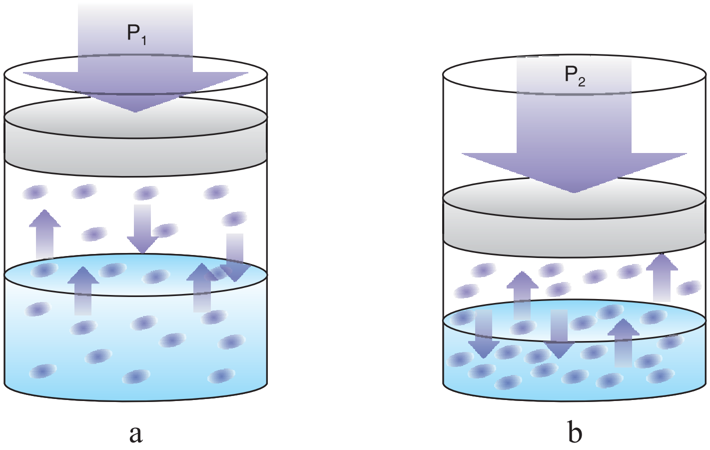
$$C_g = k_H P_g$$

where C_g is the molar concentration (mol/L) of the dissolved gas, P_g is the pressure (in atm) of the gas over the solution and k_H is Henry's law constant, which is expressed in mol/L atm.

Consider the piston-cylinder assembly in Figure 1.12, in which gas is above a saturated aqueous solution of the same gas. At a given pressure, P_1, the same number of gas molecules enters and leave the solution per unit time. i.e., the system is at equilibrium.

$$\text{Gas} + \text{Solvent} \rightarrow \text{Saturated solution}$$

If you push down the piston (*increasing pressure to P_2*), the gas volume decreases and gas particles collide with the liquid surface more often. Thus, more gas particles enter the solution per unit time. Higher gas pressure disturbs the balance of equilibrium, so more gas dissolves to reduce this disturbance until the equilibrium is established in the system.



a) *A saturated solution of a gas is in equilibrium at pressure P_1*

b) *If the pressure is increased to P_2, the volume of the gas decreases. As a result, the collisions with the surface increases, and more gas molecules enter the solution when equilibrium is re–established.*

Figure 1.12 The effect of pressure on gas solubility:

Table 1.1 Henry's Law constants for some gases in water at 20°C.

Gas	k_H (mol/L. atm)
Air	7.9×10^{-4}
Argon	1.5×10^{-3}
Carbon dioxide	3.3×10^{-2}
Helium	3.7×10^{-4}
Neon	5.0×10^{-4}
Hydrogen	8.5×10^{-4}
Nitrogen	7.0×10^{-4}
Oxygen	1.23×10^{-3}

Example 1.1

The partial pressure of carbon dioxide gas inside a bottle of mineral water is 4 atm at 25°C. What is the solubility of CO_2?

Solution:

Given:

$P_{CO_2} = 4$ atm

$k_H = 3.3 \times 10^{-2}$ mol/L atm

Required:

$C_{CO_2} = ?$

$$C_{CO_2} = k_H \cdot P_{CO_2}$$

$$= 3.3 \times 10^{-2} \text{ mol/L. } \cancel{\text{atm}} \times 4 \cancel{\text{atm}}$$

$$= 0.1 \text{ mol/L}$$

$$C_{CO_2} = 0.1 \text{ mol/L}$$

Exercise 1.4

1. If air contains 78% N_2 by volume, what is the solubility of nitrogen in water at 25°C?
2. Calculate the concentration of CO_2 in a soft drink after the bottle is opened at 25 °C under a CO_2 partial pressure of 3.0×10^{-4} atm.

1.5 WAYS OF EXPRESSING CONCENTRATIONS OF SOLUTION

At the end of this section, you should be able to:

- define terms like solution, concentration, mass percentages, ppm and ppb of a solute in a solution;
- calculate the mass percentage, ppm and ppb of a solute in a solution from given set of information;
- define mole fraction, molarity, equivalent mass, number of equivalents, normality and molality;
- calculate mole fraction, molarity, normality and molality of a solution from given set of information; and
- interconvert various concentration expressions.

What does concentration mean? How do you determine it?

The concentration of a solution is the amount of solute present in a given quantity of solvent or solution. The concentration of a solution can be expressed either qualitatively or quantitatively. The terms dilute and concentrated are used to describe a solution qualitatively. A solution with a relatively small amount of solute is said to be dilute. One with a large amount of the solutes is said to be concentrated.

The knowledge of concentration can be very useful in everyday life. For example, human beings estimate the quantity of solutes such as sugar and salt, in beverages and other food solutions by tasting. However, sometimes tasting a substance is not safe and, in general, this is not an accurate method of estimating the concentration of solute in a solution. *Why?*

Several quantitative expressions of concentration are used in chemistry. Here you are going to learn mass percentage, ppm and ppb, mole fraction, molarity, normality and molality of a solution.

1.5.1 Mass Percentage, ppm and ppb of Solute

What does mass percent mean? How do you convert it to ppm and ppb?

Percent by mass: The percent by mass, also called percent by weight or weight percent, is the ratio of the mass of a solute to the mass of the solution, multiplied by 100.

$$\text{Percent by mass of solute} = \frac{\text{Mass of solute}}{\text{Mass of solute} + \text{Mass of solvent}} \times 100$$

or

$$\text{Percent by mass of solute} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

The percent by mass has no unit because it is the ratio of two similar quantities.

Example 1.2

A solution is made by dissolving 13.5 g of glucose, $C_6H_{12}O_6$, in 0.100 kg of water. What is the mass percentage of solute in this solution?

Solution:

Given:	**Required:**
Mass of solute = 13.5 g	% by mass of solute?
Mass of solvent = 0.100 kg = 100 g	

$$\%\text{ by mass of glucose} = \frac{\text{Mass of glucose}}{\text{Mass of solution}} \times 100$$

$$= \frac{13.5\text{ g}}{13.5\text{ g} + 100\text{ g}} \times 100 = 11.9\%$$

Parts per million (ppm): When the mass of solute in the solution is very small, a widely used expression is parts per million (ppm).

$$\text{ppm of component} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

or

$$\text{ppm} = \text{Mass percentage of solute} \times 10^4$$

Example 1.3

A 2.5 g sample of ground water was found to contain 5.4 μg of Zn^{2+}. What is the concentration of Zn^{2+}, in parts per million?

Solution:

Because 1 μg is 1×10^{-6} g, 5.4 μg = 5.4×10^{-6} g

$$\text{Thus, ppm} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6 = \frac{5.4\times10^{-6}\text{ g}}{2.5\text{ g}} \times 10^6 = 2.16\text{ ppm}$$

Example 1.4

Express 5% (m/m) solution of NaCl in ppm.

Solution:

$$\text{ppm} = \text{Mass percentage} \times 10^4$$

$$= 5 \times 10^4$$

For solutions that are even more dilute, parts per billion (ppb) is used. A concentration of 1 ppb represents 1 g of solute per billion (10^9) grams of solution.

$$\text{ppb} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^9$$

Exercise 1.5

1. A sample of 0.892 g of potassium chloride, KCl, is dissolved in 54.6 g of water. What is the percent, by mass, of KCl in the solution?
2. a If 150 g of orange juice contains 120 mg of ascorbic acid (Vitamin C), what is the concentration of ascorbic acid, expressed in ppm?

   b Express the concentration of ascorbic acid given in (a) in ppb.

1.5.2 Mole Fraction (*X*)

What is the difference between mole fraction of non-electrolytes and mole-fraction of electrolytes?

The mole fraction (X) of a solute is the ratio of the number of moles of solute divided by the total number of moles of a solution (*moles of solute* + *moles of solvent*).

Mole fraction for a non-electrolyte (X) =

$$\frac{\text{Number of moles of solute}}{\text{Number of moles of solute} + \text{Number of moles of solvent}}$$

or $$X_{\text{Solute}} = \frac{n_{\text{Solute}}}{n_{\text{Solute}} + n_{\text{Solvent}}}\ ; \quad X_{\text{Solvent}} = \frac{n_{\text{Solvent}}}{n_{\text{Solvent}} + n_{\text{Solute}}}$$

A useful relation between X_{solute} and X_{solvent} is:

$$X_{\text{Solvent}} + X_{\text{Solute}} = \frac{n_{\text{Solvent}}}{n_{\text{Solvent}} + n_{\text{Solute}}} + \frac{n_{\text{Solute}}}{n_{\text{Solute}} + n_{\text{Solvent}}} = 1$$

For an electrolyte solution, the mole fraction is calculated by treating the cations and anions as individual particles; hence,

$$X_{\text{Cations}} = \frac{n_{\text{Cations}}}{n_{\text{Cations}} + n_{\text{Anions}} + n_{\text{Solvent}}}$$

A similar expression can be written for X_{Anions}.

Example 1.5

What is the mole fraction of I_2 in a solution containing 30 g of I_2 in 400 g of CCl_4?

Solution:

First find the number of moles of I_2 and the number of moles of CCl_4

$$\text{Number of moles of } I_2 = \frac{\text{Mass of } I_2}{\text{Molar mass of } I_2} = \frac{30\ \text{g}}{254\ \text{g/mol}} = 0.12\ \text{mol } I_2$$

$$\text{Number of moles of } CCl_4 = \frac{\text{Mass of } CCl_4}{\text{Molar mass of } CCl_4} = \frac{400\ \text{g}}{254\ \text{g/mol}} = 2.6\ \text{mol } CCl_4$$

$$X_{I_2} = \frac{n_{I_2}}{n_{I_2} + n_{CCl_4}} = \frac{0.12\ \text{mol}}{0.12\ \text{mol} + 2.6\ \text{mol}} = 0.044$$

Exercise 1.6

1. 1 mole of alcohol is mixed with 3 moles of water. Calculate the mole fraction of alcohol and water.
2. Determine the mole fraction of the substances in a solution containing 36 g of water and 46 g of glycerine, $C_3H_5(OH)_3$.
3. 0.1 mole of NaCl is dissolved in 10 moles of water. Calculate the mole fraction of Na^+ ions and Cl^- ions.

1.5.3 Molarity (M)

Molarity or molar concentration is the number of moles of solute in 1 L of solution. Molarity is determined by the equation

$$\text{Molarity (M)} = \frac{\text{Number of moles of solute}}{\text{Volume (L) of solution}}$$

But, $\text{Number of moles of solute} = \dfrac{\text{Mass of solute}}{\text{Molar mass of solute}}$

Therefore,

$$\text{Molarity} = \frac{\text{Mass of solute}}{\text{Molar mass of solute} \times \text{Volume (L) of solution}}$$

Example 1.6

What is the molar concentration of a solution containing 16.0 g of CH_3OH in 200 mL of solution?

Solution:

Given:	**Required:**
Mass of solute (CH_3OH) = 16 g	Molarity = ?
Volume of solution = 200 mL = 0.20 L	
Molar mass of CH_3OH = 32 g/mol	

$$\text{Molarity} = \frac{\text{Mass of } CH_3OH}{\text{Molar mass of } CH_3OH \times \text{Volume (L) of Solution}}$$

$$= \frac{16\text{ g}}{32\text{ g/mol} \times 0.20\text{ L}} = 2.50\text{ mol/L} = 2.50\text{ M}$$

Example 1.7

How many grams of potassium dichromate ($K_2Cr_2O_7$) are required to prepare 250 mL of solution whose concentration is 2.16 M?

Solution:

Given:

Volume of solution = 250 mL = 0.250 L

Molarity (M) of solution = 2.16 M

Molar mass of $K_2Cr_2O_7$ = 294 g/mol

Required:

Mass of $K_2Cr_2O_7$ = ?

$$\text{Molarity} = \frac{\text{Mass of } K_2Cr_2O_7}{\text{Molar mass of } K_2Cr_2O_7 \times \text{Volume(L) of Solution}}$$

$$\begin{aligned}\text{Mass of } K_2Cr_2O_7 &= \text{Molarity} \times \text{Molar mass of } K_2Cr_2O_7 \times \text{Volume (L) of solution}\\ &= 2.16 \text{ mol/L} \times 294 \text{ g/mol} \times 0.250 \text{ L}\\ &= 159 \text{ g } K_2Cr_2O_7\end{aligned}$$

Exercise 1.7

1. 5.85 g of sodium chloride (NaCl) is dissolved in 250 mL of solution. Calculate
   a the molarity of the solution.
   b the mass percentage of the solute.
2. How would 250 ml of 0.15 M KNO_3 solution be prepared?

1.5.4 Normality (N)

What are number of equivalents and equivalent mass? How are they used in calculating the normality of a solution?

The normality of a solution (N) is the number of equivalents of the solute contained in one litre of solution.

$$\text{Normality } (N) = \frac{\text{Number of equivalents of solute}}{\text{Volume (L) of solution}}$$

The number of equivalents can be determined from the equivalent mass.

- The equivalent mass of an acid is obtained by dividing its molar mass by the number of H^+ ions furnished by one formula unit of the acid, or by the number of hydroxide ions with which one formula unit of the acid reacts.

  The equivalent mass of HCl, for example, is the same as its molar mass, since it contains one acidic hydrogen per molecule. The equivalent mass of sulphuric acid, H_2SO_4, is usually half its molar mass, since both hydrogen are replaceable in most reactions of dilute sulphuric acid. An equivalent of phosphoric acid may be 1 mol, 1/2 mol or 1/3 mol, depending on whether one, two or three hydrogen atoms per molecule are replaced, respectively, in a particular reaction.

- The equivalent mass of a base is obtained by dividing its molar mass by the number of OH^- ions furnished by one formula unit of a base or the number of H^+ ions with which one formula unit of the base reacts. The equivalent mass of NaOH, for example, is equal to its molar mass, since one mole furnishes only one mole of OH^- ion.

- The equivalent mass of an oxidizing agent or a reducing agent for a particular reaction is equal to its molar mass divided by the total number of moles of electrons gained or lost when the redox reaction occurs. For example, the equivalent mass of $KMnO_4$ in the reaction

  $$KMnO_4 + KI + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + I_2 + H_2O$$

  is determined as follows.

The oxidation number of Mn ion is (+7) in $KMnO_4$, and is changed to (+2) in $MnSO_4$. This shows that it is a 5-electron transfer reaction.

$$\text{Equivalent mass of } KMnO_4 = \frac{\text{Molar mass of } KMnO_4}{\text{Number of Electrons gained}}$$

$$= \frac{158\ \text{g/mol}}{5\ \text{eq/mol}} = 31.6\ \text{g/eq}$$

- The equivalent mass of a salt is equal to its molar mass divided by number of total positive charges (*total positive valency*).

$$\text{Normality } (N) = \frac{\text{Number of equivalents of solute}}{\text{Volume (L) of solution}}$$

or $$\text{Normality } (N) = \frac{\text{Mass of solute}}{\text{Equivalent mass of solute} \times \text{Volume (L) of Solution}}$$

Notice that normality is molarity times *n*. It is always equal to or greater than molarity.

$$N = M \times n$$

Where *n* is

- number of ionisable hydrogen ions and hydroxide ions per molecule for acids and bases, respectively.
- total number of positive charges for salts.
- total number of electrons lost or gained in redox reactions.

Example 1.8

Calculate the number of equivalents present in 0.50 mol H_3PO_4 if the acid is

a completely neutralized to give PO_4^{3-}

b converted to $H_2PO_4^-$

c converted to HPO_4^{2-}

Solution:

a Since it is completely neutralized, a balanced equation is written as

$$H_3PO_4 \rightarrow 3H^+ + PO_4^{3-}$$

From the reaction, one mole of H_3PO_4 produces three moles of H^+ ions. Therefore,

$$\text{Number of equivalents} = \text{Moles of } H_3PO_4 \times 3$$
$$= 0.5 \times 3 = 1.5 \text{ equivalents}$$

b The reaction for the formation of $H_2PO_4^-$ is

$$H_3PO_4 \rightarrow H^+ + H_2PO_4^-$$

One mole of H_3PO_4 produces one mole of H^+. Therefore,

$$\text{Number of equivalents} = \text{moles of } H_3PO_4 \times 1$$
$$= 0.5 \times 1 = 0.5 \text{ equivalents}$$

c $H_3PO_4 \rightarrow 2H^+ + HPO_4^{2-}$

One mole of H_3PO_4 produces two moles H^+. Therefore,

$$\text{Number of equivalents} = \text{moles of } H_3PO_4 \times 2$$
$$= 0.5 \times 2 = 1 \text{ equivalent}$$

Example 1.9

Calculate the:

a normality b molarity

of 49 g of H_2SO_4 in 500 mL of solution?

Solution:

Given:

V = 500 mL = 0.5 L

Mass of H_2SO_4 = 49 g

a $\text{Normality} = \dfrac{\text{Number of equivalents}}{\text{Volume (L) of solution}}$

$$\text{Number of equivalents} = \frac{\text{Given mass}}{\text{Equivalent mass}}$$

$$\text{Equivalent mass} = \frac{\text{Molar mass}}{n}$$

Since H_2SO_4 furnishes 2 moles of H^+ ions, n equals 2.

$$\Rightarrow \text{Equivalent mass} = \frac{\text{Molar mass of } H_2SO_4}{n}$$

$$= \frac{98\ \text{g/mol}}{2\ \text{eq/mol}} = 49\ \text{g/eq}$$

$$\text{Number of equivalents} = \frac{\text{Given mass}}{\text{Equivalent mass}} = \frac{49\ \text{g}}{49\ \text{g/eq}} = 1\ \text{eq}$$

$$\text{Normality} = \frac{\text{Number of equivalents}}{\text{Volume (L) of solution}} = \frac{1\ \text{eq}}{0.5\ \text{L}} = 2\ \text{N}$$

b To find molarity, use the relation

$N = n \times M$, where n = 2 for H_2SO_4

$$M = \frac{N}{n} = \frac{2}{2} = 1\ \text{M}$$

Example 1.10

Given the unbalanced equation

$$KMnO_4 + KI + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + I_2 + H_2O$$

a How many grams of $KMnO_4$ are needed to make 500 mL of 0.250 N solution?

b How many grams of KI are needed to make 25 mL of 0.36 N solution?

Solution:

a In the example given in the note above, we have seen that the equivalent mass of $KMnO_4$ is

$$\text{Equivalent mass of } KMnO_4 = \frac{\text{Molar mass}}{\text{Number of electron gained per mole}}$$

$$= \frac{158 \text{ g / mol}}{5 \text{ eq / mol}} = 31.6$$

$$\text{Normality (N)} = \frac{\text{Mass of } KMnO_4}{\text{Equivalent mass of } KMnO_4 \times \text{Volume (L) of solution}}$$

$$\text{Mass of } KMnO_4 = \text{Normality (N)} \times \text{Equivalent mass of } KMnO_4 \times \text{Volume (L) solution}$$

$$= 0.250 \text{ eq/L} \times 31.6 \text{ g/eq} \times 0.50 \text{ L} = 3.95 \text{ g } KMnO_4$$

b In the given reaction, the oxidation state of iodine is changed from –1 in KI to 0 in I_2.

$$\text{Hence, equivalent mass of KI} = \frac{\text{Molar mass of KI}}{\text{Number of electrons lost per mole}}$$

$$= \frac{166 \text{ g / mol}}{1 \text{ eq / mol}}$$

$$\text{Mass of KI} = \text{Normality (N)} \times \text{Equivalent mass of KI} \times \text{Volume (L) of solution}$$

$$= 0.36 \text{ eq/L} \times 166 \text{ g/eq} \times 0.025 \text{ L}$$

$$= 1.49 \text{ g KI}$$

Example 1.11

What is the normality of a solution that contains 2.94 g of $K_2Cr_2O_7$ in 100 mL of solution? What is its molarity? $K_2Cr_2O_7$ is used as a salt.

Solution:

Given:	**Required:**
Mass of $K_2Cr_2O_7$ = 2.94 g	Normality (N) = ?

Volume of solution = 100 mL = 0.10 L

$$\text{Equivalent mass of } K_2Cr_2O_7 = \frac{\text{Mass of } K_2Cr_2O_7}{\text{Total positive valance per mole}}$$

$$= \frac{294\ \text{g/mol}}{2\ \text{g/eq}} = 147\ \text{g/eq}$$

$$\text{Normality (N)} = \frac{\text{Mass of } K_2Cr_2O_7}{\text{Equivalent mass of } K_2Cr_2O_7 \times \text{Volume(L) of solution}}$$

$$= \frac{2.94\ \text{g}}{147\ \text{g/eq} \times 0.10\ \text{L}} = 0.2\ \text{N}$$

$$\text{Molarity} = \frac{\text{Normality}}{n} = \frac{0.2\text{N}}{2} = 0.1\ \text{M}$$

Exercise 1.8

1. How many equivalents of solute are contained in
   - a 1 L of 2 N solution?
   - b 1 L of 0.5 N solution?
   - c 0.5 L of 0.2 N solution?
2. Calculate the mass of $Al_2(SO_4)_3$ in 250 mL of solution if the concentration is 0.48 N.
3. Calculate the molarity and normality of a solution that contains 16.2 g of the salt $Fe_2(SO_4)_3$ in 200 mL of solution.

1.5.5 Molality (m)

What is the difference between molarity and molality?

The molality of a solution is the number of moles of solute per kilogram of solvent contained in a solution.

Note that molal solutions are prepared by measuring masses of solute and solvent, not volumes of solvent or solution.

$$\text{Molality (m)} = \frac{\text{Number of moles of solute}}{\text{Mass (kg) of solvent}}, \quad \text{or}$$

$$\text{Molality (m)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute} \times \text{Mass (kg) of solvent}}$$

Example 1.12

Calculate the molality of a solution prepared by dissolving 32.0 g of $CaCl_2$ in 271 g of water.

Solution:

Given:	**Required:**
Mass of $CaCl_2$ = 32.0 g	Molality (m) =?
Mass of H_2O = 271 g = 0.271 kg	

$$\text{Molality } (m) = \frac{\text{Mass of } CaCl_2}{\text{Molar mass of } CaCl_2 \times \text{Mass (kg) of } H_2O}$$

$$= \frac{32.0 \text{ g}}{111 \text{ g/mol} \times 0.271 \text{ kg}} = 1.06\ m\ CaCl_2$$

Exercise 1.9

A solution of hydrochloric acid contains 36 percent HCl, by mass

a Calculate the mole fraction of HCl in the solution.

b Calculate the molality of HCl in the solution.

c What additional information would you need to calculate the molarity of the solution?

1.5.6 Conversion of Concentration Units

All the terms we just discussed represent different ways of expressing concentration. *How can you convert one concentration unit to another?* Observe the following guidelines when you convert one concentration unit to another.

* If the density and mass of a solution are given, you can determine the volume of the solution. Similarly, if the density and volume of a solution are given, you can calculate the mass of the solution.

* Molality involves quantity of solvent, whereas the other concentration units involve quantity of solution.

Example 1.13

Hydrogen peroxide is a powerful oxidizing agent used in concentrated solution in rocket fuels and, in dilute solution, in hair bleach. An aqueous solution of H_2O_2 is 30% by mass and has a density of 1.11 g/mL. Calculate the:

a molality of the solution

b mole fraction of H_2O_2

c molarity of the solution

Solution:

a For molality, we need the number of moles of solute and the mass (kg) of solvent. If we assume 100 g of H_2O_2 solution, we can express the mass percentage directly as mass of substance. We subtract the mass of H_2O_2 to obtain the mass of solvent. To find molality, we convert mass of H_2O_2 to moles and divide by mass of solvent.

$$\text{Mass of solvent } (H_2O) = \text{Mass of solution} - \text{Mass of solute}$$

$$= 100.0 \text{ g} - 30.0 \text{ g} = 70.0 \text{ g}$$

$$\text{Moles of } H_2O_2 = \frac{30.0 \text{ g}}{34 \text{ g/mol}} = 0.882 \text{ mol } H_2O_2$$

$$\text{Molality } (m) = \frac{\text{moles of } H_2O_2}{\text{Mass (kg) of solvent}} = \frac{0.882 \text{ mol}}{0.070 \text{ kg}}$$

$$= 12.6\ m\ H_2O_2 \text{ solution}$$

b To find the mole fraction, you use the number of moles of H_2O_2 from part a and convert the mass of H_2O to moles.

$$\text{Number of moles of } H_2O_2 = 0.882 \text{ mol } H_2O_2$$

$$\text{Number of moles of } H_2O = \frac{70.0 \text{ g}}{18 \text{ g/mol}} = 3.88 \text{ mol of } H_2O$$

$$X_{H_2O_2} = \frac{\text{moles of } H_2O_2}{\text{moles of } H_2O_2 + \text{moles of } H_2O} = \frac{0.882}{0.822 + 3.88} = 0.185$$

c To find molarity, we assume 100.0 g of solution and use the given solution density to find the volume.

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

$$\text{Volume of solution} = \frac{\text{Mass of solution}}{\text{Density of solution}}$$

$$= \frac{100.0\ \text{g}}{1.11\ \text{g/mL}}$$

$$= 90.1\ \text{mL}$$

$$\text{Molarity (M)} = \frac{\text{Number of moles of solute}}{\text{Volume (L) of solution}}$$

$$= \frac{0.882\ \text{mol}}{0.090\ \text{L}} = 9.79\ \text{M}\ H_2O_2\ \text{solution}$$

Exercise 1.10

1. A sample of commercial concentrated hydrochloric acid is 11.8 M HCl and has a density of 1.190 g/mL. Calculate
   a the mass % of HCl
   b the molality of HCl
   c the mole fraction of HCl
2. The mole fraction of ethanol in water is 0.3. Calculate
   a the molality of the solution
   b the mass percent of ethanol

1.6 PREPARATION OF SOLUTIONS

At the end of this section, you will be able to:

- Prepare molar solutions, normal solutions and molal solutions of different substances;
- Explain dilution process and calculate the volume or concentration changes during the dilution of solutions; and
- Prepare a dilute solution from a concentrated solution.

Experiment 1.5

Preparation of Solutions of Known Concentrations

Objective: To prepare a 1 molar NaCl solution and a 1 molar table-sugar solution.

Apparatus and Chemicals: 200 mL volumetric flasks, stirrers, beakers, measuring cylinders, balance, sodium chloride, sugar, and water.

Procedure 1:

1. Weigh 11.7 g of sodium chloride, using a balance, and add to a beaker.
2. Add about 50 mL of water to the beaker containing the sodium chloride and dissolve it by stirring.
3. Using a funnel, transfer the solution to the volumetric flask.
4. Slowly add more water to the volumetric flask until the solution reaches the volume mark.

Observations and analysis:

a How many moles of sodium chloride did you use to prepare the solution?
b What are the molarity and normality of the solution?

Procedure 2:

1. Weigh a beaker and record its mass. Then add 50 g of water. Perform the measurement and calculations:

   Mass of beaker __________
   Mass of beaker + mass of water __________
   Mass of water __________

2. Weigh 17.1 g of table sugar. __________
3. Dissolve the 17.1 g of table sugar in the beaker containing 50 g of water, by stirring.

Observations and analysis:

Calculate:

a mass percent of the solution.
b mole fraction of the solution.
c molality of the solution.

How do you prepare a solution of known concentration?

A common task in school, medical, industrial and other chemical laboratories is the preparation of solutions of known concentrations. For aqueous solutions, distilled, de-mineralized or de-ionized water is used. Other solvents can also be used, depending on the solution specified. Solutions are usually prepared from solutes of liquids or solids. Occasionally they are prepared from gases. First, the solute is accurately weighed and transferred to a volumetric flask, then water is added through a funnel (Figure 1.13 a). Next, the solid is slowly dissolved by gently swirling the flask (Figure 1.13 b). After all the solid has dissolved, more water is slowly added to bring the level of solution exactly to the volume mark (Figure 1.13 c). Knowing the volume of the solution in the flask and the quantity of compound (*the number of moles*), you can calculate the molarity of the solution using the formula of molarity.

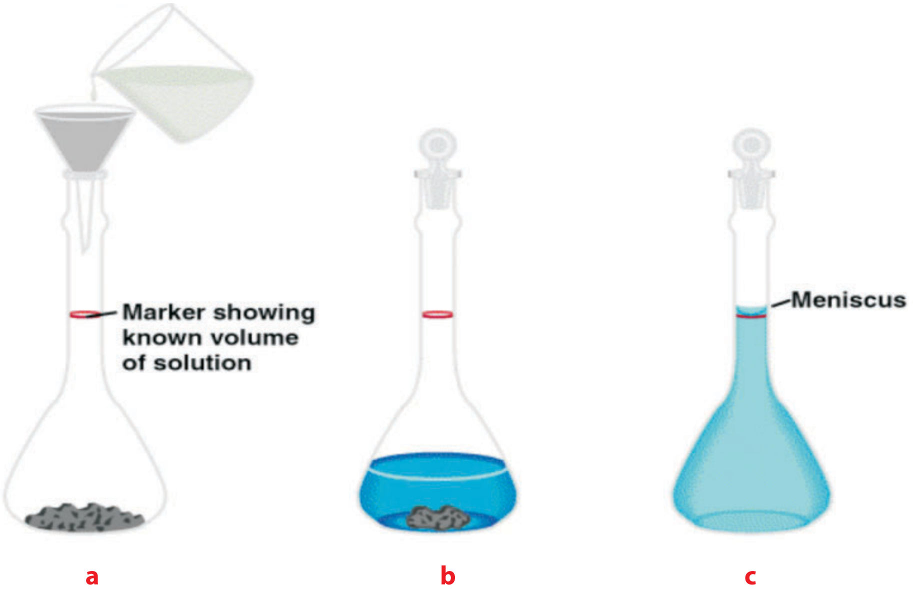


Figure 1.13 Preparation of a solution of known molarity.

A one-molar solution of NaCl can be prepared by dissolving 58.5 g of NaCl in water until the solution becomes one litre.

Activity 1.9

Dissolve 1g each of NaCl, $CuSO_4$, and $KMnO_4$ in different 50 mL measuring flasks. Note the colour intensity of the solutions.

Take 25 mL of solution from each flask and further dilute each solution to 50 mL.

Note the colour intensity again.

What did you observe? Can you correlate the colour intensity with the concentration of the solution? Does this analogy works for colourless solution also? Discuss your observations with your classmates.

Diluting Solutions

Concentrated solutions are often stored in the laboratory as "stock" solutions for use as needed. Frequently we dilute this stock solution before working with them.

Dilution is the procedure for preparing a less-concentrated solution from a more-concentrated one.

In carrying out a dilution process, it is useful to remember that adding more solvent to a given amount of the stock solution changes (*decreases*) the concentration of the solution without changing the number of moles of solute present in the solution. In other words,

Number of moles of solute before dilution = Number of moles of solute after dilution

Since number of moles of solute = molarity × volume of solution,

$$= M \times V$$

Number of of moles of solute before dilution = M_iV_i

Number of moles of solute after dilution = M_fV_f

Therefore, dilution can be expressed as

$$M_iV_i = M_fV_f$$

or, more generally,

$$C_iV_i = C_fV_f$$

Where C_i is initial concentration, C_f is final concentration, V_i is initial volume and V_f is final volume.

Example 1.14

Describe how you would prepare 5.00×10^2 mL of a 1.75 M H_2SO_4 solution, starting with an 8.61 M stock solution of H_2SO_4.

Solution:

Because the concentration of the final solution is less than that of the original one, this is a dilution process.

Given:	**Required:**
$M_i = 8.61$ M	$V_i = ?$
$M_f = 1.75$ M	

$V_f = 5.00 \times 10^2$ mL

$M_iV_i = M_fV_f$

$$V_i = \frac{M_f \times V_f}{M_i} = \frac{1.75\ M \times 5.0 \times 10^2\ mL}{8.61\ M} = 102 \text{ mL}$$

Thus, we must dilute 102 mL of 8.61 M H_2SO_4 solution with sufficient water to give a final volume of 5.0×10^2 mL.

Experiment 1.6

Preparation of Solution of Lower Concentration from Standard Stock Solution

Objective: To prepare diluted solution of H_2SO_4

Apparatus: burette, beaker, stirrer, funnel, stand with clamp

Chemicals: 18 M H_2SO_4, distilled water.

Procedure:

1. Carefully add the concentrated acid into the burette.
2. Slowly add with stirring 10.0 mL of the acid into a beaker containing 50 mL of distilled water.
3. Transfer the new solution into a volumetric flask (1 L) and add water up to the mark.

Observations and analysis:

From Procedure 1 and 2:

a Why are acid added to the water not the water to the acid?

b Explain whether volume, mass or number of moles of the solute is changed or not in the process.

c What is the new concentration of the H_2SO_4?

From Procedure 3:

d Calculate concentration of the new solution.

Exercise 1.11

a How do you prepare 60.0 mL of 0.2 M HNO_3 from a stock solution of 4 M HNO_3?

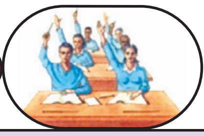
b You have 100 mL of a 0.5 M HCl solution, and you want to dilute it to exactly 0.1 M. How much water should you add?

1.7 SOLUTION STOICHIOMETRY

At the end of this section, you should be able to:

- Use stoichiometerically equivalent molar ratios to calculate the amounts of reactants and products in a reaction of pure and dissolved substances.

Activity 1.10



In Grade 9 Chemistry, you learned the stoichiometry of pure substances. What does stoichiometry mean? How can you apply it to solutions? Form a group and discuss these questions.

Since many environmental reactions and almost all biochemical reactions occur in solution, an understanding of reactions in solution is extremely important in chemistry and related sciences.

Solution stoichiometry differs from pure-substances stoichiometry in that the amount of a pure substance can be obtained by converting its mass into moles. For substances in solution, we must know the concentration to find the volume that contains a given number of moles. Thus, the concept of molarity is very important in solution stoichiometry.

You can think of molarity as a conversion factor. We use it to convert the volume of a solution to the number of moles of a solute. From the result, we can find the mass or the number of particles of a solute.

Mole-Mass Problems

The relationship between the mass of a substance and the corresponding number of moles is governed by the molar mass of the substance. But, for problems involving substances in solution, we need to know the concentration of the solution before we can find the number of moles.

Mole of a substance = Concentration × Volume

Example 1.15

What volume of 1.40 M H_2SO_4 solution is needed to react exactly with 100 g of Al? The balanced molecular equation for the reaction is

$$2Al + 2H_2SO_4 \rightarrow Al_2(SO_4)_2 + 2H_2$$

Solution:

We use the mole-mass method:

$$\text{Number of moles of Al} = \frac{100\ g}{27.0\ g/mol} = 3.70\ mol$$

From the balanced equation, 2 moles of Al reacts with 2 moles of H_2SO_4. To find the number of moles of H_2SO_4 that reacts with 3.70 moles of Al, we proceed as follows: 2 moles of Al needs 2 moles of H_2SO_4

3.7 moles Al needs X moles of H_2SO_4, therefore

$$X = \frac{3.7\ \text{mol Al} \times 2\ \text{mol}\ H_2SO_4}{2\ \text{mol Al}}$$

$$X = 3.7\ \text{mol}\ H_2SO_4$$

Volume of 1.40 M H_2SO_4 containing 3.70 mol

$$\frac{\text{Number of moles of}\ H_2SO_4}{\text{molarity}} = \frac{3.70\ \text{mol}}{1.40\ \text{mol}\ L^{-1}} = 2.64\ L$$

Exercise 1.12

1. What volume of 1M HCl solution is required to react with 6 g of magnesium?

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

2. What volume of 0.25 M NaOH solution is needed to react with 50 mL of 0.125 M H_2SO_4?

   Reaction: $2NaOH\ (aq) + H_2SO_4\ (aq) \rightarrow Na_2SO_4\ (aq) + H_2O\ (l)$

3. Calcium hydroxide is sometimes used in water treatment plants to purify water for residential use. Calculate the volume of 0.0250 M calcium hydroxide solution that can react completely with 25.0 mL of 0.125 mol L^{-1} aluminium sulphate solution.

   Reaction: $Al_2(SO_4)_3(aq) + 3Ca(OH)_2(aq) \rightarrow 2Al(OH)_3(aq) + 3CaSO_4(s)$

Mole-Volume Problems

In this type of problem, the concentration of the solution is given, and you are asked to determine the volume of the solution that contains a required number of moles or *vice versa*.

Example 1.16

Ammonium sulphate is manufactured by reacting sulphuric acid with ammonia. What concentration of sulphuric acid is needed to react with 24.4 mL of a 2.20 mol L^{-1} ammonia solution, if 50.0 mL of sulphuric acid is used?

$$H_2SO_4\,(aq) \quad + \quad 2NH_3\,(aq) \quad \rightarrow \quad (NH_4)_2SO_4\,(aq)$$

Solution:

First, we calculate the number of moles of H_2SO_4 that react with the given amount of ammonia. To do this, we need to know the number of moles of NH_3.

$$\text{Number of moles of } NH_3 = \text{Molarity of } NH_3 \times \text{Volume (L) of solution}$$

$$= 2.20 \text{ mol L}^{-1} \times 0.0244 \text{ L}$$

$$= 0.0537 \text{ mol}$$

From the balanced equation above, 2 mol NH_3 reacts with 1 mol H_2SO_4. Therefore, the number of moles of H_2SO_4 that reacts with 0.0537 moles of NH_3 is

$$\frac{0.0537 \text{ mol } NH_3 \times 1 \text{ mol } H_2SO_4}{2 \text{ mol } NH_3} = 0.0268 \text{ mol } H_2SO_4$$

$$\text{Concentration (molarity of } H_2SO_4) = \frac{0.0268 \text{ mol}}{0.05 \text{ L}} = 0.536 \text{ M}$$

Mole-Number of Particles Problems

How do you relate number of moles and number of particles?

Example 1.17

What volume of 0.5 M glucose ($C_6H_{12}O_6$) contains 3.01×10^{22} molecules of glucose?

Solution:

We first change 3.01×10^{22} molecules of glucose to moles of glucose. 1 mole of glucose contains 6.02×10^{23} molecules.

Therefore, 3.01×10^{22} molecules of glucose will be

$$\frac{1 \text{ mol} \times 3.01 \times 10^{22} \text{ molecule}}{6.02 \times 10^{23} \text{ molecule}} = 0.05 \text{ mol}$$

Since,

Number of moles = Concentration × Volume

$$\text{Volume} = \frac{\text{Number of moles}}{\text{Concentration}} = \frac{0.05 \cancel{\text{mol}}}{0.500 \cancel{\text{mol}} \text{L}^{-1}} = 0.1 \text{ L} = 100 \text{ mL}$$

1.8 DESCRIBING REACTIONS IN SOLUTION

At the end of this section, you should able to:

- explain the relationship between reacting ions, spectator ions, precipitation and solubility;
- write net ionic equations.

What is the difference between molecular equations and ionic equations? What are spectator ions?

We use chemical equations to help us describe reactions. Reaction involving ions can be presented with different types of chemical equations. The one we use depends on the kind of information we want to convey. We can represent such a reaction by a molecular equation or an ionic equation.

1.8.1 Molecular Equation

A molecular equation is a chemical equation in which the reactants and the products are written as if they were molecular substances, even though they may actually exist in solution as ions. Molecular equations are useful because they are explicit about what the *reactants* are and what *products* you obtain.

Consider the reaction between calcium chloride, $CaCl_2$, and sodium carbonate, Na_2CO_3, in aqueous solution to give solid calcium carbonate and aqueous sodium chloride. The equation for this reaction may be written as:

$$CaCl_2\,(aq) + Na_2CO_3\,(aq) \longrightarrow CaCO_3\,(s) + 2NaCl\,(aq)$$

The molecular equation closely describes what is actually done in the laboratory or in an industrial process.

1.8.2 Ionic Equation

Although a molecular equation is useful in describing the actual reactants and products, it does not give any information about what is happening at the level of ions. Since this kind of information is very useful, you often need to write the molecular equation as an ionic equation.

Consider the reaction of calcium chloride and sodium carbonate. Both are soluble ionic substances and are strong electrolytes. When they dissolve in water, they go into solution as ions. Each formula unit of $CaCl_2$ forms one Ca^{2+} ion and two Cl^- ions in solution. So, instead of $CaCl_2(aq)$, it would be better to write $Ca^{2+}(aq) + 2Cl^-(aq)$. Similarly, each formula unit of Na_2CO_3 forms two Na^+ ions and one CO_3^{2-} ion in solution, and this can be written as $2Na^+(aq) + CO_3^{2-}\,(aq)$ instead of $Na_2CO_3(aq)$. The reactant side of the reaction becomes

$$Ca^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + CO_3^{2-}\,(aq)$$

On the product side of the equation, $CaCO_3(s)$ is an ionic compound, but the ions are held together in particular sites in the crystalline solid. We leave the formula as $CaCO_3(s)$ to convey this information in the equation. On the other hand, $NaCl$ is a soluble ionic compound and is a strong electrolyte. Also it dissolves in aqueous solution to give freely moving ions. Therefore, we can write it as $Na^+(aq) + Cl^-(aq)$.

The complete equation is

$$Ca^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + CO_3^{2-}\,(aq) \rightarrow CaCO_3(s) + 2Na^+(aq) + 2Cl^-(aq)$$

The ions appearing on both sides of the equation (Na^+ and Cl^-) are called spectator ions, as they do not take part in the reaction and they can be cancelled on both sides to express the essential reaction that occurs.

$$Ca^{2+}(aq) + \cancel{2Cl^-}(aq) + \cancel{2Na^+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s) + \cancel{2Na^+}(aq) + \cancel{2Cl^-}(aq)$$

The resulting equation is:

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$$

This net ionic equation, is without spectator ions and the reaction that actually occurs at an ionic level is between calcium ions and carbonate ions which form solid calcium carbonate.

Activity 1.11

Form a group and discuss the following:

1. How are sodium carbonate and calcium hydroxide found in water solution? Write dissociation reaction for each of them.
2. Write the ionic equation for the reaction between sodium carbonate and calcium hydroxide. Are the products formed soluble in water?
3. Write the soluble product in ionic form. Are there the same ions in the reactant and product side?
4. Write the net ionic equation.

Exercise 1.13

For each of the following molecular equations, write ionic equation, write a net ionic equation, and identify the spectator ions:

a $2AgNO_3(aq) + Na_2CrO_4(aq) \longrightarrow Ag_2CrO_4(s) + 2NaNO_3(aq)$

b $2HClO_4(aq) + Ca(OH)_2(aq) \longrightarrow Ca(ClO_4)_2(aq) + 2H_2O(l)$

c $2HNO_3(aq) + Mg(OH)_2(s) \longrightarrow 2H_2O(l) + Mg(NO_3)_2(aq)$

d $Pb(NO_3)_2(aq) + Na_2SO_4(aq) \longrightarrow PbSO_4(s) + 2NaNO_3(aq)$

1.9 COLLIGATIVE PROPERTIES OF SOLUTION

At the end of this section, you should be able to:

- define colligative properties:
- list the important properties of solvents that are affected by the formation of a solution;
- state Raoult's law;

- explain the change in the colligative properties of solvent when a certain solute is added;
- describe the Van't Hoff's factor;
- calculate the vapour pressure, boiling point, and freezing point of a solvent after a given amount of solute is dissolved in it;
- define osmosis and osmotic pressure of a solution;
- calculate the osmotic pressure of a solution; and
- compare and contrast change in colligative properties of electrolytic and non electrolytic solution.

What is meant by colligative? Why does the addition of ethylene glycol lower the freezing point and raise the boiling point of water? Discuss this question with your classmates.

Certain physical properties of solutions differ in important ways from those of pure solvents. For example, pure water at 1 atm pressure freezes at 0°C, while an aqueous solutions at 1 atm pressure freezes at a lower temperature. Ethylene glycol is added to water in radiators of cars as antifreeze to lower the freezing point of the solution. This also raises the boiling point of the solution above that of pure water, permitting operation of engines at higher temperatures.

The lowering of the freezing point and the raising of the boiling point are examples of the physical properties of solutions that depend on the quantity (*concentration*) of the solute but not on the kind of solute particle. Properties that depend on the number of particles or concentration of the solute in the given amount of solvent and not on their nature are called colligative properties. (*Colligative* is a Latin word that means "*depending on the collection*".)

There are four important properties of a solution that are affected by the addition of a non-volatile solute to a solvent. These are:

1. Vapour pressure lowering
2. Boiling point elevation
3. Freezing point depression
4. Osmotic pressure

1.9.1 Vapour Pressure Lowering

How do non-volatile solutes affect the vapour pressure of the solvent?

If a solute is non-volatile i.e., it does not have a measurable vapour pressure, the vapour pressure of its solution is always less than that of the pure solvent. Vapour pressure lowering is the lowering of the vapour pressure of the solvents that results when a non-volatile solute is added to form a solution. The solute prevents (*blanket*) the tendency of the solvent to escape and it also lowers the vapour pressure of the solvent (Figure 1.14). Thus, the relationship between solution vapour pressure and solvent vapour pressure depends on the concentration of the solute in the solution.

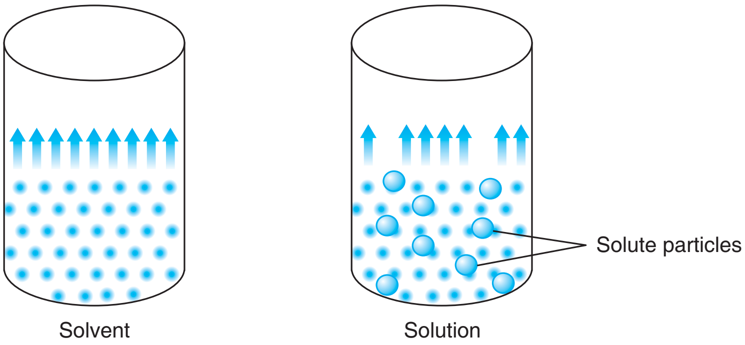


Figure 1.14 shows the lowering of the rate of vaporization of a solvent when a non-volatile solute is added.

The relationship between solution vapour pressure and solvent vapour pressure is expressed by Raoult's law. This law states that "the partial pressure of a solvent over a solution, P_1, is given by the vapour pressure of the pure solvent, times the mole fraction of the solvent in the solution, x_1, at constant temperature".

$$P_1 = x_1 P_1^\circ$$

$$\Delta P = P_1^\circ - P_1$$

where ΔP = Change in vapour pressure (vapour pressure lowering)
P° = Vapour pressure of pure solvent
P_1 = Vapour pressure of solvent in solution

Note that the vapour pressure of a solvent is not a colligative property. Only the change in vapour pressure, ΔP, which occurs when a solute is added to the solvent, is a colligative property. It can be defined as the difference between the vapour pressure of the pure solvent and the vapour pressure of solvent in the solution.

In a solution containing only one solute, $x_1 = 1 - x_2$, where x_2 is the mole fraction of the solute. Inserting this into the Raoult's-law equation gives:

$$P_1 = (1 - x_2)\, P_1^\circ$$

$$P_1 = P_1^\circ - P_1^\circ\, x_2$$

$P_1^\circ - P_1 = P_1^\circ x_2$

$\Delta P = P_1^\circ x_2$

Example 1.18

Calculate the vapour pressure of water at 90 °C in a solution containing 5.0 g of glucose ($C_6H_{12}O_6$) in 100 g of water. The *vapour pressure* of pure water at 90 °C is 525.8 Pa.

Solution:

Given:

Mass of $C_6H_{12}O_6$ = 5.0 g

Mass of water = 100 g

Vapour pressure of pure water at 90°C = 525.8 Pa

Required:

Vapour pressure of water in a solution $P_1 = ?$

First, we find mole fractions of both solute and solvent. To do this, we must find the number of moles of glucose and water.

$$\text{Number of moles of } C_6H_{12}O_6 = \frac{\text{Mass of } C_6H_{12}O_6}{\text{Molar mass of } C_6H_{12}O_6} = \frac{5.0\ \text{g}}{180\ \text{g/mol}}$$

$$= 0.028\ \text{mol}$$

$$\text{Number of moles of } H_2O = \frac{100\ \text{g}}{18\ \text{g/mol}} = 5.56\ \text{mol}$$

$$x_{C_6H_{12}O_6} = \frac{0.028\ \text{mol}}{0.028\ \text{mol} + 5.56\ \text{mol}} = 0.005$$

$$x_{H_2O} = \frac{5.56\ \text{mol}}{5.56\ \text{mol} + 0.028\ \text{mol}} = 0.995$$

$$P_1 = x_{H_2O}\, P_1^\circ$$

$$= 0.995 \times 525.8\ \text{Pa} = 523.17\ \text{Pa}$$

$$\Delta P = P^\circ - P$$

$$= 525.8\ \text{Pa} - 523.17\ \text{Pa} = 2.63\ \text{Pa}$$

Example 1.19

Calculate the vapour pressure of a solution made by dissolving 218 g of glucose in 460 mL of water at 30 °C. What is the vapour pressure lowering? (*Assume that the density of water is* 1.00 g/mL). Vapour pressure of water at 30 °C is 31.82 torr.

Solution:

Given:

Mass of solute ($C_6H_{12}O_6$) = 218 g

Volume of water = 460 mL = 0.46 L

Required:

P_1 (vapour pressure of solution) = ?

ΔP (lowering in vapour pressure) = ?

From Raoult's law

$P_1 = x_1 P_1^\circ$

To determine the number of moles of H_2O, its density is used.

$1\text{ mL} \rightarrow 1\text{ g}$ $\qquad \dfrac{460\ \cancel{\text{mL}} \times 1\text{ g}}{1\ \cancel{\text{mL}}} = 460\text{ g}$

$460\text{ mL} \rightarrow ?$

$$\text{Number of moles of } H_2O = \frac{460\text{ g}}{18\ \text{g/mol}} = 25.56\text{ mol}$$

$$\text{Number of mole of } C_6H_{12}O_6 = \frac{218\text{ g}}{180\text{ g/mol}} = 1.21\text{ mol}$$

$$x_{H_2O} = \frac{25.56\text{ mol}}{25.56\text{ mol} + 1.21\text{ mol}} = 0.955$$

$$x_{C_6H_{12}O_6} = \frac{1.2\text{ mol}}{1.21\text{ mol} + 25.56\text{ mol}} = 0.045$$

$P_1 = x_1 P_1^\circ$

P_1° is the vapour pressure of water at 30°C, which is equal to 31.82 torr.

$P_1 = 0.955 \times 31.82$ torr

$= 30.4$ torr

$\Delta P = P^\circ - P$

$= 31.82$ torr $- 30.4$ torr

$= 1.42$ torr

Exercise 1.14

1. Why is the vapour pressure of a solution less than that of the pure solvent?
2. The vapour pressure of pure water at 110°C is 1070 torr. A solution of ethylene glycol in water has a vapour pressure of 1.00 atm at 110°C. Assuming that Raoult's law is obeyed, what is the mole fraction of ethylene glycol in water?
3. Calculate the vapour pressure lowering, ΔP, when 10.0 mL of glycerol ($C_3H_8O_3$) is added to 500.0 mL of water at 50°C. At this temperature, the vapour pressure of pure water is 92.5 torr and its density is 0.988 g/mol. The density of glycerol is 1.26 g/mL.

Solutions that obey Raoult's law are said to be ideal solutions. If both components of a solution are volatile, i.e., have measurable vapour pressure, the vapour pressure of the solution is the sum of the individual partial vapour pressures. Thus, for two volatile components, A and B, the vapour pressure of each component above the solution is proportional to its mole fraction in the solution.

$$P_A = x_A P_A^\circ$$

$$P_B = x_B P_B^\circ$$

According to Dalton's law of partial pressure, at constant temperature, the pressure of a mixture of gases is equal to the sum of the partial pressures of all of the constituent gases. The total pressure, is:

$$P_T = P_A + P_B = x_A P_A^\circ + x_B P_B^\circ$$

This can be shown graphically as in Figure 1.15, assuming that A is more volatile than B.

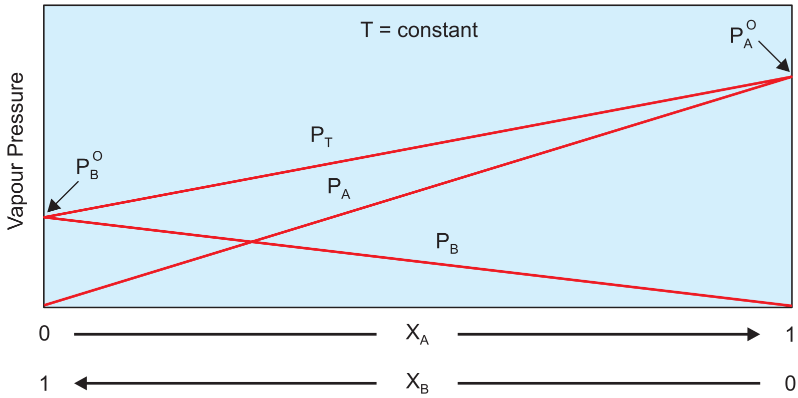


Figure 1.15 Vapour pressure versus mole fraction for an ideal solution.

Ideal solutions are characterized by the following properties:

i) The volume of an ideal solution is the sum of the volumes of its pure components. i.e., there is no expansion or contraction on mixing.

ii) The heat of a solution is zero. i.e., mixing is neither exothermic nor endothermic. Intermolecular forces between solute-solute and solute-solvent molecules are equal, as are those between solvent-solvent molecules and solute-solvent molecules.

iii) The vapour pressure above the solution is equal to the sum of the individual partial vapour pressures.

iv) The components have similarity in their chemical structures.

v) The solutions obey Raoult's law.

Can you give examples of an ideal solution?

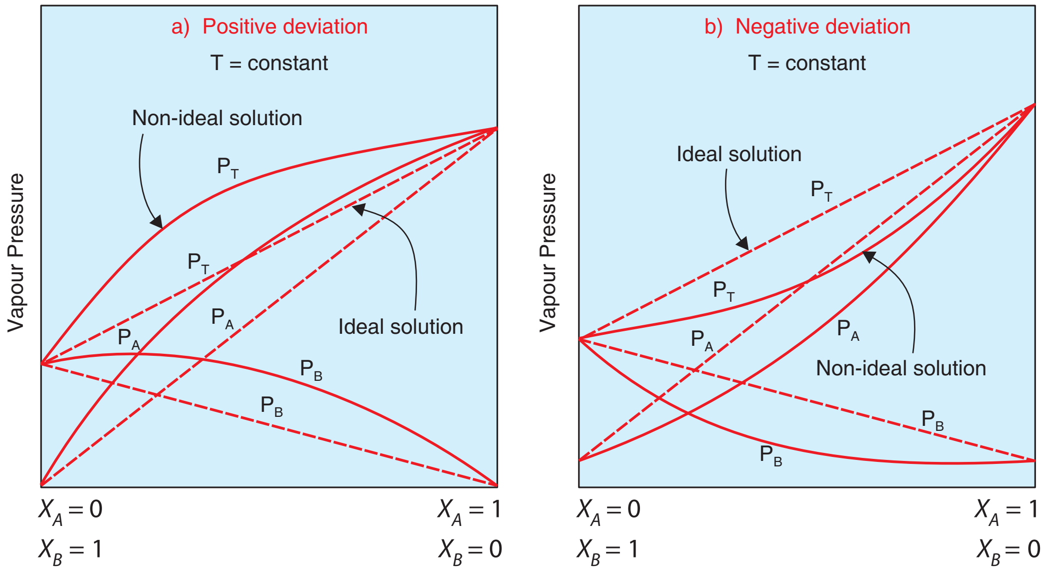
Many solutions do not behave ideally. They deviate from Raoult's law and are said to be non-ideal. Here, we can consider the following two cases.

Case 1: If the intermolecular forces between A and B molecules are weaker than those between A and A molecules and those between B and B molecules, then there is a greater tendency for A-B molecules to leave the solution, compared to the case of an ideal solution. Consequently, the vapour pressure of the solution is greater than the sum of the vapour pressures that would be predicted by Raoult's law for the same concentration.

This behaviour exemplifies the positive deviation from Raoult's law (Figure 1.16 a). In this case, the heat of mixing is an endothermic process.

Case 2: If A molecules attract B molecules more strongly than they do their own kind, then the escaping tendency decreases and the vapour pressure of the solution is less than the sum of the vapour pressures as predicted by Raoult's law.

Here, we have a negative deviation from Raoult's law, and mixing is an exothermic process (Figure 1.16 b).



(Dotted lines show the expected values and the solid lines show the observed values).

Figure 1.16 Vapour pressure versus mole fraction for real solutions.

1.9.2 Boiling Point Elevation

Which do you think has a higher boiling point, a pure solvent or a solution containing a non-volatile solute? Why?

The boiling point of a liquid is the temperature at which its vapour pressure equals the atmospheric pressure. If a non-volatile solute is added to a solvent, the solution's boiling point will be increased. This is due to the fact that the vapour pressure of a solvent at a given temperature is lowered by the presence of a non-volatile solute in it, because less number of solvent molecules are available on the surface exposed to atmosphere in presence of solute molecules, as shown in Figure 1.14. Therefore, such a solution must be heated to a higher temperature than the pure solvent in order for its vapour pressure to be equal to the atmospheric pressure.

The boiling-point elevation (ΔT_b) is defined as the boiling point of the solution (T_b) minus the boiling point of the pure solvent (T_b°).

$$\Delta T_b = T_b - T_b^\circ$$

The elevation in boiling point (ΔT_b) is directly proportional to the molality of the solution. That is:

$$\Delta T_b \ \alpha \ m$$

$$\Delta T_b = K_b m$$

where m is the molality of the solution, and K_b is the molal boiling point elevation constant for the solvent.

Table 1.2 Boiling points, molal boiling point elevation constants, freezing points and molal freezing point depression constants of some solvents at 1 atm pressure.

Solvent	Boiling point (°C)	K_b (°C/m)	Freezing point (°C)	K_f (°C/m)
Acetic acid ($C_2H_4O_2$)	118.10	3.07	16.60	3.90
Benzene (C_6H_6)	80.10	2.53	5.50	5.12
Camphor ($C_{10}H_{16}O$)	208.00	5.95	179.00	39.70
Carbon disulfide (CS_2)	46.30	2.34	– 111.50	3.83
Chloroform ($CHCl_3$)	61.26	3.63	– 63.50	4.70
Cyclohexane (C_6H_{12})	80.70	2.79	6.60	20.00
Nitrobenzene ($C_6H_5NO_2$)	210.88	5.24	5.70	7.00
Phenol (C_6H_5OH)	182.00	3.56	43.00	7.40
Water (H_2O)	100.00	0.51	0.00	1.86

Example 1.20

Calculate the boiling point of a 0.33 m solution of a solute in benzene. ($K_b = 2.53°C\ /m$).

Solution:

Given:	**Required:**
Molality = 0.33 m	Boiling point of the solution?

$K_b = 2.53°C\ /m$

$\Delta T_b = K_b m,$

$\Delta T_b = 2.53°C\ /m \times 0.33\ m = 0.83°C$

Therefore, the boiling point of the solution is determined from the boiling point of the pure solvent benzene (Table 1.2) and the change, in boiling point, ΔT_b.

Boiling point of the solution = 80.1°C + 0.83°C

= 80.93°C

Example 1.21

Calculate the boiling point of a solution that contains 200 g of sucrose, $C_{12}H_{22}O_{11}$, in 500 g of water.

Solution:

From the given masses of solute and solvent, we can find the molality of the solution.

$$\text{Molality (m)} = \frac{\text{Mass of sucrose}}{\text{Molar mass of sucrose} \times \text{Mass of } H_2O \text{ in kg}}$$

$$= \frac{200\,\text{g}}{342\,\text{g/mol} \times 0.5\ \text{kg}} = 1.17\ \text{m}$$

$\Delta T_b = K_b m$, from Table 1.2, K_b for H_2O is 0.512°C /m

Therefore, $\Delta T_b = 0.512°\text{C/m} \times 1.17\ \text{m} = 0.6°\text{C}$

Since the normal boiling point of water is 100°C, the boiling point of the solution will be equal to 100°C + 0.6°C = 100.6°C.

Exercise 1.15

1. What is the boiling point of 1.93 m solution of a non-volatile solute in nitrobenzene?
2. Automotive antifreeze consists of ethylene glycol, $C_2H_6O_2$, a non-volatile non-electrolyte solute. Calculate the boiling point of a 25.0 mass percent solution of ethylene glycol in water.

1.9.3 Freezing Point Depression

Activity 1.12

Discuss in group and account for the following processes. Report your idea to the class.

1. In countries with extremely cold conditions, anti-freezing substances like ethylene glycol ($C_2H_6O_2$) are used in the cooling system of the automobiles.
2. Salts such as NaCl or $CaCl_2$ can be used to prepare ice cream or to de-ice the roads.

When a solution begins to freeze, the component that crystalize out first is almost pure.

Pure ice, for example, crystallizes out of a solution of salt and water. Solute particles, because of their different size and shape, do not fit into the crystal lattice of the frozen solvent. They tend to concentrate in the remaining liquid, and they interfere with the freezing process by getting in the way of solvent molecules looking for lattice sites. This interference causes the solution to freeze at lower temperature than the pure solvent. The greater the concentration of the solution, the greater the interference and therefore, the lower the freezing point of the solution.

The freezing point depression (ΔT_f) is defined as the freezing point of the pure solvent (T) minus the freezing point of the solution (T_f).

$$\Delta T_f = T - T_f$$

The freezing point depression (ΔT_f) of solutions of nonelectrolytes has been found to be equal to the molality of the solution times a proportionality constant. This constant is the molal freezing point depression constant, K_f, of the solvent.

$$\Delta T_f = K_f m$$

Example 1.22

The freezing point of pure camphor ($C_{10}H_{16}O$), T_f°, is 179.0°C, and its K_f is 39.70°C kg/mol. Find the freezing point of a solution containing 1.50 g of a compound of molecular mass 125, dissolved in 35 g camphor (*solvent*).

Solution:

First we find number of moles of the compound

$$\text{Number of moles} = \frac{1.5 \text{ g}}{125 \text{ g/mol}} = 0.012 \text{ mol}$$

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Weight (kg) of solvent}} = \frac{0.012 \text{ mol}}{0.035 \text{ kg}} = 0.343 \text{ mol/kg}$$

$$\Delta T_f = K_f m = 39.7°\text{C kg/mol} \times 0.343 \text{ mol/kg}$$

$$= 13.6°\text{C}$$

The normal freezing point of camphor is lowered by 13.6°C. Therefore, the freezing point of the solution, T_f, will be:

$$\Delta T_f = T - T_f = 179.0°\text{C} - 13.6°\text{C} = 165.4°\text{C}$$

Exercise 1.16

1. Calculate the freezing point of a solution that contains 60.0 g of urea, N_2H_4CO, in 500.0 g of water.
2. Calculate the molecular mass of sulphur if 35.5 g of sulphur dissolves in 100.0 g of CS_2 to produce a solution that has a boiling point of 49.48°C.

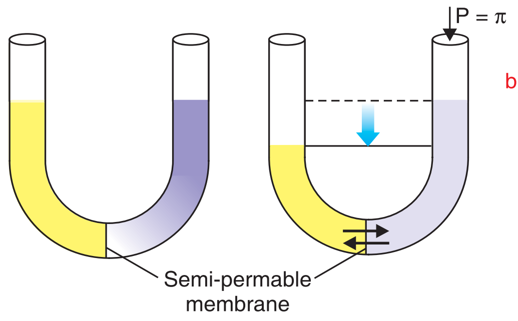
1.9.3 Osmosis and Osmotic Pressure

How do you calculate osmotic pressure?

Osmosis is the selective passage of solvent molecules through a porous (*semi- permeable*) membrane from a dilute to a more concentrated solution or from the solvent side into the solution side.

Figure 1.17 shows two solutions on equal level, separated by a semi-permeable membrane. Solvent molecules move through the membrane from left to right. As a result, the liquid levels in the two arms become uneven. Eventually, the pressure difference resulting from the unequal heights of the liquid in the two arms becomes so large that the net flow of solvent ceases. Alternatively, we may apply pressure to the right arm of the apparatus, as shown in Figure 1.17 b, to stop the net flow of solvent either way.

The pressure required to prevent osmosis is known as the osmotic pressure, π, of the solution.



a) A pure solvent and its solution are separated by a semi-permeable membrane through which solvent molecules can pass but solute molecules cannot.

b) The system at equilibrium, where the rate of solvent transfer is the same in both direction.

Figure 1.17 Apparatus for measuring osmotic pressure.

Jacobus Henricus Van't Hoff found that the osmotic pressure obeys a law similar to the ideal gas law, $PV = nRT$,

where V is the volume of the solution, n is the number of moles of solute, R is the ideal gas constant, and T is the temperature on the Kelvin scale. From the equation, we can write:

$$\pi = P = \left(\frac{n}{V}\right)RT = \mathrm{M}RT$$

where M is the molarity of the solution.

Like other colligative properties, osmotic pressure can be used to determine the molar mass of solute. Especially osmotic pressure is used in biological laboratories to determine molecular masses of huge molecules like proteins and nucleic acids.

Example 1.23

What is the osmotic pressure at 17°C of 150 mL aqueous solution containing 1.75 g of sucrose ($C_{12}H_{22}O_{11}$) per 150 mL of solution?

Solution:

First we calculate the molarity (M) of the solution

$$\text{Molarity (M)} = \frac{\text{Number of moles of solute}}{\text{Volume (L) of solution}}$$

$$= \frac{1.75\ \cancel{\text{g}}/\left(342\ \cancel{\text{g}}/\text{mol}\right)}{0.150\ \text{L}} = 0.034\ \text{mol/L}$$

$$\pi = MRT$$

$$= 0.0851\ \cancel{\text{mol}}/\cancel{\text{L}}\left(0.0821\frac{\cancel{\text{L}}\ \text{atm}}{\cancel{\text{mol}}\ \cancel{\text{K}}}\right)(290\ \cancel{\text{K}}) = 0.812\ \text{atm}$$

Example 1.24

In an experiment to measure the molar mass of polyethylene, 2.20 g of polyethylene plastic was dissolved in enough toluene to produce a 100 mL solution. Its osmotic pressure at 25°C was measured as 1.10 × 10^{-2} atm. Calculate the molar mass of polyethylene.

Solution:

From the equation, $\pi = MRT \Rightarrow M = \dfrac{\pi}{RT}$

$$M = \frac{1.10\times10^{-2}\ \text{atm}}{\left(0.0821\dfrac{\text{L.atm}}{\text{mol.K}}\right)(298\ \text{K})} = 4.5\times10^{-4}\ \text{mol/L}$$

That is, 1 L solution contains 4.5 × 10^{-4} mole of polyethylene. The amount of polyethylene in 100 mL of the solution is therefore

1 L → 4.5 × 10^{-4} mol

0.10 L → ?

$$\text{Amount of polyethylene (mol)} = \frac{0.10\ \text{L} \times 4.5 \times 10^{-4}\ \text{mol}}{1\ \text{L}}$$

$$= 4.5 \times 10^{-5}\ \text{mol}$$

$$\text{Molar mass of polyethylene } (\text{g/mol}) = \frac{2.20\ \text{g}}{4.5 \times 10^{-5}\ \text{mol}}$$

$$= 4.89 \times 10^{4}\ \text{g / mol}$$

Activity 1.13

Take 5%,10% and 20% solutions of sucrose in water.

Take 3 potatoes of almost equal size and make one cubic hole in each potato of equal dimensions.

Fill the holes with water and keep these potatoes in different solutions of sucrose.

Observe the change in the water level at different time intervals.

Discuss your observations with your teacher as well as classmates.

Exercise 1.17

1. A sample of 2.05 g of polystyrene plastic was dissolved in enough toluene to form 100 mL of solution. The osmotic pressure of this solution was found to be 1.21 kPa at 25°C. Calculate the molar mass of polystyrene.
2. What is the osmotic pressure, in atm, of a 0.30 M solution of glucose in water that is used for intravenous infusion at body temperature, 37°C?

1.9.4 Colligative Properties of Electrolytic Solutions

Activity 1.14

Form groups and discuss the following. Present the result of your discussion to the class as a report.

1. What is the difference between electrolytes and non-electrolytes?
2. How do the effects of the presence of electrolyte solute on the properties of pure solvent differ from the effect of the presence of non-electrolyte solvent? Justify your answer by giving example.

The effective number of moles of ions produced by one mole of a solute is expressed in terms of the Van’t Hoff factor (i).

$$i = \frac{\text{Measured value for electrolyte solution}}{\text{Expected value for nonelectrolyte solution}}$$

Thus, i is 1 for all solutions of nonelectrolytes, but is greater than 1 for solutions of electrolytes. Therefore, the colligative-property relationship should be modified to account for dissociation of electrolyte solutes. Consequently,

$$\Delta P = i\, x_2 P_1^\circ$$

$$\Delta T_b = i\, K_b \mathrm{m}$$

$$\Delta T_f = i\, K_f \mathrm{m}$$

$$\pi = i\, MRT$$

Table 1.3 Experimental values of the Van’t Hoff factor for some substances.

Compound	0.100 m	0.001 m
HCl	1.9	2.0
NaCl	1.87	1.97
$MgSO_4$	1.21	1.82
K_2SO_4	2.32	2.84
KBr	1.88	1.97

As can be seen in Table 1.3 the experimental Van’t Hoff factors are less than the theoretical prediction. This is mainly due to the cation-anion interaction in the solution of the electrolytes that prevents complete dissociation.

Example 1.25

If a 0.10 m $MgSO_4$ solution causes an elevation of 0.062°C in the boiling point of water, what is:

a the Van’t Hoff Factor (i)?

b the boiling point of this solution?

Solution:

a First, we find i by applying the modified colligative-property relationship for ΔT_b.

$$\Delta T_b = i\, K_b \mathrm{m}$$

Given:

$\Delta T_b = 0.062°C$

$K_{b,\ H_2O} = 0.512°C/m$

$m = 0.1\ m$

$0.062°C = i \times 0.512°C\ /m \times 0.1\ m$

$i = 1.21$. What does this indicate?

b Recall that $\Delta T_b = T_b - T_b^\circ$

$0.062°C = T_b - 100°C$

$T_b = 100°C + 0.062°C = 100.062°C$

Exercise 1.18

A 0.0622 m solution of iron (III) chloride, $FeCl_3$, in water freezes at –0.412°C. Determine the Van't Hoff's factor of $FeCl_3$ in this solution.

Unit Summary

- *Solutions are homogeneous mixtures of two or more substances.*
- *Solubility depends on the relative magnitude of solute-solute, solute-solvent, and solvent-solvent attractive forces.*
- *The relative amounts of solute and solvent in a solution can be described quantitatively in terms of mass percentage, parts per million, parts per billion, mole fraction, molarity, molality and normality.*
- *Increasing the temperature usually increases the solubility of solids in water and liquids in water while it decreases the solubility of gases in water.*
- *Raoult's law states that the partial vapour pressure of substance A over a solution is equal to the mole fraction of A,* X_A*, times the vapour pressure of pure solvent. An ideal solution obeys Raoult's law over the entire range of concentration. Non ideal solutions show positive or negative deviation from Raoult's law.*
- *Some physical properties of solutions are colligative, that is, they depend on the concentration of the solute particles that are present in a given amount*

of solvent and not on their chemical identity. These are vapour pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure.

- *The Van't Hoff factor provides a measure of the extent of dissociation of electrolyte in solution.*

Check List

Key terms of the unit

- *Boiling point elevation*
- *Colligative properties*
- *Electrolyte solution*
- *Freezing point depression*
- *Henry's law*
- *Heterogeneous solution*
- *Homogeneous solution*
- *Ideal solution*
- *Lowering of vapor pressure*
- *Mass percentage*
- *Miscible*
- *Molality*
- *Molarity*
- *Mole fraction*
- *Negative deviation from Raoult's law*
- *Nonelectrolyte*
- *Nonideal solution*
- *Normality*
- *Osmosis*
- *Osmotic pressure*
- *Parts per billion*
- *Parts per million*
- *Positive deviation from Raoult's law*
- *Raoult's law*
- *Solvation*
- *Van't Hoff factor*

REVIEW EXERCISE FOR UNIT 1

Part I: Multiple Choice Questions

1. A solution is a:

a heterogeneous mixture

b homogeneous mixture

c suspension

d colloid

2. Soda water is an example of:

a liquid-liquid solution	c gas-liquid solution
b solid-liquid solution	d gas-gas solution

3. Which of the following substances are not readily miscible within each other?

a C_6H_6 and CCl_4	c C_2H_5OH and H_2O
b C_2H_5OH and CCl_4	d CH_3OH and H_2O

4. Rate of dissolution is largely dependent upon:
   - a the inter-particle forces
   - b the surface area of solid solute
   - c the temperature of the system
   - d the pressure of the system

5. Which of the following statements is not correct?
   - a pressure has little effect on the solubility of liquids and solids
   - b the solubility of most solids increases with increasing temperature
   - c the solubility of gases in water increases with increasing temperature.
   - d none of the above

6. The quantitative relationship between gas solubility and pressure is given by:

a Raoult's law	c Hess's law
b Henry's law	d Dalton's law

7. When a non-volatile solute is added to a pure solvent the:
   - a vapour pressure of the solvent decreases.
   - b vapour pressure of the solvent increases.
   - c boiling point of the solution decreases.
   - d freezing point of the solution increases.

8. Which of the following is not true about ideal solutions?
   - a the volume of an ideal solution is the sum of the volume of its pure components
   - b there is no expansion or contraction on mixing
   - c the heat of solution is zero
   - d they deviate from Raoult's law

9. The ratio of the number of moles of solute divided by the total number of moles gives:
   - a the mole fraction of the solute
   - b the molarity of the solution
   - c the molality of the solution
   - d the normality of the solution
10. Which of the following liquid pairs shows a positive deviation from Raoult's law?
   - a octane, chloroform
   - c benzene, methanol
   - b ethanol, water
   - d water, nitric acid
11. Which of the following is not a colligative property?
   - a Osmotic pressure
   - c Boiling point elevation
   - b Vapour pressure
   - d Freezing point depression
12. The addition of a non-volatile solute to a solvent results in the lowering of:
   - a boiling point as well as freezing point
   - b freezing point as well as vapour pressure
   - c vapour pressure as well as density
   - d boiling point as well as vapour pressure
13. Phosphoric acid reacts with calcium hydroxide to form calcium hydrogen phosphate and water. The equivalent mass of phosphoric acid in this reaction will be:
   - a 98 g/eq
   - c 49 g/eq
   - b 32.6 g/eq
   - d 14 g/eq
14. A non-volatile electrolyte dissolved in an aqueous solution with the same molal proportion as a nonelectrolyte produces:
   - a the same colligative effect
   - b lower colligative effect
   - c higher colligative effect
   - d no colligative effect
15. According to Raoult's law, the relative lowering of vapour pressure of a solution by a non-volatile solute is:
   - a equal to the mole fraction of solvent
   - b equal to the mole fraction of solute

c directly proportional to mole fraction of solute

d equal to normality of solution

Part II: Short Answer Questions

16. Distinguish between solutions and colloids. Give an example of each.

17. Explain the principle "like dissolves like".

18. Explain how soaps and detergents remove dirt from clothing.

19. Indicate the type of solute-solvent interaction that is most important in each of the following solutions:

    a KBr in water

    b hexane, C_6H_{14}, in gasoline

    c ammonia in water

20. Consider the following solutions. In each case, predict whether the solubility of the solute should be high or low. Justify your answer.

    a KCl in H_2O

    b HF in H_2O

    c KCl in CCl_4

    d H_2O in CH_3OH

    e NH_4Cl in C_5H_{12}

    f CCl_4 in H_2O

21. Calculate the molarity of each of the following solutions:

    a 10.5 g NaCl in 350.0 mL of solution

    b 40.7 g $LiClO_4 \cdot 3H_2O$ in 125 mL of solution

22. The concentrated sulfuric acid we use in the laboratory is 98.0% H_2SO_4, by mass. Calculate the molality and molarity of the acid solution. The density of the solution is 1.83 g/mL.

23. Calculate the approximate volume of water that must be added to 250 mL of 1.25 N solution to make it 0.500 N.

24. a What is meant by the terms saturated and unsaturated solutions?

    b Explain how supersaturated solution can be formed.

25. State Raoult's law and explain it on a molecular basis.

26. Use the example of a solution of benzene in toluene to explain what is meant by an ideal solution.

27. What characteristic of a solution determines its colligative properties?

28 The vapour pressure of ethanol (C_2H_5OH) and 1-propanol (C_3H_7OH) at 35°C are 100 mmHg and 37.6 mmHg, respectively. Assuming ideal behaviour, calculate the partial vapour pressures of ethanol and 1-propanol over a solution, in which the mole fraction of ethanol is 0.3.

29. A solution was made by dissolving 3.75 g of a pure non-volatile solute in 95 g of acetone. The boiling point of pure acetone was observed to be 55.95°C, and that of the solution was 56.50°C. If the molar boiling point elevation constant (K_b) of acetone is 1.71°C kg/mol, what is the approximate molar mass of the solute?

30. Urea $(NH_2)_2CO$ is the product of protein metabolism in mammals. What is the osmotic pressure of an aqueous solution containing 1.10 g of urea in 100 mL of solution at 20°C?

31. Calculate the freezing point of a solution of 3.46 g of a compound, X, in 160 g of benzene. When a separate sample of X was vaporised, its density was found to be 3.27 g/L at 116°C and 773 torr. The freezing point of pure benzene is 5.45°C, and K_f is 5.12°C kg/mol.

32. Why attention given to the colligative properties of electrolyte solutions than that of nonelectrolyte solutions?

33. Pure benzene freezes at 5.45°C. A solution containing 7.24 g of $C_2Cl_4H_4$ in 115.3 g of benzene was observed to freeze at 3.55°C. From these data, calculate the molal freezing point depression constant of benzene.

34. The osmotic pressure of a 0.010 M aqueous solution of $CaCl_2$ is found to be 0.674 atm at 25°C. Calculate Van't Hoff's factor, *i*, for the solution.

35. A solution of crab hemocyanin, a pigmented protein extracted from crabs, was prepared by dissolving 0.750 g of the protein in 125 mL of water. At 4°C, a 2.6 mmHg osmotic-pressure rise of the solution was observed. The solution had a density of 1.00 g/mL. Determine the molar mass of the protein.

UNIT 12

Acid-Base Equilibria

Unit Outcomes

At the end of this unit, you will be able to:

- *understand the Arrhenius, Brønsted-Lowry and Lewis concepts of acids and bases;*
- *understand the dissociation of water, weak monoprotic and polyprotic acids, and bases;*
- *know how to solve equilibrium problems involving concentration of reactants and products, K_a, K_b, pH and pOH;*
- *understand the common-ion effect, buffer solutions, hydrolysis of salts, acid-base indicators and acid-base titrations;*
- *explain how buffering actions affect our daily lives, using some examples;*
- *determine the equivalents of acids and base, respectively, that are required to neutralize specific amounts of base and acid;*
- *predict, in qualitative terms, whether a solution of a specific salt will be acidic, basic or neutral;*
- *know how to solve problems involving concentration and pH of acid-base titration; and*
- *describe scientific enquiry skills along this unit: classifying, communicating, asking questions, applying* concepts and making generalizations.

MAIN CONTENTS

Experimental Activity

While working with your groups collect a lemon, orange and a piece of soap.

Procedure:

1. Prepare lemon and orange juices and put them in two different test tubes.
2. Put a piece of blue litmus paper in each test tubes. What did you observe? What do you conclude from this test?
3. Take a piece of soap and dissolve it in 10 mL of water. Add a piece of red litmus paper or 2-3 drops of phenolphthalein solution.

What do you observe and what do you conclude from this test?

Acids and bases are important in numerous chemical processes that occur around us. Their importance vary greatly, for example, from industrial processes to biological ones and from reactions in the laboratory to those in our environment. Proteins, enzymes, food products, medicines, blood, genetic material, and other components of living matter contain both acids and bases.

In this unit you will learn three definitions of acids and bases that will allow you to understand ever-increasing numbers of reactions in different phases of life. While dealing with the acids and the basis, you will also be able to apply the principles of chemical equilibrium to this essential group of substances.

After presenting the classical (Arrhenius) acid-base definition, we will examine the acid dissociation to see why acids vary in strength. The pH scale is introduced as a means of comparing the acidity or basicity of aqueous solutions. Then, we will notice that the short coming of the Arrhenius theory are overcome by the theory proposed independently by J.N. Brønsted in Denmark and T.M. Lowry in Great Britian.

Weak acids and weak bases are important weak electrolytes. They are found in many chemical and biological processes of interest. Amino acids, for example, are both weak acids and weak bases. In this unit, we will learn some ways of expressing concentrations of hydronium ions and of hydroxide ions in solutions of weak acids and weak bases. Then you will examine equilibria involving these weak electrolytes. You will also see that the indicators, used in titration, such as phenolphthalein, are weak acids or weak bases. Finally you will learn how to use these properties to select an appropriate indicator for a titration.

2.1 ACID-BASE CONCEPTS

At the end of this subunit, you will be able to:

- define acid by the Arrhenius concept;
- explain why proton exists bounded to water molecules, as H_3O^+, in all acid-base reactions;
- give examples of Arrhenius acids;
- define base using the Arrhenius concept;
- give examples of Arrhenius bases;
- define acid using the Brønsted-Lowry concept;
- give examples of Brønsted-Lowry acids;
- define base using the Brønsted-Lowry concept;
- give examples of Brønsted-Lowry bases;
- explain what conjugate acids and conjugate bases are;
- identify the acid-base conjugate pairs from a given reaction;
- write an equation for self-ionization of water and ammonia;
- explain what is meant by amphiprotic species;
- give examples of reactions of amphiprotic species;
- define an acid by using Lewis concept;
- give examples of Lewis acids;
- define a base using the Lewis concept;
- give examples of Lewis bases.

Activity 2.1

In grade 10 Chemistry, you have learnt the acid-base concepts. Recall this and discuss the following questions in group. After discussion write a report and present to the class:

1. Explain the concept of acid-base using examples.
2. Which of the concepts is more general?

Biography

Svante August Arrhenius

Svante August Arrhenius (1859-1927), was a Swedish chemist helped lay the foundations of modern chemistry. Born near Uppsala, Sweden, he was educated at the University of Uppsala and received his Ph.D. in 1884. While still a student, he studied the conductive properties of electrolytic (charge-conducting) solutions. In his doctoral thesis, he formulated the theory of electrolytic dissociation.

This theory holds that, in electrolytic solutions, the dissolved chemical compounds in the solution are dissociated into ions, even when there is no current flowing through the solution. Arrhenius also postulated that the degree of dissociation increases as the solution becomes more dilute. This hypothesis later turned out to be significantly true only for weak electrolytes. His theory was initially thought to be completely wrong, and his thesis was given the lowest possible passing grade. Later, however, Arrhenius' theory of electrolytic dissociation became generally accepted, and eventually became one of the cornerstones of modern physical chemistry and electrochemistry.

2.1.1 The Arrhenius Concept of Acids and Bases

Activity 2.2

Form groups and discuss the following questions and write a report of your discussion.

1. Explain Arrhenius acids and bases concepts using suitable examples?
2. Does hydrogen ion exist freely in water?

What are the drawbacks of the Arrhenius' concepts of acids and bases?

The Arrhenius definition of acids and bases has the following limitations.

* It defines acids and bases in terms of what happens when compounds dissolve in water. However, similar chemistry occurs in many reactions that take place in solvents other than water, and this definition does not work for such reactions.

* It does not explain why some compounds in which hydrogen has an oxidation number of + 1 (such as HCl) dissolve in water to give acidic solutions, whereas others (such as NH_3) do so.

- Only the compounds that contain the OH^- ion can be classified as Arrhenius bases. The Arrhenius definition does not explain why compounds such as Na_2CO_3 have basic properties.

Exercise 2.1

Based on their dissociations in water solution, classify each of the following compounds as Arrhenius acid, Arrhenius base, or as a compound that cannot be classified as an Arrhenius acid or Arrhenius base.

a $H_3PO_4(l) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$
b $NaCl(s) + H_2O(l) \rightleftharpoons Na^+(aq) + Cl^-(aq)$
c $Ca(OH)_2 + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$
d $NH_3(l) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

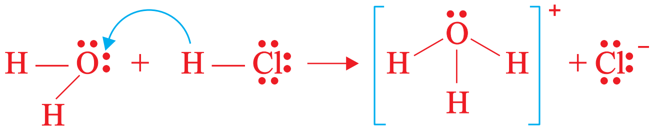
2.1.2 Brønsted-Lowry Concept of Acids and Bases

Activity 2.3

From what you have learnt in Grade 10 Chemistry discuss the following questions.

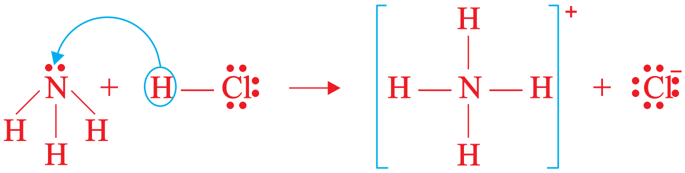
1. What are acids and bases according to Brønsted-Lowry concept?
2. How does it differ from Arrhenius definition? What are the similarities?
3. Give two Brønsted-Lowry bases that are not Arrhenius bases.
4. Are there any Brønsted acids that do not behave as Arrhenius acids?

Consider the ionization of hydrochloric acid in water:

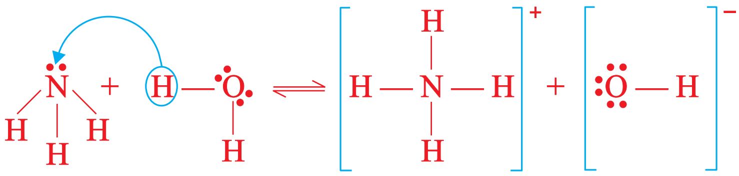


Which one is a Brønsted-Lowry acid and which one is a Brønsted-Lowry base?

The Brønsted-Lowry concept is not limited to reactions in aqueous solution. For example, HCl is an acid in liquid ammonia, $NH_3(l)$, just as it is in water.



The Brønsted-Lowry concept successfully explains how ammonia acts as a base in water, which the Arrhenius definition fails to do. In the ionization of ammonia, NH_3, water is the acid. The ionization of ammonia in water is a reversible reaction. This reversible acid-base reaction can be written as:



Once an acid has given up a proton, the remaining part can be a proton acceptor and is, now called a conjugate base. On the other hand, when a base accepts a proton, the species formed is called conjugate acid.

Every acid has a conjugate base, and every base has a conjugate acid. Thus, for any conjugate acid-base pair:

- The conjugate base has one less H and one more minus charge than the acid.
- The conjugate acid has one more H and one less minus charge than the base.

Table 2.1 The conjugate pairs in some Acid-Base Reactions.

Acid	+	Base	⇌	Conjugate base	+	Conjugate acid
HF	+	H_2O	⇌	F^-	+	H_3O^+
HCOOH	+	CN^-	⇌	$HCOO^-$	+	HCN
NH_4^+	+	CO_3^{2-}	⇌	NH_3	+	HCO_3^-
$H_2PO_4^-$	+	OH^-	⇌	HPO_4^{2-}	+	H_2O
H_2SO_4	+	$N_2H_5^+$	⇌	HSO_4^-	+	$N_2H_6^{2+}$
HPO_4^{2-}	+	SO_3^{2-}	⇌	PO_4^{3-}	+	HSO_3^-

Example 2.1

Identify the Brønsted-Lowry acids and bases and their respective conjugates in each of the following reactions.

a $H_2S + NH_3 \rightleftharpoons NH_4^+ + HS^-$

b $OH^- + H_2PO_4^- \rightleftharpoons H_2O + HPO_4^{2-}$

Solution:

To identify Brønsted-Lowry acids and bases, we look for the proton donors and proton-acceptors in each reaction.

a H_2S is converted to HS^- by donating a proton. So, H_2S is an acid, and HS^- is its conjugate base. NH_3 accepts the proton lost by the H_2S. As a result, NH_3 is a base, and NH_4^+ is its conjugate acid.

$$\underset{\text{Acid}}{H_2S} + \underset{\text{Base}}{NH_3} \rightleftharpoons \underset{\text{Conjugate acid}}{NH_4^+} + \underset{\text{Conjugate base}}{HS^-}$$

b OH^- accepts a proton from $H_2PO_4^-$. Therefore, OH^- is a base and H_2O is its conjugate acid. $H_2PO_4^-$ donates a proton to OH^-. Thus, $H_2PO_4^-$ is an acid, and HPO_4^{2-} is its conjugate base.

$$\underset{\text{Base}}{OH^-} + \underset{\text{Acid}}{H_2PO_4^-} \rightleftharpoons \underset{\text{Conjugate Acid}}{H_2O} + \underset{\text{Conjugate Base}}{HPO_4^{2-}}$$

Exercise 2.2

Identify the Brønsted-Lowry acids, bases, conjugate acids and conjugate bases in each of the following reactions.

a $NH_3 + HCO_3^- \rightleftharpoons NH_4^+ + CO_3^{2-}$

b $H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+$

c $H_2O + SO_3^{2-} \rightleftharpoons OH^- + HSO_3^-$

d $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

Strengths of Conjugate Acid-Base Pairs

The stronger the acid, the weaker is its conjugate base. Similarly, the stronger the base, the weaker is its conjugate acid. For example, HCl is a strong acid, and its conjugate base Cl^-, is a weak base. Acetic acid, CH_3COOH, is a weak acid, and its conjugate base, CH_3COO^-, is a strong base. The following chart shows the strength of conjugate acid-base pairs .

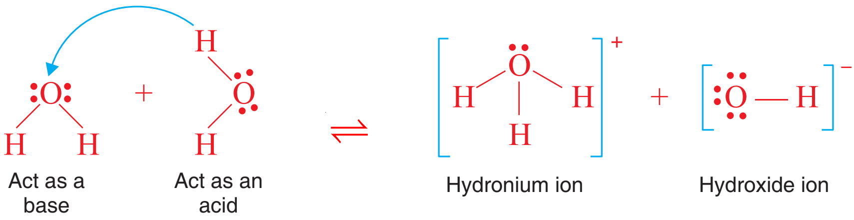
Acid strength	Acid	Base	Base strength
Strong	HCl	Cl^-	Negligible
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	H_3O^+	H_2O	
Weak	HSO_4^-	SO_4^{2-}	Weak
	H_2SO_3	HSO_3^-	
	H_3PO_4	$H_2PO_4^-$	
	HF	F^-	
	CH_3COOH	CH_3COO^-	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	HSO_3^-	SO_3^{2-}	
	$H_2PO_4^-$	HPO_4^{2-}	
	HCN	CN^-	
	NH_4^+	NH_3	
	HCO_3^-	CO_3^{2-}	
Negligible	HPO_4^{2-}	PO_4^{3-}	Strong
	H_2O	OH^-	
	HS^-	S^{2-}	
	OH^-	O^{2-}	

Chart 1.1 Strengths of Conjugate Acid-Base Pairs.

Auto-ionisation of Substances

Name the ions present in water. How are they formed?

The auto-ionisation (self-ionization) of a substance involves the transfer of a proton from one molecule of the substance to another molecule of the same substance. For example, water undergoes auto-ionisation as shown below:



This can be represented by the following equation:

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Note that, in this reaction, some water molecules behave as acids, donating protons, while the other water molecules behave as bases, accepting protons.

Amphiprotic Species

Many molecules and ions gain or lose a proton, under appropriate conditions. Such species are said to be amphiprotic. For example,

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$

$$HCO_3^-(aq) + H^+(aq) \rightleftharpoons H_2CO_3(aq)$$

In other words, amphiprotic species are species that can act as both an acid and a base. *Can you suggest more examples of amphiprotic species?*

Exercise 2.3

1. Define each of the following terms and give examples for each.
   - a autoionization
   - b amphiprotic species
2. Identify the amphiprotic species in each of the following reactions.
   - a $HPO_4^{2-}(aq) + H_3O^+(aq) \rightleftharpoons H_2O(l) + H_2PO_4^-(aq)$
     $HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$
   - b $NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
     $HCl(g) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$
3. Which of the two is the stronger base? Give your reason.
   - a HPO_4^{2-} or PO_4^{3-} b HS^- or S^{2-} c CO_3^{2-} or HCO_3^-
4. What is the weakness of the Brønsted-Lowry acids and bases theory?
5. Write the self-ionization of water and ammonia.

2.1.3 Lewis Concept of Acids and Bases

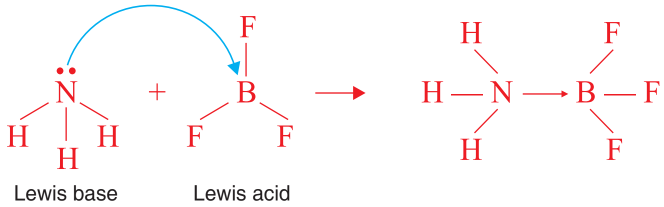
Activity 2.4

Form groups and discuss the following and report the result of your discussion to your teacher.

1. Explain Lewis concept of acids and bases.
2. How do Lewis acids and bases differ from Brønsted-Lowry acids and bases?

3. Are all Brønsted-Lowry acids and bases are also acids and bases according to Lewis concept?
4. Is there any limitation to the Brønsted-Lowry definition of acids and bases? Explain if any.

The Lewis acid-base concept includes many reactions that do not involve proton- transfer reactions. Consider, for example, the reaction between boron trifluoride (BF_3) and ammonia to form a compound, $BF_3 \leftarrow :NH_3$.



The boron atom in boron trifluoride, BF_3, has only six electrons in its valance shell and needs two electrons to satisfy the octet rule. Consequently, BF_3 (*Lewis acid*) accepts a pair of electrons from NH_3 (*Lewis base*).

This example suggests that in a Lewis acid-base reaction, we should look for:

1. a species that has an available empty orbital to accommodate an electron pair such as the B atom in BF_3, and
2. a species that has lone-pair electrons such as NH_3.

The Lewis definition allows us to consider typical Brønsted-Lowry bases, such as OH^-, NH_3, and H_2O, as Lewis bases. They all have electron pairs available to donate for electron-deficient species.

Note that any molecule or negatively charged species having an excess of electrons can be considered as a Lewis base, and any electron-deficient molecule or positively charged species can be considered as a Lewis acid.

Exercise 2.4

Identify Lewis acids and Lewis bases in each of the following reactions.

a $SiCl_4 + 2Cl^- \rightarrow [SiCl_6]^{2-}$

b $PF_5 + F^- \rightarrow [PF_6]^-$

c $Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$

d $CO_2 + H_2O \rightarrow H_2CO_3$

e $Ni + 4CO \rightarrow Ni(CO)_4$

2.2 IONIC EQUILIBRIA OF WEAK ACIDS AND BASES

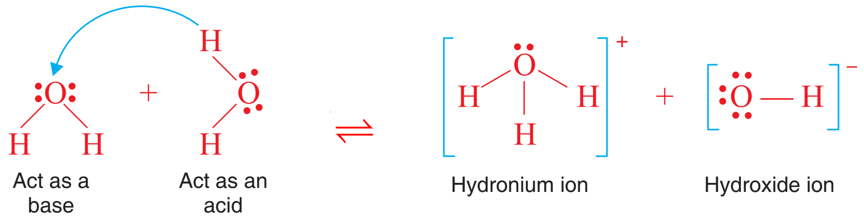
At the end of this subunit, you will be able to:

- describe the ionization of water;
- derive the expression of ion product for water, K_w;
- explain the effect of temperature on K_w;
- explain why water is a weak electrolyte;
- use K_w to calculate $[H_3O^+]$ or $[OH^-]$ in aqueous solution;
- define pH;
- define pOH;
- explain the relationship between pH and pOH;
- calculate pH from $[H^+]$ and $[H^+]$ from pH;
- calculate pOH from $[OH^-]$ and $[OH^-]$ from pOH;
- write an expression for the percent ionization of weak acids or weak bases;
- calculate the percent dissociation of weak acids and bases;
- write the expression for the acid-dissociation constant, K_a;
- calculate K_a for an acid from the concentration of a given solution and its pH;
- calculate $[H^+]$ and pH of an acidic solution from given values of K_a and the initial concentration of the solution;
- write the expression for the base-dissociation constant, K_b;
- calculate K_b for a base from the concentration of a basic solution and its pOH ; and
- calculate the $[OH^-]$ and pOH of a basic solution from a given value of K_b and the initial concentration of the solution.

2.2.1 Ionization of Water

How do you calculate the concentration of H_3O^+ ions if the concentrations of OH^- ions and K_w, at 25°C are given?

Recall that water is amphiprotic. So, to a slight extent, water molecules can transfer protons among themselves. In the self-ionization of water, the proton lost by one water molecule is gained by the other.



The self-ionization of water can be represented by the following equation:

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Since this reaction is reversible, we can apply the law of mass action to write the equilibrium constant expression.

$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$ where, K_c is the equilibrium constant, in terms of concentration.

Because only very small fractions of water molecules are ionized, the concentration of water, $[H_2O]$, remains unchanged. This equilibrium expression can be simplified by including the constant $[H_2O]^2$ term with the value of K_c to obtain a new equilibrium constant, the ion-product for water, K_w.

$$K_c [H_2O]^2 = K_W = [H_3O^+] [OH^-]$$

Note that K_w is the product of the molar concentrations of H_3O^+ and OH^- ions at a particular temperature.

Since we use $H^+(aq)$ and $H_3O^+(aq)$ interchangeably to represent the hydrated proton, the equilibrium constant can also be expressed as

$$K_w = [H^+][OH^-]$$

In pure water at 25°C, the concentrations of H^+ and OH^- ions are equal and found to be $[H^+] = 1.0 \times 10^{-7}$ M and $[OH^-] = 1.0 \times 10^{-7}$ M at 25°C,

$$K_w = [H^+][OH^-] = (1.0 \times 10^{-7}) (1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

As you have learned in your studies of chemical equilibrium in Grade 11, the value of K_c, in this case K_w, changes as temperature changes. In any aqueous solution at 25°C, no matter what it contains, the product of $[H^+]$ and $[OH^-]$ must always equal 1.0×10^{-14}. There are three possible situations.

a A neutral solution, where $[H^+] = [OH^-]$.

b An acidic solution, where $[H^+] > [OH^-]$.

c A basic solution, where $[OH^-] > [H^+]$

Activity 2.5

Form groups and discuss the following. Write a report on the discussion and present to the classs.

Many substances undergo auto-ionization in analogous to water. For example, the auto-ionization of liquid ammonia is:

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

a Write a K_c expression for auto-ionization of ammonia that is analogous to the K_w expression for water.

b Name the strongest acids and strongest bases that can exist in liquid ammonia?

c For water, a solution with $[OH^-] < [H_3O^+]$ is acidic. What are the analogous relationships in liquid ammonia?

Exercise 2.5

1. Calculate $[H^+]$ or $[OH^-]$, as required, for each of the following solutions at 25°C, and state whether the solution is neutral, acidic, or basic.
   - a $[OH^-] = 1.0 \times 10^{-4}$ M
   - b $[OH^-] = 1.0 \times 10^{-8}$ M
   - c $[H^+] = 1.0 \times 10^{-7}$ M
2. Calculate the concentration of OH^- in a solution in which
   - a $[H_3O^+] = 2.0 \times 10^{-5}$ M
   - b $[H_3O^+] = [OH^-]$
   - c $[H_3O^+] = 10^2 \times [OH^-]$
3. Calculate $[H_3O^+]$ in a solution that is at 25°C and has $[OH^-] = 6.7 \times 10^{-2}$ M. Is the solution neutral, acidic, or basic?
4. At 40°C, the value of K_w is 2.92×10^{-14}. Calculate the $[H^+]$ and $[OH^-]$ of pure water at 40°C.
5. Why water is a weak electrolyte?

The pH scale

The concentration of H^+ in aqueous solution is usually very small and inconvenient to express and to draw as graphs. Sören Sörensen, in 1909, developed the pH scale to solve this problem. The pH of a solution is defined as the negative logarithm of the hydrogen ion concentration (in mol/L):

$$pH = -\log [H_3O^+] \quad \text{or} \quad pH = -\log [H^+]$$

Note that the negative logarithm gives us positive numbers for pH. *What is the* pH *value of a neutral, basic and acidic solution?*

A pH-meter (Figure 2.1) is used to measure the pH of a solution.

Figure 2.1 pH-meter.

Activity 2.6

In your group, measure the pH of the following substances, using a pH-meter. Copy and fill in the following table. Compare your results with those of other groups. Find the pH values of the substances in reference books and other sources and compare your results with the values you observed.

Substance	pH	Acidic, Basic or Neutral
Beer		
Milk of Magnesia		
Tomato juice		
Lemon juice		
Human saliva		
Drinking water		

pH decreases as the concentration of H^+ ions increases; in other words, the more acidic the solution, the lower its pH; the more basic the solution, the higher its pH.

The pH notation has been extended to other exponential quantities. For example, hydroxide concentrations can be expressed in terms of pOH, where pOH = –log [OH^-]. Similarly, pK_w can be expressed as $-\log K_w$.

Activity 2.7

Derive the relationship, $pH + pOH = pK_w = 14$ at 25°C.

Example 2.2

Calculate the pH of a basic solution, in which $[OH^-] = 2.0 \times 10^{-3}$ at 25°C.

Solution:

From the given [OH^-], we can determine [H^+], using the relation

$$[H^+] = \frac{K_W}{[OH^-]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-3}} = 5.0 \times 10^{-12}\ M$$

$$pH = -\log(5.0 \times 10^{-12}) = 11.30$$

Example 2.3

Calculate:

a the pH and pOH of a juice solution in which $[H_3O^+]$ is 5.0×10^{-3} M

b the $[H_3O^+]$ and $[OH^-]$ of human blood at pH = 7.40

Solution:

a **Given:**

$[H_3O^+] = 5.0 \times 10^{-3}$ M

Required:

pH = ? and pOH = ?

$$pH = -\log[H_3O^+] = -\log(5.0 \times 10^{-3})$$

$$= 3 - \log 5.0 = 2.3$$

$$pH + pOH = 14$$

$$pOH = 14 - pH = 14 - 2.3 = 11.7$$

b pH = 7.40, $[H_3O^+] = ?$ $[OH^-] = ?$

$$-\log [H_3O^+] = 7.40$$

$$\log [H_3O^+] = -7.40$$

$$[H_3O^+] = 10^{-7.40}$$

$$= 4.0 \times 10^{-8}\ M$$

$$[OH^-] = \frac{K_W}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-8}} = 2.5 \times 10^{-7}\ M$$

Exercise 2.6

1. A solution formed by dissolving an antacid tablet has a pH of 9.18 at 25°C. Calculate $[H^+]$, $[OH^-]$ and pOH.
2. A solution is prepared by diluting concentrated HNO_3 to 2.0 M, 0.30 M and 0.0063 M HNO_3 at 25°C. Calculate $[H_3O^+]$, $[OH^-]$, pH and pOH of the three solutions.

2.2.2 Measures of the Strengths of Acids and Bases in Aqueous Solution

The strength of acids and bases can be described in many ways. Some of the ways are the concentration of hydrogen and hydroxide ions, pH and pOH, percent dissociation, K_a and K_b.

1. *Concentration of hydrogen and hydroxide ions*

Acid strength refers to the ability of an acid to release protons. A strong acid gives up protons more easily than a weak acid. For two acids of equal concentrations, the strongest acid produces the greater quantity of hydrogen ions. Base strength refers to the ability of a base to accept protons. A strong base accepts more protons readily than a weak base. A solution of a stronger base will contain a larger concentration of hydroxide ions than a solution of a weaker base if both solutions are of equal concentration.

Activity 2.8

In unit two of Grade 10 Chemistry, you learned about the strength of acids and bases. By referring to this text book and other chemistry books, list strong acids, strong bases, weak acids and weak bases. Then discuss what you have written with the rest of the class.

2. *pH and pOH*

If the pOH of a solution at 25°C is 12, is it acidic, neutral or basic?

It is possible to predict the strength of acids from their pH values. The smaller the pH value, the stronger the acid. The concentration of hydroxide ions in a solution can be expressed in terms of the pOH of the solution. Hence, the strength of bases can also be determined from their pOH values. The smaller the pOH value, the stronger the base.

3. *Percent Ionization*

How do you determine the percent ionization of an acid or a base?

The extent to which an acid or base ionizes is called percent ionization. Mathematically,

$$\text{Percent ionization} = \frac{\text{Ionized acid or base concentration at equilibrium}}{\text{Initial concentration of ionized acid or base}} \times 100$$

The strength of an acid depends on the percentage of the acid molecules that dissociate in water solution. If a higher percentage of the original acid molecules dissociate, then the acid is a strong acid. Strong acids and strong bases ionize nearly completely in water. However, weak acids and weak bases dissociate partially in water, and their percent of ionization is small.

4. *Dissociation (Ionization) Constants*

Acid Dissociation Constant, K_a

What is the relationship between strength of acids with their acid-dissociation constant values?

The acid-dissociation constant is a quantitative measure of the strength of the acid in a given solvent. For the dissociation of the acid, HA;

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

the dissociation-constant expression can be written as:

$$K = \frac{\left[H_3O^+\right]\left[A^-\right]}{\left[H_2O\right][HA]}$$

Since the concentration of water is nearly constant, we can write;

$$K[H_2O] = \frac{\left[H_3O^+\right]\left[A^-\right]}{[HA]}$$

The product of the two constants, K and $[H_2O]$, is itself a constant. It is designated as K_a, which is the acid-dissociation constant or the acid-ionization constant. Hence for a weak acid, HA:

$$K_a = \frac{\left[H_3O^+\right]\left[A^-\right]}{[HA]}$$

The K_a value for a strong acid is very large, because [HA] in the denominator is very small since the acid dissociates essentially completely. Similarly, the K_a value for a weak acid is relatively small, since $[H_3O^+]$ and $[A^-]$ are very small, and [HA] in the denominator is large. The ionization-constants of some weak monoprotic acids are tabulated in Table 2.2.

Table 2.2 Ionization constant of some weak monoprotic acids at 25°C.

Name of the Acid	Formula	K_a
Acetic acid	CH_3COOH	1.8×10^{-5}
Ascorbic acid	$C_6H_8O_6$	8.0×10^{-5}
Benzoic Acid	C_6H_5COOH	6.5×10^{-5}
Formic acid	$HCOOH$	1.7×10^{-4}
Hydrocyanic acid	HCN	4.9×10^{-10}
Hydrofluoric acid	HF	6.8×10^{-4}
Hypobromous acid	$HOBr$	2.5×10^{-9}
Hypochlorous acid	$HOCl$	3.0×10^{-8}
Nitrous acid	HNO_2	4.5×10^{-4}

How do you calculate the pH of weak acids?

Generally, we can calculate the hydrogen-ion concentration or pH of an acid solution at equilibrium, given the initial concentration of the acid and its K_a value. Alternatively, if we know the pH of a weak acid solution and its initial concentration, we can determine its K_a.

The following may help you to solve weak-acid dissociation problems.

1. identify the major species that can affect the pH of the solution. In most cases we can ignore the dissociation of water. Why?
2. write balanced equations for the reactions producing H_3O^+.
3. list the initial concentration of the species participating in the equilibrium.
4. define the change needed to achieve equilibrium. That is, define x.
5. write the equilibrium concentration, in terms of x.
6. write the acid dissociation constant, K_a, in terms of equilibrium concentration.

7. first solve for x by the approximation method. If the approximation is not valid, use the quadratic equation.
8. having solved for x, calculate the equilibrium concentrations of all species and/or the pH of the solution.

Example 2.4

Calculate the pH of a 0.50 M HF solution at 25°C. The ionization of HF is given by

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

Solution:

The species that can affect the pH of the solution are HF, and the conjugate base F^-, Let x be the equilibrium concentration of H_3O^+ and F^- ions in molarity (M). Thus,

	$HF(aq) + H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$F^-(aq)$
Initial, M	0.50		0.00		0.00
Change, M	$-x$		$+x$		$+x$
Equilibrium, M	$(0.50-x)$		x		x

$$K_a = \frac{[H^+][F^-]}{[HF]}$$

Substituting the concentration of HF, H^+ and F^-, in terms of x, gives:

$$K_a = \frac{(x)(x)}{0.50-x} = 6.8\times10^{-4}$$

Rearranging this expression provides:

$$x^2 + 6.8 \times 10^{-4} x - 3.4 \times 10^{-4} = 0$$

This is a quadratic equation that can be solved, using the quadratic formula, or you can use the approximation method for x. Because HF is a weak acid, and weak acids ionize only to a slight extent, x must be small compared to 0.50. Therefore, you can make this approximation:

$$0.50 - x \approx 0.50$$

Now, the ionization constant expression becomes

$$\frac{x^2}{0.50-x} \approx \frac{x^2}{0.50} = 6.8\times10^{-4}$$

Rearranging this equation gives:

$$x^2 = (0.5)(6.8 \times 10^{-4}) = 3.4 \times 10^{-4}$$

$$x = \sqrt{3.4 \times 10^{-4}} = 1.8 \times 10^{-2}\ \text{M}$$

Thus, we have solved for x without using the quadratic equation. At equilibrium, we have

$$[\text{HF}] = (0.50 - 0.018)\ \text{M} = 0.48\ \text{M}$$

$$[\text{H}_3\text{O}^+] = 0.018\ \text{M}$$

$$[\text{F}^-] = 0.018\ \text{M}$$

and the pH of the solution is

$$\text{pH} = -\log(0.018) = 1.74$$

How good is this approximation? Because K_a values for weak acids are generally known to an accuracy of only ±5%, it is reasonable to require x to be less than 5% of 0.50, the number from which it is subtracted. In other words, the approximation is valid if the percent ionization is equal to or less than 5%.

$$\frac{0.018}{0.50} \times 100\% = 3.6\%$$

Is the approximation valid?

Exercise 2.7

For a 0.036 M HNO_2 solution.

a Write a chemical equation that shows the ionization of nitrous acid in water.

b Calculate the equilibrium concentration of hydrogen ions and nitrous acid at 25°C, using the approximation method. Then check whether the approximation is valid or not.

c If the approximation is invalid, use the quadratic formula to calculate the concentration of hydrogen ions.

d Calculate the pH of the solution.

Base dissociation constant, K_b

In the same way as for acids, the dissociation of a base in water can be written as

$$\text{B(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{BH}^+\text{(aq)} + \text{OH}^-\text{(aq)}$$

which gives the equilibrium expression of the form:

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

where K_b is the base dissociation constant. K_b values for strong bases are large, while K_b values for weak bases are small. Table 2.3 shows the K_b values of some common weak bases at 25°C.

Table 2.3 Values of K_b for some Common Weak Bases at 25°C.

Base	Formula	K_b
Ammonia	NH_3	1.8×10^{-5}
Aniline	$C_6H_5NH_2$	4.0×10^{-10}
Ethylamine	$C_2H_5NH_2$	4.7×10^{-4}
Hydrazine	N_2H_4	1.7×10^{-6}
Hydroxylamine	NH_2OH	1.1×10^{-6}
Methylamine	CH_3NH_2	4.4×10^{-4}
Pyridine	C_5H_5N	1.7×10^{-9}

In solving problems involving weak bases, you should follow the same guidelines as you followed for weak acids. The main difference is that we calculate $[OH^-]$ first, instead of $[H^+]$.

Exercise 2.8

For a 0.040 M ammonia solution:

a Write a chemical equation that shows the ionization of ammonia in water.

b Calculate the equilibrium concentration of ammonia, ammonium ions and hydroxide ions, using the approximation method. Check whether the approximation is valid or not.

c If the approximation is invalid, use the quadratic formula to calculate the concentration of ammonia, ammonium ions and hydroxide ions.

d Calculate the pOH and pH of the solution.

2.3 COMMON ION EFFECT AND BUFFER SOLUTION

At the end of this subunit, you will be able to:

- define the common-ion effect;
- explain the importance of the common-ion effect;
- define buffer solution;
- give some common examples of buffer systems;
- explain the action of buffer solutions and its importance in chemical processes;
- calculate the pH of a given buffer solution; and
- demonstrate the buffer action of CH_3COOH/CH_3COONa.

2.3.1 The Common ion Effect

Activity 2.9

In Grade 11 Chemistry, you learned Le Chatelier's principle. Make a group and discuss the following and present your report to the class.

Industrially, ammonia is produced by the Haber process.

1. Write a chemical equation for the production of ammonia in the process.
2. Assume that the reaction is at equilibrium. What is the effect of
   - a adding more ammonia to the equilibrium system?
   - b removing ammonia from the equilibrium system?
   - c adding more hydrogen gas to the equilibrium system?
   - d decreasing the concentration of both hydrogen and nitrogen gases from the equilibrium system?
   - e increasing temperature?
   - f decreasing pressure?
   - g adding finely divided iron as a catalyst?

The common-ion effect is caused by the addition of a compound having an ion in common with the dissolved substance that shift the equilibrium.

The presence of the common ion suppresses the ionization of a weak acid or a weak base. For example, if sodium acetate and acetic acid are dissolved in the same solution, they both dissociate and ionize to produce CH_3COO^- ions.

$$CH_3COONa\ (s) \rightarrow CH_3COO^-\ (aq) + Na^+\ (aq)$$

$$CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons CH_3COO^-\ (aq) + H_3O^+\ (aq)$$

Sodium acetate, CH_3COONa, is a strong electrolyte, so it dissociates completely in solution, but acetic acid, CH_3COOH, is a weak acid and ionizes partially. According to Le Chatelier's principle, the addition of CH_3COO^- ions from CH_3COONa to a solution of CH_3COOH will suppress the ionization of CH_3COOH and decrease the concentration of hydrogen ions.

Therefore, a solution containing both CH_3COOH and CH_3COONa will be less acidic than a solution containing only CH_3COOH of the same concentration. The shift in equilibrium of the acetic acid ionization is caused by the acetate ions from the sodium acetate. CH_3COO^- is the common ion because it is supplied by both CH_3COOH and CH_3COONa.

Example 2.5

Determine the $[H_3O^+]$ and $[CH_3COO^-]$ in a solution that is 0.10 M in both CH_3COOH and HCl.

Solution:

0.10 M HCl ionizes completely to form 0.10 M H_3O^+ and 0.10 M Cl^- ions. The Cl^- ion is a spectator ion, and it has no influence on the concentrations of CH_3COO^- and H_3O^+.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

Initial, M	0.10		0.00	0.10
Change, M	$-x$		$+x$	$+x$
Equilibrium, M	$(0.10 - x)$		x	$0.10 + x$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(0.10 + x)(x)}{0.10 - x}$$

$$1.8 \times 10^{-5} = \frac{x(1.00 + x)}{1.00 - x}$$

If x is very small, you can approximate $(1.00 - x)$ and $(1.00 + x)$ to 1.00.

$$1.8 \times 10^{-5} = \frac{x(\cancel{1.00})}{(\cancel{1.00})}$$

$x = [H_3O^+] = 10^{-5}$ M

$$pH = -\log [H_3O^+]$$

$$= -\log (18 \times 10^{-5}) = 4.74$$

Exercise 2.9

a Calculate the pH of a solution containing 0.20 M CH_3COOH and 0.30 M CH_3COONa.

b What would be the pH of a 0.20 M CH_3COOH solution if no salt were present?

2.3.2 Buffer Solutions

How does a buffer solution resist a pH change?

A buffer solution is a solution that resists changes in pH from the addition of a limited amount of an acid or a base. Table 2.4 shows how the pH of unbuffered and buffered solutions change when a small amount of acid or base is added.

Table 2.4 Comparison of buffered and unbuffered solutions.

	Initial pH of 1.0 L sample	pH after addition of 0.010 mol NaOH	pH after addition of 0.010 mol HCl
Unbuffered solution: 1.28×10^{-5} M HCl	4.8	12.0	2.0
Buffered solution: 0.099 M CH_3COOH 0.097 M CH_3COONa	4.8	4.8	4.7

Buffers contain either a weak acid and its conjugate base or a weak base and its conjugate acid.

A buffer solution must contain a relatively large concentration of acid to react with any OH^- ions that are added to it. Similarly, it must contain a relatively large concentration of base to react with any H^+ ions. To understand the action of buffer, consider a buffer that contains approximately equal molar amounts of a weak acid, HA, and its conjugate base, A^-. When a strong acid is added to the buffer, it supplies hydrogen ions that react with the base A^-.

$$H^+ (aq) \quad + \quad A^- (aq) \quad \rightarrow \quad HA (aq)$$

On the other hand, when a strong base is added to the buffer, it supplies hydroxide ions that react with the acid, HA.

$$OH^- (aq) \quad + \quad HA (aq) \quad \rightarrow \quad H_2O (l) \quad + \quad A^- (aq)$$

Thus, a buffer solution resists changes in pH through its ability to combine with the H^+ and OH^- ions.

Buffers are very important to chemical and biological systems. The pH in the human body varies greatly from one fluid to another. For example; the pH of blood is about 7.4, whereas the gastric juice in our stomach has a pH of about 1.5. The pH values, which are crucial for proper enzyme function and the balance of osmotic pressure, are maintained by buffers in most cases.

Activity 2.10

By reading references or using other sources, write a report on the buffer system in human blood. Discuss the report with the rest of the class.

Example 2.6

1. Calculate the pH of a buffer system containing 1.0 M CH_3COOH and 1.0 M CH_3COONa.
2. What is the pH of the buffer system in (1) after the addition of 0.10 mol of gaseous HCl to 1.0 L of the solution? Assume that the volume of the solution does not change when HCl is added.

Solution:

1. In this case, you are asked to calculate the pH of the buffer system of CH_3COOH/CH_3COONa before adding HCl. Hence, you can apply the same method you have used to calculate a solution containing common ions:

	$CH_3COOH(aq)$ + $H_2O(l)$ ⇌	$H_3O^+(aq)$ +	$CH_3COO^-(aq)$
Initial, M	1.0	0	1.0
Change, M	$-x$	$+x$	$+x$
Equilibrium, M	$(1.0-x)$	x	$(1.0+x)$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(x)(1.0+x)}{1.0-x} = 1.8\times10^{-5}$$

Assuming $1.0 + x \approx 1.0$ and $1.0 - x \approx 1.0$, we obtain

$$1.8\times10^{-5} = \frac{(x)(1.0+x)}{(1.0-x)} = \frac{x(1.0)}{1.0}$$

$x = [H_3O^+] = 1.8 \times 10^{-5}$ M

$pH = -\log(1.8\times10^{-5}) = 4.74$

2. The H^+ ions provided by the strong acid, HCl, react completely with the conjugate base of the buffer, which is CH_3COO^-.

$$CH_3COO^-(aq) + H^+(aq) \rightarrow CH_3COOH(aq)$$

The moles of H^+ ions added = 0.10 mol.

The moles of acetate ions before HCl is added = 1.0 M × 1 L= 1.0 mol.

0.10 mol H^+ consumes 0.10 mol CH_3COO^-.

Therefore, the number of moles of CH_3COO^- that remains unreacted = 1.0 mol – 0.10 mol = 0.9 mol.

Moles of CH_3COOH formed = 0.10 mol

Total moles of CH_3COOH = 0.10 mol + 1.0 mol = 1.1 mol

$$[CH_3COO^-] = \frac{0.9\ \text{mol}}{1\ \text{L}} = 0.9\ \text{M}$$

$$[CH_3COOH] = \frac{1.1\ \text{mol}}{1\ \text{L}} = 1.1\ \text{M}$$

	$CH_3COOH\ (aq)$ +	$H_2O(l)$ $\rightleftharpoons$	$CH_3COO^-\ (aq)$ +	$H_3O^+\ (aq)$
Initial, M	1.1		0.90	0.00
Change, M	$-x$		$+x$	$+x$
Equilibrium, M	$(1.1 - x)$		$(0.90 + x)$	x

$$K_a = \frac{\left[CH_3COO^-\right]\left[H_3O^+\right]}{\left[CH_3COOH\right]} = \frac{(0.90 + x)(x)}{1.1 - x} = 1.8 \times 10^{-5}$$

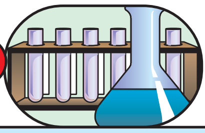
Since x is very small compared to 1.1 and 0.9, $0.90 + x \approx 0.90$ and $1.1 - x \approx 1.1$, you obtain:

$$1.8 \times 10^{-5} = \frac{(0.90 + x)x}{1.1 - x} = \frac{(0.90)x}{1.1}$$

$$x = [H_3O^+] = 2.2 \times 10^{-5}\ \text{M}$$

$$\text{pH} = -\log(2.2 \times 10^{-5}) = 4.66$$

Experiment 2.1



The Buffer Action of Solutions

Objective: To investigate the buffer action of CH_3COOH/CH_3COONa.

Apparatus: 20 mL test tubes, droppers, beakers and pH meter.

Chemicals: CH_3COOH, CH_3COONa, distilled water, 0.01 M HCl, universal indicator, 0.010 M NaOH.

Procedure:

1. Mix 5 mL of 0.10 M CH_3COONa with 5 mL of 0.10 M CH_3COOH in a 200 mL test tube. In a second test tube add 100 mL of distilled (or *de-ionized*) water. Add 5 drops of universal indicator to each sample and estimate pH.
2. Add 5 mL of 0.010 M HCl to each test tube, estimate pH, and record each pH change. If universal indicator is not available, add 2 drops of methyl orange indicator to each and record the volume (*drops*) of 0.10 M HCl to reach its end-point.
3. Again prepare a solution in step 1. Test the buffering capacity of each with 5 mL of 0.010 M NaOH. If universal indicator is not available, add 2 drops of alizarin yellow R and record the volume (*drops*) of 0.010 M NaOH to reach its end-point.

Results and discussion:

a What did you observe from procedure 1?

b What did you observe from procedure 2?

c Give your conclusion on each step.

Exercise 2.10

Calculate the pH:

a of a buffer solution containing 0.1 M acetic acid and a 0.1 M solution of sodium acetate.

b when 1.0 mL of 0.10 M HCl is added to 100 mL of the buffer in (a);

c when 1.0 mL of 0.10 M NaOH is added to 100 mL of the buffer in (a);

d of an unbuffered solution containing 1.8×10^{-5} HCl;

e change of the an unbuffered solution in (d) after adding

  i) 1.0 mL of 0.1 M NaOH to 100 mL of the solution,

  ii) 1.0 mL of 0.10 M HCl to 100 mL of the solution.

2.4 HYDROLYSIS OF SALTS

At the end of this subunit, you will be able to:

- define hydrolysis;
- explain why a salt of weak acid and strong base gives a basic solution;
- explain why a salt of strong acid and weak base gives an acidic solution; and
- explain why salts of weak acids and weak bases give acidic, basic or neutral solutions.

What does salt hydrolysis mean?

The word "hydrolysis' is derived from the Greek words hydro, meaning "water", and lyses, meaning "to split apart". Solutions of salts contain two types of ions, namely cations and anions. The term salt hydrolysis describes the reaction of an anion or a cation of a salt, or both, with water. Depending on the strengths of the parent acids and bases, the cation of a salt can serve as an acid, base or neutral.

2.4.1 Hydrolysis of Salts of Strong Acids and Strong Bases

The anions derived from strong acids are weak conjugate bases and do not undergo hydrolysis. The strong bases are the ionic hydroxides of Group IA and IIA metals. The cations of these metals also do not hydrolyze. For example, sodium chloride, NaCl, is a salt of a strong acid, HCl, and a strong base, NaOH. Since chloride ions, Cl^-, and sodium ions, Na^+, do not hydrolyze, the solution of the salt will be *neutral*. Can you give more examples?

2.4.2 Hydrolysis of Salts of Weak Acids and Strong Bases

Solutions of these salts are basic because the anion of the weak acid is a moderately strong base and can be hydrolyzed as follows.

$$X^- + H_2O \rightarrow HX + OH^-$$

Activity 2.11

Consider Na_2CO_3 and discuss the following :

a What are the 'parents' (*acid* and *base*) of this salt?

b Which ions of the salt can be hydrolyzed?

c What will be the nature of Na_2CO_3 solution? Will it be acidic, basic or neutral?

2.4.3 Hydrolysis of Salts of Strong Acids and Weak Bases

A cation (*the conjugate acid of a weak base*) hydrolyzes as an acid. As in the first case, anions of a strong acid are weak conjugate bases and do not hydrolyze.

Consider the hydrolysis of NH_4Cl. Ammonium ion, NH_4^+, is acidic and reacts with water to produce ammonia and hydronium ions.

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

What will be the pH of the solution of this salt? Is it acidic, basic or neutral?

2.4.4 Hydrolysis of Salts of Weak Acids and Weak Bases

The solution of these salts contain both a strong acid (the cation of the weak base) and a strong base (the anion of the weak acid). Whether the solution of such a salt is acidic, basic or neutral depends on the relative strengths of the acidic cation and the basic anion. If the acid is stronger than the base, the solution is acidic and if the base is stronger than the acid, the solution is basic. If they are of equal strengths, the solution is neutral.

How do you determine the strength of the acid and the base?

Activity 2.12

In the following table you are given K_a and K_b values of some cations and anions, respectively.

Anion	K_b	Cation	K_a
F^-	1.4×10^{-11}	NH_4^+	5.6×10^{-10}
CNS^-	2.0×10^{-5}		
CH_3COO^-	5.6×10^{-10}		

Using the above table, determine whether the solutions of NH_4F, NH_4CNS and CH_3COONH_4 are acidic, basic or neutral. Discuss your results with your classmates.

2.5 ACID–BASE INDICATORS AND TITRATIONS

At the end of this subunit, you will be able to:

- define acid-base indicators;
- write some examples of acid-base indicators;
- suggest a suitable indicator for a given acid-base titration;
- explain the equivalents of acids and bases;
- calculate the normality of a given acidic or basic solution;
- define acid-base titration;
- define end point;
- define equivalence point;
- distinguish between end point and equivalent point; and
- discuss titration curves.

2.5.1 Acid–Base Indicators

How do acid-base indicators change colour?

Acid-base indicators are weak organic acids or weak organic bases that indicate whether a solution is acidic, basic or neutral.

Let us consider a weak organic acid that is denoted by HIn. In order to be effective indicators, HIn, and its conjugate base, In^-, must have different colours. In solution, the acid ionizes as follows:

$$HIn(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + In^-(aq)$$

If the indicator is in sufficiently acidic medium, the equilibrium, according to Le Chatelier's principle, shifts to the left and the predominant colour of the indicator is that of nonionized form (HIn). On the other hand, in a basic medium, the equilibrium shifts to the right and the colour of the solution will be that of the ionized form (In^-).

Since the indicator molecule is a weak acid, the ratio of HIn and In^- is governed by the $[H_3O^+]$ of the test solution.

$$HIn(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + In^-(aq)$$

$$K_{In} = \frac{[H_3O^+][In^-]}{[HIn]}$$

Rearranging this equation gives

$$\frac{[HIn]}{[In^-]} = \frac{[H_3O^+]}{K_{In}}$$

To illustrate how an indicator works, consider an indicator that has a yellow colour in acid form (HIn) and a red colour in basic form (In^-). K_{In} is 1.0×10^{-6}. Thus, we have

$$\frac{[HIn]}{[In^-]} = \frac{[H_3O^+]}{1.0 \times 10^{-6}}$$

The colour we observe in a solution of this indicator depends on the ratio of [HIn] to $[In^-]$. In a solution of pH = 4.0, $[H_3O^+]$ is 1×10^{-4}, so

$$\frac{[HIn]}{[In^-]} = \frac{1.0 \times 10^{-4}}{1.0 \times 10^{-6}} = \frac{100}{1}$$

This means that the concentration on HIn is 100 times that of In^-, and so the solution appears yellow.

A solution having a pH of 5, $[H_3O^+] = 1.0 \times 10^{-5}$

$$\frac{[HIn]}{[In^-]} = \frac{1.0\times10^{-5}}{1.0 \times 10^{-6}} = \frac{10}{1}$$, still appears yellow.

At pH of 6.0, $[H_3O^+]$ is 1×10^{-6}, and $\frac{[HIn]}{[In^-]} = \frac{1.0\times10^{-6}}{1.0 \times 10^{-6}} = \frac{1}{1}$

Equal concentrations of HIn and In^- give the solution an orange colour.

At pH = 7.0, $[H_3O^+]$ is 1×10^{-7}, and $\frac{[HIn]}{[In^-]} = \frac{1.0\times10^{-7}}{1.0\times10^{-6}} = \frac{1}{10}$

Here the concentration of In^- is 10 times that of HIn, and so the solution appears red.

Indicators are used in the laboratory for estimating the pH of a solution and to reveal the equivalence point of a titration. Equivalence point is the point at which stoichiometrically equivalent quantities of an acid and a base have been brought together.

Some common indicators and their colors in acids and in bases are shown in Table 2.5.

Table 2.5 Some common indicators.

Indicator	**Acid Colour**	**Base Colour**	**pH range of Colour change**
Methyl violet	Yellow	Violet	0.0 – 1.6
Methyl orange	Red	Yellow	3.2 – 4.4
Bromcresol green	Yellow	Blue	3.8 – 5.4
Methyl red	Red	Yellow	4.8 – 6.0
Litmus	Red	Blue	5.0 – 8.0
Bromthymol blue	Yellow	Blue	6.0 – 7.6
Thymol blue	Yellow	Blue	8.0 – 9.6
Phenolphthalein	Colorless	Pink	8.2 – 10.0
Thymolphthalein	Colorless	Blue	9.4 – 0.6
Alizarin yellow R	Yellow	Red	10.1 – 12.0

The colour change of phenolphthalein in acidic and basic solutions is shown in Figure 2.2.

a

b

Figure 2.2 The colour changes of phenolphthalein in basic (a) and acidic (b) solutions.

2.5.2 Equivalents of Acids and Bases

Activity 2.13

Disucss the following quesitons in group and write a short report.

1. What is an equivalent of an acid and a base?
2. How does the equivalent mass of an acid and a base obtained?
3. What is the difference between normality and molarity? Discuss this in terms of acid-base reaction and in terms of oxidation-reduction reactions.

According to the definition of normality, the number of equivalents is the normality multiplied by the volume of solution, in litres. If we add enough acid to neutralize a given volume of base, the following equation holds:

$$N_1V_1 = N_2V_2$$

Where N_1 and V_1 refer to the normality, and volume of the acid solution, respectively, and N_2 and V_2 refer to the normality and volume of the base solution, respectively.

Example 2.7

What volume of 2.0 N NaOH is required to neutralize 25.0 mL of 2.70 N H_2SO_4?

Solution:

$$N_1V_1 = N_2V_2$$

$$V_2 = \frac{N_1V_1}{N_2} = \frac{(2.70\ \text{N}\ \ H_2SO_4)(25.0\ \text{mL})}{2.00\ \text{N}\ \ \text{NaOH}} = 33.8\ \text{mL}$$

Example 2.8

What is the number of equivalents in 4.00 mol H_2SO_4, assuming that the H_2SO_4 will react with a base to replace both hydrogen atoms?

Solution:

$$1\ \text{mol}\ H_2SO_4 \quad \rightarrow \quad 2\ \text{equiv}$$

$$4.00\ \text{mol}\ H_2SO_4 \quad \rightarrow \quad ?$$

$$\frac{4.00\ \text{mol}\ H_2SO_4 \times 2\ \text{equiv}}{1.00\ \text{mol}\ H_2SO_4} = 8.00\ \text{equiv}$$

Exercise 2.11

1. What volume of 0.1 N HNO_3 is required to neutralize 50.0 mL of a 0.15 N solution of $Ba(OH)_2$?
2. A solution of H_2SO_4 is made by dissolving 196 g of the acid in enough water to produce a 500.0 mL solution. Determine the normality of the solution.

2.5.3 Acid–Base Titrations

Experiment 2.2

Acid-base Titration

Objective: To find the normality of a given hydrochloric acid solution by titrating against 0.1 N standard sodium hydroxide solution.

Apparatus: 10 mL pipette, burette, 150 mL Erlenmeyer flask, beaker, funnel, burette clamp and metal stand.

Procedure:

1. Clean the burette with distilled water and rinse it with the 0.1 N sodium hydroxide solution; and fix the burette on the burette clamp in vertical position (Figure 2.3).
2. Using a funnel, introduce 0.1 N sodium hydroxide solution into the burette. Allow some of the solution to flow out and make sure that there are no air bubbles in the solution (why?). Record level of the solution, corresponding to the bottom of the meniscus, to the nearest 0.1 mL. Measure exactly 10 mL of hydrochloric acid solution (given) with the help of a10 mL pipette and add it into a clean 150 mL Erlenmeyer flask and add two or three drops of phenolphthalein indicator.

Caution: When you suck hydrochloric acid or any reagent solution, into a pipette, have the maximum caution not to suck it into your mouth.

Titration: First hold the neck of the Erlenmeyer flask with one hand and the stop-cock with the other. As you add the sodium hydroxide solution from the burette, swirl the content of the flask gently and continuously. Add sodium hydroxide solution until the first faint pink colour comes which disappears on swirling. Add more sodium hydroxide drop wise until the pink colour persists for a few seconds. Find the difference between the initial level and the end point level of the burette.

Observations and analysis:

1. Colour change at the end point is from ___________ to __________.
2. What is the volume of sodium hydroxide added at the end point?
3. What is the normality of hydrochloric acid at the end point?
4. What is the similarity and difference between equivalence point and end point level after reaching the end point.

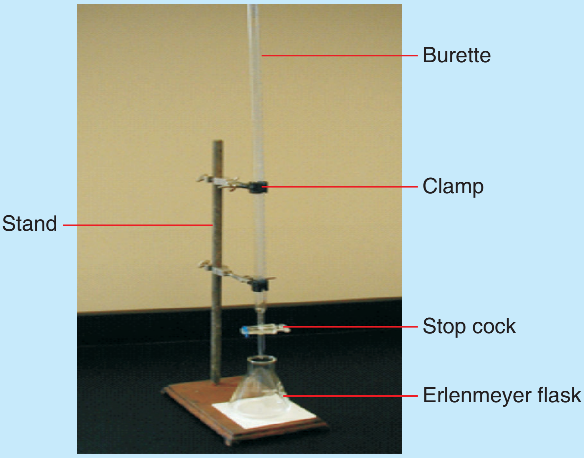


Figure 2.3 Titration Setup.

A titration is a technique in which a solution of known concentration is used to determine the concentration of an unknown solution. Typically, the titrant (the *known solution*) is added from a burette to a known quantity of the analyte (the *unknown solution*) until the neutralization reaction is complete. The point at which the acid has completely reacted with or been neutralized by the base, or vice versa, is called the equivalence point of the titration.

Knowing the volume of titrant added allows the determination of the concentration of the unknown. Often, an indicator is used to signal the end of the reaction, the end point. The end point of titration is the pH at which the indicator changes colour. A graph of pH as a function of the added titrant is called a titration curve. Figure 2.4 shows the technique of titration.

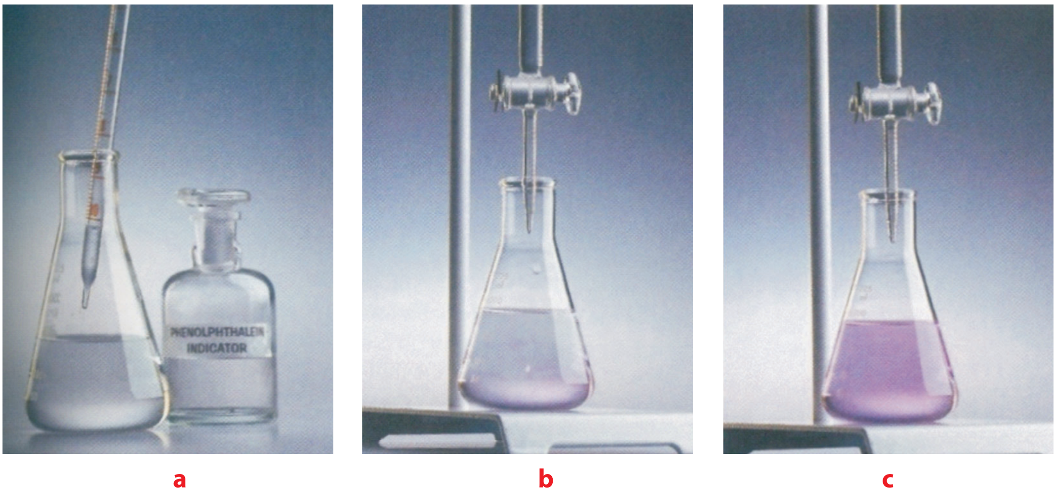


Figure 2.4 The Techinques of Titration.

a A precisely measured volume HCl(aq) is discharged from a pipette into a quantity of water in small flask. Then a few drops of phenolphthalein indicator solution are added. The solution is colourless. What does this indicate?

b NaOH(aq) is slowly added from a burette into the flask. Until all of the HCl has been neutralized, the HCl is in excess and the NaOH is the limiting reactant. The solution remains colourless, indicating that it is still acidic.

c At the point when the acid has just been completely neutralized, which is the equivalence point, HCl and NaOH are in stoichiometric proportions. An additional drop of NaOH(aq) beyond this point makes the solution slightly basic, and the indicator turns to a light pink colour. The titration is stopped, and the volume of solution delivered from the burette is recorded.

To perform a successful titration, we must use an indicator that changes color at the equivalence point.

Strong Acid-Strong Base Titrations

What is the pH of a solution of strong acid-strong base titration at the equivalence point? What are the indicators used in this type of titration?

Take 20 mL of 0.5 M HCl (a strong acid), in a small flask and slowly add 0.5 M NaOH (a strong base) to it. To establish data for a titration curve, we can calculate the pH of the accumulated solution at different points in the titration. Then we can plot these pH values *versus* the volume of NaOH(aq) added. From the titration curve, we can establish the pH at the equivalence point and identify appropriate indicators for the titration. The pH at different points in the titration of 20 mL of 0.5 M HCl with 0.5 M NaOH can be calculated as follows:

a *Before the addition of any NaOH*

Because HCl is a strong acid, it ionizes completely. Therefore, the initial solution has $[H_3O^+] = 0.5$ M

$$\text{pH} = -\log [H_3O^+] = -\log (0.5) = 0.3$$

b *After the addition of 5 mL of 0.5 M NaOH*

The total number of moles of H_3O^+ to be titrated is:

$$0.02\ \cancel{L} \times 0.5\ \text{mol}/\cancel{L} = 0.01\ \text{mol}$$

The number of moles of OH^- in 5 mL of 0.5 M NaOH is:

$$0.005\ \cancel{L} \times 0.5\ \text{mol}/\cancel{L} = 0.0025\ \text{mol}$$

Since 0.0025 moles of NaOH neutralizes 0.0025 moles of HCl, the number of moles of H_3O^+ ion unneutralized is 0.01 mol – 0.0025 mol = 0.0075 mol.

The total volume is 20 mL + 5 mL = 25 mL = 0.025 L.

Concentration of H_3O^+ unneutralized is:

$$\frac{0.0075\ \text{mol}}{0.025\ \text{L}} = 0.3\ \text{mol/L}$$

$$\text{pH} = -\log 0.3 = 0.52$$

c *pH after the addition of 10.0 mL NaOH*

The moles of H_3O^+ to be titrated is again 0.02 L × 0.5 M = 0.01 mol.

The moles of OH^- added is 0.01 L × 0.5 M = 0.005 mol

Since 0.005 mol OH^- neutralizes 0.005 mol H_3O^+, then the amount of H_3O^+ that remains unneutralized is 0.01 mol – 0.005 mol = 0.005 mol.

The total volume of the solution is 20 mL + 10 mL = 30 mL = 0.03 L.

The concentration of unneutralized H_3O^+ is:

$$\frac{0.005\text{ mol}}{0.030\text{ L}} = 0.17\text{ M}$$

$$\text{pH} = -\log[H_3O^+] = -\log 0.17 = 0.77$$

d *pH after the addition of 15.0 mL NaOH*

The number of mole of H_3O^+ here is also 0.01 mol.

The moles of OH^- ion added is 0.5 M × 0.015 L = 7.5×10^{-3} mol.

7.5×10^{-3} moles OH^- ions neutralizes 7.5×10^{-3} mol H_3O^+ ions.

Then, the amount of H_3O^+ ions that remain unneutralized is:

$$0.01\text{ mol} - 7.5 \times 10^{-3}\text{ mol} = 2.5 \times 10^{-3}\text{ mol}$$

Total volume is 20 mL + 15 mL = 35 mL = 0.035 L

The concentration of H_3O^+ unneutralized is:

$$\frac{2.5\times10^{-3}\text{ mol}}{0.035\text{ L}} = 0.07\text{ M}$$

$$\text{pH} = -\log[H_3O^+] = -\log 0.07 = 1.15$$

e *pH after the addition of 20 mL NaOH*

This is a simple calculation, because it involves a complete-neutralization reaction, and the salt (NaCl) does not undergo hydrolysis. *What do you call this point*?

At this point, $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$

$$\text{pH} = -\log[H_3O^+] = -\log(1.0\times 10^{-7}) = 7$$

f *pH after the addition of 25 mL NaOH*

Do any moles of H_3O^+ remain unneutralized here?

The moles of OH^- ions added is 0.5 M × 0.025 L = 0.0125 mol. Since all the H_3O^+ ions are neutralized, there is only 0.0125 mol OH^-.

The total volume here is 20 mL+ 25 mL = 45 mL = 0.045 L.

Concentration of OH^- is:

$$\frac{0.0125\text{ mol}}{0.045\text{ L}} = 0.28\text{ M}$$

$$pOH = -\log[OH^-] = -\log 0.28 = 0.55$$

$$pH = 14 - 0.55 = 13.45$$

Can you now calculate the pH after the addition of 30 mL of 0.5 M NaOH?

Now you have the data for a titration curve.

Volume of 0.5 M NaOH added (mL)	0.00	5.00	10.00	15.00	20.00	25.00	30
pH	0.30	0.52	0.77	1.15	7.00	13.45	?

Figure 2.5 shows the titration curve of 20.00 mL of 0.5 M HCl by 0.5 M NaOH.

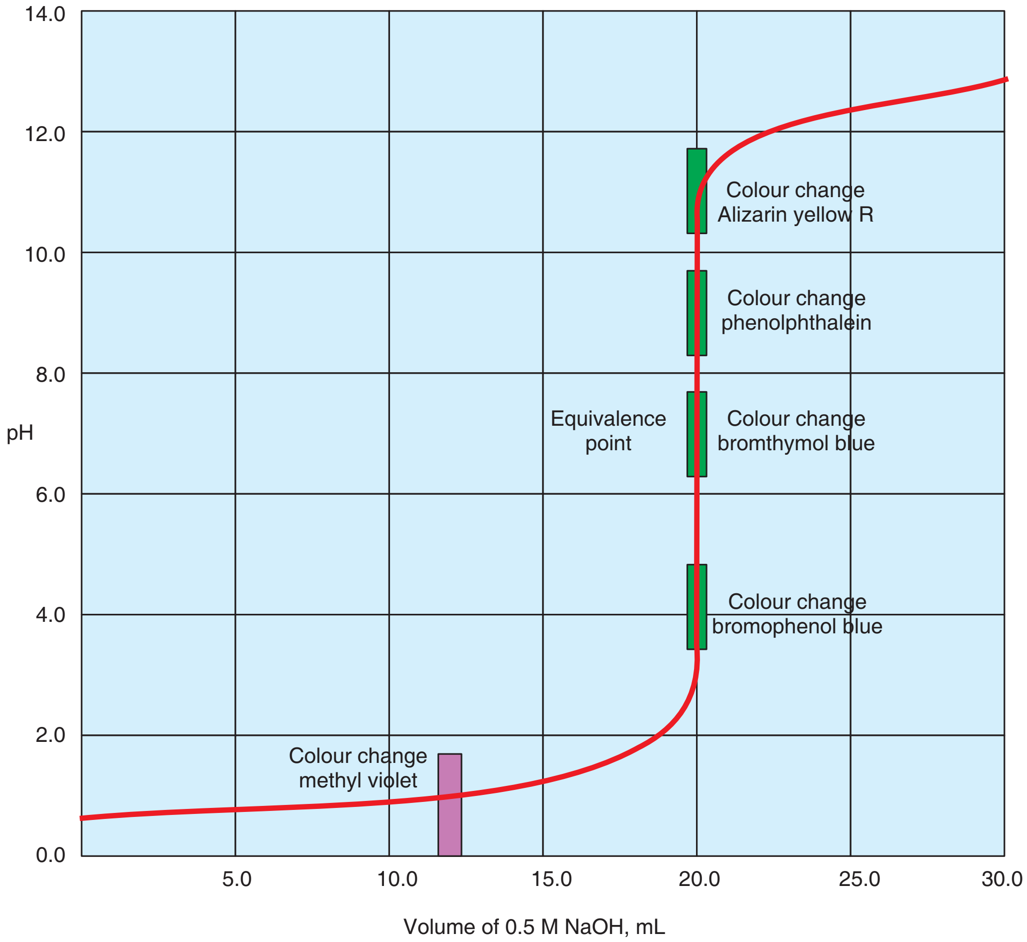


Figure 2.5 Titration curve of 20 mL of 0.5 M HCl by 0.5 M NaOH.

Features of the titration curve for the titration of a strong acid with a strong base.

- The pH is low at the beginning of the titration.
- The pH change slowly until just before the equivalence point.
- Just before the equivalence point, the pH rises sharply.
- At the equivalence point, the pH is 7.00.
- Just past the equivalence point, the pH continues its sharp rise.
- Further beyond the equivalence point, the pH continues to increase, but much less slowly.
- Any indicator whose colour changes in the pH range from about 4 to 10 can be used in the titration of a strong acid with a strong base. Methyl violet changes colour too soon, and alizarin yellow R too late. So, bromthymol blue and phenolphthalein are preferred for this titration.

Exercise 2.12

Calculate the pH when the following quantities of 0.1 M NaOH solution have been added to 50 mL of 0.1 M HCl solution.

a 49.00 mL b 49.90 mL c 50.00 mL d 50.10 mL

Weak Acid-Strong Base Titrations

Can you predict the pH range at the equivalence point?

The titration of a weak acid by a strong base is slightly more complicated than the titration of a strong acid by a strong base. The conjugate base of a weak acid will undergo hydrolysis, which will affect the pH of the solution. Thus, we need to consider the stoichiometric reaction between the acid and the base and the equilibrium reaction of the species that remain.

In contrast to the titration of a strong acid with a strong base, the titration of a weak acid with a strong base, has these features:

- The initial pH is higher because the weak acid is only partially ionized.
- At the half-neutralization, pH = pK_a. The solution at this point is a buffer solution in which the concentration of the weak acid and its conjugate base are equal.
- The pH is greater than 7 at the equivalence point because the anion of the weak acid hydrolyzes.

* The steep portions of the titration curve just prior to and just beyond the equivalence point is confined to a smaller pH range.

* The choice of indicator for the titration is more limited. The color change must occur in a basic solution. Generally, the midpoint of the pH range in which the indicator changes colour must be well above pH 7.

As an example, let us consider the titration of 20 mL of 0.5 M acetic acid, CH_3COOH, with 0.5 M NaOH. To establish data for the titration curve, we calculate the pH at different points in the titration, as follows:

a pH before addition of any NaOH

Here we have only 0.5 M acetic acid, and we calculate the equilibrium concentration of H_3O^+ ions to calculate the pH.

	$CH_3COOH(aq)$ +	$H_2O(l)$ ⇌	$H_3O^+(aq)$ +	$CH_3COO^-(aq)$
Initial, M	0.5		0	0
Change, M	$-x$		$+x$	$+x$
Equilibrium, M	$(0.5 - x)$		x	x

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{x^2}{0.5 - x} = 1.8 \times 10^{-5}$$

We can make the actual assumption, that is $x << 0.5$.

$$K_a = \frac{x^2}{0.5 - x} = 1.8 \times 10^{-5}$$

$$x^2 = 0.5 \times 1.8 \times 10^{-5}$$

$$x^2 = 9.0 \times 10^{-6}$$

$$x = \sqrt{9.0 \times 10^{-6}} = 3.0 \times 10^{-3} = [H_3O^+]$$

$pH = -\log [H_3O^+] = -\log (3.0 \times 10^{-3}) = 2.57$

b pH after the addition of 5.00 mL NaOH

The original number of moles of CH_3COOH is 0.5 M × 0.020 L = 0.01 mol.

The moles of OH^- added is 0.5 M × 0.005 L = 0.0025 mol.

All the OH^- ions have reacted, converting 0.0025 mol CH_3COOH to CH_3COO^-. So, at this point we have 0.0025 mol CH_3COO^- and (0.01 – 0.0025) mol CH_3COOH or 0.0075 mol CH_3COOH.

The total volume of the solution is 20 mL + 5 mL = 25 ml = 0.025 L.

The concentration of CH_3COO^- and CH_3COOH in 0.025 L solution can be calculated as

$$[CH_3COOH] = \frac{0.0075\,\text{mol}}{0.025\text{L}} = 0.3\ \text{M}$$

$$[CH_3COO^-] = \frac{0.0025\,\text{mol}}{0.025\text{L}} = 0.1\ \text{M}$$

	$CH_3COOH(aq)$ +	$H_2O(l)$ ⇌	$CH_3COO^-(aq)$ +	$H_3O^+(aq)$
Initial, M	0.3		0.1	0
Change, M	$-x$		$+x$	$+x$
Equilibrium, M	$0.3 - x$		$0.1 + x$	x

$$K_a = \frac{(0.1+x)x}{0.3-x} = 1.8\times10^{-5}$$

Assuming that x is very small when compared to 0.1 and 0.3, then $0.1 + x = 0.1$, and $0.3 - x = 0.3$, respectively. Thus,

$$1.8\times10^{-5} = \frac{0.1x}{0.3}$$

$$x = \frac{0.3\times1.8\times10^{-5}}{0.1} = 5.4\times10^{-5} = [H_3O^+]$$

$pH = -\log [H_3O^+] = -\log (5.4 \times 10^{-5}) = 4.26$

c pH after the addition of 10 mL of 0.5 M NaOH

Number of moles of the original CH_3COOH = 0.01 mol.

Number of moles of OH^- ions added 0.5 M × 0.01 L = 0.005 mol.

0.005 mol OH^- ions convert 0.005 mol of CH_3COOH to CH_3COO^-. So, at this point, we have 0.005 mol CH_3COO^- and (0.01 – 0.005) mol CH_3COOH or 0.005 mol CH_3COOH.

The total volume of the solution is 20 mL + 10 mL = 30 mL = 0.03 L.

Concentration of CH_3COOH and CH_3COO^- in 0.03 L solution is

$$[CH_3COOH] = \frac{0.005 \text{ mol}}{0.03 \text{L}} = 0.17 \text{ M}$$

$$[CH_3COO^-] = \frac{0.005 \text{ mol}}{0.03 \text{ L}} = 0.17 \text{ M}$$

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

Initial, M	0.17	0.17	0
Change, M	$-x$	$+x$	$+x$
Equilibrium, M	$(0.17-x)$	$(0.17+x)$	x

$$K_a = \frac{(0.17+x)x}{0.17-x} = 1.8 \times 10^{-5}$$

By assuming that x is very small

$$0.17 + x \approx 0.17,\ 0.17 - x \approx 0.17$$

$$1.8 \times 10^{-5} = \frac{(\cancel{0.17})x}{\cancel{0.17}}$$

$$x = 1.8 \times 10^{-5} = [H_3O^+]$$

$$\text{pH} = -\log 1.8 \times 10^{-5} = 4.47$$

d pH, after addition of 20 mL of 0.5 M NaOH

This is the equivalence point. Do you think that the pH at this point equals 7?

Number of moles of OH^- ions added

$$0.5 \text{ M} \times 0.020 \text{ L} = 0.01 \text{ mol}$$

Since 0.01 mol OH^- converts 0.01 mol of CH_3COOH to CH_3COO^-, no more CH_3COOH remains at this point. But now we have 0.01 M CH_3COO^-.

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

Initial, M	0	0	0
Change, M	$-x$	$+x$	$+x$
Equilibrium, M	$(0.01-x)$	x	x

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$5.6 \times 10^{-10} = \frac{x^2}{0.01 - x}$$

Assuming that x is very small, $0.01 - x \approx 0.01$

$$5.6 \times 10^{-10} = \frac{x^2}{0.01}$$

$x^2 = 0.01 \times 5.6 \times 10^{-10} = 5.6 \times 10^{-12}$

$x = \sqrt{5.6 \times 10^{-12}} = 2.37 \times 10^{-6} = [OH^-]$

$pOH = -\log 2.37 \times 10^{-6} = 5.63$

$pH = 14 - 5.63 = 8.37$

e pH after the addition of 25 mL of 0.5 M NaOH

number of mole of OH^- added 0.5 M × 0.025 L = 0.0125 mol

Now the equivalence point is passed, and there is no more CH_3COOH to react with the excess OH^- ion that are added.

The number of moles of OH^- in excess is (0.0125 – 0.01) mol or 0.0025 mol.

Total volume of the solution is 20 mL + 25 mL = 45 mL = 0.045 L

The concentration of the excess OH^- ions is

$$\frac{0.0025\ \text{mol}}{0.045\ \text{L}} = 0.055 = [OH^-]$$

$pOH = -\log [OH^-] = -\log 0.055 = 1.26$

$pH = 14 - 1.26 = 12.74$

Can you calculate the pH after the addition of 30 mL of 0.5 M NaOH?

From the volume of NaOH added and the pH values calculated, you can tabulate as follows:

Volume of NaOH added (mL)	0.00	5.00	10.00	20.00	25.00	30.00
pH	2.57	4.26	4.47	8.37	12.74	?

Figure 2.6 shows the titration curve for 20.00 mL of 0.5 M CH_3COOH by 0.5 M NaOH.

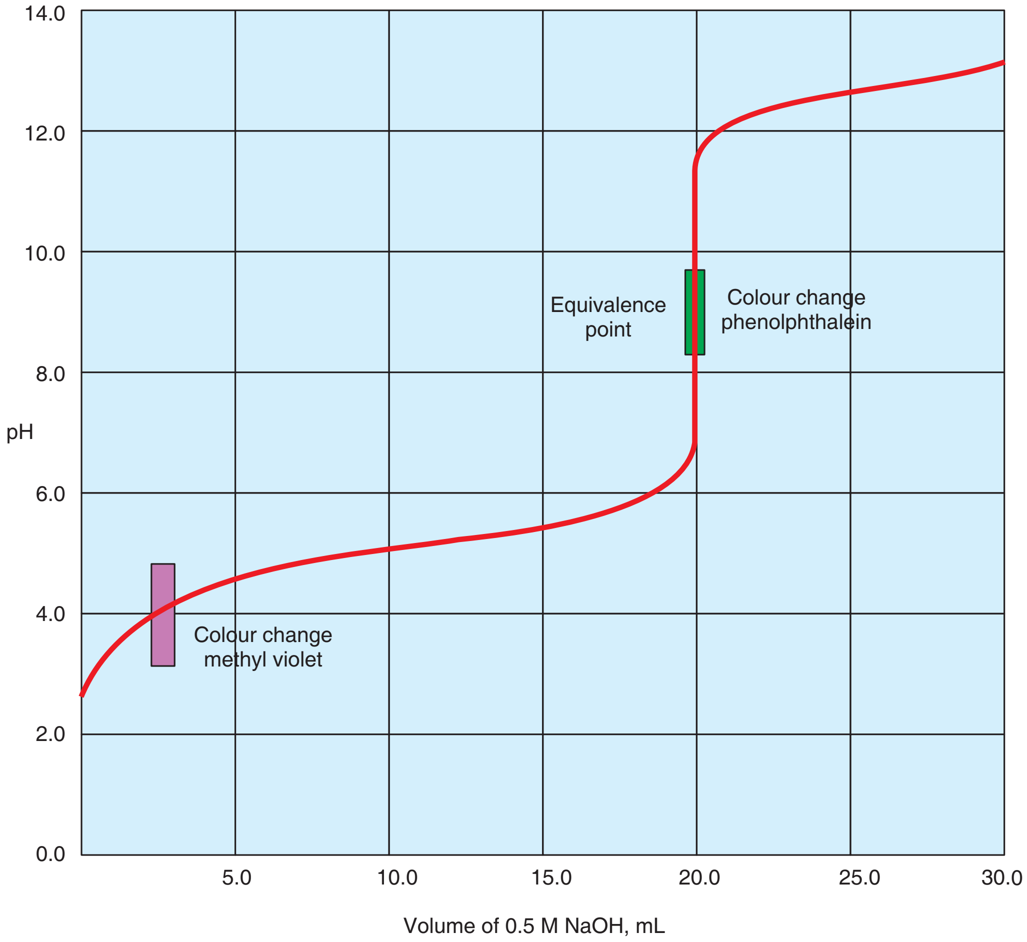


Figure 2.6 Titration curve of 20.00 mL of 0.5 M CH_3COOH by 0.5 M NaOH.

Exercise 2.13

Calculate the pH when the following quantities of 0.1 M NaOH solution have been added to 25.0 mL of 0.1 M acetic acid:

a 10.00 mL
b 25.00 mL
c 35.00 mL

Weak Base-Strong Acid Titrations

How does the titration curve of a weak base with a strong acid differ from the titration curves you have seen so far? What is the pH at equivalence point?

Consider the titration of ammonia, NH_3, with a strong acid, HCl.

$$HCl\,(aq) \quad + \quad NH_3\,(aq) \quad \rightarrow \quad NH_4Cl\,(aq)$$

or simply

$$H^+\,(aq) \quad + \quad NH_3\,(aq) \quad \rightarrow \quad NH_4^+\,(aq)$$

The pH at the equivalence point is less than 7. Why?

Activity 2.14

A 25.0 mL sample of 0.1 M NH_3 is titrated with 0.1 M HCl.

a Calculate the pH values of the solution after the following volumes of 0.1 M HCl are added. 0.00 mL, 5.00 mL, 10.00 mL, 15.00 mL, 20.00 mL, 22.00 mL, 24.00 mL, 25.00 mL and 26.00 mL.

b Draw a table and put the pH values corresponding to each volume in the table.

c Draw the titration curve.

d Name the appropriate indicator for this titration.

Unit Summary

- *The classical (Arrhenius) definition of acids and bases has many limitations but still we cannot ignore it.*
- *The Brønsted-Lowry definition is more general, and considers an acid as a proton donor and a base as a proton acceptor. In this definition, every acid has a conjugate base and every base has a conjugate acid. The stronger the acid, the weaker its conjugate base. Similarly, the stronger a base, the weaker its conjugate acid.*
- *According to Lewis, a base is any species that donates an electron pair, and an acid is any species that accepts an electron pair.*
- *Water spontaneously ionizes to a slight extent (self-ionization or autoionization), forming* H_3O^+*(aq) and* OH^-*(aq). The extent of ionization is expressed by the ion-product constant for water,* K_w.

- *The strength of acids and bases in aqueous solution depends on several factors such as the percent of dissociation, the dissociation constant, the concentration of hydrogen ions and hydroxide ions,* pH *and* pOH.
- *The extent to which a weak acid ionizes can be expressed by using the equilibrium constant for the ionization reaction.*
- *Generally, we can calculate the hydrogen-ion concentration or* pH *of an acid solution at equilibrium, given the initial concentration of the acid and its* K_a *value.*
- *The common-ion effect tends to suppress the ionization of a weak acid or a weak base. This action can be explained by Le Chatelier's principle.*
- *A buffer solution is a combination of either a weak acid and its conjugate base or a weak base and its conjugate acid. The solution reacts in such a way that the* pH *of the solution remains nearly constant. Buffer systems play a vital role in maintaining the* pH *of body fluids.*
- *Acid-base indicators are weak organic acids or bases. They change colour near the equivalence point in an acid-base neutralization reaction.*
- *The* pH *at the equivalence point of an acid-base titration depends on hydrolysis of the salt formed in the neutralization reaction. For strong acid-strong base titrations, the* pH *at the equivalence point is 7. For weak acid strong base titrations, the* pH *at equivalence point is greater than 7. For weak base–strong acid titrations, the* pH *at the equivalence point is less than 7.*

Check List

Key terms of the unit

- *Acid-base titration*
- *Acids*
- *Amphiprotic species*
- *Arrhenius acid-base concept*
- *Autoionization*
- *Bases*
- *Brønsted-Lowry concept of acid and bases*
- *Buffer solution*
- *Common ion effect*
- *Conjugate acid*
- *Conjugate base*
- *Equivalents of acids and bases*
- *Hydrolysis of salts*
- *Lewis concept of acids and bases*
- *percent ionization*
- *pH scale*
- *Solvation*
- *Titration curve*

REVIEW EXERCISE FOR UNIT 2

Part I: Multiple-Choice Questions

1. A Brønsted-Lowry base is defined as a substance that:

   a acts as a proton donor

   b increases $[H^+]$ when placed in water

   c decreases $[H^+]$ when placed in water

   d acts as a proton acceptor

2. Given the reaction

   $HC_2O_4^-(aq) + H_2O\,(l) \rightarrow H_3O^+(aq) + C_2O_4^{2-}(aq)$

   which of the following is a conjugate acid-base pair?

   a $HC_2O_4^-$ and H_2O

   b $HC_2O_4^-$ and H_3O^+

   c H_2O and $C_2O_4^{2-}$

   d $HC_2O_4^-$ and $C_2O_4^{2-}$

3. In the reaction

   $AlCl_3 + Cl^- \rightarrow AlCl_4^-$, $AlCl_3$ acts as a:

   a Salt

   b Lewis base

   c Lewis acid

   d Brønsted base

4. Which of the following is the conjugate base of HCO_3^-?

   a OH^-

   b H_2CO_3

   c CO_3^{2-}

   d HCO_3^+

5. What is the pH of an aqueous solution at 25°C in which $[OH^-]$ is 0.00250 M?

   a 2.60

   b 3.60

   c 11.4

   d 12.4

6. A substance that is capable of acting as both an acid and a base is:

   a amphiprotic

   b conjugated

   c diprotic

   d binary acid-base

7. The magnitude of K_w indicates that:

   a water autoionizes very slowly

   b water autoionizes very quickly

   c water autoionizes only to a very small extent

   d water autoionizes completely

8. When sodium acetate is added to an aqueous solution of acetic acid its pH:

   a increases
   c remains constant
   b decreases
   d may increase or decrease

9. pK_a values of three acids A, B and C, are 4.5, 3.5 and 6.5, respectively. Which of the following represents the correct order of acid strength?

   a $A > B > C$
   c $C > A > B$
   b $B > A > C$
   d $C > B > A$

10. An acid buffer can be prepared by mixing solutions of:

    a sodium chloride and hydrochloric acid
    b sodium borate and boric acid
    c sodium sulfate and sulfuric acid
    d sodium hydroxide and hydrochloric acid

11. Which of the following is not true about strong acid-strong base titration?

    a the pH is low at the beginning of the titration
    b at the equivalence point, the pH is 7.00
    c any indicator whose color changes in the pH range from about 4 to 10 can be used
    d none of the above

12. Which of the following salts will yield a basic solution on dissolution in water?

    a a salt of weak acid and weak base
    b a salt of strong acid and strong base
    c a salt of weak acid and strong base
    d a salt of strong acid and weak base

13. A more generalized acid-base concept is that of:

    a Brønsted and Lowry
    c Lewis
    b Arrhenius
    d none of these

14. Which of the following anions is the weakest base?

    a NO_2^-
    c CH_3COO^-
    b NO_3^-
    d PO_4^{3-}

15. Which of the following buffer solutions has a pH greater than 7?

    a CH_3COOH/CH_3COONa
    b HCOOH/HCOOK

c CH_3COOH/CH_3COONH_4

d NH_4OH/NH_4Cl

Part II: Short Answer Questions

16. Define acid and base according to:

    a Arrhenius concept

    b Brønsted-Lowry concept

    c Lewis concept

17. Given the following species, identify the acids and bases according to the Brønsted-Lowry concept.

    a HNO_3 b OCl^- c NH_2^-

    d NH_4^+ e $CH_3NH_3^+$

18. Write the conjugate acids of the following bases.

    a OH^- b Cl^- c OCl^- d CN^-

    e HCO_3^- f HPO_4^{2-} g HS^-

19. What are the conjugate bases of the following acids?

    a H_2S b $HCOOH$ c HSO_3^- d HSO_4^-

    e HS^- f HNO_2 g HCN

20. Write the equation for the reaction of sulphuric acid and water, and identify the acid, the base, the conjugate acid and the conjugate base.

21. Identify the conjugate acid-base pairs in the following reactions using notation such as acid (1) and base (1)

    a $H_2S(aq) + NH_3(aq) \rightleftharpoons HS^-(aq) + NH_4^+(aq)$

    b $CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$

    c $H_2C_2O_4(aq) + H_2O(l) \rightleftharpoons HC_2O_4^-(aq) + H_3O^+(aq)$

    d $HCO_3^-(aq) + OH^-(aq) \rightleftharpoons CO_2^{3-}(aq) + H_2O(l)$

22. a What is meant by amphiprotic substance?

    b Write an equation for the autoionization of water that demonstrates that water is amphiprotic.

23. Which of the following are amphiprotic?

    a OH^- b NH_3 c H_2O d H_2S

    e NO_3^- f HCO_3^- g CH_3COO^- h HNO_3

24. Rank the base in each of the following groups in order of increasing base strength, and explain the reason for the order you assign.

    a H_2O, OH^-, H^-, Cl^-

    b ClO_4^-, ClO^-, ClO_2^-, ClO_3^-

    c NH_2^-, HS^-, HTe^-, PH_2^-

    d BrO_2^-, ClO_2^-, lO_2^-

25. Which of the following acids are classified as Lewis acids but not as Brønsted-Lowry acids?

    a $HBrO_3$ b $SbCl_3$

    c HSO_4^- d AlF_3

26. Calculate $[OH^-]$ for each of the following solutions:

    a $[H^+] = 0.005$ M

    b $[H^+] = 1.3 \times 10^{-9}$ M

    c A solution in which $[OH^-]$ is 100 times greater than $[H^+]$.

27. Calculate the pH of each of the following:

    a $[H^+] = 3.6 \times 10^{-3}$ M b $[H^+] = 0.047$ M

    c pOH = 5.33 d $[OH^-] = 6.7 \times 10^{-2}$ M

28. What is the pOH of each of the following solutions?

    a 1.0×10^{-2} M NaOH b 0.00520 M $Ba(OH)_2$

    c 0.0068 M LiOH d 3.51×10^{-4} M HCl

29. Hydrogen cyanide, HCN, is a weak acid with a dissociation constant of 4.8×10^{-10}. Calculate the percent dissociation, the pH, and the OH^- concentration of a 0.15 M solution of HCN in water.

30. Calculate the $[OH^-]$ in a 1.0×10^{-3} M solution of the weak base methylamine (CH_3NH_2), whose $K_b = 4.4 \times 10^{-4}$. What percentage of the base has dissociated?

31. A 0.01 M butanoic acid solution is 3.9% dissociated at 298 K. Calculate the K_a value for butanoic acid.

32. a What is meant by the common-ion effect?

    b Give an example of a salt that can decrease the ionization of HCl in solution.

    c Explain why the ionization of a weak acid is suppressed by the presence of its conjugate base.

33. Describe the effect on pH (increase, decrease or no change) that results from each of the following additions.

   a Sodium formate, NaCOOH, to a solution of formic acid, HCOOH.

   b Ammonium perchlorate, NH_4ClO_4, to a solution of ammonia, NH_3.

   c Potassium bromide, KBr, to a solution of potassium nitrite, KNO_2.

   d Hydrochloric acid, HCl, to a solution of sodium acetate, $NaCOOCH_3$.

34. Explain why a mixture of HCl and KCl does not function as a buffer, whereas a mixture of $HC_2H_3O_2$ and $NaC_2H_3O_2$ does.

35. Calculate the pH of the buffer system made up of 0.15 M NH_3/0.35 M NH_4Cl.

36. The pH of a sodium acetate/acetic acid buffer is 4.5. Calculate the ratio of $[CH_3COOH]/[CH_3COO^-]$.

37. A buffer is prepared by adding 20.0 g of acetic acid, CH_3COOH, and 20.0 g of sodium acetate; CH_3COONa, to enough water to form 2.00 L of solution.

   a Determine the pH of the buffer.

   b Write the complete ionic equation for the reaction that occurs when a few drops of hydrochloric acid are added to the buffer.

   c Write the complete ionic equation for the reaction that occurs when a few drops of potassium hydroxide solution are added to the buffer.

38. A buffer is prepared by adding 1.00 g of acetic acid, CH_3COOH, and 1.50 g of sodium acetate, CH_3COONa, to enough water to form a 0.10 L solution.

   a What is the pH of this buffer?

   b What is the pH after the addition of 1.00 mL of a 1.00 M HCl solution?

   c What is the pH after the addition of 1.00 mL of 1.00 M KOH solution?

39. How does the titration of a strong acid with a strong base differ from the titration of a weak acid with a strong base, with respect to the following points?

   a Quantity of base required to reach the equivalence point.

   b pH at the beginning of the titration.

   c pH at the equivalence point.

   d pH after addition of a slight excess of base.

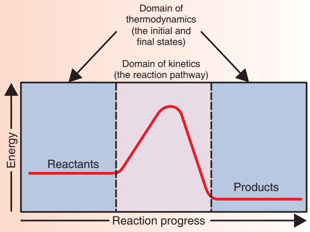
   e Choice of indicator for determining the equivalence point.

40. A 20.0 mL sample of 0.2 M HBr solution is titrated with 0.2 M NaOH solution. Calculate the pH of the solution after the following volumes of the base have been added; draw the titration curve.

   a 15.0 mL b 19.9 mL c 20.0 mL

   d 20.1 mL e 35.0 mL.

UNIT 3



Introduction to Chemical Thermodynamics

Unit Outcomes

After completing this unit, you will be able to:

- *understand the terms system, open system, closed system and isolated system, spontaneous process, state and path function, intensive and extensive property, internal energy, heat and work;*
- *understand the first and second laws of thermodynamics;*
- *compare the energy change observed when chemical bonds are formed and broken, and relate these changes to endothermic and exothermic reactions;*
- *identify ways in which the terms reactant, product, and heat are combined to form thermodynamic equations representing endothermic and exothermic chemical change;*
- *understand concepts such as enthalpy change, entropy change and free-energy changes;*
- *determine the spontaneity of a given reaction; and*
- *demonstrate scientific enquiry skills including: communicating, measuring, applying concepts and asking questions.*

MAIN CONTENTS

3.1 Common Thermodynamic Terms
3.2 The First Law of Thermodynamics and Some Thermodynamic Quantities
3.3 Thermochemistry
3.4 Entropy and the Second Law of Thermodynamics
– *Unit Summary*
– *Review Exercises*

Start-up Activity

Form a group and discuss the following issues:

How do you describe the following in relation to energy? How do they benefit the society? Which of them are widely used in Ethiopia?

1. Fuels such as oil, wood, coal and natural gas.
2. Fertilizers.
3. Plastics, fiber glass and ceramic materials.
4. Solar energy.
5. Hydroelectric power.

Write a short report and present it to the class.

In Grade 11 Chemistry, you learned about chemical kinetics. What are the main concerns of chemical kinetics? How do you relate it to thermodynamics?

Thermodynamics is the study of energy and its transformation. In a chemical reaction, thermodynamics determines whether a reaction is possible and how much product can be formed.

Thermodynamics deals with energy changes and applies to physical as well as chemical changes. However, it does not give any information about the duration of time required for the related processes. ***Which area of chemistry is concerned with that topic?***

Figure 3.1 depicts the concern of chemical kinetics and chemical thermodynamics.

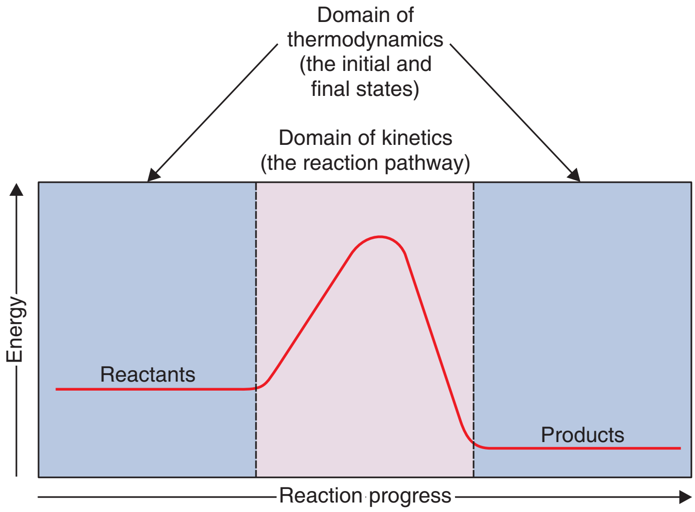


Figure 3.1 Concerns of kinetics and thermodynamics.

Activity 3.1

Read chemistry books and other resource materials, and define the following terms:

a thermodynamics
b system
c surroundings
d isothermal process
e adiabatic process
f state
g equation of state
h heat capacity
i specific heat
j state function
k state variable

Try to explain these terms verbally to your classmates.

3.1 COMMON THERMODYNAMIC TERMS

At the end of this topic, you will be able to:

- define chemical thermodynamics;
- define system;
- give examples of system;
- explain open, closed and isolated systems;
- classify system as open, closed and isolated;

- define state function and path function;
- distinguish between intensive and extensive properties; and
- define spontaneous and non-spontaneous process.

When we study a set of energy changes, we focus our attention on a limited and well-defined part of the universe. In your discussion of Activity 3.1, have you recognized that we are considering systems? A thermodynamic system may be a solution in a beaker, a gas in a cylinder, a reaction vessel, an engine, an electrochemical cell, a biological cell, etc.

What do you call the rest of the universe outside a system? Because energy is neither created nor destroyed, any gain or loss of energy by a system must be accompanied by an equivalent loss or gain of energy in the surroundings.

There are three types of thermodynamic systems based on the boundary between the system and its surroundings.

An open system – is a system that can exchange mass and energy, usually in the form of heat, with its surroundings.

For example, an open system may consist of a quantity of water in an open container, as shown in Figure 3.2 a.

A closed system – is a system which transfers energy, but not mass across its boundary with its surroundings. If you close the flask, as in Figure 3.2 b, so that no water vapor can escape from or condense into the container, you create a closed system.

An isolated system – is a system in which neither the transfer of mass nor that of energy takes place across its boundary with the surroundings. By placing the water in a totally insulated container, as shown in Figure 3.2 c, we construct an isolated system.

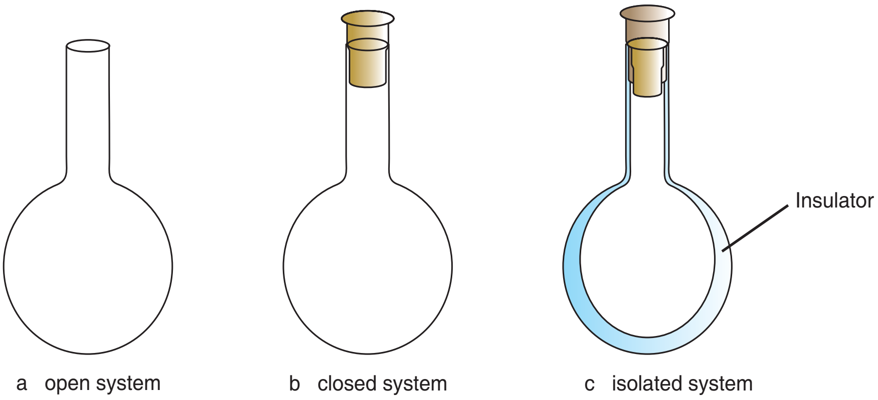


Figure 3.2 The three classes of system.

A system is said to be in a certain state if T, P, V, n (*observable variables*) do not change with time. An equation that relates these observable variables is called an equation of state. An ideal-gas equation is an example of equation of state. A thermodynamic function (*expressed in quantity*) that depends on the initial and final state of a system, regardless of how that condition was achieved, is called a *state function*. Examples are energy, volume, pressure, etc. Functions that depend on the path are *path functions*. Examples are heat, work, etc.

The properties of a system can be intensive or extensive based on its dependence on amount of a substance.

Intensive properties are those that do not depend on the amount of matter present. Some examples include colour, temperature and density.

Extensive properties are those properties, that depend on the amount of matter, for example, mass, internal energy, volume, and pressure.

Activity 3.2

In your group list properties of a system you know. Classify them as intensive or extensive. Record your conclusions by coping and filling out the following table. Follow the example that is given in the first line of the tabulation.

Properties	Intensive	Extensive
Colour	✓	

A spontaneous process is a process that occurs without external influence. Once started, requires no action from outside in order to continue. On the other hand, a non-spontaneous process will not occur unless some external action is continuously applied.

A rock that is rolling down from the top of a hill continues to roll down. Heat flows from an object of high temperature to an object of low temperature. Iron rusts in moist air. Each of these processes occurs spontaneously, without requiring an outside force or agency. If these processes were to go in the opposite direction, they would be non spontaneous. ***Can you mention some other examples of spontaneous and nonspontaneous processes you encounter in your daily life?***

An isothermal process is a process in which temperature remains constant, $\Delta T = 0$. This typically occurs when a system in contact with an outside thermal reservoir (*heat bath*), and the change occurs slowly enough to allow the system to continually adjust to the temperature of the reservoir through heat exchange.

An alternative special case in which a system exchanges no heat with the surroundings ($\Delta q = 0$) is called an adiabatic process. In an isothermal process, the value of $\Delta T = 0$ but $\Delta q \neq 0$, while in an adiabatic process, $\Delta T \neq 0$ but $\Delta q = 0$.

3.2 THE FIRST LAW OF THERMODYNAMICS AND SOME THERMODYNAMIC QUANTITIES

At the end of this topic, you will be able to:

- explain internal energy in relation to the concepts of thermodynamics;
- explain heat in relation to the concepts of thermodynamics;
- explain work in relation to the concepts of thermodynamics;
- state the first law of thermodynamics;
- explain the first law of thermodynamics; and
- calculate the change in the internal energy of a system based on a given information.

3.2.1 Internal Energy (E)

Activity 3.3

If you have pumped air into a bicycle tyre, you probably noticed a warming effect in the valve stem. Discuss in a group from where this heat is originated and write a short report and present to the class.

The internal energy (E) of a system is the total energy contained within a system, partly as kinetic energy and partly as potential energy. When a chemical system changes from reactants to products and the product return to the starting reactant, the internal energy has changed. To determine this change, ΔE, we measure the difference between the systems internal energy after the change (E_{final}) and before the change (E_{initial}).

$$\Delta E = E_{\text{final}} - E_{\text{inital}}$$

The kinetic energy component of internal energy consists of various types of molecular motion and the movement of electrons within molecules.

Potential energy is a factor of:

- attractive and repulsive interaction between molecules;
- attractive interactions between electrons and nuclei within molecules;
- repulsive interactions between electrons within molecules; and
- repulsive interactions between nuclei within molecule.

Activity 3.4

Take ordinary electric bulbs of 100 W, and 150 W; put separate white papers (of equal size and weight) above the bulbs; after noting the initial temperature of the paper, switch the bulbs on. Note the temperature of the papers after 15 minutes and 30 minutes respectively. Do you observe any change in temperature of the papers? Discuss the results with your classmates.

3.2.2 Heat (Q)

Heat (*thermal energy*) is the energy transferred between a system and its surroundings as a result of a difference in their temperatures. Heat passes spontaneously from the region of higher temperature to the region of lower temperature. Heat transfer stops when the system and surroundings reach the same temperature and therefore the system and surroundings are at thermal equilibrium.

Heat and Calorimetry

A chemical reaction or a physical change that releases heat is said to be an exothermic process. The burning of charcoal, for example, is an exothermic process. A reaction or a physical change that absorbs heat is an endothermic process. The melting of ice is an endothermic process, because heat is absorbed when ice melts. The SI unit of heat is joule (J). Another unit of heat is calorie. A calorie (Cal) is the amount of heat, or other energy, necessary to raise the temperature of 1 g of water by 1 degree Celsius. A kilocalorie (kCal) is 1000 calories, and 4.184 Joules is equivalent to 1.0 calorie.

Experimentally, we can determine the heat flow associated with chemical reaction by measuring the temperature change it produces. The measurement of heat flow is called calorimetry. An apparatus that measures heat is called a calorimeter.

The temperature change experienced by an object when it absorbs a certain amount of energy is determined by its heat capacity. Heat capacity is defined as the amount of heat energy required to raise its temperature by 1° (or 1 K). For pure substances, heat capacity is usually given for a specified amount of the substance. The heat capacity of 1 mol of a substance is called its molar heat capacity. In all thermodynamic calculations temperature must be expressed in Kelvin (K).

The heat capacity of 1g of a substance is called its specific heat. Specific heat of a substance can be determined experimentally by measuring the temperature change (ΔT) for a known mass (m) of a substance that gains or loses a specific quantity of heat, q.

$$\text{Specific heat} = \frac{\text{quantity of heat transferred}}{(\text{ grams of substance })\times(\text{temperature change})}$$

$$= \frac{q}{m \times \Delta T}$$

Table 3.1 shows the specific heat of some common substances.

Table 3.1 The specific heat of some common substances.

Substance	Specific heat $[Jg^{-1}K^{-1}]$
Aluminum, Al (s)	0.90
Gold, Au (s)	0.13
Carbon (*graphite*)	0.72
Carbon (*diamond*)	0.50
Copper, Cu (s)	0.38
Iron, Fe (s)	0.45
Mercury, Hg (l)	0.14
Water, H_2O (l)	4.18
Ethanol, C_2H_5OH (l)	2.46

Example 3.1

A 466 g sample of water is heated from 8.5°C to 74.6°C. Calculate the amount of heat absorbed by the water in kilojoules.

Solution:

We know the quantity of water and the specific heat of water (4.18 J/g.K). On applying the equation:

$$\text{Specific heat} = \frac{q}{m \times \Delta T}$$

$$4.18\,\text{J/g.K} = \frac{q}{466\,\text{g} \times (347.60\,\text{K} - 281.5\,\text{K})}$$

$$q = 4.18\,\text{J/g.K} \times 466\,\text{g} \times 66.1\,\text{K} = 129\,\text{kJ}$$

Exercise 3.1

1. How much heat is required to raise the temperature of 250 g of water from 22°C to near its boiling point, 98°C?
2. What is the molar heat capacity of water?

Activity 3.5

Take 50 mL water in two different beakers; heat one beaker to 10°C above room temperature and cool the other beaker 10°C below room temperature. Note the time taken by both the beakers to attain the room temperature. Discuss the results with your teacher.

3.2.3 Work (*W*)

How do you determine the pressure-volume work of a gas?

Work, like heat, is an energy transferred between a system and its surroundings. There are several types of work, but here we will consider only the pressure-volume work that is done when gases are compressed or expanded.

Suppose we have a gas confined to a cylindrical container that is fitted with a movable piston as shown in Figure 3.3, where F is the force acting on the piston of area A. Since pressure is defined as force per unit area, the pressure of the gas is $P = \frac{F}{A}$.

Work is defined as a force applied over a given distance, so if the piston moves a distance Δh, as shown in Figure 3.3, then the magnitude of the work is

$$\text{Work} = \text{force} \times \text{distance} = F \times \Delta h$$

$$\text{Since } P = \frac{F}{A}, \text{ or } F = P \times A, \text{ then}$$

$$\text{Work} = F \times \Delta h = P \times A \times \Delta h$$

The product of the cross-sectional area of the cylinder, A, and the height, Δh, represents the change in volume of the gas, which is designated by the symbol ΔV. By replacing $A \times \Delta h$ with its equivalent, ΔV, we see that the work associated with a gas that expands at constant pressure is described by the following equation.

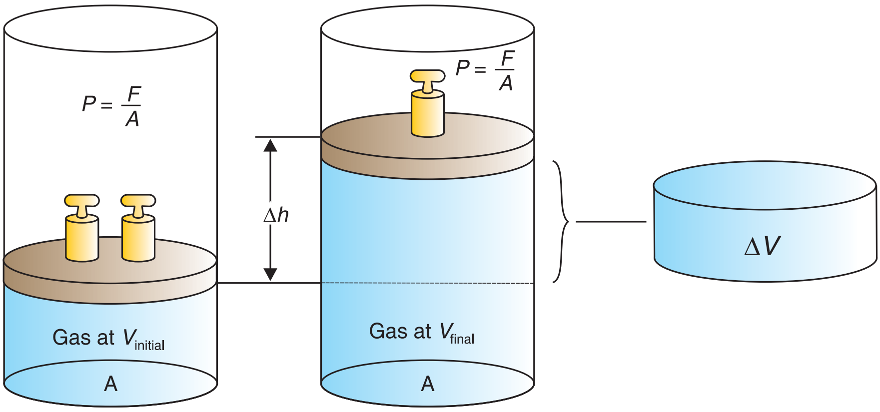
$$\text{Work} = P \times A \times \Delta h = P\Delta V$$

The product of pressure and a change in volume is usually called "pressure-volume" work. When a gas expands, ΔV is positive, and the work is negative.

$$\text{Work } (W) = -P\Delta V$$

A negative quantity of work signifies that the system loses energy, and that this, energy is transferred from the system to the surroundings.

When a gas is compressed by its surroundings, ΔV is negative, the quantity of work is positive and energy is gained by the system.



a Initial state b Final state

Figure 3.3 a The piston, moving a distance Δh against a pressure P, does work on the surroundings.

b Since the volume of a cylinder is the area of the base times its height, the change in volume of the gas (ΔV) is given by $A \times \Delta h$.

Activity 3.6

Observe different types of energy transformations occurring at home and around you, and make a list of these. Discuss the nature and type of transformations with your friends and present your findings in the class.

3.2.4 The First Law of Thermodynamics

What are the concepts studied in the first law of thermodynamics?

The first law of thermodynamics, which is a restatement of the law of conservation of energy, states that the total amount of energy in the universe is constant. When a system undergoes any chemical or physical change, the accompanying change in its internal energy, ΔE, is given by the heat added to the system, q, plus the work done by the system, W.

$$\Delta E = q + W$$

Thermodynamic quantities always consist of two parts:

- a number plus units, which gives the magnitude of the change; and
- a sign that indicates the direction of the flow.

The sign reflects the system's point of view. For example, if a quantity of energy flows into the system as heat, q is equal to $+q$, where the positive sign indicates that the system's energy is increasing. On the other hand, when energy flows out of the system as heat, q equal to $-q$, where the negative sign indicates that the system's energy is decreasing.

This suggests that we need sign conventions to be used with the first law of thermodynamics. The conventions are as follows:

- If heat is absorbed by the system, $q > 0$. If work is done on a system, $W > 0$.
- If heat is given off by a system, $q < 0$. If work is done by a system, $W < 0$.

Example 3.2

A gas does 135 J of work while expanding and at the same time, it absorbs 156 J of heat. What is the change in internal energy?

Solution:

Note that heat is absorbed by the system (a positive quantity, + 156 J) and work is done by the system (a negative quantity, – 135 J). Because more heat is absorbed than work done, the internal energy increases:

$$\Delta E = q + W = (+156\ \text{J}) + (-135\ \text{J}) = +21\ \text{J}$$

Exercise 3.2

1. Calculate ΔE for a process in which the system absorbs 65 J of heat and 12 J of work is done on it by the surroundings.
2. A balloon is inflated to its full extent by heating the air inside it. In the final stages of this process, the volume of the balloon changes from 4.00×10^6 L to 4.50×10^6 L by addition of 1.3×10^8 J of energy as heat. Assuming the balloon expands against a constant pressure of 1.0 atm, calculate ΔE for the process.

3.3 THERMOCHEMISTRY

At the end of this topic, you will be able to:

- define enthalpy change, ΔH;
- derive an expression for the enthalpy change of an ideal gas, based on the first law of thermodynamics;
- calculate enthalpy change for ideal gases, from a given information;
- define standard state;
- define standard molar enthalpy of combustion, ΔH°_{C};
- describe how heats of combustion can be used to estimate the energy available from foods;
- define standard molar enthalpy of formation, ΔH°_{f};
- define standard molar enthalpy of neutralization, ΔH°_{neut};
- carry out an activity to measure standard molar enthalpy of neutralization;
- state Hess's law;
- apply Hess's law to solve problems on enthalpy changes of chemical reactions;
- explain bond energy;
- calculate the bond energies of substances in a given chemical reaction; and
- calculate the standard enthalpy changes of reaction from given enthalpy changes of reactants and products.

Activity 3.7

Form a group and discuss the following questions:

Can water freeze at room temperature; why?

When ice melts at room temperature, the enthalpy decreases or increases? Explain.

Write a short report and present it to the class.

Thermochemistry is the study of energy changes that occur during chemical reactions. Usually we assess these energy changes in terms of losing and gaining energy in a system.

When we warm our cold hands over a campfire, the burning wood gives off energy *as heat* and our hands gain energy, raising their temperature.

3.3.1 Heats of Reactions

In the first law of thermodynamics, you have learned that,

$$\Delta E = q + p\Delta V$$

If a reaction occurs at constant volume, then $\Delta V = 0$ and no pressure-volume work is done. Thus, $\Delta E = (q)_{V.}$ Where the subscript V indicates a constant-volume process.

Constant volume conditions are often inconvenient, and sometimes impossible, to measure.

What is enthalpy?

Most physical and chemical changes, including those in living systems, take place under the constant pressure of the earth's atmosphere. In the laboratory, for example, reactions are generally carried out in containers that are open to the atmosphere, such as beakers and test tubes. For most processes, especially those that do not involve gases, only small amount of work is performed as the system expands or contracts slightly against the pressure of the atmosphere. Thus, most of the energy gained or lost by the system during these processes is in the form of heat. The heat absorbed or released by a system at constant pressure is called enthalpy (H).

Enthalpy is defined as the sum of the internal energy and the pressure-volume product of a system.

$$H = E + PV$$

or $$\Delta H = \Delta E + P\Delta V \text{ (}\textit{at constant pressure}\text{)}$$

$$\Delta E = q - P\Delta V$$

then $$\Delta H = q - P\Delta V + P\Delta V$$

$$\Delta H = (q)_P$$

Thus, the change in enthalpy equals the heat gained or lost at constant pressure.

What is the relationship between ΔH and ΔE?

In case of an ideal gas, we can express change in enthalpy, using the ideal-gas law:

$$PV = nRT$$

$$\Delta H = \Delta E + \Delta(PV)$$

$$\Delta H = \Delta E + \Delta(nRT)$$

If the temperature is constant

$$\Delta H = \Delta E + \Delta nRT$$

or $$\Delta E = \Delta H - \Delta nRT$$

where $\Delta n = \sum n_P - \sum n_R$ of the gaseous substances.

Example 3.3

Calculate the change in enthalpy when 2 moles of CO is converted to 2 moles of CO_2 at 1 atm and 25°C.

$$2CO\ (g) \quad + \quad O_2\ (g) \rightarrow 2CO_2\ (g) \qquad \Delta E = -\ 563.5\ \text{kJ}$$

Solution:

Given T $= 25°C = 298$ K

$\Delta E = -\ 563.5$ kJ

Δn = number of moles of gaseous products – number of moles of gaseous reactants

$= 2 - 3 = -1$

$$R = 0.082\ \frac{\text{L.atm}}{\text{mol.K}} = 8.314\ \text{J/mol.K}$$

$$\begin{aligned}\Delta H &= \Delta E + \Delta nRT \\ &= -\ 563.5\ \text{kJ} + (8.314\text{J}/\cancel{\text{mol}}.\cancel{\text{K}} \times 298\ \cancel{\text{K}} \times -1\ \cancel{\text{mol}}) \\ &= -\ 563.5\ \text{kJ} - (8.314 \times 298)\ \text{J} \\ &= -\ 563.5\ \text{kJ} - 2477.6\ \text{J} \\ &= -\ 563.5\ \text{kJ} - 2.5\ \text{kJ} \\ &= -\ 566.0\ \text{kJ}\end{aligned}$$

Is there a significant difference between the values of ΔH and ΔE?

Note that if a physical process or reaction occurs under constant-volume conditions, then the heat change, $(q)_V$, is equal to ΔE. On the other hand, when a physical process or reaction is carried out at constant pressure, the heat change, $(q)_P$, is equal to ΔH.

Consider the combustion of methane:

$$CH_4(g) \quad + \quad 2O_2(g) \rightarrow CO_2(g) \quad + \quad 2H_2O(l); \qquad \Delta H^\circ_C = -890.3\,\text{kJ}$$

We say that the enthalpy change in the combustion of 1 mol $CH_4(g)$ at 25°C is 890.3 kJ. The negative value of ΔH shows that the combustion of methane at constant pressure is an exothermic reaction.

Some Properties of Enthalpy

1. Enthalpy is an extensive property. The enthalpy of a system depends on the quantities of substances present. Consider the formation of ammonia from nitrogen and hydrogen;

   $1/2N_2(g) + 3/2H_2(g) \rightleftharpoons NH_3(g); \qquad \Delta H_f = -45.9 \text{ kJ/mol}$

   It is found experimentally that –45.9 kJ of heat is produced when 1/2 mole of nitrogen reacts with 3/2 moles of hydrogen to produce 1 mole of ammonia at constant pressure system.

   1 mole of nitrogen reacts with 3 moles of hydrogen to form 2 moles of NH_3 and – 91.8 kJ of heat is produced.

2. The enthalpy change for a reaction is equal in magnitude but opposite in sign to ΔH for the reverse reaction. For example, if we assume for the reverse reaction of the formation of ammonia (forward reaction for decompostion of ammonia):

   $NH_3(g) \rightleftharpoons 1/2N_2(g) + 3/2H_2(g); \qquad \Delta H_r = +45.9 \text{ kJ/mol}$

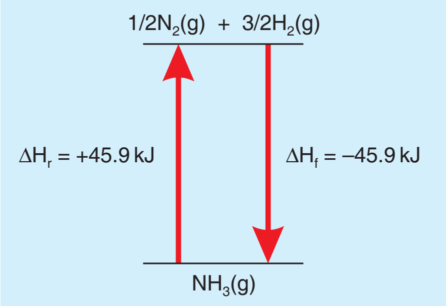


Figure 3.4 Reversing a reaction changes the sign but not the magnitude of the enthalpy change: $\Delta H_r = -\Delta H_f$.

3. The enthalpy change for a reaction depends on the state of the reactants and the products. If the product in the combustion of methane were gaseous H_2O instead of liquid H_2O, ΔH would be – 802 kJ instead of – 890.3 kJ. This is due to the absorption of 88 kJ of heat when 2 mol of liquid water is changed to gaseous water.

   $2H_2O(l) \rightarrow 2H_2O(g); \qquad \Delta H = +88 \text{ kJ}$

Therefore, the states of the reactants and products must be specified.

3.3.2 Standard States

Is there any difference between standard states of ideal gases and standard states of thermodynamic properties?

The standard state for a substance is the most stable form at temperature of 25°C and at atmospheric pressure of 1 atm. We can define the standard enthalpy of combustion, ΔH°_C, as the change in enthalpy that accompanies the combustion of 1 mole of a substance in oxygen at standard conditions. Most chemical reactions that produce heat are combustion reactions. The food we eat is combusted in our bodies in order to give us energy. Most of the energy our bodies need comes from carbohydrates and fats. Carbohydrates are decomposed in the intestines into glucose, $C_6H_{12}O_6$.

Glucose is soluble in blood and is known as blood sugar. It is transported by the blood to cells, where it reacts with O_2 in a series of steps, eventually producing $CO_2(g)$, $H_2O(l)$, and energy.

$$C_6H_{12}O_6(s) \quad + \quad 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l); \qquad \Delta H^\circ_C = -2816\,\text{kJ}$$

The breakdown of carbohydrates is rapid, so their energy is quickly supplied to the body.

Standard Enthalpies of Formation

The standard enthalpy of formation, ΔH°_f, is the change in enthalpy in the reaction when one mole of a substance is formed from the elements in their standard states. By definition, the standard enthalpy of formation of the most stable form of any element is zero.

Table 3.2 Standard enthalpies of formation, ΔH°_f, of some substances at 25°C.

Substance	Formula	ΔH°_f (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7
Ammonia	$NH_3(g)$	– 46.11
Benzene	$C_6H_6(l)$	48.99
Calcium carbonate	$CaCO_3(s)$	– 1207.1
Calcium oxide	CaO(s)	– 635.5
Carbon dioxide	$CO_2(g)$	– 393.5
Diamond	C(s)	1.88
Ethane	$C_2H_6(g)$	– 84.68
Ethanol	$C_2H_5OH(l)$	– 277.7
Ethylene	$C_2H_4(g)$	52.26
Glucose	$C_6H_{12}O_6(s)$	– 1260

Substance	Formula	ΔH_f° (kJ/mol)
Hydrogen bromide	HBr(g)	– 36.23
Hydrogen chloride	HCl(g)	– 92.30
Hydrogen fluoride	HF(g)	– 271.1
Hydrogen iodide	HI(g)	26.48
Methane	$CH_4(g)$	– 74.85
Methanol	$CH_3OH(l)$	– 238.6
Nitric oxide	NO(g)	90.25
Nitrous oxide	$N_2O(g)$	82.05
Nitrogen dioxide	$NO_2(g)$	33.18
Propane	$C_3H_8(g)$	– 103.85
Silver chloride	AgCl(s)	– 127.0
Sodium bicarbonate	$NaHCO_3(s)$	– 947.7
Sodium carbonate	$Na_2CO_3(s)$	– 1130.9
Sodium chloride	NaCl(s)	– 441.0
Sulfur dioxide	$SO_2(g)$	– 296.8
Sulfur trioxide	$SO_3(g)$	– 395.7
Water	$H_2O(l)$	– 285.8
Water vapor	$H_2O(g)$	– 241.8

Now let us explore how we can use standard enthalpies of formation to determine standard enthalpy changes of chemical reactions.

We sum the enthalpies of formation of all reaction products, taking care to multiply each molar enthalpy of formation by the coefficient of that substance in a balanced equation. From this, we subtract a similar sum of the enthalpies of formation for the reactants:

$$\Delta H^\circ_{rxn} = \sum n\Delta H^\circ_{f(products)} - \sum m\Delta H^\circ_{f(reactants)}$$

where, n and m are the stoichiometric coefficients of the chemical reaction.

Example 3.4

The standard enthalpies of formation of NH_3, H_2O and NO are –46.2, –241.8 and 90.3 kJ/mol, respectively. Calculate the enthalpy of the reaction:

$$4NH_3\,(g) \;+\; 5O_2\,(g) \rightarrow 6H_2O(l) \;+\; 4NO\,(g)$$

Solution:

The convenient way to begin this kind of calculation is to list ΔH_f° under the formula of each substance in the equation.

$$\begin{array}{ccccccc} 4NH_3\,(g) & + & 5O_2\,(g) & \rightarrow & 6H_2O\,(l) & + & 4NO\,(g) \\ -46.2\text{ kJ} & & 0 & & -241.8\text{ kJ} & & 90.3\text{ kJ} \end{array}$$

Now we can multiply these ΔH_f° values by the numbers of moles given by the coefficients in the equation. In substituting these values into the general equation for ΔH_f°, remember that we must subtract the sum of the terms for the reactants from the sum of the terms for products.

$$\Delta H_{rxn}^\circ = 6\left[\Delta H_f^\circ(H_2O)\right] + 4\left[\Delta H_f^\circ(NO)\right] - 4\left[\Delta H_f^\circ(NH_3)\right] - 5\left[\Delta H_f^\circ(O_2)\right]$$

$$= 6\,(-241.8\text{ kJ/mol}) + 4\,(90.3\text{ kJ/mol}) - 4\,(-46.2\text{ kJ/mol}) - 5\,(0\text{ kJ/mol})$$

$$= -1450.8\text{ kJ} + 361.2\text{ kJ} + 184.8\text{ kJ} - 0$$

$$= -904.8\text{ kJ}$$

Example 3.5

Calculate ΔH° for combustion of propane, C_3H_8, from the ΔH_f° values of the products and reactants.

$$C_3H_8\,(g) + 5O_2\,(g) \rightarrow 3CO_2\,(g) + 4H_2O\,(l)$$

Solution:

As usual, first we list ΔH_f° under the formula of each substance in the equation:

$$\begin{array}{ccccccc} C_3H_8(g) & + & 5O_2(g) & \rightarrow & 3CO_2(g) & + & 4H_2O(l) \\ -103.8\text{ kJ} & & 0 & & -393.5\text{ kJ} & & -285.8\text{ kJ} \end{array}$$

$$\Delta H_{rxn} = 3(-393.5\text{ kJ/mol}) + 4\,(-285.8\text{ kJ/mol}) - (-103.8\text{ kJ/mol}) - 5(0)$$

$$= (-2324) - (-103.8)$$

$$= -2220\text{ kJ}$$

Exercise 3.3

1. Using the standard enthalpies of formations given in Table 3.2, calculate the ΔH° for the reaction:

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l)$$

2. Compare the quantity of heat produced by combustion of 1.00 g of propane, C_3H_8, with that produced by 1.00 g of benzene, C_6H_6. (*Hint: refer to* Example 3.5, *above*).

The standard molar enthalpy of neutralization is the change in enthalpy, ΔH_{neut}, when one mole of an acid or a base is completely neutralized. For example, the heat of neutralization for

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l) \quad \Delta H_{neut} = -56.2 \text{ kJ/mol}$$

Example 3.6

1.00×10^2 mL of 0.5 M HCl was mixed with 1.00×10^2 mL of 0.5 M NaOH. The initial temperature of the HCl and NaOH solution was the same, i.e., 22.5°C, and the final temperature of the mixed solution was 25.86°C. Calculate the heat change for the neutralization reaction on a molar basis.

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

Assume that the densities and specific heats of the solutions are the same as for water (1.00 g/mL, and 4.184 J/g°C, respectively)

Solution:

Assuming no heat lost to the surroundings, $q_{sys} = q_{soln} + q_{rxn} = 0$, so $q_{rxn} = -q_{soln}$, where q_{soln} is the heat absorbed by the combined solution. Because the density of the solution is 1.00 g/mL, the mass of a 100 mL solution is 100 g. Thus

$$\text{Specific heat} = \frac{q}{m \times \Delta T}$$

$$\begin{aligned} q_{soln} &= m \times C\Delta T \\ &= (1.00 \times 10^2\text{ g} + 1.00 \times 10^2\text{ g})(4.184\text{ J/g°C})(25.86\text{°C} - 22.50\text{°C}) \\ &= 2.81 \times 10^3\text{ J} = 2.81\text{ kJ} \end{aligned}$$

Because $q_{rxn} = -q_{soln}$, $q_{rxn} = -2.81\text{kJ}$

The number of moles of both HCl and NaOH in 1.00×10^2 mL solution is:

$$\frac{0.5\text{ mol}}{1\text{ L}} \times 0.1\text{ L} = 0.05\text{ mol}$$

Therefore, the heat of neutralization when 1.00 moles of HCl react with 1.00 moles of NaOH is $-\dfrac{2.81\text{kJ}}{0.05\text{mol}} = -56.2\text{kJ/mol}$

Exercise 3.4

2.00×10^2 mL of 0.862 M HCl is mixed with 2.00×10^2 mL of 0.431 M $Ba(OH)_2$ in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of the HCl and $Ba(OH)_2$ solution is the same, at 20.48°C.

For the process

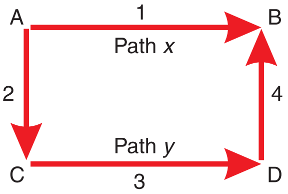
$$H^+(aq) \quad + \quad OH^-(aq) \rightarrow H_2O(l)$$

the heat of neutralization is –56.2 kJ/mol. What is the final temperature of the mixed solution?

3.3.3 Hess's Law

Hess's law states that if different processes are used to bring about the same change the enthalpy changes during these processes are the same.

Consider the following cycle, in which Path x from step $A \rightarrow B$, represents one process, and path y represents second process through three steps: $A \rightarrow C$, $C \rightarrow D$, and $D \rightarrow B$. Both paths result in the same change.



$$\Delta H_1 = H_B - H_A$$

If we know how to calculate the enthalpy from A to C, from C to D, and from D to B, then we can calculate the enthalpy from A to B for path x. This is possible because enthalpy is a state function. By definition,

$$\Delta H_2 = H_C - H_A$$
$$\Delta H_3 = H_D - H_C$$
$$\Delta H_4 = H_B - H_D$$

According to Hess's Law, if we add up ΔH_2, ΔH_3 and ΔH_4, we get:

$$\Delta H_2 + \Delta H_3 + \Delta H_4 = \left(\cancel{H_C} - H_A\right) + \left(\cancel{H_D} - \cancel{H_C}\right) + \left(H_B - \cancel{H_D}\right) = H_B - H_A = \Delta H_1$$

$$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$$

This shows that the change in the heat of a reaction is constant, whether the reaction is carried out directly in one step or through a number of steps.

To apply Hess's law, you can generally expect to do the following.

Reverse certain equations and change the signs of their ΔH values. Multiply certain quantities and their ΔH values by appropriate factors. The factors may be whole numbers or fractions.

Example 3.7

The enthalpies of combustions, of C to CO_2 and CO to CO_2 are –393.5 kJ/mol and –283.0 kJ/mol, respectively.

1. $C(s) + O_2(g) \rightarrow CO_2(g); \quad \Delta H = -393.5 \text{ kJ}$
2. $CO(g) + 1/2\ O_2(g) \rightarrow CO_2(g); \quad \Delta H = -283.0 \text{ kJ}$

Using these data, calculate the enthalpy of combustion of C to CO.

$$C(s) + 1/2\ O_2(g) \rightarrow CO(g)$$

Solution:

To apply Hess's Law, we need to arrange the above equations, (Equation (1) and equation (*2*)) so that C(s) on the reactant side and CO(g) on the product side of the arrow are the same, as we can see in the target equation.

To do this, we need to reverse *equation* (*2*) so that CO(g) is a product. Remember that when reactions are reversed, the sign of ΔH is also reversed. We arrange the two equations so that they can be added to give the target equation:

$$C(s) + O_2(g) \rightarrow \cancel{CO_2}(g); \quad \Delta H = -393.5 \text{ kJ}$$

$$\cancel{CO_2}(g) \rightarrow CO(g) + 1/2\ O_2(g); \quad \Delta H = 283.0 \text{ kJ}$$

$$C(s) + 1/2O_2(g) \rightarrow CO(g); \quad \Delta H = -110.5 \text{ kJ}$$

Example 3.8

Calculate the enthalpy for the following reaction:

$$C(\textit{graphite}) \rightarrow C(\textit{diamond})$$

Given the data:

1. $C(\textit{graphite}) + O_2(g) \rightarrow CO_2(g); \quad \Delta H = -393.5 \text{ kJ}$
2. $C(\textit{diamond}) + O_2(g) \rightarrow CO_2(g); \quad \Delta H = -395.4 \text{ kJ}$

Solution:

To get the target equation C (graphite) → C (diamond) from equation (1) and (2), we reverse equation (2) and add to equation (1).

$$\mathrm{C\ (graphite)} + \cancel{O_2}\,(g) \rightarrow \cancel{CO_2}\,(g); \qquad \Delta H = -393.5\ \mathrm{kJ}$$

$$CO_2\ \cancel{(g)} \rightarrow \mathrm{C\ (diamond)} + \cancel{O_2}\ (g); \qquad \Delta H = 395.4\ \mathrm{kJ}$$

$$\mathrm{C\ (graphite)} \rightarrow \mathrm{C\ (diamond)}; \qquad \Delta H = 1.9\ \mathrm{kJ}$$

Exercise 3.5

1. From the following enthalpies of reaction:

a $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g); \quad \Delta H = -196\ \mathrm{kJ}$

b $2S(s) + 3O_2(g) \rightarrow 2SO_3(g); \quad \Delta H = -790\ \mathrm{kJ}$

Calculate the enthalpy change for the reaction:

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

2. Calculate ΔH for the reaction:

$$2C(s) + H_2(g) \rightarrow C_2H_2(g)$$

Given the following reactions and their respective enthalpy changes:

a $C_2H_2(g) + 5/2O_2(g) \rightarrow 2CO_2(g) + H_2O(l); \quad \Delta H = -1296.6\ \mathrm{kJ}$

b $C(s) + O_2(g) \rightarrow CO_2(g); \quad \Delta H = -393.5\ \mathrm{kJ}$

c $H_2(g) + 1/2O_2(g) \rightarrow H_2O(l); \quad \Delta H = -285.9\ \mathrm{kJ}$

3.3.4 Bond Energies

Why is bond energy defined only for gases?

Bond energy is the enthalpy required to break a particular bond in 1 mole of gaseous molecules. This energy is generally expressed in kilojoules per mole of bonds (kJ/mol).

It is easy to understand bond-dissociation energy (D) for diatomic molecules because there is only one bond (single, double or triple) per molecule. We can represent bond-dissociation energy as an enthalpy change or a heat of reaction. The enthalpy change for the reverse reaction, which is bond formation, is the negative of the bond-dissociation energy. For example

Bond breaking: $Cl_2\,(g) \rightarrow 2Cl\,(g); \qquad \Delta H = +243\ \mathrm{kJ/mol}$

Bond forming: $2Cl\,(g) \rightarrow Cl_2\,(g)$; $\Delta H = -243$ kJ/mol

Notice that the bond energy is always a positive quantity; energy is always required to break chemical bonds. Conversely, energy is released when a bond forms between two gaseous atoms or molecular fragments. Of course, the greater the bond energy, the stronger the bond.

Calculations Involving Bond Energies

How do we apply bond energies to calculate ΔH?

For chemists, reactions involve the breaking and remaking of bonds. So, we can imagine a process in which we break all the reactant molecules into their respective atoms, and then recombine the atoms in the way we want. In other words the process we follow is:

Gaseous reactants → gaseous atoms → gaseous products

The enthalpy of the reaction is estimated as the total energy required to break the bonds minus the total bond energies of the new bonds formed.

$$\Delta H = \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed})$$

Table 3.3 Average bond energies of some substances (kJ/mol).

Bond	Bond Energy	Bond	Bond Energy
H—H	436	N—H	389
H—F	565	N—N	163
H—Cl	427	N—O	201
H—Br	366	N—F	272
H—I	295	N—Br	243
C—H	413	N—I	159
C—C	348	O—H	463
C—N	305	O—F	190
C—O	358	O—Cl	203
C—F	485	O—I	234
C—Cl	328	F—F	155
C—Br	276	Cl—F	253
C—I	240	Br—Br	193
Multiple bonds			
C=C	614	N=N	418
C≡C	839	N=O	607
C≡N	615	O=O	498
C=O	799	N≡N	945
C≡O	1072		

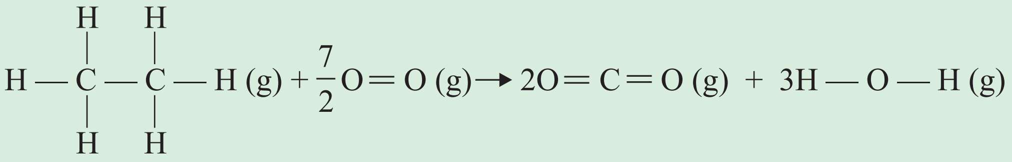
Example 3.9

Estimate ΔH for the following reaction:

$$C_2H_6\,(g) \;+\; \frac{7}{2}O_2\,(g) \rightarrow 2CO_2\,(g) \;+\; 3H_2O\,(g)$$

Solution:

Among the reactants, we must break six C – H bonds and one C – C bond in C_2H_6. We also break $\frac{7}{2}$ O = O bonds. Among the products, we form four C = O bonds (two in each CO_2) and six O – H bonds (two in each H_2O). We may rewrite the equation, using Lewis structures of each substance involved in the reaction.



$$\mathrm{H_3C{-}CH_3}\,(g) + \frac{7}{2}\,\mathrm{O{=}O}\,(g) \longrightarrow 2\,\mathrm{O{=}C{=}O}\,(g) + 3\,\mathrm{H{-}O{-}H}\,(g)$$

$$\Delta H = \left(6(\mathrm{C-H}) + (\mathrm{C-C}) + \frac{7}{2}(\mathrm{O=O})\right) - \left(4(\mathrm{C=O}) + 6(\mathrm{H-O})\right)$$

$$= 6(413\ \mathrm{kJ}) + 348\ \mathrm{kJ/mol} + \frac{7}{2}(498\ \mathrm{kJ/mol}) - 4(799\ \mathrm{kJ/mol}) - 6(463\ \mathrm{kJ/mol})$$

$$= 4558\ \mathrm{kJ/mol} - 5974\ \mathrm{kJ/mol} = -1416\ \mathrm{kJ/mol}$$

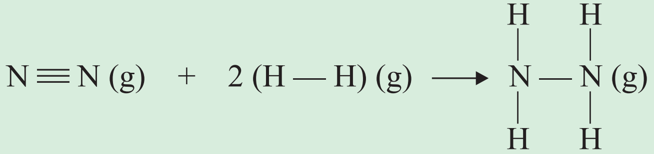
Example 3.10

Estimate the enthalpy of the formation of gaseous hydrazine, $N_2H_4(g)$

$$N_2(g) \;+\; 2H_2(g) \;\rightarrow\; N_2H_4(g)$$

Solution:

To know the bond energies, we need to write a Lewis structure for each substance involved in the reaction.



$$\mathrm{N{\equiv}N}\,(g) \;+\; 2\,(\mathrm{H{-}H})\,(g) \longrightarrow \mathrm{H_2N{-}NH_2}\,(g)$$

$$\Delta H = 945\ \mathrm{kJ} + 2(436\ \mathrm{kJ}) - 4(389\ \mathrm{kJ}) - 163\ \mathrm{kJ}$$

$$= 1818\ \mathrm{kJ} - 1719\ \mathrm{kJ}$$

$$= 99\ \mathrm{kJ}$$

Exercise 3.6

Using bond energies given in Table 3.3, estimate ΔH for each of the following gas-phase reactions.

a $CH_3OH(g) + HBr(g) \rightarrow CH_3Br(g) + H_2O(g)$

b $CO(g) + H_2O(g) \rightarrow H_2(g) + CO_2(g)$

Experiment 3.1

Measuring the standard molar enthalpy of neutralization

Objective: To measure the standard molar enthalpy of the neutralization of sodium hydroxide and hydrochloric acid.

Apparatus: Plastic cup, beaker, thermometer, measuring cylinder, cotton wool.

Chemicals: Sodium hydroxide, hydrochloric acid.

Procedure:

1. Measure 50 mL of 1M NaOH solution and put it in the plastic cup. Measure its initial temperature and record it.
2. Add 50 mL of 1 M HCl to the beaker containing 50 mL of 1 M NaOH and stir the solution with the thermometer. Record the maximum temperature of the mixture.

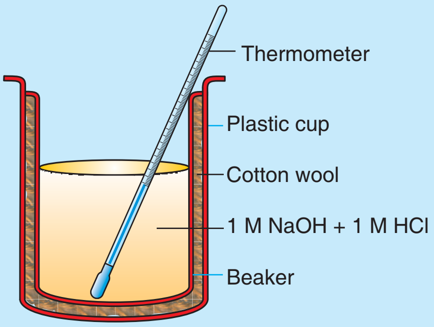


Figure 3.5 Apparatus to measure standard molar enthalpy of neutralization.

3. Record the temperature as follows:

Initial temperature of NaOH ....

Temperature of the mixture of NaOH and HCl ....

Change in temperature, $\Delta T =$ ....

4. The total mass of the solution is 100 g (100 mL), and the specific heat of the solution is ....

   [Given: Specific heat of water = 4.18 J/g.°C]

Observations and analysis:

1. Calculate the heat of neutralization.
2. Is the value obtained for the heat of neutralization larger or smaller than 57.3 kJ? Why?
3. If more acid is added after neutralization, no more rise in temperature will take place. What is the reason?

3.4 ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

At the end of this topic, you will be able to:

- explain entropy and entropy change;
- calculate entropy change, from the given standard entropies of substances;
- state the second law of thermodynamics;
- explain the second law of thermodynamics;
- calculate the entropy changes from the given enthalpy changes of the system and absolute temperature;
- explain free energy and free-energy change;
- calculate the standard free-energy change, $\Delta G°$, from given standard free energies of reactants and products;
- describe the relationship between $\Delta G°$, $\Delta H°$ and S° of a reaction; and
- determine the spontaneity of a given reaction.

3.4.1 Entropy and Spontaneous Process

Activity 3.8

Discuss the following issues in group and present your ideas to the class.

1. Why a ball rolls down a hill but not up?

2. Does this rolling of ball down a hill need any action from outside to occur?
3. List any process that can occur in a system by itself.
4. Decide whether the following become ordered or disordered.
   a Solids melt to liquids.
   b Solids or liquids vaporize to form gases.
   c Solids or liquids dissolve in a solvent to form solutions.
   d A chemical reaction produces more number of molecules of gases.

A spontaneous process (change) is a change in a system that proceeds without any outside influence on the system. For example, when we add solid salt to water, the solid dissolves without any outside influence. The dissolution is spontaneous. Liquid water freezes to ice spontaneously below 0°C; ice melts spontaneously at 25°C. When a solution of an acid is added to a solution of a base, the hydronium ions and hydroxide ions combine spontaneously.

We know well that certain other processes don't occur by themselves. They are said to be non-spontaneous. For example, water does not freeze to form ice at room temperature. The iron oxide of a rusty nail does not revert to iron metal and oxygen gas, solid sodium chloride does not decompose into sodium metal and chloride gas.

A non-spontaneous process is one that cannot take place without outside influence on the system.

The fact that a process is spontaneous does not mean that it will occur at an observable rate. A spontaneous reaction may be very fast, as in the case of acid-base neutralization, or very slow, as in the case of the rusting of iron. Thermodynamics can tell us the direction and extent of a reaction, but it can say nothing about its speed. Which field of chemistry studies the rates of reactions?

What factors make a process spontaneous?

In the previous section, we have seen that the enthalpy change, ΔH, for a process is an important factor in determining whether the process is favorable. Those exothermic processes for which ΔH is very negative are frequently spontaneous. For example, enough heat to melt and ignite the metal may be produced by the spontaneous reaction of sodium with water, and the reaction is exothermic.

$$2Na\ (s) \ + \ 2H_2O\ (l) \ \rightarrow \ 2NaOH\ (s) \ + \ H_2\ (g); \quad \Delta H^\circ_{298} = -281.9\ kJ$$

However, we shall see that considering only the enthalpy change of a process is not enough. The spontaneity of a process also depends on how the disorder of the system changes during the process.

Entropy and Entropy Change

Entropy (S) is the thermodynamic property of a system that is related to its degree of randomness, or disorder. The greater the randomness, or disorder, in a system, the higher is its entropy. Entropy is one of the most important scientific concepts.

The SI unit of entropy is JK^{-1} (Joule per Kelvin), which is the same unit as that of heat capacity. Every substance has entropy as one of its characteristic properties, just as it has colour, hardness, volume, melting point, density and enthalpy. Is entropy an intensive or extensive property?

The entropy change, ΔS, for a chemical change is equal to the sum of the entropies of the products minus the sum of the entropies of the reactants.

$$\Delta S_{rxn} = \sum mS_{(product)} - \sum nS_{(reactant)}$$

where *m* and *n* are the amounts of the individual species represented by their coefficients in the balanced equation. For a reaction,

$aA + bB \rightarrow cC + dD$, the entropy change is

$$\Delta S = \left[(c \times S_C) + (d \times S_D)\right] - \left[(a \times S_A) + (b \times S_B)\right]$$

where S_A is the entropy of A, S_B is the entropy of B, and so on.

* $\Delta S > 0$ indicates an increase in randomness, or disorder, during the change.

* $\Delta S < 0$ indicates a decrease in randomness, or an increase in order.

In Activity 3.8, in which case does the entropy increase? In which case does the entropy have a negative sign?

The difference between the entropy change for a process at 298 K and that same process at some other temperature is generally small and is often ignored. It is common practice to make the approximation that ΔS°_{298} equals ΔS° for the same process.

$$\Delta S^\circ_{rxn} = \sum mS^\circ_{(product)} - \sum nS^\circ_{(reactant)}$$

Example 3.11

Predict whether each of the following leads to an increase or decrease in the entropy.

a $H_2O(l) \rightarrow H_2O(g)$

b $C_{12}H_{22}O_{11}(s) \rightarrow C_{12}H_{22}O_{11}(aq)$

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

d $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

Solution:

a The vaporization of a liquid is accompanied by an increase in volume, because the molecules are distributed throughout a much larger volume in the gaseous state than in the liquid state, an increase in disorder accompanies vaporization, thus producing an increase in entropy.

b Sucrose molecules are highly ordered in the solid state, however they are randomly distributed in aqueous solution. We predict an increase in entropy.

c In this process, the ions that are free to move about the larger volume of the solution form a solid in which the ions are confined to highly ordered positions. Thus there is a decrease in entropy.

d Four moles of gaseous reactants produce two moles of gaseous products. Because two moles of gas in a highly disorganized state of matter are lost, we predict a decrease in entropy.

Exercise 3.7

1. Indicate whether each of the following reactions produces an increase or decrease in the entropy of the system, and predict whether ΔS is positive or negative in each case.
   a $CO_2(s) \rightarrow CO_2(g)$
   b $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$
   c $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$
   d $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$
2. Predict the sign of entropy change for each of the following processes:
   a cooling nitrogen gas from 80°C to 20°C
   b freezing liquid bromine below its melting point
   c evaporating ethanol

3.4.2 The Second Law of Thermodynamics

Activity 3.9

Write a brief paragraph on the following topic and present it to the class.

If the processes of the universe are not at equilibrium, what would be the effect of the solar energy on living things?

The connection between entropy and the spontaneity of a reaction is expressed by the second law of thermodynamics, which states that "*The entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.*" Because the universe is made up of the system and its surroundings, the entropy change in the universe (ΔS_{univ}) for any process is the sum of the entropy changes in the system (ΔS_{sys}) and the surroundings (ΔS_{sur}).

Mathematically, we can express the second law of thermodynamics as follows:

For a spontaneous process: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{sur} > 0$

For an equilibrium process: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{sur} = 0$

For a spontaneous process, the second law says that ΔS_{univ} must be greater than zero, but it does not place a restriction on either ΔS_{sys} or ΔS_{sur}. Thus it is possible for either ΔS_{sys} or ΔS_{sur} to be negative, as long as the sum of these two quantities is greater than zero. For an equilibrium process, ΔS_{univ} is zero. In this case ΔS_{sys} and ΔS_{sur} must be equal in magnitude but opposite in sign.

Free Energy and Free Energy Change

We have seen that the spontaneity of a reaction involves two thermodynamic concepts, enthalpy and entropy. A new quantity that tells us whether a reaction will be spontaneous was first developed by the American mathematician J. Willard Gibbs. He proposed a new state function, now called the Gibbs free energy, or just free energy, designated by G.

The Gibbs free energy, G, is defined as

$$G = H - TS$$

where T is the absolute temperature, S is an entropy and H is an enthalpy.

For a process occurring at constant temperature, the change in free energy is given by the expression

$$\Delta G = \Delta H - T\Delta S$$

The Gibbs free energy change gives an unambiguous prediction of the spontaneity of a chemical reaction run at constant temperature and pressure, because it combines the effect of both ΔH and ΔS. Since temperature, T, has positive value, ΔS determines the sign of $T\Delta S$ terms, and the following can be summarized for $\Delta G = \Delta H - T\Delta S$:

* For a change in which $\Delta H < 0$ and $\Delta S > 0$, the change in Gibbs free energy becomes less than zero ($\Delta G < 0$), and the process is spontaneous.

* If $\Delta H > 0$ and $\Delta S < 0$, the change in Gibbs free energy becomes positive ($\Delta G > 0$), and the process is non-spontaneous.

* If $\Delta H > 0$ and $\Delta S > 0$, ΔG may or may not be negative, but only if $\Delta H < T\Delta S$, $\Delta G < 0$.

* If $\Delta H < 0$ and $\Delta S < 0$, $\Delta G < 0$ if $T\Delta S$ is small. This occurs at small value of temperature.

* If ΔG is zero, the process is at equilibrium and there is no driving force tending to make the reaction go in either direction.

Table 3.4 Criterion for spontaneous change: $\Delta G = \Delta H - T\Delta S$.

Case	ΔH	ΔS	ΔG	Result	Example
1.	–	+	–	Spontaneous at all T	$2O_3(g) \rightarrow 3O_2(g)$
2.	– –	– –	– +	Spontaneous toward low T Non-spontaneous toward high T	$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
3.	+ +	+ +	+ –	Non-spontaneous toward low T Spontaneous toward high T	$2H_2O(g) \rightarrow 2H_2(g) + O_2(g)$
4.	+	–	+	Non-spontaneous at all T	$2C\,(\text{graphite}) + 2H_2(g) \rightarrow C_2H_4(g)$

Activity 3.10

Do the following as a group assignment:

1. Given the following ΔH and ΔS values, determine the temperatures at which these reactions would be spontaneous:

   a $\Delta H = 10.5$ kJ; $\Delta S = 30$ J/K b ΔH = 1.8 kJ; ΔS = 113 J/K

c ΔH = –11.7 kJ; ΔS = –105 J/K

2. Consider the reaction:

$2HI\,(g) \rightarrow H_2\,(g) + I_2\,(g)$

a Is $\Delta S^\circ > 0$, $\Delta S^\circ = 0$ or $\Delta S^\circ < 0$?

b Indicate the sign of ΔG° at high and low temperature, and predict whether the reaction is spontaneous or non-spontaneous

c What is the answer for the questions a and b if the reaction is reversed?

Example 3.12

The reaction of calcium oxide with the pollutant sulfur trioxide has been proposed as one way of removing SO_3 from burning high sulfur coal.

$$CaO(s) + SO_3(g) \rightarrow CaSO_4(s)$$

Using the following ΔH_f° and S_{298}° values, calculate the standard free-energy change for the reaction under standard state conditions and predict whether the reaction is spontaneous or non spontaneous.

$CaO(s)$: $\Delta H_f^\circ = –635.5$ kJ/mol; $S_{298}^\circ = 40$ J/mol K

$SO_3(g)$: $\Delta H_f^\circ = –395.7$ kJ/mol; $S_{298}^\circ = 256.6$ J/mol K

$CaSO_4(s)$; $\Delta H_f^\circ = –1432.7$ kJ/mol; $S_{298}^\circ = 107$ J/mol K

Solution:

We calculate ΔH_{298}° and S_{298}° for the reaction from the data and then calculate ΔG_{298}° from the free energy equation.

$$\Delta H_{298}^\circ = \sum \Delta H^\circ_{f\,(product)} - \sum \Delta H^\circ_{f\,(reactant)}$$

$$= \Delta H_f^\circ\, CaSO_4(s) - \Delta H_f^\circ\, CaO(s) - \Delta H_f^\circ SO_3(g)$$

$$= 1\text{ mol }(–1432.7\text{ kJ/mol}) – 1\text{ mol }(–635.5\text{ kJ/mol}) – 1\text{ mol }(395.7\text{ kJ/mol})$$

$$= –401.5\text{ kJ} = –401{,}500\text{ J}$$

$$\Delta S_{298}^\circ = \sum S^\circ_{(products)} - \sum S^\circ_{(reactants)}$$

$$= S^\circ_{CaSO_4(s)} - S^\circ_{CaO(s)} - S^\circ_{SO_3(g)}$$

$$\Delta S_{298}^\circ = 1\text{ mol }(107\text{ J/mol K}) – 1\text{mol }(40\text{ J/mol K}) – 1\text{mol }(256.6\text{ J/mol K})$$

$$= –189.6\text{ J/K}$$

The free-energy change of a chemical process equals the sum of the free energies of formation of the products minus the sum of the free energies of formation of the reactants.

For the reaction

$$aA + bB \rightarrow cC + dD$$

the free energy change is

$$\Delta G^{\circ}_{298} = \sum \Delta G^{\circ}_{(\text{products})} - \sum \Delta G^{\circ}_{(\text{reactants})}$$

$$= \left[\left(c \times \Delta G^{\circ}_{fC}\right) + \left(d \times \Delta G^{\circ}_{fD}\right) - \left(a \times \Delta G^{\circ}_{fA}\right) - \left(b \times \Delta G^{\circ}_{fB}\right)\right]$$

The standard molar free energy of formation of any free element in its most stable state is zero. So, for the above example,

$$\Delta G^{\circ}_{298} = \Delta H^{\circ}_{298} - T\Delta S^{\circ}_{298}$$

$$= -401{,}500\ \text{J} - (298.15\ \text{K}) \times (-189.6\ \text{J/K})$$

$$= -344{,}971\ \text{J} \approx -345.0\ \text{kJ}$$

Since, ΔG°_{298} is negative, therefore, the reaction will be spontaneous.

Exercise 3.8

Classify each of the following reactions as belonging to the four possible cases summarized in Table 3.4.

1 $N_2(g) + 3F_2(g) \rightarrow 2NF_3(g)$

$\Delta H^{\circ} = -249$ kJ; $\Delta S^{\circ} = -278$ J/K

2 $N_2(g) + 3Cl_2(g) \rightarrow 2NCl_3(g)$

$\Delta H^{\circ} = 460$ kJ; $\Delta S^{\circ} = -275$ J/K

3 $N_2F_4(g) \rightarrow 2NF_2(g)$

$\Delta H^{\circ} = 85$ kJ; $\Delta S^{\circ} = 198$ J/K

4 Calculate the standard free energy change, for the reaction

$$2Ag_2S(s) + 2H_2O(l) \rightarrow 4Ag(s) + 2H_2S(g) + O_2(g)$$

Standard molar free energies of formation of Ag_2S, H_2O and H_2S are -40.7, -237.2 and -33.6 kJ/mol, respectively.

Unit Summary

- *Thermodynamics is the study of heat, work, and energy and the rules that govern their inter-conversion. Among its basic ideas are the notion of a system and its surroundings, the concepts of kinetic energy, potential energy, and the internal energy and the distinction between two types of energy exchanges, heat* (q) *and work* (W).
- *The first law of thermodynamics* (*the law of conservation of energy*) *tells us that the energy is conserved. That is the energy lost by a system equals that gained by its surroundings and vice versa.*
- *Enthalpy change* (ΔH) *can be written into chemical equations and incorporated into conservation factors that relate amounts of substances with quantities of heat released or absorbed in chemical reactions. In an exothermic reaction, enthalpy of the system decreases and heat is given off to the surroundings. In an endothermic reaction, enthalpy increases and heat is absorbed from the surroundings.*
- *The standard enthalpy change,* ΔH°, *and the standard enthalpy of formation* (*heat of formation*), ΔH_f°, *are important thermodynamic quantities. The standard enthalpy of formation of a substance is defined as the enthalpy change for the formation of 1 mole of that substance from the elements, with all reactants and products in their standard states.*

$$\Delta H^\circ_{\text{rxn}} = \sum n\Delta H^\circ_{f\,\text{(products)}} - \sum \text{m}\,\Delta H^\circ_{f\,\text{(reactants)}}$$

- *A spontaneous change in a system occurs by itself without outside intervention. The enthalpy change of a system,* ΔH, *is a measure of the heat change in a process. Exothermic processes* ($\Delta H < 0$) *tend to occur spontaneously. The spontaneous character of a reaction is also determined by the change in randomness or disorder of the system, measured by the entropy,* S. *Processes that produce an increase in randomness or disorder of the system* ($\Delta S > 0$) *tend to occur spontaneously.*
- *The second law of thermodynamics tells us that in any spontaneous process the entropy of the universe increases. That is*

  $$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$
- *The standard entropy change in a system,* ΔS°, *can be calculated from tabulated standard entropy values,* S°, *as follows:*

$$\Delta S^\circ = \sum nS^o_{\text{(products)}} - \sum \text{m}S^o_{\text{(reactants)}}$$

- *The Gibbs free energy, G, is a thermodynamic state function that combines the two state functions enthalpy and entropy:*
- $G = H - TS$. *For processes that occur at constant temperature,*

  $\Delta G = \Delta H - T\Delta S$
- *For a spontaneous process at constant temperature and pressure, ΔG must be negative, that is $\Delta G < 0$. In many cases, the sign of ΔG can be predicted just by knowing the signs of ΔH and ΔS.*
- *The standard free energy change, $\Delta G°$, for any process can be calculated from tabulated standard free energies of formation, ΔG°_f.*

$$\Delta G^\circ = \sum n\Delta G^\circ_{f\,(\text{products})} - \sum m\Delta G^\circ_{f\,(\text{reactants})}$$

Check List

Key terms of the unit

- *Calorie*
- *Calorimeter*
- *Closed system*
- *Endothermic process*
- *Enthalpy*
- *Entropy*
- *Exothermic process*
- *First law of thermodynamics*
- *Free energy change*
- *Gibbs free energy*
- *Heat of reaction*
- *Internal Energy*
- *Open system*
- *Specific heat*
- *Standard state*
- *State function*
- *Surroundings*
- *System*
- *Thermochemistry*
- *Work*

REVIEW EXERCISE ON UNIT 3

Part I: Multiple Choice Questions

1. In themodynamics, a quantity whose value simply depends upon the initial and final state of the system is called:

   a thermodynamic quantity
   c adiabatic quantity
   b state function
   d path funciton

2. All naturally-occurring processes proceed spontaneously in a direction which leads to:
   - a increase in enthalpy of a system
   - b decrease in entropy of a system
   - c decrease in free energy of a system
   - d increase in free energy of a system
3. A system absorbs 20 kJ of heat and also does 10 kJ of work. The net internal energy of the system:
   - a increases by 10 kJ
   - b increases by 30 kJ
   - c decreases by 10 kJ
   - d decreases by 30 kJ
4. A hypothetical reaction $X \rightarrow 2Y$ proceeds by the following sequence of steps:

$$\frac{1}{2}X \rightarrow Z; \quad \Delta H = q_1$$
$$Z \rightarrow 2W; \quad \Delta H = q_2$$
$$W \rightarrow \frac{1}{2}Y; \quad \Delta H = q_3$$

   after applying Hess' law, the value of ΔH for the hypothetical reaction above is:
   - a $q_1 + q_2 + q_3$
   - b $2(q_1 + 2q_2 + 2q_3)$
   - c $2q_1 + 2q_2 + 2q_3$
   - d $2(q_1 + q_2 + 2q_3)$
5. A certain system which can exchange energy but not matter with the surroundings is classified as:
   - a open system
   - b closed system
   - c isolated system
   - d hetrogeneous system
6. A human being requires 2700 kcal of energy per day. If ΔH_C of glucose is –1350 kcal/mol, how many grams of glucose a person has to consume every day:
   - a 360 g
   - b 36.0 g
   - c 3.6 kg
   - d 360 mg
7. In a certain chemical process both ΔH and ΔS have values greater than zero. Under what conditions, the reaction would not be spontaneous?
   - a $\Delta H > T\Delta S$
   - b $\Delta H = T\Delta S$
   - c $T\Delta S - \Delta H > 0$
   - d None

8. A mode of transference of energy involved when petrol undergoes combustion in an internal combustion engine is:

   a heat as well as light

   b heat

   c work as well as heat

   d heat as well as electricity

9. If ΔH°_{CO} and $\Delta H^\circ_{CO_2}$ are –111.3 kJ/mol and –393.5 kJ/mol respectively, the ΔH°_C of CO (g) will be

   a –282.2 kJ   b +282.2 kJ   c 28.2 kJ

   d unpredictable because $\Delta H^\circ_{O_2}$ is not given

10. Which of the following processes involve decrease in the entropy of system?

    a $Br_2(l) \rightarrow Br_2(g)$

    b diamond to graphite

    c $N_2(g)\ (1\,atm) \rightarrow N_2(g)\ (10\,atm)$

    d none

Part II: Short Answer Questions

11. Define the following terms:

    a system

    b surroundings

    c open system

    d closed system

    e isolated system

    f thermochemistry

    g enthalpy

    h entropy

    i thermodynamics

    j adiabatic process

12. a What is work?

    b How do we determine the amount of work done given the magnitude of the associated force?

13. What is the change in internal energy of a system that absorbs 455 J of heat and does 325 J of work?

14. How much heat, in J, is needed to raise the temperature of 324 g of H_2O from 15.3°C to 67.1°C.

15. a What is meant by the term state function?

    b Give an example of a quantity that is a state function and one that is not?

    c Is temperature a sate function? Why?

16. State Hess's law. Explain with one example the usefulness of Hess's law in thermochemistry.

17. A large bed of rocks are used in some solar heated homes to store heat. Calculate the quantity of heat absorbed by 50.0 kg of rocks if their temperature increases by 12.0°C (Assume that the specific heat of the rock is 0.82 J/g.K.

18. a What is the specific heat of water?

    b How many kilojoules of heat are needed to raise the temperature of 2.06 kg of water from 35.14°C to 76.37°C?

19. From the following enthalpies of reaction:

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g) \quad \Delta H = -196 \text{ kJ}$$
$$2S(s) + 3O_2(g) \rightarrow 2SO_3(g) \quad \Delta H = -790 \text{ kJ}$$

Calculate the enthalpy change for the reaction

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

20. Determine the enthalpy change for the oxidation of ammonia

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$$

From the following data

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g); \quad \Delta H = -92.221 \text{ kJ}$$
$$N_2(g) + O_2(g) \rightarrow 2NO(g); \quad \Delta H = +180.5 \text{ kJ}$$
$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l); \quad \Delta H = -571.6 \text{ kJ}$$

21. If a reaction is spontaneous, does this imply that it occurs rapidly? Explain.

22. Rank the three physical states in order of increasing entropies.

23. How does the entropy of the system change when the following processes occur?

    a A solid is melted.

    b A liquid is vaporized.

    c A solid is dissolved in water.

    d A gas is liquidified.

24. Given the following bond energy data:

$N-N$	$\Delta H = 160$ kJ/mol
$N=N$	$\Delta H = 481$ kJ/mol
$N\equiv N$	$\Delta H = 941$ kJ/mol
$F-F$	$\Delta H = 154$ kJ/mol

and the enthalpy change for the reaction $\frac{1}{2}N_2(g) + \frac{3}{2}F_2(g) \rightarrow NF_3(g)$; $\Delta H = -103$ kJ/mol; what is the bond energy for NF_3?

25. Find the temperature at which reactions with the following ΔH and ΔS values would become spontaneous.
    a $\Delta H = -126$ kJ/mol, $\Delta S = 84$ J/K.mol
    b $\Delta H = -117$ kJ/mol, $\Delta S = -105$ J/K.mol

26. Calculate the standard free energy change, $\Delta G°$, for the complete combustion of methane.

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l)$$

The standard free energies of formation for CH_4 (g), CO_2 (g) and H_2O (l) are –51 kJ/mol, –394 kJ/mol and –237 kJ/mol, respectively.

27. From the following heats of combustion,

$$CH_3OH\,(l) + \frac{3}{2}O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O(l); \quad \Delta H° = -726.4\text{ kJ}$$
$$C\,(\text{graphite}) + O_2\,(g) \rightarrow CO_2\,(g); \quad \Delta H° = -393.5\text{ kJ}$$
$$H_2\,(g) + \frac{1}{2}O_2\,(g) \rightarrow H_2O(l); \quad \Delta H° = -285.8\text{ kJ}$$

calculate the enthalpy of formation of methanol (CH_3OH) from its elements.

$$C\,(\text{graphite}) + 2H_2(g) + \frac{1}{2}O_2\,(g) \rightarrow CH_3OH\,(l)$$

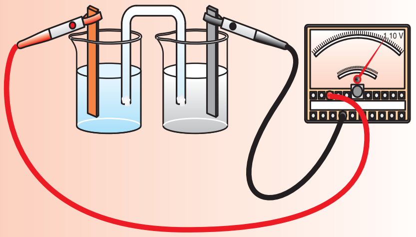
28. From the data given below:

$$S\,(\text{rhombic}) + O_2\,(g) \rightarrow SO_2\,(g) \quad \Delta H° = -296.06\text{ kJ}$$
$$S\,(\text{monoclinic}) + O_2\,(g) \rightarrow SO_2\,(g) \quad \Delta H° = -296.36\text{ kJ}$$

Calculate the enthalpy change for the transformation

$$S\ (\text{rhombic}) \rightarrow S\ (\text{monoclinic})$$

UNIT 4



Electrochemistry

Unit Outcomes

After completing this unit, you will be able to:

- *understand the fundamental concepts related to oxidation-reduction reactions;*
- *know the application of redox reactions in the production of new substances and electrical energy;*
- *demonstrate an understanding of fundamental concepts related to the interconversion of chemical and electrical energy;*
- *understand the difference between metallic conduction and electrolytic conduction;*
- *identify and describe the function of the components of Electrolytic and Galvanic cells;*
- *understand the difference between electrolytic and Galvanic cells;*
- *know how to solve problems based on Faraday's first and second laws;*
- *measure, through experimentation, the mass of the metal deposited by electroplating(example copper to copper (II) sulphate), and apply Faraday's Law to relate the mass of the metal deposited to the amount of charge passed;*
- *predict spontaneity of redox reactions and overall cell potentials by studying a table of half-cell reduction potentials;*
- *determine the emf of an electrochemical cell, experimentally or from given data;*
- *explain the application of electrochemistry in our daily lives and in industry;*
- *explain corrosion as an electrochemical process, and describe corrosion-inhibiting techniques (e.g. painting, galvanizing, cathodic protection);*
- *describe examples of common Galvanic cells and evaluate their environmental and social impact; and*
- *describe scientific enquiry skills: observing, classifying, comparing and contrasting, communicating, asking questions, measuring, relating cause and effect and problem solving.*

MAIN CONTENTS

4.1 OXIDATION-REDUCTION REACTIONS

After completing this subunit, you will be able to:

- define a redox reaction;
- define oxidation, in terms of electron transfer and change in oxidation number;
- define reduction, in terms of electron transfer and change in oxidation number;
- describe the oxidizing and reducing agents;
- identify the species that are oxidized and reduced in a given redox reaction and determine the oxidizing and reducing agents;
- balance a given redox reaction, using the change in oxidation-number method; and
- balance a given redox reaction, using the ion-electron method.

Start-up Activity

Form a group and discuss the following questions,

1. What are oxidation-reduction (redox) reactions?
2. List the redox-reactions taking place in your body, and the surroundings.

After discussion, share your idea with other groups.

4.1.1 Oxidation

When do we say a substance is oxidized?

The term oxidation was originally used to describe reactions in which an element combines with oxygen. For example, the reaction between magnesium and oxygen involves the oxidation of magnesium: $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$. However, nowadays it has a broader meaning that includes reactions not involving only oxygen. Now, oxidation is the loss of electrons and is identified by an increase in oxidation number.

4.1.2 Reduction

When do we say a substance is reduced? Can oxidation occur without reduction and vice versa?

The term reduction was originally used to describe the production of a metal from an ore. The term has been modified through time to include other reactions. Now, reduction is the gain of electrons and is identified by a decrease in oxidation number.

Activity 4.1

In Grade 10 chemistry, you have learnt oxidation-reduction reactions. Form a group. Discuss the following questions and present your answers to the class.

1. Define each of the following terms.
   - a Oxidizing agent
   - b Reducing agent
   - c Oxidation Number
2. What will happen if a zinc rod is immersed in a solution of copper (II) sulphate?
3. Which of the following reactions are redox reactions? Explain your answer for each case.
   - a $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$
   - b $H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$
   - c $Si(s) + 2Cl_2(g) \rightarrow SiCl_4(l)$
   - d $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$
4. Use the given chemical equation to answer the following questions;

   $Mg(s) + Zn^{2+}(aq) \rightarrow Zn(s) + Mg^{2+}(aq)$

   identify the:
   - a oxidized substance.
   - b reduced substance.
   - c oxidizing agent.
   - d reducing agent.
5. Calculate the oxidation number of:
   - a C in $C_2O_4^{2-}$
   - b Cr in K_2CrO_4
   - c N in N_2O_5
   - d S in H_2SO_4
   - e Cl in $HClO_4$

4.1.3 Balancing Oxidation-Reduction (Redox) Reactions

What scientific law is used in balancing chemical equations?

Because atoms are neither created nor destroyed in an ordinary chemical reaction, chemical equation must have an equal number of atoms of each element on the reactant and product sides. In addition, the net electrical charges in the reactant side must be equal to the net electrical charges in the product side.

Balancing Redox Reactions Using Change in Oxidation-Number Method

How do you balance redox reactions, using the change in the oxidation-number method?

In a redox reaction, the total number of electrons gained by the oxidizing agent is equal to the total number of electrons lost by the reducing agent. The change in oxidation number method for balancing redox reaction is based on this fact.

This method is used to balance redox reactions that do not occur in aqueous solutions, and also reactions that do not involve ions.

Use the following steps to balance chemical equations, using the change in oxidation state method.

Step 1: Write an unbalanced chemical equation.

Step 2: Assign oxidation numbers to each atom, and determine which atoms are changing their oxidation numbers.

Step 3: Determine the number of electrons lost by each atom per molecule undergoing oxidation and the number of electrons gained by each atom per molecule being reduced.

Step 4: Balance the number of electrons lost in oxidation with those gained in reduction by adjusting the coefficients of substances being oxidized and reduced.

Step 5: Balance the remaining substances by counting atoms.

Step 6: Check the final equation to be sure that each atom as well as the net charges on either side is balanced.

Example 4.1

Balance the following chemical equation, using the change in oxidation-number method.

$$C + H_2SO_4 \rightarrow CO_2 + SO_2 + H_2O$$

Solution:

Step 1: $C + H_2SO_4 \rightarrow CO_2 + SO_2 + H_2O$

Step 2: $\overset{0}{C} + \overset{+1\,+6\,-2}{H_2SO_4} \longrightarrow \overset{+4\,-2}{CO_2} + \overset{+4\,-2}{SO_2} + \overset{+1\,-2}{H_2O}$

Changes in oxidation number are observed in carbon and sulphur.

Step 3: $\overset{0}{C} + \overset{+6}{H_2SO_4} \longrightarrow \overset{+4}{CO_2} + \overset{+4}{SO_2} + H_2O$

4 electrons lost

2 electrons gained

Step 4: $C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + H_2O$

1 × 4 = 4 electrons lost

2 × 2 = 4 electrons gained

Step 5: Balance hydrogen atoms by making the coefficient of water 2.

$$C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$$

Step 6:

Reactants	Products
C (1)	C (1)
H (4)	H (4)
S (2)	S (2)
O (8)	O (8)

The chemical equation is balanced, because the number of atoms in the reactant side is equal to the number of atoms in the product side. It can also be confirmed that the net charge is zero on each side.

Example 4.2

Balance the following chemical equation by using the change in oxidation-number method.

$$Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$$

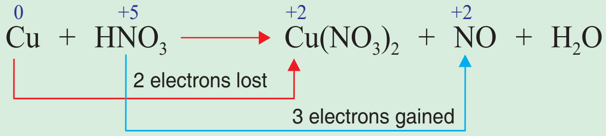
Solution:

Step 1: $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$

Step 2: $\overset{0}{Cu} + \overset{+1+5\,-2}{HNO_3} \longrightarrow \overset{+2\quad +5\,-2}{Cu(NO_3)_2} + \overset{+2\,-2}{NO} + \overset{+1\,-2}{H_2O}$

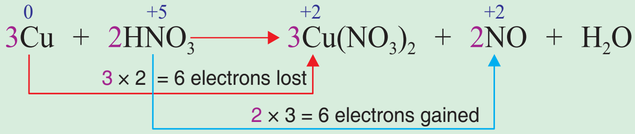
Changes in oxidation number are observed in copper and nitrogen.

Step 3:



$$\overset{0}{Cu} + \overset{+5}{H}NO_3 \rightarrow \overset{+2}{Cu}(NO_3)_2 + \overset{+2}{N}O + H_2O$$

Step 4:



$$3\overset{0}{Cu} + 2\overset{+5}{H}NO_3 \rightarrow 3\overset{+2}{Cu}(NO_3)_2 + 2\overset{+2}{N}O + H_2O$$

In this case, two NO_3^- ions are converted to two NO, but we need six NO_3^- to balance the six NO_3^- ions that are present in three $Cu(NO_3)_2$. Therefore, the coefficient of HNO_3 becomes 8.

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + H_2O$$

Step 5: Hydrogen atoms can be balanced by making the coefficient of water as 4.

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

Step 6:

Reactants	**Products**
Cu (3)	Cu (3)
H (8)	H (8)
N (8)	N (8)
O (24)	O (24)

Is the chemical equation balanced?

Exercise 4.1

Balance each of the following chemical equations, using the change in oxidation number method.

a $Na_2Cr_2O_7 + FeCl_2 + HCl \rightarrow CrCl_3 + NaCl + FeCl_3 + H_2O$

b $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$

c $H_2S + HNO_3 \rightarrow S + NO + H_2O$

d $Cu + H_2SO_4 \rightarrow CuSO_4 + SO_2 + H_2O$

e $P_4 + HNO_3 \rightarrow H_3PO_4 + NO_2 + H_2O$

4.1.4 The Ion-Electron Method for Balancing Redox Reactions

This method is useful if the net ionic equation is given or no spectator ions are present. For example,

$$Na^+(aq)+S^{2-}(aq)+H^+(aq)+Cl^-(aq)+NO_3^-(aq) \rightarrow Na^+(aq)+Cl^-(aq)+S(s)+NO(g)+H_2O(l)$$

In this reaction, $Na^+(aq)$ and $Cl^-(aq)$ ions are spectator ions, because they appear on both the reactant and product sides. Therefore, the net ionic equation becomes:

$$S^{2-}(aq)+H^+(aq)+NO_3^-(aq) \rightarrow NO(g)+S(s)+H_2O(l)$$

Steps for balancing redox reaction using the ion-electron method:

Step 1: Identify the element undergoing oxidation and reduction; write separate equations for oxidation and reduction half-reactions.

Step 2: Balance the element oxidized or reduced.

Step 3: Determine the change in oxidation number of the element oxidized or reduced. Add the electrons gained or lost to the side on which the redox element has the higher oxidation number.

Step 4: Balance any elements other than hydrogen and oxygen that may be present.

Step 5: Balance charges by adding H^+ ions if the solution is acidic and OH^- ions if the solution is basic.

Step 6: Balance hydrogen by adding water molecules.

Step 7: Multiply each half-reaction by appropriate coefficients so that the number of electrons lost in oxidation equals the number of electrons gained in reduction.

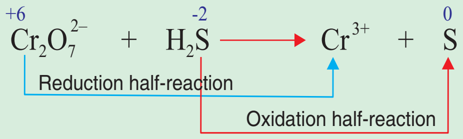
Step 8: Add the two half-reactions together and eliminate anything that appears in identical form on both sides of the equation.

Example 4.3

Balance the following chemical equation using the ion-electron method.

$$Cr_2O_7^{2-} + H_2S \rightarrow Cr^{3+} + S \quad (\textit{in acidic solution})$$

Solution:



Reduction half-reaction

Step 1: $Cr_2O_7^{2-} \rightarrow Cr^{3+}$

Step 2: $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$

Step 3: $Cr_2O_7^{2-} + 6e^- \rightarrow 2Cr^{3+}$

Step 4: There is no element other than oxygen.

Step 5: $Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+}$

Step 6: $Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

Here, the reduction half-reaction is balanced.

Oxidation half-reaction

Step 1: $H_2S \rightarrow S$

Step 2: Sulphur is already balanced.

Step 3: $H_2S \rightarrow S + 2e^-$

Step 4: There is no element other than hydrogen.

Step 5: $H_2S \rightarrow S + 2e^- + 2H^+$

Step 6: Hydrogen is already balanced and the oxidation half-reaction is also balanced.

Step 7: *Oxidation half-reaction*

$(H_2S \rightarrow S + 2e^- + 2H^+) \times 3$

$3H_2S \rightarrow 3S + 6e^- + 6H^+$

Reduction half-reaction

$Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+}$

Step 8: Add the two half-reactions.

$$\begin{array}{r}
3H_2S \rightarrow 3S + \cancel{6e^-} + \cancel{6H^+} \\
Cr_2O_7^{2-} + \cancel{6e^-} + \overset{8}{\cancel{14}}H^+ \rightarrow 2Cr^{3+} + 7H_2O \\
\hline
\end{array}$$

Overall reaction : $Cr_2O_7^{2-} + 3H_2S + 8H^+ \rightarrow 3S + 2Cr^{3+} + 7H_2O$

Exercise 4.2

Balance the following chemical equations, using the ion-electron method.

a $MnO_4^- + SO_3^{2-} \rightarrow Mn^{2+} + SO_4^{2-}$ (*in acidic solution*)

b $Sn^{2+} + Bi^{3+} \rightarrow [Sn(OH)_6]^{2-} + Bi$ (*in basic solution*)

4.2 ELECTROLYSIS OF AQUEOUS SOLUTIONS

After completing this subunit, you will be able to:

- recall the concepts metallic conductivity, electrolytic conductivity and electrolysis of molten electrolytes;
- draw and label diagrams of electrolytic cell ;
- define preferential discharge;
- explain factors that affect preferential discharge;
- describe the effects of nature of ions on the electrolysis of aqueous solutions of dilute H_2SO_4 and NaOH;
- describe the effect of the concentrations of ions on the electrolysis of dilute and concentrated solutions of NaCl;
- describe the effects of types of electrodes on the electrolysis of $CuSO_4$ solution, using Ni and Cu electrodes;
- write the electrode half-reactions and overall reactions for the electrolysis of dilute H_2SO_4, dilute NaOH, dilute NaCl, concentrated NaCl and $CuSO_4$ solutions; and
- distinguish between molten electrolytes and aqueous solutions of electrolytes.

Before we study the electrolysis of aqueous solutions, let us consider some important concepts about conductivity. As you learned in Grade 10 Chemistry, electrical conductivity is the ability of a substance to transmit electricity. Generally, there are two major types of electrical conductors: metallic conductors and electrolytic conductors.

Activity 4.2

Form a group. Discuss the following points and present your answers to the class. Your teacher might help you to form groups.

1. How does conduction occur in metals and in electrolytes?
2. What do substances need in order to conduct electricity?
3. What are the physical states in which metals and electrolytes conduct electricity?
4. Can ionic compounds conduct electricity in the solid state? If your answer is "No", why?

Aqueous solutions can be tested for the presence of mobile ions by using an electric circuit like the one in Figure 4.1.

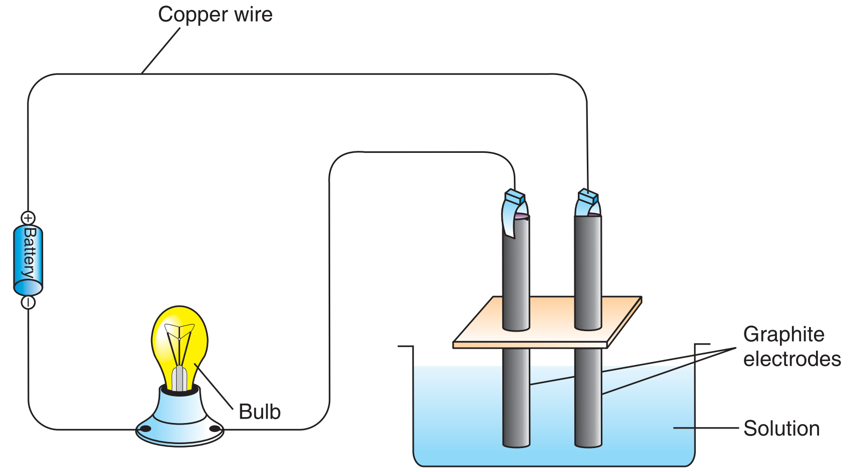


Figure 4.1 Electrical Conductivity Apparatus.

This circuit consists of a current source, a light bulb, and two graphite rods called electrodes that dip into the solution. If the solution contains ions, current flows through the circuit and the light bulb glows. The brightness of the bulb increases with current strength, which increases with the number of ions in the solution.

The ability of different solutes to provide ions can be compared by comparing the brightness of the light bulb at the same concentration.

Note that metallic conduction is a *physical process*, but electrolytic conduction causes *chemical changes* to occur on the surface of the electrodes.

Exercise 4.3

Which of the following substances are capable of conducting electricity? Give reason for your answer.

a Iron
b Sulphur
c Solid sodium chloride
d Molten calcium chloride

Experiment 4.1

Electrical Conductivity Test

Objective: To classify substances as electrical conductors and insulators.

Apparatus: Copper wire, light bulb, power supply (DC) or dry cells, scotch tape, distilled water, 1M NaCl solution, 1 M H_2SO_4 solution, 1 M CH_3COOH solution, 1 M sugar solution, magnesium ribbon and an iron nail.

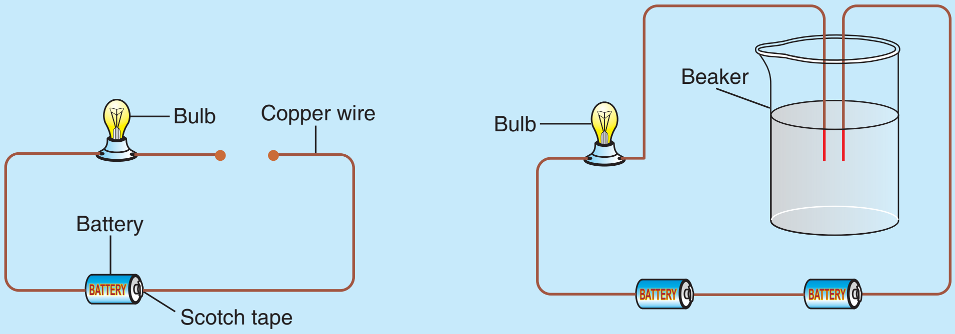


Figure 4.2 (a) Electrical conductivity apparatus for solid materials. (b) Electrical conductivity apparatus for liquids and solutions.

Procedure:

1. Polish the strip of magnesium and connect the two ends of the copper wire as shown in Figure 4.2a. Do the same thing for iron nail. Record your observations.
2. Rinse the 100 mL beaker thoroughly with distilled water and fill to the 50 mark and insert the two ends of the copper wire as shown in Figure 4.2b. Record your observations.
3. Clean the two ends of the copper wire in Figure 4.2b with distilled water and insert them into a beaker containing 50 mL of 1 M NaCl solution. Repeat the same thing for the 1 M H_2SO_4, 1 M CH_3COOH and 1 M sugar solutions. Record your observation.

Results and Discussion:

1. Why is it important to polish the magnesium ribbon and iron nail before use?
2. Classify the materials you used as conductors, strong electrolytes, weak electrolytes and nonelectrolytes.
3. Label the two ends of the wire in Figure 4.2b as cathode and anode.

4.2.1 Electrolytic cells

Activity 4.3

Form a group, and discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. Describe the migration of ions during electrolysis?
2. Observe Figure 4.3 and answer the following questions.

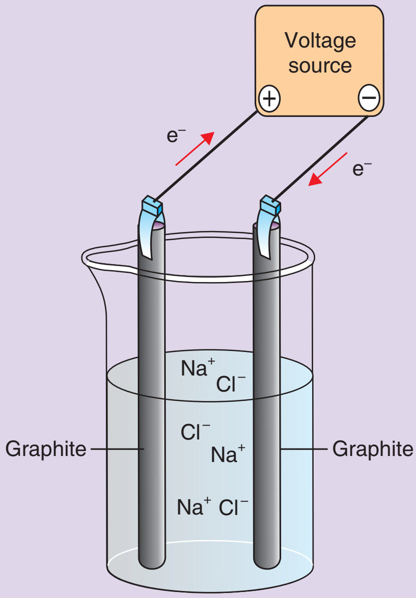


Figure 4.3 Electrolytic cell containing molten sodium chloride.

a Label the anode and the cathode.

b Indicate the migration of sodium ions and chloride ions.

c Write the reduction half-reaction, oxidation-half reaction, and the overall reaction.

d What are the products of electrolysis of molten NaCl?

4.2.2 Preferential Discharge

What does preferential discharge mean? What are the factors that affect preferential discharge of ions?

The preferential discharge of ions is affected by the nature of the electrodes, the positions of the ions in the electrochemical series and the concentration of the ions in the electrolyte. Let us discuss these factors one by one.

1. *Nature of the electrodes*

How do electrodes affect the preferential discharge of ions?

Inert electrodes, like graphite or platinum, do not affect the product of electrolysis, but reactive or active electrodes, like copper, can affect the product of electrolysis.

For example, in the electrolysis of copper sulphate solutions, using graphite electrodes, oxygen gas is liberated at the anode and copper metal is deposited at the cathode, as shown below.

$$CuSO_4(aq) \longrightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$$

Anode : $4OH^-(aq) \longrightarrow O_2(g) + 2H_2O(l) + 4e^-$

Cathode : $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

However, if the electrolysis of copper sulphate is performed using copper electrodes, the copper electrode at the anode dissolves and copper metal will be deposited at the cathode, as indicated below.

Anode : $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$

Cathode : $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

2. *The position of the ions in the electrochemical series*

The reactivity series or activity series is an empirical series of metals, in order of "reactivity" from highest to lowest. It is used to summarize information about the reactions of metals with acids and water, single displacement reactions and the extraction of metals from their ores. The electrochemical series is built up by arranging various redox equilibria in order of their standard electrode potentials (*redox potentials*). The values of standard electrode potentials are given in the Table 4.2 in volts relative to the standard hydrogen electrode. You will learn more about standard electrode potentials in this unit.

The reactivity series is sometimes quoted in the reverse order of standard electrode potentials:

Li > K > Sr > Ca > Na > Mg > Al > Zn > Cr > Fe > Cd > Co > Ni > Sn > Pb > H > Cu > Ag > Hg > Pt > Au

The positions of lithium and sodium are changed on such a series; gold and platinum are also inverted, although this has little practical significance as both metals are highly unreactive.

Standard electrode potentials offer a quantitative measure of the power of a reducing agent, rather than the qualitative considerations of other reactivity series. However, they are only valid for standard conditions. In particular, they only apply to reactions in aqueous solution. Even with this provision, the electrode potentials of lithium and sodium, and hence their positions in the electrochemical series, appear anomalous. The order of reactivity, as shown by the vigor of the reaction with water or the speed at which the metal surface tarnishing in air, appears to be:

potassium > sodium > lithium > alkaline earth metals

Table 4.1 The ease of discharge of some common cations and anions.

Cations	Anions
The ease of discharge increase downward Li^+ K^+ Na^+ Mg^{2+} Al^{3+} Mn^{2+} Zn^{2+} Cr^{3+} Fe^{2+} Cd^{2+} Pb^{2+} Fe^{3+} H^+ Cu^{2+} Ag^+ Au^{3+}	The ease of discharge increase downward F^- SO_4^{2-} NO_3^- CO_3^{2-} Cl^- Br^- I^- OH^- S^{2-}

The ions that are lower in the electrochemical series get discharged in preference to those above them.

For example, if a solution has potassium ions and copper ions, the copper ions will accept electrons, and get discharged as copper atoms first. The potassium ions will not be affected.

In general, if two or more positive ions migrate to the cathode, the ion lower in the series is discharged preferentially. Similarly, if two or more negative ions migrate to the anode, the ion lower in the series is discharged preferentially.

3. *Concentration of the ions in the electrolyte*

If an electrolyte contains a higher concentration of ions that are higher in the electrochemical series than of those that are lower, then the higher ions get discharged in preference to the lower ones.

For example, a solution of sodium chloride in water contains two types of anions i.e., the chloride (Cl^-) ions and the hydroxide (OH^-) ions. The hydroxide ions are lower in the electrochemical series than the chloride ions. But if the concentration of chloride ions is much higher than that of the hydroxide ions, then the chloride ions get discharged first.

Exercise 4.4

1. Define the following terms:
    - a perferential discharge
    - b inert electrode
    - c reactive or active electrode.
2. What gases are liberated at the cathode and anode if concentrated hydrochloric acid is electrolyzed? Write the reduction half-reaction, oxidation half-reaction and the overall reaction.

4.2.3 Electrolysis of Some Selected Aqueous Solutions

Activity 4.4

Form a group, and discuss each of the following:

1. Prior to electrolysis, why sodium chloride must be in molten state?
2. Why water must be excluded in the electrolytic preparation of active metals such as potassium. What will happen if water gets into the cell?
3. For the electrolysis of molten KCl, write a balanced equation for the:
    - a anode reaction
    - b cathode reaction
    - c overall reaction
4. Why are H^+ and Cl^- ions discharged in preference to Na^+ and OH^- ions in concentrated sodium chloride solution?

After the discussion, share your ideas with the rest of the class.

Electrolysis of concentrated sodium chloride solution (brine solution)

Concentrated solution of sodium chloride (brine solution) contains Na^+, Cl^-, H^+ and OH^- ions. However, the concentrations of H^+ and OH^- are very small. Why? When a potential difference is established across the two electrodes, Na^+ and H^+ ions move towards the cathode, and Cl^- and OH^- ions move towards the anode. At the cathode, the H^+ ions are discharged in preference to the Na^+ ions. Similarly, Cl^- ions are discharged at the anode in preference to the OH^- ions because the concentration of Cl^- ions is very high.

$$\begin{array}{lll} \textbf{\textit{Cathode (reduction)}} & : & 2H^+(aq) + 2e^- \rightarrow H_2(g) \\ \textbf{\textit{Anode (oxidation)}} & : & 2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- \\ \hline \textbf{\textit{Overall reaction}} & : & 2H^+(aq) + 2Cl^-(aq) \rightarrow H_2(g) + Cl_2(g) \end{array}$$

Since the Na^+ and OH^- ions remain in the solution, the solution yields NaOH, as shown in Figure 4.4.

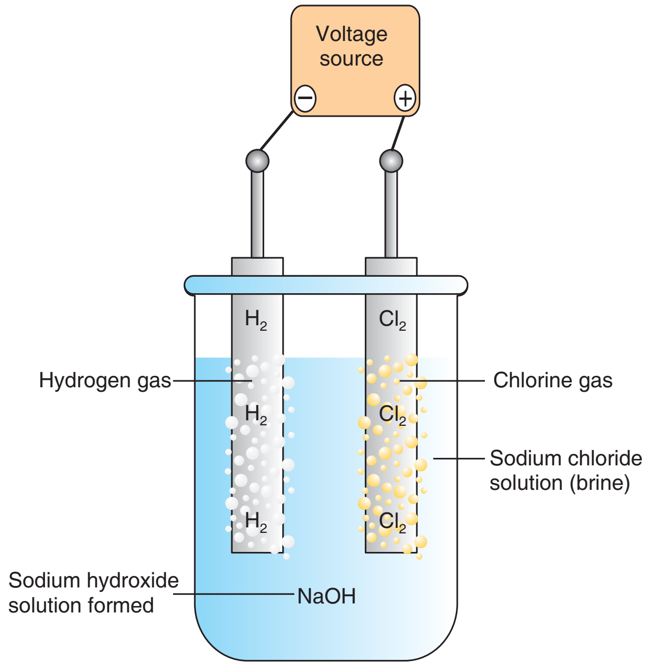


Figure 4.4 Electrolysis of brine solution.

Electrolysis of Dilute Sodium Chloride Solution

Activity 4.5

Form a group, and discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. What is meant by dilute solution?
2. a List all ions present in dilute sodium chloride solution.
   b Identify ions that migrate towards the anode and the cathode.
   c Which ions listed in (a) will discharge at the cathode and at the anode?
3. Write the electrode half-reactions and overall reaction for the electrolysis of dilute solution of sodium chloride.

Experiment 4.2

Investigating electrolysis of sodium chloride solution

Objective: To electrolyze sodium chloride solution and observe the reaction occurring at the electrodes.

Apparatus and Chemicals: Water, sodium chloride, beakers, measuring cylinder, graphite electrodes, batteries and connecting wires.

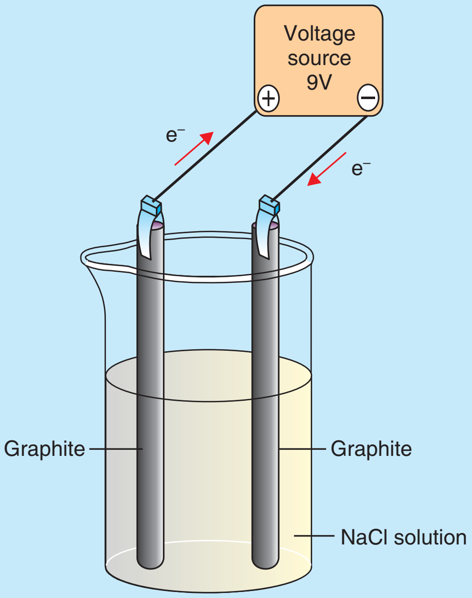


Figure 4.5 Electrolysis of sodium chloride solution

Procedure:

1. Prepare 0.1 M sodium chloride solution.
2. Transfer the solution to the beaker.
3. Immerse the graphite electrodes in the sodium chloride solution.
4. Arrange the setup as shown in the Figure 4.5.

Results and Discussion:

1. What do you observe at the surface of the electrodes?
2. Identify the cathode and anode in the Figure 4.5.
3. Name the gases evolved at the cathode and anode.
4. Write the equations for anode and cathode reactions.

Electrolysis of Dilute Sulphuric Acid Solution

Which ions are discharged at the cathode and anode?

Dilute sulphuric acid solution contains H^+, OH^- and SO_4^{2-} ions. When a potential difference is applied across the two electrodes (anode and cathode), only H^+ ions migrate towards the cathode, and OH^- and SO_4^{2-} ions migrate towards the anode.

At the cathode, H^+ ions are discharged, and at the anode, OH^- ions are discharged in preference to SO_4^{2-} ions because the hydroxide ion is below the SO_4^{2-} ion in the electrochemical series.

Anode (oxidation) : $4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^-$

Cathode (reduction) : $[2H^+(aq) + 2e^- \rightarrow H_2(g)] \times 2$

Overall reaction : $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

Note that the electrolysis of dilute NaCl and dilute H_2SO_4 solutions results in the decomposition of water to oxygen and hydrogen gases.

Electrolysis of Copper (II) Sulphate, Using Inert Electrodes

Which ions are liberated at the cathode and anode if copper sulphate solution is electrolysed, using platinum (inert) electrodes?

Copper sulphate solution contains Cu^{2+}, H^+, SO_4^{2-} and OH^- ions. When a potential difference is established between the two electrodes, Cu^{2+} and H^+ ions migrate towards the cathode, and SO_4^{2-} and OH^- ions migrate towards the anode.

At the cathode, the Cu^{2+} ions are discharged in preference to the H^+ ions, because copper is below hydrogen in the electrochemical series. Similarly, at the anode, the OH^- ions are discharged in preference to the SO_4^{2-} ions.

Anode (oxidation) : $4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^-$

Cathode (reduction) : $[Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)] \times 2$

Overall reaction : $2Cu^{2+}(aq) + 4OH^-(aq) \rightarrow 2Cu(s) + 2H_2O(l) + O_2(g)$

Since copper ions are deposited at the cathode, and hydroxide ions at the anode, the solution becomes acidic due to the formation of H_2SO_4.

Electrolysis of Copper (II) Sulphate Solution, Using Copper Electrodes

Activity 4.6

Form a group, and discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. What is the difference between inert electrodes and reactive electrodes?
2. Are the copper electrodes reactive or inert in the electrolysis of copper (II) sulphate solution?
3. a List all the ions present in copper (II) sulphate solution.
   b Identify the ions that migrate towards the anode and the cathode.
   c Which ions you listed in (a) will discharge at the cathode and at the anode?
4. Write the reactions ocurring at the anode and at the cathode during the electrolysis of copper (II) sulphate solution, using copper electrodes.
5. What is the net result of the electrolysis of copper (II) sulphate solution, using copper electrodes?

Exercise 4.5

1. For the electrolysis of dilute NaOH solution,
   a write the balanced chemical equations for the reduction half-reaction and oxidation half-reactions.
   b write the balanced overall cell reaction.
2. What happens to the concentration of the dilute H_2SO_4 solution after electrolysis?
3. Does the concentration of copper sulphate increase, decrease or remain the same after the electrolysis of copper sulphate, using inert electrodes? Explain.

4.3 QUANTITATIVE ASPECTS OF ELECTROLYSIS

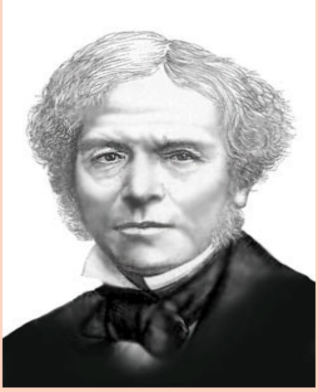
After completing this subunit, you will be able to:

- state Faraday's first law of electrolysis;
- write the mathematical expressions for the Faraday's first law of electrolysis;
- do calculations related to Faraday's first law of electrolysis;
- state Faraday's second law of electrolysis;
- write the mathematical expressions for Faraday's second law of electrolysis; and
- do calculations related to Faraday's second law of electrolysis.

Is it possible to calculate the amount of product formed at the electrodes?

The quantitative treatment of electrolysis was developed primarily by Michael Faraday in the year 1834. His early research on electrolysis led him to propose a relationship between the amount of current passed through a solution and the amount of substance decomposed or produced by the current.

Biography


Faraday, Michael

Michael Faraday (1791-1867), was a British physicist and chemist, best known for his discoveries of electromagnetic induction and of the laws of electrolysis.

Faraday was born on September 22, 1791, in Newington, Surrey, England. He was the son of a blacksmith and received little formal education. While apprenticed to a bookbinder in London, he read books on scientific subjects and experimented with electricity. In 1812, he attended a series of lectures given by the British chemist Sir Humphry Davy and forwarded the notes he took at these lectures to Davy, together with a request for employment. Davy employed Faraday as an assistant in his chemical laboratory at the Royal Institution, and in 1813 took Faraday with him on an extended tour of Europe. Faraday was elected to the Royal Society in 1824, and the following year he was appointed director of the laboratory of the Royal Institution. In 1833, he succeeded Davy as professor of chemistry at the institution. Two years later he was given a pension of 300 pounds per year for life. Faraday was the recipient of many scientific honors, including the Royal and Rumford medals of the Royal Society; he was also offered the presidency of the society but declined the honour. He died on August 25, 1867, near Hampton Court, Surrey.

4.3.1 Faraday's First Law of Electrolysis

Faraday's First Law states that "the amount of substance consumed or produced at one of the electrodes in an electrolytic cell is directly proportional to the amount of electricity that passes through the cell".

If m is the mass of a substance librated or deposited at an electrode due to the passage of charge Q, then according to Faraday's first law of electrolysis,

$$m \propto Q \quad \text{or} \quad m = zQ$$

Where z is a constant of proportionality and is called electrochemical equivalent of the substance. It has the same charge which passes due to a steady current I flowing for time t, then the above equation can be written as:

$$\begin{aligned} m &= z \times I \times t \\ &= z \times Q \end{aligned}$$

Show that the general formula of Faraday's first law is given by : $m = \frac{MIt}{nF}$. where, m is mass of the substance deposited or liberated, I is current in amperes, t is time in seconds, F is Faradays constant, n is the number of moles of electrons lost or gained, and M is the molar mass of the substance.

For example, in the electrolysis of molten NaCl, the cathode reaction tells us that one Na atom is produced when one Na^+ ion accepts an electron from the cathode. To reduce 1 mole of Na^+ ions, we must supply one mole of electrons (6.02×10^{23} electrons) to the cathode.

Example 4.4

How many moles of chlorine, magnesium and aluminium are formed when 2, 2 and 3 moles of charge are passed through three different solution containing chloride, magnesium and aluminium ions respectively?

Solution:

The stoichiometry of the anode reaction shows that oxidation of two Cl^- ions yields one chlorine molecule and releases two electrons. Therefore, the formation of 1 mole of chlorine results in 2 moles of electrons supplied by the Cl^- ions to the anode. Similarly, it takes 2 moles of electrons to reduce 1 mole of Mg^{2+} ions and 3 moles of electrons to reduce 1 mole of Al^{3+} ions:

$$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$$

$$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$$

$$Al^{3+}(l) + 3e^- \rightarrow Al(s)$$

In an electrolysis experiment, we generally measure the current in amperes (A) that pass through an electrolytic cell in a given period of time. By definition, 1 coulomb of charge is transferred when a 1 ampere current flows for 1 second:

$$1\ C = 1\ A \times 1\ s$$

The charge on 1 mole of electrons is 96,500 C, which is obtained by multiplying 1 mol (6.02×10^{23} electrons) with the charge of electron (1.602×10^{-19} C).

Charge of 1 mol of electrons = 6.02×10^{23} electrons $\times\ 1.602 \times 10^{-19}$ C

$$= 96,485\ C \approx 96,500\ C = 1\ F\ \text{(one faraday)}$$

Therefore, $1F = 96,500\ C.mol^{-1}$.

Example 4.5

Calculate the mass of calcium metal and chlorine gas that can be produced when a current of 0.452 A is passed through molten $CaCl_2$ for 1.5 h.

Solution:

In solving electrolysis problems of this type, the first step is to determine which species will be oxidized at the anode and which species will be reduced at the cathode. Here the choice is straightforward because we only have Ca^{2+} and Cl^- ions in molten $CaCl_2$. Thus, we write the half and overall reactions as:

Anode (oxidation) : $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

Cathode (reduction) : $Ca^{2+}(l) + 2e^- \rightarrow Ca(l)$

Overall reaction : $Ca^{2+}(l) + 2Cl^-(l) \rightarrow Ca(l) + Cl_2(g)$

The quantities of calcium metal and chlorine gas formed depend on the number of electrons that pass through the electrolytic cell, which in turn depends on current × time or charge.

Charge (Q) = current (I) in A × time (t) in s

$Q = I \times t = (0.452\ \text{A}) \times (1.5 \times 60 \times 60\ \text{s})$

$= 2.44 \times 10^3\ \text{A s} = 2.44 \times 10^3\ \text{C}$

$1\ \text{mol e}^- = 96{,}500\ \text{C}$

$x? = 2.44 \times 10^3\ \text{C}$

$$\Rightarrow x = \frac{2.44 \times 10^3\ \cancel{\text{C}} \times 1\ \text{mol e}^-}{96{,}500\ \cancel{\text{C}}} = 0.0253\ \text{mol e}^-$$

2 moles of electrons are required to produce 1 mole, or 40 g, of calcium metal at the cathode. Hence, the mass of calcium formed is

$2\ \text{mol e}^- = 1\ \text{mole Ca} = 40.08\ \text{g Ca}$

$0.0253\ \text{mol e}^- = x?$

$$\Rightarrow x = \frac{0.0253\ \cancel{\text{mol e}^-} \times 40.08\ \text{g Ca}}{2\ \cancel{\text{mol e}^-}} = 0.507\ \text{g Ca}$$

The anode reaction indicates that 1 mole, or 71 g, of chlorine is produced by giving 2 moles of electrons to the anode. Hence, the mass of chlorine gas formed is

$2\ \text{mol e}^- = 71\ \text{g Cl}_2 = 1\ \text{mole Cl}_2$

$0.0253\ \text{mol e}^- = x?$

$$\Rightarrow x = \frac{0.0253\ \cancel{\text{mol e}^-} \times 71\ \text{g Cl}_2}{2\ \cancel{\text{mol e}^-}} = 0.898\ \text{g Cl}_2$$

Example 4.6

A current of 1.26 A is passed through an electrolytic cell containing an aqueous solution of H_2SO_4 for 7.44 h. Write the half-cell reactions and calculate the volume of the gases generated at STP (Note that at STP, $P = 1$ atm, and $T = 0°\text{C}$ or 273 K).

Solution:

Recall that, from the electrolysis of dilute H_2SO_4, we have:

Anode (oxidation) : $4OH^-(aq) \rightarrow 2H_2O\,(l) + O_2(g) + 4e^-$

Cathode (reduction) : $4H^+(aq) + 4e^- \rightarrow 2H_2(g)$

Overall reaction : $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

First let us calculate the total charge.

Given: $I = 1.26$ A

$t = 7.44\ h = 7.44 \times 60 \times 60\ \text{s} = 26{,}784\ \text{s}$

$Q = It = (1.26\ \text{A}) \times (26{,}784\ \text{s}) = 3.37 \times 10^4\ \text{C}$

The above balanced chemical equation shows that for 1 mole of O_2 formed at the anode, 4 moles of electrons are generated. Now let us calculate the number of moles of electrons.

$1\ \text{mol e}^- = 96{,}500\ \text{C}$

$x? = 3.37 \times 10^4\ \text{C}$

$$\Rightarrow x = \frac{1\ \text{mol e}^- \times 3.37 \times 10^4\ \cancel{\text{C}}}{96{,}500\ \cancel{\text{C}}} = 0.350\ \text{mol e}^-$$

The number of moles of oxygen becomes:

$4\ \text{mol e}^- = 1\ \text{mol O}_2$ (Observe the anode reaction)

$0.350\ \text{mol e}^- = x?$

$$\Rightarrow x = \frac{0.350\ \cancel{\text{mol e}^-}\ x\ 1\ \text{mol O}_2}{4\ \cancel{\text{mol e}^-}} = 0.0875\ \text{mole of O}_2$$

The volume of 0.0875 mol O_2 at STP is given by

$$V = \frac{nRT}{P} = \frac{0.0875\ \cancel{\text{mol}} \times \left(0.0821\ \frac{\text{L.}\ \cancel{\text{atm}}}{\cancel{\text{mol}}\ .\ \cancel{\text{K}}}\right) \times (273\ \cancel{\text{K}})}{1\ \cancel{\text{atm}}}$$

$V = 1.96$ L or since the volume of 1 mol of a gas at STP is 22.4 L, the volume occupied by 0.0875 mol of O_2 can be obtained using the following relation.

$$1 \text{ mol} = 22.4 \text{ L}$$

$$0.0875 \text{ mol} = x?$$

$$\Rightarrow \quad x = \frac{0.0875 \cancel{\text{mol}} \times 22.4 \text{ L}}{1 \cancel{\text{mol}}} = 1.96 \text{ L}$$

Similarly, for hydrogen, we write

$$4 \text{ mol e}^- = 2 \text{ mol } H_2 \text{ (Observe the cathode reaction)}$$

$$0.35 \text{ mol e}^- = x?$$

$$x = \frac{0.35 \cancel{\text{mol e}^-} \times 2 \text{ mol } H_2}{4 \cancel{\text{mol e}^-}}$$

$$x = 0.175 \text{ mol } H_2$$

The volume of 0.175 mol of H_2 at STP is given by

$$V = \frac{nRT}{P} = \frac{0.175 \cancel{\text{mol}} \times \left(0.0821 \frac{\text{L.} \cancel{\text{atm}}}{\cancel{\text{mol}} \,.\, \cancel{\text{K}}}\right) \times (273 \cancel{\text{K}})}{1 \cancel{\text{atm}}}$$

$$V = 3.92 \text{ L}$$

Note that the volume of H_2 is twice that of O_2.

Exercise 4.6

1. Calculate the volume of H_2 and O_2 gases at 25°C and 1.00 atm that will be collected at the cathode and anode, respectively, when an aqueous solution of Na_2SO_4 is electrolyzed for 2 hours with 10 ampere current.
2. Calculate the mass of copper and volume of oxygen (at 25°C and 760 mmHg) that would be produced by passing a current of 0.5 A through a $CuSO_4$ solution between Pt electrodes for 3 hours.
3. What mass of aluminium is deposited electrolytically in 30 minutes by a current of 40 A?

4.3.2 Faraday's Second Law of Electrolysis

Faraday's second law of electrolysis states that "when the same quantity of charge (Q) is passed through different electrolytes, then the masses of different substances deposited (m_1, m_2, m_3,...) at the respective electrodes will be directly proportional to their equivalent masses (E_1, E_2, E_3,...)."

$$m \propto E$$

or, $$m_1 \propto E_1,\ m_2 \propto E_2, \text{ and } m_3 \propto E_3 \text{ etc.}$$

Replacing the proportionality by a proportionality constant k, the equations become:

$$M_1/E_1 = M_2/E_2 = M_3/E_3 = \cdots = k$$

The law can be illustrated by passing the same quantity of electric current through three solutions containing H_2SO_4, $CuSO_4$ and $AgNO_3$, connected in series, as shown in Figure 4.6.

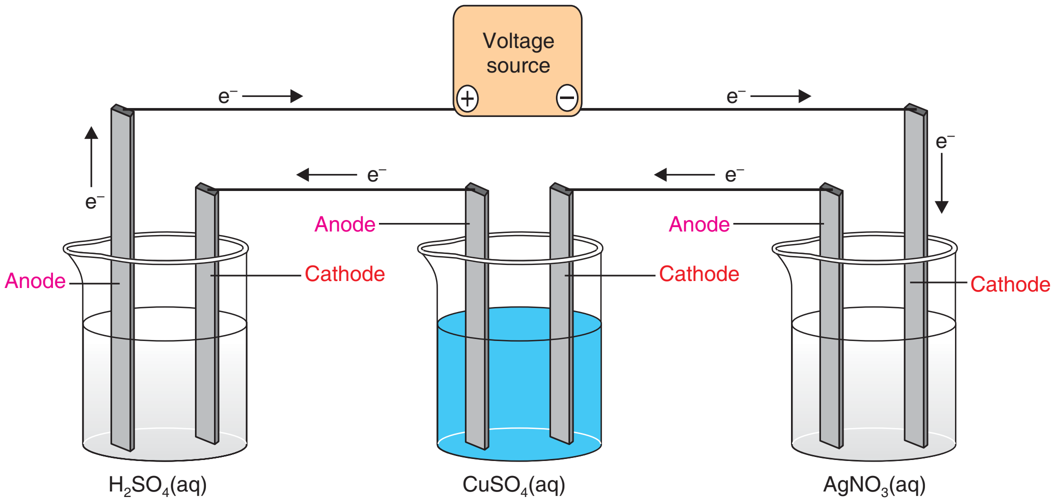


Figure 4.6 Solutions connected in series to a battery.

In the first solution, hydrogen and oxygen are liberated. In the second solution copper is deposited and in the third, silver is deposited.

$$\frac{\text{Mass of hydrogen}}{\text{Equivalent mass of } H_2} = \frac{\text{Mass of copper}}{\text{Equivalent mass of copper}} = \frac{\text{Mass of silver}}{\text{Equivalent mass of silver}}$$

Example 4.7

Calculate the mass of copper deposited by the electrolysis of copper (II) sulphate solution placed in series with a silver nitrate solution, when 0.108 g of silver is being deposited.

Solution:

The equivalent mass of silver and copper can be obtained from their reduction half-reaction:

$$Ag^+(aq) + 1e^- \rightarrow Ag(s),\ E_{Ag} = \frac{108\ g/mol}{1} = 108\ g/eq$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s),\ E_{Cu} = \frac{63.5\ g/mol}{2} = 31.75\ g/eq$$

The mass of Ag is 0.108 g, and you are asked to find the mass of copper.

$$\frac{m_{Ag}}{E_{Ag}} = \frac{m_{Cu}}{E_{Cu}} \Rightarrow m_{Cu} = \frac{E_{Cu} \times m_{Ag}}{E_{Ag}}$$

$$= \frac{31.75\ \cancel{g/eq} \times 0.108\ g}{108\ \cancel{g/eq}} = 0.032\ g \text{ of Cu is deposited}$$

Exercise 4.7

1. Two cells are connected in series. One contains $AlCl_3$, and the other contains $AgNO_3$ as the electrolytes. What mass of Ag is deposited when 18 g of Al is deposited at cathode?
2. 0.2 moles of electrons are passed through three electrolytic cells in series that contain silver ions, zinc ions and iron (III) ions. How many grams of each metal will be deposited at cathode?

4.4 INDUSTRIAL APPLICATION OF ELECTROLYSIS

After completing this subunit, you will be able to:

- mention the industrial applications of electrochemistry;
- explain electroplating and electrorefining;

- demonstrate copper refining; and
- explain how electrolysis is used in the production of some metals, nonmetals and compounds.

4.4.1 Electroplating and Electrorefining of Metals

Activity 4.7

Form a group. Discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. Define electroplating and electrorefining.
2. What are the purposes of electroplating and electrorefining?
3. Where do we put the plating metal and the metal to be plated, during electroplating?
4. Does the electrolyte contain dissolved ions of the plating metal or the metal to be plated?
5. What is chrome plating? How is it done?
6. Describe the electrorefining of copper. Include the appropriate chemical equations.

4.4.2 Extraction of Metals

Activity 4.8

Discuss each of the following questions. After the discussion, share your ideas with your classmates.

1. List active metals that can be extracted from their compounds by electrolysis.
2. Explain why electrolytic reduction rather than chemical reduction is often used to obtain active metals from their compounds.
3. Why are molten metal chlorides used as electrolytes rather than using other molten salts?

4.4.3 Manufacture of Nonmetals and Some Compounds

Activity 4.9

Form a group. Discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. List nonmetals and compounds that are prepared by electrolysis.
2. Write the cathode and anode reactions during the electrolysis of molten mixture of potassium fluoride and hydrogen fluoride.
3. Using chemical equations, write the preparation of:
   a sodium hydroxide from the electrolysis of brine solution.
   b hydrogen and oxygen from the electrolysis of dilute sodium chloride solution.
4. Why is a small amount of solute added in the electrolysis of water?

4.5 VOLTAIC (GALVANIC) CELLS

After completing this subunit, you will be able to:

- define Voltaic cell and salt bridge;
- draw and label Zn-Cu Voltaic cell;
- define electrode potential and cell potential;
- construct Zn-Cu Voltaic cell;
- measure the cell potential of Zn-Cu cell using voltmeter;
- explain how standard electrode potential is measured;
- describe the reactivity of metal from its position in the activity series or electromotive series;
- calculate cell potential;
- decide whether a given redox reaction is spontaneous or not;
- explain the effect of concentration on cell potential;
- mention the different types of Voltaic cells;
- give examples of each type of Galvanic cell;
- describe how a hydrogen-oxygen fuel cell operates;

- distinguish between primary and secondary cells;
- identify the cathode, anode and electrolyte of a given Galvanic cell;
- compare and contrast electrolytic and Galvanic cells;
- explain metallic corrosion in terms of redox reactions;
- explain the negative effects of corrosion; and
- explain the different methods of the prevention of corrosion.

What makes a Galvanic cell different from an electrolytic cell?

A Galvanic cell is a device in which chemical energy is transformed into electrical energy.

4.5.1 Construction of Zn-Cu Galvanic Cell

Activity 4.10

Form a group. Discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. Describe the basic features of an electrochemical cell. Why are the two components of the cell separated from each other?
2. Given the following chemical reaction,

   $Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$:

   a write equations for the oxidation and reduction half-reactions.

   b which half-reaction occurs in the anode compartment and which occurs in the cathode compartment?

What happens if zinc metal is immersed in copper (II) sulphate solution?

When zinc metal is immersed in copper sulphate solution, some zinc dissolves and some copper metal forms on the surface of the remaining zinc.

The net reaction,

$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$

is an oxidation-reduction reaction (redox reaction) in which electrons are transferred from zinc atoms to copper ions.

The half-reaction equations are:

Oxidation half-reaction **:** $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Reduction half-reaction **:** $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Since the copper sulphate solution is in contact with the zinc metal, the electrons flow directly from the zinc metal atoms to the copper ions without doing useful work. If the half-reactions could be made to occur in separate compartments, and the electrons were transferred through an external wire from one compartment to the other, then we would have a Galvanic cell capable of doing electrical work.

A Galvanic cell was invented by the British Chemist John Daniell in 1836. It is called the Daniell cell. A diagram of this cell is as shown in Figure 4.7.

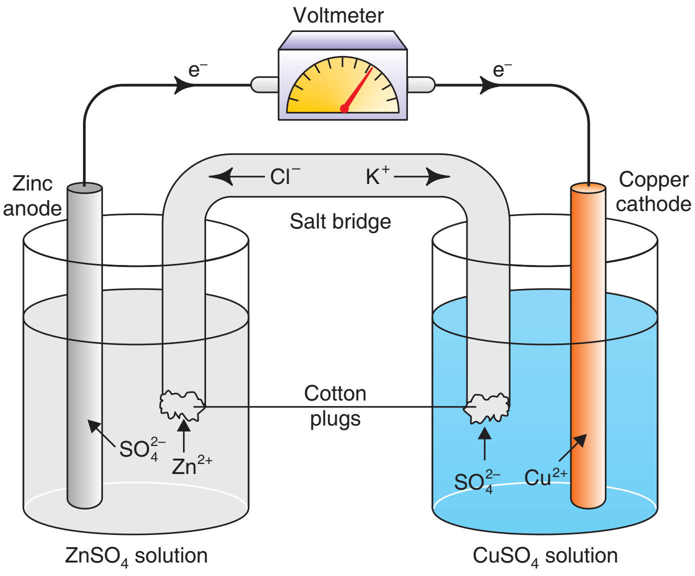


Figure 4.7 Daniell cell.

One compartment of the Daniell cell contains a zinc electrode immersed in a solution of zinc sulphate ($ZnSO_4$). The other compartment contains a copper electrode in a solution of copper sulphate ($CuSO_4$). When the two electrodes are connected by a wire, the zinc atoms give up electrons, forming positive ions:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

The zinc ions repel each other and enter the solution. The negative electrons also repel each other and travel through the external wire to the copper electrode, where they are accepted by copper ions from the surrounding solution:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

The resulting copper atoms deposit as the copper metal on the surface of copper electrode. The Daniell cell reaction is identical to the reaction that occurs when zinc metal is dipped directly into copper sulphate solution (zinc atoms are oxidized and copper ions are reduced), but the cell is constructed so that the electrons pass through an external circuit where they can do useful work.

The solutions in the two halves of a Galvanic cell must be connected in order to complete the circuit, but they must not mix. The connection can be made through a salt bridge (see Figure 4.7).

A salt bridge is an inverted U-tube filled with an electrolyte, such as NH_4NO_3 or KCl, chosen so that it does not interfere with the operation of the cell. Regardless of how the cell is constructed, the solutions in each compartment remain more or less separated. Furthermore, because ions can move into and out of the salt bridge, the solutions remain electrically neutral.

How does the salt bridge maintain the electroneutrality of a solution?

Consider the zinc compartment. The oxidation of zinc atoms tends to build up the concentration of positive zinc ions in a solution around the zinc electrode. Some of the charge is neutralized by negative ions flowing out of the salt bridge and enter into the zinc compartment, and the rest of zinc ions flow out of the compartment into the salt bridge.

Now consider the copper compartment. The reduction of copper ions tends to decrease the concentration of positive copper ions around the copper electrode. The resulting negative charge is neutralized, partially by positive ions flowing from the salt bridge and enter into the copper compartment, and partially by negative sulphate ions flowing out of the compartment. If the flow of ions did not occur, a charge difference would build up between the compartments, and the reaction would stop. Every Galvanic cell has an oxidation half-reaction and a reduction half-reaction. The compartments in which these reactions occur (and their associated electrodes) are referred to as half-cells.

What are the anode and the cathode in a Galvanic cell?

The electrode where oxidation takes place is called the anode, and the electrode where reduction takes place is the cathode. In the Daniell cell, the zinc electrode is the anode and the copper electrode is the cathode. The anode sends electrons through the connecting wire (it is the electron source or negative terminal of the cell). The cathode receives electrons, so it is a positive terminal. When the terminals of a Galvanic cell are connected by an external circuit, there will always be a flow of electrons from anode to cathode through the external circuit.

Note that the electrode polarities in Galvanic cells are the reverse of those in an electrolytic cell.

	Cathode	Anode
Galvanic cell	+	–
Electrolytic cell	–	+

4.5.2 Cell Notation

How do you represent Galvanic cells without drawing a diagram?

A cell notation allows us to describe a Galvanic cell without drawing a diagram. It is a shorthand representation of a Galvanic cell. For example, a Daniell cell in which the electrolyte concentrations are each 1 molar is represented as

$$\mathrm{Zn(s)}\,\big|\,\mathrm{Zn^{2+}(1\,M)}\,\big\|\,\mathrm{Cu^{2+}\ (1\,M)}\,\big|\,\mathrm{Cu(s)}$$

The anode is written on the left. The cathode on the right and concentrations and other data are given in parentheses. The vertical line (|) indicates phase boundaries, and the double vertical line (||) indicates a salt bridge or a porous partition.

The cell notation for the Daniell cell tells us that the zinc anode is dipped into a 1 M solution of zinc ions, the copper cathode is dipped into a 1 M solution of copper ions, and the two half-cells are separated by a salt bridge or a porous partition. If the two half-cells were in direct contact, the double vertical line would be replaced by single line. The notation for any Galvanic cell has the following form:

anode | anode electrolyte (M) || cathode electrolyte (M) | cathode

Every redox reaction is the sum of an oxidation half-reaction and a reduction half-reaction written in such a way as to cancel out the electrons by suitably multiplying the half-reactions by the minimum integers.

Example 4.8

Write the cell notation for a Galvanic cell, based on this reaction:

$$\mathrm{Fe(s) + Hg_2{}^{2+}(aq) \longrightarrow Fe^{2+}(aq) + 2Hg(l)}$$

Assume that the solution concentrations are 0.10 M.

Solution :

Write the oxidation half-reaction and the reduction half-reaction separately.

Oxidation half-reaction (anode) : $\mathrm{Fe(s) \longrightarrow Fe^{2+}\ (aq,\ 0.1\ M) + 2e^-}$

Reduction half-reaction (cathode) : $\mathrm{Hg_2^{2+}\ (aq,\ 0.1\ M) + 2e^- \longrightarrow 2Hg(l)}$

The cell notation is : $\mathrm{Fe(s)}\,\big|\,\mathrm{Fe^{2+}\ (0.10\,M)}\,\big\|\,\mathrm{Hg_2^{2+}\ (0.10\,M)}\,\big|\,\mathrm{Hg(l)}$

Exercise 4.8

1. Write the cell notation for a Galvanic cell consisting of an Al electrode placed in 1 M $Al(NO_3)_3$ solution and a Ag electrode placed in a 1 M $AgNO_3$ solution.
2. Explain the use of a salt bridge.
3. a Explain the difference between a Galvanic cell and an electrolytic cell.

   b Indicate the electrode polarity of each cell.

4.5.3 Standard Reduction Potentials

What is the difference between standard reduction potential and cell potential?

The cell potential is the difference between two electrode potentials, one associated with the cathode and the other associated with the anode.

By convention, the potential associated with each electrode is chosen to be the potential for reduction to occur at the electrode. Thus, standard electrode potentials (electrode potentials at a concentration of 1 M) are tabulated for reduction reactions and are denoted as E^o_{red}. The cell potential (E^o_{cell}) is E^o_{red} (*cathode*) minus the standard reduction potential of the anode reaction, E^o_{red} (*anode*):

$$E^o_{cell} = E^o_{red}\,(\text{cathode}) - E^o_{red}\,(\text{anode})$$

Because every Galvanic cell involves two half-cells, it is not possible to directly measure the standard reduction potential of a half-reaction. However, if we assign a standard reduction potential to a certain reference half-reaction, we can then determine the standard reduction potentials of the other half-reactions, relative to that reference. The reference half-reaction is the reduction of $H^+(aq)$ to $H_2(g)$ under standard conditions, which is given a standard reduction potential of exactly 0.0 V.

$$2H^+\,(aq,\ 1M) + 2e^- \rightarrow H_2(g,\ 1\ atm);\ E^o_{red} = 0.0\ V$$

An electrode designed to produce this half-reaction is called a standard hydrogen electrode (SHE). As depicted in Figure 4.8, SHE consists of platinum wire connected to a piece of platinum foil covered with finely-divided platinum that serves as an inert surface for the reaction. The electrode is encased in a glass tube, so that hydrogen gas can bubble over the platinum, and the solution contains $H^+(aq)$ under standard (1 M) conditions.

Can you indicate the cathode and the anode in Figure 4.8?

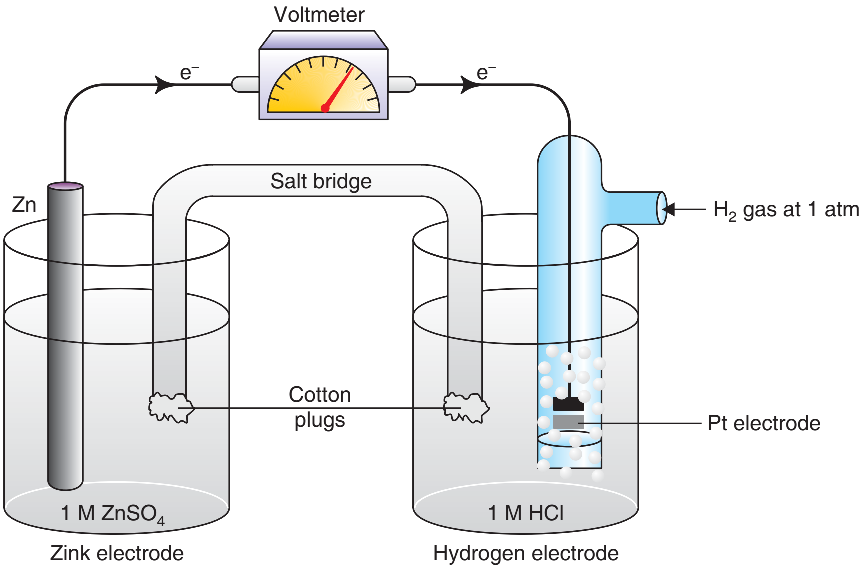


Figure 4.8 Standard Hydrogen Electrode

The spontaneous reaction in Figure 4.8, is the oxidation of zinc and the reduction of H^+ :

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

In the Figure 4.8, above;

i) The $Zn^{2+} | Zn$ electrode is the anode, and the SHE is the cathode.

ii) The cell voltage is 0.76 V.

By using the defined standard reduction potential of H^+ , we can determine the standard reduction potential for $Zn^{2+} | Zn$ half-reaction:

$$E^o_{cell} = E^o_{red}\,(cathode) - E^o_{red}\,(anode)$$

$$0.76\ V = 0.0\ V - E^o_{red}\,(anode)$$

$$\Rightarrow \quad E^o_{red}\,(anode) = -0.76\ V$$

Therefore, a standard reduction potential of –0.76 V can be assigned to the reduction of Zn^{2+} to Zn:

$$Zn^{2+}\ (aq,\ 1M) + 2e^- \rightarrow Zn(s);\ E^o_{red} = -0.76\ V$$

Note that we write the reaction as a reduction, even though it occurs in reverse as oxidation. Whenever we assign a potential to a half-reaction, we write the reaction as a reduction.

The standard reduction potentials for other half-reactions are established in the way that we did for the $Zn^{2+} | Zn$ half-reaction. In Table 4.2, the standard reduction potentials of some of the half-reactions are given.

Table 4.2 Standard Reduction Potential in Aqueous Solution at 25°C.

Half-reaction	Volts
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	+2.87
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	+1.82
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$	+1.70
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	+1.07
$2Hg^{2+}(aq) + 2e^- \rightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \rightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O_2(aq)$	+0.68
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+} + e^- \rightarrow Cu^+(aq)$	+0.15

Half-reaction	**Volts**
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	−0.41
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.76
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \rightarrow Na(s)$	−2.71
$Li^+(aq) + e^- \rightarrow Li(s)$	−3.05

In your calculations, be sure to understand these points about the information in Table 4.2:

1. The E^o_{red} values apply to the half-cell reactions as read in the forward (*left to right*) direction.
2. The more positive E^o_{red} is the greater tendency for the substance to be reduced.

   For example, the reaction,

   $F_2(g,\ 1\ atm) + 2e^- \rightarrow 2F^-(1M),\ E^o_{red} = +2.87\ V$

has the highest E^o value for all of the half-cell reactions. Thus, F_2 is the strongest oxidizing agent because it has the greatest tendency to be reduced. At the other extreme is the reaction,

$$Li^+ (1M) + e^- \rightarrow Li(s),\ E^o_{red} = -3.05\ V$$

which has the most negative E^o_{red} value. Thus, Li^+ is the weakest oxidizing agent, because it is the most difficult species to be reduced. Alternatively, Li metal is the strongest reducing agent since it gets oxidized most readily.

3. Under standard state conditions, any species on the left of a given cell reaction reacts spontaneously with a species that appears on the right of any half-cell reaction that is located below it in Table 4.2. This principle is sometimes called the diagonal rule. In the case of the Daniell cell,

$$Cu^{2+} (1\ M) + 2e^- \rightarrow Cu(s); \quad E^o_{red} = +0.34\ V$$

$$Zn^{2+} (1\ M) + 2e^- \rightarrow Zn(s); \quad E^o_{red} = -0.76\ V$$

We see that the substance on the left of the first half-cell reaction is Cu^{2+}, and on the right in the second half-cell reaction is Zn. Therefore, Zn spontaneously reduces Cu^{2+} to form Zn^{2+} and Cu.

4. Changing the stoichometric coefficients of a half-cell reaction does not affect the value of E^o_{red}, because electrode potentials are intensive properties. This means that the value of E^o_{red} is unaffected by the size of the electrodes or the amount of solutions present but is dependent on the concentration of the solutions and the pressure of a gas (if any).

For example,

$$I_2(s) + 2e^- \rightarrow 2I^- (1M);\ E^o_{red} = +0.53\ V$$

but E^o does not change if we multiply the half-reaction by 2:

$$2I_2(s) + 4e^- \rightarrow 4I^- (1M);\ E^o_{red} = +0.53\ V$$

5. The sign of E^o_{red} changes, but its magnitude remains the same when we reverse a reaction.

6. The more positive the reduction potential, the greater the tendency to accept electrons. As a result, when two half-cells are coupled, the reaction with higher (more positive) reduction potential proceeds as reduction, while the other proceeds as oxidation.

Example 4.9

A Galvanic cell consists of a Mg electrode in 1.0 M $Mg(NO_3)_2$ solution and a Ag electrode in 1.0 M $AgNO_3$ solution. Calculate the standard cell potential (*emf*) of this cell at 25°C.

Solution:

Using Table 4.2, it can be noticed that Ag^+ will oxidize Mg:

Anode (oxidation) : $Mg(s) \rightarrow Mg^{2+}\ (1\ M) + 2e^-$; $E^o_{red} = +2.37\ V$

Cathode (reduction) : $2Ag^+\ (1\ M) + 2e^- \rightarrow 2Ag(s)$; $E^o_{red} = +0.80\ V$

Overall reaction : $Mg(s) + 2Ag^+\ (1\ M) \rightarrow Mg^{2+}\ (1\ M) + 2Ag(s)$

$$E^o_{cell} = 2.37\ V + 0.80\ V = +3.17\ V$$

Note that, in order to balance the overall reaction, we multiplied the cathode reaction by 2. We can do so because, E^o_{red} is an intensive property, which means it is not affected by this procedure. We can also find the E^o_{cell} by using the principle stated in number 6 above.

$Ag^+ (1.0\ M) + e^- \rightarrow Ag^+(s), E^o_{red} = +0.80\ V$ (*Cathode: higher reduction potential*)

$Mg^{2+} (1.0\ M) + 2e^- \rightarrow Mg(s), E^o_{red} = -2.37\ V$ (*Anode: lower reduction potential*)

$$E^o_{red} = E^o_{red}\ (\text{cathode}) - E^o_{red}\ (\text{anode})$$

$$= E^o_{red}\ (Ag^+/Ag) - E^o_{red}\ (Mg^{2+}/Mg)$$

$$= 0.80\ V - (-2.37\ V) = +3.17\ V$$

The positive value of E^o_{cell} shows that the forward reaction is favoured.

Experiment 4.3

Determination of Cell Potential of Daniell Cell

Objective: To determine cell potential of Daniell cell and to identify the cathode and anode.

Apparatus: Voltmeter, copper strip, zinc strip, 1 M $ZnSO_4$, 1 M $CuSO_4$, saturated KCl solution, two 100 mL beakers, U-tube, a fine sandpaper or file and cotton.

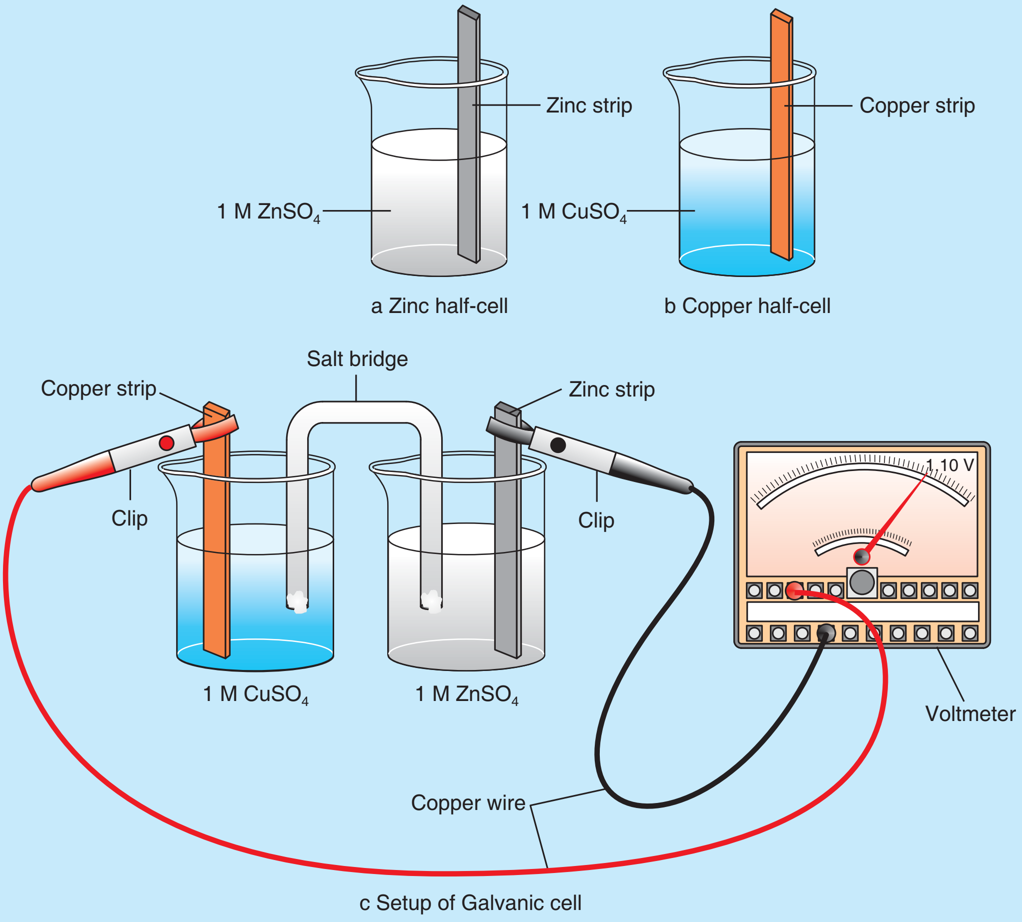


Figure 4.9 Daniell Cell.

Procedure:

1. Fill each U-tube with saturated KCl and plug each end with cotton. Be sure not to trap of any air bubbles in the tube. The cotton also helps to prevent the leakage of KCl solution.

2. Clean the metal strips (Zn and Cu) with a fine sandpaper or file, if needed. These strips are to be used as electrodes.

3. Assemble a Zn half-cell as shown in Figure 4.9a. Dip one end of the Zn metal strip in a 50 mL of 1 M $ZnSO_4$ in a 100 mL beaker. Then, attach one end of the copper wire with the strip of zinc and the other to terminal of a voltmeter. Do the same thing to construct the copper half-cell shown in Figure 4.9b. Connect the two half-cells using a salt bridge as shown in Figure 4.9c. Read the voltage and note the deflection of the voltmeter needle. Record your observations and give explanations for those observations.

Results and discussion:

1. What happens to the needle in the voltmeter when current flows in the external circuit? What does the deflection of needle indicate? Label the cathode and anode.
2. Write the half-reactions at each half cells.
3. Is there any colour change in the intensity of copper sulphate solution?
4. What are the factors that affect cell potential?

Exercise 4.9

1. What is the standard emf (E^{o}_{cell}) of a Galvanic cell which is made of a Cd electrode in a 1.0 M $Cd(NO_3)_2$ solution and a Cr electrode in a 1.0 M $Cr(NO_3)_3$ solution at 25°C?
2. Given the following overall reaction,

   $Cu^{2+}(1\ M) + Mg(s) \rightarrow Cu(s) + Mg^{2+}(1\ M)$

   a Sketch the Galvanic cell based on the reaction.

   b Identify the cathode and anode.

   c Show the direction of electron flow through the external circuit.

4.5.4 Electromotive Force (emf)

Activity 4.11

Form a group. Discuss the following question.

Why does water in a river flow downhill rather than uphill? How do you relate this concept to the movement of electrons in a wire? After the discussion, share your ideas with the rest of the class.

When electrons move through a wire, they encounter resistance from localised atoms in their paths. The driving force that allows the electrons to overcome this resistance and move around the circuit is called electromotive force (emf).

The electromotive force in a Galvanic cell comes from the redox reaction that pushes electrons from the anode to a cathode through the external circuit. Electrons on the negative electrode repel each other and have more potential energy than electrons on the positive electrode. This potential difference causes electrons to flow through the external circuit from the negative terminal (*anode*) to the positive terminal (*cathode*). The energy of the moving electrons is used to overcome resistance in the external circuit, and it can be used to do various forms of electrical work. Energy that overcomes resistance appears as heat or as light emitted by a glowing filament. Electrical work is used for starting cars, running watches, radios, and computers etc.

Electrical work (W) is the product of the emf of the cell and the total charge (in coulombs) that passes through the cell:

$$W = Q \times E$$

where Q is the charge and E is electrical potential.

$$\text{Electrical energy} = \text{coulombs} \times \text{volts} = \text{joules}$$

The total charge is determined by the number of moles of electrons (n) that pass through the circuit.

By definition,

$$Q = nF$$

where F, the Faraday constant, is the total electrical charge contained in 1 mole of electrons.

$$1\ \text{F} = 96{,}500\ \text{C/mol e}^-$$

Because $1\ \text{J} = 1\ \text{C} \times 1\ \text{V}$,

We can also express the unit of Faraday as $1\ \text{F} = 96,\ 500\ \text{J/V. mol e}^-$.

The measured emf is the maximum voltage that the cell can achieve. This value is used to calculate the maximum amount of electrical energy that can be obtained from the chemical reaction. This energy is used to do electrical work (W_{ele}), so

$$W_{max} = W_{ele} = -\,nFE_{cell}$$

where, W_{max} is the maximum amount of work that can be done.

What does the negative sign indicate?

The change in free energy (ΔG) represents the maximum amount of useful work that can be obtained from a reaction.

$$\Delta G = W_{max}$$

$$\Rightarrow \quad \Delta G = W_{max} = -\,nFE_{cell}$$

$$\Delta G = -\,nFE_{cell}$$

Both n and F are positive quantities, and ΔG is negative for a spontaneous process, so E_{cell} must be positive. Therefore, a positive E_{cell} value corresponds to a negative ΔG value, which is the condition for spontaneity.

For standard state conditions,

$$\Delta G^\circ = -\,nFE^\circ_{cell}$$

Now we can relate E°_{cell} to the equilibrium constant (K) of a redox reaction. The standard free energy change, ΔG°, for a reaction is related to its equilibrium constant, as follows.

$$\Delta G^\circ = -\,RT\ \ln K$$

If we substitute ΔG° by $-\,nFE^\circ_{cell}$ it becomes $+\,nFE^\circ_{cell} = +\,RT\ \ln K$

$$\Rightarrow \quad nFE^\circ_{cell} = RT\ \ln K$$

$$E^\circ_{cell} = \frac{RT}{nF}\ \ln K$$

When $T = 298$ K, the equation can be simplified by substituting for R and F.

$$E^\circ_{cell} = \frac{(8.134\text{J/mol K})\times(298\text{ K})}{n\,(96{,}500\text{J/V mol})}\ \ln K = \frac{0.0257\text{ V}}{n}\ \ln K$$

The natural logarithm (ln) is related to the common logarithm (log) as follows:

$$\ln x = 2.303\ \log x$$

$$\left(\frac{0.0257\text{V}}{n}\right)\times 2.303\log K = \frac{0.0592\text{ V}}{n}\log K$$

Therefore, $E^\circ_{cell} = \dfrac{0.0592\text{ V}}{n}\log K.$

Thus, if any one of the three quantities ΔG°, K or E°_{cell} is known, the other two quantities can be calculated, using the equations $\Delta G^\circ = -\,RT\ln K, \Delta G^\circ = -\,nFE^\circ_{cell}$ or $E^\circ_{cell} = \dfrac{-\Delta G^\circ}{nF}$.

Let us summarize the relationships among ΔG°, K and E°_{cell} and characterize the spontaneity of a redox reaction.

Table 4.3 Relationship among ΔG^o, K and E^o_{cell}

ΔG^o	K	E^o_{cell}	Reaction under standard state conditions
Negative	> 1	Positive	Favours the formation of products.
Zero	= 1	Zero	Reactants and products are equally favoured.
Positive	< 1	Negative	Favours the formation of reactants.

Example 4.10

Calculate the equilibrium constant for the following reaction at 25°C.

$$Sn(s) + 2Cu^{2+}(aq) \rightleftharpoons Sn^{2+}(aq) + 2Cu^{+}(aq)$$

Solution :

The equilibrium constant (K) can be calculated, using the equation,

$$\ln K = \frac{nE^o_{cell}}{0.0257\ V} \Rightarrow K = e^{\left(\frac{nE^o_{cell}}{0.0257\ V}\right)}$$

The half-reactions are:

$$\textit{Anode (oxidation)} \quad : \quad Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$$

$$\textit{Cathode (reduction)} \quad : \quad 2Cu^{2+}(aq) + 2e^- \rightarrow 2Cu^{+}(aq)$$

From the above reaction and using Table 4.2, we can calculate the cell potential,

$$E^\circ_{cell} = E^\circ_{red}\ (cathode) - E^\circ_{red}\ (anode)$$

$$= E^\circ_{red}\ (Cu^{2+}/Cu^{+}) - E^\circ_{red}\ (Sn^{2+}/Sn)$$

$$= 0.15\ V - (-\ 0.14\ V) = +0.29\ V$$

E°_{cell} is 0.29 V, and $n = 2$ (because 2 mol of electrons are consumed in the reaction), then,

$$\ln K = \frac{nE^o_{cell}}{0.0257\ V} = \frac{2 \times 0.29\ \cancel{V}}{0.0257\ \cancel{V}} = 22.6$$

$$\Rightarrow K = e^{22.6} = (2.72)^{22.6} = 7 \times 10^9$$

The reaction favours the products.

Example 4.11

Calculate the standard free-energy change for the following reaction at 25°C.

$$2Au(s) + 3Ca^{2+}\ (1.0\ M) \rightarrow 2Au^{3+}(1.0\ M) + 3Ca(s)$$

Solution :

The relationship between the standard free energy change and the standard cell potential is given by $\Delta G^o = -nFE^o_{cell}$. First, let us determine E^o_{cell}

The half-reactions are:

Anode (*oxidation*) : $2Au(s) \rightarrow Au^{3+}\ (1.0\ M) + 6e^-$

Cathode (*reduction*) : $3Ca^{2+}\ (1.0\ M) + 6e^- \rightarrow 3Ca(s)$

$$E^\circ_{cell} = E^\circ_{red}\ (cathode) - E^\circ_{red}\ (anode)$$

$$E^\circ_{cell} = E^\circ_{red}\ (Ca^{2+}/Ca) - E^\circ_{red}\ (Au^{3+}/Au)$$

$$= -2.87\ V - 1.50\ V = -4.37\ V$$

The overall reaction shows that n = 6 (6 moles of electrons are involved). Now we can calculate ΔG°, using the following equation:

$$\Delta G^\circ = -nFE^\circ_{cell}$$

$$= -6 \times (96500\ J/V\ mol) \times (-4.37\ V)$$

$$= 2.53 \times 10^6\ J/mol = 2.53 \times 10^3\ kJ/mol$$

Therefore, the large positive value of ΔG° tells us that the reaction favours the reactants at equilibrium. The forward reaction is non-spontaneous, that is, gold cannot reduce calcium.

Exercise 4.10

By referring to Table 4.2, calculate ΔG° for the following reaction at 25°C.

$$2Al^{3+}(aq) + 3Mg(s) \rightleftharpoons 2Al(s) + 3Mg^{2+}(aq)$$

4.5.5 Dependence of emf on Concentration

What is the effect of changing the concentration of reactants on cell potential?

A change in concentration affects the change of cell potential which is a result of free energy change. According to chemical thermodynamics

$$\Delta G = \Delta G^{o} + RT \ln Q$$

Where, Q is the reaction quotient, and Q was used to calculate the effect of concentration on ΔG. Since $\Delta G = -nFE_{cell}$ and $\Delta G^{o} = -nFE^{o}_{cell}$, the equation becomes

$$-nFE_{cell} = -nFE^{o}_{cell} + RT \ln Q$$

Dividing each side of the equation by $-nF$ gives

$$E = E^{o}_{cell} - \frac{RT}{nF} \ln Q$$

This equation gives the relationship between the cell potential and the concentrations of the cell components and is called the Nernst equation.

At 25°C:

$$E_{cell} = E^{o}_{cell} - \frac{(8.314 \text{ J/mol K}) \times (298 \text{ K})}{(n)\,(96,500 \text{ J/V mol})} \ln Q$$

$$E_{cell} = E^{o}_{cell} - \frac{0.0257 \text{ V}}{n} \ln Q \quad \text{or} \quad E = E^{\circ}_{cell} - \frac{0.0592}{n} \log Q$$

During the operation of a Galvanic cell, electrons flow from the anode to the cathode, resulting in product formation and a decrease in reactant concentration. Thus Q increases, which means that E_{cell} decreases. Eventually, the cell reaction reaches equilibrium. At equilibrium, there is no net transfer of electrons, so $E_{cell} = 0$ and $Q = K$, where K is the equilibrium constant.

The above equation enables us to calculate E_{cell} as a function of reactant and product concentrations in a redox reaction. For monovalent ions ten-fold changes in concentration of solution will cause a change of 0.0592 volts and bivalent a change of 0.0592/2 volts. For example, for the Daniell cell,

$$\text{Zn(s)} + \text{Cu}^{2+}\text{(aq)} \rightarrow \text{Zn}^{2+}\text{(aq)} + \text{Cu(s)},\ \text{E}^{o}_{cell} = 1.10 \text{ V}$$

The equation for this cell at 25°C can be written as:

$$E_{\text{cell}} = 1.1\text{ V} - \frac{0.0592}{2}\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Note that the concentration of liquids and solids is constant and does not appear in the equilibrium constant expression. If the ratio $[\text{Zn}^{2+}]/[\text{Cu}^{2+}]$ is less than 1, then log $([\text{Zn}^{2+}]/[\text{Cu}^{2+}])$ is a negative number. Therefore, the second term on the right-hand side of the preceding equation is positive. Under this condition, E_{cell} is greater than the standard cell potential. If the ratio is greater than 1, E_{cell} is smaller than E°_{cell}.

Example 4.12

Predict whether the following reaction would proceed spontaneously, as written at 298 K, given that $[\text{Co}^{2+}] = 0.15$ M and $[\text{Fe}^{2+}] = 0.68$ M :

$$\text{Co(s)} + \text{Fe}^{2+}\text{(aq)} \rightarrow \text{Co}^{2+}\text{(aq)} + \text{Fe(s)}$$

Solution :

Because the reaction is not run under standard state conditions (concentrations are not 1 M), we need the equation to calculate the emf (E_{cell}) of Galvanic cell. The standard emf (E°_{cell}) can be calculated, using the standard reduction potentials in Table 4.2.

The half-cell reactions are

Anode (oxidation) : $\text{Co(s)} \rightarrow \text{Co}^{2+}\text{(aq)} + 2e^-$

Cathode (reduction) : $\text{Fe}^{2+}\text{(aq)} + 2e^- \rightarrow \text{Fe(s)}$

$$E^{o}_{\text{cell}} = E^{o}_{\text{red}}(\textit{cathode}) - E^{o}_{\text{red}}(\textit{anode})$$

$$= E^{o}_{\text{red}}(\text{Fe}^{2+}/\text{Fe}) - E^{o}_{\text{red}}(\text{Co}^{2+}/\text{Co})$$

$$= -0.44\text{ V} - (-0.28\text{ V}) = -0.16\text{ V}$$

Using the equation,

$$E_{\text{cell}} = E^{o}_{\text{cell}} - \frac{0.0257\text{ V}}{n}\ln Q$$

$$= E^{o}_{\text{cell}} - \frac{0.0257\text{ V}}{n}\ln\frac{[\text{Co}^{2+}]}{[\text{Fe}^{2+}]}$$

$$= -0.16\text{ V} - \frac{0.0257\text{ V}}{2}\ln\left(\frac{0.15}{0.68}\right)$$

$$= -0.16\text{ V} + 0.019\text{ V} = -0.14\text{ V}$$

The reaction is not spontaneous in the direction written. Why?

Exercise 4.11

1. Will the following reaction occur spontaneously at 25°C, given that $[Fe^{2+}]$ = 0.60 M and $[Cd^{2+}]$ = 0.010 M? (Hint: Use the Nernst equation)

   $$Cd(s) + Fe^{2+} \rightarrow Cd^{2+}(aq) + Fe(s)$$

2. Complete the following table. State whether the cell-reaction is spontaneous, non-spontaneous, or at equilibrium.

E	ΔG	Cell reaction
> 0		
	> 0	
= 0		

4.5.6 Batteries

Activity 4.12

Form a group. Discuss the following questions, and share your idea with other groups.

1. What are the advantages of batteries?
2. When do we say a battery is "dead"?
3. Collect some used and disposed batteries;
   - i classify them as:
     - a primary battery or secondary battery.
     - b dry cell or alkaline battery etc.
   - ii Identify the parts of the batteries, which you have collected.
   - iii Describe the type of electrodes as well as physical and chemical nature of the electrolyte present in each battery.

Caution! Wear gloves while collecting the disposed batteries.

A battery is a Galvanic cell, or a series of combined Galvanic cells, that can be used as a source of direct current at a constant voltage.

The principal advantages offered by batteries are convenience and portability, rather than efficient use of energy.

Based on their rechargeability, we can classify batteries as primary and secondary. Primary batteries use redox reactions that cannot be returned to their original state by recharging, so when the reaction is complete, the batteries become "dead" and must be discarded. Secondary batteries are often called storage batteries, or rechargeable batteries. The reactions in these batteries can be reversed, which means that the batteries can be recharged. They have the advantage of being more cost-efficient in the long term although the individual batteries are more expensive.

PROJECT 4.1

Go to a nearby automobile garage and ask the garage mechanic:

1. about working of car battery;
2. how do they come to know whether a car battery needs recharging;
3. what components serve as electrolyte, anode and cathode in a car battery?

Write the project report and submit it to your teacher.

In this section, you will learn the various types of batteries that are widely used.

The Dry Cell Battery

Activity 4.13

In your Grade 10 chemistry, you have learnt about dry cell batteries. Form a group. Discuss the following questions, and share your idea with other groups.

1. What are the components that serve as electrolyte, anode and cathode in a dry cell?
2. For a dry cell, write the:
   - a oxidation half-reaction,
   - b reduction half-reaction, and
   - c overall reaction.

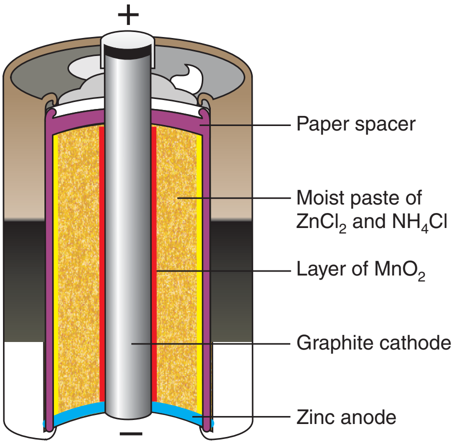


Figure 4.10 The interior section of a dry cell battery.

The voltage produced by a dry cell is about 1.5 V. The LeClanchè cells are widely used because of their low cost, but they have several disadvantages. If the current is drawn from the battery very rapidly, the gaseous products cannot be consumed immediately. As a result, the cell resistance increases and the voltage drop. In addition, since an ammonium ion is a weak conjugate acid, the zinc electrode and ammonium ion react very slowly. Because of this reaction, these voltaic cells cannot be stored indefinitely. You have probably learned from experience that, when the zinc outer cover deteriorates, the electrolyte can leak out and damage the flashlight or other appliances in which it contained.

Alkaline Battery

Alkaline batteries are more expensive than LeClanchè batteries. Why? They can generate current up to 50% longer than the same size of dry cell batteries. The chemistry of alkaline cells is quite similar to that of LeClanchè cells, except that the material inside the cell is basic or alkaline. Alkaline cells use the oxidation of zinc and reduction of MnO_2 to generate a current, but NaOH or KOH is used in the cell instead of the acidic salt NH_4Cl.

Anode : $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$

Cathode : $2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$

Write the overall balanced chemical equation.

The additional advantage of alkaline cells is that the cell potential does not decline under high current loads, because no gases are formed.

Mercury cells are alkaline cells that are typically used in calculators, cameras, watches and other devices. The anode in a mercury cell is again metallic zinc, but the cathode is mercury (II) oxide.

Anode : $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$

Cathode : $HgO(s) + H_2O(l) + 2e^- \rightarrow Hg(s) + 2OH^-(aq)$

Write the overall balanced chemical equation.

The cell produces 1.35 V. These cells are widely used, but their disposal is an environmental problem, and there are ongoing efforts to phase them out. Mercury and its compounds are poisonous. So, mercury batteries should be reprocessed to recover the metal at the end of their useful lives.

Nickel-Cadmium Battery

Because dry cells are not rechargeable, they have to be replaced frequently. The nickel-cadmium battery is rechargeable and especially is used in battery-operated tools and portable computers.

The cadmium metal serves as the anode, and the $NiO_2(s)$, which is reduced to $Ni(OH)_2(s)$, serves as the cathode. The cell reactions are:

Anode : $Cd(s) + 2OH^-(aq) \rightleftharpoons Cd(OH)_2(s) + 2e^-$

Cathode : $NiO_2(s) + 2H_2O(l) + 2e^- \rightleftharpoons Ni(OH)_2(s) + 2OH^-(aq)$

Overall reaction : $NiO_2(s) + Cd(s) + 2H_2O(l) \rightleftharpoons Ni(OH)_2(s) + Cd(OH)_2(s)$

The solid reaction products, $Ni(OH)_2$ and $Cd(OH)_2$, adhere to the electrodes. This permits the reactions to be readily reversed during charging.

The Lead Storage Battery

The lead storage battery commonly used in automobiles consists of six identical cells joined together in series. This is an example of a secondary rechargeable cell. The reactions within the cell can be reversed. Each cell has a lead anode and a cathode made up of lead oxide (PbO_2) packed on a metal plate.

Both the cathode and the anode are immersed in an aqueous solution of sulphuric acid which acts as the electrolyte. Figure 4.11 depicted the typical lead storage battery. The cell reactions are:

Anode : $Pb(s) + SO_4^{2-}(aq) \rightleftharpoons PbSO_4(s) + 2e^-$

Cathode : $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$

Overall reaction : $Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \rightleftharpoons 2PbSO_4(s) + 2H_2O(l)$

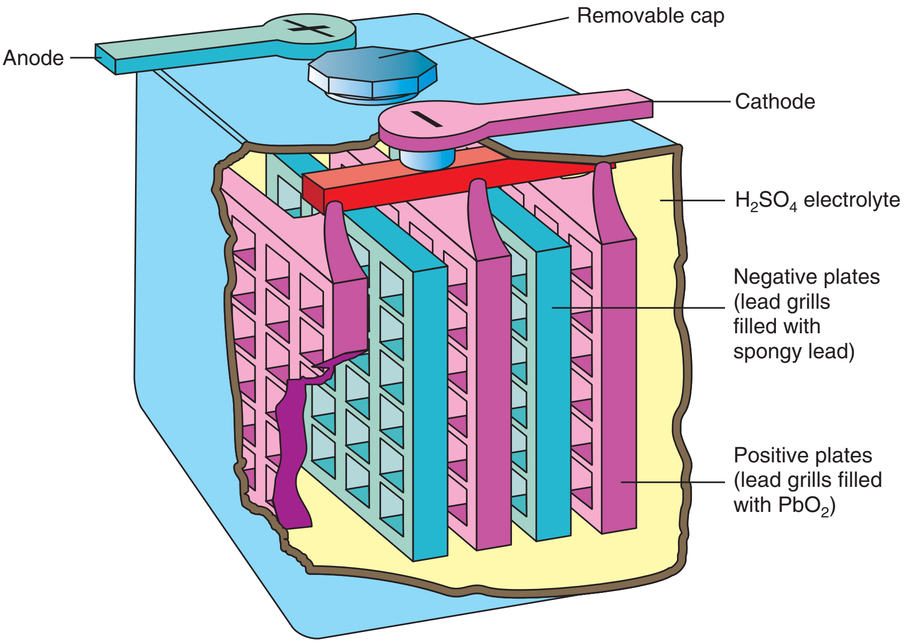


Figure 4.11 Interior section of a lead storage battery.

Under normal operating conditions, each cell produces 2 V. Therefore a total of 12 V is supplied by the six cells. Lead storage battery is used to power the ignition circuit of automobile and other electrical systems. The lead storage battery can deliver large amounts of current in short time, such as the time it takes to start up the engine. The lead storage battery is rechargeable.

Activity 4.14

Form a group. Discuss the chemical reactions occurring at the cathode and anode during the charging of the car battery. Do these reactions differ from the reactions occurring during discharge of the battery? Share your idea with the class.

Activity 4.15

Form a group. Discuss the following:

The electrolyte in a discharged lead storage battery freezes at higher temperature than a fully charged battery. Explain this observation to your class.

Fuel Cells

What makes a fuel cell different from other types of batteries?

Fossil fuels are major sources of energy, but the conversion of fossil fuel into electrical energy is a highly inefficient process.

Consider the combustion of methane:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) + \text{Energy}$$

To generate electricity, heat produced by the reaction is first used to convert water to steam, which then drives a turbine that drives a generator. A significant fraction of the energy released in the form of heat is lost to the surroundings at each step. Even the most efficient power plants convert only about 40% of the original chemical energy into electricity. Because combustion reactions are redox reactions, it is more desirable to carry them out directly by electrochemical means, thereby greatly increasing the efficiency of the power production. This objective can be accomplished by a device known as a fuel cell.

A fuel cell is a Galvanic cell that requires a continuous supply of reactants to keep functioning. In its simplest form, a hydrogen-oxygen fuel cell consists of an electrolyte solution such as sodium hydroxide solution, and two inert electrodes. The hydrogen and oxygen gases are bubbled through the anode and cathode compartments. See Figure 4.12.

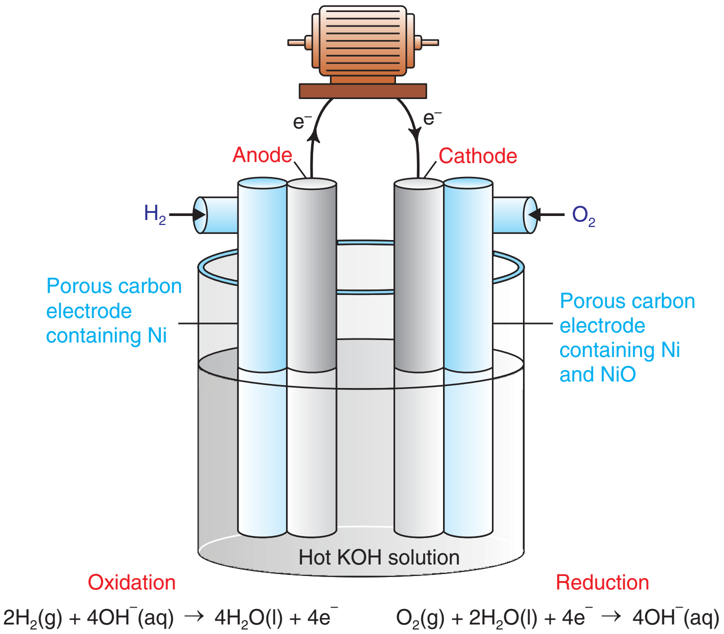


Figure 4.12 A Hydrogen-oxygen fuel cell.

The reactions are

Anode : $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$

Cathode : $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Overall reaction : $2H_2(g) + O_2(aq) \rightarrow 2H_2O(l)$

The standard cell potential, can be calculated using the data from Table 4.2.

$$\begin{aligned} E°_{cell} &= E°_{red}\,(cathode) - E°_{red}\,(anode) \\ &= 0.40\text{ V} - (-0.83\text{ V}) \\ &= +1.23\text{ V} \end{aligned}$$

Thus, the cell reaction is spontaneous under standard state conditions. Note that the reaction is the same as the hydrogen combustion reaction, except that the oxidation and reduction are carried out separately at the anode and the cathode. Unlike batteries, fuel cells do not store chemical energy. Reactants must be continuously supplied, and products must be continuously removed from a fuel cell.

Exercise 4.12

1. Explain the difference between a dry cell and a lead storage battery.
2. Write the reactions that occur at the cathode and anode during the charging of a lead storage battery.
3. a What is the electrolyte in a dry cell?
   b Write the half-reactions for the reducing and oxidizing agents in a dry cell.

4.5.7 Corrosion of Metals

What are the causes of corrosion?

Corrosion is the term usually applied to the deterioration of metals by an electrochemical process. It causes enormous damage to buildings, bridges, ships, and cars.

Can you give more examples of materials that can be damaged by corrosion from your environment?

Corrosion reactions are redox reactions in which a metal is attacked by some substance in its environment and is converted to an unwanted compounds. For nearly all metals, oxidation in air is a thermodynamically favourable process at room temperature. If the oxidation process is not inhibited, it can be very destructive. However, oxidation can also result in the formation of an insulating protective oxide layer that prevents further reaction of the underlying metal. For example, on the basis of the standard reduction potential for Al^{3+}, we would expect aluminium metal to be readily oxidized. The exceptional stability of this metal in air is due to the formation of a thin protective coat of oxide (a hydrated form of Al_2O_3) on the surface of the metal. The oxide coat is impermeable to the passage of O_2 or water and so protects the underlying metal from further corrosion. Magnesium metal is similarly protected.

Corrosion of Iron

The most familiar example of corrosion is the rusting of iron. Oxygen gas and water must be present for iron to rust. Although the reactions involved are quite complex and not completely understood, the main steps are believed to be as follows:

A region of the metal's surface serves as the anode, where oxidation occurs.

Anode **:** $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$;

The electrons given up by iron reduce atmospheric oxygen to water at the cathode, which is another region of the same metal surface.

Cathode **:** $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$;

The overall reaction is

$$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$

With data from Table 4.2, we find the standard emf for this process:

$$E^\circ_{cell} = E^\circ_{red}(cathode) - E^\circ_{red}(anode)$$

$$= 1.23\ V - (-0.44\ V)$$

$$= +1.67\ V$$

Note that this reaction occurs in an acidic medium, and the H^+ ions are supplied, in part, by the reaction of atmospheric carbon dioxide with water to form H_2CO_3.

Can you write the dissociation of carbonic acid in water?

The Fe^{2+} ions formed at the anode are further oxidized by oxygen:

$$4Fe^{2+}(aq) + O_2(g) + (4 + 2x)\ H_2O(l) \rightarrow 2Fe_2O_3 . xH_2O(s) + 8H^+(aq)$$

This hydrated form of iron (III) oxide is known as rust. The amount of water associated with the iron oxide varies, so we represent the formula as $Fe_2O_3.xH_2O$. Figure 4.13 shows the mechanism of rust formation.

Why does rusting of iron occur rapidly in salt water?

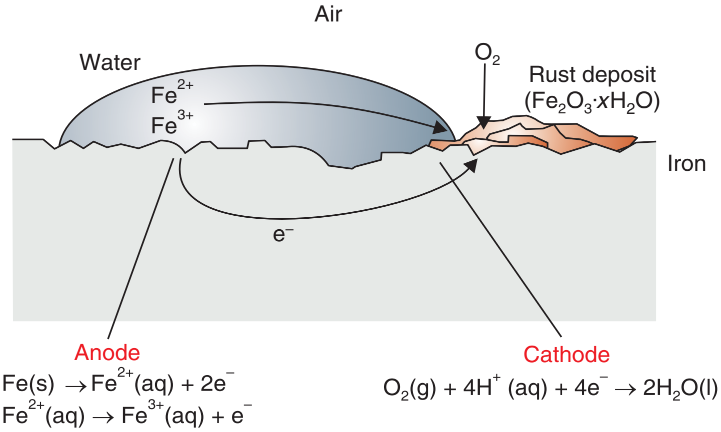


Figure 4.13 Corrosion of iron in contact with oxygen.

The electrical circuit is completed by the migration of electrons and ions.

Exercise 4.13

1. Define corrosion.
2. Explain the negative effects of corrosion.
3. Aluminium does not rust as iron does. Why?

Prevention of Corrosion

Activity 4.16

Form a group and discuss each of the following questions. After the discussion, share your ideas with the other groups.

1. List the methods that help to prevent the rusting of iron.
2. What is common in all methods of preventing the rusting of iron?

Activity 4.17

Form a group and discuss the following:

1. What does sacrificial anode mean?
2. Which of the following metals are suitable for uses as sacrificial anodes to protect against corrosion of underground iron pipes? If any are not suitable, explain why.

   Al, Pb, Mn, Mg and Cd.
3. What is the role of magnisum in the Figure 4.14?
4. Write chemical reactions occuring during protection of iron pipes, using magnisum as anode.
5. Would you advise to replace a section of damaged iron pipe with copper pipe? Explain?
6. Explain why galvanized iron, which contains a thin coating of zinc metal, corrodes much more slowly than iron.

After discussion, share your idea with rest of the class.

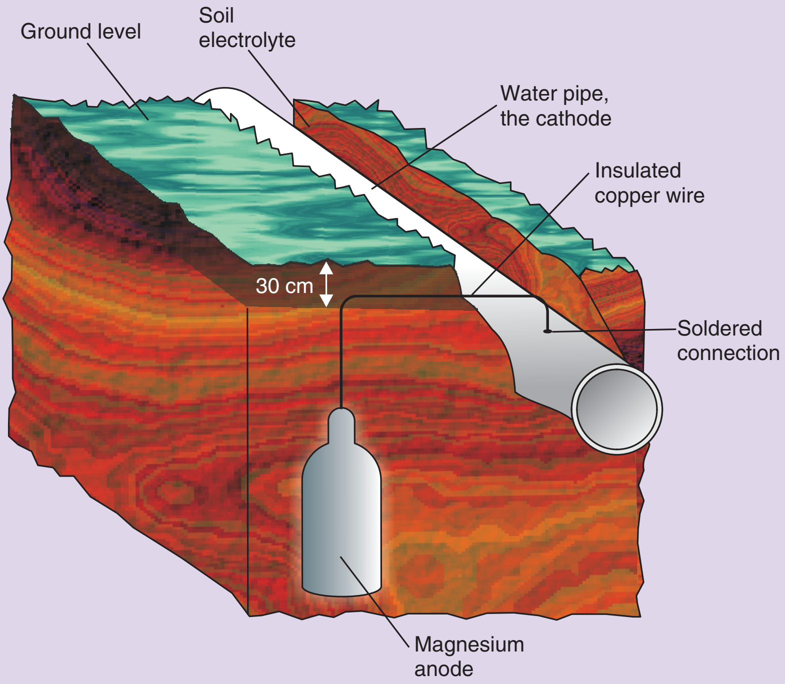


Figure 4.14 Protection of iron using magnesium.

Unit Summary

- *Oxidation is loss of electrons, and reduction is gain of electrons.*
- *A reduced substance is an oxidizing agent and an oxidized substance is a reducing agent.*

- *Redox reactions are balanced, using the oxidation number change method or the ion- electron method.*
- *Metals can conduct electricity because they have delocalized electrons, and electrolytes can also conduct electricity, due to the presence of free ions.*
- *In the electrolytic cell, electrical energy is used to bring about a chemical change.*
- *The cathode is the electrode at which reduction takes place and the anode is the electrode at which oxidation takes place.*
- *In an electrolytic cell, the anode is positive and the cathode is negative. In Galvanic cells, the electrode polarity is reversed.*
- *The preferential discharge of ions is affected by the nature of the electrodes, the position of the ions in the electrochemical series and the concentration of the ions in the electrolyte.*
- *In the electrolysis of molten sodium chloride, sodium is discharged at the cathode, and chlorine is released at the anode. But, in the electrolysis of concentrated brine solution, hydrogen is discharged at the cathode, and chlorine is discharged at the anode.*
- *In the electrolysis of dilute sodium chloride solution and dilute sulphuric acid solution, hydrogen gas discharges at the cathode and oxygen gas discharges at the anode.*
- *The Faraday's Laws are used to calculate the amount of substance deposited or liberated at the cathode or anode during electrolysis.*
- *Some of the applications of electrolysis are electroplating, electrorefining and extraction of metals and non-metals.*
- *A Galvanic cell is a device in which chemical energy is transformed to electrical energy.*
- *A salt bridge preserves the electroneutrality of a solution.*
- *A cell notation allows us to describe a Galvanic cell without drawing a diagram. The anode is written on the left and the cathode on the right.*
- *Cell potential is the difference between the electrode potentials of the cathode and anode.*

- *For spontaneous cell reactions,* $\Delta G < 0$ *and* $E_{cell} > 0$.
- *The Nernst equation enables us to calculate* E_{cell} *as a function of reactant and product concentrations in a redox reaction.*
- *A battery is a Galvanic cell that gives a direct current at a constant voltage.*
- *A battery can be either primary or secondary.*
- *Corrosion is the deterioration of metals by electrochemical processes. It is a redox reaction.*
- *Corrosion can be prevented by painting, electroplating and by way of cathodic protection.*

Check List

Key terms of the unit

- *Anion*
- *Anode*
- *Battery*
- *Brine solution*
- *Cathode*
- *Cation*
- *Cell notation*
- *Concentrated solution*
- *Conductivity*
- *Corrosion*
- *Daniell cell*
- *Dilute solution*
- *Dry cell*
- *Electrochemical series*
- *Electrolysis*
- *Electrolyte*
- *Electrolytic cell*
- *Electroplating*
- *Faraday's first law*
- *Faraday's second law*
- *Galvanic cell*
- *Galvanizing*
- *Nernst equation*
- *Oxidation*
- *Oxidation number*
- *Oxidizing agent*
- *Preferential discharge*
- *Primary batteries*
- *Redox reaction*
- *Reducing agent*
- *Reduction*
- *Salt bridge*
- *Secondary batteries*
- *SHE*
- *Standard electrode potential*

REVIEW EXERCISE ON UNIT 4

Part I: Multiple Choice Questions

1. What is the oxidation number of chromium in $(NH_4)_2Cr_2O_7$?

   a + 7 c +5

   b + 3 d + 6

2. In the following half-reaction,

   $$C_2O_4^{2-} \rightarrow CO_2 + xe^-$$

   The value of 'x' is:

   a 1 c 4

   b 2 d 3

3. Balance the following equation, using the lowest possible whole number coefficients;

   $$Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$$

   The sum of the coefficients is:

   a 8 c 12

   b 10 d 7

4. Which one of the following statements is not true regarding the electrolysis of concentrated sodium chloride solution?

   a chlorine gas is produced at the anode.

   b hydrogen gas is formed at the cathode.

   c oxygen gas is produced at the anode.

   d after the electrolysis, the remaining solution becomes basic.

5. Which one of the following statements about the Daniell cell is false?

   a zinc metal immersed in zinc sulphate solution acts as the anode.

   b copper metal dipped in copper sulphate solution acts as the cathode.

   c anode is the positive electrode and cathode is the negative electrode.

   d electrons flow from anode to cathode in the external circuit.

6. Given the following reaction:

$$Mg(s) + Zn^{2+}(aq) \rightarrow Mg^{2+}(aq) + Zn(s)$$

The correct cell notation for the reaction is:

a $Zn^{2+}(aq) \mid Zn(s) \parallel Mg(s) \mid Mg^{2+}(aq)$

b $Mg(s) \mid Mg^{2+}(aq) \parallel Zn^{2+}(aq) \mid Zn(s)$

c $Mg(s) \mid Mg^{2+}(aq) \parallel Zn(s) \mid Zn^{2+}(aq)$

d $Zn^{2+}(aq) \mid Zn(s) \parallel Mg^{2+}(aq) \mid Mg(s)$

7. Which of the following statements is correct about ΔG^{o}, K and E^{o}_{cell}?

a If K is less than one, ΔG^{o} is negative.

b If ΔG^{o} is zero, K is greater than one.

c If K is greater than one, the ΔG^{o} is negative.

d If a reaction is spontaneous, then ΔG^{o} is positive.

8. Which one of the following equations shows the relationship between standard Gibbs free energy and equilibrium constant?

a $K = \Delta G^{o}$

c $\Delta G^{o} = -RT \ln K$

b $K = RT \ln \Delta G^{o}$

d $\Delta G^{o} = RT \ln K$

9. Which of the following statements is true about E^{o}_{red}?

a When we reverse a reduction half-reaction, both the magnitude and sign of E^{o}_{red} change.

b The more positive the reduction potential, the higher the tendency to become a reducing agent.

c Its value does not change as we change the stochiometric coeffiecients of the half-reaction.

d All of the above

10. In the standard reduction potential table, the strongest oxidizing agent is:

a lithium

c ozone

b sodium

d fluorine

11. When does a spontaneous cell reaction occur:
    - a $\Delta G < 0$
    - b $E_{\text{cell}} > 0$
    - c $E_{\text{cell}} < 0$
    - d a and b

12. A battery is "dead" if:
    - a reactants and products reach their equilibrium concentrations.
    - b E_{cell} is equal to zero.
    - c ΔG is equal to zero.
    - d all of the above.

13. One of the basic differences between a fuel cell and a battery is:
    - a a fuel cell is rechargeable, while a battery is not.
    - b a fuel cell does not store chemical energy, but a battery can store chemical energy.
    - c both a fuel cell and a battery are rechargeable.
    - d a and c.

14. A metal corrodes if:
    - a it serves as cathode in the corrosion process.
    - b it serves as anode in the corrosion process.
    - c it does not react with oxygen.
    - d all of the above.

Part II: Short Answer Questions

15. Define each of the following terms:
    - a oxidation
    - b reduction
    - c anode
    - d cathode
    - e electrolytic cell
    - f Galvanic cell
    - g corrosion

16. How is corrosion of iron prevented?

17. Balance each of the following chemical equations, using oxidation state change method.

a $K_2CrO_4 + H_2O + S \rightarrow SO_2 + KOH + Cr_2O_3$

b $CuO + NH_3 \rightarrow Cu + N_2 + H_2O$

c $H_2SO_4 + NaBr \rightarrow Br_2 + SO_2 + Na_2SO_4 + H_2O$

18. Balance each of the following chemical equations in basic medium, using ion-electron method.

a $Mn^{2+} + BiO_3^- \rightarrow MnO_4^- + Bi$

b $H_2O_2 + Cl_2O_7 \rightarrow ClO_2^- + O_2$

19. Balance each of the following chemical equations in acidic medium, using ion-electron method.

a $MnO_4^- + CH_3OH \rightarrow Mn^{2+} + HCOOH$

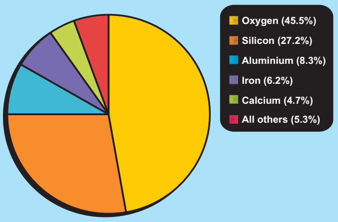
b $NO_2^- + Cr_2O_7^{2-} \rightarrow Cr^{3+} + NO_3^-$

20. Calculate the standard free energy change for the following reaction at 25°C. (Hint use Table 4.2.).

$Mg(s) + Zn^{2+}(1.0\ M) \rightarrow Zn(s) + Mg^{2+}\ (1.0\ M)$

21. Calculate the volume of H_2 and O_2 gases that, at 25°C and 1.00 atm, will collect at the cathode and anode, respectively, when an aqueous solution of Na_2SO_4 is electrolyzed for 1.5 h with a 10 A current.

UNIT 5



Some Elements in Chemistry and Industry

Unit Outcomes

After completing this unit, you will be able to:

- *describe the occurrence and abundance of the elements in nature;*
- *explain how carbon, nitrogen and phosphorus cycles in nature;*
- *understand metallurgical processes;*
- *understand the occurrence, extraction, chemical properties and uses of sodium, calcium, tin, lead, zinc and chromium;*
- *describe the occurrence, extraction, chemical properties and main uses of silicon;*
- *explain the major steps in the industrial production of ammonia, nitric acid, sulphuric acid and diammonium monohydrogen phosphate; and*
- *demonstrate scientific enquiry skills: classifying, communicating, asking questions, relating cause and effect and making generalizations.*

MAIN CONTENTS

5.1 Some Elements in Nature
5.2 Some Elements in Industry
– *Unit Summary*
– *Review Exercise*

5.1 SOME ELEMENTS IN NATURE

After completing this subunit, you will be able to:

- define the terms mineral and ore;
- describe the forms of occurrences of metals;
- discuss the distribution and relative amounts of the elements in the earth's crust;
- define the term fixation; and
- discuss the carbon cycle, the nitrogen cycle and the phosphorus cycle.

Start up Activity

1. Collect pieces of metals and non-metals from your neighbourhood. Explain how you classified these samples as metals and non-metals to the class.
2. Refer to chemistry books available in your school library, or to any other sources and;
   a identify three man-made elements and describe two physical properties for each element.
   b based on their positions in the periodic table, predict their chemical properties. Present your investigation to the class.

There are 113 elements known at present. 92 elements occur in nature, while the rest are man-made. All the materials on the earth are made of the naturally occurring elements. The elements are classified as metals, non-metals and metalloids.

A solid substance that occurs naturally in the earth's crust is called mineral. All minerals are not suitable for the extraction of elements. Minerals from which elements can be extracted easily and economically are called ores. Thus, all ores are minerals, but all minerals are not ores, because a mineral may not contain sufficient percentage of an element for economic extraction. In economic extraction, the cost of obtaining the element out of the ore is significantly less than the amount of money to be made by selling the element.

5.1.1 Occurrence of Elements

Activity 5.1

Try to find out:

a various gaseous elements around you;

b different metallic elements in your home and school;

c physical states in which the elements exist; and

d different non-metallic elements present in your body.

Make a list of metallic elements which you come across in your daily life, and discuss their importance with your friends.

Are all elements found free in nature?

The twelve most abundant elements that constitute 99.7% by mass of the earth's crust are, in decreasing order of abundance: oxygen (O), silicon (Si), aluminium (Al), iron (Fe), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), titanium (Ti), hydrogen (H), phosphorous (P), and manganese (Mn).

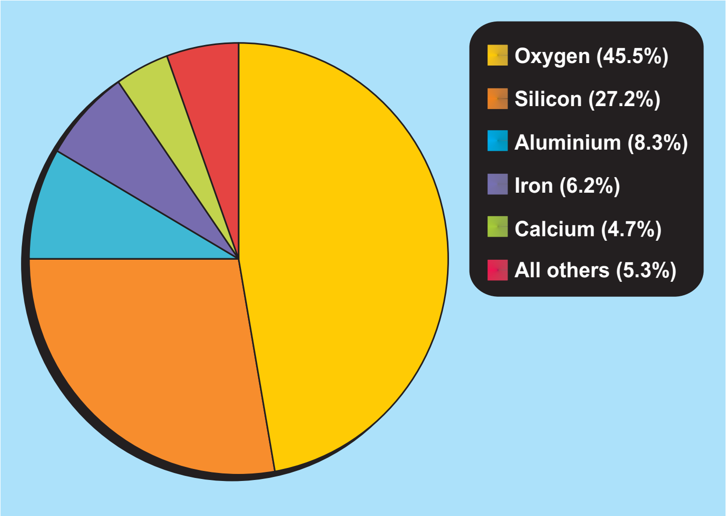


Figure 5.1 Abundance of elements in the Earth's crust.

The earth's atmosphere contains mainly nitrogen (78%), oxygen (21%), argon, carbon dioxide, and other trace gases.

Very few elements exist in the free or native state. The most unreactive metals, i.e., those that are not affected by air and water, such as silver, gold, platinum, palladium, ruthenium and osmium, are generally found in the native state. Most metals, however, occur in combined form as compounds such as oxides, carbonates, sulphides, sulphates, silicates, chlorides, nitrates and phosphates etc. A variety of physical and chemical methods can be applied to separate the pure forms of elements from their ores. However, the financial cost of mining, separating and purifying an element is the major consideration before a process is chosen for implementation.

Metals at the top of the reactivity series (K, Na, Ca, Mg, and Al) are so reactive that they are never found in nature as free elements. The metals in the middle of the reactivity series (Zn, Fe, Sn, and Pb) are moderately reactive and also exist in the combined state. Copper and silver are the two metals that occur in free as well as in combined states, such as as sulphide, oxide or halide ores.

Table 5.1 Reactivity series of elements (the most reactive is at the top and the least reactive is at the bottom).

Elements	Symbol
Potassium	K
Sodium	Na
Lithium	Li
Calcium	Ca
Magnesium	Mg
Aluminium	Al
Carbon	C
Zinc	Zn
Iron	Fe
Tin	Sn
Lead	Pb
Hydrogen	H
Copper	Cu
Silver	Ag
Gold	Au
Platinum	Pt

Table 5.2 Main type of minerals.

Type	Minerals
Uncombined metals	Ag, Au, Cu, Pd, Pt, Ru, Os
Carbonates	$BaCO_3$ (witherite), $CaCO_3$ (calcite, limestone), $MgCO_3$ (magnesite), $CaCO_3.MgCO_3$ (dolomite),
Halides	CaF_2 (fluorite), NaCl (halite), KCl (sylvine or silvite), Na_3AlF_6 (cryolite)
Oxides	$Al_2O_3.2H_2O$ (bauxite), Al_2O_3 (corundum), Fe_2O_3 (hematite), Fe_3O_4 (magnetite), Cu_2O (cuprite), SnO_2 (Cassiterite), TiO_2 (rutile), ZnO (zincite).
Phosphates	$Ca_3(PO_4)_2$ (phosphate rock), $Ca_5(PO_4)_3OH$ (hydroxylapatite)
Sulphides	Ag_2S (argentite), CdS (greenockite), Cu_2S (chalcocite), FeS_2 (pyrites), HgS(cinnaber), PbS (galena), ZnS (sphalerite)
Sulphates	$BaSO_4$ (barite), $CaSO_4$ (anhydrite), $PbSO_4$ (anglesite), $CaSO_4 . 2H_2O$ (gypsum), $MgSO_4 . 7H_2O$ (epsomite)

Exercise 5.1

1. Explain why some elements exist free in nature while others exist in the form of compounds.
2. List, in order, the six most abundant elements in the earth's crust and classify them as metals, non-metals and metalloids.
3. What is the distinction between a mineral and an ore?
4. Write the names of the minerals containing:

a	PbS	e	Fe_2O_3
b	FeS_2	d	HgS
c	$MgSO_4.7H_2O$	f	$CaCO_3.MgCO_3$

5.1.2 The Recycling of Elements in Nature

How do elements recycle in nature?

Living organisms interact with the environment. The key part of this interaction is the cycling of nutrients in the ecosystem.

An ecosystem consists of all organisms living in a community as well as the abiotic (non-living) factors with which they interact.

Nutrients provide substances to organisms that help them to grow, but nutrients can be very limited in the environment. It is through this exchange of necessary elements between the living and non-living world that sustains life. The major cycles that you will study are the carbon cycle, nitrogen cycle and phosphorus cycle. Note that the law of conservation of mass is obeyed in the recycling of substances.

Activity 5.2

Form a group, and discuss the following question. After the discussion, share your ideas with your classmates.

What are the impacts of afforestation, deforestation and the building of large numbers of cement factories, on global warming?

1. *The Carbon Cycle*

The Earth's atmosphere contains 0.035% carbon dioxide (CO_2), and the biological environment depends upon plants to convert carbon dioxide into sugars, proteins and fats.

As shown in Figure 5.2, green plants convert atmospheric carbon dioxide and water into glucose and oxygen in a process called photosynthesis.

$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6\ (aq) + 6O_2(g);\ \Delta H = +2803\ \text{kJ mol}^{-1}$$

Photosynthesis is an endothermic reaction. Solar energy from the sun provides the necessary energy for the above reaction to proceed.

Animals (including humans) eat plants, or eat other animals that have eaten plants, and incorporate the plants' carbon atoms into their cells.

Carbon returns to the physical environment in a number of ways. Both plants and animals respire, and they release carbon dioxide during respiration.

$$C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l);\ \Delta H = -2803\ \text{kJ mol}^{-1}$$

Respiration is an exothermic reaction, releasing 2803 kJ/mol of energy.

The process of decomposition of organic matter also releases carbon dioxide back into the atmosphere.

Over a very long period of time, dead organisms under high pressure and in the absence of air can be converted into fossil fuels such as coal, oil and gas. Humans combust these fossil fuels as energy sources which releases carbon dioxide back into the atmosphere. The complete combustion of coal, oil, or natural gas results in the formation of carbon dioxide gas:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

The combustion of fossil fuels is exothermic, and therefore, releases energy in the form of heat.

According to law of conservation of mass, the total number of carbon atoms (in the atmosphere) is always constant; but there is a growing concern over the amount of carbon that exists as carbon dioxide, because carbon dioxide is a greenhouse gas and is a major contributor to global warming.

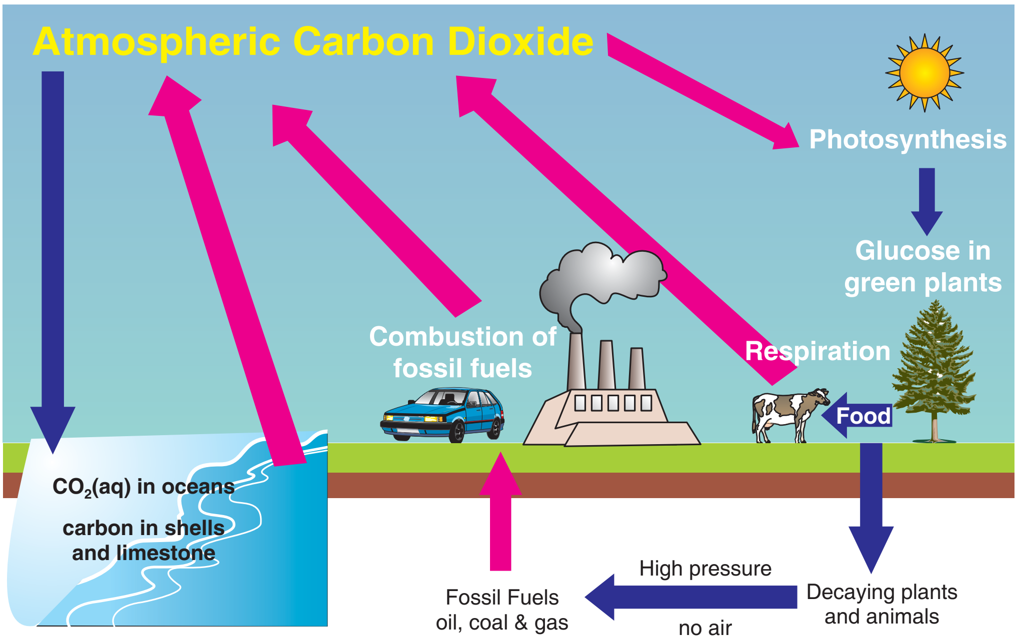


Figure 5.2 Carbon cycle.

Exercise 5.2

1. a Discuss how green plants and animals incorporate carbon atoms from atmospheric carbon dioxide gas.

   b Describe how carbon returns to the atmosphere.

2. One of the possible consequences of global warming is an increase in the temperature of ocean water. The oceans serve as a “sink” for CO_2 by dissolving a large amount of the substance. How would the solubility of CO_2 in the oceans be affected by an increase in the temperature of water?

Activity 5.3

In your group, discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. Why are fertilisers like urea and diammonium monohydrogen phosphate extensively used in agriculture?
2. What role do the nitrogen-fixing bacteria play in legumes in the nitrogen cycle?

2. *The Nitrogen Cycle*

Proteins and nucleic acids contain nitrogen, so nitrogen is a very important atom in biological organisms. Nitrogen makes up 78% of the earth’s atmosphere, but most organisms cannot use nitrogen (N_2). This is because the $N \equiv N$ triple bond has large dissociation energy ($945\ kJ\ mol^{-1}$), and N_2 is quite inert.

Nitrogen fixation refers to the conversion of nitrogen gas into nitrogen compounds.

Natural fixation reactions can be initiated by lightning, which breaks nitrogen molecules and enables their atoms to combine with oxygen in the air, forming nitrogen oxides. These compounds are then washed into the soil by rain.

Bacteria found in nodules in the roots of leguminous plants, such as beans, lentils, and peas, can convert atmospheric nitrogen gas into nitrates (NO_3^-), which plants use to make plant proteins. Generally, soluble nitrogen compounds in the soil can be taken up by plants to make plant proteins.

Animals eat plants and convert plant proteins into animal proteins. Animals excrete nitrogenous wastes, partially as urea or uric acid, which is returned to the soil.

Industrial chemical processes involving the fixation of atmospheric nitrogen include the Haber's process for the manufacture of ammonia, and the formation of calcium cyanamide, which involves the use of high temperatures and pressures. Bacteria can fix atmospheric nitrogen easily at room temperature and atmospheric pressure, yet man requires expensive industrial plants with high temperatures and pressures to do the same thing.

Once atmospheric nitrogen is fixed by chemical industries, it can be converted to nitrogen-containing fertilisers, which can be used by plants for their metabolism.

When plants and animals die, specialized decomposing bacteria will start to convert them back into ammonia and water-soluble ammonium salts. After the nutrients are converted back into ammonia, anaerobic bacteria will convert it back into nitrogen gas. This process is known as denitrification.

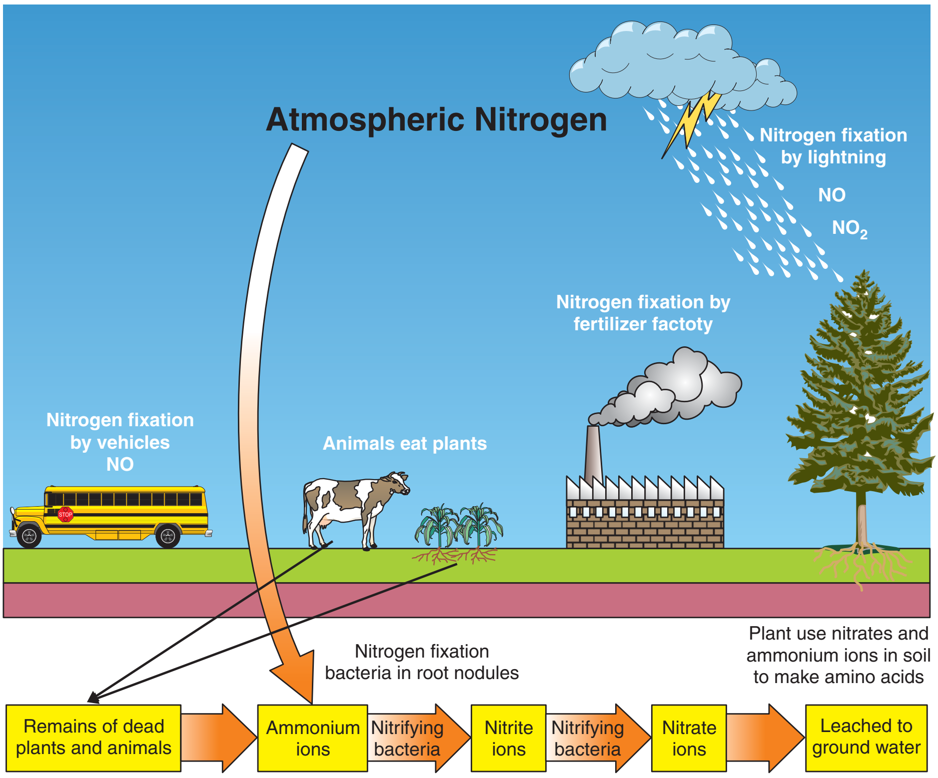


Figure 5.3 Nitrogen cycle.

Exercise 5.3

1. For what purpose do plants and animals need nitrogen?
2. Why is atmospheric nitrogen less reactive?
3. What is the difference between nitrogen fixation and denitrification? Use examples to explain your answer.
4. How is nitrogen fixed naturally and synthetically?

3. *The Phosphorus Cycle*

The phosphorus cycle differs from the nitrogen and carbon cycles primarily in that phosphorus is not found in the atmosphere in the gaseous state.

Phosphorus is mainly found in water, soil and sediments. It is an essential nutrient for plants and animals in the form of PO_4^{3-} and HPO_4^{2-} ions. It is part of DNA (deoxyribo nucleic acid) molecules, molecules that store energy-rich ATP (adenosine triphosphate) and fats of cell membranes. Phosphorus is a building block of certain parts of the human and animal body, such as bones and teeth.

Phosphate salts are released when phosphate rocks are eroded by rainfall, weathering and runoff. The release of phosphate salts into the soil results in a constant phosphorus supply for plants. Phosphate salts are absorbed through the roots of plants and are used to make organic compounds. Animals absorb phosphates by eating plants or plant-eating animals. When plants and animals die, they decompose and return phosphorus into the soil or water and complete the cycle.

In comparison to the nitrogen and carbon cycles, the rate at which phosphate salts are released is extremely slow. Phosphorus can remain in rocks or sediments for millions of years. As a result, the need of phosphate salts for plant growth outweighs the amount of phosphate salts being released. To alleviate the phosphate demand, the addition of phosphate fertilisers has been devised by humans to maintain and increase crop production.

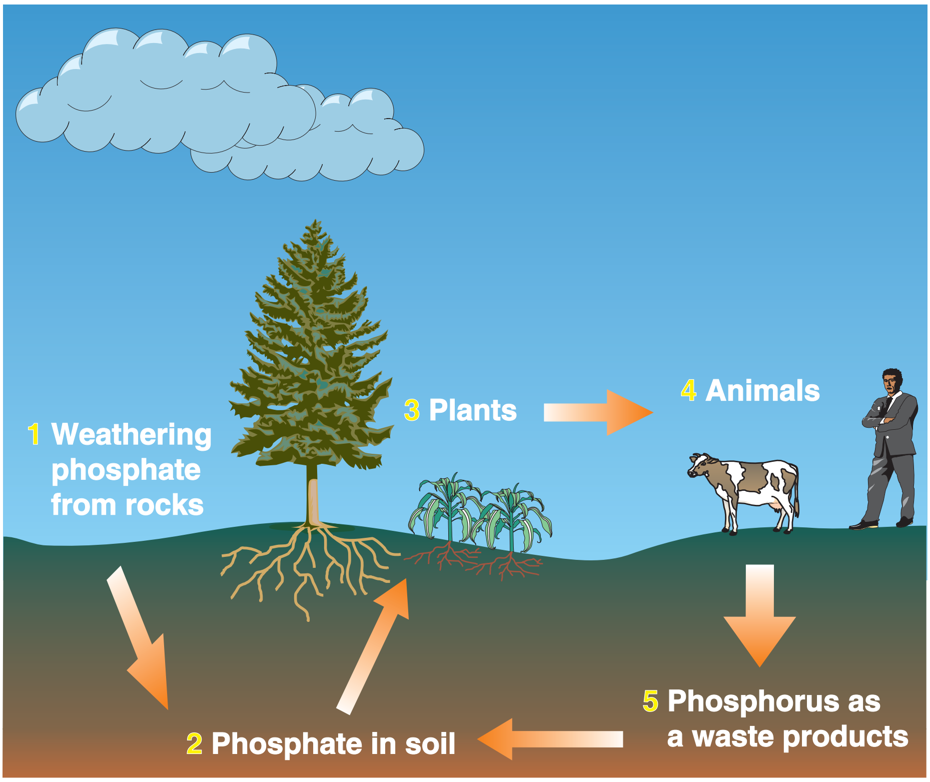


Figure 5.4 Phosphorus cycle.

Exercise 5.4

1. What are the effects of using phosphate fertilisers on the environment?
2. What makes the phosphorus cycle different from the carbon and nitrogen cycles?
3. What are the major uses of phosphorus in living organism?

5.2 Some Elements in Industry

After completing this subunit, you will be able to:

- define metallurgy;
- explain the major steps in metallurgical processes;
- describe the manufacture of sodium by Down's cells;

- explain the chemical properties of sodium;
- describe the uses of sodium;
- describe the manufacture of calcium;
- explain the chemical properties of calcium;
- describe the uses of calcium;
- describe the manufacture of tin;
- explain the chemical properties of tin;
- describe the uses of tin;
- describe the manufacture of lead;
- explain the chemical properties of lead;
- describe the uses of lead;
- describe the manufacture of zinc;
- explain the chemical properties of zinc;
- describe the uses of zinc;
- describe the manufacture of chromium;
- explain the chemical properties of chromium;
- describe the uses of chromium;
- describe the production of silicon;
- explain the chemical properties of silicon;
- describe the uses of silicon;
- explain the steps in the Haber process in the industrial production of ammonia and describe the uses of ammonia;
- explain the steps in the Ostwald's process in the industrial production of nitric acid and describe the uses of nitric acid;
- explain the steps in the Contact process in the industrial production of sulphuric acid and describe the uses of sulphuric acid; and
- explain the steps in the industrial production of diammonium monohydrogen phosphate and describe its uses.

Activity 5.4

Discuss each of the following questions in your group; after the discussion, share your ideas with the rest of the class.

1. How are metals extracted from their ores?
2. What property determines the application of chemical or electrolytic reduction?
3. Why are some elements extracted by electrolysis and others by chemical reduction? Give examples for each type.

5.2.1 Metallurgy

Metallurgy is the science and technology of extracting metals from their natural sources and preparing them for practical use.

The principal steps that are carried out to obtain a metal from its ore are: concentrating the ore, pre-treatment, extracting the metal and refining (*purifying*) the crude metal.

1. *Concentrating the Ore*

What physical and chemical methods are employed to concentrate an ore?

Concentrating an ore increases the fraction of metal-bearing ore by eliminating most of the accompanying rock and soil, called gangue. A gangue is undesired material or impurity, which is found together with the ore.

The ore must first be finely divided by crushing and grinding, and then the gangue can be removed in a number of ways.

i) Gravity Separation

Gravity separation depends on the difference in density between the mineral and the gangue. For example, since gold has a very large density (19.3 g/mL), it can be separated from its gangue by this method.

ii) Magnetic Separation

Magnetic separation can be used for separating ferromagnetic minerals from their impurities.

For example, the mineral magnetite (Fe_3O_4) can be separated from gangue by using a strong electromagnet.

iii) Froth Floatation

In this process, the ore is finely ground and added to water containing oil and detergent. Because of the differences in the surface characteristics of mineral particles and the silicate rock particles, the oil wets only the mineral particles. A stream of air blown through the mixture causes tiny bubbles to form on the oil-covered pieces, which then float to the surface in the form of froth or foam, while the gangue settles to the bottom. The froth is skimmed off, allowed to collapse, and then is dried to recover the mineral particles. For example, sulphide ores are concentrated by froth flotation.

iv) Amalgamation

An amalgam is an alloy of mercury with another metal or metals.

How are metals recovered from an amalgam?

Mercury forms amalgams with a number of metals and can be used to extract these metals from their ores. For example, mercury dissolves silver and gold in an ore to form a liquid amalgam, which is easily separated from the remaining ore. The gold or silver is recovered by distilling off the mercury.

v) Leaching

How does leaching differ from other methods of concentrating ore?

The methods we have seen so far are physical methods of concentrating ore. In contrast, leaching is a chemical process of concentrating ore. In this method, the ore is treated with a reagent that dissolves the target substance, leaving the impurities undissolved. For example, aluminium oxide, Al_2O_3, is separated from bauxite ($Al_2O_3·2H_2O$) and oxides of iron and silicon impurities. When the crushed ore is treated with hot 30% aqueous solution of sodium hydroxide, the amphoteric aluminium oxide dissolves.

$$Al_2O_3(s) + 2NaOH\ (aq\ 30\%) + 3H_2O \xrightarrow{150°C\ to\ 220°C} 2Na^+(aq) + 2Al(OH)_4^-(aq)$$

Why is aluminium oxide soluble in excess strong bases like NaOH?

Iron oxide and other basic oxides are not affected by the base, and the silicate impurities are converted to insoluble aluminosilicates. The solution is filtered, cooled, and diluted to reduce the OH^- concentration. Aluminium hydroxide then precipitates and the anhydrous oxide is obtained by heating.

$$Al(OH)_4^-\ (aq) \longrightarrow Al(OH)_3(s) + OH^-\ (aq)$$

$$2Al(OH)_3(s) \xrightarrow{heat} Al_2O_3(s) + 3H_2O(g)$$

Gold is sometimes found in ores in the elemental state, but it usually occurs in relatively small concentrations. A process called cyanidation treats the crushed ore with an aqueous cyanide solution in the presence of air. This process dissolves the gold by forming the complex ion $Au(CN)_2^-$.

$$4Au(s) + 8CN^-(aq) + O_2(g) + 2H_2O(l) \longrightarrow 4Au(CN)_2^-(aq) + 4OH^-(aq)$$

Pure gold is then recovered by reacting the solution of $Au(CN)_2^-$ with zinc powder to reduce Au^+ in the complex to Au.

$$2Au(CN)_2^-(aq) + Zn(s) \longrightarrow 2Au(s) + Zn(CN)_4^-(aq)$$

Activity 5.5

Discuss the following in your group; after the discussion, share your ideas with the rest of the class.

1. Which elements can form amalgam with mercury?
2. Can non-metals form amalgam; if not why?
3. What are the uses of amalgams in our daily life?

Exercise 5.5

1. Define metallurgy.
2. Describe and give an example of each of the following methods of concentrating ores.
   - a Gravity separation
   - b Magnetic separation
   - c Froth flotation
   - d Amalgamation
   - e Leaching

2. *Pre-treatment*

Pre-treatment converts a mineral to a form that is easy to reduce. For example, sulfides are converted to reducible oxides by heating them in dry air, a process called roasting:

$$2PbS(s) + 3O_2(g) \xrightarrow{heat} 2PbO(s) + 2SO_2(g)$$

If a metal is to be obtained by electrolytic reduction, its oxide, hydroxide, or carbonate is often treated with HCl to convert it to chloride. Chlorides are preferred for electrolytic reductions because they usually melt at low temperatures, except for aluminium chloride, to form conductive liquids. Molten aluminium chloride is a poor conductor of electricity. This pre-treatment method is used in the Dow process for obtaining magnesium metal from seawater.

Seawater contains about 1.3 g of magnesium ions per litre. These ions are first precipitated as magnesium hydroxide and then converted to magnesium chloride.

The chemical equations are:

$$CaCO_3(s) \xrightarrow{\text{heat}} \underset{\text{Lime}}{CaO(s)} + CO_2(g)$$

$$CaO(s) + H_2O(l) \longrightarrow \underset{\text{Saturated solution}}{Ca(OH)_2(aq)}$$

$$\underset{\text{Seawater}}{Mg^{2+}(aq)} + Ca(OH)_2(aq) \longrightarrow Mg(OH)_2(s) + Ca^{2+}(aq)$$

The magnesium hydroxide is filtered and converted to magnesium chloride with HCl.

$$Mg(OH)_2(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + 2H_2O(l)$$

Pure $MgCl_2$, for electrolysis, is recovered by evaporating the water.

3. *Production of Metals*

By what methods are metals extracted from their pre-treated ores?

Because metals in their combined form always have positive oxidation numbers, the production of a free metal usually involves a reduction process. How a particular pure metal is obtained by reduction from its combined form depends on the standard reduction potential of the metal. The production of metals by reduction may be accomplished either chemically or electrolytically.

a Chemical Reduction

A more electropositive metal can be used as a reducing agent to separate a less electropositive metal from its compound at high temperatures.

For example:

$$V_2O_5(s) + 5Ca(l) \longrightarrow 2V(l) + 5CaO(s)$$

$$TiCl_4(s) + 2Mg(l) \longrightarrow Ti(s) + 2MgCl_2(l)$$

$$Cr_2O_3(s) + 2Al(s) \longrightarrow 2Cr(l) + Al_2O_3(s)$$

The less electropositive metals like copper, tin, lead, zinc, manganese, cobalt, nickel and iron are obtained by reducing their oxides with coke (carbon) at high temperature.

$$ZnO(s) + C(s) \xrightarrow{\text{heat}} Zn(l) + CO(g)$$

Carbon is used as a reducing agent because it is readily available and is cheap. However, it can not be used to reduce all the metal oxides.

Hydrogen may also be used to reduce metals that are lower than itself in the reactivity series. But since hydrogen is more expensive than carbon, it is only used on a large scale for the extraction of tungsten because this process avoids the formation of tungsten carbide.

$$WO_3(s) + 3H_2(g) \longrightarrow W(s) + 3H_2O(g)$$

b Electrolytic Reduction

How can we prepare metals by electrolysis?

Electrolytic reduction is suitable for highly electropositive metals, such as sodium, magnesium and aluminium. Aluminium is extracted by the electrolysis of molten aluminium oxide (Al_2O_3) with cryolite (Na_3AlF_6). Cryolite is added to aluminium oxide to enhance electrical conductivity and to lower the melting point. However, the many metals are extracted by the electrolysis of anhydrous molten halides. At the cathode, metal ions are reduced and at the anode, anions are oxidized.

4. *Refining and Alloying*

Metals prepared by reduction usually need further treatment to remove impurities. The extent of purification, of course, depends on how the metal will be used. The three common purification procedures are distillation, electrolysis, and zone refining.

a Distillation

What kind of metals can be separated by distillation?

Metals that have low boiling points, such as mercury, magnesium, and zinc, can be separated from other metals by fractional distillation.

b Electrolysis

Electrolysis is another important purification technique. For example, the copper metal obtained by roasting copper sulphide usually contains impurities such as zinc, iron, silver, and gold. The more electropositive metals are removed by an electrolysis process in which the impure copper acts as anode and pure copper acts as the cathode. (Refer to the electrolysis of copper sulphate, using copper electrodes, in Unit 4).

c Zone Refining

Another method of obtaining pure metals is zone refining. In this process, a metal rod containing a few impurities is drawn through an electrical heating coil that melts the metal in the metal rod. Most impurities dissolve in the molten metal. As the metal rod comes out from the heating coil, it cools and the pure metal crystallizes, leaving the impurities in the molten metal portion that is still in the heating coil.

Purification of the metal occurs because as the crystal reforms, the metal ions are likely to fit much better in the crystal lattice than are atoms of impurities. Several repetitions of this process give a very pure metal.

High purity of metals is not always required, because pure metals possess undesirable properties for most practical applications. For instance, as you learned in Unit 4, iron deteriorates by corrosion. Therefore, iron is generally more useful when it is alloyed or coated with other metals.

To make alloys, metals are melted together to form a molten solution, and the solution is cooled to the solid state. The resulting alloy possesses the same general characteristics as the parent metals. However, because the alloy is a mixture in the form of a solid solutions, it is stronger than its parent metals.

Activity 5.6

Form a group. Discuss the following questions in your group. After the discussion, share your ideas with the rest of class.

1. Make a list of various elements present in sea water and river water.
2. Are carbonates and bicarbonates also present in sea water?
3. Which elements are economically recovered from sea water by electrolysis?

Exercise 5.6

1. Discuss the main steps in obtaining a pure metal from its ore.
2. What is meant by pre-treatment of an ore? Give some examples of pre-treatment.
3. Describe, with examples, the chemical and electrolytic reduction processes used in the production of metals.
4. Describe the process by which a metal is purified by zone refining.
5. A copper sample containing gold, lead, silver, and zinc as impurities, is refined electrolytically using a copper sulphate as electrolyte. Use Table 4.2 and state which substances will be found in the anode sludge.

5.2.2 Extraction, Properties and Uses of Some Selected Metals

1. Sodium

Activity 5.7

Form a group. Discuss the following questions in your group. After the discussion, share your ideas with the rest of class.

1. What are the main ores of sodium?
2. Which of the ores you listed in question (1) are found in Lake Afdera and Lake Abiyata?
3. Which regions in Ethiopia are the potential sources of table salt?
4. Why is sodium metal kept under kerosene or paraffin oil?
5. For the electrolysis of molten sodium chloride, write a balanced chemical equation for:

   a anode reaction b cathode reaction c overall reaction

Extraction of Sodium

How is sodium metal extracted from sodium chloride?

Sodium is a very reactive metal and is not found free in nature. It exists in the form of compounds. It is a strong reducing agent and cannot be reduced by carbon. Sodium is obtained by the electrolysis of a molten mixture of about 40% $NaCl$ and 60% $CaCl_2$ in a Downs cell as shown in Figure 5.5. Calcium chloride ($CaCl_2$) is added to lower the melting point of $NaCl$ from 800°C to 600°C.

The sodium metal formed at the cathode is in liquid state. Because sodium metal is less dense than molten NaCl, the sodium floats to the surface and is collected. Chlorine gas forms at the anode and is collected at the top of the Downs cell.

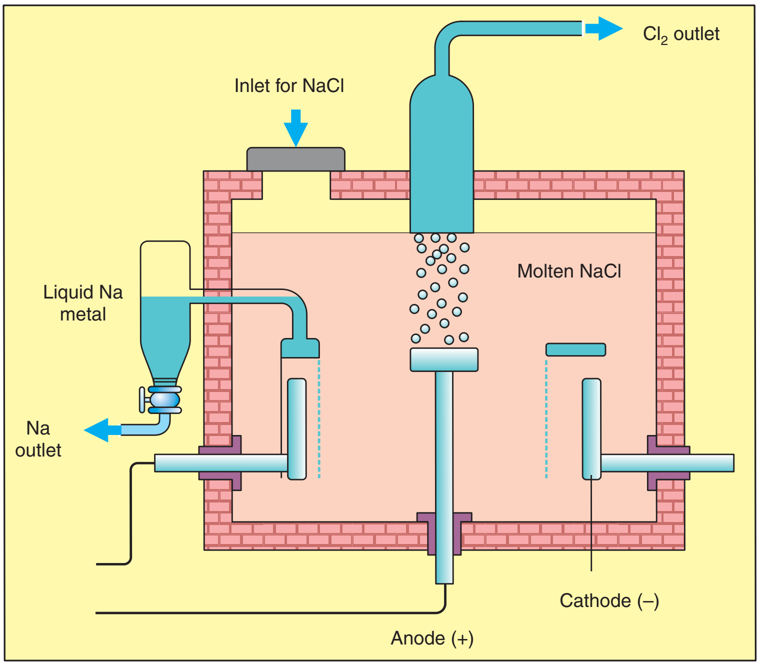


Figure 5.5 Downs cell for electrolysis of molten NaCl.

Chemical Properties of Sodium

a Reaction with water

Sodium reacts with water, liberating hydrogen and forming sodium hydroxide solution.

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$

b Reaction with air

Sodium tarnishes readily in dry air to form sodium peroxide and sodium oxide.

$$6Na(s) + 2O_2(g) \longrightarrow \underset{\text{major product}}{Na_2O_2(s)} + \underset{\text{minor product}}{2Na_2O(s)}$$

c Reaction with hydrogen

Sodium reacts with hydrogen to form sodium hydride.

$$2Na(s) + H_2(g) \longrightarrow 2NaH(s)$$

d Reaction with halogens (F_2, Cl_2, Br_2 and I_2)

Sodium reacts with halogens to form sodium halides.

$$2Na(s) + F_2(g) \longrightarrow 2NaF(s)$$

Uses of Sodium

The largest use of sodium is to make a Na/Pb alloy needed to make tetraethyl lead ($PbEt_4$) and tetramethyl lead ($PbMe_4$). These compounds are used as anti-knock additives to petrol. Another important use is to reduce $TiCl_4$ and $ZnCl_4$ to the metals. Liquid sodium metal is used as a coolant in nuclear reactors. It is also used to make Na_2O_2 and NaH, and for street lights.

Exercise 5.7

1. Write the chemical formulas of the following ore:

   a borax b trona c rock salt

2. Why is calcium chloride added in the electrolysis of molten sodium chloride?
3. Assume that a piece of sodium catches a fire in the laboratory. Why shouldn't you try to extinguish with water?
4. Write balanced chemical reactions for the reaction of sodium with:

   a chlorine b bromine c iodine

5. State the uses of sodium metal.

2. *Calcium*

Occurrence of Calcium

Calcium is the 5th most abundant element in the earth's crust. The main ores of calcium are: limestone, chalk, and marble ($CaCO_3$), dolomite ($CaCO_3.MgCO_3$), gypsum ($CaSO_4.2H_2O$), fluorite (CaF_2), and hydroxylapatite, $Ca_5(PO_4)_3OH$. In Ethiopia, gypsum deposits are found in the Danakil depression.

Extraction of Calcium

Explain why sodium and calcium cannot be extracted by using carbon as a reducing agent?

Calcium is prepared by the electrolysis of molten calcium chloride ($CaCl_2$).

Anode (oxidation) : $2Cl^-(l) \longrightarrow Cl_2(g) + 2e^-$

Cathode (reduction) : $Ca^{2+}(l) + 2e^- \longrightarrow Ca(l)$

Overall reaction : $Ca^{2+}(l) + 2Cl^-(l) \longrightarrow Ca(l) + Cl_2(g)$

Calcium can also be prepared by the reduction of CaO by aluminium in vacuum, where the calcium produced distills off.

Based on the above information, write an equation that shows the reaction between calcium oxide and aluminium metal.

Chemical properties of Calcium

a Reaction with water

Calcium reacts with cold water quite readily, liberating hydrogen gas and forming calcium hydroxide.

$$Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$$

b Reaction with oxygen

Calcium reacts with oxygen to form calcium oxide.

$$2Ca(s) + O_2(g) \longrightarrow 2CaO(s)$$

c Reaction with nitrogen

Calcium reacts with nitrogen at high temperatures to form calcium nitride.

$$3Ca(s) + N_2(g) \xrightarrow{\text{high temperature}} Ca_3N_2(s)$$

d Reaction with halogens

Calcium reacts with F_2, Cl_2, Br_2 and I_2 to form CaF_2, $CaCl_2$, $CaBr_2$ and CaI_2 respectively.

$$Ca(s) + F_2(g) \longrightarrow CaF_2(s)$$

e Reaction with hydrogen

Calcium combines with hydrogen to form calcium hydride.

$$Ca(s) + H_2(g) \longrightarrow CaH_2(s)$$

Uses of Calcium

Calcium is an essential element in living matter. It is the major component of bones and teeth. A characteristic function of Ca^{2+} ions in living systems is in the activation of a variety of metabolic processes. For example, calcium plays a vital role in heart action, blood clotting, muscle contraction, and nerve-impulse transmission.

Exercise 5.8

1. List the common ores of calcium.
2. When exposed to air, calcium first forms calcium oxide, which is then converted to calcium hydroxide, and finally to calcium carbonate. Write a balanced chemical equation for each step.
3. Write a balanced chemical equation to show the reaction between calcium and:

   a chlorine
   c iodine
   b bromine
   d nitrogen
4. Describe the uses of calcium metal.

3. *Tin*

Occurrence

The only important ore of tin is cassiterite, SnO_2.

Extraction of Tin

Activity 5.8

Refer to chemistry books available in your school library, or to any other sources, and write a report how tin occurs in nature and how it is extracted from cassiterite. After discussing it with your teacher, present your report to the class.

Chemical Properties of Tin

a Reaction with water

Tin does not react with cold water, but it reacts with steam to form SnO_2 and H_2.

$$Sn(s) + 2H_2O(g) \xrightarrow{heat} SnO_2(s) + 2H_2(g)$$

b Reaction with acids

Tin reacts with dilute and concentrated acids.

$$Sn(s) + \textit{dil. } 2HCl(aq) \longrightarrow SnCl_2(aq) + H_2(g)$$

$$Sn(s) + \textit{conc. } 4HNO_3(aq) \longrightarrow Sn(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

c Reaction with halogens

Tin reacts with Cl_2 and Br_2 in the cold and with F_2 and I_2 on warming, forming the corresponding tin tetrahalide.

$$Sn(s) + 2Cl_2(g) \xrightarrow{\text{cold}} SnCl_4(s)$$

$$Sn(s) + 2F_2(g) \xrightarrow{\text{warm}} SnF_4(s)$$

Uses of Tin

The main uses of tin are for electroplating steel, to make tin-plate, and alloys. Tin-plate is extensively used for making cans for food. Tin is a constituent of many alloys, including type metal (Sn, Sb and Pb), bronze (Sn and Cu), and solder (Sn and Pb).

Exercise 5.9

1. Write balanced chemical equation to show the extraction of tin from cassiterite.
2. Write the reactions of tin with steam and dilute HNO_3.
3. Write the reactions of tin with chlorine, bromine and iodine.
4. Describe the uses of tin metal.

4. *Lead*

Occurrence of Lead

The main ore of lead is galena, PbS. It is black, shiny and very dense.

Extraction of Lead

Galena is mined and separated from its impurities by froth flotation. There are two methods of extracting the element:

According to first method, the ore is roasted in air to give PbO, which is then reduced with coke or carbon monoxide in a furnace.

$$2PbS(s) + 3O_2(g) \longrightarrow 2PbO(s) + 2SO_2(g)$$

$$2PbO(s) + C(s) \xrightarrow{\Delta} 2Pb(l) + CO_2(g)$$

In second method, PbS is partially oxidized by heating and blowing air through it. After some time the air is turned off and heating is continued, and the mixture undergoes self–reduction.

$$3PbS(s) + O_2(g) \xrightarrow{\text{heated in air}} PbS(s) + 2PbO(s) \xrightarrow[\text{of air}]{\text{heated in absence}} 3Pb(l) + SO_2(g)$$

Chemical Properties of Lead

Lead is not affected by water because the metal is covered by a thin oxide film. It dissolves slowly in dilute HCl, forming the sparingly soluble $PbCl_2$ and quite readily in dilute HNO_3, forming $Pb(NO_3)_2$ and oxides of nitrogen. However, it does not dissolve in dilute H_2SO_4 because a surface coating of $PbSO_4$ is formed. Lead is slowly attacked by cold alkali, and rapidly by hot alkali, giving the plumbates $Na_2Pb(OH)_6$. Thus, lead is amphoteric. It also reacts with F_2 in the cold, forming PbF_2, and with Cl_2 on heating, giving $PbCl_2$.

Uses of Lead

The major use of lead is to make lead-acid storage batteries. It is also used in the manufacture of $PbEt_4$ as an additive for petrol, in paints and pigments. In addition, lead is used for the production of lead sheets, lead pipes and solder.

Exercise 5.10

1. Show the extraction of lead from galena, using chemical equations.
2. Write balanced chemical equations to show the reaction between lead and
   a H_2O b HCl c HNO_3
3. Describe the uses of lead metal.

5. *Zinc*

Occurrence of Zinc

Zinc is the 24th most abundant element in the earth's crust. The most important ore of zinc is zinc blende (ZnS).

Extraction of Zinc

How is zinc metal extracted from zinc blende?

ZnS is concentrated by froth flotation and then roasted in air to give ZnO and SO_2. The SO_2 is used to make H_2SO_4. Zn is extracted from the oxide by two different processes.

1. ZnO may be reduced by carbon monoxide at 1200°C

$$ZnO(s) + CO(g) \longrightarrow Zn(g) + CO_2(g)$$

2. ZnS is heated in air at a lower temperature, yielding ZnO and $ZnSO_4$. These are dissolved in H_2SO_4. Zinc dust is added to precipitate Cd, and then the $ZnSO_4$ solution is electrolyzed to give pure zinc. This method is more expensive than the first.

Chemical Properties of Zinc

Zinc is a silvery solid that tarnishes rapidly in moist air. It dissolves in dilute HCl and liberates hydrogen gas.

$$Zn(s) + HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$$

Zinc also reacts with aqueous solution of sodium hydroxide and forms sodium zincate, $Na_2Zn(OH)_4$. Hence, zinc shows amphoteric properties.

On heating, it reacts with oxygen to form zinc oxide.

$$2Zn(s) + O_2(g) \xrightarrow{\text{heating}} 2ZnO(s)$$

Uses of Zinc

Zinc is used in large amounts for coating iron to prevent it from rusting. A thin coating of zinc may be applied electrolytically. This process is called galvanizing. A thicker layer may be applied by dipping a metal in molten zinc. Large amounts of Zn are used to make alloys. The most common alloy is brass, which is an alloy of copper and zinc.

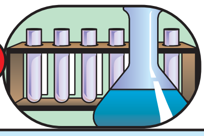
Can you list the other alloys of zinc?

Zinc is also used as the negative electrode (anode) in sealed 'dry' batteries such as Le clanche' cells, mercury cells and alkaline manganese cells. Zinc oxide is sometimes used as a white pigment in paint. It is particularly bright as it absorbs UV light and re-emits it as white light.

Exercise 5.11

1. Describe the extraction of zinc from zinc blende.
2. Explain the amphoteric properties of zinc.
3. State the uses of zinc metal.

Experiment 5.1



Studying Chemical Properties of Some Metals

Objective: To study some chemical properties of sodium, calcium, lead, tin and zinc metals.

Chemicals: Na, Ca, Sn, Pb, and Zn metals; 2 M HCl, water.

Apparatus: Test tubes and beakers.

1. *Reaction of cold water with sodium*

   Take about 5 mL of water in a test tube and place a small piece of sodium metal to the water. Check the basicity of the solution using litmus paper.

2. *Reaction of cold water with calcium*

   Take about 50 mL of water in a beaker and add a small piece of calcium metal in the water. Check the basicity of the solution by using litmus paper.

3. Reaction of tin, lead and zinc with 2M HCl

   Place 1 mL of 2M HCl in three test tubes and then add a small piece of tin metal in the first test tube, lead metal in the second test tube, and zinc metal in the third test tube. What do you observe?

Results and Discussion:

1. What is the gas liberated? How do you confirm it?
2. Write a chemical equation that shows:

   a the burning of hydrogen gas.

   b the reaction between zinc and dilute hydrochloric acid.

6. Chromium

Occurrence

Chromium is the 21st most abundant element, by weight, in the Earth's crust. The most important ore of chromium is chromite ($FeCr_2O_4$).

Extraction

Chromium is produced in two forms which are ferrochrome and pure chromium metal. Ferrochrome is mainly an alloy of chromium and iron. It is prepared by reducing chromite with carbon.

$$FeCr_2O_4(s) + 4C(s) \xrightarrow[\text{furnance}]{\text{electric}} \underbrace{Fe + 2Cr}_{\text{ferrochrome}} + 4CO$$

Four basic steps are followed to get pure chromium.

Step 1: When chromite is fused with NaOH in air, chromium (III) is oxidized to chromium (VI).

$$4FeCr_2O_4(s)+16NaOH(s)+7O_2(g) \xrightarrow{1100°C} 8Na_2CrO_4(s)+2Fe_2O_3(s)+8H_2O(l)$$

Step 2: Ferric oxide (Fe_2O_3) is insoluble, but sodium chromate (Na_2CrO_4) is soluble in water. Thus the sodium chromate is separated from ferric oxide by dissolving with water, followed by decantation or filtration. The sodium chromate solution is acidified to convert it to a less soluble sodium dichromate.

$$2Na_2CrO_4(aq) + 2HCl(aq) \longrightarrow Na_2Cr_2O_7(s) + 2NaCl(aq) + H_2O(l)$$

Step 3: The sodium dichromate is reduced to Cr_2O_3 by heating with carbon.

$$Na_2Cr_2O_7(s) + 2C(s) \longrightarrow Cr_2O_3(s) + Na_2CO_3(s) + CO(g)$$

Step 4: Finally, Cr_2O_3 is reduced to the metal by Al.

$$Cr_2O_3(s) + 2Al(s) \longrightarrow 2Cr(s) + Al_2O_3(s)$$

Chemical Properties

Chromium is an active metal but it is protected from corrosion by a very thin transparent oxide film.

$$4Cr(s) + 3O_2(g) \longrightarrow 2Cr_2O_3(s)$$

Concentrated nitric acid and other oxidizing agents build up the oxide film to the point where chromium becomes passive, that is, it no longer dissolves in the acid solution.

Chromium dissolves in HCl and dilute H_2SO_4 to form blue chromium (II) ions, which are stable only in the absence of air.

$$Cr(s) + 2H^+(aq) \longrightarrow Cr^{2+}(aq) + H_2(g)$$

The unstable chromium (II) state is readily oxidized to the chromium (III) state.

It can remove traces of oxygen by bubbling the gas through a solution containing chromium (II) ions.

$$4Cr^{2+}(aq) + O_2(g) + 4H^+(aq) \longrightarrow 4Cr^{3+}(aq) + 2H_2O(l)$$

Uses

Nichrome wire, commonly used in chemistry laboratories for flame tests, is an alloy of nickel and chromium. Ferrochrome, iron–chromium alloy, is used in the production of stainless steel. Cr_2O_3 is dissolved in H_2SO_4 and deposited electrolytically (*electroplating*) on the surface of a metal. This protects the metal from corrosion and gives it a shiny appearance.

Sodium and potassium chromates and dichromates are used as pigments and corrosion inhibitors in heating systems and air-conditioning systems.

Chromium (VI) oxide, CrO_3, appears as a bright-red precipitate when saturated potassium dichromate is treated with excess of concentrated sulphuric acid.

$$Cr_2O_7^{2-}(aq) + 2H^+(aq) \longrightarrow 2CrO_3(s) + H_2O(l)$$

$$CrO_3(s) + H_2O(l) \rightleftharpoons H_2CrO_4$$

The resulting acid mixture (also known as chromic acid) is a powerful oxidizing agent. It can oxidize grease and was used as a cleaning solution for laboratory glassware.

Exercise 5.12

1. Write equations for the reduction of chromite ore with carbon, and Cr_2O_3 with aluminium.
2. Pure chromium can also be prepared from chromite by the following steps. Write the equations for each step.

Step 1: The ore is fused with sodium carbonate in the presence of air, yielding sodium chromate, iron (III) oxide, and carbon dioxide gas.

Step 2: The sodium chromate is converted to sodium dichromate by the addition of acid.

Step 3: The sodium dichromate is recrystallised, dried and reduced to chromium (III) oxide with carbon.

Step 4: The chromium (III) oxide is reduced to chromium metal with aluminium.

5.2.3 Silicon

Occurrence

Silicon is the second most abundant element, after oxygen, in the Earth's crust. It occurs as silica (SiO_2) and silicate compounds containing the silicate ion, (SiO_4^{4-}). Quartz is a pure crystalline form of silica, and flint is a hard amorphous form.

Extraction

Silicon is prepared by heating silica with coke to approximately 3000°C in an electric furnace:

$$SiO_2(s) + 2C(s) \longrightarrow Si(l) + 2CO(g)$$

The molten silicon is taken from the bottom of the furnace and allowed to cool producing a shiny blue-gray solid.

Extremely high-purity silicon is needed for the electronics industry. Purifying raw silicon requires additional steps. First, the silicon in the impure sample is allowed to react with chlorine to convert the silicon to liquid silicon tetrachloride.

$$Si(s) + 2Cl_2(g) \longrightarrow SiCl_4(l)$$

Silicon tetrachloride (*boiling point* 57.6°C) is carefully purified by distillation and then reduced to silicon, using magnesium:

$$SiCl_4(g) + 2Mg(s) \longrightarrow 2MgCl_2(s) + Si(s)$$

The magnesium chloride is washed out with water, and the silicon is remelted and cast into bars. A final purification is carried out by zone refining.

Chemical Properties

Silica is resistant to attack by all acids except HF, with which it reacts to give SiF_4 and H_2O. This chemical attack is involved in the etching of glass. It also dissolves slowly in hot, molten NaOH or Na_2CO_3 to give Na_4SiO_4:

$$SiO_2(s) + 4HF(l) \longrightarrow SiF_4(g) + 2H_2O(l)$$

$$SiO_2(s) + 2Na_2CO_3(l) \longrightarrow Na_4SiO_4(s) + 2CO_2(g)$$

Silicon and methyl chloride (CH_3Cl) react at 300°C in the presence of copper powder as a catalyst. The main product of this reaction is $(CH_3)_2SiCl_2$.

$$Si(s) + 2CH_3Cl\ (g) \longrightarrow (CH_3)_2SiCl_2(l)$$

When it reacts with water, initially it produces $(CH_3)_2Si(OH)_2$, and the reaction continues to form a polymer.

$$(CH_3)_2SiCl_2(l) + 2H_2O(l) \longrightarrow (CH_3)_2Si(OH)_2(l) + 2HCl(g)$$

$$n(CH_3)_2Si(OH)_2(l) \longrightarrow [(CH_3)_2SiO]_n(s) + nH_2O(l)$$

Silicone polymers are non-toxic and have good stability to heat, light, moisture, and oxygen.

Uses

Silicon is a semiconductor and is used in the construction of transistors and microprocessors. Quartz crystals are used to control the frequency of radio and television transmissions. Silicone polymers are used in making lubricants, lipstick, car polish and other materials.

Activity 5.9

Form a group. Discuss the following question. After the discussion, share your ideas with the rest of the class.

Explain why elements like tin, lead, zinc, chromium and silicon can be extracted from their ores using carbon as a reducing agent, but sodium and calcium cannot.

Exercise 5.13

1. Describe how ultra pure silicon can be produced from silica.
2. State major uses of silicon and its compounds.

Activity 5.10

Have a look at the Periodic Table of elements and make a list of various metals, which at room temperature:

1. do not react with acids, bases or air;
2. vigorously react with water;

3. react with air and water, and hence are stored under kerosene; and
4. react with chlorine.

Discuss your findings with your teacher and share them with your classmates.

5.2.4 Some Important Compounds of Selected Non-metals

1. *Ammonia* (NH_3)

Historical Note

Haber, Fritz (1868-1934), was a German chemist and Nobel laureate. He is best known for his development of an economical method of ammonia synthesis. Haber was born in Breslau (now Wroclaw, Poland) and educated at the Technische Hochschule in Berlin. He was appointed as professor of physical chemistry at the University of Berlin in 1911. Subsequently, he became director of the Kaiser Wilhelm Institute for Physical Chemistry in Berlin. During World War I, Haber was chief of the German chemical warfare service, and he directed the chlorine gas attack at the Second Battle of Ypres. In 1933, because of anti-Semitic policies in Germany, Haber resigned and went to Switzerland, where he died the following year. Haber's greatest achievement was his discovery, in 1913, of a process for synthesizing ammonia by the direct combination of nitrogen and hydrogen. The method was adapted to commercial use in the 1930s by the German chemist Karl Bosch. The Haber-Bosch process is used in the manufacture of explosives and in the production of fertilizers. Haber also made fundamental contributions to the field of electrochemistry. He was awarded the 1918 Nobel Prize in chemistry.

Haber Fritz

Activity 5.11

In your group, discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. Write a balanced chemical equation for the formation of ammonia by Haber process.
2. What is the purpose of adding finely divided iron in the Haber process?
3. Why is ammonia highly soluble in water?

4. What conditions are required to get high yield of ammonia using Le Chatelier's principle?
5. What conditions are required to get economically feasible yields of ammonia?
6. Discuss the uses of ammonia.

2. *Nitric Acid (HNO_3)*

Pure nitric acid is a colourless liquid, but on exposure to light it turns brown because of slight decomposition into NO_2 (*brown*) and O_2.

$$4HNO_3(l) \longrightarrow \underset{\text{brown}}{4NO_2(g)} + O_2(g) + 2H_2O(l)$$

Nitric acid is a strong acid and dissociates completely to give H_3O^+ and NO_3^- in dilute aqueous solution.

Nitric acid forms a large number of salts, called nitrates, which are typically very soluble in water.

Nitric acid is a strong oxidizing agent, particularly when it is hot and concentrated. Nitric acid is produced industrially from ammonia by the three-step Ostwald process:

Step 1: Ammonia is burned in excess oxygen over a platinum catalyst to form nitric oxide (NO):

$$4NH_3(g) + 5O_2(g) \xrightarrow[\text{Pt}]{850\,°\text{C, 5 atm}} 4NO(g) + 6H_2O(g)$$

Step 2: Additional air is added to cool the mixture and oxidize NO to NO_2:

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

Step 3: The NO_2 gas is bubbled into warm water where it reacts to give nitric acid and nitric oxide:

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + \underset{\text{recycled}}{NO(g)}$$

The nitric oxide (NO) is recycled in Step 2.

The largest percentage of nitric acid is used to synthesize ammonium nitrate, a water soluble fertiliser. Large quantities are also used to make plastics, drugs, and explosives such as trinitrotoluene (TNT) and nitroglycerine.

Exercise 5.14

1. Describe the properties of nitric acid.
2. Show the preparation of nitric acid by the Ostwald process.
3. What are the main uses of nitric acid?

3. *Sulphuric Acid* (H_2SO_4)

Sulphuric acid is the world's most important industrial chemical, and the rate of consumption of sulphuric acid is a measure of a country's industrialization. Pure H_2SO_4 melts at 10.5°C and boils at 338°C. Anhydrous H_2SO_4 and concentrated H_2SO_4 mix with water in all proportions and release large amounts of heat energy (880 kJ/mol).

If water is poured into concentrated acid, the heat evolved leads to boiling of the water and causes violent splashing. The safe way to dilute strong acids is to carefully pour the acid into the water while stirring. Concentrated H_2SO_4 has strong oxidizing properties.

Do you know where sulphuric acid is manufactured in Ethiopia?

Sulphuric acid is prepared industrially by the contact process, using four steps:

Step 1: Burning sulphur in air:

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

Step 2: Converting SO_2 to SO_3

$$2SO_2(g) + O_2(g) \xrightarrow[400°C]{V_2O_5 \text{ catalyst}} 2SO_3(g)$$

The conversion of SO_2 to SO_3 is slow, but it is increased by heating the reaction mixture to 400ºC in the presence of V_2O_5 catalyst. Because the SO_2 and O_2 molecules react on contact with the surface of V_2O_5, the process is called Contact process.

Step 3: Passing SO_3 into concentrated H_2SO_4:

$$SO_3(g) + H_2SO_4(l) \longrightarrow \underset{\substack{\text{Pyrosulphuric acid} \\ \text{(oleum or fuming sulphuric acid)}}}{H_2S_2O_7(l)}$$

Step 4: Addition of water to pyrosulphuric acid

$$H_2S_2O_7(l) + H_2O(l) \longrightarrow 2H_2SO_4(aq)$$

Uses of sulphuric acid

Sulphuric acid is used in the production of fertilisers, detergents, plastics and paints. It is used in the production of a number of explosives. Sulphuric acid is an oxidizing agent and a good dehydrating agent. It is often used to dry neutral and acidic gases such as nitrogen, oxygen, and carbon dioxide. It is also used as electrolyte in car batteries. It is also used as a catalyst in the manufacture of many chemicals.

Exercise 5.15

1. Describe the industrial production of H_2SO_4. Write the equations and state the conditions of each step.
2. State the properties and major uses of sulphuric acid.

Activity 5.12

Form a group and discuss each of the following questions:

1. What are some of the indications that the soil in which plants grow, is deficient in:
   a nitrogen? b phosphorus ? c potassium?
2. Why the large-scale use of synthetic fertilizers can be harmful to the environment?

After the discussion, share your ideas with the rest of the class.

4. *Diammonium monohydrogen phosphate (DAP), $(NH_4)_2HPO_4$*

Diammonium monohydrogen phosphate (DAP) is a white crystalline compound that is completely soluble in water. *How is DAP produced industrially*? It can be produced when ammonia reacts with phosphoric acid by the following two steps:

Step 1: Anhydrous ammonia reacts with phosphoric acid to form monoammonium dihydrogen phosphate and diammonium monohydrogen phosphate

$$3NH_3(g) + 2H_3PO_4(l) \longrightarrow NH_4H_2PO_4(s) + (NH_4)_2HPO_4(s)$$

Step 2: Recycling monoammonium dihydrogen phosphate for further reaction with anhydrous ammonia yields DAP:

$$NH_4H_2PO_4(s) + NH_3(g) \longrightarrow (NH_4)_2HPO_4(s)$$

DAP is used as a fertiliser. When applied as plant food, it temporarily increases soil acidity, but over the long term, the soil becomes more acidic than before upon nitrification of the ammonium. DAP has the advantage of having both nitrogen and phosphorus, which are essential for plant growth.

DAP can be used as fire retardant. It lowers the combustion temperature of the material, decreases weight-loss rates, and causes an increase in the production of residue or char.

DAP is also used as a yeast nutrient in wine making and beer brewing.

Exercise 5.16

1. Describe the industrial production of DAP. Write the chemical equations.
2. State properties and major uses of DAP.
3. Calculate the percentage composition of phosphorus and nitrogen in diammonium monohydrogen phosphate.

Unit Summary

- *There are 113 elements in the periodic table. Of these, 92 elements occur in nature, and the others are man-made.*
- *Minerals that are suitable for the extraction of elements are called ores.*
- *All ores are minerals, but not all minerals are ores.*
- *The twelve most abundant elements in the earth's crust, in decreasing order of abundance, are: oxygen, silicon, aluminium, iron, calcium, magnesium, sodium, potassium, titanium, hydrogen, phosphorus and manganese.*
- *Metals found in the Earth's crust are in the form of oxides, carbonates, sulphides, halides, sulphates and phosphates.*
- *Nutrients are limited in nature, and they are exchanged between living and nonliving things.*
- *In the carbon cycle, atmospheric carbon dioxide is converted to glucose by green plants. Animals incorporate carbon by eating plants or other animals. Carbon returns to the physical environment during respiration, the burning of wood or fossil fuels, and the decomposition of plants and animals.*
- *In the nitrogen cycle, atmospheric nitrogen is converted to nitrogen compounds by lightning, through the Haber process or by bacteria on*

root nodules of leguminous plants. Plants use these compounds to prepare their proteins and nucleic acids. Animals also prepare their proteins and nucleic acids through eating plants or other animals. Nitrogen returns to the atmosphere during the decomposition of plants and animals through the action of denitrifying bacteria.

- *The phosphorus cycle differs from the nitrogen and carbon cycles primarily because phosphorus cannot exist in gaseous form in the atmosphere. Plants absorb phosphates, using their roots, and make DNA, and ATP. Animals get phosphates by eating plants or other animals. When plants and animals die, they decompose and return phosphates into the soil or water.*
- *Metallurgy is the science and technology of extracting metals from their natural sources and preparing them for practical use. This process has three main steps: concentrating the ore, extracting the metal and purifying the crude metal.*
- *Sodium is the 7th most abundant element in the Earth's crust and is extracted from molten sodium chloride using Downs cell.*
- *Calcium is the 5th most abundant element in the Earth's crust and is extracted from molten calcium chloride. It is a major component in bones and teeth.*
- *Tin is mainly extracted from cassiterite (SnO_2), using coke as reducing agent. It is used to make alloys.*
- *Lead can be extracted from galena (PbS) by partially oxidizing galena and self-reduction. It is used to make lead /acid storage batteries.*
- *Zinc is extracted from zinc blende (ZnS) by roasting, followed by reduction with carbon monoxide. Large amounts of zinc are used for coating iron.*
- *Chromium is extracted from chromite ore ($FeCr_2O_4$): First it is oxidized to sodium chromate (Na_2CrO_4). Then sodium chromate is converted to sodium dichromate by the addition of acids. Next the sodium dichromate is reduced to chromium (III) oxide, using carbon. Finally, Cr_2O_3 is reduced to chromium metal by aluminium. Chromium is used to make alloys.*

- *Silicon is the* 2^{nd} *most abundant element in the Earth's crust and is extracted from silica, using carbon as reducing agent. Silicon is used in the construction of transistors and microprocessors.*
- *Ammonia is prepared by the Haber process and is mainly used to make fertilisers.*
- *Nitric acid is prepared by the Ostwald process, and is used to make fertilizers, plastics and explosives.*
- *Sulphuric acid is produced by the Contact process, and is mainly used to make fertilizers, detergents and paints.*
- *Diammonium monohydrogen phosphate (DAP) is prepared by reacting anhydrous ammonia with phosphoric acid in two steps. DAP is mainly used as a fertilizer.*

Check list

Key terms of the unit

- *Amalgamation*
- *Borax*
- *Carbon cycle*
- *Cassiterite*
- *Chemical reduction*
- *Chromite*
- *Concentrating ore*
- *Contact process*
- *Denitrification*
- *Dolomite*
- *Downs cell*
- *Economic extraction*
- *Electrolysis*
- *Electrolytic reduction*
- *Extraction of metals*
- *Fixation*
- *Froth flotation*
- *Galena*
- *Gravity separation*
- *Gypsum*
- *Haber process*
- *Leaching*
- *Magnetic separation*
- *Marble*
- *Metallurgy*
- *Mineral*
- *Nitrogen cycle*
- *Ore*
- *Ostwald process*
- *Phosphorus cycle*
- *Pretreatment*
- *Purification of metals*
- *Reactivity series*
- *Silica*
- *Trona*
- *Zinc blende*
- *Zone refining*

REVIEW EXERCISE FOR UNIT 5

Part I: Multiple Choice Questions

1. Which of the following statements is incorrect?
   - a all the materials on earth are made of the 92 naturally-occurring elements.
   - b all minerals are ores.
   - c most metals are solids at 25°C.
   - d None of the above.
2. The four most abundant elements, in increasing order of abundance, are:
   - a silicon, oxygen, iron and aluminium
   - b oxygen, silicon, aluminium, and iron
   - c iron, aluminium, silicon, and oxygen
   - d aluminium, iron, silicon, and oxygen
3. Which of the following elements does not exist in native state in nature?
   - a platinium
   - b gold
   - c silver
   - d sodium
4. The element that is a liquid at 25°C is:
   - a oxygen
   - b bromine
   - c chlorine
   - d nitrogen
5. Which of the following ores contains carbonates?
   - a dolomite
   - b bauxite
   - c epsomite
   - d cassiterite
6. Which of the following processes fix atmospheric carbon dioxide?
   - a Photosynthesis
   - b Respiration
   - c Burning of fossil fuels
   - d b and c
7. Which one of the following statements is incorrect about the nitrogen cycle?
   - a nitrogen is the most abundant gas in the atmosphere
   - b atmospheric nitrogen is less reactive
   - c the process of releasing nitrogen gas back into the atmosphere is called nitrogen fixation
   - d lightning converts atmospheric nitrogen into nitrogen oxides

8. What makes the phosphorus cycle different from the nitrogen and carbon cycles?
   - a The phosphorus cycle is very slow
   - b Phosphorus cannot be found in the atmosphere in the gaseous state
   - c It is not an essential element for plants and animals
   - d a and b
9. If a mineral is denser than its gangue, the appropriate method of separation is:
   - a magnetic separation
   - b froth floatation
   - c amalgamation
   - d gravity separation
10. If a metal is to be obtained by electrolytic reduction, its oxide, hydroxide or carbonate is often treated with HCl to convert it to the chloride. The reason for doing this conversion is that:
    - a most chlorides usually melt at high temperatures to form conductive liquids
    - b most chlorides usually melt at low temperatures to form conductive liquids
    - c only aluminium chloride melts at low temperatures to form a conductive liquid
    - d all of the above
11. Metals that have low melting points, such as mercury, magnesium, and zinc can be purified from other metals that have high melting points by:
    - a zone refining
    - b electrolysis
    - c distillation
    - d leaching
12. Which of the following statements is incorrect about sodium?
    - a It is the 7th most-abundant element in the earth's crust
    - b Its main ores are borax, trona and rock salt
    - c It is obtained by reducing molten sodium chloride by coke
    - d It reacts with both air and water
13. Which of the following statements is incorrect about calcium?
    - a It is extracted by the electrolysis of molten calcium chloride
    - b It reacts with both oxygen and water
    - c It reacts with nitrogen at high temperature to form calcium nitride
    - d None of the above
14. Tin does not react with:
    - a cold water
    - b dilute hydrochloric acid
    - c concentrated nitric acid
    - d chlorine

15. Which element is extracted from its ore by self-reduction?

    a tin
    b lead
    c chromium
    d zinc

16. Which one of the following statements is false about zinc?

    a It is mainly extracted from galena
    b It reacts with dilute hydrochloric acid to give zinc chloride and hydrogen gas
    c It shows amphoteric property
    d It is used for coating iron to prevent the iron from corrosion

17. Which of the following statements is incorrect about chromium?

    a Ferrochrome contains chromium and cobalt
    b It is passive towards oxidizing acids like concentrated nitric acid
    c It is produced by reducing chromium (III) oxide with aluminium metal
    d It is used for electroplating

18. Which of the following statements is incorrect about silicon and its compounds?

    a It is extracted by heating silica and coke at very high temperatures
    b It is a semiconductor and extensively used by the electronics industry to produce computer chips
    c Silicone polymers are used in making lubricants
    d None of the above

Part II: Short Answer Questions

19. Define each of the following terms:

    a Mineral
    b Ore
    c Metallurgy
    d Roasting

20. List the twelve most abundant elements in the Earth's crust.

21. Explain the carbon, nitrogen and phosphorus cycles using diagrams.

22. Explain the three major steps that are carried out to obtain a metal from its ore.

23. Describe the occurrence of:

    a sodium
    b calcium
    c tin
    d lead
    e chromium
    f silicon

24. Describe the extraction of each of the following elements from their respective ore:
    - a sodium
    - b calcium
    - c tin
    - d lead
    - e chromium
    - f silicon
25. Describe the chemical properties of:
    - a sodium
    - b calcium
    - c tin
    - d lead
    - e chromium
    - f silicon
26. Describe the major uses of:
    - a sodium
    - b calcium
    - c tin
    - d lead
    - e chromium
    - f silicon
27. Using chemical equations, describe the manufacturing process of:
    - a ammonia, by the Haber process
    - b nitric acid, by the Ostwald process
    - c sulphuric acid, by the Contact process
    - d diammonium monohydrogen phosphate
28. Describe the major uses of:
    - a ammonia
    - b nitric acid
    - c sulphuric acid
    - d diammonium monohydrogen phosphate

UNIT 6

Polymers

Unit Outcomes

After completing this unit, you will be able to:

- *understand the processes of addition polymerization and condensation polymerization ;*
- *list a variety of synthetic polymers and natural polymers and explain their differences;*
- *classify synthetic polymers as addition polymers or condensation polymers and identify their monomers;*
- *describe monomers, properties and uses of plastics, rubbers, carbohydrates and proteins;*
- *analyze the risks and benefits of the development of and application of synthetic polymers (example, plastics) and suggest possible methods of control;*
- *demonstrate scientific enquiry including classifying, comparing and contrasting, communicating, asking questions, applying concepts and making generalizations.*

MAIN CONTENTS

6.1 INTRODUCTION TO POLYMERS

After completing this subunit, you will be able to:

- define the terms monomer and polymer;
- classify polymers into synthetic and natural polymers; and
- give examples of synthetic and natural polymers.

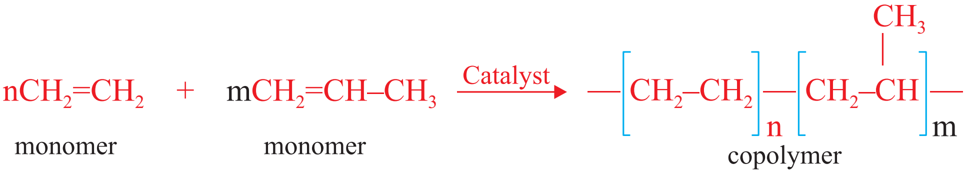
Polymers are *macro (large) molecules* made from smaller repeating units called monomers. Hence, monomers are the building blocks of polymers. A polymer might be made from identical monomers or different types of monomers. Homopolymers are made from only one type of monomer. For example, polyethylene is synthesized by the polymerization of one type monomer, ethene (ethylene).

$$\underset{\substack{\text{Ethene (ethylene)}\\\text{(monomer)}}}{nCH_2 = CH_2} \xrightarrow{\text{Catalyst}} \underset{\substack{\text{Polyethylene}\\\text{(homopolymer)}}}{-\left[CH_2 - CH_2\right]_n-}$$

Activity 6.1

Assume that 2000 students are standing in the school play ground and each student is treated as a monomer unit of polyethylene. The students are asked to hold the hands of each other in a linear fashion. In this way, the students will form a linear chain of polyethylene molecule. Calculate the molecular mass of the polyethylene molecule, using this analogy.

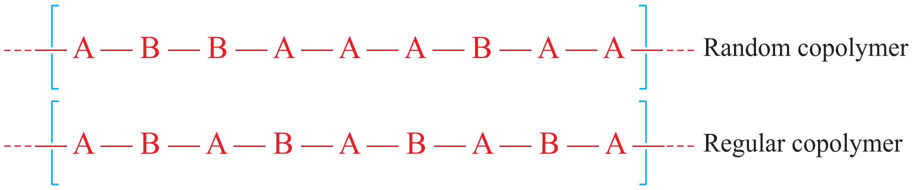
Copolymers are prepared by polymerizing more than one kind of monomer unit. For instance, ethene ($H_2C=CH_2$) and propene ($H_2C=CH-CH_3$) can be copolymerized to produce a polymer that has two kinds of repeating units:



$$\underset{\text{monomer}}{nCH_2=CH_2} + \underset{\text{monomer}}{mCH_2=CH-CH_3} \xrightarrow{\text{Catalyst}} \underset{\text{copolymer}}{-\left[CH_2-CH_2\right]_n-\left[CH_2-\overset{\overset{CH_3}{|}}{CH}\right]_m-}$$

Copolymers are classified as random or regular, based on the way the monomers are arranged along the polymer chain (Figure 6.1.).

Random polymers contain repeating units arranged in a random fashion. Regular polymers contain a sequence of monomers in regular alternating repeating units.



where, A and B represent monomer units.

Figure 6.1 Random and regular copolymers.

On the basis of their source, polymers are classified as synthetic and natural. Natural polymers, as their name indicates, are found in nature. For example, proteins, carbohydrates, nucleic acids and natural rubber are natural polymers. You will study them in the last section of this unit.

Synthetic polymers are man–made polymers. Most synthetic polymers are organic compounds. Some of the examples are nylon, polyester (Dacron), Teflon, Bakelite, polyethylene, and polyvinyl chloride.

Can you list more examples of synthetic and natural polymers?

Exercise 6.1

1. Define each of the following terms:
   - a monomer
   - b polymer
   - c homopolymer
   - d copolymer
   - e natural polymer
   - f synthetic polymer
2. List examples of natural and synthetic polymers in daily life.
3. Classify each of the following polymers as natural or synthetic:
   - a wool
   - b dacron
   - c insulin
   - d teflon
   - e cellulose
   - f polyvinyl chloride
   - g bakelite
   - h glycogen
   - i DNA
4. Draw the structure of the copolymer of:

   $HO\text{–}CH_2CH_2\text{–}OH$ and $HOOC\text{–}CH_2CH_2\text{–}COOH$.

6.2 POLYMERIZATION

After completing this subunit, you will be able to:

- explain polymerization;
- mention the two types of polymerization;
- explain how addition polymerization takes place; and
- explain how condensation polymerization takes place.

Polymerization is the process by which monomer units combine together to form polymers. Polymerization can be carried out either through addition polymerization or condensation polymerization.

Activity 6.2

Perform the following activity. Then, share your ideas with the rest of the class.

a Distinguish between addition and condensation reactions.

b Prepare list of monomers used in polymerization and have a look at their structures and functional groups. Explain their special features that allow them to form large molecules.

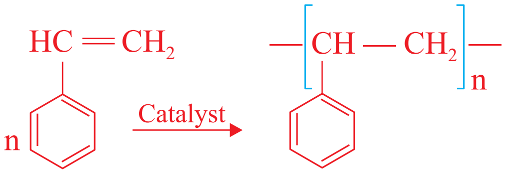
6.2.1 Addition Polymerization

Addition polymerization requires a large number of monomer molecules which can be polymerized by addition reactions. This type of polymerization is also known as chain-growth polymerization.

For example, the addition polymerization of many ethylene molecules yields polyethylene and that of styrene molecules gives polystyrene.

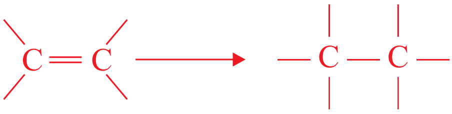
$$nCH_2=CH_2 \xrightarrow{\text{Catalyst}} -\!\left[CH_2-CH_2\right]_n\!-$$

Ethylene Polyethylene



Styrene Polystyrene

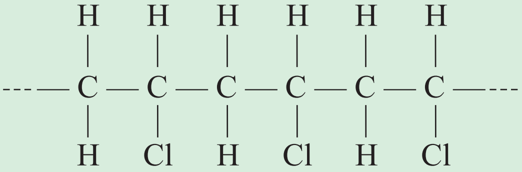
Note that the molecular formula of a polymer is *n* times that of the monomer and upon polymerization, the double bond is converted to a single bond.



Note also that, if a polymer is given, you can identify the monomer unit that is repeated in it.

Example 6.1

The addition polymer polyvinyl chloride (PVC) has the structure



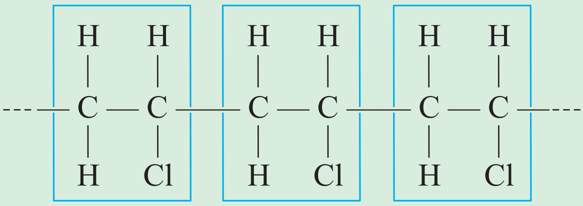
$$\cdots-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\underset{|}{\overset{|}{\mathrm{C}}}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\underset{|}{\overset{|}{\mathrm{C}}}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\underset{|}{\overset{|}{\mathrm{C}}}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\underset{|}{\overset{|}{\mathrm{C}}}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\underset{|}{\overset{|}{\mathrm{C}}}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\underset{|}{\overset{|}{\mathrm{C}}}}}-\cdots$$

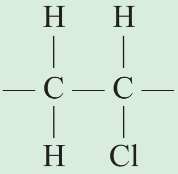
a Draw the structure of the monomer from which PVC is made.

b How many monomer units are in a PVC polymer that has a molar mass of 1.33×10^5 g/mol?

Solution:

a We need to find the repeating unit from which this polymer chain is constructed



The repeating unit is  $-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\underset{|}{\overset{|}{\mathrm{C}}}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\underset{|}{\overset{|}{\mathrm{C}}}}}-$, and the monomer has carbon-carbon double bond.

b To find the number of monomer units, we have to divide the molar mass of the polymer (PVC) by the molar mass of monomer.

The molar mass of the monomer CH_2CHCl is calculated as follows:

$$\text{Number of monomer units} = \frac{\text{Molar mass of the polymer}}{\text{Molar mass of the monomer}}$$

$$= \frac{1.33 \times 10^5 \text{ g/mol}}{62.5 \text{ g/mol}} = 2128$$

$$C = 12 \times 2 = 24$$

$$H = 1 \times 3 = 3$$

$$Cl = 35.5 \times 1 = 35.5 = 62.5 \text{ g/mol}$$

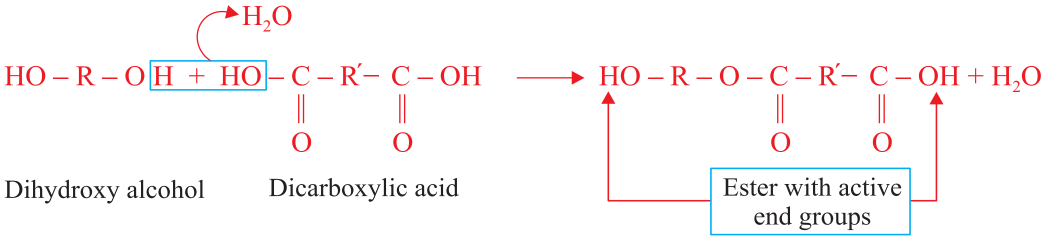
Which means that 2128 vinyl chloride molecules combine to form the polymer.

6.2.2 Condensation Polymerization

Condensation polymerization involves the combination of monomer molecules, with the elimination of simple molecules like water. This polymerization is also known as step growth polymerization. In order to produce a condensation polymer, the monomers involved must have two or more functional groups.

Can you give examples of condensation polymers?

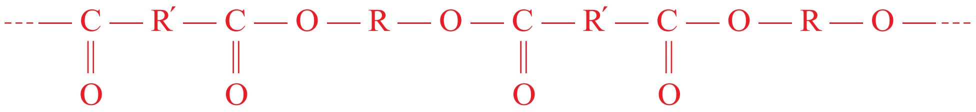
Consider what happens when an alcohol with two –OH groups, HO–R –OH, reacts with a dicarboxylic acid, HOOC–R′–COOH. In this case the ester formed still has a reactive group at both ends of the molecule.



$$HO-R-O\overset{\curvearrowright H_2O}{\boxed{H + HO}}-\underset{\underset{O}{\|}}{C}-R'-\underset{\underset{O}{\|}}{C}-OH \longrightarrow HO-R-O-\underset{\underset{O}{\|}}{C}-R'-\underset{\underset{O}{\|}}{C}-OH + H_2O$$

The COOH group at one end of the ester molecule can react with another alcohol molecule. This process can continue, leading eventually to a long-chain polymer containing large number of ester groups.

The general structure of the polyester can be represented as



$$\text{---}-\underset{\underset{O}{\|}}{C}-R'-\underset{\underset{O}{\|}}{C}-O-R-O-\underset{\underset{O}{\|}}{C}-R'-\underset{\underset{O}{\|}}{C}-O-R-O-\text{---}$$

Section of the polyester

Example 6.2

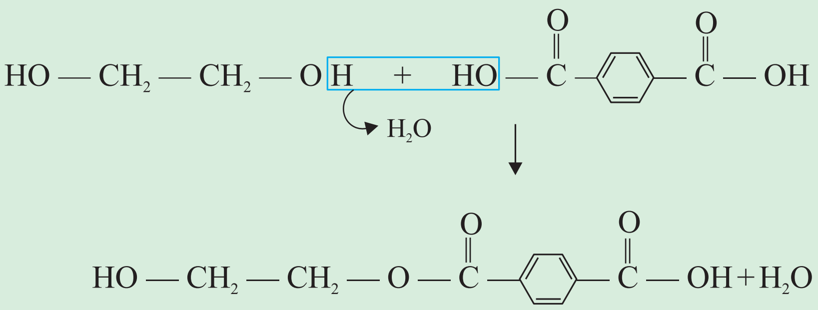
Polyethylene terephthlate or Dacron is prepared from ethylene glycol ($HO–CH_2–CH_2–OH$) and terephthalic acid.

a Write the structural formula of the ester that formed when one molecule of ethylene glycol reacts with one molecule of terephthalic acid.

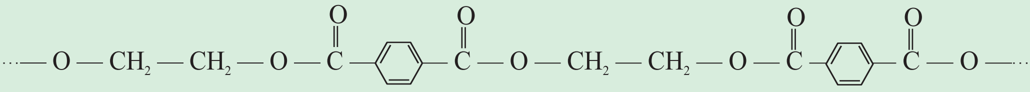
b Draw a section of polyethylene terephthalate.

Solution :

a



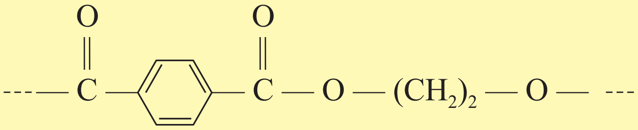
b



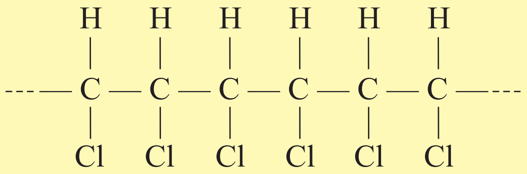
Exercise 6.2

1. Draw the structures of the monomers that would be used to make the following polymers.

a

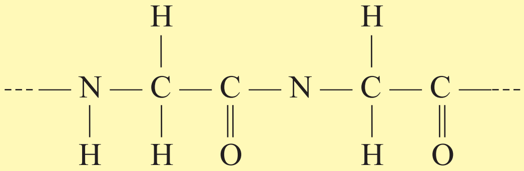


b



$$\cdots-\overset{H}{\underset{Cl}{C}}-\overset{H}{\underset{Cl}{C}}-\overset{H}{\underset{Cl}{C}}-\overset{H}{\underset{Cl}{C}}-\overset{H}{\underset{Cl}{C}}-\overset{H}{\underset{Cl}{C}}-\cdots$$

c



$$\cdots-\underset{H}{N}-\overset{H}{\underset{H}{C}}-\underset{O}{\overset{}{\underset{\|}{C}}}-N-\overset{H}{\underset{H}{C}}-\underset{O}{\underset{\|}{C}}-\cdots$$

2. Consider a polymer made from tetrachloroethylene.

   a Draw a portion of the polymer chain.

   b What is the molar mass of the polymer if it contains 3.2×10^3 tetrachloroethylene?

   c Calculate the percentage of C and Cl in the polymer?

6.3 SYNTHETIC POLYMERS

After completing this subunit, you will be able to:

- give examples of addition polymers;
- tell the monomers of each of the given addition polymers;
- explain common uses of addition polymers;
- give examples of condensation polymers;
- tell the monomers of each of the given condensation polymers;
- explain the uses of these condensation polymers: nylon, polyester and Bakelite;
- describe thermoplastics and thermosetting polymers; and
- give examples of thermoplastics and thermosetting polymers.

During the 1800s, scientists began to chemically modify natural polymers to produce new substances. The first semi-synthetic polymer produced was Bakelite in 1909. You will study the preparation and uses of Bakelite in this subunit. In 1911, Bakelite was followed by rayon, the first synthetic fiber. Despite these important developments, it was not until World War II that significant changes took place in the polymer industry. Since then, the polymer industry has continued to evolve as one of the fastest growing industries in the world.

6.3.1 Addition Polymers

Activity 6.3

Form a group and discuss each of the following questions:

1. What problems do you think are arising with the rapid development of synthetic polymers?
2. What necessary steps should be taken to protect the environment from synthetic polymers?

After the discussion, share your ideas with the rest of the class.

Discuss the following question in a group:

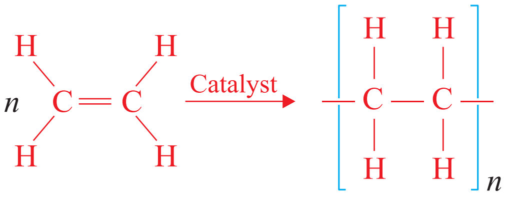
Usually ethene is obtained from petroleum by cracking. An alternative source of ethene is to make it from ethanol, which is obtained by fermentation. Why do you think that this is a feasible alternative in Ethiopia at the moment? Write an equation to show the synthesis of ethene from ethanol.

After the discussion, share your ideas with the rest of the class.

Polyethylene

Have you observed polyethylene materials in your surrounding?

Polyethylene is a polymer made by the addition polymerization of ethylene.



Ethylene (Ethene) Polyethylene

where, n is a very large number.

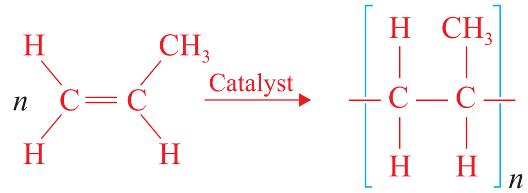
Polyethylene has no taste or odour and is lightweight, nontoxic and relatively cheap. Some of its primarily uses are in making squeeze bottles, plastic wrapping, garment bags, trash bags and electrical insulation.

Polyethylene trash bags Squeeze bottle (wash bottle) Polyethylene tube

Figure 6.2 Some polyethylene materials.

Polypropylene

The monomer of polypropylene is propylene (propene). It is produced by the addition polymerization of propylene.



Propylene (propene)   Polypropylene

Polypropylene is stronger than polyethylene. It is used for making food containers that can safely be washed in a dishwasher. It can also be used for making ropes, fishing nets, carpets, and bottles.

Polypropylene rope   Polypropylene carpet   Polypropylene bottles

Figure 6.3 Some polypropylene products.

Polyvinyl Chloride (PVC)

Activity 6.4

Form a group. Discuss the following questions. After the discussion, share your ideas with other groups.

1. Draw the structure of vinyl chloride.
2. Write a chemical equation that shows the preparation of vinyl chloride from acetylene and hydrogen chloride.
3. Write a chemical equation that indicates the polymerization of vinyl chloride to polyvinyl chloride.

Polyvinyl chloride is the third most widely produced plastic, after polyethylene and polypropylene. It is commonly used for making pipes, leather-like materials, shoes, raincoats, aprons, wallpaper, floor tile, and phonograph records.

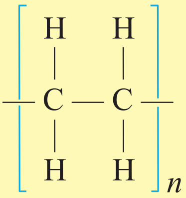
PVC pipes PVC floor tile PVC raincoat

Figure 6.4 Some polyvinyl chloride products.

Exercise 6.3

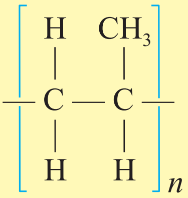
1. Write the molecular formula and structure of monomers of each of the following polymers.

a



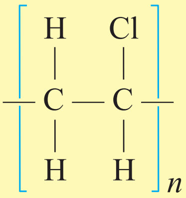
$$-\!\!\left[\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\|\\\mathrm{H}\end{array}\!-\!\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\|\\\mathrm{H}\end{array}\right]\!\!-_{n}$$

b



$$-\!\!\left[\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\|\\\mathrm{H}\end{array}\!-\!\begin{array}{c}\mathrm{CH_3}\\|\\\mathrm{C}\\|\\\mathrm{H}\end{array}\right]\!\!-_{n}$$

c



$$-\!\!\left[\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\|\\\mathrm{H}\end{array}\!-\!\begin{array}{c}\mathrm{Cl}\\|\\\mathrm{C}\\|\\\mathrm{H}\end{array}\right]\!\!-_{n}$$

2. Describe major uses of:

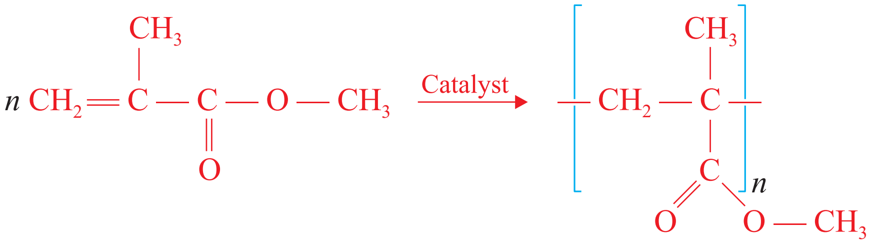
   a polyethylene b polypropylene c polyvinyl chloride

3. Make a list of materials in your home made of PVC.

4. What is the basic structural difference between low density polyethylene (LDPE) and high density polyethylene (HDPE)?

Polymethyl methacrylate (Perspex)

Polymethyl methacrylate, PMMA, is sold under the trade name Lucite or plexiglass. It is prepared by the polymerization of methyl methacrylate.

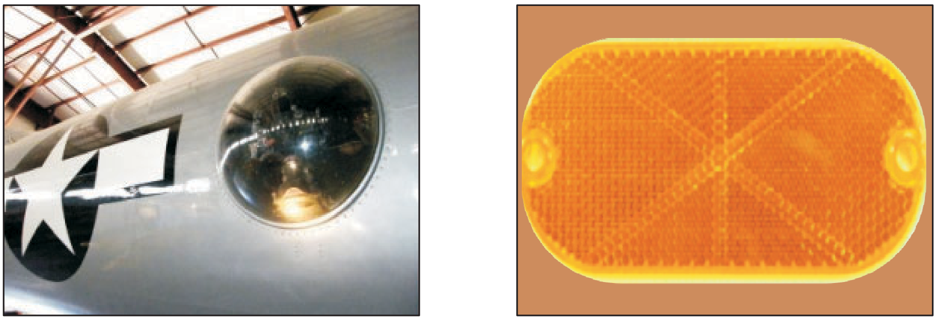


Methyl methacrylate

Polymethyl methacrylate
(Lucite or Plexiglass)

Note that acrylic acid is the common name of 2-propenoic acid, $CH_2{=}CHCOOH$

PMMA is a lightweight glass-like polymer used as a glass substitute for example, in airplane windows and streetlights.



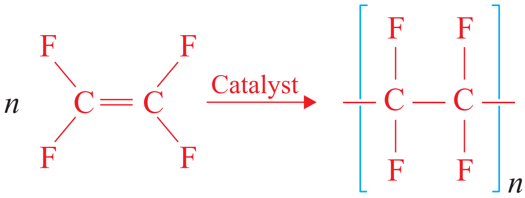
PMMA as airplane window

PMMA as reflector in streetlight

Figure 6.5 Some polymethyl methacrylate materials.

Polytetrafluoroethylene, PTFE, Teflon

Teflon is prepared by the addition polymerization of tetrafluoroethylene.



Tetrafluoroethylene Polytetrafluoroethylene (Teflon)

Teflon has good resistance to chemical attack, and it can be used at any temperature between –73°C and 260°C with no effect on its properties. It also has a very low coefficient of friction, which makes it waxy or slippery to touch. As a result, it is particularly suited to applications in food preparation. For example, bread dough does not stick to a Teflon-coated surface. Teflon is used for coating cooking utensils and for making electrical insulation.

Teflon coated dish **Teflon tape**

Figure 6.6 Some Teflon materials.

Polystyrene

Activity 6.5

Make a list of some materials made of polystyrene. Discuss with your classmates, the physical and chemical behaviour of polystyrene and PVC.

Polystyrene is produced by the addition polymerization of styrene. It is one of the most widely used polymers. For example, it is used for making packing materials especially for impact-absorbent. Its other uses include preparing CD and DVD cases, toys, flowerpots and architectural models.

Polystyrene used for packing a cup

Polystyrene CD case

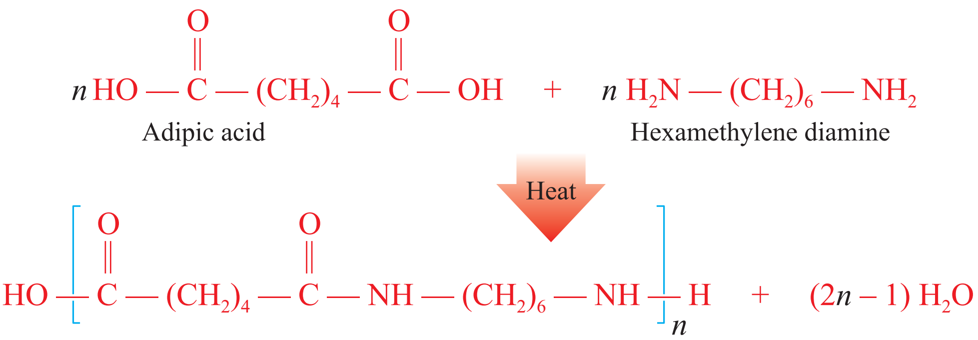
Architectural model of building, using Styrene

Figure 6.7 Some Polystyrene Materials.

6.3.2 Condensation Polymers

Nylons

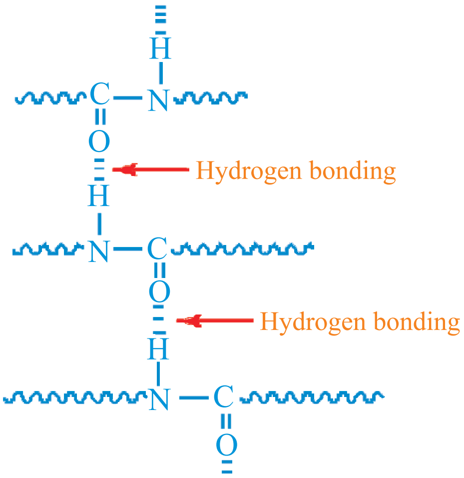
Nylons are polyamides. They can be produced by the condensation reaction of diacids and diamines. One of the most common polyamides is nylon 66. It is a copolymer and is prepared by the condensation of 1,6-diaminohexane (hexamethylene diamine) and 1,6-hexanedioic acid (adipic acid). The basic amine reacts with the acid to form a salt. Heating removes water and forms the amide bonds.



$$n\,HO-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-OH + n\,H_2N-(CH_2)_6-NH_2 \xrightarrow{\text{Heat}} HO\left[\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-NH-(CH_2)_6-NH\right]_n H + (2n-1)\,H_2O$$

Nylon 66 (the numbers indicate there are six carbon atoms each in hexamethylene diamine and adipic acid).

There are hydrogen bondings between the polymer chains.



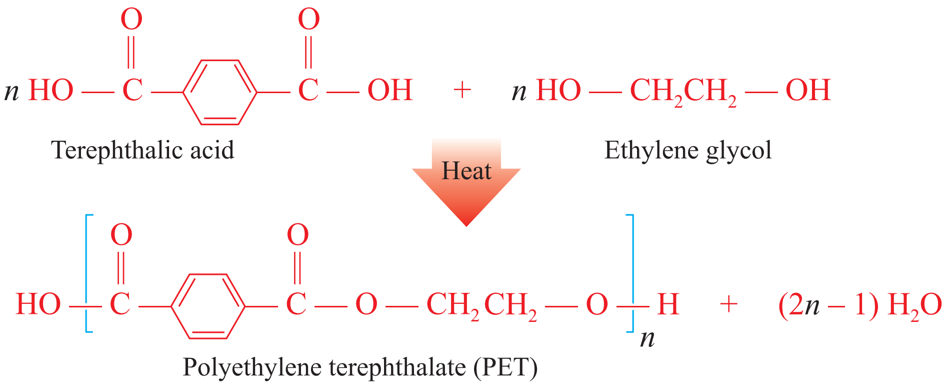
Uses of nylon include making parachutes, ropes, clothes, stockings, hair combs, and rugs. They are also used to reinforce automobiles tires.

Nylon cloth **Nylon rug** **Stockings**

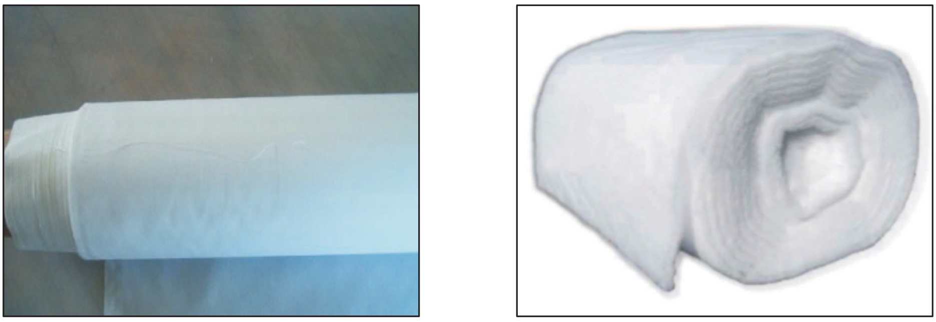
Figure 6.8 Some nylon materials.

Polyester (Polyethylene terephthalate or Dacron)

Dacron is a copolymer and is formed when equimolar amounts of 1, 4-benzene dicarboxylic acid (terephthalic acid) and 1, 2-ethanediol (ethylene glycol) react.



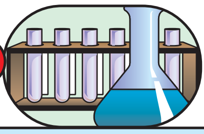
Dacron is a strong and impact resistant. It is colourless and has high transparency. It is mainly used for synthetic fibers. Mixing it with various amounts of cotton gives fabrics that are durable, easily dyed and crease-resistant. It is also used for making bottles and packaging materials.



Dacron cloth (Polyester) Dacron wrap

Figure 6.9 Some Dacron materials.

Experiment 6.1



Synthesis of Nylon

Objective: To prepare nylon and study its properties.

Apparatus and Chemicals: 250 ml beakers, dropping funnel, glass rod, forceps or copper wire hooks, 0.5 M basic solution of hexamethylenediamine , 0.5 M NaOH solution and adipoyl chloride.

Caution: Wear gloves while doing this experiment.

***Procedure*:**

1. Place 5 mL of Solution A in a small beaker.

   Solution A: Prepare a 0.5 M basic solution of hexamethylenediamine (or 2,6 – diaminohexane, $H_2N(CH_2)_6(NH_2)$ as follows: weigh 6 g of hexamethylene diamine in a large beaker and dilute to 100 mL with 0.5 M NaOH solution.

2. Place 5 mL of Solution B in a second beaker.

   Solution B: Weigh 5 g of adipoyl chloride and dissolve in 100 mL of cyclohexane.

3. Slowly add solution B to solution A using dropping funnel, pouring it down the side of the slanted beaker. Do not stirr the mixture of solution A and solution B.
4. Nylon will form at the interface of the two solutions.
5. Draw a thread out of the interface using a forceps or a copper wire hook, and draw the thread out of the beaker using glass rod as a pool and slowly windup the thread as you draw it out.
6. After nylon has been collected, wash it thoroughly with water, dry it superficially with towel then let it dry.

Results and discussion

1. Why the two solutions are not able to mix?
2. Why is adipoyl chloride used instead of adipic acid?

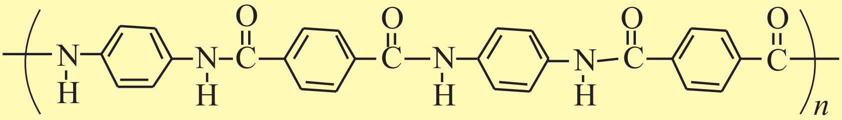
Exercise 6.4

1. Write the structure of the following polymers and also indicate the monomer units involved in the formation of these polymers.

   a Nylon 66 b Dacron

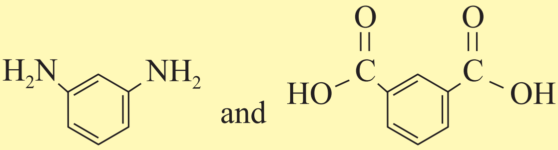
2. Describe the major uses of nylons and polyethylene terephthalate.

3. Kevlar is used in bulletproof vests. The structure of Kevlar is:



   Which monomers are used to make Kevlar?

4. Nomex is used in fire-resistant clothing. It is a copolymer of:



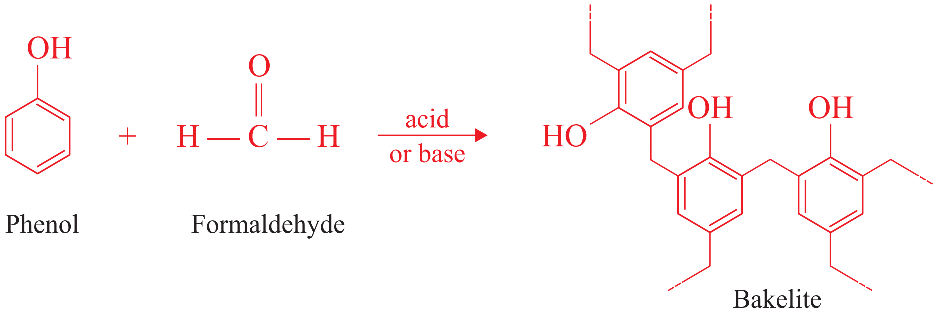
   draw the structure of the Nomex polymer.

5. How do Kevlar and Nomex differ in their structure?

Bakelite

The monomers of Bakelite are phenol and formaldehyde. The reaction between phenol and formaldehyde is not a simple reaction. The reaction takes place in the presence of an acid or a base as a catalyst.

The chemical representation of the reaction is:



Bakelite

Bakelite has been used for making rotary-dial telephones, whistles, billard balls, dominos, chess, checkers, porcelain etc.

Bakelite chess pieces Bakelite phone Bakelite purses

Figure 6.10 Bakelite products.

Thermoplastics and Thermosetting Polymers

What is the basic difference between thermoplastics and thermosetting polymers?

Based on their response to heat, polymers can be divided into two groups: thermoplastics and thermosetting plastics.

Thermoplastics soften on heating and can be moulded into different shapes. They become hard on cooling. The process of heating and cooling can be repeated many times without causing any change in their properties. For example, polyethylene, polypropylene, polyvinyl chloride, Teflon, polymethyl methacrylate, nylon and polyester (Dacron) are thermoplastics.

Thermosetting plastics can be moulded into different shapes by heating and they become hard when cooled. However, once solidified and set they cannot be softened or remoulded by heating. For example, Bakelite is a thermosetting plastic.

What makes this difference?

Thermoplastics consist of linear or slightly branched molecules which do not chemically bond with each other when heated. Instead, the polymer molecules are held together by weak Van der Waals forces. In contrast, thermosetting plastics consist of chain molecules that chemically bond, or cross-link, with each other when heated.

Which forces are stronger, Van der Waals forces or covalent bonds? Why?

Thermoplastic materials can be recycled, whereas thermosetting cannot.

What are the advantages of recycling?

Table 6.1 Difference between thermoplastics and thermosetting plastics.

Thermoplastics	Thermosetting plastics
• On heating, they do not soften and can be reshaped and reused several times. • They are generally long chain linear polymers. • They are generally weak, soft and less brittle. • They can be recycled.	• On heating, they soften readily and once shaped cannot be remoulded again. • They have three dimensional cross-linked structure • Thermosetting plastics are hard, strong, and brittle • They cannot be recycled.

Exercise 6.5

1. What are the monomers of Bakelite?
2. Write the major uses of Bakelite.
3. Explain the difference between thermoplastics and thermosetting polymers, using examples.
4. What makes thermoplastic materials recyclable, whereas thermosetting ones are not?

Impacts of Synthetic Polymers on Environment

Activity 6.6

1. Collect some discarded plastic materials and identify the materials of which these items are made. Discuss the impact of these materials on the environment. Share your ideas with the rest of your classmates.
2. What should be done to alleviate the problems caused by plastics?

It is common to use plastic bags to carry materials that we buy from supermarkets or shops.

If you discarded plastic materials to the environment, what problems would they cause to the environment?

Synthetic polymers or plastics are extensively used throughout the world. Although they are very important for humans, there are many environmental concerns about their use. Study of fields like environmental science and environmental chemistry are mainly concerned with protecting the environment.

The production of plastic produces substantial amounts of toxic chemicals (*e.g.* ethylene oxide, benzene and xylenes) to air and water. Many of the toxic chemicals released in plastic production can cause cancer and birth defects and damage the nervous system, blood, kidneys and immune systems. These chemicals can also cause serious damage to environment.

Direct disposal (littering or dumping) and incineration (burning) of these wastes is a common practice. Each is harmful to the health of people and the environment. For example, dumping plastic wastes in urban drainage systems pollutes water courses and causes flooding. When these water bodies are contaminated, they carry disease into the household. The burning of plastics encourages airborne pollution, the majority of which is extremely toxic and can cause a host of health problems (cancer, asthma, etc.). Although landfilling and recycling reduce the waste problem, each has considerably negative consequences: landfills leak and often contaminate the ground water with toxic liquids and residues. Recycling of plastic is associated with skin and respiratory problems, resulting from exposure to and inhalation of toxic fumes, especially hydrocarbons and residues released during the process.

One of the features that we value in plastics, their durability, is also a problem for us. When plastics are disposed into the environment, they remain there for a very long time, degrading very slowly, and continue to pollute our environment.

Figure 6.11 Plastics discarded to the environment.

Exercise 6.6

1. What are the major problems caused by plastics?
2. Is there any relationship between durability of plastics and pollution? Explain your answer.

6.4 NATURAL POLYMERS

After completing this subunit, you will be able to:

- give examples of addition polymers;
- describe natural rubber;
- tell the monomer of natural rubber;
- explain vulcanization;

- explain the use of natural rubber;
- give three examples of synthetic rubber;
- explain the uses of synthetic rubbers;
- compare and contrast synthetic and natural rubber;
- define the term carbohydrate;
- describe monosaccharide;
- draw the structures of monosaccharides;
- give examples of monosaccharides and disaccharides;
- describe disaccharides;
- draw the structures of disaccharides;
- describe polysaccharides;
- draw the structure of starch and cellulose;
- explain the difference between starch, glycogen and cellulose;
- define the terms amino acid, peptide and protein;
- describe the structure of amino acids;
- explain how proteins are formed; and
- list types of proteins.

Natural polymers are found in nature. They are mainly produced by plants and animals.

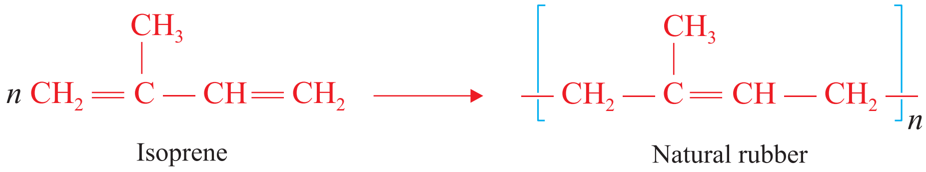
Activity 6.7

Prepare a list of natural polymers found in the environment and in human body. Classify them as condensation polymer or addition polymer. Then, share your ideas with your classmates.

Note that most synthetic polymers have been made only since 1909. However, natural polymers appeared on the earth about a million years ago. In addition, the number of natural polymers is almost constant, but number of new synthetic polymers is growing very fast.

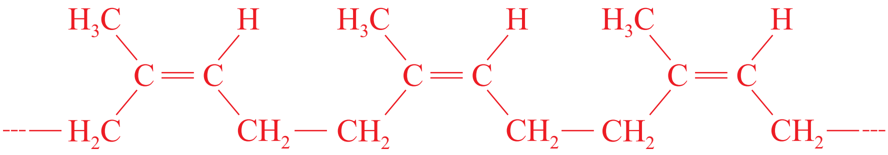
6.4.1 Natural Rubber

Natural rubber is obtained from rubber tree. The monomer of natural rubber is isoprene or 2-methyl-1,3-butadiene.



$$n\,CH_2=\overset{\overset{\large CH_3}{|}}{C}-CH=CH_2 \longrightarrow \left[-CH_2-\overset{\overset{\large CH_3}{|}}{C}=CH-CH_2-\right]_n$$

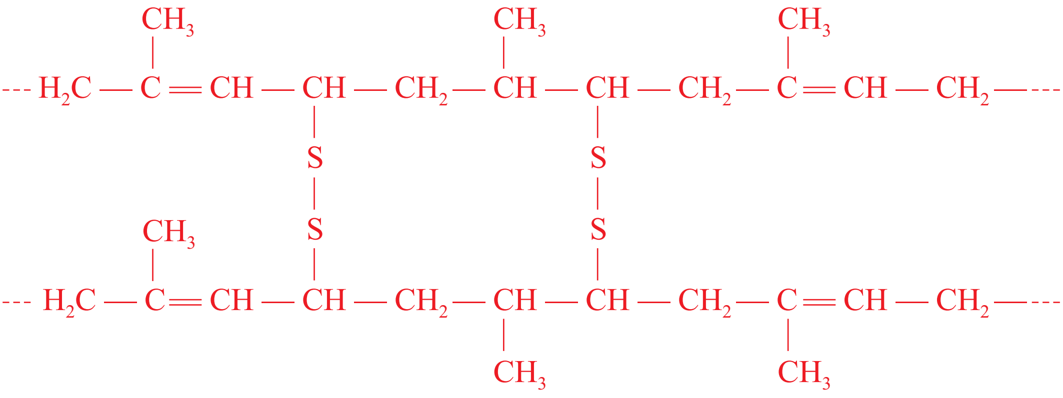
Since isoprene has two double bonds, it retains one of the double bonds after polymerization reaction. Natural rubber has the cis-configuration of methyl groups.



Rubber is an example of elastomer type of polymer, in which the polymer can return to its original shape after being stretched. Natural rubber is a soft and sticky solid.

Rubber softens in hot weather and gets hard in cold weather. It is soluble in organic solvents such as carbon disulfide, petrol, ether and so on.

The properties of natural rubber are improved by introducing cross linkages between its polymer chains. This can be achieved by heating natural rubber with sulphur. This process is known as vulcanization. Vulcanization establishes cross-links between linear polymer chains.



Vulcanized rubber has the following properties.

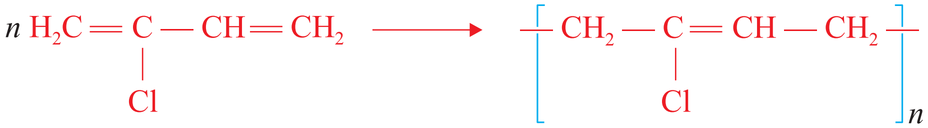
- It is hard and nonsticky.
- It has higher elasticity, which occurs over a higher range of temperature.
- It has high tensile strength.
- It is insoluble in solvents.
- It is not oxidized readily .

6.4.2 Synthetic Rubber

Synthetic rubber is produced either by the polymerization of conjugated dienes in the presence of a catalyst or by copolymerization of conjugated dienes with other olefinic compounds.

Neoprene

Neoprene is a polymer of 2-chloro-1,3-butadiene and is obtained by addition polymerization.



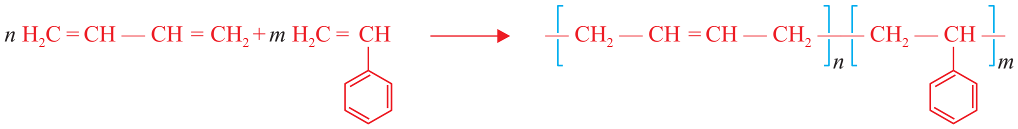
$$n\,H_2C{=}\underset{\underset{Cl}{|}}{C}-CH{=}CH_2 \longrightarrow \left[CH_2-\underset{\underset{Cl}{|}}{C}{=}CH-CH_2\right]_n$$

Chloroprene (2-chloro-1,3-butadiene) Neoprene (polychloroprene)

Neoprene is a linear thermoplastic polymer. Because of its resistance to chemicals, it is used for making hoses for chemicals, petrols, and oils.

Styrene Butadiene Rubber (SBR)

It is a copolymer of styrene with butadiene.

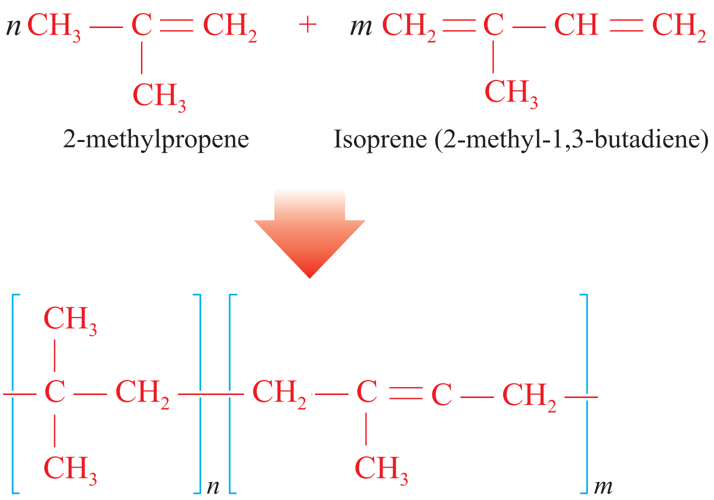


1,3-Butadiene Styrene Styrene-butadiene rubber

It is vulcanized in a similar manner as natural rubber. This rubber is superior to natural rubber with regard to mechanical strength. Its primary application is in the manufacture of tires and other mechanical goods.

Butyl Rubber

Butyl rubber is a polymer made by the polymerization of 2-methylpropene (isobutylene) with 1-2% of 2-methyl-1,3-butadiene (isoprene).



$$n\,CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + m\,CH_2=\underset{\underset{CH_3}{|}}{C}-CH=CH_2 \longrightarrow \left[-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\right]_n\left[-CH_2-\underset{\underset{CH_3}{|}}{C}=C-CH_2-\right]_m$$

Butyl Rubber

Exercise 6.7

1. What are the monomers of
   a natural rubber?
   b neoprene?
   c SBR?
   d butyl rubber?
2. What is vulcanization of rubber and how does it affect the properties of rubber?
3. What are the major uses of neoprene and SBR ?

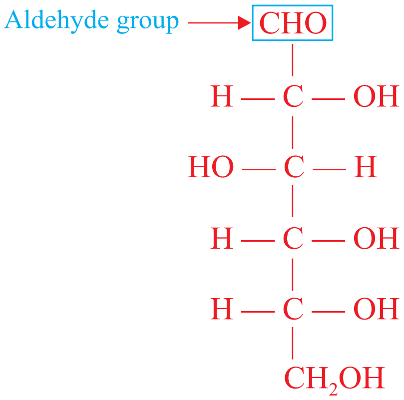
6.4.3 Carbohydrates

Carbohydrates are compounds that contain carbon, hydrogen and oxygen. Green plants produce carbohydrates by photosynthesis. In this process, carbon dioxide from air and water from the soil are the reactants and sunlight absorbed by chlorophyll is the energy source.

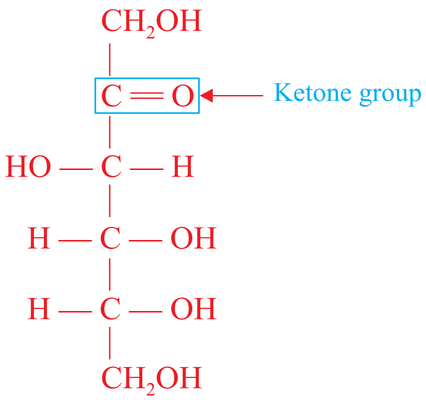
$$CO_2 + H_2O + \text{solar energy} \xrightarrow[\text{plant enzymes}]{\text{chlorophyll}} \text{carbohydrate} + O_2$$

Earlier, carbohydrates that were purified and analysed had molecular formulas that corresponds to $C_nH_{2n}O_n$ or $C_n(H_2O)_n$. As a result, they were considered to be "hydrates of carbon" or carbohydrates. However, examination of the structures of carbohydrates shows that this view is inaccurate. Even though this definition is no more used, the name carbohydrate is still used.

Today, carbohydrates are defined as polyhydroxy aldehydes, polyhydroxy ketones or compounds that yield such substance upon hydrolysis. For example, glucose is a polyhydroxy aldehyde, and fructose is a polyhydroxy ketones.



Glucose (Polyhydroxy aldehyde)



Fructose (Polyhydroxy ketone)

Carbohydrates are classified on the basis of their acid-catalyzed hydrolysis products as monosaccharide, disaccharides and polysaccharides.

a *Monosaccharides*

Monosaccharides, or simple sugars, are carbohydrates that cannot be hydrolyzed into smaller compounds. Monosaccharides with three to seven carbon atoms are found in nature. A three-carbon monosaccharides is called a triose, and those that contain four, five and six carbon atoms are called tetroses, pentoses, and hexoses, respectively.

Monosaccharides are classified as aldoses and ketoses based on the carbonyl group present.

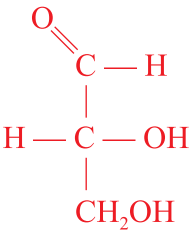
Aldoses are monosaccharides that contain an aldehyde functional group. Ketoses are monosaccharides that contain a ketone functional group.

Monosaccharides are often classified by both their number of carbon atoms and their functional group.

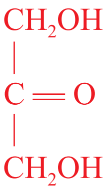
A six-carbon monosaccharide with an aldehyde functional group is an *aldohexose*. A five-carbon monosaccharide with a ketone functional group is a *ketopentose*.

Monosaccharides are also often called sugars. The word sugar is associated with "*sweetness*" and most monosaccharides have a sweet taste. Both monosaccharides and disaccharides are called sugars.

The simplest aldotriose and ketotriose are glyceraldehyde and dihydroxylacetone.

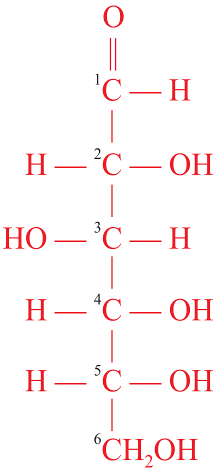


Glyceraldehyde
(Aldotriose)

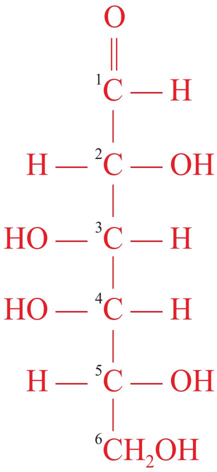


Dihydroxylacetone
(Ketotriose)

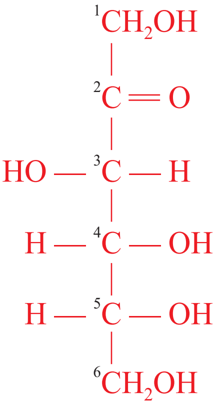
The most common monosaccharides are glucose, galactose, fructose and ribose. Glucose and galactose are aldohexoses, fructose is a ketohexose, and ribose is aldopentose. All four of these monosaccharides are water soluble, white and crystalline solids.



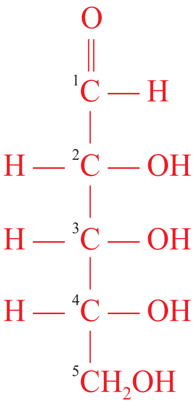
Glucose (Aldohexose)



Galactose (Aldohexose)



Fructose (ketohexose)

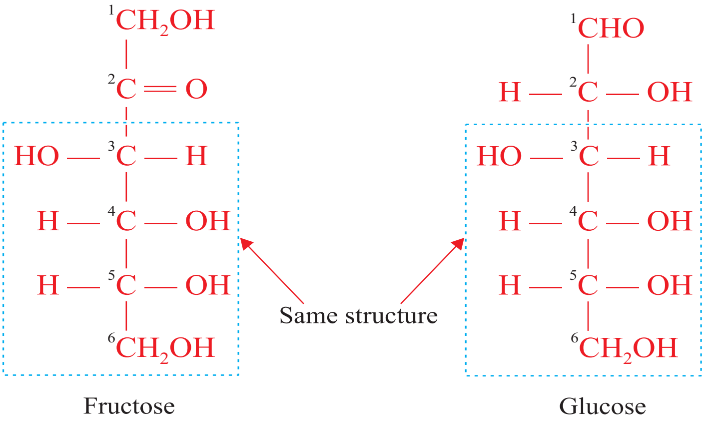


Ribose (Aldopentose)

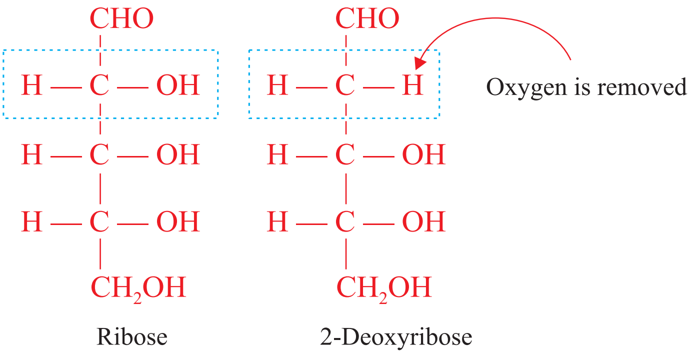
Note that glucose and galactose differ only in the configuration of the – OH group and – H group on carbon-4. Glucose is the most abundant monosaccharide in nature. It is called blood sugar because blood contains dissolved glucose. Its concentration in the blood ranges from 70-100 mg per 100 ml of blood. Cells use this glucose as a primary energy source.

In the human body, galactose is synthesized from glucose in the mammary glands for use in lactose (*milk sugar*). Fructose is the sweetest-tasting of all sugars and is found in many fruits. It is also present in honey, in equal amounts with glucose.

From the third to the sixth carbon the structure of fructose is identical to that of glucose. Differences at carbons 1 and 2 are related to the presence of a ketone functional group in fructose and of an aldehyde functional group in glucose.



Ribose is a component of ribonucleic acid (RNA) and adenosine triphosphate (ATP). The compound 2-deoxyribose is a component of deoxyribonucleic acid molecules (DNA). The prefix deoxy indicates that the oxygen at carbon-2 is removed.

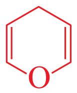


Experimental evidence indicates that, for monosaccharides containing five or more carbon atoms, their open-chain structures are in equilibrium with two cyclic structures and the cyclic structures are the dominant forms at equilibrium. The cyclic forms of monsaccharides result from the ability of their carbonyl group to react intramolecularly (*within the molecule*) with the hydroxyl group. The result is a cyclic hemi-acetal or cyclic hemi-ketal.

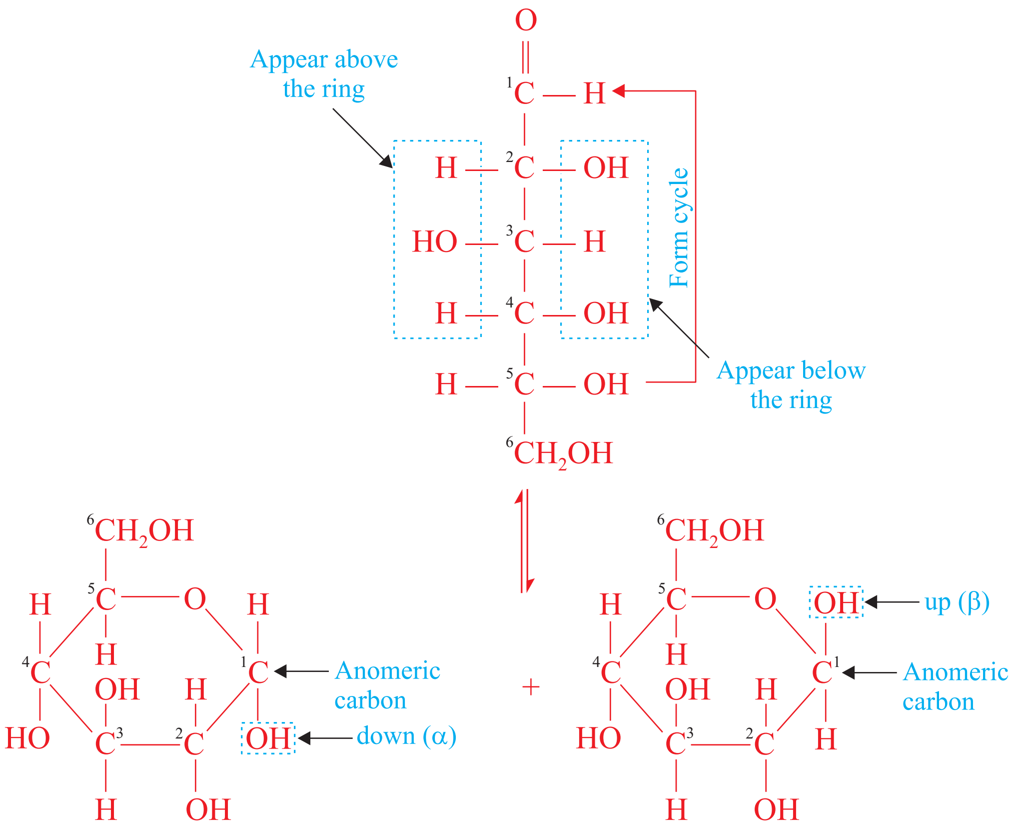
If a six member ring is formed, it is called pyranose. The pyranose ring is formed by the reaction of the –OH group on carbon-5 with the carbonyl group on carbon-1.

Is there any structural similarity between Pyran and Pyranose?

The name pyranose is derived from pyran, which is the name of the six-member heterocyclic ether.



Pyran

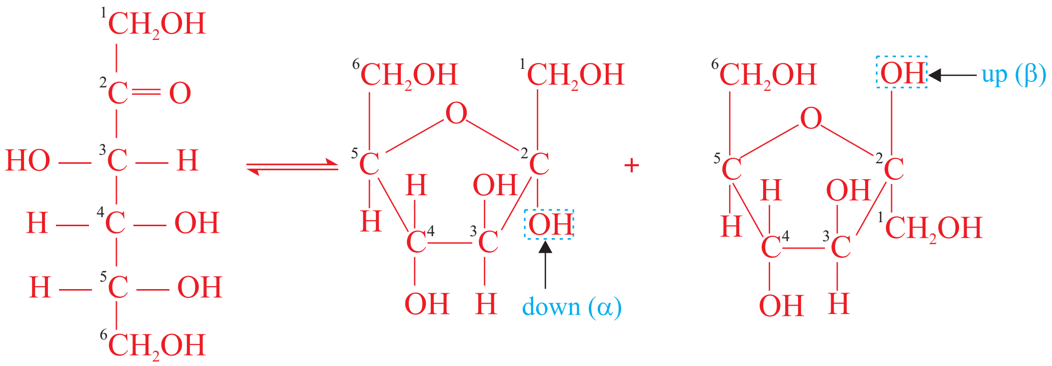


α-Glucopyranose β-Glucopyranose

If the –OH attached to anomeric carbon is below the ring or down, we use α and when –OH is above the ring, we use β. Galactose, like glucose, forms a six membered ring, but both fructose and ribose form a five-member ring sugar called furanose. This name derived from furan, which is the name of five-member heterocyclic ether.

Furan

The furanose ring is formed by the reaction of the –OH group on C–5 with the carbonyl group on C–2.

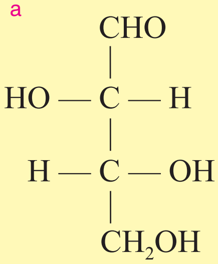


Fructose α-Fructofuranose β-Fructofuranose

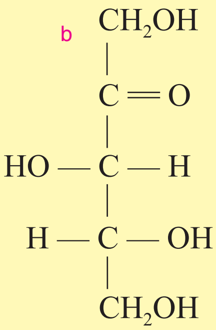
Exercise 6.8

1. Are carbohydrates "hydrates of carbon"? Explain your answer.
2. Classify each of the following monosaccharides by its number of carbon atoms and its type of carbonyl group.

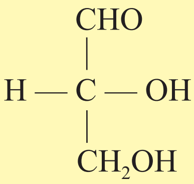
a



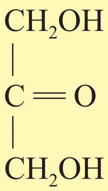
b



c



d



3. Write the cyclic forms of galactose and ribose.
4. Write the molecular formula of ribose, glucose, galactose and fructose.
5. What are reducing sugars? Which of the following monosaccharides behave as reducing sugars?

a Glucose	c Galactose
b Fructose	d Ribose

b Disaccharides

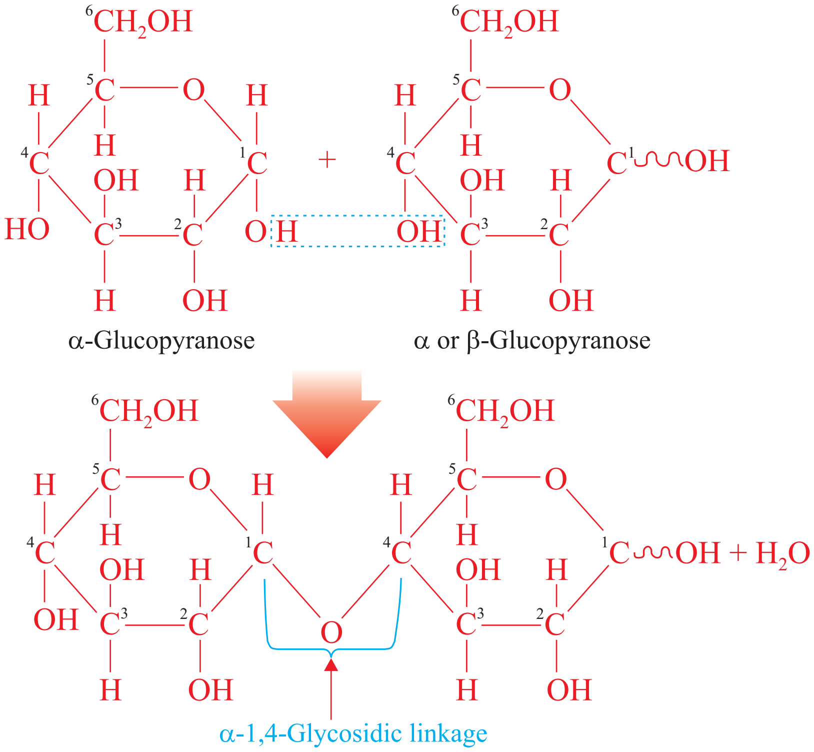
They are dimers made up of two monosaccharide molecules. The monosaccharides may be either the same or different. The monosaccharides are joined by glycosidic linkage between anomeric carbon of one monosaccharide and the – OH group of the other.

The most glycosidic linkage is between the 4-hydroxyl group of one monsaccharide and the α or β position of the anomeric carbon. This kind of linkage is called α-1,4- or β-1,4-glycosidic linkage or bond depending on the configuration at the anomeric carbon atom.

Maltose

Maltose, often called malt sugar, is produced whenever the polysaccharide starch breaks down. This happens when seed germinates in plants and during starch digestion in human beings.

Maltose is made of two glucose units, one of which must be α-glucose and the other can be α or β glucose. Note that since the orientation of OH at carbon-1 is either α or β, we represent it by (∿OH).

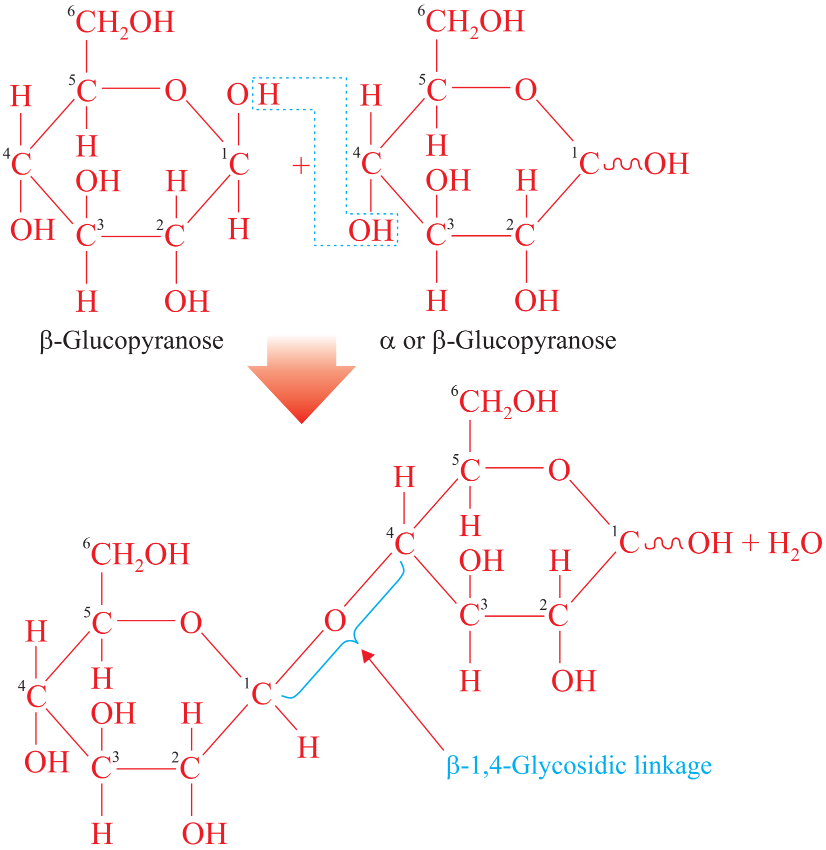


Maltose

The glycosidic linkage between the two glucose units is called an α-1, 4- linkage. The two –OH groups that form the linkage are attached, respectively, to carbon-1 of the first glucose unit (*in the α-configuration*) and to carbon-4 of the second glucose unit.

Cellobiose

Like maltose, cellobiose contains two glucose units. It differs from maltose in that the glycosidic linkage is β-1,4-linkage.

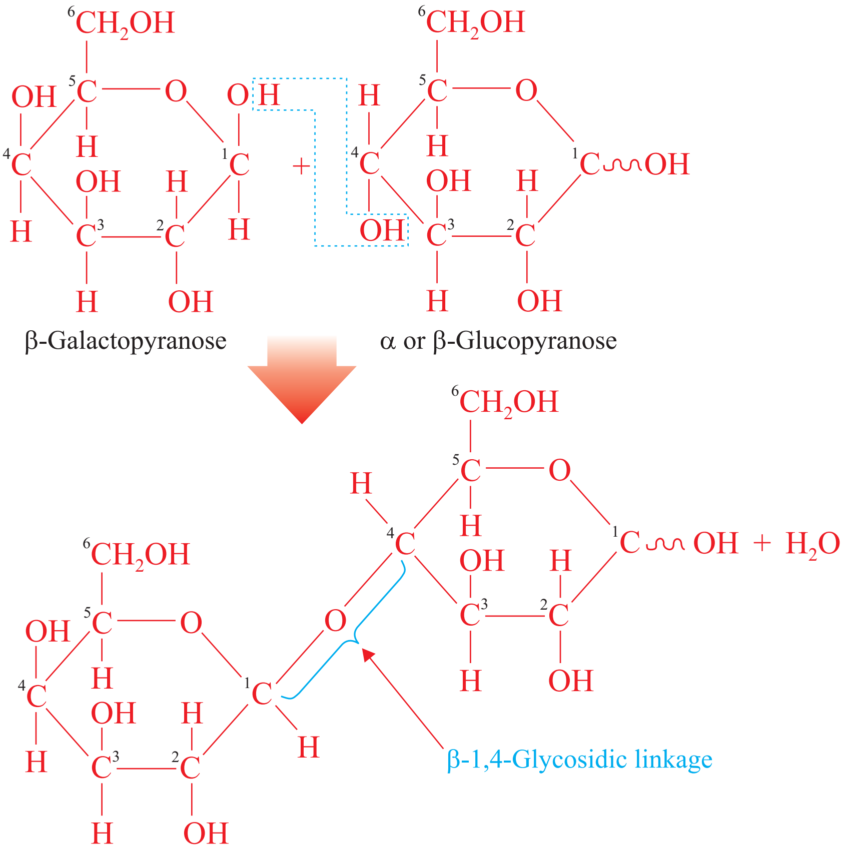


Cellobiose

Maltose and cellobiose have different biological behaviors. Maltase, the enzyme that breaks the glucose-glucose α-1,4-linkage present in maltose, is found both in the human body and yeast. As a result, maltose is digested easily by humans and is readily fermented by yeast. Both the human body and yeast lack the enzyme cellobiase needed to break the glucose-glucose β-1,4-linkage of cellobiose. Therefore, cellobiose cannot be digested by humans or fermented by yeast.

Lactose

Lactose is made up of a β-galactose unit and an α or a β glucose unit joined by a β-1,4-linkage.

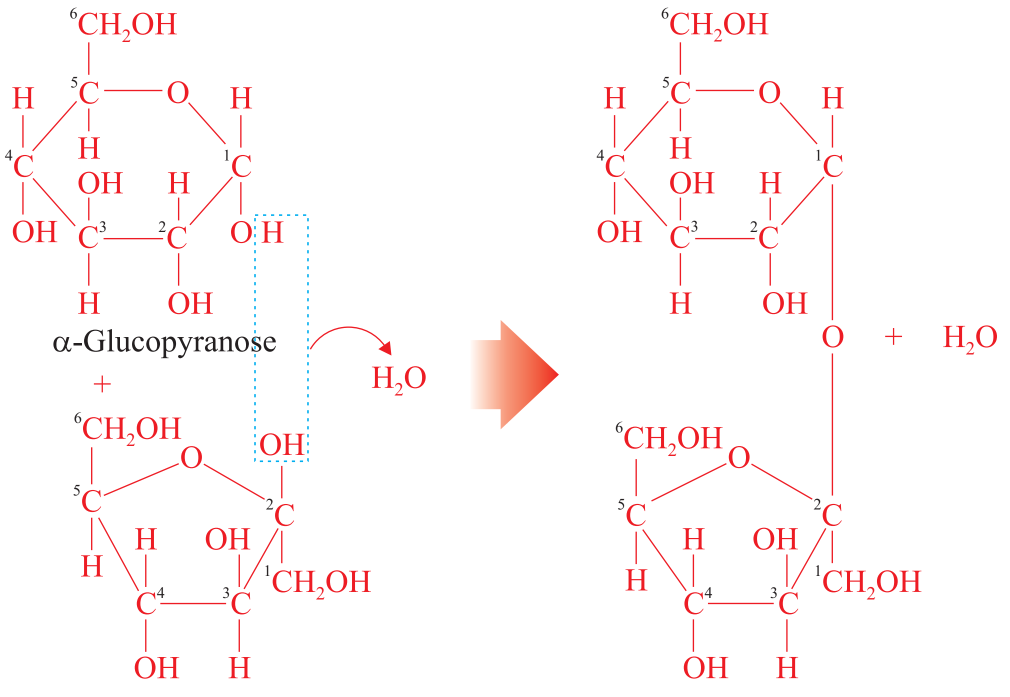


Lactose

Lactose is the major sugar found in milk. The souring of milk is caused by conversion of lactose to lactic acid by bacteria in the milk.

Sucrose

Sucrose, common table sugar, is the most abundant of all the disaccharides. The two monosaccharide units in sucrose molecule are α-glucose and β-fructose. The glycosidic linkage is α, β-1,2-linkage. The –OH group on carbon-2 of β-fructose reacts with the –OH group on carbon-1 of α-glucose.



Sucrose is commercially produced from the juice of sugar cane and sugar beets.

Exercise 6.9

1. What monosaccharides are produced from the hydrolysis of the following disaccharides?
   - a sucrose
   - b maltose
   - c lactose
   - d cellobiose
2. What type of glycosidic linkage is present in the following disaccharides?
   - a sucrose
   - b maltose
   - c lactose
   - d cellobiose
3. Write the molecular formula of:
   - a sucrose
   - b maltose
   - c lactose
   - d cellobiose
4. In making candy, sucrose is boiled in water with little acid, such as lemon juice.
   - a What is the purpose of adding the lemon juice?
   - b Why does the product mixture taste sweater than the starting sucrose solution?

c Polysaccharides

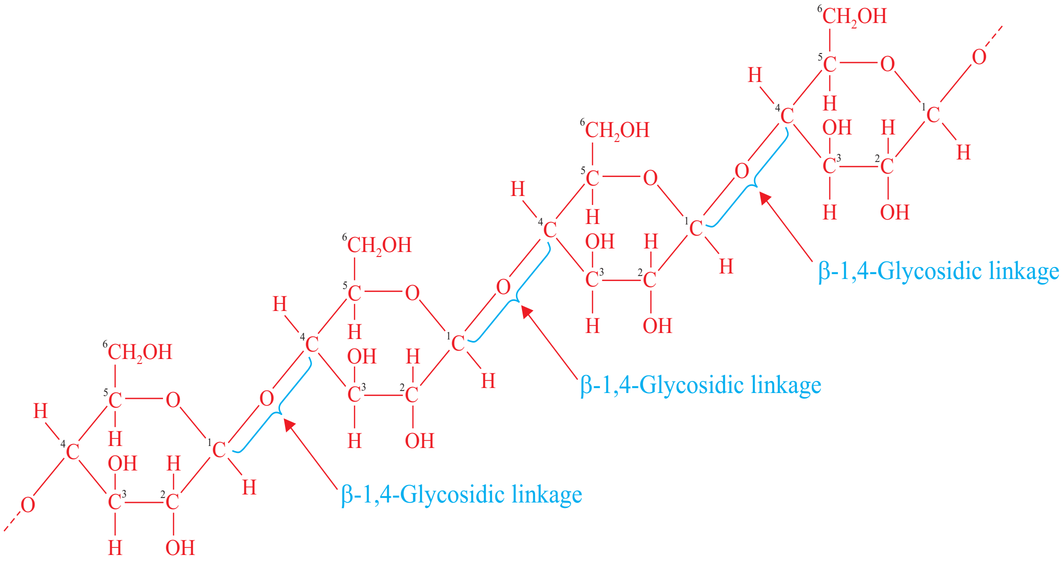
Are polysaccharides condensation polymers or addition polymers?

Polysaccharides are polymers. They consist of a large number of monosaccharide units bonded together by glycosidic bonds. The three important polysaccharides, all made up of glucose units, are cellulose, starch and glycogen.

Are polysaccharides homopolymers or copolymers?

Cellulose

Cellulose is the most abundant polysaccharide. It is the structural component of the cell walls of plants. Structurally, cellulose is a linear (unbranched) glucose polymer in which the glucose units are linked by β-1,4-glycosidic bonds.



Cellulose

Cellulose is not a source of nutrition for humans because humans lack the enzyme cellulase which can hydrolyze the β-1,4-glycosidic bonds and produce free glucose from cellulose.

However, animals such as horses, cows and sheep contain bacteria in their intestine that produce cellulase and produce free glucose from cellulose. Thus, grasses and other plant materials are sources of nutrition for these animals. Cotton is composed of pure cellulose. The cotton fibre forms around the seeds of the cotton plant as indicated in Figure 6.12 and is designed to help carry the seeds long distances on the wind so that the plant can distribute itself. It is the most widely used natural-fibre for clothing.

Figure 6.12 Cotton.

Activity 6.8

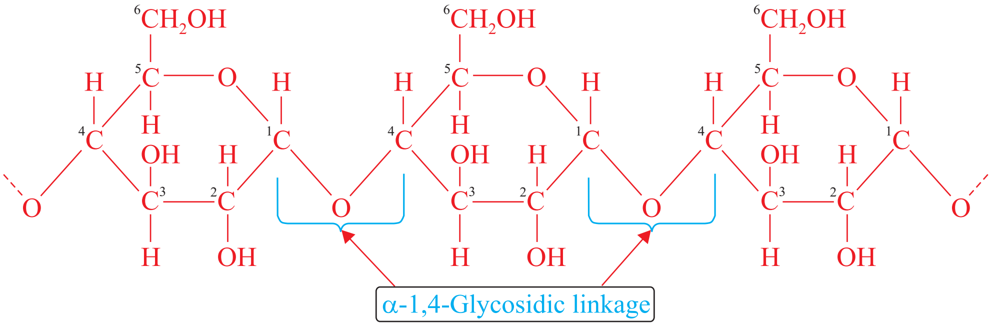
1. Give examples of synthetic fibres used for clothing that were developed on principles learned from carbohydrates.
2. What is the simplest method to differentiate woollen fibre from a cotton fibre?

Starch

Starch is used for energy storage in plants. If excess glucose enters a plant cell, it is converted to starch and stored for later use.

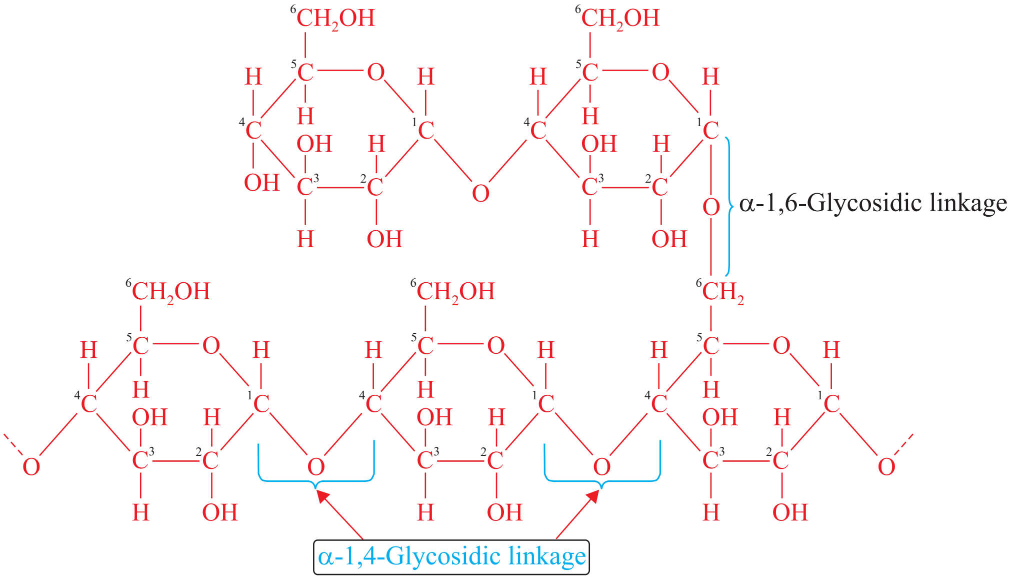
Starch can be separated into two principal polysaccharides, amylose and amylopectin.

Amylose is a straight-chain glucose polymer and accounts for 20-25% of starch. The glucose units in amylose are connected by α-1,4-glycosidic bonds. The number of glucose units present in amylose chain depends on the source of the starch.



Starch (Amylose)

Amylopectin is a highly branched glucose polymer, which accounts for 75-80% of starch. Similar to the case in amylose, all the linkages in amylopectin are α-linkages. A branch occurs in amylopectin about once in every 25-30 glucose units. The branch points involve α-1,6-linkages. Because of the branching, amylopectin has a large average molecular mass than the linear amylose.



Starch (Amylopectin)

Note that all of the glycosdic linkages in starch (*both amylose and amylopectin*) are of the α-type. In amylose, they are all α-1,4-linkages and in amylopectin both α-1,4 and α-1,6-likages are present.

Glycogen

It is a glucose storage polysaccharide in humans and animals. It is called animal starch. Liver cells and muscle cells are the storage sites for glycogen in humans.

Like amylopectin, glycogen units are joined by α-1,4- and α-1,6-glycosdic bonds. However, glycogen is about three times more highly branched than amylopectin.

When excess glucose is present in the blood, the liver and muscle tissues convert the excess glucose to glycogen, which is then stored in these tissues. If the glucose blood level decreases, some stored glycogen is hydrolyzed back to glucose.

Exercise 6.10

1. Describe the structural differences and similarities between the following pairs of polysaccharides:

   a glycogen and amylopectin
   b amylose and amylopectin
   c amylose and cellulose
   d amylose and glycogen

2. Match each of the following structural characteristics to the polysaccharides. You can use the characteristics in column B more than once.

Column A	Column B
i Amylopectin	A Contains both α-1,4-and α-1,6-glycosidic linkages
ii Amylose	B Composed of glucose monosaccharide units
iii Glycogen	C Composed of unbranched glucose chains
iv Cellulose	D Contains only β-1,4-glycosidic linkage

3. Humans can digest starch but not cellulose. Why?

6.4.4 Proteins

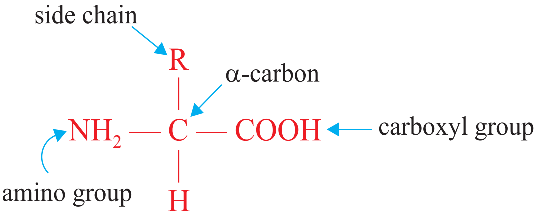
What are proteins?

The name protein comes from the Greek word "*proteios*" which means "*primary*". This indicates the relative importance of these compounds. All proteins contain carbon, hydrogen, oxygen and nitrogen. Many proteins also contain sulphur.

Proteins are made by the polymerization of the twenty naturally occurring amino acids. An amino acid is a compound that contains both an amino ($-NH_2$) group and a carboxylic acid ($-COOH$) group.

The amino acids found in proteins are always α-amino acids (*the amino group is attached to the carbon atom adjacent to the carboxyl group*).

The structural formula for an α-amino acid is:

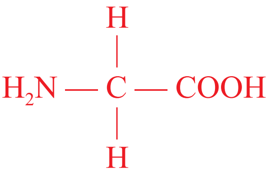


The R group present in an α- amino acid is called the amino acid side chain. The nature of this side chain distinguishes α- amino acids from each other. Based on the side chain polarity, amino acids can be grouped into four categories:

1. Nonpolar amino acids;
2. Polar neutral amino acids;
3. Polar acidic amino acids; and
4. Polar basic amino acids.

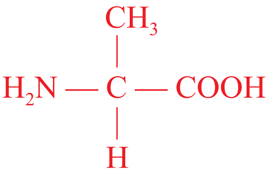
Nonpolar amino acids

Nonpolar amino acids contain one amino group, one carboxyl group, and a nonpolar side chain. When they are incorporated into a protein, these amino acids are hydrophobic or "*water-fearing*" and are not attracted to water molecules. They are generally found on the interior of proteins, where there is limited contact with water. There are eight nonpolar amino acids.



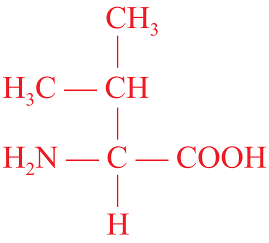
$$H_2N-\overset{H}{\underset{H}{C}}-COOH$$

Glycine (Gly, G)

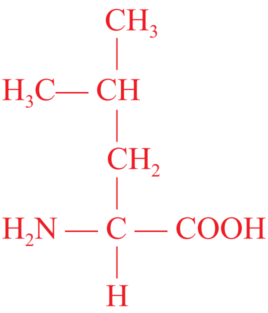


$$H_2N-\overset{CH_3}{\underset{H}{C}}-COOH$$

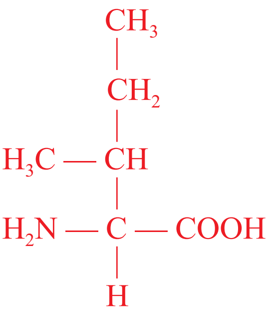
Alanine (Ala, A)



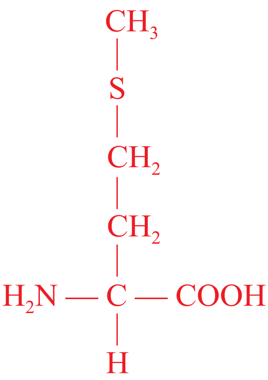
Valine (Val, V)



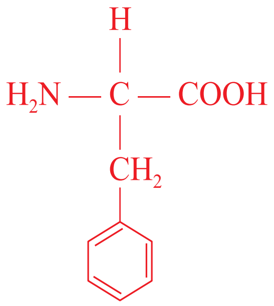
Leucine (Leu, L)



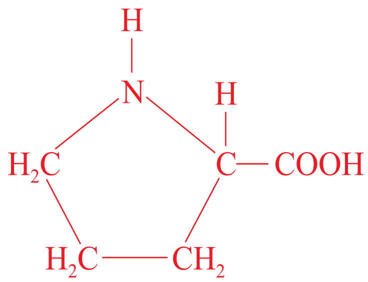
Isoleucine (Ile, l)



Methionine (Met, M)



Phenylalanine (Phe, F)



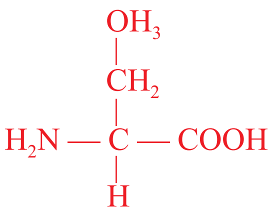
Proline (Pro, P)

Note that either three letters or one letter can represent each amino acid.

Polar neutral amino acids

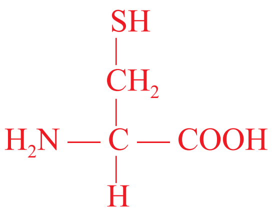
What will happen if polar neutral amino acids are incorporated into a protein?

Polar neutral amino acids contain one amino group, one carboxyl group, and a side chain that is polar but neutral. There are seven polar neutral amino acids.



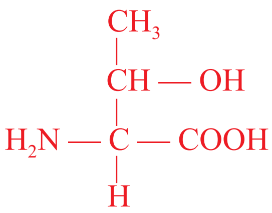
$$\begin{array}{ccc} & OH_3 & \\ & | & \\ & CH_2 & \\ & | & \\ H_2N - & C & - COOH \\ & | & \\ & H & \end{array}$$

Serine (Ser, S)



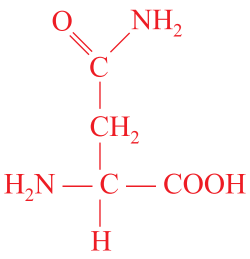
$$\begin{array}{ccc} & SH & \\ & | & \\ & CH_2 & \\ & | & \\ H_2N - & C & - COOH \\ & | & \\ & H & \end{array}$$

Crysteine (Cyst, C)

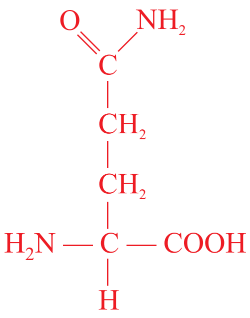


$$\begin{array}{ccc} & CH_3 & \\ & | & \\ & CH - OH & \\ & | & \\ H_2N - & C & - COOH \\ & | & \\ & H & \end{array}$$

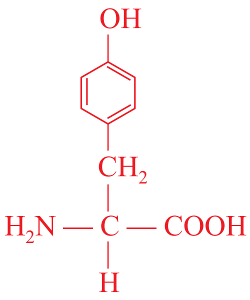
Threonine (Thr, T)



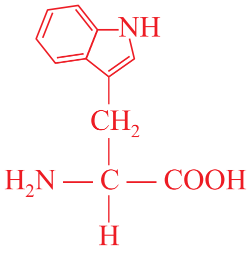
Asparagine (Agn, N)



Glutamine (Gln, Q)



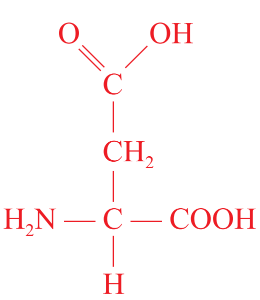
Tyrosine (Tyr, Y)



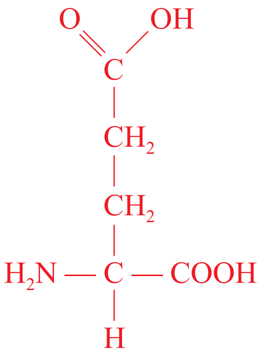
Tryptophan (Trp, W)

Polar acidic amino acids

Polar acidic amino acids contain one amino group and two carboxyl groups. The second carboxyl group is part of the side chain. There are two polar acidic amino acids.



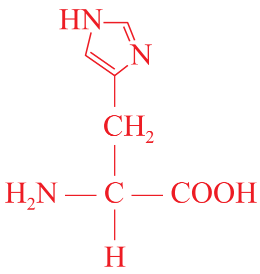
Aspartic acid (Asp, D)



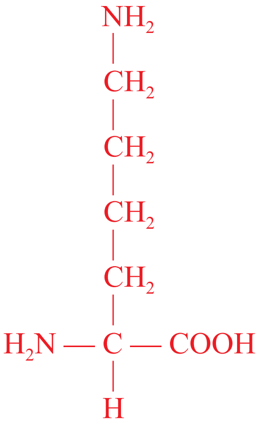
Glutamic acid (Glu, E)

Polar basic amino acids

Polar basic amino acids contain two amino groups and one carboxyl group. The second amino group is part of the side chain. There are three polar basic amino acids.

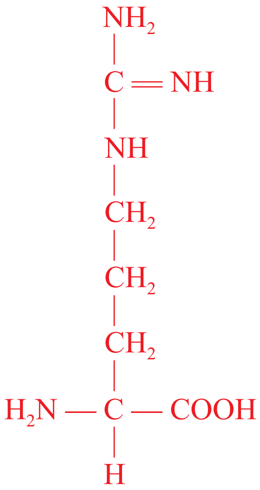


Histidine (His, H)



$$\begin{array}{ccccc} & & NH_2 & & \\ & & | & & \\ & & CH_2 & & \\ & & | & & \\ & & CH_2 & & \\ & & | & & \\ & & CH_2 & & \\ & & | & & \\ & & CH_2 & & \\ & & | & & \\ H_2N & - & C & - & COOH \\ & & | & & \\ & & H & & \end{array}$$

Lysinee (Lys, K)



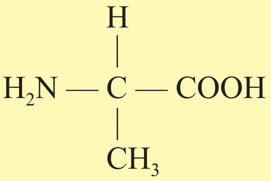
$$\begin{array}{ccccc} & & NH_2 & & \\ & & | & & \\ & & C & = & NH \\ & & | & & \\ & & NH & & \\ & & | & & \\ & & CH_2 & & \\ & & | & & \\ & & CH_2 & & \\ & & | & & \\ & & CH_2 & & \\ & & | & & \\ H_2N & - & C & - & COOH \\ & & | & & \\ & & H & & \end{array}$$

Arginine (Arg, R)

Exercise 6.11

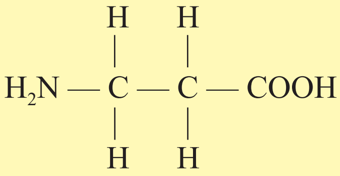
1. Which of the following structures represents α-amino acids?

a



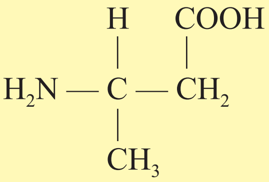
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H_2N & - & C & - & COOH \\ & & | & & \\ & & CH_3 & & \end{array}$$

b



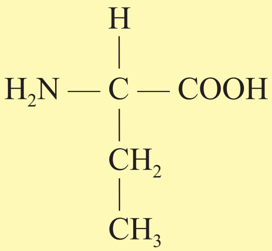
$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H_2N & - & C & - & C & - & COOH \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

c



$$\begin{array}{ccccc} & & H & & COOH \\ & & | & & | \\ H_2N & - & C & - & CH_2 \\ & & | & & \\ & & CH_3 & & \end{array}$$

d



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H_2N & - & C & - & COOH \\ & & | & & \\ & & CH_2 & & \\ & & | & & \\ & & CH_3 & & \end{array}$$

2. Give two examples for each of the following amino acids, together with their structures.
   - a Nonpolar amino acids
   - b Polar neutural amino acids
   - c Polar acidic amino acids
   - d Polar basic amino acids

Physical Properties of Amino Acids

Amino acids have the following properties.

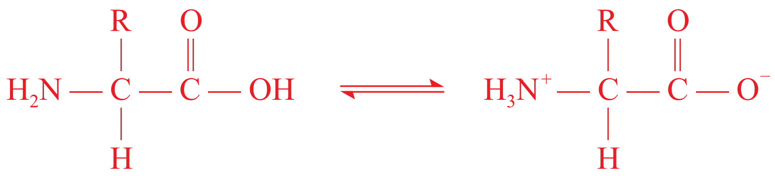
i) They have high melting points.

ii) They are colourless crystalline substances.

iii) They are soluble in water but insoluble in nonpolar solvents.

Thus, they resemble ionic compounds. This occurs due to the fact that amino acids contain both an acid (–COOH) and a base (–NH_2) functional groups. These acids and basic groups react with each other to form a dipolar ion or internal salt. The dipolar ion of an amino acid is called zwitterion.

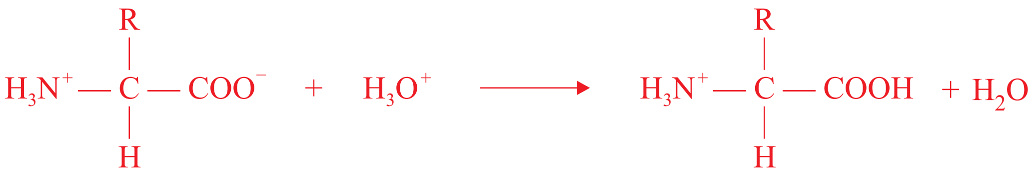
A zwitterion has no net charge.



$$H_2N-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OH \rightleftharpoons H_3N^+-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-O^-$$

Zwitterion form

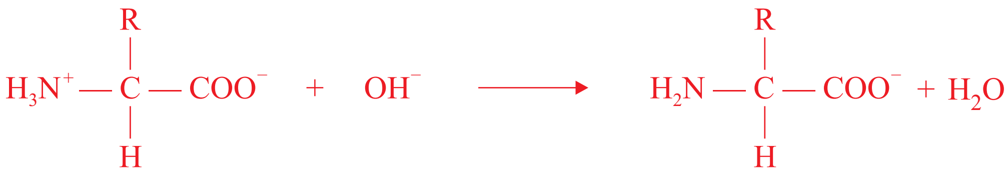
A zwitterion structure changes when the pH of a solution containing an amino acid is changed from neutral either to acidic (low pH), by adding an acid such as HCl, or to basic (high pH), by adding a base such as NaOH. In acidic solution, the zwitterion accepts a proton (H^+) to form a positively charged ion.



$$H_3N^+-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}-COO^- + H_3O^+ \longrightarrow H_3N^+-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}-COOH + H_2O$$

Zwitterion (no net charge) Positively charged ion

In a basic solution, the – NH_3^+ of zwitterion loses a proton, and a negatively charged species is formed.

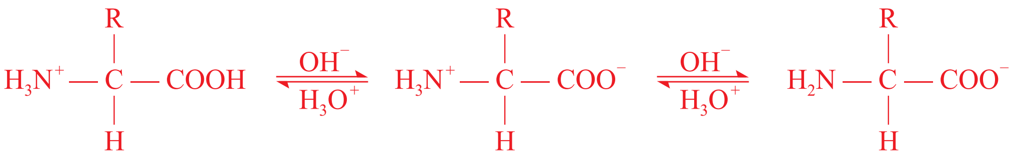


$$H_3N^+-\underset{H}{\overset{R}{C}}-COO^- + OH^- \longrightarrow H_2N-\underset{H}{\overset{R}{C}}-COO^- + H_2O$$

Zwitterion (no net charge) Negatively charged ion

Thus, in a solution, three different amino acid forms can exist (*zwitterion, negative ion, and positive ion*).

The three species are in equilibrium with each other and the equilibrium shift with pH change.



$$H_3N^+-\underset{H}{\overset{R}{C}}-COOH \xrightleftharpoons[H_3O^+]{OH^-} H_3N^+-\underset{H}{\overset{R}{C}}-COO^- \xrightleftharpoons[H_3O^+]{OH^-} H_2N-\underset{H}{\overset{R}{C}}-COO^-$$

Acidic solution (low, pH) Neutral solution (pH = 7) Basic solution (high pH)

In acidic solution, the positively charged species on the left predominates. Nearly neutral solutions have the middle species (*the zwitterion*) as the dominant species. In basic solution, the negatively charged species on the right predominates.

Peptide Bond Formation

Activity 6.9

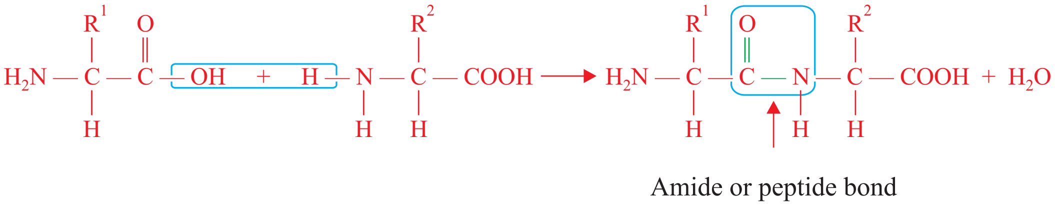
Form a group and discuss each of the following questions.

1. Why amino acids form zwitterions?
2. How many different tripeptides can be obtained by various combinations of three amino acid residues?
3. How do amino acids join together to form proteins?
4. What type of polymerization is it?
5. What are the differences between different proteins?

After the discussion, share your ideas with the rest of the class

A peptide (*amide*) is a bond formed between the carboxyl group of one amino acid and the amino group of another amino acid.

If two amino acids are allowed to react, the carboxyl group of one amino acid reacts with the amino group of the other amino acid. The products are a molecule containing the two amino acids linked by an amide bond or a peptide bond and water.



$$H_2N-CH(R^1)-C(=O)-OH + H-NH-CH(R^2)-COOH \longrightarrow H_2N-CH(R^1)-C(=O)-NH-CH(R^2)-COOH + H_2O$$

A compound containing two amino acids joined by a peptide bond is called a *dipeptide*. Either end of the dipeptide can undergo a condensation reaction with another amino acid to form a tripeptide, tetrapeptide and so on.

Recall that, in the preparation of nylon 66, adipic acid contains two acid functional groups and hexamethylene diamine contains two amine functional groups.

A polypeptide is a sequence of amino acids, containing up to 50 amino acid units, in which the amino acids are joined together through amide (peptide) bonds. Proteins are polypeptides that contain more than 50 amino acid units.

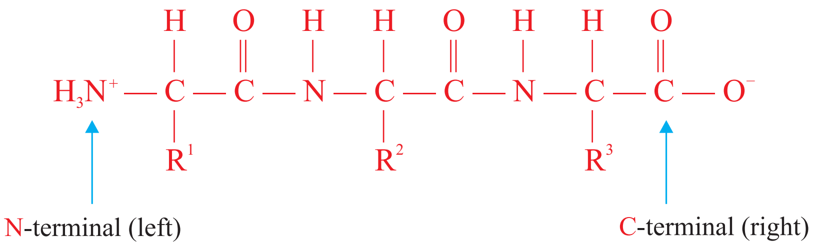
Are proteins condensation polymers or addition polymers? Which small molecule is mostly expelled in the synthesis of protein?

Proteins have many functions, as shown in Table 6.2.

Table 6.2 Some Functions of Proteins.

Type of protein	Example	Function
Enzymes	amylase	Promotes the breakdown of starch to the simple sugar glucose.
Structural proteins	keratin, collagen	Promotes the formation of hair, wool, nails, horns, tendons and cartilage.
Contractile proteins	actin, myosin	Contracting fibers in muscle.
Hormones	insulin, glucagon	Regulates use of blood sugar.
Storage proteins	ferritin	Stores iron in spleen.
Transport proteins	hemoglobin	Carries oxygen in blood.
	serum albumin	Carries fatty acids in blood.
Immunological proteins	antibodies	Defends the body from foreign invaders.

By convention the sequence of amino acids in a peptide is written with the N-terminal amino acid at the left and the C-terminal amino acid at the right. The individual amino acids within a peptide chain are called amino acid residues.



$$H_3N^+-CH(R^1)-C(=O)-NH-CH(R^2)-C(=O)-NH-CH(R^3)-C(=O)-O^-$$

Exercise 6.12

1. Draw the appropriate structural form for the amino acid alanine that predominates in a solution at each of the following pH values.

   a pH = 1 b pH = 7

   c pH = 11

2. What two functional groups are involved in the formation of a peptide bond?
3. How do amino acids, peptides, and protein differ?
4. Write a chemical equation that indicates the formation of a dipeptide from glycine and alanine.

Unit Summary

- *Monomers are the building blocks of polymers.*
- *Homopolymers are made from identical monomers, and copolymers are synthesized from more than one kind of monomer.*
- *Based on their sources, polymers can be classified as synthetic or natural. Synthetic polymers are man-made, while natural polymers exist naturally.*
- *Polymerization is the process of combining monomer units to form large molecules called polymers.*
- *Polymerization can be effected through either addition polymerization or condensation polymerization.*
- *Each of the following polymers are made by addition polymerization.*
  - ◆ *Polyethylene*
  - ◆ *Polypropylene*

  - *Polyvinyl chloride (PVC)*
  - *Polymethyl methacrylate (PMMA)*
  - *Teflon*
  - *Polystyrene*
  - *Natural rubber*
  - *Neoprene*
  - *Styrene-butadiene rubber and*
  - *Butyl rubber*
- *Polymers that are synthesized by condensation polymerization are.*
  - *Nylons*
  - *Polyesters*
  - *Bakelite*
  - *Carbohydrates, and*
  - *Proteins.*
- *Thermoplastics soften on heating and can be molded into different shapes, and the process of heating and cooling can be repeated several times, but once thermosetting plastics are solidified they cannot be softened or remolded on heating.*
- *Synthetic polymers pollute the environment during their preparations, use and disposal.*
- *Monosaccharides are the building blocks of carbohydrates.*
- *Proteins are made from the twenty naturally occurring amino acids.*

Check list

Key terms of the unit

- *Addition polymerization*
- *Adipic acid*
- *Amino acids*
- *Bakelite*
- *Butyl rubber*
- *Carbohydrates*
- *Catalyst*
- *Copolymer*
- *Disaccharides*
- *Ethylene*

- *Ethylene glycol*
- *Formaldehyde*
- *Hexamethylene diamine*
- *Homopolymer*
- *Isoprene*
- *Methyl methacrylate*
- *Monomer*
- *Monosaccharides*
- *Natural polymer*
- *Natural rubber*
- *Nylon*
- *Peptides*
- *Phenol*
- *Polyester*
- *Polyethylene*
- *Polymer*
- *Polymerization*
- *Polymethyl methacrylate (PMMA)*
- *Polypropylene*
- *Polysaccharides*
- *Polystyrene*
- *Polyvinyl chloride (PVC)*
- *Propylene*
- *Protiens*
- *Repeating unit*
- *SBR*
- *Styrene*
- *Synthetic polymer*
- *Teflon*
- *Terephthaleic acid*
- *Tetrafluoroethylene*
- *Thermoplastic and thermosetting plastics*
- *Vinyl chloride*
- *Vulcanization*

REVIEW EXERCISE FOR UNIT 6

Part I: Mutiple Choice Questions

1. Which of the following statement is incorrect about polymers?
   a they are macromolecules made from smaller units.
   b they can be prepared by either condensation or addition polymerization.
   c most condensation polymers are hompolymers.
   d disposing synthetic polymers can pollute the environment.
2. The process by which monomer units combine to form polymers, is:
   a condensation
   b thermoplastic
   c thermosetting
   d evaporation

3. What is the molar mass of a polyethylene sample, $-\!\!\left(CH_2-CH_2\right)\!\!-_{n}$, when $n = 4600$? (Atomic mass, H = 1 and C = 12).

a 1.288×10^3 g/mol
b 1.288×10^5 g/mol
c 1.196×10^3 g/mol
d 1.196×10^4 g/mol

4. Which one of the following is not formed by addition polymerization?

a polyethylene
b polyvinyl chloride
c teflon
d dacron

5. Which one of the following polymer-monomer pairs is incorrectly matched?

a Teflon-propylene
b PVC-chloroethene
c Plexiglass-methyl methacrylate
d Bakelite-phenol and formaldehyde

6. Which one of the following is not a synthetic polymer?

a nylon
b cotton
c teflon
d dacron

7. Polyethylene is not used for making:

a squeeze bottles
b trash bags
c electrical insulation
d airplane windows

8. Dacron is made by the polymerization of ___________ and ______________.

a terephthalic acid, ethylene
b adipic acid, ethylene glycol
c terephthalic acid, ethylene glycol
d adipic acid, hexamethylene diamine

9. Which one of the following is a thermosetting plastic?

a polyethylene
b polypropylene
c dacron
d bakelite

10. Which of the following structures represents the monomer of $-\!\!\left(CH_2-CH_2=CH_2-CH_2\right)\!\!-_{n}$?

a $CH_3CH=CHCH_3$
b $CH_2=CH-CH=CH_2$
c $CH_2=CH-CH_2-CH_3$
d none of the above

11. The monomer of natural rubber is:

a	isoprene	c	chloroprene
b	2-methyl-1,3-butadiene	d	a and b are correct answers

12. Which one of the following statements is incorrect about synthetic and natural polymers?

    a Nucleic acids, proteins and carbohydrates are natural polymers

    b Natural polymers are the major pollutants of the environment

    c Synthetic polymers have wide applications

    d None of the above

13. Which one of the following is not the characteristic of vulcanized rubber?

    a It is a sticky solid

    b It is hard

    c It has high tensile strength

    d It has higher elasticity over a higher range of temperature

14. Which of the following statement is correct about natural and synthetic rubbers?

    a Natural rubber is a copolymer but synthetic rubbers are hompolymers.

    b Natural rubber is superior to styrene-butadiene rubber with regard to mechanical strength.

    c Butyl rubber holds air better than natural rubber and is used for inner tubes.

    d All of the above.

15. Which of the following statement is false about carbohydrates?

    a They are prepared by green plants during photosynthesis.

    b They are polyhydroxyl ketones or aldehydes or substances that yield such substances upon hydrolysis.

    c All carbohydrates are polymers.

    d None of the above.

16. Which of the following monosaccharides is a ketohexose?

a	Ribose	c	Galactose
b	Glucose	d	Fructose

17. An amino acid differs from the others by:

a the amine functional group
b the acid functional group
c the side-chain
d a and b are correct answers

18. Pyranose ring can be formed by:

a galactose
b fructose
c ribose
d a and b are correct answers

19. A disaccharide made from two glucose units that are linked by α-1,4 glycosidic bond is:

a cellulose
b maltose
c lactose
d sucrose

20. Which one of the following disaccharide is prepared from two different monosaccharide units?

a Cellulose
b Maltose
c Lactose
d Fructose

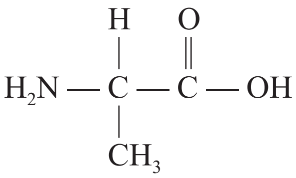
21. Which one of the following statement is incorrect about polysaccharides?

a Cellulose, starch and glycogen are hompolymers.
b Cellulose is a linear polymer in which the glucose units are linked by β-1,4 glycosidic bonds.
c Amylose and amylopectin are the two forms of glycogen.
d Glycogen is a glucose storage polysaccharide in humans and animals.

22. Which type of amino acids contain two amino groups and one carboxyl group?

a Non-polar
b Polar neutral
c Polar basic
d Polar acidic

23. What is the charge on the following amino acid at pH 14?



$$H_2N-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OH$$

a +1
b +2
c –1
d –2

24. A bond that is formed between amino acids is called:
    - a hydrogen bond
    - b amide bond
    - c peptide bond
    - d b and c are correct answers

Part II: Short Answer Questions

25. Define each of the following terms and give an example for each:
    - a Monomer
    - b Polymer
    - c Carbohydrate
    - d Amino acid
    - e Polypeptide
    - f Protein

26. Classify each of the following polymers as natural or synthetic.
    - a Polyethylene
    - b Polypropylene
    - c Cellulose
    - d Polyvinyl chloride
    - e Deoxyribonucleic acid
    - f Polytetrafluoroethylene
    - g Polystyrene
    - h Nylons
    - i Cotton
    - j Dacron

27. Classify each polymer in Question 26 as an addition polymer or a condensation polymer.

28. What functional groups are involved in the addition and condensation polymerization processes?

29. Mention major uses of each of the following synthetic polymers.
    - a Polypropylene
    - b Polyvinyl chloride
    - c Teflon
    - d Polystyrene
    - e Bakelite
    - f Nylons
    - g Plexiglass

30. Draw the open chain and cyclic structures of each of the following compounds.
    - a Galactose
    - b Fructose
    - c Ribose
    - d Maltose
    - e Sucrose
    - f Cellulose
    - g Phenylalanine