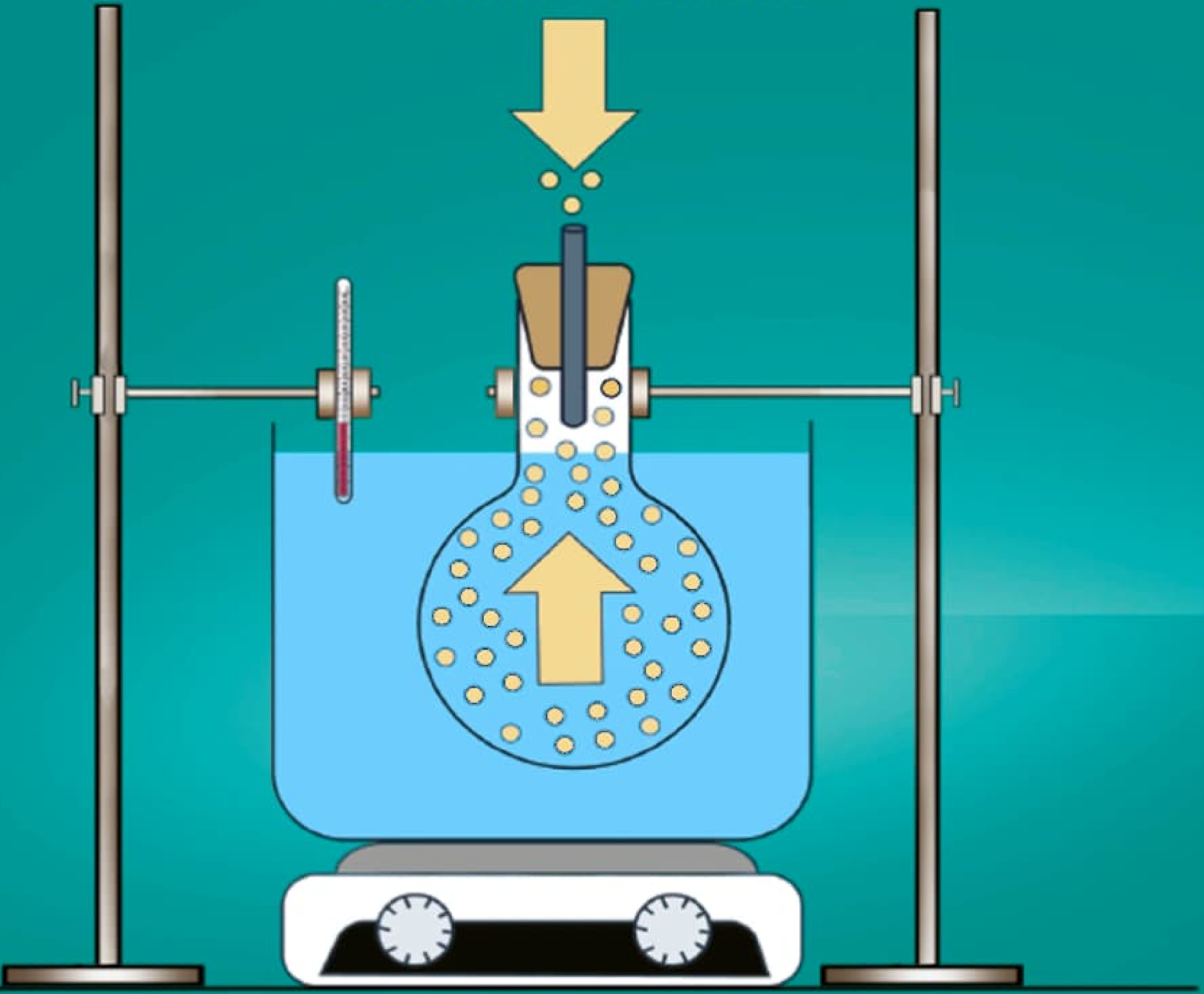
Physical Chemistry

for Advanced Secondary Schools

Student's Book
Form Five and Six



Tanzania Institute of Education

Physical Chemistry

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Student's Book

Form Five and Six

THE UNITED REPUBLIC OF TANZANIA
MINISTRY OF EDUCATION,
SCIENCE AND TECHNOLOGY

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Commissioner for Education

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Tanzania Institute of Education
Mikocheni Area
132 Ali Hassan Mwinyi Road
P. O. Box 35094
14112 Dar es Salaam

Mobile numbers: +255 735 041 168/ +255 735 041 170
E-mail: director.general@tie.go.tz
Website: www.tie.go.tz

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Writers: Dr Grace A. Kinunda, Dr Mtabazi G. Sahini, Dr Gerald E. Shija, Dr Aldo Kitalika, Mr Fixon E. Mtelesi, Ms Marietha Belege, Mr Peter Kyabwazi, Ms Galasia Lunyungu, Mr Jumanne Mwanga, Mr Chrisant Kayogolo & Ms Auguster F. Kayombo

Editors: Dr Joseph Y.N. Philip, Dr James E. Mgaya, Dr Ginena B. Shombe, Ms Renatha M. Mahega, Mr Elias B. Singano & Mr Mbonyo H. Zaidi

Designers: Mr Katalambula F. Hussein & Mr Silvanus A. Mihambo

Illustrators: Dr Mtabazi G. Sahini, Mr Fixon E. Mtelesi, Mr Fikiri A. Msimbe, Alama Art and Media Production Co. Ltd & Mr Hance E. Wawar

Coordinator: Ms Auguster F. Kayombo

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Dr Aneth A. Komba
Director General
Tanzania Institute of Education

Preface

This textbook, *Physical Chemistry for Advanced Secondary Schools*, is written specifically for Form Five and Six Students in the United Republic of Tanzania. The book is prepared in accordance with the 2023 Chemistry Syllabus for Advanced Level Secondary Education, Form V-VI, issued by the Ministry of Education, Science and Technology (MoEST). It is a revised edition of Physical Chemistry for Secondary Schools Student's Book for Form Five and Six that was published in 2019 in accordance with the 2009 syllabus issued by the then, Ministry of Education and Vocational Training (MoEVT).

The book consists of eight chapters, namely: Gases, Colligative properties of solutions, Two components liquid systems, Energetics, Chemical equilibrium, Ionic equilibrium, Chemical kinetics, and Electrochemistry. In addition to the contents, the chapters contain illustrations, activities, tasks, and exercises. You are encouraged to do all the activities, tasks, and attempt all questions in the exercises. You are also required to prepare a portfolio for keeping records of activities performed in different lessons. This will enhance your understanding and development of the intended competencies for this level.

Additional learning resources are available in the TIE e-Library at

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Chapter One

Gases

Introduction

Many reactions performed in the laboratory or industries involve gases as reactants or products. This means that a chemist must be well equipped with the knowledge of gases to successfully handle such reactions. In this chapter, you will learn about the parameters of gases, gas laws, the kinetic theory of gases, the relative molecular masses of gases and the applications of gas laws in daily life. The competencies developed will enable you to manipulate, predict and associate the behaviour of gases to unlock and tackle various challenges that drive innovations in the manufacturing and transport industries.

Think

A world with unknown behaviour of gases

1.1 Gas parameters

Task 1.1

Use online resources to study properties of gases.

Despite their wide differences in chemical properties, all gases more or less obey the gas laws. These laws show the relationship between macroscopic physical properties of gases, such as volume, pressure, temperature, and number of moles of a gas.

(a) *Volume (V)* – Gases have no definite volume as they expand to fill the volume of a container. Therefore, the volume of a gas is equal to the volume of a container occupied by the gas. The SI unit of volume is cubic metre (m^3); however, other units such as litre (L), cubic decimetre (dm^3), cubic centimetre (cm^3) and millilitres (mL) are commonly used depending on the context and the precision required.

(b) *Pressure (P)* – The pressure of a gas is the force exerted by the impacts of its molecules per unit area of the wall of the container.

The pressure of a gas in a container is measured by using a *manometer*. The pressure for gases in the atmosphere is measured by using a *barometer*. The manometer and the barometer can be electronic or digital. An example of a manometer is shown in Figure 1.1.

In the manometer, the gas container is connected to a U-tube containing a non-toxic liquid such as water, oil or glycol with a vacuum at the top end. When the cock is opened, the gas flows from the container and pushes the liquid upward. The gas pressure is proportional to the difference in the heights of the liquid columns in the two arms of the manometer.

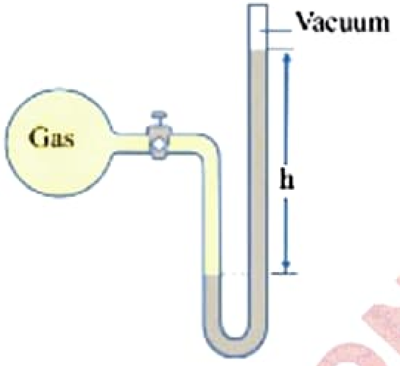


Figure 1.1: *Manometer for measurement of gas pressure*

The pressure can be calculated using the equation:

$$P = h\rho g$$

where h = height difference between the liquid levels in the U-tube, ρ is the density of the liquid in the manometer and g is the acceleration due to gravity.

The SI units of pressure are Pascal (Pa) and (Nm^{-2}). The relationship among the units of pressure is:

$$1\ \text{atm} = 760\ \text{Torr} = 1.01 \times 10^5\ \text{Pa} = 1.01 \times 10^5\ \text{N/m}^2$$

For the measurement of gas pressure in the atmosphere, mercury barometers are the most common. However, their use has been restricted due to health issues associated with mercury. Currently, mercury barometers have been replaced by electronic or digital barometers. These devices use electronic sensors to measure the atmospheric pressure and display the reading digitally.

(c) *Temperature (T)* – The temperature of a gas is measured in Celsius degree or centigrade degree (°C). The SI unit of temperature is Kelvin (K). The Kelvin temperature (or absolute temperature) of a gas can be obtained using the following expression:

$T(\text{K}) = T(^{\circ}\text{C}) + 273$

(d) *Number of moles of a gas (n)* – The number of moles of a gas in a container is equal to the mass of the gas (m) divided by its molecular/atomic mass (M).

$$\text{Moles of a gas} = \frac{\text{mass of a gas}}{\text{molecular/atomic mass of a gas}} \text{ or simply, } n = \frac{m}{M}$$

1.2 The gas laws

Task 1.2

Use online sources to study different gas laws.

The parameters needed to characterise a gas are inter-related. Any change in one parameter causes a change in one of the other parameters. The relationship between various properties of gases, such as pressure, temperature, volume and amount of gas molecules (moles) are described by the gas laws. These laws include *Boyle's law*, *Charles' law*, *Gay Lussaac law*, *Avogadro's law* and *ideal gas equation*. Other gas laws are *Dalton's law of partial pressure* and *Graham's law of diffusion and effusion*.

1.2.1 Boyle's law

The *Boyle's law* was named after an Anglo-Irish philosopher and scientist, Robert Boyle (1627 – 1691), who published the law in 1662. The law states that at constant temperature, the volume of a fixed mass of a gas is inversely proportional to its pressure. This means that, if pressure increases, volume decreases and vice versa. In this law, temperature (T) and the number of moles (n) are kept constant. The change in the volume of a gas with pressure is illustrated in Figure 1.2.

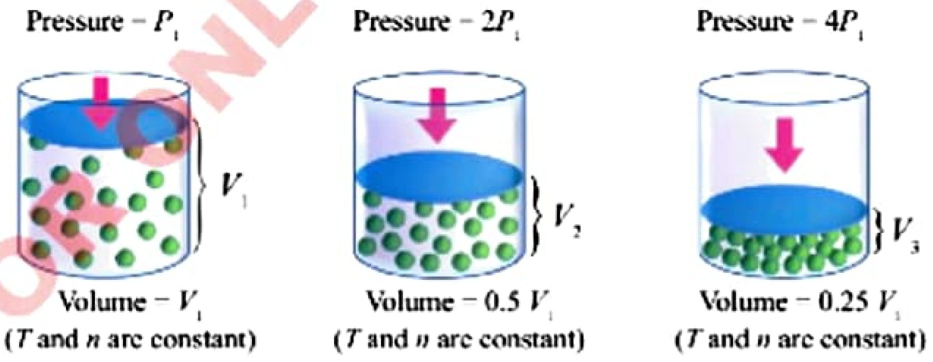


Figure 1.2: *Change in volume of a gas with pressure at constant temperature*

Mathematically, the Boyle's law can be expressed as:

$$V \propto \frac{1}{P} \; (T \text{ and } n \text{ are constant})$$

This means, $V = \frac{k}{P}$,

hence, $PV = k$

where k is a proportionality constant which is specific for a given gas sample at specified temperature. For two sets of pressures and volumes:

$$P_1V_1 = k \text{, and } P_2V_2 = k$$

Therefore,

$$P_1V_1 = P_2V_2 \qquad (1.1)$$

If the volume of a gas at a certain pressure is known, the unknown volume at any other pressure can be calculated using Equation 1.1.

Graphically, Boyle's law can be represented in two ways: the first is by plotting pressure against volume where a hyperbola is obtained as shown in Figure 1.3. The plot indicates that when volume increases, pressure is lowered and vice versa.

The other way is by plotting volume versus the inverse of pressure (Equation 1.2).

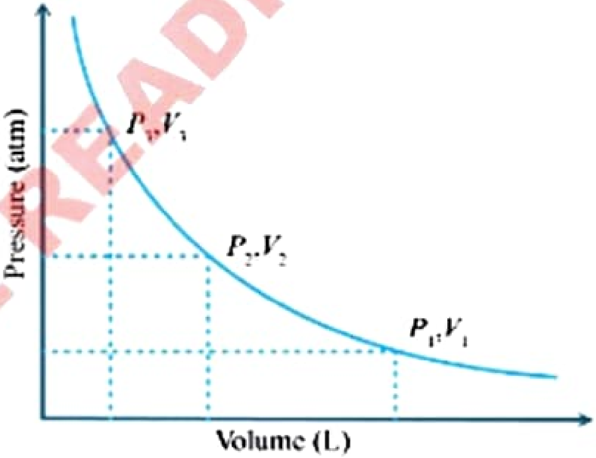


Figure 1.3: *Variation of pressure and volume at constant temperature*

Rewriting Boyle's Law as:

$$V = k\frac{1}{P} \qquad (1.2)$$

the equation takes the form of an equation of a straight line; $y = mx + c$, where, m is the slope, and c is the y-intercept.

Therefore, a plot of V against $\frac{1}{P}$ is a straight line with an intercept of zero (Figure 1.4).

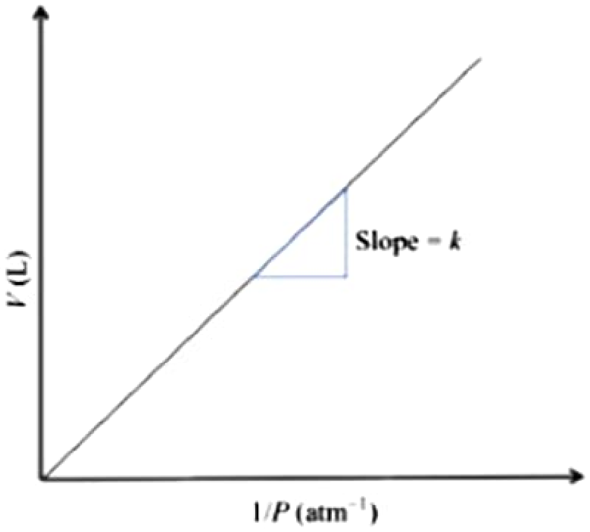


Figure 1.4: *Variation of volume with the inverse of pressure at constant temperature*

Example 1.1

A chemist observed that the air trapped in a U-tube occupies 25.5 cm3 at 1.15 atm. After adding a liquid to the tube, the pressure of the trapped air increased to **2.61 atm**. What is the new volume of air in litres if the temperature remained constant?

Solution

Given that,

$V_1 = 25.5\ \text{cm}^3 = 0.0255\ \text{L}$

V_2 = unknown,

$P_1 = 1.15$ atm, $P_2 = 2.61$ atm, and temperature (T) is constant

From Boyle's law,

$$P_1V_1 = P_2V_2 \Rightarrow V_2 = \frac{P_1V_1}{P_2} = \frac{1.15\ \text{atm} \times 0.0255\ \text{L}}{2.61\ \text{atm}} = 0.0112\ \text{L}$$

Therefore, the new volume of air is 0.0112 litres.

Example 1.2

A sample of an inert gas occupies 100 mL at 0.875 atm. If temperature remains constant, what would be the new volume of the gas at 26.5 kPa?

Solution

Data given:

$V_1 = 100$ mL, $V_2 =$ unknown

$P_1 = 0.875$ atm, $P_2 = 26.5$ kPa

Change units of P_2 to Pascal by the relation 1 kPa = 10^3 Pa

Therefore, 26.5 kPa = 26500 Pa

Then, change P_2 from Pascal to atm;

1 atm = 101325 Pa

? atm = 26500 Pa

$$= \frac{1\text{ atm} \times 26500\text{ Pa}}{101325\text{ Pa}}$$

$$P_2 = 0.2615\text{ atm}$$

From Boyle's law,

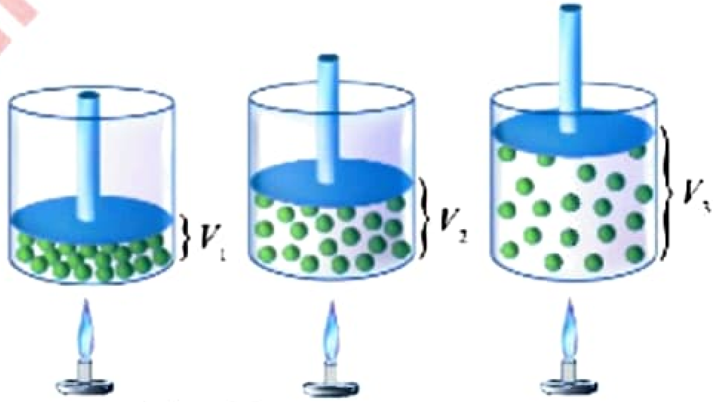
$$P_1V_1 = P_2V_2 \Rightarrow V_2 = \frac{P_1V_1}{P_2} = \frac{0.875\text{ atm} \times 100\text{ mL}}{0.2615\text{ atm}} = 334.6\text{ mL}$$

Therefore, the new volume of the gas would be 334.6 mL.

1.2.2 Charles' law

The *Charles' law* was named after a French, scientist, Jacques Alexander Cesar Charles (1746 –1823). The law states that at constant pressure, the volume of a fixed mass of a gas is directly proportional to the absolute temperature. This means, if temperature increases at constant pressure, volume also increases and vice versa.

In this law, two parameters are kept constant, pressure and the number of moles. The change in volume of a gas with temperature is shown in Figure 1.5.



Temperature = T_1 (P and n are constant) Temperature = T_2 (P and n are constant) Temperature = T_3 (P and n are constant)

$T_1 < T_2 < T_3$, $V_1 < V_2 < V_3$

Figure 1.5: *Changes in volume of a gas with temperature at constant pressure and number of moles*

Mathematically, Charles' law can be expressed as:

$$V \propto T \ (P \text{ and } n \text{ are constant})$$

$$V = kT, \quad k = \frac{V}{T} \tag{1.3}$$

For two sets of temperature and volume:

$$\frac{V_1}{T_1} = k, \qquad \frac{V_2}{T_2} = k$$

Therefore, $$\frac{V_1}{T_1} = \frac{V_2}{T_2} \tag{1.4}$$

If the volume of a gas at a certain temperature is known, the unknown volume at any other temperature can be calculated by using Equation 1.4. The graphical representation of Charles' law is shown in Figure 1.6.

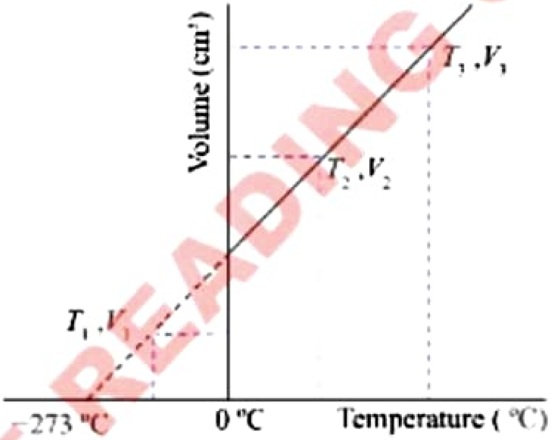


Figure 1.6: *Change in volume with temperature at constant pressure*

The important feature of the graph in Figure 1.6 is that when the graph is extrapolated, the temperature at the point where the volume is zero is obtained. This is true for all gases which obey the Charles' law. The temperature where all the extrapolated lines meet (–273 °C, or 0 K on the Kelvin temperature scale) is the *absolute zero temperature*. Below the absolute zero temperature, the extrapolated volume of a gas would be negative which is never attained as there is no gas with negative volume.

Activity 1.1

Aim: To investigate the effect of temperature on the volume of a gas

Requirements: Balloon, balloon filler, two steady objects like small stones or bricks, and freezer or ice

Procedure

1. Inflate the balloon with air using your mouth or the balloon filler and tie it.
2. Put the two steady objects side by side leaving the space in between, enough to fit the size of the filled balloon.
3. Fit the balloon between the two objects by allowing it to barely touch the objects on each side.
4. Remove the balloon and put it in a freezer or ice for about thirty minutes. Leave the steady objects on their position undisturbed.
5. Remove the balloon from the freezer or ice and place it between the two objects as in step 3. Record your observation.

Questions

1. What variables were controlled in the experiment? Explain.
2. If you were to conduct the experiment again with a different gas, what would be the results? Explain.

1.2.3 Gay-Lussac's law

The Gay-Lussac's law was named after the French chemist, Joseph Louis Gay-Lussac, who laid its foundation in 1802. The law states that the pressure of a gas is directly proportional to its absolute temperature provided that the volume and the amount of the gas are kept constant.

Mathematically, Gay-Lussac's law can be expressed as:

$$P \propto T \text{ (}V\text{ and }n\text{ are constant)}$$

$$P = kT$$

$$\frac{P}{T} = k \qquad (1.5)$$

For two sets of pressure and temperature:

$$\frac{P_1}{T_1} = k \text{ and } \frac{P_2}{T_2} = k$$

Therefore, $$\frac{P_1}{T_1} = \frac{P_2}{T_2} \qquad (1.6)$$

If the pressure of a gas at a certain temperature is known, the pressure at any other temperature can be calculated using Equation 1.6. The graphical representation of Gay Lussac's law is shown in Figure 1.7.

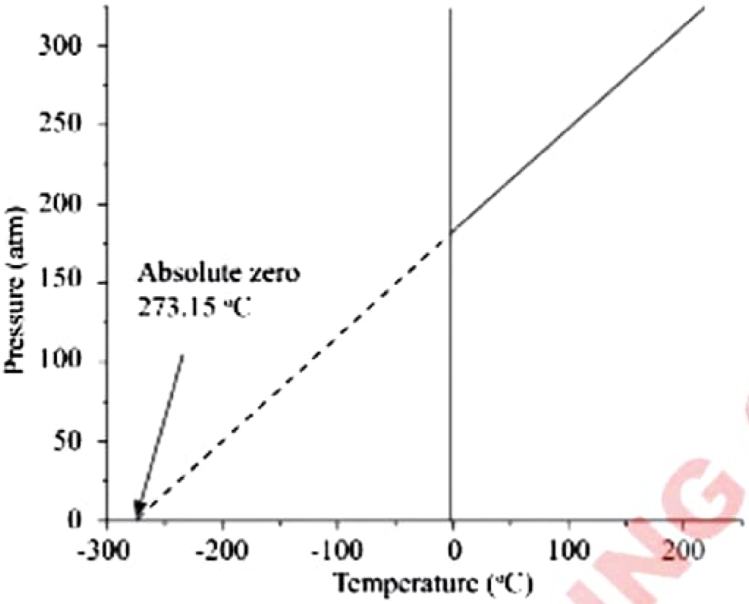


Figure 1.7: *Change in pressure with temperature at constant volume*

For the Gay Lussac's law, the absolute zero temperature is obtained when the graph is extrapolated to the point where the pressure is zero. Below the absolute temperature, the extrapolated pressure of the gas will be negative which is never attained as no gas will exist with negative pressure. In reality, as gases cool down and approach absolute zero, they often condense into a liquid or solidify and the gas law no longer applies.

Gay-Lussac's law finds practical applications in various everyday situations. One common example is the use of pressure cookers. When the temperature inside a pressure cooker increases, the tight fitting lid prevents the water vapour produced from escaping leading to a rise in pressure. This increased pressure causes the inside temperature to rise above normal allowing food to cook faster. If the pressure inside the pressure cooker exceeds the set value, it may lead to explosion hence the safety valve of a pressure cooker should be left open to allow some of the vapour to escape.

Another instance is observed in car tires. As a car is driven, the friction between the tires and the road generates heat, causing the air inside the tires to heat up. Since the volume of the tires remains relatively constant, according to Gay-Lussac's law, the pressure inside the tires increases due to the high temperature posing the risk of tire rupture. This explains why drivers are advised to check their tires regularly after a long drive. Another application of Gay Lussac's law involves pressurized aerosol cans like spray paint or deodorant cans which have warning labels to keep them away from heat. When these cans are exposed to heat, the pressure inside increases, potentially causing the container to rupture.

Activity 1.2

Aim: To investigate the effect of temperature on the pressure of a gas

Requirements: Balloon, balloon filler

Procedure

1. Inflate the balloon with air.
2. Place the air-filled balloon outside your classroom at a hot temperature.
3. Observe the balloon.

Question

How were the volume and number of moles of the gas kept constant in the experiment?

1.2.4 Combined gas law

According to Boyle's law, pressure and volume of a gas are inversely related; and according to Charles' law, the absolute temperature and volume of a gas are directly related. These two relationships can be combined into a single equation known as the *combined gas law*.

$$\text{Boyle's law:}\ V \propto \frac{1}{P}\ (T \text{ and } n \text{ are constant})$$

$$\text{Charles' law:}\ V \propto T\ (P \text{ and } n \text{ are constant})$$

$$\text{Therefore,}\quad V \propto \frac{T}{P}\ (n \text{ is constant})$$

The *combined gas law* can be stated as for a fixed mass of a gas, the volume is directly proportional to the absolute temperature and inversely proportional to the pressure.

$$V \propto \frac{T}{P}$$

$$V = \frac{kT}{P}$$

$$\frac{PV}{T} = k$$

For two sets of pressure, temperature and volume:

$$\frac{P_1V_1}{T_1} = k, \quad \frac{P_2V_2}{T_2} = k$$

Therefore, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ (1.7)

The combined gas law can be used to solve problems involving a change in the three variables for a fixed mass of a gas.

Example 1.3

A 25.8 L quantity of gas has a pressure of 690 Torr and a temperature of 17 °C. Calculate the volume of the gas if the pressure is changed to 1.85 atm and the temperature to 345 K.

Solution

Data given:

$$V_1 = 25.8\ \text{L}, V_2 = \text{Unkown}$$

$$T_1 = 17\ °\text{C} = (17 + 273)\ \text{K} = 290\ \text{K}, \ T_2 = 345\ \text{K}$$

$$P_1 = 690\ \text{torr} = \frac{690\ \text{Torr} \times 1\ \text{atm}}{760\ \text{Torr}} = 0.908\ \text{atm}$$

$$P_2 = 1.85\ \text{atm}$$

From,

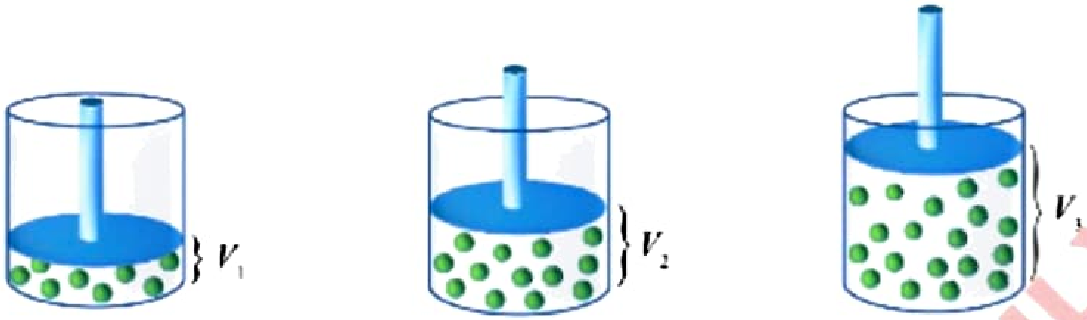
$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \Rightarrow V_2 = \frac{P_1V_1T_2}{P_2T_1}$$

$$V_2 = \frac{0.908\ \text{atm} \times 25.8\ \text{L} \times 345\ \text{K}}{1.85\ \text{atm} \times 290\ \text{K}} = 15.1\ \text{L}$$

Therefore, the volume of the gas is 15.1 L.

1.2.5 Avogadro's law

Avogadro's law was stated in 1811 by an Italian Chemist, Amedeo Avogadro (1776–1856). The law states that equal volume of gases at the same temperature and pressure contain equal number of particles. That is, at constant temperature and pressure, increasing the amount of a gas increases the volume occupied by the gas. The change of the amount of a gas with volume is illustrated in Figure 1.8.



Number of moles, n_1
(P, T are constant)

Number of moles, n_2
(P, T are constant)

Number of moles, n_3
(P, T are constant)

$$n_1 < n_2 < n_3 \qquad V_1 < V_2 < V_3$$

Figure 1.8: *Changes in volume of a gas with number of molecules at constant temperature and pressure*

Mathematically, the Avogadro's law can be expressed as:

$$V \propto n \ (P \text{ and } T \text{ are constant})$$

$$V = kn \Rightarrow \frac{V}{n} = k \tag{1.8}$$

where, n is the number of moles of a gas

k is the proportionality constant, and

V is the gas volume.

Equation 1.8 shows that the volume of a gas at constant temperature and pressure is directly proportional to the number of moles of the gas. For two sets of volume and number of moles at constant temperature and pressure;

$$\frac{V_1}{n_1} = k, \quad \frac{V_2}{n_2} = k$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \tag{1.9}$$

If the number of moles of a gas at a certain volume is known, the unknown number of moles of the gas at any other volume can be calculated by using Equation 1.9.

The graphical representation of Avogadro's law is shown in Figure 1.9.

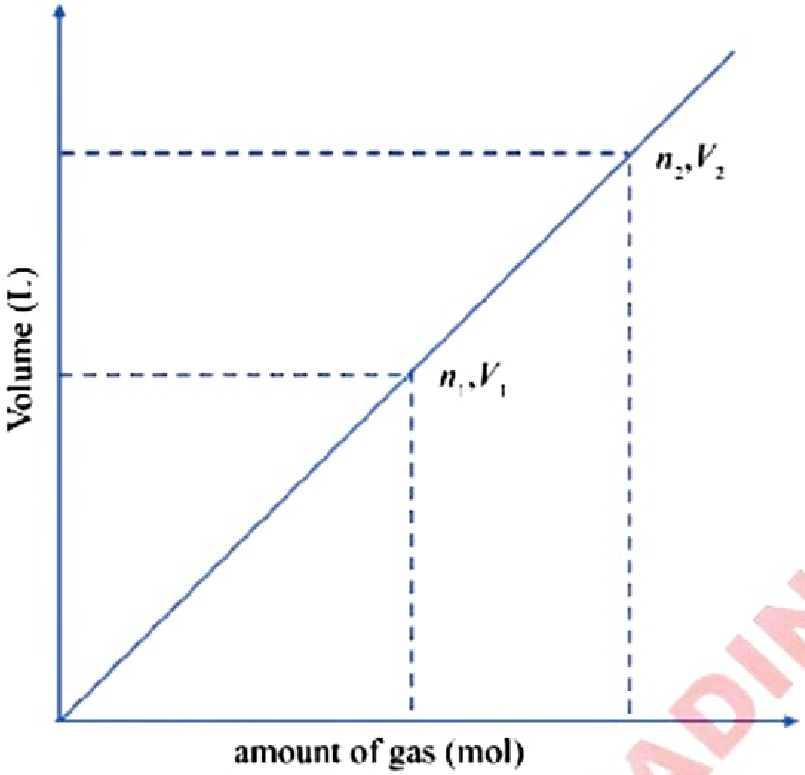


Figure 1.9: *Change in volume with number of moles at constant temperature and pressure*

Avogadro's law finds numerous practical applications in everyday life. For instance, when air is blown into a balloon, it expands as the number of gas molecules increases. The opposite takes place when the air is evacuated. Similarly, when a flat tire is filled with air, the increased gas volume helps the tire regain its original shape. Another example is in vehicle airbags, where a certain chemical reaction produces gas when triggered. Avogadro's law guarantees that the resulting gas volume remains constant, ensuring inflation for occupant safety. Furthermore, Avogadros law finds application in the carbonation process of beverages such as soda where carbon dioxide gas is dissolved in the liquid under pressure. The amount of the gas dissolved in the liquid affects the level of carbonation and the taste of the beverage. Likewise, in baking, yeast produces carbon dioxide causing dough to rise. The lightness and softness of baked goods depend on the volume of carbon dioxide gas produced.

Example 1.4

An expandable container has a volume of 275 mL and contains 0.012 mol of air. What will the volume of the container be after a piece of dry ice (solid CO_2) weighing 1.0 g is added and allowed to sublime?

Solution

Data given:

$$V_1 = 275\,\text{mL}, V_2 = \text{Unknown}$$

$$n_1 = \text{mole of air} = 0.012\,\text{mol}$$

$$\text{Moles of CO}_2\text{ gas} = \frac{1.0\,\text{g}}{44\,\text{g mol}^{-1}} = 0.023\ \text{mol}$$

n_2 = moles of air + moles of CO_2 = 0.012 mol + 0.023 mol = 0.035 mol

From,

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \Rightarrow V_2 = \frac{V_1 \times n_2}{n_1}$$

$$= \frac{275\ \text{mL} \times 0.035\ \text{mol}}{0.012\ \text{mol}} = 802.1\ \text{mL}$$

Therefore, the volume of the container is 802.1 mL.

The molar gas volume

The *molar gas volume* is the volume occupied by one mole of any gas at a given temperature (T) and pressure (P). This volume is also known as *molar volume*. To be able to compare the molar volume of gases, a fixed reference temperature and pressure called standard temperature and pressure (STP) is used. The standard temperature and pressure are 273 K (0 °C) and 1 atm, respectively. At STP, one mole of any gas occupies a volume of 22.4 litres.

Relative molecular mass of a gas and relative vapour density

The relative vapour density (RVD) of a gas is the ratio of the mass of a certain volume of the gas to the mass of the same volume of hydrogen gas at the same temperature and pressure.

$$\text{Relative vapour density (RVD)} = \frac{\text{mass of volume '}V\text{' of the gas}}{\text{mass of volume '}V\text{' of hydrogen}}$$

If V (mL) of any gas contains n molecules (Avogadro's law), then

$$\text{RVD} = \frac{\text{mass of } n \text{ molecules of the gas}}{\text{mass of } n \text{ molecules of hydrogen}}$$

$$\text{RVD} = \frac{\text{mass of 1 molecule of the gas}}{\text{mass of 1 molecules of hydrogen}}$$

$$= \frac{\text{mass of 1 molecule of the gas}}{2 \times \text{mass of 1 atom of hydrogen}}$$

$$2\text{RVD} = \frac{\text{mass of 1 molecule of the gas}}{\text{mass of 1 atom of hydrogen gas}}$$

By definition, mass of 1 atom of hydrogen = $\frac{1}{12^{th}}$ the mass of 1 atom of carbon-12

$$2\text{RVD} = \frac{\text{mass of 1 molecule of the gas}}{\frac{1}{12^{th}} \text{ mass of 1 carbon} - 12 \text{ atom}}$$

But relative molecular mass $= \dfrac{\text{mass of 1 molecule of the gas}}{\frac{1}{12^{th}} \text{ mass of 1 carbon} - 12 \text{ atom}}$

$$2\text{RVD} = \text{relative molecular mass of the gas}$$

Thus, $\text{RVD} = \dfrac{\text{relative molecular mass of the gas}}{2}$ (1.10)

1.2.6 Ideal gas equation

The behaviour of any gas can be described by considering four variables (temperature, pressure, volume and number of moles) whose relationships are studied by the gas laws. A combination of Boyle's, Charles' and Avogadro's laws gives an equation known as *ideal gas equation* which indicates how the four variables are related to each other.

Consider the expression for each gas law:

Boyle's law; $V \propto \frac{1}{p}$ (T and n are constant)

Charles' law; $V \propto T$ (P and n are constant)

Avogadro's law: $V \propto n$ (P and T are constant)

Combining the three gas laws gives Equation 1.11,

$$V \propto \frac{nT}{p} \qquad (1.11)$$

which is the statement of the *ideal gas law*. The ideal gas law states that, the volume of a given amount of a gas is directly proportional to the number of moles of the gas and the absolute temperature, and inversely proportional to the pressure. It is the equation of state for a gas where the state of a gas is its condition at a given time.

Rearranging Equation 1.11 gives:

$$V \propto \frac{nT}{P} \Rightarrow V = R\frac{nT}{P}$$

where R is a proportionality constant called a universal gas constant. The preceding equation can be further rearranged into a more general form of the equation called an *ideal gas equation* (Equation 1.12).

$$PV = nRT \qquad (1.12)$$

A gas that obeys this equation is called an *ideal gas* (i.e., behaves ideally). The law is based on empirical evidence and is sometimes considered the *limiting law* as it prescribes the behaviour which real gases approach at low pressures and high temperatures. Thus, an ideal gas is an imaginary substance.

Derivation of gas constant, *R*

Making R the subject of the formula from the ideal gas equation, gives:

$$R = \frac{PV}{nT}$$

Assuming that there are standard conditions of temperature and pressure (STP), one mole of any gas occupies a volume of 22.4 litres. At STP, standard temperature is equal to 273 K (0 °C) and standard pressure is equal to 1 atm.
Therefore,

$$R = \frac{(1\ \text{atm})\times(22.4\ \text{L})}{(1\ \text{mol})\times(273\ \text{K})} = \frac{0.0821\ \text{L atm}}{\text{mol K}} = 0.0821\ \text{L atm mol}^{-1}\text{K}^{-1}$$

R can also be derived in units of joules per mole per Kelvin (J $\text{mol}^{-1}\ \text{K}^{-1}$)

1 joule (J) = 1 Newton meter (N m)

1 atm = $1.01325 \times 10^5\ \text{Nm}^{-2}$

Volume of 1 mole of a gas at STP is equal to 22.4 L.

$$\text{Volume } (V) = 22.4\ \text{dm}^3 = 0.0224\ \text{m}^3$$
$$T = 273\ \text{K}$$
$$n = 1\ \text{mol}$$

Therefore,

$$R = \frac{PV}{nT} = \frac{(1.01325 \times 10^5\ \text{N m}^{-2}) \times (0.0224\ \text{m}^3)}{(1\ \text{mol}) \times (273\ \text{K})} = \frac{8.314\ \text{N m}}{\text{mol K}} = 8.314\ \text{N m mol}^{-1}\ \text{K}^{-1}$$

But 1 N m = 1 joule. This gives the value of *R* equals to 8.314 J $\text{mol}^{-1}\text{K}^{-1}$.

Other values of *R* include 62.36 L Torr $\text{mol}^{-1}\text{K}^{-1}$ and 8.314 m^3 Pa $\text{mol}^{-1}\text{K}^{-1}$.

Because of the various values of *R*, it is important to match the values of pressure, volume, number of moles and temperature with the units of *R*. For example, if *R* is 0.0821 atm L $\text{mol}^{-1}\text{K}^{-1}$, the units of pressure, volume, and temperature must be atm, litre, and Kelvin, respectively. If *R* is 8.314 J $\text{mol}^{-1}\text{K}^{-1}$, the units of pressure, volume and temperature must be N/m^2, cubic meter (m^3), and Kelvin (K), respectively.

Example 1.5

What is the temperature in °C of a 9.65 g of oxygen gas in a 4560 mL container if the pressure is 895 Torr?

Solution

Data given:

Mass of oxygen = 9.65 g, Volume of the container = 4560 mL

Pressure = 895 Torr, Temperature = unknown

$$\text{Pressure}\,(P) = 895\ \text{Torr} = \frac{1\,\text{atm} \times 895\ \text{Torr}}{760\ \text{Torr}} = 1.18\ \text{atm}$$

$$\text{Number of moles}\,(n) = \frac{\text{mass (m)}}{\text{molar mass (M)}} = \frac{9.65\,\text{g}}{32.0\,\text{g mol}^{-1}} = 0.302\ \text{mol}$$

$$\text{Volume}\,(V) = 4560\ \text{mL} = \frac{4560\,\text{mL} \times 1\,\text{L}}{1000\ \text{mL}} = 4.560\ \text{L}$$

From,

$$PV = nRT \Rightarrow T = \frac{PV}{nR} = \frac{1.18\ \text{atm} \times 4.56\ \text{L}}{0.302\ \text{mol} \times 0.0821\ \text{L atm mol}^{-1}\text{K}^{-1}} = 217\ \text{K}$$

$$T(^\circ\text{C}) = T(\text{K}) - 273\ \text{K}$$

$$= 217\ \text{K} - 273\ \text{K} = -56\ ^\circ\text{C}$$

Therefore, the temperature of oxygen gas is −56 °C.

Exercise 1.1

1. A sample of neon occupies a volume of 461 mL at STP. What will the volume of neon be if pressure is reduced to 93.3 kPa?
2. How does Boyle's law relate to the operation of a syringe or a bicycle pump?
3. A gas tank holds 2785 L of propane (C_3H_8) at 830 Torr. If the temperature is constant, calculate the volume of the propane at standard pressure.
4. Why is the understanding of Gay-Lussac's law important for ensuring the safe storage and transportation of compressed gases?
5. What is the density of helium gas at 298 K and 0.987 atm if its molar mass is 4.003 g/mol?
6. A 6.0 L sample at 25 °C and 2.00 atm contains 0.5 moles of a gas. If 0.25 moles of the gas at the same pressure and temperature are added, calculate the final total volume of the gas.
7. How does the application of Charles's law contribute to the design and operation of hot air balloons?
8. A container holds 50.0 mL of nitrogen gas at 25 °C at a constant pressure of 736 Torr. What will its volume be if the temperature increases by 35 °C?
9. Why are divers advised to ascend slowly as they return to the surface?

1.2.7 Dalton's law of partial pressure

The concept of partial pressure was invented by an English chemist called John Dalton (1766–1844). Dalton proposed that in a mixture of gases which do not react chemically, each component exerts pressure as if it were the only component occupying the container. This pressure is called *partial pressure*. The partial pressure is pressure exerted by an individual gas component as part of the total pressure of the mixture. *Dalton's law of partial pressure* states that the total pressure of a mixture of gases equals to the sum of the partial pressures of all the gases in the mixture.

If the mixture consists of three gases A, B, and C, the total pressure (P_T) of all the gases in a container is expressed as:

$$P_T = P_A + P_B + P_C \qquad (T \text{ and } V \text{ are constant}) \qquad (1.13)$$

where P_A, P_B, and P_C are the partial pressures of gases A, B, and C, respectively. The Dalton's law of partial pressure is illustrated in Figure 1.10.

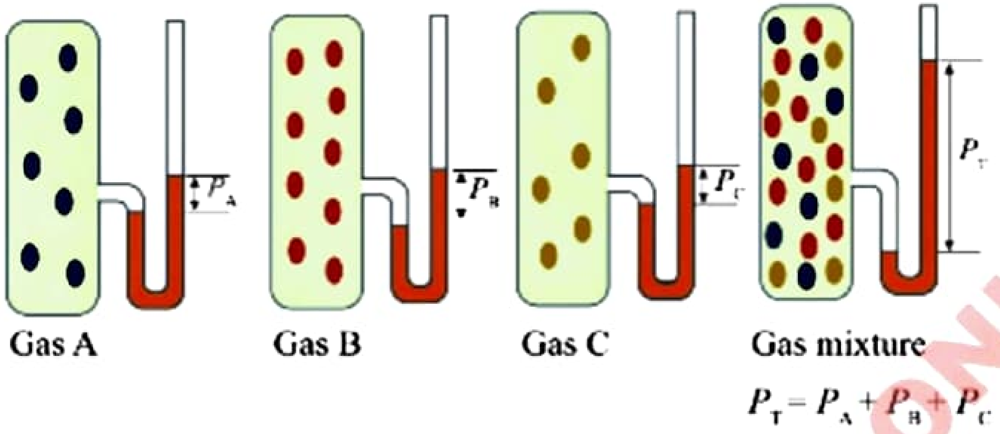


Figure 1.10: *Description of Dalton's law of partial pressure*

If the gas mixture consists of ideal gases, the ideal gas equation can be deduced from Dalton's law of partial pressure. From the ideal gas equation:

$$PV = nRT \Rightarrow P = \frac{nRT}{V} \qquad (1.14)$$

For gas components A, B, and C with partial pressures P_A, P_B, and P_C, the ideal gas equation in terms of partial pressures will be:

$$P_A = n_A\frac{RT}{V}, \quad P_B = n_B\frac{RT}{V}, \text{ and } \quad P_C = n_C\frac{RT}{V} \qquad (1.15)$$

where n_A, n_B, and n_C are the numbers of moles of gases A, B, and C, respectively. Note that Dalton's law of partial pressure applies at constant temperature and volume.

According to Dalton's law of partial pressure, the total pressure of the mixture of ideal gases will be:

$$P_T = P_A + P_B + P_C = n_A\frac{RT}{V} + n_B\frac{RT}{V} + n_C\frac{RT}{V} \qquad (1.16)$$

$$P_T = (n_A + n_B + n_C)\frac{RT}{V}$$

$$P_T = n_T\frac{RT}{V} \qquad (1.17)$$

where n_T is the sum of the numbers of moles of the various gases. Equation 1.17 indicates that for a mixture of ideal gases, the valuable factor is the total number of moles of the particles that gives the total pressure of the gas mixture but not the identity or composition of the involved gases.

Mole fraction of a gas

The mole fraction of a gas is the ratio of the number of moles of the gas to the total number of moles of gases in the mixture. The mole fraction is denoted by the symbol χ. If the mixture consists of gases, the expression for the mole fraction of one component can be derived using Dalton's law of partial pressure and the ideal gas equation.

If Equation 1.15 is divided by Equation 1.17 for one component, Equation 1.18 is obtained.

$$\frac{P_A}{P_T} = \frac{n_A(RT/V)}{n_T(RT/V)} = \frac{n_A}{n_T} \qquad (1.18)$$

The ratio $\frac{n_A}{n_T}$ in Equation 1.18 is called the *mole fraction* (χ_A) of component A and it is defined as the number of moles of individual gas A divided by the total number of moles of all components.

If the mixture consists of three gases (A, B, and C), the mole fraction for each component can be expressed as follows:

The mole fraction of component A (χ_A):

$$\chi_A = \frac{n_A}{n_A + n_B + n_C} = \frac{n_A}{n_T}$$

where, n_A, n_B, and n_C are the numbers of moles of gases A, B, and C, respectively, and n_T is the total number of moles.

Similarly, the mole fraction of components B and C:

$$\chi_B = \frac{n_B}{n_A + n_B + n_C} = \frac{n_B}{n_T} \quad \text{and}$$

$$\chi_C = \frac{n_C}{n_A + n_B + n_C} = \frac{n_C}{n_T}$$

Rearrangement of Equation 1.18 gives:

$$\frac{P_A}{P_T} = \frac{n_A}{n_T} = \chi_A \Rightarrow P_A = \chi_A P_T \qquad (1.19)$$

Equation 1.19 indicates that the partial pressure of a gas is the product of its mole fraction and total pressure of the gases in the mixture. For the gas mixture containing gases A, B, and C,

$$P_A = P_T \times \chi_A, \quad P_B = P_T \times \chi_B \quad \text{and} \quad P_C = P_T \times \chi_C \qquad (1.20)$$

where P_A, P_B, and P_C, and, χ_A, χ_B, and χ_C are the partial pressures of gases A, B, and C, and the mole fractions of gases A, B, and C, respectively.

Substituting Equation 1.13 with Equation 1.20 gives:

$$P_T = P_T \times \chi_A + P_T \times \chi_B + P_T \times \chi_C = P_T(\chi_A + \chi_B + \chi_C)$$

Dividing by P_T on both sides:

$$\frac{P_T}{P_T} = \frac{P_T}{P_T}(\chi_A + \chi_B + \chi_C) \Rightarrow 1 = \chi_A + \chi_B + \chi_C$$

$$\chi_A + \chi_B + \chi_C = 1 \qquad (1.21)$$

Therefore, the sum of the mole fractions of all gases in the mixture is equal to 1.

Example 1.6

A mixture of noble gases consisting of 5.7 g He, 15.2 g Ne, and 37.0 g Ar is placed in a container at room temperature and a pressure of 1 atm. Calculate:

(a) The partial pressure of each gas component.

(b) The total pressure of the gas mixture.

(c) The mole fraction of each gas component.

(Molar mass of He = 4.003, Ne = 20.18 and Ar = 39.95).

Solution

(a) Given that:

Temperature, $T = 25\ ^{\circ}\text{C} = (25+273)\,\text{K} = 298\,\text{K}$

Volume, $V = 22.4\,\text{dm}^3$ and pressure $= 1\,\text{atm}$

Since each gas behaves independently, from Dalton's law of partial pressure;

$$P_T = P_{He} + P_{Ne} + P_{Ar}$$

where, P_T is the total pressure of the mixture and P_{He}, P_{Ne}, and P_{Ar} are partial pressures of helium, neon, and argon, respectively.

$$P_{He} = \frac{n_{He}RT}{V} = \frac{mRT}{M \times V} = \frac{5.70\ \text{g} \times 0.0821\ \text{L atm mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}}{4.003\ \text{g mol}^{-1} \times 22.4\ \text{L}} = 1.5553\ \text{atm}$$

$$P_{Ne} = \frac{n_{Ne}RT}{V} = \frac{mRT}{M \times V} = \frac{15.20\ \text{g} \times 0.0821\ \text{L atm mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}}{20.18\ \text{g mol}^{-1} \times 22.4\ \text{L}} = 0.8227\ \text{atm}$$

$$P_{Ar} = \frac{n_{Ar}RT}{V} = \frac{mRT}{M \times V} = \frac{37.00\ \text{g} \times 0.0821\ \text{L atm mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}}{39.95\ \text{g mol}^{-1} \times 22.4\ \text{L}} = 1.0116\ \text{atm}$$

Therefore, the partial pressures of He, Ne, and Ar are 1.5553, 0.8227 and **1.0116 atm**, respectively.

(b) From Dalton's law of partial pressure:

The total pressure;

$$P_T = P_{He} + P_{Ne} + P_{Ar} = 1.5553\ \text{atm} + 0.8226\ \text{atm} + 1.0116\ \text{atm} = 3.3895\ \text{atm}$$

(c) Mole fraction:

$$n_{He} = \frac{m_{He}}{M_{He}} = \frac{5.70\ \text{g}}{4.003\ \text{g mol}^{-1}} = 1.424\ \text{mol}$$

$$n_{Ne} = \frac{m_{Ne}}{M_{Ne}} = \frac{15.20\ \text{g}}{20.18\ \text{g mol}^{-1}} = 0.753\ \text{mol}$$

$$n_{Ar} = \frac{m_{Ar}}{M_{Ar}} = \frac{37.0\ \text{g}}{39.95\ \text{g mol}^{-1}} = 0.926\ \text{mol}$$

$$n_T = (1.424 + 0.753 + 0.926) = 3.103\ \text{mol}$$

$$\chi_{He} = \frac{n_{He}}{n_{He} + n_{Ne} + n_{Ar}} = \frac{n_{He}}{n_T} = \frac{1.424\ \text{mol}}{3.103\ \text{mol}} = 0.4589$$

$$\chi_{Ne} = \frac{n_{Ne}}{n_{He} + n_{Ne} + n_{Ar}} = \frac{n_{Ne}}{n_T} = \frac{0.753\ \text{mol}}{3.103\ \text{mol}} = 0.2427$$

$$\chi_{Ar} = \frac{n_{Ar}}{n_{He} + n_{Ne} + n_{Ar}} = \frac{n_{Ar}}{n_T} = \frac{0.926\ \text{mol}}{3.103\ \text{mol}} = 0.2984$$

Therefore, the mole fractions of He, Ne, and Ar are 0.4589, 0.2427, and 0.2984, respectively.

1.2.8 Graham's laws of diffusion and effusion

Diffusion is a net movement of atoms or molecules from the region of high concentration to the region of low concentration (Figure 1.11).

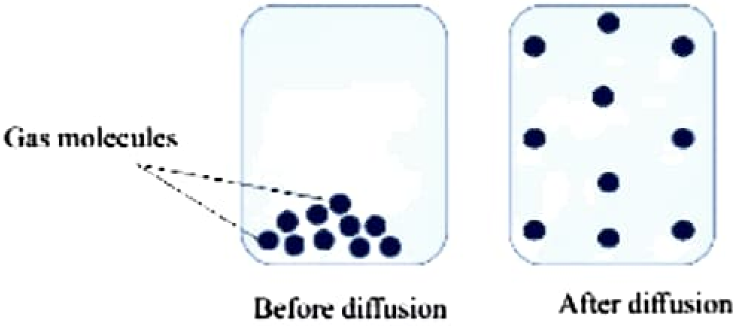


Figure 1.11: *Diffusion of gas molecules*

Effusion is the process by which gas molecules escape from their container through a tiny hole into an evacuated space (Figure 1.12).

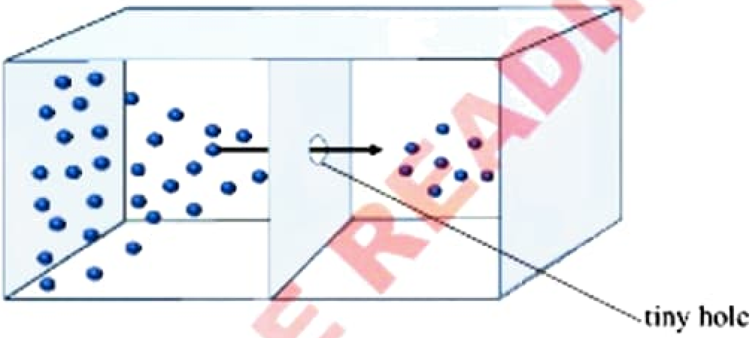


Figure 1.12: *Effusion of gas molecules through a tiny hole*

Both diffusion and effusion involve the movement of gas molecules/atoms from the region of high concentration to the region of low concentration. The only difference is that in effusion, the gas molecules/atoms pass through a tiny hole while in diffusion, they move through an open space.

The Graham's law of diffusion and effusion was named after the Scottish Chemist, Thomas Graham (1805 – 1869), who in 1846, studied the effusion process and concluded that the rate of effusion is inversely proportional to the square root of gas density.

Mathematically,

Rate, $R \propto \frac{1}{\sqrt{\text{density } (\rho)}} \Rightarrow R = \frac{k}{\sqrt{\rho}}$

where k is the proportionality constant. For two sets of gases A and B,

$$R_A = \frac{k}{\sqrt{\rho_A}} \quad \text{and} \quad R_B = \frac{k}{\sqrt{\rho_B}}$$

$$R_A\sqrt{\rho_A} = k,\ R_B\sqrt{\rho_B} = k$$

Therefore; $R_A\sqrt{\rho_A} = R_B\sqrt{\rho_B}$ Or

$$\frac{R_A}{R_B} = \sqrt{\frac{\rho_B}{\rho_A}} \tag{1.22}$$

Since density is proportional to molar mass, Graham's law can also be stated in terms of the molar mass of the effusing or diffusing gaseous substance. The law states that the rate of diffusion or effusion of a gaseous substance is inversely proportional to the square root of its molar mass.

Mathematically,

$$\text{Rate of diffusion, } R \propto \frac{1}{\sqrt{\text{Molar mass (M)}}} \Rightarrow R = \frac{k}{\sqrt{\text{M}}}$$

where k is the proportionality constant. For two sets of gases A and B,

$$R_A = \frac{k}{\sqrt{\text{M}_A}} \quad \text{and} \quad R_B = \frac{k}{\sqrt{\text{M}_B}}$$

$$R_A\sqrt{\text{M}_A} = k,\ \ R_B\sqrt{\text{M}_B} = k$$

This gives:

$$\frac{R_A}{R_B} = \sqrt{\frac{\text{M}_B}{\text{M}_A}} \tag{1.23}$$

The ratio of the diffusion rates of the two gases A and B is equal to the square root of the inverse ratio of their molar masses:

$$\frac{\text{Rate of diffusion of gas A}}{\text{Rate of diffusion of gas B}} = \sqrt{\frac{\text{M}_B}{\text{M}_A}}$$

This expression also applies for the effusion process. Thus,

$$\frac{\text{Rate of effusion of gas A}}{\text{Rate of effusion of gas B}} = \sqrt{\frac{\text{M}_B}{\text{M}_A}}$$

Since the rate is the amount of the gas effused or diffused per unit time, therefore it is inversely proportional to time (t). Mathematically,

$$R \propto \frac{1}{t} \Rightarrow R = \frac{k}{t}$$

For the two gases A and B,

$$R_A = \frac{k}{t_A} \quad \text{and} \quad R_B = \frac{k}{t_B}$$

where t_A and t_B are the times taken for gases A and B, respectively, to diffuse or effuse, and k is the proportionality constant.

$$R_A t_A = k \quad \text{and} \quad R_B t_B = k$$

$$R_A t_A = R_B t_B$$

Thus,

$$\frac{R_A}{R_B} = \frac{t_B}{t_A}$$

But, $$\frac{R_A}{R_B} = \sqrt{\frac{M_B}{M_A}}$$

Therefore, $$\frac{t_A}{t_B} = \sqrt{\frac{M_A}{M_B}} \qquad (1.24)$$

Graham's law of effusion or diffusion can be used to determine the molar mass of an unknown gas by comparing its diffusion or effusion rate with that of a known gas. The law applies mainly to effusion because the process occurs at very low pressure for gases to escape individually through the hole; and the hole is so tiny that the gases do not collide when they pass through it.

Example 1.7

A flammable gas is found to effuse through a porous barrier in 1.50 min. Under the same temperature and pressure conditions, it takes 4.73 min for an equal volume of bromine vapour to effuse through the same barrier. Calculate the molar mass of the unknown gas.

Solution

Data given:

Time taken by unknown gas = 1.50 min

Time taken by equal volume of Br_2 to effuse = 4.73 min

Molar mass of bromine = 159.8 g/mol

Required to calculate the molar mass of unknown gas

Let the unknown gas be A and bromine be B.

Using Equation 1.24: $\frac{t_A}{t_B} = \sqrt{\frac{M_A}{M_B}}$

$$\frac{1.50\,\text{min}}{4.73\,\text{min}} = \sqrt{\frac{M_A}{158.9\,\text{g/mol}}}$$

$$M_A = 16.1\ \text{g/mol}$$

Therefore, the molar mass of the unknown gas is 16.1 g/mol.

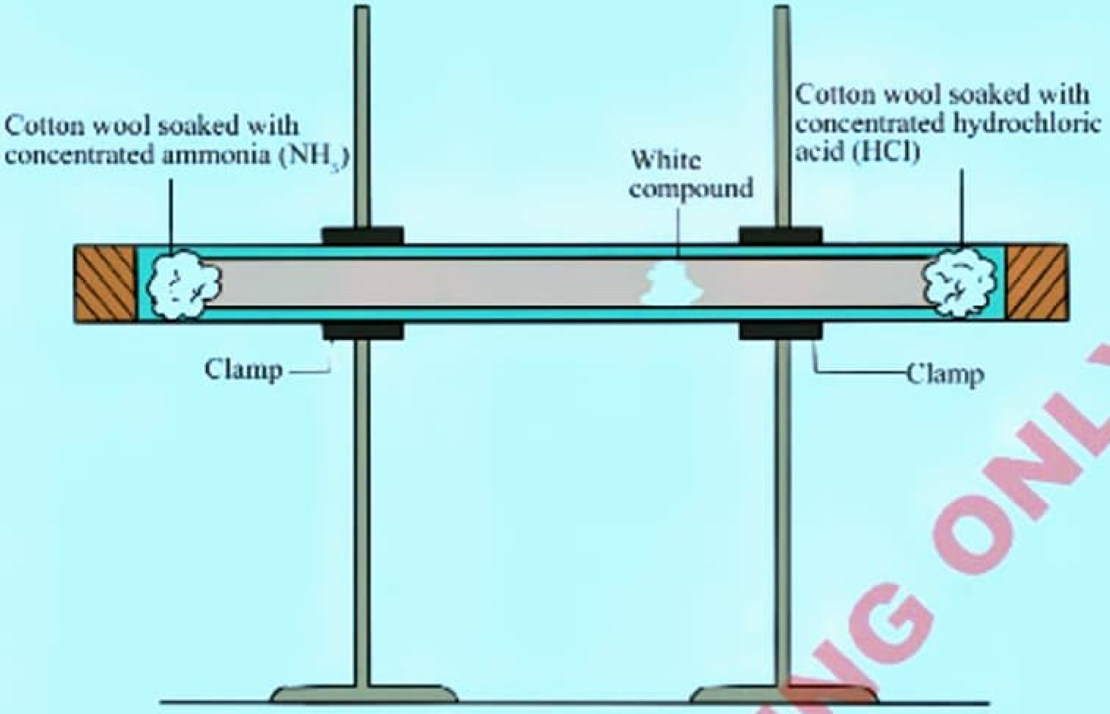
Activity 1.3

Aim: To investigate the diffusion of two gases

Requirements: Glass tube (1 m), corks, droppers, cotton wool, stop watch, concentrated ammonia solution, concentrated hydrochloric acid and stands with clamps

Procedure

1. Clamp a 1 m long glass tube in a horizontal position as shown in the following figure.



Rates of diffusion of NH_3 and HCl

2. Insert cotton wool plugs at both ends of a horizontal tube.
3. Add a few drops of concentrated HCl on one cotton plug and the other with concentrated ammonia solution and cork both ends of the tube.
4. Start the stopwatch immediately and stop it when a white ring of smoke is formed. Record the time.
5. Mark the point where the ring appears first and measure the distance of this point from both ends.
6. Record the following observations:
    (a) Initial time (t_1) when drops are introduced and the final time (t_2) when the white ring appears first
    (b) Time taken for diffusion (t)
    (c) The distance travelled by HCl (d_1) and the distance travelled by NH_3 (d_2)
    (d) The rate of diffusion of HCl (d_1/t) and the rate of diffusion of NH_3 (d_2/t)

Questions

1. How will you verify Graham's law using the recorded observations?
2. How is the knowledge from this activity applicable in the formulation of perfumes or air fresheners?

Exercise 1.2

1. If 3 moles of N_2 and 4 moles of O_2 are placed in a 35 L container at 25 °C, calculate the pressure of the resulting gas mixture.
2. A container with two gases, helium and argon, is 30.0% by volume of helium. Calculate the partial pressure of helium and argon if the total pressure inside the container is 4.00 atm.
3. In what ways does Dalton's law of partial pressure contribute to the understanding of gas behaviour in the atmosphere, particularly in relation to air quality monitoring or atmospheric studies?
4. Blast furnaces give off different gases. If the total air pressure is 0.99 atm, the partial pressure of carbon dioxide is 0.05 atm, and the partial pressure of hydrogen sulfide is 0.02 atm, what is the partial pressure of the remaining air in the blast furnace?
5. Suppose you have a container holding 100 litres of air. If you fill this container with 3 moles of oxygen gas at a pressure of 1 atmosphere, what will the temperature of the container be?
6. In what ways does Graham's law of effusion contribute to the understanding of gas behaviour in industrial processes or environmental monitoring?
7. Two perfumes are released simultaneously from their containers, and you are standing 7.5 meters away from them. Molecule of perfume A has a mass of 275 a.m.u, and that of B has a mass of 205 a.m.u.
    (a) Which perfume will you smell first and why?
    (b) If you smell the first perfume in 15 seconds, how long will it take for you to smell the second perfume?
8. An unknown gas diffuses 0.25 times as fast as helium. What is the molecular mass of the unknown gas?
9. Which gas between NH_3 and He has a higher effusion rate? Explain.

1.3 The kinetic theory of gases

The gas laws are useful for predicting the behaviour of gases, but they do not tell what happens at the molecular level to cause the observed changes, such as the expansion of a gas upon heating. The kinetic theory was developed in the 19th century by James Clerk Maxwell (1831–1879) and Ludwig Boltzmann

(1844 –1906) who found that the physical properties of gases can be explained at the molecular level in terms of the motion of individual molecules as the pressure, volume, and temperature changes.

1.3.1 Relationships among volume, pressure, and temperature

The kinetic theory of gases explains how individual gas particles create a force on the surface, which is measured as gas pressure. According to Boyle's law, when gas pressure increases, the volume occupied by the gas decreases. The theory also explains what happens to the gas particles leading to the change in gas volume when pressure changes. It also clarifies the contribution of each individual gas to the total pressure as stated by Dalton's law. The increase in volume due to an increase in temperature as stated in Charles' law is also part of this theory. The dependence of gas volume or pressure on the number of moles present, and not on the nature or size of the gas molecules is also explained by the kinetic theory of gases.

1.3.2 Assumptions of the kinetic theory

Task 1.3

Use online sources to perform simulations on kinetic theory of gases and record the assumptions of the theory observed.

The following are the assumptions (postulates) of the kinetic theory of gases:

1. A gas consists of tiny particles called atoms or molecules, scattered throughout the container. Due to their small size, the volume of individual gas molecules is negligible compared to the volume of the container.
2. Gas molecules are in constant random motion and travel with uniform velocities and their direction changes on collision with other gas molecules or with the walls of the container (Figure 1.13). This dynamic behaviour is fascinating and forms the basis of our understanding of gases.
3. All collisions between gas molecules are perfectly elastic, hence no loss of kinetic energy during collision.
4. The distance between gas molecules is very large and independent of the 'van der Waals' forces of attraction. As a result, the gas molecules can move freely, independent of each other.
5. Gas pressure is caused by gas molecules colliding with the walls of the container.

6. The average kinetic energy $\left(\frac{1}{2}mv^2\right)$ of the gas molecules is directly proportional to the absolute temperature. This means that the average kinetic energy of gas molecules is the same at a specific temperature.

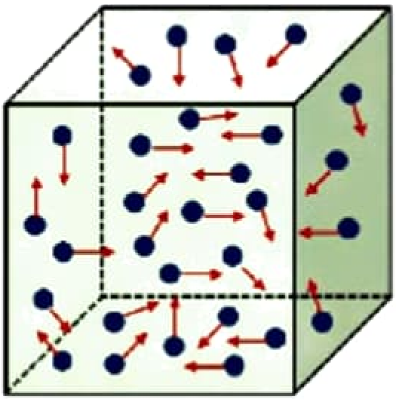


Figure 1.13: *Random motion of gas molecules in a container*

1.3.3 Relationship between the kinetic gas equation and the gas laws

The kinetic gas equation is useful in accounting for the general properties of substances in the gaseous state. It successfully explains the gas laws.

Boyle's law

According to the kinetic theory of gases, the average kinetic energy of gas molecules is directly proportional to the absolute temperature.

The kinetic gas equation is:

$$PV = \frac{1}{3}mNv^2 \tag{1.25}$$

where m is the mass of the individual gas molecule, N is the number of molecules, and v is the molecular speed. The derivation of the kinetic gas equation is beyond the scope of this book.

Expressing the right-hand side of the equation in terms of kinetic energy,

$$\frac{1}{3}mNv^2 = \frac{1}{3} \times \frac{2}{2} \times mNv^2 = \frac{2}{3} \times \left(\frac{1}{2}mNv^2\right)$$

Note that the total mass of the gas molecules is equal to the mass of an individual molecule times the total number of molecules (mN). Therefore,

$$\frac{1}{2}mNv^2 = \text{kinetic energy } (KE)$$

Since $KE \propto T$,

$$\frac{1}{2}\text{mN}v^2 \propto T \Rightarrow \frac{1}{2}\text{mN}v^2 = kT$$

But,

$$PV = \frac{1}{3}\text{mN}v^2 = \frac{2}{3}\times\left(\frac{1}{2}\text{mN}v^2\right)$$

Therefore,

$$PV = \frac{2}{3}\times(kT) = \frac{2}{3}kT$$

Since Boyle's law applies at constant temperature,

$$PV = \frac{2}{3}kT = \text{constant}$$

If T is constant and k is constant, therefore, the whole $\frac{2}{3}kT$ is also constant.

PV = constant; meaning that, $P \propto \frac{1}{V}$ (This is the Boyle's law).

Charles' law

According to Charles' law, pressure and the number of moles of gases are constant. From:

$$PV = \frac{2}{3}kT \Rightarrow \frac{PV}{T} = \frac{2}{3}k \Rightarrow \frac{V}{T} = \frac{2k}{3P}$$

If P and k are constant, then $\frac{2k}{3P}$ is also constant.

Therefore,

$$\frac{V}{T} = \frac{2k}{3P} = \text{Constant}$$

$\frac{V}{T}$ = Constant; meaning that $V \propto T$ (This is the Charles' law).

Avogadro's law

In the Avogadro's law, temperature and pressure are constant. For two gases (1 and 2),

$$PV = \frac{1}{3}\text{m}_1\text{N}_1v_1^2 \text{ for gas 1 and } PV = \frac{1}{3}\text{m}_2\text{N}_2v_2^2 \text{ for gas 2}$$

The Avogadro's law considers equal volumes of gases at the same temperature and pressure. Therefore, pressure is the same and volume is also the same. This implies that,

$$\frac{1}{3}\mathrm{m}_1\mathrm{N}_1v_1^2 = PV = \frac{1}{3}\mathrm{m}_2\mathrm{N}_2v_2^2$$

Therefore,

$$\frac{1}{3}\mathrm{m}_1\mathrm{N}_1v_1^2 = \frac{1}{3}\mathrm{m}_2\mathrm{N}_2v_2^2 \tag{1.26}$$

Since the two sets of gases are at the same temperature, the average kinetic energy of gas molecules will be the same.

$$\frac{1}{2}\mathrm{m}_1v_1^2 = \frac{1}{2}\mathrm{m}_2v_2^2 \tag{1.27}$$

Dividing Equation 1.26 by Equation 1.27 gives:

$$\frac{2}{3}\frac{\mathrm{m}_1\mathrm{N}_1v_1^2}{\mathrm{m}_1v_1^2} = \frac{2}{3}\frac{\mathrm{m}_2\mathrm{N}_2v_2^2}{\mathrm{m}_2v_2^2}$$

The values of m and v for both gases cancel each other. Therefore,

$\mathrm{N}_1 = \mathrm{N}_2$ (This is the Avogadro's law).

Graham's law of diffusion or effusion

Consider the kinetic gas equation:

$$PV = \frac{1}{3}\mathrm{mN}v^2$$

For gases 1 and 2,

$$PV = \frac{1}{3}\mathrm{m}_1\mathrm{N}_1v_1^2 \text{ for gas 1, and } PV = \frac{1}{3}\mathrm{m}_2\mathrm{N}_2v_2^2 \text{ for gas 2.}$$

If m_1 and m_2 are the masses, and v_1 and v_2 are the velocities of the molecules of gases 1 and 2, respectively, then at the same volume and pressure:

$$\frac{1}{3}\mathrm{m}_1\mathrm{N}_1v_1^2 = \frac{1}{3}\mathrm{m}_2\mathrm{N}_2v_2^2$$

But, from Avogadro's law, $\mathrm{N}_1 = \mathrm{N}_2$. Therefore,

$$\mathrm{m}_1v_1^2 = \mathrm{m}_2v_2^2 \Rightarrow \frac{v_1^2}{v_2^2} = \frac{\mathrm{m}_2}{\mathrm{m}_1} \Rightarrow \left(\frac{v_1}{v_2}\right)^2 = \frac{\mathrm{m}_2}{\mathrm{m}_1}$$

Taking the square root on both sides gives:

$$\frac{v_1}{v_2} = \sqrt{\frac{\mathrm{m}_2}{\mathrm{m}_1}}$$

But the rate of diffusion (R) is proportional to the velocity (v) of the molecules.

Therefore,

$$\frac{\text{Rate of diffusion of gas 1}}{\text{Rate of diffusion of gas 2}} = \frac{R_1}{R_2} = \sqrt{\frac{m_2}{m_1}}$$

This is the Graham's law of diffusion or effusion.

1.4 Relative molecular masses of gases

The molecular mass is the sum of the atomic masses (in a.m.u, i.e., atomic mass unit) in the molecule. It is numerically equal to the molar mass (in grams) of a compound. The most convenient currently used method to determine molecular mass is *mass spectrometry*. However, in the 19th century (before the invention of mass spectrometer), several methods were developed based on the gas laws to determine molecular masses. These methods include the Duma's and Victor Meyer's Methods.

1.4.1 Determination of molecular mass by Dumas' method

Dumas' method of determining the molecular mass was named after a French Chemist, John Dumas (1800 – 1884). This method is used to determine the molecular mass of gases. Since liquids are much easier to handle than gases, volatile liquids are used as sources of gases. For this method to work well, the volatile liquid must have a boiling point above the room temperature and below the boiling point of water. Examples of volatile liquids with this criterion are acetone, ethanol, and diethyl ether.

The experimental setup for the determination of the molar mass of an unknown volatile liquid by Dumas' method as depicted in Figure 1.14 is straight forward and practical. A small amount of volatile liquid is introduced in a pre-weighed flask of a known volume. The flask is sealed with a stopper containing a narrow tube and heated in a boiling water bath to vaporise the liquid. As the liquid vaporises, the vapour first displaces all of the air out of the flask and then begins to flow out through the narrow tube until the pressure inside the bulb equals the atmospheric pressure.

When all the liquid is vaporised, and no more vapour is observed to escape the flask, the vapour pressure inside the flask is equal to the atmospheric pressure. The volume of the vapour inside the flask is equal to the volume of the flask. The flask is quickly removed from the boiling water bath to cool and condense the gas into liquid. The flask is re-weighed to obtain the mass of the liquid which is equal to the mass of the gas remaining in the flask. During the experiment, the temperature (T), the water bath, and the atmospheric pressure (P) are measured directly. This information is then used to calculate the molecular mass of the gas by using the ideal gas equation (Equation 1.14).

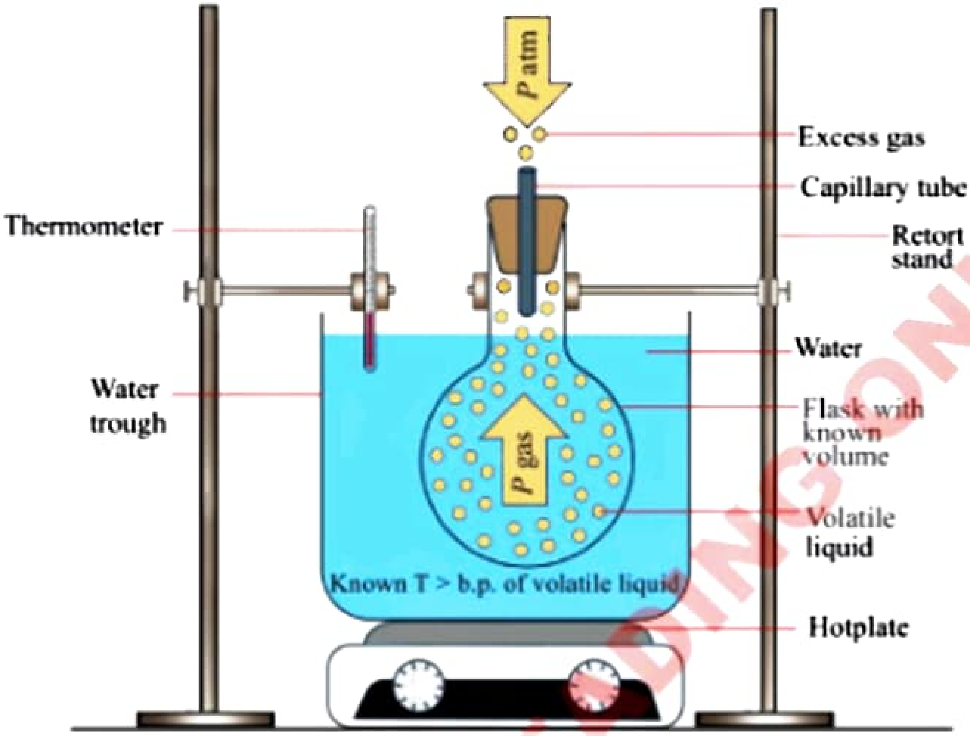


Figure 1.14: *Experimental setup for the determination of molar mass of unknown volatile liquid*

Example 1.8

In one experiment, a colourless liquid was isolated from a petroleum sample and observed to have the properties of cyclohexane (C_6H_{12}). To determine the molar mass of the isolated liquid, Dumas' method was used and the following data were recorded:

Volume (V) of flask = 213 mL
Mass of flask + gas = 78.416 g
Mass of empty flask = 77.834 g
Temperature (T) = 100 °C
Pressure, (P) = 754 Torr

Calculate the molar mass to verify if the liquid was consistent with the suspected cyclohexane molecule.

Solution

Mass (m) of the gas = (Mass of flask + gas) – (mass of flask)

$$\mathrm{m} = 78.416\ \mathrm{g} - 77.834\ \mathrm{g} = 0.582\ \mathrm{g}$$

$$\text{Volume } (V) \text{ of the gas} = 213\ \mathrm{mL} = 213\ \mathrm{mL} \times \frac{1\ \mathrm{L}}{1000\ \mathrm{mL}} = 0.213\ \mathrm{L}$$

$$\text{Pressure } (P) = 754\ \mathrm{Torr} = 754\ \mathrm{Torr} \times \frac{1\ \mathrm{atm}}{760\ \mathrm{Torr}} = 0.992\ \mathrm{atm}$$

$$\text{Temperature } (T) = 100\ ^\circ\mathrm{C} = (100\ ^\circ\mathrm{C} + 273.15) = 373.15\ \mathrm{K}$$

Gas constant (R) = 0.0821 L atm $\mathrm{mol^{-1}\,K^{-1}}$

From ideal gas equation,

$$PV = nRT$$

$$PV = \frac{\mathrm{m}RT}{\mathrm{M}} \Rightarrow \mathrm{M} = \frac{\mathrm{m}RT}{PV}$$

$$\mathrm{M} = \frac{0.582\ \mathrm{g} \times 0.0821\ \mathrm{L\ atm\ mol^{-1}K^{-1}} \times 373.15\ \mathrm{K}}{0.992\ \mathrm{atm} \times 0.213\ \mathrm{L}} = 84.4\ \mathrm{g\ mol^{-1}}$$

Calculation of molecular mass from the molecular formula of cyclohexane (C_6H_{12}):

$$C_6H_{12} = (6 \times 12.01\ \mathrm{g\ mol^{-1}}) + (12 \times 1.008\ \mathrm{g\ mol^{-1}})$$

$$C_6H_{12} = (72.06\ \mathrm{g\ mol^{-1}}) + (12.096\ \mathrm{g\ mol^{-1}}) = 84.156\ \mathrm{g\ mol^{-1}}$$

Therefore, the experimentally determined molar mass is consistent with the liquid being cyclohexane with minor experimental error.

Activity 1.4

Aim: To determine molecular mass of volatile liquid by Dumas' method

Requirements: Volatile liquid, thermometer, heat source, flat bottomed flask, capillary tube, stopper, paper towel, water trough, barometer, stopwatch, and weighing balance

Procedure

1. Measure about 5 $\mathrm{cm^3}$ of unknown volatile liquid and put into a pre-weighed flat-bottomed flask of known volume.

2. Close the flat bottomed flask with the stopper containing a narrow tube.
3. Set the apparatus as shown in Figure 1.14.
4. Clamp the flat-bottomed flask so that it is as deep in the water trough as possible, but the bottom of the flat bottomed flask should not touch the trough.
5. Heat the water in the trough to the boiling and record its temperature.
6. Vaporise the liquid until all the liquid has vaporised and continue heating for another 4 minutes.
7. Quickly remove the flask from boiling water and cool it.
8. Using a paper towel, dry the outside of the flask thoroughly.
9. Reweigh the flask (with the condensed unknown liquid inside) and record this mass.
10. Measure the atmospheric pressure using a barometer.

Questions

1. What is the molecular mass of the unknown volatile liquid?
2. How would each of the following possible sources of error be expected to affect the obtained molecular mass?
    (a) Air was not completely swept out of the flask by the unknown liquid after it had completely vaporised.
    (b) The volume of the flask at 100 °C was more significant than that at room temperature because of the expansion of the glass.

1.4.2 Determination of molecular mass by Victor-Meyer's method

Victor-Meyer's method of determining the molecular mass was named after a German Chemist, Victor Meyer (1848–1897). This method is used for determining the molecular weights of volatile liquids. Figure 1.15 shows the experimental setup of the Victor Meyer's method.

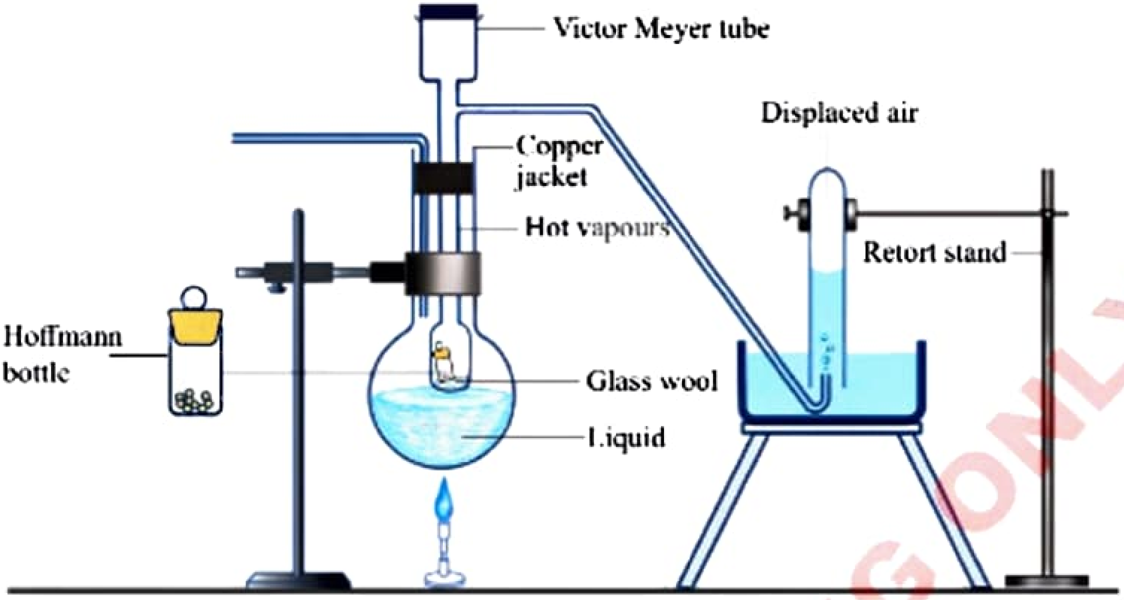


Figure 1.15: *Experimental setup for determination of molecular mass by Victor-Meyer's method*

The setup consists of an inner Victor-Meyer's tube surrounded by an outer jacket, with the lower end of the tube in the shape of a bulb. The upper end of the tube is connected to a side tube leading to a water trough. The outer jacket consists of a liquid with a boiling temperature of at least 30 °C higher than that of the volatile substance being studied. At the bottom of the Victor-Meyer's tube, a small quantity of glass wool or asbestos fibre is placed in order to prevent breakage when the bottle containing the liquid substance is dropped in.

This method involves the vaporisation of a known mass of volatile liquid by heating in a Victor Meyer's tube. The vapour generated displaces the same volume of air, which is then measured at the recorded experimental temperature and pressure. The liquid in the jacket is boiled to allow the trapped air inside the tube to escape. When no more air escapes from the side tube, a graduated tube filled with water is inverted on top of the side tube dipped in a water trough. A small quantity of the volatile substance to be studied is weighed in a small stoppered bottle and quickly dropped in the heated Victor-Meyer's tube. Then, the opening at the top of the tube is immediately corked. When the bottle falls on the asbestos fibre, its content changes into vapour and blows out the stopper, displacing an equal volume of air, which is then collected in the inverted graduated tube. To measure the volume of air in the graduated tube, the latter is taken out by closing its opening with the thumb and dipping it in a jar full of water. The volume of air displaced is noted when the water levels outside and inside the tube are the same.

Calculations

The mass of the volatile substance = X (g)

The volume of air displaced = volume of vapour = (m^3)

Laboratory temperature = (K)

R = gas constant = 0.0821 L atm mol^{-1} K^{-1}

Required is the molar mass of the volatile liquid

P_{T} is the total pressure

$P_{\text{volatile liquid}}$ is pressure of dry vapour

(P_{water}) is pressure of water

From Dalton's law of partial pressures

$$P_{\text{T}} = P_{\text{water}} + P_{\text{volatile liquid}} \text{, and}$$

$$P_{\text{Volatile liquid}} = P_{\text{Total}} - P_{\text{Water}}$$

The molar mass of volatile liquid is then obtained by using ideal gas equation:

$$PV = nRT = \frac{\text{m}RT}{\text{M}} \Rightarrow \text{M} = \frac{\text{m}RT}{PV}$$

Example 1.9

In a Victor-Meyer's method for determining molar mass, a 0.156 g of volatile liquid displaced 47.0 cm^3 of air measured over water at 14 °C and 762 Torr pressure. What is the relative molecular mass of the volatile liquid? (Vapour pressure of water at 14 °C is 13 Torr).

Solution

Data given:

Weight of volatile liquid = 0.156 g, volume of air displaced = 47.0 cm^3 = 0.047 L

Total pressure = 762 Torr, Vapour pressure of water at 14 °C = 13 Torr

The absolute temperature = (14 + 273) K = 287 K

$$P_{\text{total}} = P_{\text{water}} + P_{\text{volatile liquid}}$$

$$762\ \text{Torr} = 13\ \text{Torr} + P_{\text{volatile liquid}}$$

$$P_{\text{volatile liquid}} = 762\ \text{Torr} - 13\ \text{Torr} = 749\ \text{Torr}$$

$$= \frac{749\ \text{Torr} \times 1\ \text{atm}}{760\ \text{Torr}} = 0.9855\ \text{atm}$$

From ideal gas equation,

$$PV = nRT = \frac{mRT}{M} \Rightarrow M = \frac{mRT}{PV}$$

$$M = \frac{0.156\ \text{g} \times 0.08215\ \text{L atm mol}^{-1}\text{K}^{-1} \times 287\ \text{K}}{0.9855\ \text{atm} \times 0.047\ \text{L}} = 79.41\ \text{g mol}^{-1}$$

Therefore, the relative molecular mass of the liquid is 79.41 g mol^{-1}.

1.4.3 Abnormal vapour density and molecular mass

The vapour density and molar mass found by vaporising volatile solid or liquid substances using Victor Meyer, or Duma's methods may be greater or less than expected. For example, when heated to above boiling point, a substance like $FeCl_3$ associates to form a dimer, which doubles its vapour density and molecular mass.

$$2FeCl_3 \longrightarrow Fe_2Cl_6$$

Examples of molecules that can undergo association are aluminium chloride (Al_2Cl_6) and hydrogen fluoride (H_2F_2).

Sometimes substances dissociate into smaller molecules and thus the vapour density and molecular mass are smaller than expected. For example, the sublimation of ammonium chloride.

$$NH_4Cl \longrightarrow NH_3 + HCl$$

Calculation of the degree of dissociation

The degree of dissociation is the fraction of the original molecules that have undergone dissociation. It is usually expressed as a decimal, fraction, or as a percentage. In all cases where dissociation takes place with an increase in volume, the density (or vapour density) decreases, and the extent of the decrease depends on the degree of dissociation.

Consider the dissociation of N_2O_4 to form $2NO_2$. Let the degree of dissociation be α. Then the fraction of N_2O_4 molecules remaining is $1-\alpha$. If there were N molecules of N_2O_4 before dissociation, there would be $N(1-\alpha)$ molecules of N_2O_4 after dissociation. Since each molecule of N_2O_4 that dissociates furnishes two molecules of NO_2, there will be $2N\alpha$ molecules of NO_2 after dissociation.

$$\begin{array}{lcl} N_2O_4 & \rightleftharpoons & 2NO_2 \\ N(1-\alpha) & & 2N\alpha \end{array}$$

The total number of molecules after dissociation are

$$= N(1-\alpha)+2N\alpha$$

$$= N(1-\alpha+2\alpha)$$

$$= N(1+\alpha)$$

Now, for a given mass of the gas, the density is inversely proportional to the number of molecules present. Let ρ_1 = density before dissociation, and ρ_2 = the observed density after dissociation.

Then, $\rho_1 \propto \frac{1}{N}$, and $\rho_2 \propto \frac{1}{N(1+\alpha)}$

Thus, $$\frac{\rho_1}{\rho_2} = \frac{N(1+\alpha)}{N} = \frac{1+\alpha}{1}$$

Therefore, $$\alpha = \frac{\rho_1}{\rho_2} - 1$$

Example 1.10

The vapour density of dinitrogen tetraoxide at 26.7 °C is 38.3. The vapour density of undissociated dinitrogen tetraoxide, N_2O_4 is 46. Find the degree of dissociation.

Solution

The degree of dissociation: $\alpha = \frac{\rho_1}{\rho_2} - 1 = \frac{46}{38.3} - 1$

$$= 1.20 - 1 = 0.20$$

$$= 20\%$$

Therefore, the degree of dissociation is 20%.

When dissociation occurs so that one of the initial vapours give more than two volumes of gaseous products, the formula for the degree of dissociation must be modified accordingly.

Generally, if n gaseous molecules are formed from one molecule,

$$\frac{\rho_1}{\rho_2} = \frac{1-\alpha+n\alpha}{1}$$

$$\alpha = \frac{\rho_1-\rho_2}{\rho_2(n-1)}$$

The degree of dissociation cannot be calculated by this method for molecules whose dissociation results in the same number of molecules as before dissociation. This is because there is no change in volume.

Exercise 1.3

1. Use the kinetic theory to explain the origin of gas pressure.
2. Use the kinetic theory of gases to elucidate how a gas uniformly fills a container of any shape.
3. The speed of a given molecule in a gas remains constant at a given temperature. Explain.
4. Describe what happens to the average kinetic energy of ideal gas molecules when the conditions are changed as follows:
   (a) The gas pressure increases by reducing the volume at a constant temperature.
   (b) The pressure increases by increasing the temperature at a constant volume.
   (c) The average velocity of the molecules is increased by a factor of 2.
5. If $SO_2(g)$ moves with the same speed as $O_2(g)$, what is the ratio of the average kinetic energy of the SO_2 molecule to that of the O_2 molecule in a mixture of two gases?
6. A 1.0 L sample of CO initially at STP is heated to 546 °C, and its volume increased to 2 L. What is the effect of these changes on the number of collisions of the gas molecules per unit area of the container's wall?

7. Show that the ratio of the rate of diffusion of gas 1 to the rate of diffusion of gas 2, R_1/R_2 is the same at 0 °C and 100 °C.

8. A gas sample with a volume of 512 cm^3 weighs 1.236 g at a temperature of 20 °C and a pressure of 1 atmosphere. Calculate its relative molecular mass if the molar gas constant is $R = 8.314$ J mol^{-1} K^{-1}.

9. A volatile organic compound weighs 0.2 g. On heating in Victor Meyer's tube, it displaces 30 mL of air at 27 °C and 756 Torr atmospheric pressure. Determine the molecular mass of the compound (aqueous tension at 27 °C equals 26 Torr).

Revision exercise 1

1. 352 mL of chlorine at a pressure of 680 Torr is placed in a container at a pressure of 1210 Torr. The temperature remains constant at 296 K. What is the volume of the container in litres?

2. Explain the practical applications of Charles's law in real life.

3. A sample of helium has a volume of 521 dm^3 at a pressure of 750 Torr and a temperature of 18 °C. Calculate the volume of helium when temperature is increased to 23 °C.

4. In the context of Boyle's law, what happens to the volume of a gas-filled container as a diver descends deeper into the water?

5. A 20.0 L container is filled with helium at a pressure of 150 atm and a temperature of 30 °C. How many 5.0 L balloons can be filled when the temperature is 22 °C, and the atmospheric pressure is 755 Torr?

6. A sample of nitrogen gas occupies a volume of 2.0 L at 756 Torr and 0.0 °C. The volume increases by 2.0 L and the temperature decreases to 137 K. What is the final pressure exerted by the gas?

7. A chemist adds 3.13 moles of argon to a 5.29 L container with 2.51 moles of argon. What is the volume of the container after the addition of extra gas?

8. A 25.5-litre container holding 3.5 moles of carbon dioxide leaks. If 1.9 moles of carbon dioxide escape before the container is sealed, what is the new volume of the container?

9. A 3.0 L container is filled with neon gas at 770 Torr and 27 °C. If a 0.633 g sample of carbon dioxide vapour is added to this container:

   (a) What are the partial pressures of carbon dioxide and neon in atm?

   (b) What is the total pressure in the container in atm?

10. A glass tube with a stopcock joins two flasks at the same temperature. Flask A is a 4.0 L flask containing $N_2(g)$ at 2.0 atm, while flask B is a 10.0 L flask containing CO(g) at 1.4 atm. What is the final pressure in the flasks after the stopcock is opened?

11. Hydrogen chloride particles (HCl) have a mass of 36.5 a.m.u and ammonia particles (NH_3) have a mass of 17.0 a.m.u. If hydrogen chloride and ammonia particles are released at opposite ends of a 100.0 cm tube, where will they meet in the tube?

12. Food cooks more quickly at higher altitudes compared to lower altitudes. Explain.

13. Under the same temperature and pressure, how fast will hydrogen effuse compared to carbon dioxide?

14. It is not safe to put aerosol canisters in a campfire. Explain.

15. Some fire extinguishers operate under gas laws. Explain.

Chapter Two

Colligative properties of solutions

Introduction

Colligative properties of solutions are fascinating phenomena that occur when solute particles interact with solvent particles, leading to changes in the solution's physical properties. In this chapter, you will learn about the four types of colligative properties and their applications in water purification, dialysis, food preservation and antifreeze. The competencies developed will enable you to apply the colligative properties to understand the solution's responses to environmental changes.

Think

Universality of colligative properties

2.1 Properties of solutions exhibiting colligative properties

Task 2.1

Use online simulation to explore colligative properties and their applications in various systems.

Colligative properties are the properties of solutions that depend on the number of solute particles dissolved and not on the nature of solute particles. For a solution to exhibit colligative properties, it must fulfil the following conditions:

(a) The solution should be dilute with a concentration less than or equal to 0.2 M.

Colligative properties require that solute particles do not interact with each other, or at least that their interactions do not change with concentration. A high concentration of solution means that there is a large number of solute particles, and therefore, there will be extensive solute-solute interactions.

(b) The solute should be non-electrolyte.

Electrolyte solutes tend to form ions in a solution. Because colligative properties depend on the number of solute particles and not on the nature of particles, the formation of ions by a solute which is an electrolyte would increase the number of particles and hence the interaction between particles of the solute.

(c) The solute should be non-volatile.

The solute is required to be non-volatile because the focus is on the effect of solute particles on the properties of the solvent. When a non-volatile solute is added to a solvent, it does not readily evaporate into the vapour phase. Therefore, it will not contribute to the vapour pressure of the solution.

2.2 Types of colligative properties

There are four colligative properties: vapour pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. These properties change in accordance with the amount of the solute added to the solvent to form a solution.

2.2.1 Vapour pressure lowering

A vapour is the gaseous state of a substance. For molecules of liquids to escape into the vapour phase, they have to overcome the intermolecular forces of attraction in liquids. If a container is closed, the molecules of the liquid escaping from the surface remain above the surface of the liquid. The molecules in the vapour phase collide with each other, with the walls of the container and with the surface of the liquid and return to the liquid state, leading to a continuous evaporation-condensation process. After some time, an equilibrium is established between the liquid phase and the vapour phase, where the rate of evaporation is equal to the rate of condensation. The pressure exerted by the vapour on the liquid surface is called *vapour pressure*. The vapour pressure of a liquid increases with an increase in temperature and does not depend on the volume of the liquid or the amount of vapour present. At room temperature, volatile liquids have higher vapour pressures, whereas non-volatile liquids have lower vapour pressures.

Concept of lowering of the vapour pressure of a solvent

When a non-volatile solute is dissolved in a liquid solvent, the vapour pressure of the solvent is lowered. Unlike in pure solvents, the surface area in the solution is not completely available for a volatile solvent because it is partly occupied by a non-volatile solute. As a result, the rate of evaporation of the solution is lower than that of pure solvent. *Lowering of vapour pressure* is the difference between the vapour pressure of the pure solvent and the vapour pressure of the solution.

Mathematically, the lowering of vapour pressure (ΔP) is expressed as:

$$\Delta P = P^\circ - P \qquad (2.1)$$

where P° is the vapour pressure of pure solvent and P is the vapour pressure of the solution.

Vapour pressure lowering and the Raoult's law

Raoult's law was named after a French Chemist called François–Marie Raoult (1830–1901). In the 1880s, Raoult discovered that when a substance is dissolved in a solvent, the vapour pressure of the solution decreases. He further observed that the decrease in vapour pressure of the solvent in a solution is dependent on the amount of the dissolved solute and hence the mole fraction of the solute and the vapour pressure of pure solvent. These observations were summarised into what is called *Raoult's law* which states that the vapour pressure of a solvent in a solution (P_{solvent}) is equal to the vapour pressure of pure solvent (P°_{solvent}) times the mole fraction of the solvent (χ_{solvent}).

Mathematically,

$$P_{\text{solvent}} = P^\circ_{\text{solvent}} \times \chi_{\text{solvent}} \qquad (2.2)$$

$$\chi_{\text{solvent}} = \frac{n_{\text{solvent}}}{n_{\text{solvent}} + n_{\text{solute}}} = \frac{n_{\text{solvent}}}{n_{\text{total}}}$$

Similarly, χ_{solute} is the mole fraction of solute.

$$\chi_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solvent}} + n_{\text{solute}}} = \frac{n_{\text{solute}}}{n_{\text{total}}}$$

In the solution, the mole fraction of a solvent (χ_{solvent}) is always less than 1. Therefore, the vapour pressure of the solvent in a solution (P_{solvent}) is always less than the vapour pressure of pure solvent (P°_{solvent}). A solution which obeys Raoult's law is called an *ideal solution*. However, most solutions deviate from the ideal behaviour at a certain concentration, and the Raoult's law works better for dilute solutions only. Since a solution consists of a solvent and a solute, the sum of their mole fractions is equal to 1. That is,

$$\chi_{\text{solvent}} + \chi_{\text{solute}} = 1 \Rightarrow \chi_{\text{solvent}} = 1 - \chi_{\text{solute}} \qquad (2.3)$$

Substituting Equation 2.3 in 2.2:

$$P_{\text{solvent}} = P^\circ_{\text{solvent}} \times \chi_{\text{solvent}} \Rightarrow P_{\text{solvent}} = P^\circ_{\text{solvent}} \times (1 - \chi_{\text{solute}})$$

$$P_{\text{solvent}} = P^\circ_{\text{solvent}} - (P^\circ_{\text{solvent}} \times \chi_{\text{solute}})$$

and rearranging, gives:

$$P^\circ_{\text{solvent}} - P_{\text{solvent}} = P^\circ_{\text{solvent}} \times \chi_{\text{solute}} \Rightarrow \Delta P = P^\circ_{\text{solvent}} \times \chi_{\text{solute}} \qquad (2.4)$$

Equation 2.4 shows that the vapour pressure lowering depends on the mole fraction of the solute as illustrated in Figure 2.1.

The graph of vapour pressure against mole fraction shows that as the mole fraction of the solvent decreases (increasing mole fraction of solute) the vapour pressure of the solvent in the solution decreases relative to the pure solvent. As a result, the lowering of vapour pressure (ΔP) increases.

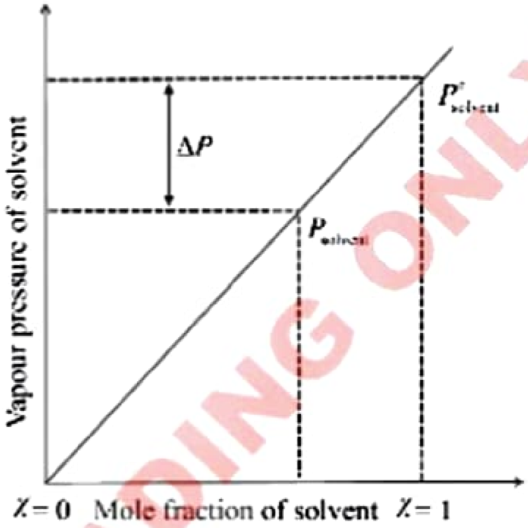


Figure 2.1: *Lowering of vapour pressure with increasing mole fraction of solute*

Therefore, the lowering of vapour pressure (ΔP) is directly proportional to the mole fraction of the solute in a solution.

Mathematically, $\Delta P \propto \chi_{solute}$

The ratio of the lowering of vapour pressure (ΔP) to the vapour pressure of pure solvent is called the *relative lowering of vapour pressure*. That is,

$$\frac{\Delta P}{P^{o}_{solvent}} = \frac{P^{o}_{solvent} - P_{solvent}}{P^{o}_{solvent}} = \chi_{solute} \tag{2.5}$$

The relative lowering of vapour pressure can also be expressed in terms of the number of moles of solute and solvent molecules as:

$$\frac{\Delta P}{P^{o}_{solvent}} = \frac{n}{n + \mathrm{N}} \tag{2.6}$$

where n is the number of moles or molecules of the solute and N is the number of moles or molecules of solvent. Therefore, combining Equations 2.5 and 2.6 gives:

$$\frac{\Delta P}{P^{o}_{solvent}} = \frac{P^{o}_{solvent} - P_{solvent}}{P^{o}_{solvent}} = \frac{n}{n + \mathrm{N}} \tag{2.7}$$

If the solution is very dilute, $n + N \approx N$, and Equation 2.7 approximates to:

$$\frac{\Delta P}{P^{o}_{solvent}} = \frac{P^{o}_{solvent} - P_{solvent}}{P^{o}_{solvent}} = \frac{n}{\mathrm{N}} \tag{2.8}$$

If m_1 is the mass of the solute, m_2 is the mass of the solvent and M_1 and M_2 are the molar masses of solute and solvent, respectively, then:

$$\frac{P^{\circ}_{\text{solvent}} - P_{\text{solvent}}}{P^{\circ}_{\text{solvent}}} = \frac{m_1/M_1}{m_2/M_2} = \frac{m_1 M_2}{m_2 M_1} \tag{2.9}$$

Equation 2.9 is applicable for very dilute solutions.

Example 2.1

Calculate the lowering of vapour pressure caused by the addition of 100 g of sucrose (molecular mass = 342 g mol^{-1}) to 1000 g of water if the vapour pressure of pure water at 25 °C is 23.8 Torr.

Solution

Given that,

$P^{\circ}_{\text{solvent}} = 23.8$ Torr

ΔP = lowering of vapour pressure $= P^{\circ}_{\text{solvent}} - P_{\text{solvent}}$

N = Number of moles of solvent = 42 g mol^{-1}

m_1 = Mass of solute, M_1 = Molar mass of solute

m_2 = Mass of water, M_2 = Molar mass of water

n = Number of moles of solute

The relative lowering of vapour pressure is expressed as:

$$\frac{\Delta P}{P^{\circ}_{\text{solvent}}} = \frac{P^{\circ}_{\text{solvent}} - P_{\text{solvent}}}{P^{\circ}_{\text{solvent}}} = \frac{n}{n+N} = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2}$$

$$n = \frac{m_1}{M_1} = \frac{100\ \text{g}}{342\ \text{g mol}^{-1}} = 0.29\ \text{mol}$$

$$N = \frac{m_2}{M_2} = \frac{1000\,\text{g}}{18\,\text{g mol}^{-1}} = 55.56\ \text{mol}$$

$$\frac{\Delta P}{23.8\ \text{Torr}} = \frac{0.29\ \text{mol}}{0.29\ \text{mol} + 55.6\ \text{mol}}$$

$$\Delta P = \left(\frac{0.29\ \text{mol}}{0.29\ \text{mol} + 55.6\ \text{mol}}\right) \times 23.8\ \text{Torr} = 0.124\ \text{Torr}$$

Therefore, the lowering of vapour pressure is 0.124 Torr.

Example 2.2

The vapour pressure of water at 50 °C is 92.5 Torr. At the same temperature, a solution containing 9.14 g of urea in 150 g of water has a vapour pressure of 90.8 Torr. Determine the molecular mass of urea.

Solution

Data given:

$P^{o}_{\text{solvent}} = 92.5$ Torr, $P_{\text{solvent}} = 90.8$ Torr,

$\Delta P = 92.5 - 90.8\ \text{Torr} = 1.7\ \text{Torr}$,

n = the number of moles of solute

m_1 = the mass of solute = 9.14 g

N = the number of moles of solvent

m_2 = the mass of solvent = 150 g

M_1 = the molar mass of solute = ?

M_2 = the molar mass of solvent (H_2O) = 18 gmol^{-1}

The relative lowering of vapour pressure is expressed as:

$$\frac{\Delta P}{P^{o}_{\text{solvent}}} = \frac{P^{o}_{\text{solvent}} - P_{\text{solvent}}}{P^{o}_{\text{solvent}}} = \frac{n}{n+N} = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2}$$

Assuming very dilute solution:

$$\frac{\Delta P}{P^{o}_{solvent}} = \frac{P^{o}_{solvent} - P_{solvent}}{P^{o}_{solvent}} = \frac{n}{N} = \frac{m_1/M_1}{m_2/M_2} = \frac{m_1 M_2}{m_2 M_1}$$

where,

$\Delta P =$ lowering of vapour pressure $\left(P^{o}_{solvent} - P_{solvent}\right)$

$$\frac{1.7\text{ Torr}}{92.5\text{ Torr}} = \frac{9.14\text{ g} \times 18\text{ g mol}^{-1}}{150\text{ g} \times M_1}$$

$$M_1 = \frac{9.14\text{ g} \times 18\text{ g mol}^{-1} \times 92.5\text{ Torr}}{150\text{ g} \times 1.7\text{ Torr}} = 59.7\text{ g mol}^{-1}$$

Therefore, the molar mass of urea is 59.7 g mol^{-1}.

Exercise 2.1

1. How does the vapour pressure lowering affect cooking processes?
2. A solution is made by dissolving 218 g of glucose (molar mass = 180.2 g/mol) in 460 mL of water at 30 °C. If the vapour pressure of pure water at 30 °C is 31.82 Torr, calculate:
    (a) The vapour pressure of the solution
    (b) The vapour pressure lowering of the solution. Assume the density of the solution is 1.0 g/mL.
3. The vapour pressure of a 5% aqueous solution of a non-volatile organic substance at 373 K is 745 Torr. What is the molar mass of the organic substance? (The vapour pressure of pure water at 373 K is 760 Torr).
4. When 40.0 g of rhombic sulfur is dissolved in 1.0 kg of CS_2, the vapour pressure of CS_2 falls to 0.3868 atm. If the vapour pressure of pure liquid CS_2 at 20 °C is 0.3914 atm, what is the molecular formula of the sulfur molecules dissolved?
5. Adding of 114 g of sucrose to 1000 g of water lowers the vapour pressure of water from 17.540 atm to 17.435 atm. Compute the molecular weight of sucrose.

2.2.2 Boiling point elevation

The boiling point of a liquid is the temperature at which the vapour pressure of the liquid is equal to the atmospheric pressure. The vapour pressure of a solvent in a solution of non-volatile solute is always less than that of a pure solvent ($P_{solvent} < P^o_{solvent}$). This means that the solution has less tendency of forming vapour than the pure solvent. Therefore, the solution will boil at a temperature higher than the boiling point of pure solvent. For the solution to boil, its vapour pressure must be increased to the external atmospheric pressure. The increase in temperature is denoted by ΔT_b (the subscript b stands for boiling), which is equal to $T–T^o$, where T is the boiling point of solution and T^o is the boiling point of the pure solvent. Since T is greater than T^o, therefore ΔT_b is the elevation of the boiling point.

The *elevation of the boiling point* is defined as the difference between the boiling point of a solution and that of pure solvent. The elevation of the boiling point of a solution is illustrated in Figure 2.2.

The vapour pressure–temperature curve of a solution (curve C–D) is always below that of a pure solvent (curve A–B). Point E is the boiling point of pure solvent, and its corresponding temperature is T^o. At this point, the vapour pressure of the solvent is equal to the atmospheric pressure which is 760 Torr. At this temperature, the vapour pressure of a solution is below the atmospheric pressure as shown by point G. For the solution to reach its boiling point (point F), the temperature is raised from T^o to T. This increase in temperature from T^o to T is what is referred to as the elevation of boiling point (ΔT_b).

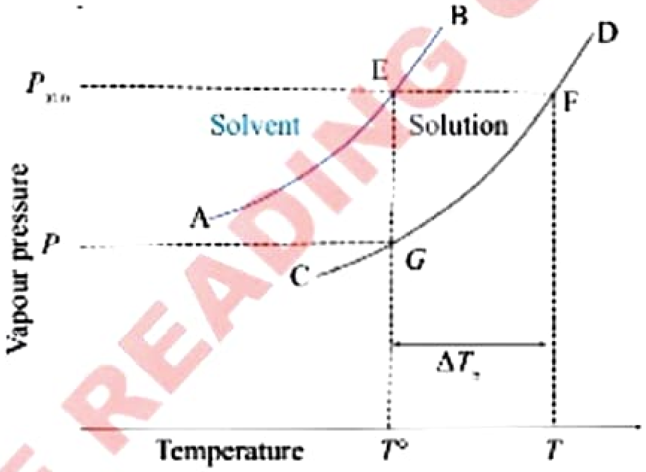


Figure 2.2: *Elevation of boiling point of a solution*

The magnitude of the boiling point elevation is proportional to the molal concentration (m) of solute particles.

Mathematically,

$$\Delta T_b \propto m \Rightarrow \Delta T_b = K_b m \qquad (2.10)$$

where K_b is the *molal boiling point elevation constant* or *ebullioscopic constant*.

Molality or molal concentration (*m*) is the number of moles of a solute dissolved in 1 kg of a solvent. Ebullioscopic constant is defined as the ratio of the elevation of the boiling point of a solvent to the molality of the solution, or is the amount of temperature elevated when one mole of a solute is dissolved in one kilogram of a solvent.

$$K_b = \frac{\Delta T_b}{m}$$

The units of K_b are degree Celsius per molal unit (°C/*m*), which is degree Celsius kilogram per mole (°C kg mol^{-1}) or Kelvin kilogram per mole (K kg mol^{-1}).

Activity 2.1

Aim: To investigate the effect of the amount of solute on the boiling point of pure solvent

Requirements: Thermometer, glass beakers, glass rod, source of heat, measuring cylinder, analytical balance, tripod stand, wire gauze, sugar and water

Procedure

1. Measure 20 mL of water and pour it into a 100-mL beaker.
2. Heat the water on the heat source and record the temperature at which the water starts to boil.
3. Dissolve 5 g of sugar in another 20 mL of water.
4. Heat the sugar solution and record the temperature at which the water boils.
5. Repeat steps 3 and 4 using 10 g of sugar.

Questions

1. What is the boiling point elevation of the solution when:
   (a) 5 g of sugar was added?
   (b) 10 g of sugar was added?
2. What will be the boiling point of the solution if the same amount of sucrose is used in the place of glucose? **Note**: The density of water is 1 g/cm^3, and the Ebullioscopic constant of water is 0.512 °C/*m*.
3. In what industries is the investigated phenomenon applicable?

Example 2.3

The boiling temperature of a solution prepared by dissolving 5.0 g of an organic solid in 100.0 g of benzene is 82.42 °C. If the boiling temperature of pure benzene is 80.10 °C, what is the molecular weight of the organic solid? ($K_b = 2.53\ °C/m$).

Solution

Data given:

Mass of an organic solid = 5.0 g

Mass of benzene = 100.0 g

Boiling temperature of benzene solution = 82.42 °C

Boiling temperature of pure benzene = 80.10 °C

Determine the change in boiling temperature (between the solution and pure solvent).

$$\Delta T_b = T_{\text{solution}} - T_{\text{pure solvent}} = 82.42\ °C - 80.10\ °C = 2.32\ °C$$

Calculate the molality using the change in boiling point and the elevation constant.

$$\Delta T_b = K_b m \Rightarrow m = \frac{\Delta T_b}{K_b}$$

$$m = \frac{2.32\ °C}{2.53\ °C\, m^{-1}} = 0.917\ \text{mol kg}^{-1}$$

Find the moles of a solute from molality by multiplying with the mass of a solvent.

From:

Number of moles of solute = Molality × Mass of solvent in kg,

$$\text{Number of moles of solute} = 0.917\ \text{mol kg}^{-1} \times 100.0\ \text{g benzene} \times \frac{1\ \text{kg}}{1000\ \text{g}} = 0.0917\ \text{mol}$$

$$\text{From: number of moles of solute} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}}$$

$$\text{Molar mass of solute} = \frac{\text{Mass of solute}}{\text{Number of moles of solute}}$$

$$\text{Molar mass} = \frac{5.0\ \text{g}}{0.0917\ \text{mol}} = 54.5\ \text{g mol}^{-1}$$

Therefore, the molecular weight of the organic solid is 54.5 g mol^{-1}.

Example 2.4

Propanone has a boiling point of 56.2 °C. When 1.0 g of a non-volatile solute was dissolved in 10 g of propanone, the solution boiled at 57.4 °C. Calculate the molar mass and thus the relative molecular mass of the solute given that the ebullioscopic constant of propanone is 1.71 K kg mol^{-1}.

Solution

Given that:

Mass of solvent $(m_{\text{solvent}}) = 10\ \text{g}$

Mass of solute $(m_{\text{solute}}) = 1.0\ \text{g}$

Boiling point of pure propanone = 56.2 °C

Boiling point of propanone solution = 57.4 °C

The elevation of boiling point:

$$\Delta T_b = T_{\text{solution}} - T_{\text{pure solvent}} = 57.4\ °\text{C} - 56.2\ °\text{C} = 1.2\ °\text{C} = 1.2\ \text{K}$$

Ebullioscopic constant, $K_b = 1.71\ \text{K kg mol}^{-1}$

Find the molality of the solution:

From $\Delta T_b = K_b m$,

$$m = \frac{\Delta T_b}{K_b} = \frac{1.2\ \text{K}}{1.71\ \text{K kg mol}^{-1}} = 0.7017\ \text{mol kg}^{-1}$$

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

Number of moles of solute = Molality × Mass of solvent (kg)

$$\text{Number of moles} = 0.7017\ \text{mol kg}^{-1} \times 10\ \text{g (propanone)} \times \frac{1\ \text{kg}}{1000\ \text{g}} = 7.017 \times 10^{-3}\ \text{mol}$$

$$\text{Number of moles of solute} = \frac{\text{Mass of solute (g)}}{\text{Molar mass of solute}\ (\text{g mol}^{-1})}$$

$$\text{Molar mass of solute (g mol}^{-1}) = \frac{\text{Mass of solute (g)}}{\text{Number of moles of solute (mol)}}$$

$$\text{Molar mass of solute (g mol}^{-1}) = \frac{1\,\text{g}}{7.017\times10^{-3}\,\text{mol}} = 142.51\,\text{g mol}^{-1}$$

Thus, the molar mass of the non-volatile solute is 142.51 g mol^{-1} and its relative molecular mass is 142.51.

Exercise 2.2

1. Calculate the boiling point of a solution made by dissolving 45.0 g of a non-volatile and non-electrolyte solute with molar mass of 40 g/mol in 500 g of water (K_b for water = 0.512 °C/m).
2. Describe the practical application of boiling point elevation in automotive engineering.
3. Two solutions were prepared, one containing 105 g of sucrose ($C_{12}H_{22}O_{11}$) in 500 g of water, and the other containing 35.0 g of NaCl in 500 g of water. Which solution will have a higher boiling point? Comment on your answer (K_b = 0.512 °C/m).
4. When 25.0 g of an unknown, non-volatile and non-electrolyte solute was dissolved in 130 g of water, the boiling point of the solution reached 102.5 °C. Find the molar mass of the unknown solute (K_b = 0.512 °C/m).

2.2.3 Freezing point depression

Freezing point of a liquid is the temperature at which the vapour pressure of solid is equal to the vapour pressure of liquid. As explained previously, the vapour pressure of pure solvent is higher than the vapour pressure of solution. Therefore, a solution freezes at lower temperatures than pure solvent. This difference in the freezing point between

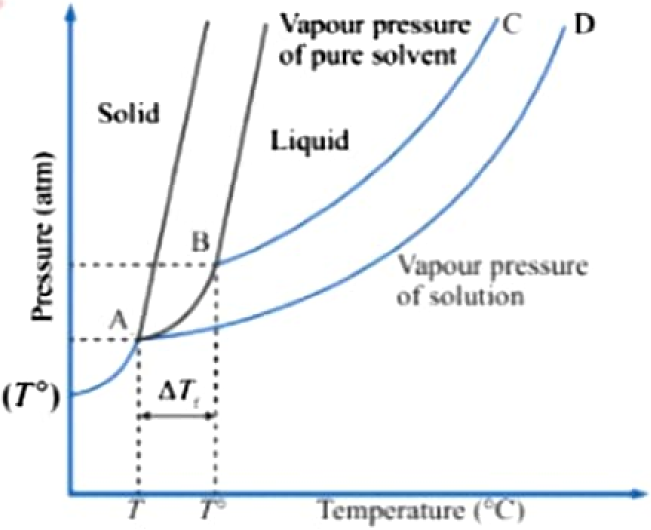


Figure 2.3: *Depression of freezing point of a solution*

pure solvent and a solution containing non-volatile solute is called *freezing point depression*, denoted by ΔT_f or $T^\circ - T$, where the subscript *f* stands for freezing, T is the freezing point of a solution and T° is the freezing point of pure solvent.

The depression of the freezing point of the solution is illustrated in Figure 2.3, where AB is the solid-vapour sublimation curve of the solid-solvent, and BC is the liquid–vapour pressure curve of pure liquid solvent. AD is the liquid–vapour pressure curve of a solution containing a non-volatile solute. At point B, pure liquid solvent and solid solvent have the same vapour pressure. Therefore, the temperature corresponding to point B is the freezing point of pure solvent (T°). When a non-volatile solute is added to a pure liquid solvent and forms a solution, the vapour pressure of the solvent is lowered and the solvent can no longer freeze at a temperature T°. At point A, the vapour pressure of a solvent from the solution of a non-volatile solute and the solid solvent are the same. Therefore, the temperature corresponding to point A is the freezing point of the solution (T).

The vapour pressure curve of pure solvent (BC) is always found above the vapour pressure curve of the solution (AD). Therefore, the point at which the vapour pressure curve of a solution and that of a solid solvent meet is always lower than T°. As a result, the freezing point of a solution (T) is always lower than that of pure solvent (T°). The magnitude of the depression of the freezing point is proportional to the molal concertation (m) of solute particles.

Mathematically,

$$\Delta T_f \propto m \Rightarrow \Delta T_f = K_f m \qquad (2.11)$$

where K_f is the *molal freezing point depression constant* or *cryoscopic constant*. Cryoscopic constant is the ratio of the depression of the freezing point of a solvent to the molality of the solution or is the quantity of the freezing point depressed when one mole of a solute is dissolved in one kilogram of the solvent.

$$K_f = \frac{\Delta T_f}{m}$$

The units of K_f are degrees Celsius per molal unit (°C/m), which is degree Celsius kilogram per mole (°C kg mol^{-1}) or Kelvin kilogram per mole (K kg mol^{-1}) .

Example 2.5

Determine the freezing point depression of methyl alcohol (CH_3OH) in a solution made by dissolving 18.5 g methyl alcohol in 850 g of water (K_f for water = 1.86 °C kg mol^{-1}).

Solution

Data given:

Mass of methyl alcohol =18.5 g

Mass of water = 850 g

$$\text{Moles of solute} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} = \frac{18.5\ \text{g}}{32.0\ \text{g mol}^{-1}} = 0.578\ \text{mol of solute}$$

$$\text{Molality} = \frac{\text{Number of moles}}{\text{Mass of solvent in kg}} = \frac{0.578\ \text{mol}}{850\ \text{g}} \times \frac{1000\ \text{g}}{1\ \text{kg}} = 0.680\ \text{mol kg}^{-1}$$

$$\Delta T_f = K_f m = 1.86\ ^\circ\text{C kg mol}^{-1} \times 0.68\ \text{mol kg}^{-1} = 1.26\ ^\circ\text{C}.$$

Therefore, freezing point depression of methyl alcohol solution is 1.26 °C.

Example 2.6

Determine the freezing point of an aqueous solution containing 468 g of sucrose ($C_{12}H_{22}O_{11}$) in 350 g of water (K_f for water = 1.86 °C kg mol^{-1}).

Solution

Data given:

Mass of sucrose = 468 g

Mass of water 350 g

K_f for water = 1.86 °C kg mol^{-1}

$$\text{Moles of solute} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} = \frac{468\ \text{g}}{342\ \text{g mol}^{-1}} = 1.3684\ \text{mol of solute}$$

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}} = \frac{1.3684\ \text{mol}}{350\ \text{g}} \times \frac{1000\ \text{g}}{1\ \text{kg}} = 3.91\ \text{mol kg}^{-1}$$

$$\Delta T_f = K_f\ m = 1.86\ ^\circ\text{C kg mol}^{-1} \times 3.91\ \text{mol kg}^{-1} = 7.27\ ^\circ\text{C}$$

$$\Delta T_f = T_{\text{pure solvent}} - T_{\text{solution}} \Rightarrow T_{\text{solution}} = T_{\text{pure solvent}} - \Delta T_f$$

$$T_{solution} = 0.00\,°C - 7.27\,°C = -7.27\,°C$$

Therefore, the freezing point of an aqueous solution is $-7.27\,°C$.

The relationship between freezing points and melting points

Melting point is the temperature at which the solid substance melts. At this temperature, the solid phase and liquid phase are at equilibrium. The transitions between the solid and liquid phases is very sharp for small samples of pure substances where melting points can be measured to 1 °C. The substance can exist as either a solid or liquid at a particular temperature. A substance exists as a solid at the temperature below the melting point or freezing point and as a liquid at the temperature above the melting point or freezing point. Since the transition between liquid and solid is very sharp, the melting point of a solid substance is considered the same as the freezing point of the corresponding liquid.

Exercise 2.3

1. Ethanoic acid has a freezing point of 16.63 °C. On adding 2.5 g of an organic solute to 40 g of the acid, the freezing point was lowered to 15.48 °C. Calculate the relative molecular mass of the solute.
   (K_f for ethanoic acid = 3.9 °C/*m*)
2. Salts such as NaCl or $CaCl_2$ are spread on ice-covered roads or sidewalks during winter. Explain.
3. How many grams of ethylene glycol ($C_2H_6O_2$), a non-electrolyte anti-freeze, must be added to 4000 g of water to reduce the melting point to -40 °C? (K_f for water = 1.86 °C/*m*).
4. Ethylene glycol is an anti-freeze in car radiators in cold climates. How much ethylene glycol should be added to 1 kg of water to prevent it from freezing at -10 °C? The molal depression constant for water is $1.86\,°C\,kg\,mol^{-1}$.
5. A solution is made by mixing 45 g of ethylene glycol ($C_2H_6O_2$) with 600 g of water. Evaluate the freezing point depression and freezing point of the solution (K_f for water = 1.86 °C/*m*).
6. The melting point constant for benzene is 4.90 °C/*m* and the normal melting point of benzene is 5.50 °C. Calculate the melting point of a solution of 9.30 g of sucrose, a non-electrolyte solute in 250 g of benzene.

2.2.4 Osmotic pressure

Task 2.2

Use online resources to study the process of water purification.

A cook can tell why salt is not added to the pot at the start of cooking beans. The obvious reason is that the beans will take a long time to cook. What happens when a peeled potato with a depression at the top containing salt is immersed in a solution containing pure water? The salt will dissolve and increase the water level in the depression, suggesting that there is a net movement of water through the potato to the salt solution through the process called osmosis.

Osmosis is the movement of solvent molecules from an area of the dilute solution to an area of concentrated solution through a semi–permeable membrane. The concept of osmosis can be understood by considering Figure 2.4. This figure separates two sides by a semi–permeable membrane. One side consists of a dilute solution, and the other contains a concentrated solution. With time, the volume of the concentrated solution will increase while that of the dilute solution will decrease. The small pores of the semi-permeable membrane allow the solvent molecules to pass on either side of the membrane but not the larger solute molecules. Because of the presence of solute and fewer solvent molecules in the concentrated solution, the chance of the solvent molecules touching the semi–permeable membrane is low. Therefore, fewer solvent molecules leave the concentrated solution side to enter the dilute solution side at a given time than the solvent molecules entering the concentrated solution. As a result, there is a net flow of solvent molecules into the concentrated solution, which increases the volume of the concentrated solution, thereby diluting it.

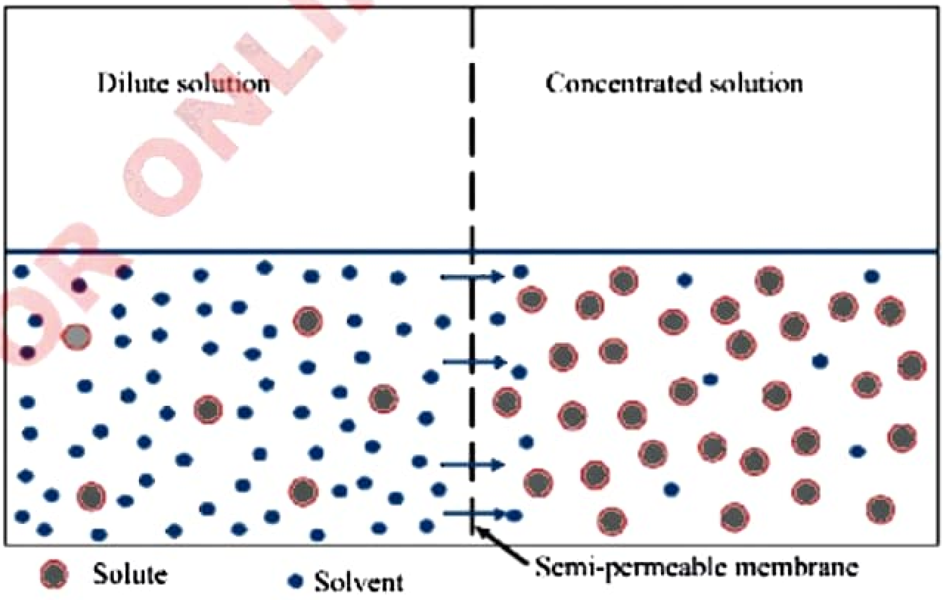


Figure 2.4: *Osmosis process*

Suppose a pressure greater than that leading to osmosis is applied on the concentrated solution side, the flow of solvent into the concentrated solution will stop. The pressure which is applied on the side of a concentrated solution to stop the net flow of the solvent into the concentrated solution through a semi-permeable membrane is called *osmotic pressure*. Recall that because of osmosis, there is a difference between the level of liquid in dilute solution and in the concentrated solution separated by a semi–permeable membrane. The difference in liquid level results in a pressure difference, which pushes the solvent molecules from the concentrated solution back to the dilute solution through the semi-permeable membrane. An equilibrium is reached when the flow rate of the solvent molecules from the dilute solution to the concentrated solution is the same as that from the concentrated solution back to the dilute solution as indicated by two arrows pointing at each direction (Figure 2.5). Therefore, such a pressure difference is the osmotic pressure.

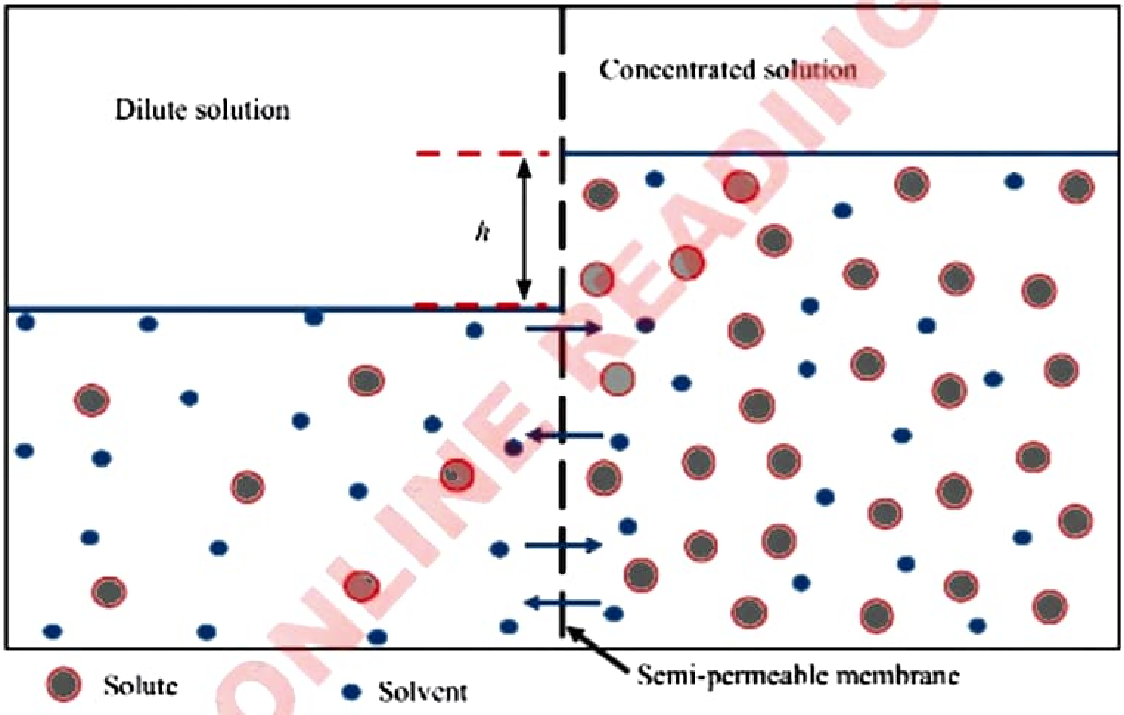


Figure 2.5: *Equilibrium between solvent and solution*

According to Figure 2.5, the pressure created by the difference in heights (h) of two liquids is the osmotic pressure. The value of osmotic pressure is equivalent to the external pressure which is applied to restore the liquid into the same level while maintaining the equilibrium as shown in Figure 2.6.

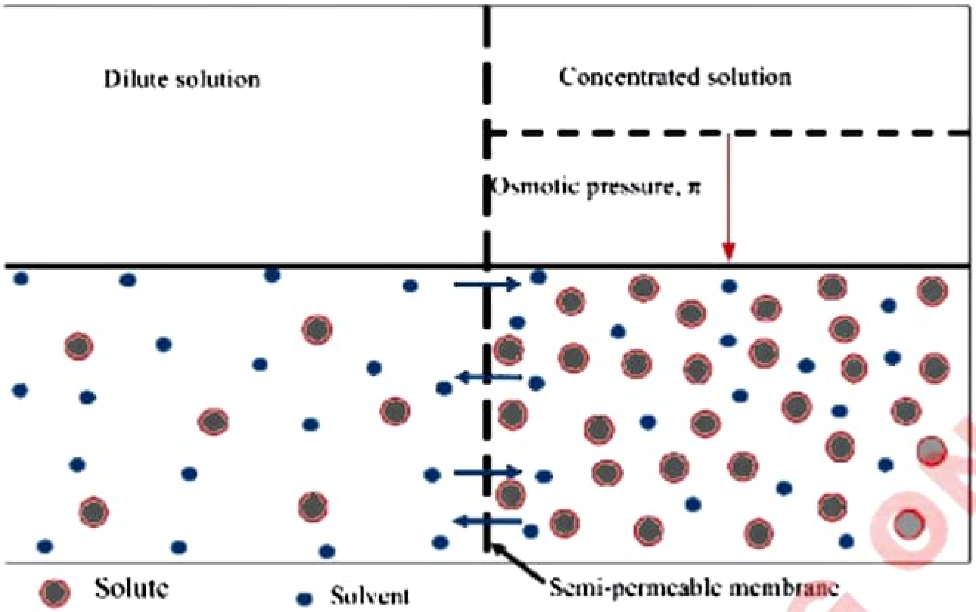


Figure 2.6: *External pressure applied to restore the level of liquids*

The van't Hoff's law of osmotic pressure

Quantification of the osmotic pressure on solutions can be seen from the work of the Dutch Chemist, Jacobus Henricus van't Hoff (1852–1911), in the law called the *van't Hoff's law of osmotic pressure*. The law states that the magnitude of osmotic pressure is proportional to the number of solute particles present in a given volume of solution.

Mathematically,

$$\pi \propto \frac{n_{\text{solute}}}{V_{\text{solution}}}$$

The number of particles per unit volume is equal to molarity (M). Therefore,

$$\pi \propto M \Rightarrow \pi = kM$$

where k is a proportionality constant which is equal to gas constant (R) times the absolute temperature T, that is $k = RT$.

Therefore,

$$\pi V = nRT \qquad (2.12)$$

This is called the *van't Hoff's Equation* which is derived from van't Hoff's law of osmotic pressure and is analogous to the ideal gas equation $PV = nRT$.

The van't Hoff's law of osmotic pressure is related to the gas laws that were discussed in Chapter One.

The van't Hoff – Boyle's law

The van't Hoff – Boyle's law states that the osmotic pressure (π) of a dilute solution is directly proportional to its molar concentration (M) at constant temperature or inversely proportional to the volume of the solution provided that temperature and number of moles remain constant.

Mathematically,

$$\pi \propto M \ (T \text{ constant})$$

$$\text{Molar concentration } (M) = \frac{\text{number of moles of solute } (n)}{\text{Volume of solution } (V)}$$

Therefore,

$$\pi \propto \frac{n}{V} \ (T \text{ constant}) \text{ or}$$

$$\pi \propto \frac{1}{V} \ (T, n \text{ constant})$$

$$\pi = \frac{k}{V} \Rightarrow \pi V = k$$

The above equation is analogous to the Boyle's law $PV = k$.

The van't Hoff-Charles' law

The van't Hoff-Charles' law states that the osmotic pressure of a dilute solution is directly proportional to the absolute temperature provided that the concentration remains constant.

Mathematically,

$$\pi \propto T (M \text{ constant})$$

$$\pi = kT \Rightarrow \frac{\pi}{T} = k$$

where k is the proportionality constant. This equation is similar to the Charles' law, $\left(k = \frac{V}{T}\right)$ in which the osmotic pressure is related to volume.

The van't Hoff – Avogadro's law

The van't Hoff – Avogadro's law states that two solutions of equal concentrations of different solutes exert the same osmotic pressure at the same temperature.

From $\pi V = nRT$,

For two sets of solutions 1 and 2,

$$\pi_1 V_1 = n_1 RT_1 \quad \text{and} \quad \pi_2 V_2 = n_2 RT_2$$

where n_1 and n_2 are the numbers of moles of solutes 1 and 2, and V_1 and V_2 are volumes in litres of solutions 1 and 2, respectively. If $\pi_1 = \pi_2$, $T_1 = T_2$ and $V_1 = V_2$, then from van't Hoff's Equation:

$$n_1 = n_2$$

Thus, when temperature and osmotic pressure are kept constant, equal volumes of solutions will contain equal number of moles of the solute (Avogadro's law).

Example 2.7

A sugar solution with a concentration of 2.5 g dm^{-3} gave an osmotic pressure of 8.3×10^{-4} atm at 25 °C. Calculate the molar mass of the solute.

Solution

Data given:

Temperature, $T = 25\ ^\circ\text{C} = (25 + 273)\ \text{K} = 298\ \text{K}$, $R = 0.08215\ \text{L atm mol}^{-1}\ \text{K}^{-1}$

$$\pi V = nRT = \frac{\text{m}}{\text{M}} RT \text{ therefore, } \text{M} = \frac{\text{mRT}}{\pi V}$$

$$\text{M} = \frac{\text{m}RT}{\pi V} = \frac{2.5\,\text{g} \times 0.0821\ \text{L atm mol}^{-1}\text{K}^{-1} \times 298\,\text{K}}{8.3 \times 10^{-4}\ \text{atm} \times 1\,\text{L}} = 7.37 \times 10^{4}\ \text{g mol}^{-1}$$

Therefore, the molar mass of the solute is 7.37×10^4 g mol^{-1}.

2.3 Abnormal molecular masses

You have seen in the previous sections that colligative properties such as lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure exist in dilute solutions of non-electrolytes. In these solutions, the solutes remain in normal molecular conditions and neither undergo dissociation nor association. A good example is the solution of urea and glucose in water. Recall that colligative properties of solutions of non-volatile electrolyte solutes depend on the actual number of solute particles present in the solution, hence, the molecular mass of solute. The mathematical relations show that the colligative property is inversely proportional to the molecular mass of a solute.

This value of the molecular mass of the solute is theoretical.

For solutions of electrolytes, the values of the observed colligative properties can either be higher or lower than the theoretically expected value because the electrolyte solutes such as acid, base or salt can undergo dissociation or association when dissolved in a solvent.

When a solute undergoes dissociation, the number of particles in the form of ions is more than the ones actually dissolved. This increase in the number of particles increases the value of colligative properties. If the dissociation produces 2, 3, 4 and so on ions, the observed molecular mass becomes $\frac{1}{2}, \frac{1}{3}, \frac{1}{4}$ and so on of the theoretical molecular mass of electrolyte solute. When the solutes associate together to form large aggregate molecules, the effective number of particles of the solute in the solution decreases. As a result, the observed molecular mass is double, triple and so on the theoretical molecular mass. In general, the dissociation of solutes lowers the observed molecular mass and the association increases the observed molecular mass of the solutes, and these observed molecular masses together are called *abnormal molecular masses*.

2.3.1 Osmotic pressure of electrolytes

The observed osmotic pressure of the electrolyte solutes (π) in aqueous solution is higher than the osmotic pressure calculated using van't Hoff's equation $\pi_o V = n_o RT$.

From the van't Hoff's Equation,

$$\pi_o V = n_o RT$$

$$\pi_o = \frac{n_o RT}{V} \text{ for non-electrolytes}$$

$$\pi V = nRT$$

$$\pi = \frac{nRT}{V} \text{ for electrolytes}$$

$$\pi > \pi_o \text{ because } n_o < n$$

where n_o is the number of moles of non-electrolyte solutes and n is the number of moles of electrolyte solute which dissociates to give a large number of particles.

The ratio between the observed osmotic pressure of electrolytes (π) and the calculated osmotic pressure (π_o) is called the *van't Hoff's factor, i*.

The van't Hoff's factor is expressed as:

$$i=\frac{\pi}{\pi_o}=\frac{\text{moles of particles in solution}}{\text{moles of particles in formula units dissolved}}$$

As a result, the van't Hoff's Equation for electrolyte solutions becomes $\pi = iMRT$.

Due to the dissociation of electrolytes in the solution, the total number of particles increases compared to the number of particles in the absence of dissociation. Therefore, the van't Hoff's factor can also be expressed as:

$$i=\frac{\pi}{\pi_o}=\frac{\text{Actual number of particles in solution after dissociation}}{\text{Number of particles in absence of dissociation}}$$

Consider the dissociation of electrolyte AB in which the degree of dissociation is represented by symbol α.

$$\begin{array}{lll} \mathrm{AB} \rightleftharpoons & \mathrm{A}^{+}(aq) + & \mathrm{B}^{-}(aq) \\ 1-\alpha & \alpha & \alpha \end{array}$$

The total number of moles of particles in aqueous solution will be $1-\alpha+\alpha+\alpha=1+\alpha$ compared to 1 mole of particles before dissociation.

Therefore,

$$i=\frac{\pi}{\pi_o}=\frac{1+\alpha}{1}=1+\alpha$$

The value of i will be greater than one and less than two because α must be less than one.

Note: $i>1$ means electrolytes undergo dissociation in the solution.

$i<1$ means electrolytes undergo association in the solution.

$i=1$ means electrolytes undergo neither dissociation nor association.

Example 2.8

The osmotic pressure of equimolal solutions of $CaCl_2$ and sucrose at 298.15 K are 0.605 atm and 0.224 atm, respectively. Calculate the van't Hoff's factor and the degree of dissociation of $CaCl_2$.

Solution

Data given:

$\pi = 0.605$ atm and $\pi_o = 0.224$ atm

$$i = \frac{\pi}{\pi_o} = \frac{0.605 \text{ atm}}{0.224 \text{ atm}} = 2.70$$

Therefore, van't Hoff's factor (i) is equal to 2.7.

Let α be the degree of dissociation of $CaCl_2$

$$\begin{array}{ccc} CaCl_2(aq) & \rightleftharpoons & Ca^{2+}(aq) + 2Cl^-(aq) \\ 1-\alpha & & \alpha \qquad\quad 2\alpha \end{array}$$

The total number of particles $= 1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha$.

Then,

$$i = \frac{1+2\alpha}{1} = 1 + 2\alpha = 2.7$$

$$\alpha = \frac{2.7-1}{2} = 0.85$$

Therefore, the degree of dissociation of $CaCl_2$ is 0.85 or 85%.

Example 2.9

Calculate the osmotic pressure of an aqueous solution of $BaCl_2$ at 298 K containing 0.39 g in 60 mL solution. The degree of dissociation of salt is 60% (Ba = 137; Cl = 35.5).

Solution

Data given:

Temperature = 298 K

Mass of $BaCl_2$ = 0.39 g

Volume = 60 mL

For an electrolyte solution, the van't Hoff's equation is:

$$\pi = iMRT$$

where i is the van't Hoff's Factor.

$$\text{Volume} = 60 \text{ mL} = 60 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.06 \text{ L}$$

$$\text{Molarity} = \frac{\text{mass (g)}}{\text{molar mass (g mol}^{-1}) \times \text{volume (L)}}$$

$$\text{Molarity} = \frac{0.39\text{ g}}{208\text{ g mol}^{-1} \times 0.06\text{ L}} = 0.03125\text{ mol L}^{-1}$$

From the dissociation equation of $BaCl_2$

$$\begin{array}{ccc} BaCl_2(aq) & \rightleftharpoons & Ba^{2+}(aq) + 2Cl^{-}(aq) \\ 1-\alpha & & \alpha \qquad\qquad 2\alpha \end{array}$$

Total number of particles in electrolytes is equal to $1-\alpha+\alpha+2\alpha = 1+2\alpha$

$$i = \frac{1+2\alpha}{1} = 1+2\alpha$$

Since α is equal to 60% or 0.6,

$$i = \frac{1+2\times0.6}{1} = 2.2$$

From:

$$\pi = iMRT = 2.2 \times 0.0313\text{ mol L}^{-1} \times 0.0821\text{ L atm mol}^{-1}\text{K}^{-1} \times 298\text{ K} = 1.68\text{ atm}$$

Therefore, the osmotic pressure of an aqueous solution of $BaCl_2$ is 1.68 atm.

2.3.2 Freezing point depression and Blagden's law

In 1788, Sir Charles Brian Blagden (1948 – 1820), a British physician, studied the effects of dissolved inorganic solutes in the freezing point depression of water. He revealed that the dissolved inorganic solutes like salts affect the freezing point of water. This discovery led to the formulation of *Blagden's law*. According to the law, the depression of freezing point of a dilute solution is directly proportional to the concentration of the dissolved solutes.

Mathematically,

$$\Delta T_f = K_f m i$$

where:

ΔT_f = freezing point depression.

K_f = freezing point constant called cryoscopic constant.

m = Molality

i = van't Hoff's factor (the number of ions particles formed)

Example 2.10

A solution of 20 g sodium chloride is added to 200 g of water to depress the freezing point. Calculate the freezing point depression of the solution; given that, K_f of water = 1.86 °C/*m*.

Solution

Data given:

Mass of solute = 20 g

Mass of solvent = 200 g

K_f of water = 1.86 °C/*m*

Using Blagden's Law:

$$\Delta T_f = K_f \, m \, i$$

$$\text{Molality } (m) = \frac{\text{number of moles of solute}}{\text{mass of solvent (kg)}}$$

$$\text{But, number of moles of solute} = \frac{\text{mass of solute (g)}}{\text{molar mass of solute (g/mol)}}$$

$$= \frac{20.0 \text{ g}}{58.5 \text{ g/mol}}$$

$$= 0.342 \text{ mol}$$

$$\text{Then, molality} = \frac{0.342 \text{ mol}}{0.2 \text{ kg}}$$

$$= 1.71 \text{ mol/kg}$$

Consider dissociation of NaCl solution:

$$\text{NaCl}(aq) \longrightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)$$

Then, the number of ionic particles formed (i) = 2

From $\Delta T_f = K_f mi$

$$\Delta T_f = 1.86 \text{ °C}/m \times 1.71 \text{ mol/kg} \times 2$$

$$= 6.36 \text{ °C}$$

Therefore, the freezing point of sodium chloride solution is 6.36 °C.

Generally, to obtain colligative property of ionic solutions, multiply the van't Hoff's factor (i) in each of the following equations:

Vapour pressure lowering $(\Delta P) = i\chi_{\text{solute}}P^{\circ}_{\text{Solvent}}$

Freezing point depression $(\Delta T_{\text{f}}) = imK_{\text{f}}$

Boiling point elevation $(\Delta T_{\text{b}}) = imK_{\text{b}}$

Osmotic pressure $(\pi) = iMRT$

Task 2.3

Review literature (from various sources) on creating coolants for various household uses. Compile a report and share it with your peers. Submit the **report** to your subject teacher for evaluation.

Exercise 2.4

1. How is the concept of osmotic pressure utilised in medical treatment such as dialysis?
2. Explain how osmotic pressure plays a role in the absoption of water by plant roots.
3. If a solution containing 30.0 g L^{-1} of protein has a measured osmotic pressure of 9.4 Torr at 25 °C, calculate the molar mass of the protein.
4. Haemoglobin is a large molecule that carries oxygen in human blood. A water solution that contains 0.263 g of haemoglobin in 10.0 mL of solution has an osmotic pressure of 7.51 Torr at 25 °C. Calculate the molar mass of haemoglobin.
5. Calculate the concentration in mol/L of non-electrolyte solutes in a human body if the osmotic pressure of human blood is 7.3 atm at a body temperature of 37 °C.
6. How many grams of glucose $(C_6H_{12}O_6)$ per litre should be used for an intravenous solution to match the 7.65 atm osmotic pressure of blood at 37 °C?
7. The osmotic pressure of 0.01 M potassium iodide (KI) solution at 25 °C is 0.465 atm. Calculate the van't Hoff's factor for KI at this concentration.

Revision exercise 2

1. Propose a laboratory activity to demonstrate the concept of vapour pressure lowering using everyday materials. Describe how you would measure and analyse the results.

2. Evaluate the limitations of colligative properties for determining molecular weight or concentration of solutes in real-world scenarios.

3. How are colligative properties applicable in food preservation?

4. The vapour pressure of water at 25.0 °C is 23.8 Torr. What is the vapour pressure of a solution of 10.0 g of glucose ($C_6H_{12}O_6$, 180.2 g mol^{-1}) dissolved in 100.0 g of water?

5. Ethylene glycol ($C_2H_6O_2$) is a common automobile anti–freeze. It is water soluble and relatively non-volatile, with a boiling point of 197 °C. Calculate the freezing point of a solution containing 651 g of this substance in 2505 g of water (K_f of water =1.86 °C/*m*).

6. Pure toluene (C_7H_8) has a normal boiling point of 110.60 °C. A solution of 7.80 g of anthracene ($C_{14}H_{10}$) in 100.0 g of toluene has a boiling point of 112.06 °C.

   (a) What is the molality of the solution?

   (b) What is the molal boiling point elevation constant for toluene?

7. A 2.60 g sample of a compound known to contain only indium and chlorine is dissolved in 50.0 g of tin (IV) chloride (K_b = 9.43 °C/*m*). The normal boiling point is raised from 114.1 °C for pure $SnCl_4$ to 116.3 °C for the solution. What is the molecular weight and probable molecular formula for the solute?

8. A solution of glucose (molar mass = 180.18 g mol^{-1}) in 500 g of water had a boiling point of 102.25 °C. Given K_b of water = 0.512 °C/*m*;

   (a) What is the molality of the solution?

   (b) How many moles of glucose were added?

   (c) How many grams of glucose were added?

9. An aqueous solution was found to have a freezing point of –2.15 °C. What was the molality of the solution? (Given K_f of water = 1.86 °C/*m*).

10. The freezing point depression of a 0.10 *m* aqueous solution of HF is – 0.201 °C. Calculate the percentage dissociation of HF(*aq*) (Given K_f of water = 1.86 °C/*m*).

11. What is the molarity of a solution in which the osmotic pressure is 80.7 atm at 27 °C? Assume the solute is a non-electrolyte.

12. At what temperature in Celsius would the osmotic pressure be 347.5 kPa to stop osmosis if there were 24.37 g of glucose (molar mass =180.18 g mol^{-1}) dissolved in enough water to make a 1.00 L solution?

13. An aqueous solution contains 3.00% by mass phenylalanine ($C_9H_{11}NO_2$) (molar mass =165.21 g mol^{-1}) at 25.0 °C. Assume phenylalanine is non-ionic and non–volatile and that the density of the solution is 1.00 g/mL (Given K_f of water = 1.86 °C/*m*, K_b of water = 0.512 °C /*m*). Calculate the following:
    (a) The freezing point of the solution (T_f)
    (b) The boiling point of the solution (T_b)
    (c) The osmotic pressure of the solution (π)

Chapter Three

Two-component liquid systems

Introduction

*The preceding chapter focused on the properties of solutions that do not depend on the identity of particles but only on their relative concentrations. This chapter focuses on the properties of the liquid mixtures that depend on the identity of the individual components. In this chapter, you will learn about completely miscible liquids, immiscible liquids, and the distribution of solutes in immiscible solvents. The competencies developed will enable you to **apply steam** distillation, solvent extraction, and chromatography in the extraction, separation and purification of substances in everyday life.*

Think

Liquid systems with unknown behaviour.

3.1 Completely miscible liquids

Miscible liquids dissolve completely in one another in all proportions to form a homogeneous solution. The resulting solution can be ideal or non-ideal depending on the strength of intermolecular forces of attraction between the components involved in forming the solution.

Task 3.1

Use online resources such as scientific databases, research articles, educational websites, and interactive simulations to study the interactions in two-component liquid systems and the way they affect the system's behaviour.

3.1.1 Formation of miscible liquid mixture

Miscible liquids are formed between compounds which have similar types of intermolecular forces. For example, ethanol and water are miscible because they can form hydrogen bonds with each other. Likewise, ethane (C_2H_6) and propane (C_3H_8) are miscible because they both exhibit dispersion forces. An illustration of the formation of a miscible liquid mixture is shown in Figure 3.1.

Figure 3.1: *The formation of miscible liquid mixture*

3.1.2 Ideal solutions

An ideal solution is one that is made from entirely miscible liquids whose intermolecular forces are the same as the intermolecular forces within the liquids involved in forming the solution. An ideal solution obeys *Raoult's law* which states that the partial vapour pressure of a volatile component of an ideal solution is equal to the vapour pressure of the pure component multiplied by its mole fraction in the solution.

For an ideal solution formed by liquids A and B,

$$P_A = \chi_A \times P_A^o \quad \text{and} \quad P_B = \chi_B \times P_B^o \tag{3.1}$$

where,

P_A and P_B are the partial vapour pressures of components A and B over the solution.

χ_A and χ_B are the mole fractions of components A and B in the solution.

P_A^o and P_B^o are the vapour pressures of pure components A and B.

According to *Dalton's law of partial pressure*, the total vapour pressure above the solution containing the volatile components A and B is the sum of the partial vapour pressures of the two components:

$$P_T = P_A + P_B \tag{3.2}$$

Figure 3.2 illustrates the partial and total vapour pressures of the components of an ideal solution.

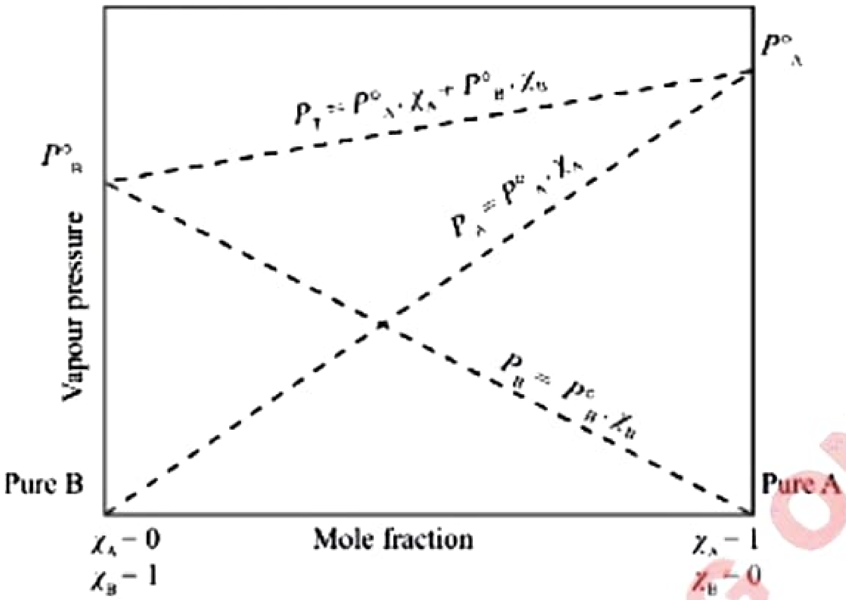


Figure 3.2: *Partial and total vapour pressures of the components of ideal solution*

From Figure 3.2, pure component A has more vapour pressure than pure component B. This implies that component A is more volatile than component B. As the mole fraction of component A (χ_A) increases from zero to one, the corresponding partial vapour pressure increases, accompanied by a decreasing vapour pressure of component B. Similarly, when the mole fraction of component B (χ_B) increases, the corresponding partial vapour pressure also increases. Once an equilibrium is reached, the total vapour pressure is obtained as the sum of the partial vapour pressures of the components A and B:

$$P_T = \chi_A \times P^\circ_A + \chi_B \times P^\circ_B = P_A + P_B \tag{3.3}$$

Properties of ideal solutions

The following are the properties of ideal solutions:

(a) Ideal solutions obey Raoult's law at any concentration.

(b) Heat is neither evolved nor absorbed during the mixing of the liquid components to form an ideal solution. Therefore, the heat change is equal to zero.

(c) The total volume of the solution is equal to the sum of the volumes of the liquid components. In other words, the volume change is equal to zero.

(d) The sum of the partial vapour pressures of the components, say A and B, is equal to the total vapour pressure of the solution.

(e) The forces of interactions in individual components (A – A) and (B – B) are the same as the interactive forces in the solution (A – B); in other words, A and B are identical in shape, size, and character.

Examples of ideal solutions include the solutions of benzene and toluene, *n*-hexane and *n*-heptane, chlorobenzene and bromobenzene, and *n*-butylchloride and *n*-butylbromide.

3.1.3 Non-ideal solution

A *non-ideal solution* is a solution that is made from completely miscible liquids whose intermolecular forces of attraction are different from the intermolecular forces of the liquid components that form the solution. In other words, the A – A or B – B interactions differ from A – B interactions. Non-ideal solutions do not obey Raoult's law. Therefore, these solutions are said to exhibit deviations from the Raoult's law such that:

$$P_A \neq \chi_A \times P_A^\circ \text{ and } P_B \neq \chi_B \times P_B^\circ$$

The deviations from Raoult's law can be positive or negative depending on the strength of the interactions in the resulting solution compared to those in individual components.

Positive deviation from Raoult's law

Positive deviation from Raoult's law occurs when the intermolecular forces of attraction between particles in the solution (A – B) are less than those in pure components (A – A or B – B). Due to weaker intermolecular forces of attraction in the solution than in pure liquids, the solution tends to form vapour more than any of the individual components. Therefore, the vapour pressure above the solution is higher than expected from Raoult's law. This occurs when a polar molecule is mixed with a non-polar molecule. Two liquids that show positive deviation from Raoult's law in solution form vapour pressures at low temperatures. Examples of non-ideal solutions which show positive deviations from Raoult's law include the solutions of acetone (C_3H_6O) and ethanol (C_2H_5OH), acetone and carbon disulfide (CS_2), water (H_2O) and methanol (CH_3OH), carbon tetrachloride (CCl_4) and toluene ($C_6H_5CH_3$), and cyclohexane (C_6H_{12}) and ethanol.

Properties of non-ideal solutions with positive deviation from Raoult's law

The following are the properties of non-ideal solutions which exhibit a positive deviation from Raoult's law:

(a) The solutions do not obey Raoult's law at any concentration.

(b) Heat is absorbed during mixing of the liquid components to form a solution. Therefore, the heat change is greater than zero (endothermic).

(c) The total volume of the solution is increased. Therefore, the volume change is greater than zero.

(d) The partial vapour pressures of the components, say A and B, are greater than the products of their mole fractions and their vapour pressures when pure, i.e.,

$$P_A > \chi_A \times P_A^o \text{ and } P_B > \chi_B \times P_B^o \text{ Therefore, } P_A + P_B > \chi_A \times P_A^o + \chi_B \times P_B^o$$

(e) The forces of attraction between molecules in the solution (A – B) are weaker than those in pure components (A – A or B – B).

An illustration of the positive deviation from Raoult's law by non-ideal solutions is shown in Figure 3.3.

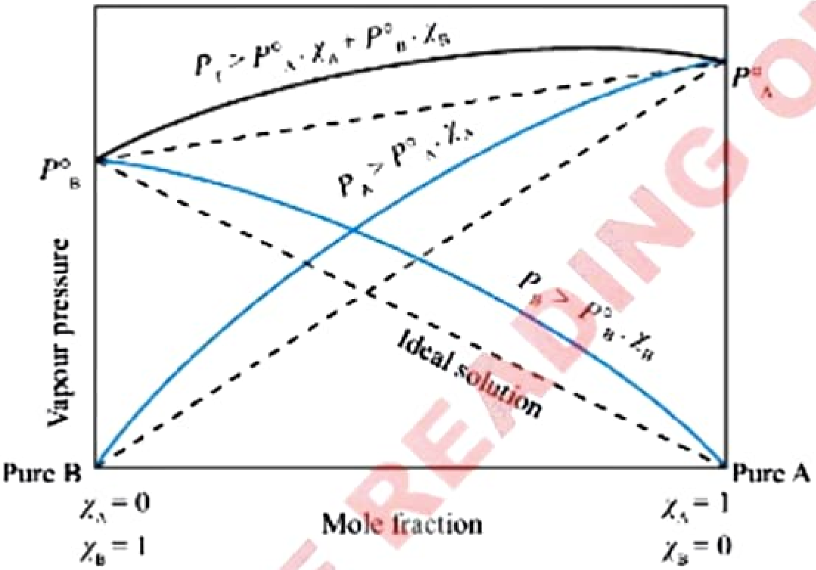
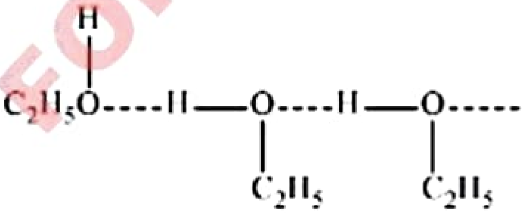


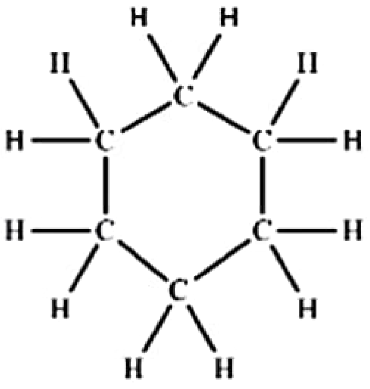
Figure 3.3: *Positive deviation from Raoult's law by non-ideal solution*

For further explanation of the positive deviation from Raoult's Law, consider a solution of ethyl alcohol (ethanol) and cyclohexane.



$$C_2H_5\overset{\displaystyle H}{\overset{|}{O}}\text{----}H-\underset{\underset{\displaystyle C_2H_5}{|}}{O}\text{----}H-\underset{\underset{\displaystyle C_2H_5}{|}}{O}\text{-----}$$

ethanol molecules



cyclohexane

In ethanol, the molecules are held together by hydrogen bonds. When cyclohexane is added to ethanol, cyclohexane molecules tend to occupy spaces between ethanol molecules. As a result, some hydrogen bonds in ethanol molecules break and weaken their attractive forces. Breaking the hydrogen bonds involves absorbing specific amounts of energy; therefore, the dissolution process is endothermic ($\Delta H_{mix} > 0$). In this process, there is an increase in volume ($\Delta V_{mix} > 0$) and a slight increase in vapour pressure.

Negative deviation from Raoult's law

Negative deviation from Raoult's law occurs when the intermolecular forces of attraction between molecules in the solution (A – B) are stronger than those between pure components (A – A or B – B). Stronger intermolecular forces in a solution rather than in pure liquids make the solution to have less tendency of forming vapour pressure than pure components. This means that the escaping tendency of A and B molecules from the solution becomes less than from pure liquids because much energy must be supplied to break the attractive forces and set the molecules free. Because of that, the solution has lower total vapour pressure than expected from Raoult's law. Such solutions form vapour pressure at higher temperatures than that of pure components.

Examples of non-ideal solutions which show negative deviations from Raoult's law include the solutions of acetone (C_3H_6O) and chloroform ($CHCl_3$), nitric acid (HNO_3) and water (H_2O), acetic acid ($C_2H_4O_2$) and pyridine (C_5H_5N), and chloroform and benzene (C_6H_6).

Properties of non-ideal solutions with negative deviation from Raoult's law

The following are the properties of non-ideal solutions which exhibit negative deviations from Raoult's law:

(a) The non-ideal solutions do not obey Raoult's law at any concentrations.

(b) During mixing of liquid components to form a solution, heat is evolved. Therefore, the heat change is less than zero (exothermic).

(c) The total volume of the solution is decreased; therefore, the change in volume is less than zero ($\Delta V_{mix} < 0$).

(d) The partial vapour pressures of components A and B are less than the products of their mole fractions and the vapour pressures when pure.

$P_A < \chi_A \times P_A^o$ and $P_B < \chi_B \times P_B^o$. Therefore, $P_A + P_B < \chi_A \times P_A^o + \chi_B \times P_B^o$

(e) The forces of attraction between molecules in the solution (A–B) are stronger than those in the pure components (A–A or B–B).

An illustration of the negative deviation from Raoult's law by non-ideal solutions is shown in Figure 3.4.

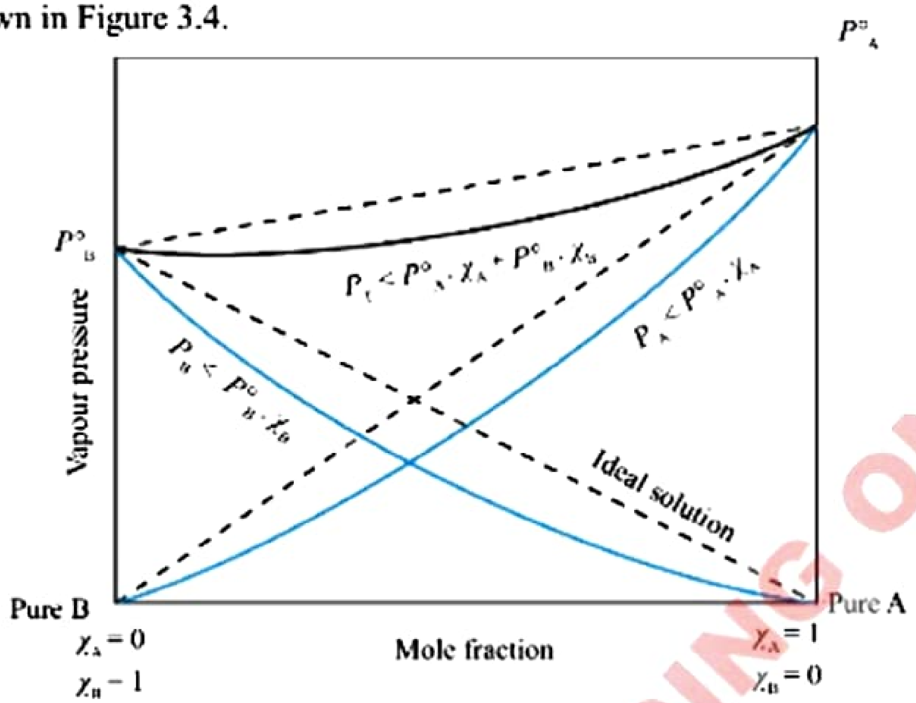
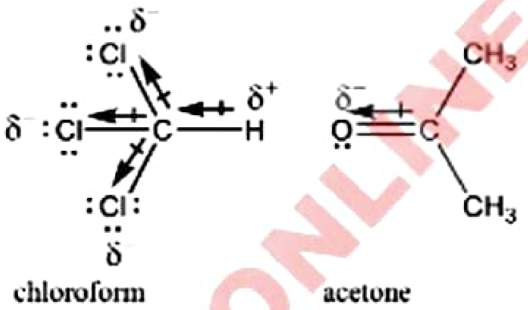
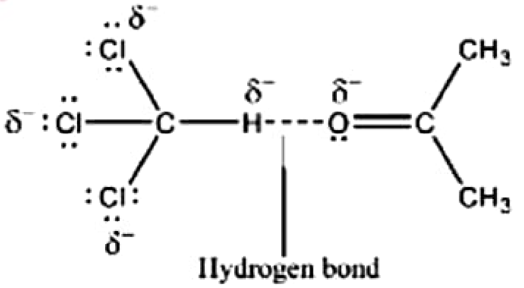


Figure 3.4: *Negative deviation from Raoult's law by non-ideal solution*

Negative deviation happens in two possible ways: dipole-dipole interactions and ionisation. Consider the solutions of acetone and chloroform as well as pyridine and acetic acid in which negative deviation occurs by dipole-dipole interactions.



Structure (a)

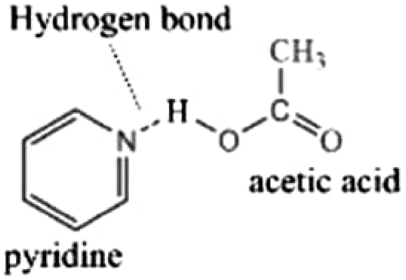


Structure (b)

In the case of acetone and chloroform solutions, three chlorine atoms in chloroform make the carbon atom partially positive (δ^+). As a result, electrons are withdrawn away from the bonding side between carbon and hydrogen (C–H), as shown in structure (a), thereby making the hydrogen partially positive (δ^+). Then, the partially positive hydrogen atom allows the partially negative oxygen atom (δ^-) on acetone to interact by forming a hydrogen bond, as shown in structure (b). The formed hydrogen bond is not as strong as in compounds like H_2O, NH_3, and HF.

The formation of hydrogen bond leads to the decrease in the volume ($\Delta V_{mix} < 0$) and the decrease in the vapour pressure than the expected for an ideal solution.

For pyridine and acetic acid solution, the effect of hydrogen bond is also observed.



Nitrogen atom in pyridine forms hydrogen bond with hydrogen atom in acetic acid.

Another way in which the negative deviation from Raoult's law occurs is the formation of ions in solutions. A good example is a solution of nitric acid (HNO_3) and water (H_2O). Both water and nitric acid react to form ions when mixed together and these ions interact by ionic bonds.

$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$

The resultant ionic attractions are greater than the attraction between pure water or pure nitric acid molecules. Hence, few molecules escape, leading to low vapour pressure.

Activity 3.1

Aim: To investigate positive and negative deviation from Raoult's law in non-ideal solutions

Requirements: Acetone, ethanol, water, methanol, cyclohexane, chloroform, nitric acid, sulfuric acid, hydrochloric acid, thermometers, beakers and 50-mL measuring cylinders

Procedure

1. Measure 10 mL of acetone, ethanol, water, methanol, cyclohexane, chloroform, hexane, sulfuric acid, and nitric acid, each in separate 100 mL beakers.
2. Record the temperature of each liquid.

3. Mix the liquids in (1) to form the following solutions:
    (a) Ethanol and hexane
    (b) Acetone and ethanol
    (c) Water and methanol
    (d) Acetone and chloroform
    (e) Cyclohexane and ethanol
    (f) Nitric acid and water
    (g) Water and sulfuric acid
4. Record the volume and the temperature of the solutions prepared in (3).

Questions

1. Which solution(s) obey(s) the Raoult's law?
2. Which solution(s) deviate(s) from Raoult's law? Specify the kind of deviation.
3. How might the deviations impact industrial processes or everyday applications involving liquid mixtures?

Large deviation from Raoult's law

Recall that non-ideal solutions deviate positively or negatively from Raoult's law due to the difference in intermolecular forces in the solution relative to pure liquid components. The mixtures that exert vapour pressures that are slightly greater than Raoult's law are said to show a positive deviation, and those that exert vapour pressures slightly less than that predicted by Raoult's law are said to show a negative deviation. However, under a slight deviation from Raoult's law, the highest vapour pressure at any composition is still the vapour pressure of the more volatile pure component.

Some liquid mixtures exhibit very large deviations from Raoult's law such that the curves become much distorted. For the case of a very large positive deviation, the vapour pressures of the solutions at some compositions are higher than the vapour pressure of even the more volatile pure component. That is, the maximum vapour pressure is no longer that of one of the pure liquids (more volatile liquids).

An illustration of large positive deviation from Raoult's law is shown in Figure 3.5. (Note: Only the total vapour pressure of a solution of components A and B is shown, not the partial vapour pressures).

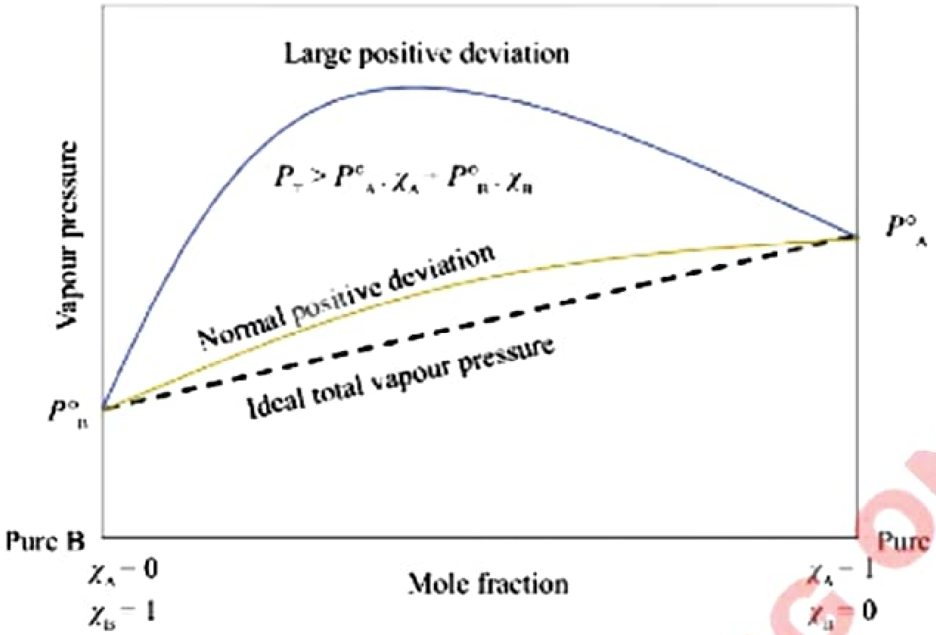


Figure 3.5: *Large positive deviation from Raoult's law*

The vapour pressure is much higher than the ideal in these mixtures. This means that intermolecular forces between molecules A and B are weaker than in pure liquids; therefore, they can easily be broken. For the case of very large negative deviations, the vapour pressures of the solutions at some compositions are lower than the vapour pressure of even the less volatile component when pure. That is, the minimum vapour pressure is no longer that of one of the pure liquids (less volatile liquid). An illustration of large negative deviation from Raoult's law is shown in Figure 3.6.

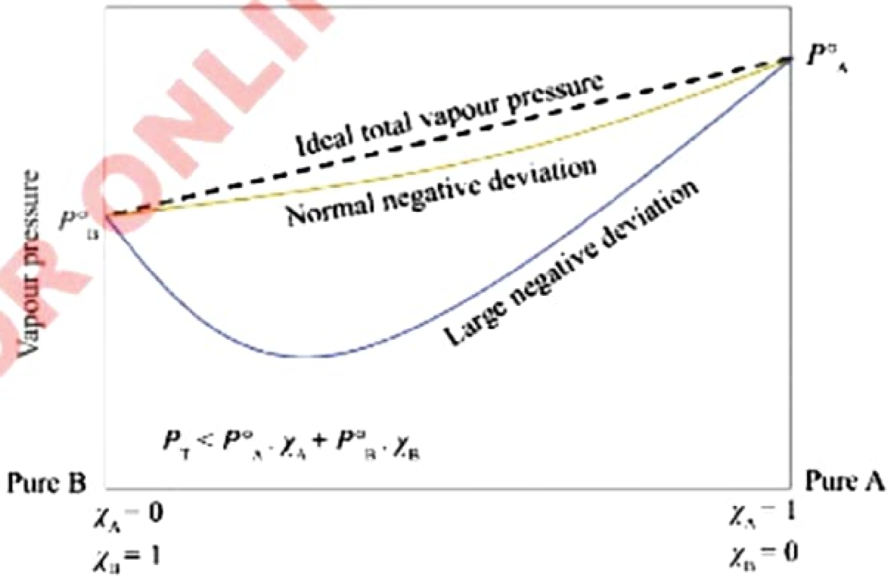


Figure 3.6: *Large negative deviation from Raoult's law*

In this case, only the total vapour pressure of components A and B is shown, and not the partial vapour pressures. Since the vapour pressure is much lower than that of the ideal solution in these mixtures, the intermolecular forces between molecules A and B are stronger than in pure liquids. Therefore, they are difficult to break.

Exercise 3.1

1. How does the understanding of ideal solutions contribute to the development of pharmaceutical formulations?
2. What factors influence the miscibility of liquids?
3. Which of the following substances would be the most soluble in CCl_4?
   (a) CH_3CH_2OH
   (b) H_2O
   (c) NH_3
   (d) $C_{10}H_{22}$
   (e) NaCl
4. Non-ideal solutions can introduce expected complexities into experimental setup or industrial processes. Explain.

Azeotropic mixtures

An *azeotropic mixture* is a mixture of liquids that boils at a constant temperature, behaves like a pure liquid, and exhibits the same composition in the liquid phase and the vapour phase. The boiling point of an azeotropic mixture is either higher or lower than the boiling point of the pure liquids that form the mixture.

Maximum boiling azeotropic mixture

The maximum boiling azeotropic mixture boils at a higher temperature than the boiling points of pure components, giving lower vapour pressure. An example of a maximum boiling azeotropic mixture is a mixture of water (H_2O) and nitric acid (HNO_3) with a composition of 32%:68%, respectively. An illustration of this azeotropic composition is shown in Figure 3.7.

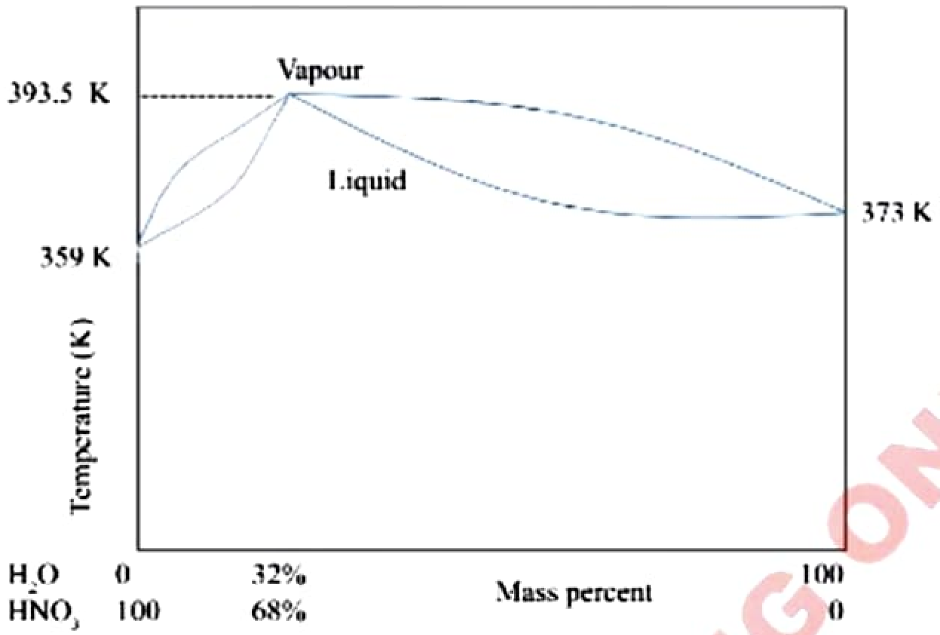


Figure 3.7: *Maximum boiling azeotropic mixture of nitric acid and water*

The boiling point of pure nitric acid (HNO_3) is 86 °C (359 K) and the boiling point of water (H_2O) is 100 °C (373 K). The liquid mixture with 32% H_2O and 68% HNO_3 has a boiling point of 120.5 °C (393.5 K). This boiling point is higher than that of pure components, and the liquid phase's composition is the same as in a vapour phase. The 32% H_2O and 68% HNO_3 form what is called a *maximum boiling azeotropic mixture*.

Minimum boiling azeotropic mixture

The minimum boiling azeotropic mixture boils at a lower temperature than the boiling points of pure components, giving higher vapour pressure. A good example of a minimum boiling azeotropic mixture is a mixture of ethanol (C_2H_5OH) and water (H_2O) with a composition of 95.6% and 4.4%, respectively. Figure 3.8 illustrates this azeotropic composition.

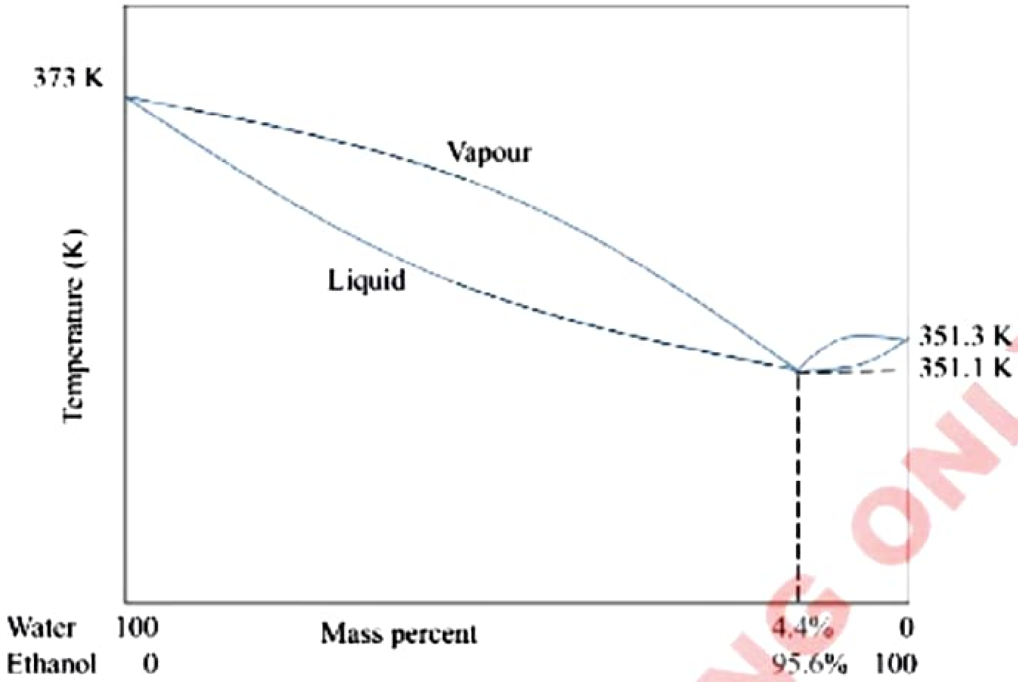


Figure 3.8: *Minimum boiling azeotropic mixture of water and ethanol*

The boiling point of pure water is 100 °C (373 K), and the boiling point of ethanol is 78.3 °C (351.3 K). The liquid mixture with 4.4% H_2O and 95.6% C_2H_5OH has a boiling point of 78.1 °C (351.1 K). This boiling point is lower than that of pure components, and the composition in the liquid phase is the same as that in the vapour phase. The 4.4% H_2O and 95.6% C_2H_5OH form what is called *minimum boiling azeotropic mixture.*

3.1.4 Separation of miscible liquid mixture by distillation

Task 3.2

Search on the internet or any other resources about useful products obtained by distillation and explain the principle behind their production.

Distillation is a method of separating and purifying liquid mixtures into their individual components based on their differences in boiling points. The distillation process involves heating a liquid mixture to form vapour and then condensing the vapour into liquid. The vapour composition will be richer in the more volatile component, which has a lower boiling point than the less volatile component. The composition of the condensed liquid will be the same as the composition of the vapour, which contains more volatile components. If the difference in the boiling points of the liquids is large, a simple distillation can be used. *Simple distillation* involves heating the liquid mixture to form vapour and condensing the vapour to form liquid. Illustrations of the simple distillation setup and the corresponding distillation curve are shown in Figures 3.9(a) and 3.9(b), respectively.

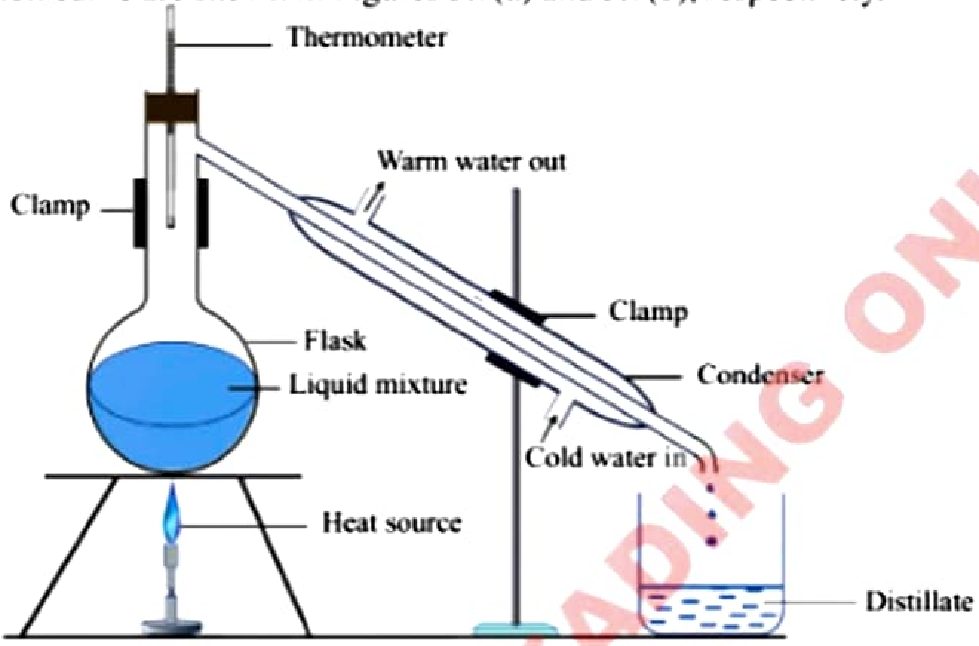


Figure 3.9 (a): *Simple distillation setup*

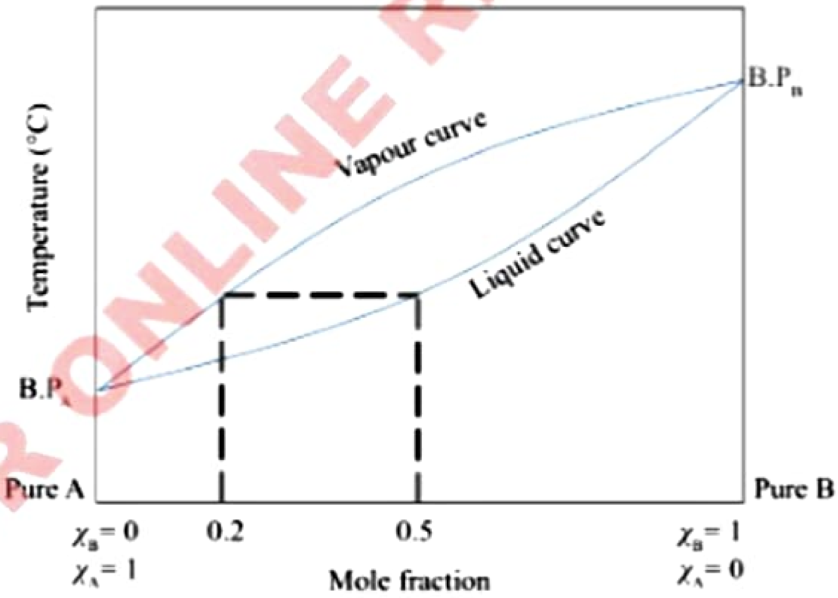


Figure 3.9 (b): *Distillation curve*

The distillation curve (Figure 3.9 (b)) shows that the liquid mixture consists of liquids A and B with 50% each. When this mixture is heated, the vapour composition consists of 0.8 (80%) of liquid A and 0.2 (20%) of liquid B. This implies that it is difficult to get pure liquid components by using simple distillation. In order to get pure liquid components from the mixture with high purity, successive reflux operations are required. This can be done by a series of repeated simple distillation processes. However, in repeated distillations, some materials are lost by evaporation into the air or getting stuck into the apparatus in each distillation run. At the end of the distillation, it may be found that many materials have been lost. There is a method for carrying out several simple distillations in one apparatus, resulting in high yields of pure liquid components with minimum loss. This method is called *fractional distillation*. An illustration of the fractional distillation setup is shown in Figure 3.10.

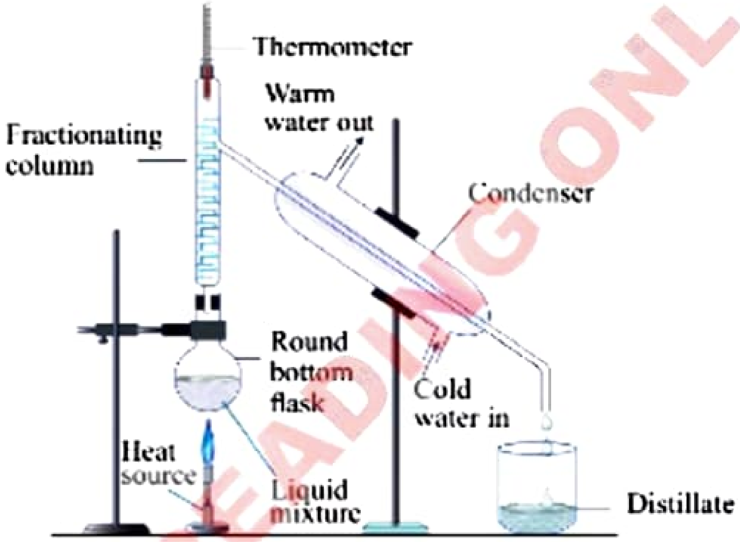


Figure 3.10: *Fractional distillation setup*

In this technique, vapours of a liquid mixture are passed through a fractionating column before condensation. The vapours rising in the fractionating column become richer in the more volatile liquid component. After successive distillations, the remaining liquid in the distillation flask is enriched with the high boiling liquid component.

A fractionating column

In fractional distillation, successive distillations occur in a fractionating column. The fractionating column consists of a glass tube with the attached disks inside. When the liquid mixture boils, some vapour condenses at each disk since the temperature decreases with an increase in the height of the column. When ascending the column, the vapour condenses and re-evaporates repeatedly, making it richer in the more volatile liquid. The condensed liquid on disks becomes richer in the less volatile liquid when descending from one disk to the next along the column. Once all the more volatile liquids have been distilled off, the temperature is raised to the boiling point of the less volatile liquid. If the distillation is stopped at this point, the less volatile liquid remains in the distillation flask while the more volatile liquid is collected in the receiver. The difference in boiling points between the liquid components in the mixture determines the length of the fractionating column, and hence, the number of plates required. The temperature versus composition phase diagram for the fractional distillation process is shown in Figure 3.11.

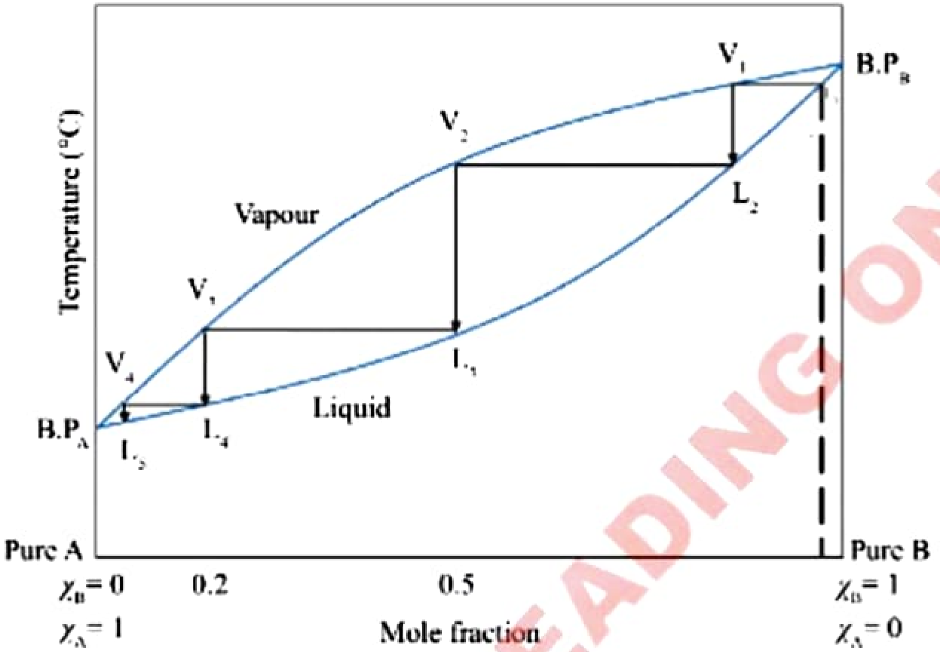


Figure 3.11: *Composition phase diagram for fractional distillation process*

If a liquid mixture with composition L_1 is boiled, it forms vapour with composition V_1. When the vapour V_1 is condensed, it gives a liquid composition L_2 which has the same composition as the vapour. Boiling of liquid L_2 gives the corresponding vapour V_2 with a different composition from liquid L_2. Generally, the vapour and the corresponding liquid get richer in the more volatile liquid component at each progressive boiling and condensing stage. At L_3, for example, liquid components A and B have a composition of 0.5. Boiling of this liquid mixture forms vapour V_3, whose composition is 0.2 (20%) for liquid component B and 0.8 (80%) for liquid component A. Condensing vapour V_3 gives liquid mixture L_4 with the same composition. Then, when liquid mixture L_4 is boiled and condensed, liquid L_5 is obtained, which is nearly pure liquid component A. This pure liquid component A is collected in the receiver, leaving the less volatile liquid component B in the flask. Liquid component B can be boiled to its boiling point and then condensed and collected in a separate receiver.

Activity 3.2

Aim: To separate a mixture of acetone and water by simple distillation method

Requirements: Round-bottomed flask, thermometer, condenser, rubber tubing, beaker, conical flask, heat source, acetone, water and measuring cylinder

Procedure

1. Measure about 100 cm^3 of each solvent (acetone and water) and transfer them into a clean round-bottomed flask.
2. Set the apparatus as shown in Figure 3.9 (a).
3. Heat the mixture gently to about 70 °C.
4. Collect the distillate using a beaker/conical flask.

Questions

1. What is the composition of the distillate collected?
2. What is the basic principle behind simple distillation?
3. How can the simple distillation affect the yield of the distillate?
4. How can the principles and skills acquired from the activity be applied to separate other mixtures with different chemical compositions?

Fractional distillation of miscible liquids which form azeotropic mixtures

Azeotropic mixtures boil at constant temperatures and behave as pure liquids with the same compositions in liquid and vapour phases. Consider the minimum boiling azeotrope, which boils at a lower temperature than the boiling point of pure components. An example of this azeotropic mixture is the ethanol–water mixture with a composition of 95.6% and 4.4%, respectively, as shown in Figure 3.8. The boiling point of water is 100 °C (373 K) and that of ethanol is 78.3 °C (351.3 K). These boiling points are higher than the boiling point of the azeotropic mixture, which is 78.1 °C (351.1 K). If a mixture of the solution containing less than 95.6% ethanol which is a more volatile component is distilled by fractional distillation, the azeotropic mixture that is collected in the receiver will exhaust the volatile component (ethanol), leaving pure water in the flask. This is because the amount of ethanol in the mixture is less than what is needed to form the azeotropic mixture with water. Therefore, the proportion of water that is needed to form azeotropic mixture with ethanol is also lowered.

If the composition with greater than 95.6% ethanol is distilled, the azeotropic mixture which is collected in the receiver will exhaust all the water contents in the solution, leaving pure ethanol in the flask. This is because the proportion of water available to form azeotropic mixture with ethanol is less than 4.4 %.

For the maximum boiling azeotrope, the boiling point of the azeotropic mixture is higher than the boiling point of pure components. An example is the azeotropic mixture of water–nitric acid with a composition of 32% and 68%, respectively, as shown in Figure 3.7. The boiling point of water is 100 °C (373 K) and that of nitric acid is 86 °C (359 K). These boiling points are lower than the boiling point of the azeotropic mixture, which is 120.5 °C (393.5 K). If a solution containing less than 68% nitric acid is distilled, pure water is distilled and collected in the receiver, and the azeotropic mixture remains in the flask. This is because the boiling point of pure water is less than that of an azeotropic mixture, and all the nitric acid is used to form an azeotropic mixture. If the composition with greater than 68% nitric acid is distilled, the acid distils off, and its concentration in the distillation flask decreases. The temperature rises until the boiling point of the azeotropic mixture is reached. Pure nitric acid is collected in the receiver while the azeotropic mixture remains in the distillation flask.

The examples show that, azeotropic mixtures can only be collected as pure components in the receiver or left in the distillation flask, depending on their boiling points relative to pure components. Therefore, normal fractional distillation can not separate the composition of azeotropic mixtures. The following are the methods that can be used to separate azeotropic mixtures:

(a) Distillation with a third component

Consider the azeotropic mixture of ethanol and water containing 95.6% ethanol at a normal atmospheric pressure. If benzene is added in the distillation flask, a new minimum boiling azeotrope with 23.8% ethanol, 23.3% water, and 52.9% benzene is formed. The low boiling point of 64.86 °C (337 K) allows the mixture to be collected in the receiver and leaves pure ethanol in the flask.

(b) By chemical methods

Quicklime (CaO) may be used to remove water from an azeotropic mixture of ethanol and water as shown in the following reaction:

$$\mathrm{CaO}(s) + \mathrm{H_2O}(l) \longrightarrow \mathrm{Ca(OH)_2}(s)$$

The formed precipitate of calcium hydroxide can be separated from the ethanol by physical means.

(c) Adsorption: Charcoal or silica gel may adsorb one of the components.

(d) Solvent extraction: One component can be separated from the solution by solvent extraction where solvents with similar attractive forces are used.

3.1.5 Applications of fractional distillation

There are numerous practical application of fractional distillation in our daily lives. One of the most significant industrial uses of fractional distillation is the separation of crude oil into its various components. This process is also utilised in chemical plants for large-scale manufacturing of chemicals, natural gas processing, separation of pure gas from the mixture of gases (cryogenic separation), and purification of organic compounds. Moreover, fractional distillation plays a crucial role in the purification of water, removing many dissolved impurities. It is fascinating to note that fractional distillation is applicable even on the production of alcoholic beverages such as whisky and the like.

Fractional distillation of crude oil

Fractional distillation separates various components of crude oil, including bitumen, fuel and lubricating oil, diesel, kerosene, naphtha, petrol and refinery gas. An illustration of the fractional distillation column or tower of crude oil is shown in Figure 3.12. The crude oil is heated, and the mixture starts to boil. The temperature decreases as ascending the fractionating column. The crude oil evaporates, and its vapours are allowed to condense at different temperatures in the fractionating column. Each fraction contains hydrocarbon molecules with a similar number of carbon atoms. Fractions with lower boiling points rise to the top of the column, cool down and condense to form liquid. Gases condense at the top of the column, the liquids in the middle, and solids stay at the bottom. Bitumen, which remains as a solid at the bottom of the column, is used as material for road construction and roofing. Heavy fuel oils are used in the operation of ships and factories due to their high energy content. Above the fuel oil, the lubricating oil is collected. The lubricating oil works to reduce wear and tear in various machine parts in contact.

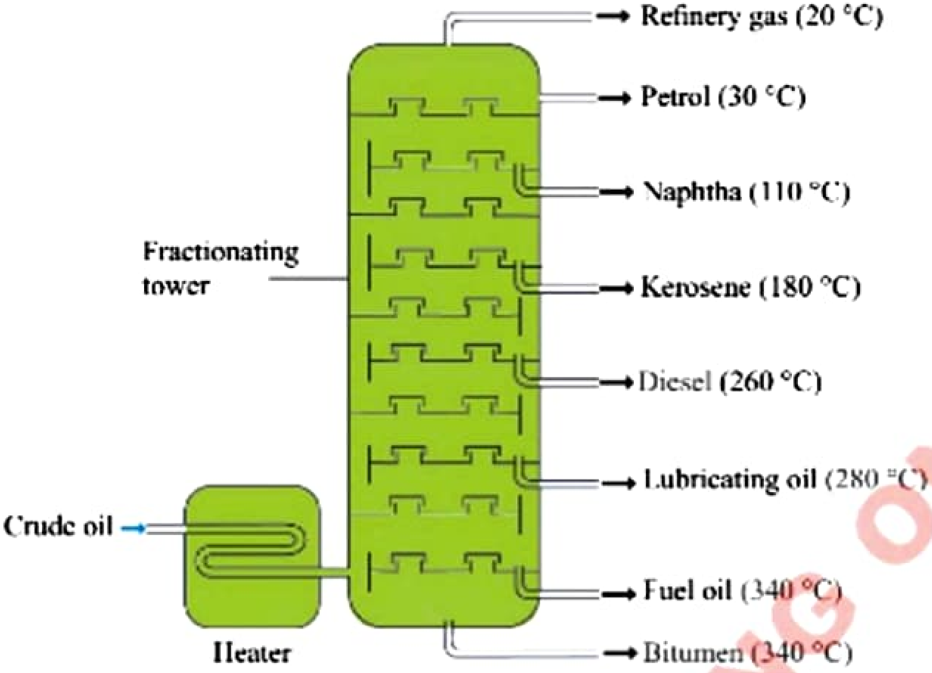
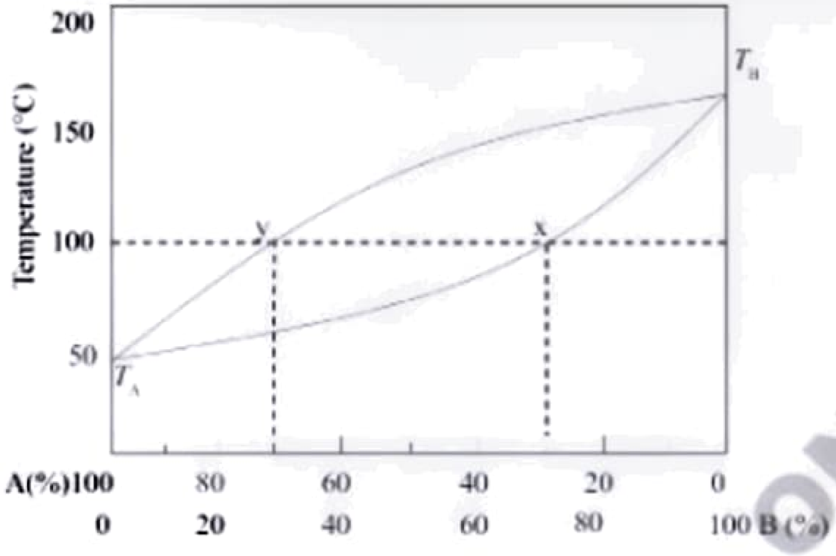


Figure 3.12: Fractional distillation of crude oil

Above the lubricating oil, the sequence of the fractions follows this trend: diesel, kerosene, naphtha, petrol, and finally, refinery gas. Diesel is a source of energy to drive heavy duty vehicles such as lorries, tractors and buses. Kerosene is used as jet fuel for lighting and heating. Naphtha, which is collected above the kerosene in the fractionating column, is used in the production of various chemicals. Petrol oil, which is above the naphtha in the fractionating column, is used as fuel for light-duty machines and vehicles. The refinery gases, which are condensed at the top of the column, are used as fuels for industrial and domestic purposes such as cooking.

Exercise 3.2

1. With examples, explain any liquid mixtures that can be separated into pure components by fractional distillation.
2. How does fractional distillation contribute to producing purified chemicals and solvents in chemical manufacturing processes?
3. The following figure shows a phase diagram for a mixture of liquids A and B. Use the figure to answer the questions that follow.



(a) What is the boiling point of pure A?

(b) Consider a solution with a composition of 40% B.

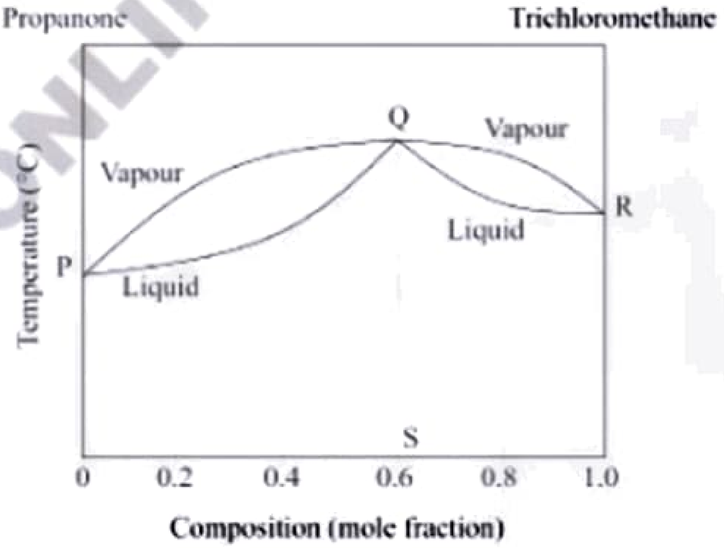
(i) What is the boiling point of this solution?

(ii) If the solution is boiled, what will the composition of the vapour phase be?

(iii) If the vapours are condensed, what will the composition of the distillate be?

(c) What does the line x – y represent?

4. Study the given diagram and answer the questions that follow:



(a) What do the letters P, Q, R, and S represent?

(b) What would end as a distillate at the end of a series of distillations that started with a solution of composition with mole fraction = 0.72R?

3.2 Immiscible liquids

Immiscible liquids are liquids which when mixed together in any proportions form two separate phases. The two liquids are mutually insoluble in each other due to the differences in polarity, intermolecular forces and molecular structure.

3.2.1 Formation of immiscible liquid mixture

Liquids are immiscible with each other when the intermolecular forces are not alike. For example, water and butane are immiscible because the types of intermolecular forces in the two compounds are different. Water exhibits hydrogen bonding while butane exhibits only the *dispersion forces*. In a mixture of immiscible liquids such as chloroform and ethyl acetate, the less dense liquid (ethyl acetate) forms the upper layer, and the denser liquid (chloroform) forms the bottom layer. An illustration of the formation of an immiscible liquid mixture is shown in Figure 3.13.

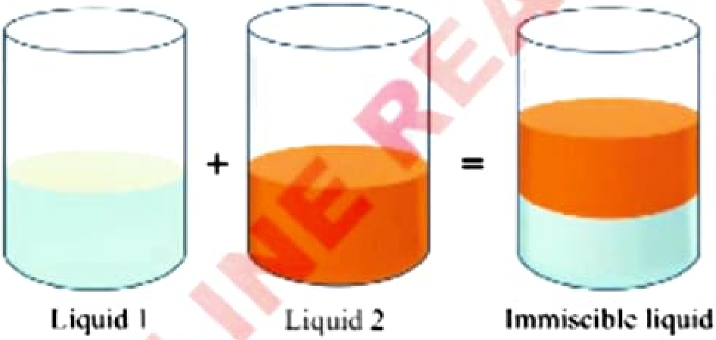


Figure 3.13: *Formation of immiscible liquid mixture*

3.2.2 Properties of immiscible liquids

When immiscible liquids are mixed, they form two layers. The lower layer is the liquid with the highest density, and the upper layer is the less dense liquid (Activity 3.3). The boiling point of a mixture of immiscible liquids is lower than that of either liquid, and the liquids show a sharp boiling point (boils at constant temperature). Bromobenzene–water mixture, for example, has a boiling point of 95 °C, which is less than that of bromobenzene (156 °C) and water (100 °C). The total vapour pressure (P_T) above the mixture of liquids is the sum of individual vapour pressures of liquids at a given temperature, that is, for a mixture of immiscible liquids A and B, $P_T = P_A^\circ + P_B^\circ$ where P° is the vapour pressure of the pure liquids.

Activity 3.3

Aim: To investigate the differences between miscible and immiscible liquids

Requirements: Ethanol, distilled water, diethyl ether, measuring cylinder ($100\ cm^3$), beakers ($250\ cm^3$), and separating funnel ($200\ cm^3$)

Procedure

1. Measure $100\ cm^3$ of water and $100\ cm^3$ of ethanol using two measuring cylinders and put them into the separating funnel.
2. Fix the stopper on the separating funnel and shake the mixture thoroughly for two minutes.
3. Clamp the separating funnel on the retort stand.
4. Leave the mixture to settle and observe.
5. Repeat steps 1 to 3 but use diethyl ether instead of ethanol.

Questions

1. What are the observations of the experiment? Give reasons.
2. How might the results of this activity be applicable in industry or everyday life?

3.2.3 Mixture of partially miscible liquids

Partially miscible liquids dissolve in one another to a limited extent. Examples are mixtures of phenol and water, and ether and water. If a few drops of phenol are shaken in water, a clear solution of phenol in water is obtained, the same as for a few drops of water in phenol. Similarly, ether dissolves 1.2% of water and water dissolves about 6.5% of ether. When equal volumes of ether and water are shaken together, two layers are formed: a saturated solution of ether in water and a saturated solution of water in ether. In addtion, for equal volumes of phenol and water, a saturated solution of phenol in water (top layer) and a saturated solution of

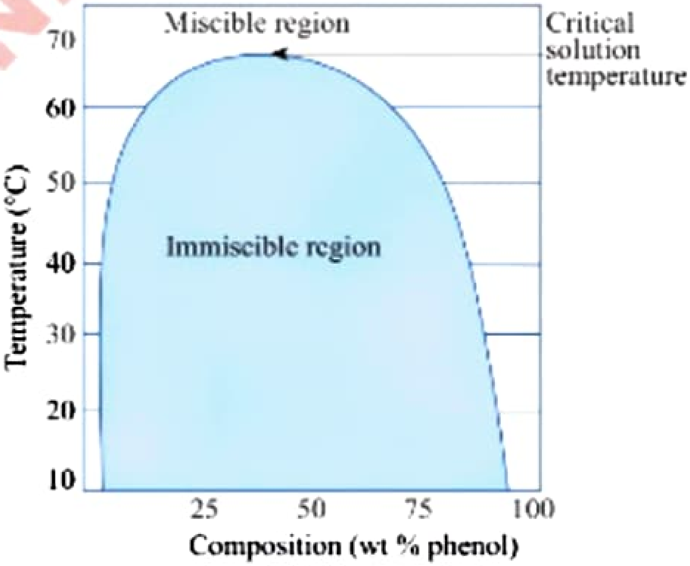


Figure 3.14: *Temperature versus composition phase diagram for phenol-water system*

water in phenol (bottom layer) is formed. These two partially miscible solutions can be treated as immiscible liquids. The solubility and hence miscibility of the partially miscible liquids depend on the temperature and fractional composition of the liquid components. A phenol-water mixture will be used to discuss this phenomenon (Figure 3.14).

The solubility of phenol in water and water in phenol increases with temperature until the *critical solution temperature* (CST) is reached. The critical solution temperature is the temperature at which the two liquid layers merge into one another to form one phase. Phenol and water are miscible in all proportions above the critical solution temperature. The critical solution temperature of the phenol-water system is about 67 °C. Below this temperature, the percentage composition of the two components determines the number of layers. For the phenol water mixture below 50 °C, a mixture of 90% phenol and 10% water or 5% phenol and 95% water will be completely miscible. The coloured part of the phenol-water phase diagram indicates the temperatures and compositions at which the two liquids behave as completely immiscible liquids. The addition of a certain amount of phenol to the $5\%-95\%$ phenol water system causes a shift in the fractional composition into the region of immiscible liquids from the left. Similarly, adding of a certain amount of water to the $90\%-10\%$ phenol-water system causes a shift in the fractional composition into the region of immiscible liquids from the right.

3.2.4 Applications of the knowledge of immiscible liquids

The understanding of immiscible liquids is mainly applicable in steam distillation for the separation of mixtures and the determination of molar masses of compounds with high boiling points or compounds that decompose at their boiling temperatures.

Steam distillation

Steam distillation is the process whereby steam is passed through an impure liquid that is immiscible with water and in the presence of steam, where the liquid compound is made volatile and distils with steam. It is a special type of distillation for temperature sensitive materials. Many high boiling point organic compounds cannot be purified at their boiling points since they tend to decompose near their boiling points. Hence, they can be distilled by steam distillation below 100 °C. Since the mixture boils at a constant temperature, it yields a distillate of constant composition. Therefore, steam distillation is used to purify organic liquids that are steam-volatile and immiscible with water. The experimental setup of steam distillation is shown in Figure 3.15.

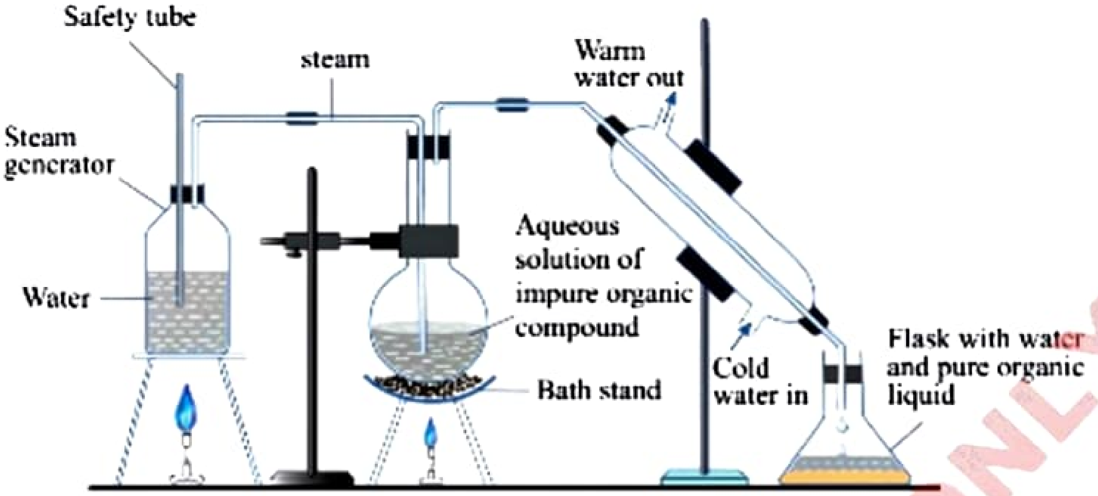


Figure 3.15: *Steam distillation setup*

The impure organic liquid containing non-volatile impurities is mixed with water, heated, and steam passes into it. The aim of mixing organic liquid with water is to avoid the decomposition of its molecules by lowering the boiling temperature. The boiling point of the given liquid is reached when the vapour pressure of the liquid is equal to the atmospheric pressure. For a mixture of two immiscible liquids, each component exerts its vapour pressure. The total vapour pressure (P_T) over the mixture equals the sum of the individual vapour pressures (P_A, P_B) at that temperature. Hence, the total vapour pressure is given by the following equation:

$$P_T = P_A + P_B$$

Since $P_T > P_A$ or P_B, the boiling point of the mixture of two liquids will be lower than either of the pure components. For example, in the mixture of aniline and water, the boiling point of water is 100 °C, and that of aniline is 184 °C, but the steam distillation temperature of aniline is 98 °C. Following the steam distillation process, the vapour of the organic liquid and steam rising from the boiling mixture pass through the condenser. The distillate collected in the receiver consists of two layers, one of the pure organic liquid and the other of water. The pure liquid is then removed using a separating funnel. The steam distillation process can extract natural products from plant materials. Examples include the extraction of eucalyptus oil from the eucalyptus plant, citrus oil from lemon or orange peel, and the extraction of oils from various plants such as *Rosa damascena* (Rose plant) and Jasmine plant, which are used for making perfumes. The steam distillation is also used in the purification of organic liquids with high boiling points and those which can easily decompose on heating at high temperatures.

Task 3.3

Use online sources or textbooks to study Soxhlet extraction.

Activity 3.4

Aim: To extract essential oil from plant material using steam distillation

Requirements: Plant materials (e.g., cloves, lemongrass, mint leaves, citrus peels), distillation apparatus, heat source, distilled water, separating funnel, beakers, graduated cylinders, and thermometer

Procedure

1. Assemble the distillation apparatus as shown in Figure 3.15.
2. Place the plant material in the flask and add distilled water until the material is submerged.
3. Heat the flask gently using a hot plate. Monitor the temperature using a thermometer and adjust the heat source to maintain a steady temperature.
4. Collect the distillate in the receiver flask as a mixture of water and essential oil.
5. Once sufficient distillate has been collected, remove the receiver flask from the apparatus and separate the essential oil from the water layer.
6. Repeat steps 2 to 5 for other plant materials available.

Questions

1. How does the steam distillation facilitate the extraction of essential oils from the given plant materials?
2. What are the reasons for choosing the given plant materials?
3. How relevant are the skills developed from the activity to your society?

Determination of molar mass of high boiling point liquids by steam distillation

It has been discussed previously that if a mixture of two immiscible liquids is heated, both components can contribute to the vapour pressure and express their full saturated vapour pressure because by being immiscible, they act independently. So, at a given temperature, the total vapour pressure is the sum of the vapour pressures of the pure liquid components. That is, for immiscible liquids A and B,

$$P_T = P_A^o + P_B^o$$

For steam distillation, one component is water and the second component is an organic liquid with high boiling point. Therefore,

$$P_T = P_{H_2O}^0 + P_{organic}^0$$

At normal atmospheric conditions, P_T = 760 Torr. If the distillation temperature is known, the composition of the distilled mixture can be determined from the vapour pressure ratios. The vapour pressure of a liquid component is directly proportional to the number of moles of that component (Equation 3.4).

$$P \,\alpha\, n, \quad P = kn, \quad k = \frac{P}{n} \qquad (3.4)$$

where, P is the vapour pressure of a liquid, n is the number of moles of liquid, and k is the proportionality constant.

For two liquid components A and B,

$$\frac{P_A}{n_A} = k, \quad \frac{P_B}{n_B} = k, \quad \frac{P_A}{P_B} = \frac{n_A}{n_B} \qquad (3.5)$$

Therefore,

$$\frac{P_A}{P_B} = \frac{m_A/M_A}{m_B/M_B} = \frac{m_A M_B}{M_A m_B} \Rightarrow \frac{m_A}{m_B} = \frac{P_A M_A}{P_B M_B} \qquad (3.6)$$

where, m_A and m_B are masses of A and B, respectively, and M_A and M_B are molar masses of A and B, respectively. For steam distillation, one component is water and another component which is being distilled is an organic liquid. Let component A be an organic liquid and B be water:

$$\frac{m_{organic\ liquid}}{m_{water}} = \frac{P_{organic\ liquid} \times M_{organic\ liquid}}{P_{water} \times M_{water}}$$

But molar mass (M) of water = 18 $g\,mol^{-1}$. Therefore,

$$\frac{m_{organic\ liquid}}{m_{water}} = \frac{p_{organic\ liquid} \times M_{organic\ liquid}}{p_{water} \times 18\ g\,mol^{-1}} \qquad (3.7)$$

Example 3.1

At a pressure of 760 Torr, a mixture of nitrobenzene ($C_6H_5NO_2$) and water boils at 99 °C. The vapour pressure of water at this temperature is 733 Torr. Find the ratio of water to nitrobenzene in the distillate obtained by steam distillation of impure nitrobenzene.

Solution

Data given:

Vapour pressure of nitrobenzene (P_n) = 760 Torr – 733 Torr = 27 Torr

Molecular mass of nitrobenzene (M_n) = 123 g mol^{-1}

Vapour pressure of water (P_w) = 733 Torr

Mass of nitrobenzene = unknown

Mass of water = unknown

From,

$$\frac{m_{\text{organic liquid}}}{m_{\text{water}}} = \frac{P_{\text{organic liquid}} \times M_{\text{organic liquid}}}{P_{\text{water}} \times 18\ \text{g mol}^{-1}} = \frac{27\ \text{Torr} \times 123\ \text{g mol}^{-1}}{18\ \text{g mol}^{-1} \times 733\ \text{Torr}} = 0.25$$

Therefore, the ratio of water to nitrobenzene in distillate is 4:1.

Example 3.2

Calculate the percentage by mass of bromobenzene (C_6H_5Br) in the distillate when the mixture of bromobenzene and water distils in a steam at 95 °C. The vapour pressures of bromobenzene and water at 99 °C are 1.59×10^4 N m^{-2} and 8.50×10^4 N m^{-2}, respectively.

Solution

Data given:

Vapour pressure of bromobenzene (P_b) = 1.59×10^4 Nm^{-2}

Molecular mass of bromobenzene (M_b) = 157 g mol^{-1}

Vapour pressure of water (P_w) = 8.50×10^4 Nm^{-2}

Mass of bromobenzene = unknown

Mass of water = unknown

From:

$$\frac{m_{\text{organic liquid}}}{m_{\text{water}}} = \frac{P_{\text{organic liquid}} \times M_{\text{organic liquid}}}{P_{\text{water}} \times 18\ \text{g mol}^{-1}}$$

$$= \frac{1.59 \times 10^4\ \text{N m}^{-2} \times 157\ \text{g mol}^{-1}}{18\ \text{g mol}^{-1} \times 8.50 \times 10^4\ \text{N m}^{-2}} = \frac{1.63}{1}$$

The proportion by mass between bromobenzene and water is 1.63:1.

Thus, total mass = 1.63 + 1 = 2.63 g.

$$\%\ \text{by mass of bromobenzene} = \frac{\text{Mass of bromobenzene}}{\text{Total mass}} \times 100\%$$

$$= \frac{1.63}{2.63} \times 100\% = 61.97\% \approx 62\%$$

Therefore, the distillate contains 62% by mass of bromobenzene.

Exercise 3.3

1. How practical is steam distillation in the pharmaceutical industry during drug formulations?
2. Analyse the advantages and limitations of steam distillation compared to other extraction techniques, such as solvent extraction or cold pressing.
3. Why is steam distillation proper for thermally unstable compounds?
4. Nitrobenzene is completely immiscible with water. A mixture of the two liquids boils at 99 °C and 753 Torr. The vapour pressure of water is 733 Torr at this temperature. Calculate the percentage composition by weight of the liquid mixture.
5. Calculate the molecular mass of compound B whose mixture with water distils at 95.2 °C. At this temperature, the vapour pressures of compound B and water are 119 Torr and 641 Torr, respectively. The ratio by mass in which the liquid distils (B:water) is equal to 1.62:1.
6. Liquid A distils in steam, and at the boiling point. The partial pressures of the two liquids are A = 6.59×10^3 N m^{-2} and water = 9.44×10^4 N m^{-2}. If the molar mass of A is 95 g mol^{-1}, calculate the percentage by mass of A in the distillate.

7. Calculate the percentage by mass of phenylamine in the distillate when a mixture of phenylamine ($C_6H_5NH_2$) and water distils at 98 °C. The vapour pressures of phenylamine and water are 1.01×10^5 N m^{-2} and 9.40×10^4 N m^{-2}, respectively.

3.3 Distribution of solutes in immiscible solvents

In the previous section, you learnt that when two immiscible liquids are mixed in the same container, they separate into two layers. The denser liquid forms the lower layer, and the lighter liquid forms the upper layer. For example, water is denser than many organic solvents but less dense than some organic solvents such as chloroform. Therefore, if chloroform and water are mixed in the same container, two layers are formed with water being the top layer and chloroform the bottom layer.

3.3.1 The distribution law

When a solute X, which is soluble in both solvents, is added to the mixture of immiscible liquids and shaken, it distributes itself between the two solvents. There is a continuous interchange of solute between the liquid layers until a dynamic equilibrium is established. The equilibrium is heterogeneous since the solute is distributed between two distinct layers. At equilibrium, the rate (R_1) at which molecules of X pass from solvent 1 to solvent 2 is proportional to its concentration (C_1) in solvent 1.

$$R_1 \propto C_1 \Rightarrow R_1 = k_1\, C_1 \qquad (3.8)$$

where k_1 is a proportionality constant. Similarly, the rate (R_2) at which molecules of X pass from solvent 2 to solvent 1 is proportional to its concentration (C_2) in solvent 2.

$$R_2 \propto C_2 \Rightarrow R_2 = k_2\, C_2 \qquad (3.9)$$

where, k_2 is a proportionality constant. At equilibrium, the two rates are equal and combining Equations 3.8 and 3.9, you get:

$$R_1 = R_2 \Rightarrow k_1\, C_1 = k_2\, C_2 = \frac{C_1}{C_2} = \frac{k_2}{k_1} \qquad (3.10)$$

where k_1 and k_2 are constants at the same temperature, and the ratio between k_2 and k_1 is called the *distribution coefficient* (K_D) The value of K_D is constant if the temperature is fixed. Thus, the *distribution or partition law* states that the ratio of the concentrations of a solute X distributed between two immiscible liquids 1 and 2 at constant temperature is constant if the molecular state of the solute is the same in both solvents.

$$K_D = \frac{C_1}{C_2} \tag{3.11}$$

where C_1 and C_2 are concentrations of solutes in solvents 1 and 2, respectively.

The distribution or partition coefficient (K_D), expresses how much a solute distributes itself between the two layers. If the K_D value is less than 1, the solute is dissolved more in solvent 2 than in solvent 1, and if the K_D value is greater than 1, the solute dissolves more in solvent 1. For example, non-polar iodine dissolves more in a non-polar organic solvent than in the highly polar solvents.

$$I_2(aq) \rightleftharpoons I_2(CCl_4)$$

$$K_D = \frac{C_1}{C_2} = \frac{[I_2(aq)]}{[I_2(CCl_4)]} = 0.0116$$

Because the value of K_D obtained is less than one, iodine dissolves more in tetrachloromethane.

The following conditions govern the distribution law:

(a) Non-miscibility of solvents

The two solvents in which the solute is distributed should be immiscible or partially miscible with each other, and the addition of solute should not alter the immiscibility.

(b) Equilibrium concentrations

The actual values of solute concentrations are obtained after the distribution of solute between the two immiscible liquids reaches equilibrium. If the equilibrium is not reached, the value of K_D will not be correct.

(c) Dilute solution

The law does not apply at high concentrations of solute. Therefore, the concentration should be kept low.

(d) Constant temperature

The temperature is maintained constant during the experiment because any change in temperature will affect the solubility of the solute in the two liquids.

(e) Same molecular state

The molecular state of the solute should be the same in all the solvents. There should be no dissociation or association of solutes in any of the solvents.

Example 3.3

A solid X is added to a mixture of benzene and water. After shaking well and allowing the mixture to stand, 10 mL of the benzene layer was found to contain 0.13 g of X and 100 mL of water layer contained 0.22 g of X.

(a) Calculate the distribution coefficient value of X between benzene and water. The density of benzene = 0.8765 $g\,cm^{-3}$ and the density of water = 1.0 $g\,cm^{-3}$.

(b) Comment on the value of the distribution coefficient obtained.

Solution

(a) Data given:

Volume of benzene = 10 mL, Mass of X in benzene = 0.13 g

Therefore, the concentration of X in benzene$(C_{benzene}) = \frac{0.13\ g}{10\ mL} = 0.013\ g\,mL^{-1}$

Volume of water = 100 mL, Mass of X in water = 0.22 g

Therefore, the concentration of X in water$(C_{water}) = \frac{0.22\ g}{100\ mL} = 0.0022\ g\,mL^{-1}$

According to the distribution law,

$$K_D = \frac{C_{benzene}}{C_{water}} = \frac{0.013\ g\,mL^{-1}}{0.0022\ g\,mL^{-1}} = 5.9$$

(b) This value of distribution coefficient is greater than 1 implying that the solute X dissolves more in benzene than in water.

Example 3.4

In the distribution of succinic acid between ether and water at 15 °C, 20 mL of the ether layer contains 0.092 g of the acid. If the distribution coefficient of succinic acid between ether and water is 5.2, calculate the weight of the acid present in 50 mL of the aqueous solution at equilibrium with the ether layer.

Solution

Let the mass of succinic acid in aqueous layer be X.
Volume of ether = 20 mL, Mass of X in ether = 0.092 g

Therefore, the concentration of X in ether, $(C_{ether}) = \frac{0.092\ g}{20\ mL} = 0.0046\ g\,mL^{-1}$

Volume of water = 50 mL, Mass of X in water = unknown = m (g)

Therefore, the concentration of X in water, $\left(C_{\text{water}}\right) = \frac{\text{m (g)}}{\text{50 mL}}$

According to the distribution law,

$$K_D = \frac{C_{\text{ether}}}{C_{\text{water}}} = \frac{0.0046\ \text{g mL}^{-1}}{\left(^{\text{m}}/_{50}\right)\text{g mL}^{-1}} = \frac{50\ \text{mL} \times 0.0046\ \text{g mL}^{-1}}{\text{m (g)}} = 5.2$$

$$\text{m} = \frac{50\ \text{mL} \times 0.0046\ \text{g mL}^{-1}}{5.2} = 0.044\ \text{g}$$

Therefore, the mass of succinic acid present in 50 mL of aqueous solution is 0.044 g.

The distribution law in terms of solubility

The distribution coefficient (K_D) can also be expressed in terms of solubility. This is because solubility also represents the concentration of solute in a solvent.

$$K_D = \frac{S_1}{S_2} \qquad (3.12)$$

where S_1 and S_2 are solubilities of solute in solvents 1 and 2, respectively. The solubility of the solute in one solvent can be determined if the value of the distribution coefficient and the solubility of the solute in another solvent are known.

Example 3.5

Given that the solubility of iodine in water at 25 °C is 0.34 g/L and the aqueous solution of iodine containing 0.0516 g/L is in equilibrium with carbon tetrachloride (CCl_4) solution containing 4.412 g/L, calculate the solubility of iodine in carbon tetrachloride.

Solution

Data given:

Concentration of iodine in water (C_{water}) = 0.0516 g/L

Concentration of iodine in (C_{CCl_4}) = 4.412 g/L

Use the concentrations to find K_D.

$$K_D = \frac{C_{H_2O}}{C_{CCl_4}} = \frac{0.0516\ \text{g/L}}{4.412\ \text{g/L}} = 0.0117$$

Then use the value of K_D obtained to calculate the solubility of iodine in CCl_4.

$$K_D = \frac{S_{H_2O}}{S_{CCl_4}} \Rightarrow S_{CCl_4} = \frac{S_{H_2O}}{K_D} = \frac{0.34\text{ g/L}}{0.0117} = 29.06\text{ g/L}$$

The solubility of iodine in CCl_4 is 29.06 g/L.

The results obtained indicate that iodine dissolves more in carbon tetrachloride (CCl_4) than in water.

Activity 3.5

Aim: To determine the distribution coefficient of ethanedioic acid (oxalic acid) in diethyl ether-water solvent system

Requirements: Oxalic acid, diethyl ether, distilled water, 0.1 M sodium hydroxide, phenolpthalein indicator, retort stand, burette, conical flask, separating funnel, thermometer, beaker (100 cm^3), measuring cylinder, dropper and pipette (10 cm^3)

Procedure

1. Measure 100 cm^3 of diethyl ether and 100 cm^3 of distilled water and transfer them into the 250 cm^3 separating funnel.
2. Add 5 g of oxalic acid into the separating funnel and fix the stopper on the separating funnel.
3. Shake the mixture vigorously until all solid particles dissolve completely.
4. Allow the mixture to settle.
5. Separate the organic layer from the aqueous layer.
6. Measure 10 cm^3 of the aqueous layer using a measuring cylinder and transfer it into a conical flask.
7. Titrate the aqueous layer with sodium hydroxide solution using a POP indicator and record the results in the following table. Use phenolphthalein indicator.

Titration	Pilot	1	2	3
Final volume (cm^3)				
Initial Volume (cm^3)				
Volume used (cm^3)				

8. Titrate 10 mL of the organic layer with a sodium hydroxide solution using phenolphthalein indicator and record the results as in step 7.

Questions

1. In which solvent does the acid dissolve more? Why?
2. What value of K_D would be expected if 2.5 g of the acid had been shaken with 50 cm^3 of each solvent at 25 °C ?
3. How is the knowledge from this activity applicable to drug development?

Activity 3.6

Aim: To determine the distribution coefficient of succinic acid between water and diethylether

Requirements: Separating funnel with its stopper, measuring cylinder, pipette, burette, beakers, conical flasks, 0.1M NaOH, 0.4M phenolphthalein indicator, diethyl ether and 0.4 M aqueous solution of succinic acid solution (butane-1,4-dioic acid).

Procedure

1. Measure 75 mL of succinic acid into a clean separating funnel.
2. Add 75 mL of diethyl ether to the separating funnel containing the succinic acid solution, stopper the separating funnel, mix the contents thoroughly, and leave them to settle.
3. Empty the two layers into separate clean beakers.
4. Pipette 25.00 mL of the lower layer into a clean conical flask and add 2 to 3 drops of phenolphthalein indicator.
5. Fill the burette with 0.1M NaOH and record the initial volume.
6. Titrate the contents in the burette against the contents in the flask, and record the volume used when the colour changes from colourless to pink.
7. Repeat step 4 and 6 to obtain two more readings.
8. Record your result in tabular form.

Questions

1. What is the molarity of succinic acid present in aqueous and diethyl ether layers?
2. What is the distribution coefficient of succinic acid between the aqueous layer and the diethyl ether layer?
3. In which layer does the succinic acid dissolve more? Explain your answer.

Deviations from the distribution law

It has been explained that one of the conditions governing the distribution law is that, the molecular state of the solute should be maintained throughout the experiment. This means the solute should neither associate nor dissociate in any solvents. If the solute undergoes an association or a dissociation in any of the solvents, the ratio of the upper to lower layer concentrations would change. As a result, the value of the distribution coefficient would also change.

The distribution coefficient when solute undergoes association

The distribution of a solute between two immiscible solvents when the solute undergoes association in one of the solvents (lower layer) is shown in Figure 3.16. Suppose the solute X distributes itself between solvent A and solvent B. In solvent A, the solute X exists in a non-associated state, while in solvent B, n molecules of X associate to form X_n molecules. At equilibrium, a few free molecules of X are also present in solvent B.

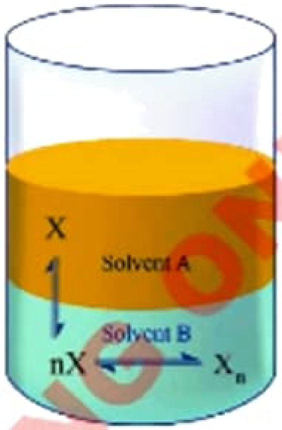


Figure 3.16: *Distribution of solute X when it undergoes association*

Let C_1 be the concentration of solute X in solvent A, C_2 be the concentration of solute X_n in solvent B, and C_3 be the concentration of solute X in solvent B.

According to the distribution law.

the amount of X in solvent A $\rightleftharpoons$ the amount of X in solvent B

The distribution coefficient, (K_D) is given by:

$$K'_D = \frac{C_1}{C_3} \tag{3.13}$$

where K'_D is the distribution constant in which the solute undergoes an association with one of the solvents.

By applying the law of mass action,

$$nX \rightleftharpoons X_n \Rightarrow K_C = \frac{[\text{product}]}{[\text{reactants}]} \tag{3.14}$$

where K_C is the equilibrium constant.

$$K_C = \frac{[X_n]}{[X]^n} = \frac{C_2}{C_3^n} \tag{3.15}$$

Taking nth root on both sides of Equation 3.15 gives Equation 3.16.

$$\sqrt[n]{K_C} = \frac{\sqrt[n]{C_2}}{C_3} \tag{3.16}$$

Dividing Equation 3.13 by Equation 3.16 gives the following:

$$\frac{K'_D}{\sqrt[n]{K_C}} = \frac{C_1 \times C_3}{C_3 \times \sqrt[n]{C_2}} = \frac{C_1}{\sqrt[n]{C_2}}$$

The $\frac{K'_D}{\sqrt[n]{K_C}}$ is constant and is equal to the overall distribution constant (K_D).

Therefore, in the presence of the association of solute X in one of the solvents, the distribution law is modified as

$$K_D = \frac{C_1}{\sqrt[n]{C_2}} \tag{3.17}$$

Example 3.6

During an experiment, benzoic acid was shaken with a mixture of benzene and water at constant temperature. The following results were recorded:

Type of solvent used	Number of experiments		
	1	2	3
Concentration of acid in benzene (C_1)	0.24	0.55	0.93
Concentration of acid in water (C_2)	0.015	0.022	0.029

Comment on the results obtained.

Solution

Assuming that $K_D = \frac{C_1}{C_2}$, the values of K_D for three sets of data are

$$K_D = \frac{0.24}{0.015} = 16, \quad K_D = \frac{0.55}{0.022} = 25 \quad \text{and} \quad K_D = \frac{0.93}{0.029} = 32$$

From these data, it is observed that the distribution coefficient is not constant. Thus, benzoic acid does not exist as free molecules in both solvents.

Activity 3.7

Aim: To determine the distribution coefficient of iodine between water and isobutyl alcohol

Requirements: Separating funnel with its stopper, measuring cylinder, pipette, burette, beakers, conical flasks, 1.524 g of iodine in 1 dm^3 of water, 0.001 M sodium thiosulfate solution, isobutyl alcohol and starch indicator.

Procedure

1. Measure 50 mL of iodine solution into a clean separating funnel.
2. Add 50 mL of isobutyl alcohol to the separating funnel containing the iodine solution, stopper the separating funnel, mix the contents thoroughly, and leave them to settle.
3. Empty the two layers into separate clean beakers.
4. Pipette 25.00 mL of the lower layer into a clean conical flask, and add 2 to 3 drops of starch indicator.
5. Fill the burette with 0.001 M $Na_2S_2O_3$; then record the initial volume.
6. Titrate the contents in the burette against the contents in the flask and record the volume used when the blue colour just disappears.
7. Repeat the procedure, but in step 4, pipette 20.00 mL of the upper layer into the conical flask, and record your results in a tabular form.

Questions

1. What is the concentration of iodine in the aqueous layer?
2. What is the K_D of iodine between organic and aqueous layers?
3. What factors can influence the distribution of solute between immersible solvents?

The distribution coefficient when solute undergoes dissociation

The solute distribution between two immiscible solvents is shown in Figure 3.17, where the solute undergoes dissociation in one of the solvents (the lower layer). Suppose solute X distributes itself between solvent A and solvent B; in solvent A, the solute X exists in a non-dissociated state while in solvent B, the molecules of X dissociate into A + B molecules. At equilibrium, few single molecules of X are also present in solvent B, together with A and B molecules.

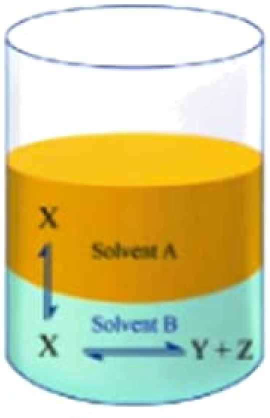


Figure 3.17: *Distribution of solute when undergoes dissociation*

Let the concentration of X in solvent A be C_1 and C_2 be the total concentration of X (dissociated and undissociated) in solvent B. If the degree of dissociation in solvent B is α,

$$\begin{array}{lcl} X & \rightleftharpoons & Y + Z \\ 1-\alpha & & \alpha \quad \alpha \end{array}$$

Thus, the undissociated molecules of X have a concentration of C_2 (1 − α) in solvent B. According to the distribution law for normal solutes in two solvent,

$$\frac{C_1}{C_2} = K_D \quad \text{but } C_2 = C_2(1-\alpha)$$

Therefore,

$$K_D = \frac{C_1}{C_2(1-\alpha)} \tag{3.18}$$

This is the modified distribution law when there is dissociation in one of the solvents.

3.3.2 Applications of the distribution law in solvent extraction

Solvent or liquid-liquid extraction is a method by which a compound is pulled out from one solvent to another where the two solvents are immiscible. With this method, the compounds which are poorly miscible in organic solvents but highly miscible in water can be extracted into organic compounds by repetitive extraction with the separating funnel or liquid- liquid extractor. Assume that an organic substance is present in aqueous solution. If this solution is mixed with an organic solvent that is immiscible with water, for example, ether, and shaken, some or all of the organic substances will be extracted from the water and transfered into the organic phase. On standing, the two liquids separate into layers with some solute from the aqueous layer dissolved in the organic layer. The aqueous layer (in this case, the lower layer) is transferred out of the separating funnel, leaving the ether layer behind. The ether layer is transferred to the distillation flask, which is distilled to obtain the organic substance targeted. If desired, the process may be repeated by returning the collected aqueous layer to the separating funnel and shaking it with ether. Solvents such as chloroform, carbon disulfide and hexane can also be used in solvent extraction. The solvent extraction setup is shown in Figure 3.18.

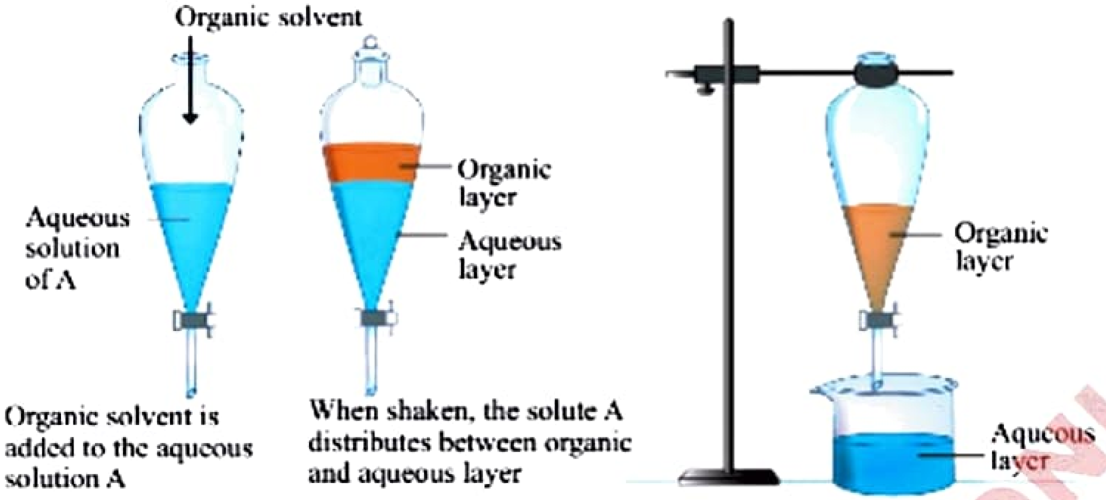


Figure 3.18: *Solvent extraction setup*

Multiple extraction

Multiple extraction is the process by which solvent extraction is done repeatedly by introducing the aqueous layer back into the separating funnel and shaking it again with organic solvent immiscible with water. This method recovers the maximum amount of organic substance from the aqueous phase. The aqueous solution is first extracted with a portion of organic solvent in the separating funnel. This aqueous layer is then transferred to another separating funnel and shaken with another portion of the same organic solvent. This process is repeated several times until the maximum amount of organic substance is recovered. This demonstrates that multiple solvent extraction is more efficient than using the same volume of organic solvent in a single extraction.

Suppose you have 100 mL of an aqueous solution containing m grams of an organic substance to be extracted with 100 mL of ether. The value of the distribution coefficient between ether and water is 2.

Case 1: Using all the ether in one lot

Let the volume of ether to be used = 100 mL and the mass of organic substance extracted using ether be x grams. The concentration of an organic substance in ether layer = $\frac{x\text{ g}}{100\text{ mL}}$. Therefore, the concentration left in the aqueous layer is equal to $\frac{(m-x)\text{ g}}{100\text{ mL}}$.

From the distribution law:

$$K_D = \frac{C_{ether}}{C_{water}} = \frac{\left({}^{x}\!/_{100}\right)\text{g mL}^{-1}}{\left(m - {}^{x}\!/_{100}\right)\text{g mL}^{-1}} = \frac{100x}{100(m-x)} = \frac{x}{(m-x)}$$

$$K_D = \frac{x}{(m-x)} = 2$$

$$\frac{x}{(m \quad x)} = 2 \Rightarrow x = \frac{2}{3}m$$

Since m is the original mass and x is the mass of organic substance extracted, therefore, 66%, $\left(\frac{2}{3}\right)$ has been extracted.

Case 2: Using 50 mL of ether twice

(a) First extraction

Again, use m grams as the original mass and x grams as the mass of organic substance extracted. The concentration of organic substance in ether layer $= \frac{x\text{ g}}{50\text{ mL}}$. Therefore, the concentration left in the aqueous layer is equal to $\frac{(m-x)\text{ g}}{100\text{ mL}}$.

From the distribution law:

$$K_D = \frac{C_{ether}}{C_{water}} = \frac{\left({}^{x}\!/_{50}\right)\text{g mL}^{-1}}{\left(m - {}^{x}\!/_{100}\right)\text{g mL}^{-1}} = \frac{100x}{50(m-x)} = \frac{2x}{(m-x)}$$

$$K_D = \frac{2x}{(m-x)} = 2$$

$$\frac{2x}{(m-x)} = 2 \Rightarrow x = \frac{1}{2}m$$

Therefore, 50% of the organic substance has been extracted and the organic substance left in water is equal to $\frac{1}{2}m$.

(b) Second extraction

Let y be the mass of organic substance during the second extraction. Then, the concentration of organic substance in ether layer = $\frac{y\text{ g}}{50\text{ mL}}$. The concentration of

organic substance in aqueous layer = $\frac{\left(\frac{1}{2}m - y\right)\text{g}}{100\text{ mL}}$.

From the distribution law:

$$K_D = \frac{C_{\text{ether}}}{C_{\text{water}}} = \frac{\left(\frac{y}{50}\right)\text{g mL}^{-1}}{\left(\left(\frac{1}{2}m - y\right)\Big/100\right)\text{g mL}^{-1}} = \frac{100y}{50(\frac{1}{2}m - y)} = \frac{2y}{(\frac{1}{2}m - y)}$$

$$K_D = \frac{2y}{(\frac{1}{2}m - y)} = 2 \quad \Rightarrow y = \frac{1}{4}m$$

Therefore, 25% of the organic substance was extracted using 50 mL of ether during the second extraction. For the two portions of extraction, 75% of the organic substance was extracted against 66% when one lot of 100 mL ether was used. This implies that the amount of substance extracted is maximised as you increase the number of portions of the solvent.

Example 3.7

The distribution coefficient of y between benzene and water is 10. Calculate the amount of y extracted if 1 g of it dissolved in 100 mL of water is equilibrated in a separating funnel with 100 mL of benzene.

Solution

Data given:

$K_D = 10$

Let x g be the amount of y extracted with 100 mL of benzene. Then, the amount of y left in 100 mL of water = $(1-x)$ g.

From the distribution law:

$$K_D = \frac{C_{\text{benzene}}}{C_{\text{water}}} \Rightarrow \frac{x\!\!\diagup\!100\text{ g mL}^{-1}\ 100x}{\left(1-x\!\!\diagup\!100\right)\text{g mL}^{-1}\ 100(1-x)} = 10 = \frac{100x}{100(1-x)}$$

$$10(1-x) = x \Rightarrow 10 - 10x = x$$

$$\frac{10}{11} = \frac{11x}{11}$$

$$x = \frac{10}{11}$$

Hence, the amount of y extracted with 100 mL of benzene is 0.909 g.

Example 3.8

An aqueous solution contains 10 g/L of solute. When 1 litre of the solution is treated with 100 mL of ether, 6 g of the solute is extracted. Assume that the molecular state of the solute is the same in ether and water. How much more solute would be extracted from the aqueous solution by a further 100 mL of ether?

Solution

Data given:

Concentration of solute in ether $(C_{ether}) = \frac{6}{100}\ \text{g mL}^{-1} = 0.06\ \text{g mL}^{-1}$

Concentration of solute in water $(C_{H_2O}) = \frac{10-6}{1000}\ \text{g mL}^{-1} = 0.004\ \text{g mL}^{-1}$

Applying the distribution law,

$$K_D = \frac{C_{ether}}{C_{H_2O}} = \frac{0.06}{0.004} = 15$$

To find the amount of solute removed after the first extraction, let the mass extracted in the second extraction be x g.

Concentration of solute in ether $(C_{ether}) = \frac{x}{100}\ \text{g mL}^{-1}$

Concentration of solute in water $= \frac{4-x}{1000}\ \text{g mL}^{-1}$

Applying the distribution law,

$$K_D = \frac{C_{ether}}{C_{water}} = \frac{\left(\frac{x}{100}\right)\text{g mL}^{-1}}{\left(\frac{4-x}{1000}\right)\text{g mL}^{-1}} \Rightarrow 15 = \frac{1000x}{100(4-x)} = \frac{10x}{4-x}$$

$$15 = \frac{10x}{4-x} \Rightarrow x = \frac{60}{25} = 2.4$$

Therefore, 2.4 g of the solute will be extracted at the second extraction with ether.

General formula for calculating the mass of organic substance left un-extracted

You have seen that as the number of portions of the solvents which are used for the extraction increases, the amount of organic substance extracted from the aqueous layer also increases relative to a single extraction using the same volume of organic solvent. There is a general formula for calculating the mass left un-extracted after several number of extractions. Knowing the mass left un-extracted, the mass extracted can also be calculated.

In the first extraction

Let the mass of organic substance in aqueous solution be m g, and the mass left un-extracted be x_1.

The concentration of an organic substance in the aqueous layer is equal to $\frac{x_1}{V_1}$, where V_1 is the volume of the aqueous layer. The concentration of an organic substance extracted in organic solvent will be equal to $\left(\frac{m-x_1}{V_2}\right)$ g mL^{-1}, where V_2 is the volume of the portion of organic solvent used. Considering the mixture in which the organic solvent is less dense than water. The distribution law will be

$$K_D = \frac{C_{\text{organic}}}{C_{\text{water}}} = \frac{(m-x_1)/V_2}{x_1/V_1} = \frac{(m-x_1)}{V_2} \times \frac{V_1}{x_1}$$

$$K_D V_2 x_1 = (m-x_1)V_1 = mV_1 - x_1V_1$$

$$x_1 = m\left(\frac{V_1}{K_D V_2 + V_1}\right) \qquad (3.19)$$

In the second extraction

The initial mass of organic substance in the aqueous layer is the mass left un-extracted in the first extraction, which is equal to x_1. The mass left un-extracted in the second extraction is x_2. The volume of the aqueous layer is the same (V_1). In each portion, the volume of organic solvent used is the same (V_2). Therefore,

$$C_{\text{aqueous}} = \frac{x_2}{V_1} \quad \text{and} \quad C_{\text{organic}} = \frac{(x_1 - x_2)}{V_2}$$

From the distribution law:

$$K_D = \frac{C_{\text{organic}}}{C_{\text{aqueous}}} = \frac{\frac{(x_1 - x_2)}{V_2}}{\frac{x_2}{V_1}} \Rightarrow K_D = \frac{(x_1 - x_2)}{V_2} \times \frac{V_1}{x_2}$$

$$K_D V_2 x_2 = (x_1 - x_2)V_1 = x_1V_1 - x_2V_1$$

$$x_2 = \frac{x_1V_1}{K_DV_2 + V_1} \qquad (3.20)$$

Substituting the value of x_1 from Equation 3.19 into Equation 3.20 gives

$$x_2 = m\left(\frac{V_1}{K_DV_2 + V_1}\right) \times \left(\frac{V_1}{K_DV_2 + V_1}\right) = m\left(\frac{V_1}{K_DV_2 + V_1}\right)^2$$

Therefore, the mass left un-extracted after the second extraction is

$$x_2 = m\left(\frac{V_1}{K_DV_2 + V_1}\right)^2$$

In the third extraction,

$$x_3 = m\left(\frac{V_1}{K_DV_2 + V_1}\right)^3$$

Therefore, for *n* number of extractions:

$$x_n = m\left(\frac{V_1}{K_DV_2 + V_1}\right)^n \qquad (3.21)$$

For the case where the organic solvent is denser than water:

$$x_n = m\left(\frac{K_DV_1}{K_DV_1 + V_2}\right)^n \qquad (3.22)$$

This general formula is applicable only when equal portions of the extracting solvent are used.

Example 3.9

The distribution coefficient of an alkaloid between chloroform and water is 20 in favour of chloroform. Compare the weights of the alkaloid remaining in the aqueous solution when 100 mL containing 1 gram of it has been shaken with (a) 100 mL chloroform and (b) two successive 50 mL portions of chloroform.

Solution

Chloroform is denser than water. Therefore, the distribution law is

$$K_D = \frac{C_{H_2O}}{C_{CHCl_3}} = \frac{1}{20} = 0.05$$

From the general formula in the mass left un-extracted,

$$x_n = m\left(\frac{K_D V_1}{K_D V_1 + V_2}\right)^n$$

where,

V_1 = volume of aqueous layer

V_2 = volume of the portions of chloroform

n = number of extractions

m = mass of organic substance before extraction

Data given,

$V_1 = 100$ mL, $m = 1$ g and $K_D = 0.05$

(a) $V_2 = 100$ mL (extraction done using one portion)

$$x_1 = 1\,g \times \left(\frac{0.05 \times 100\text{ mL}}{0.05 \times 100\text{ mL} + 100\text{ mL}}\right)^1 = 0.0476\,g$$

(b) $V_2 = 50$ mL

$n = 2$ (extraction done twice using 50 mL portions)

$$x_2 = 1\,\text{g} \times \left(\frac{0.05 \times 100\ \text{mL}}{0.05 \times 100\ \text{mL} + 50\ \text{mL}} \right)^2 = 1\,\text{g} \times \left(\frac{5}{5 + 50} \right)^2 = 0.0083\ \text{g}$$

Therefore, the mass left after extracting once using 100 mL of organic solvent is 0.0476 g, and the mass left after extracting twice using 50 mL portions of organic solvent is 0.0083 g. These results also support the proposition that extracting several times in small portions increases the amount of the organic substance extracted.

3.3.3 Applications of distribution law in chromatography

Chromatography is a technique that separates the components of a mixture due to the difference in the affinity between the two phases which are the mobile phase and the stationary phase. This technique is used to identify, separate, and purify organic substances from a mixture. It is based on the difference in the extent of adsorption of various mixture components on an adsorbent. Common adsorbents include magnesium oxide, cellulose paper, silica gel and alumina. The adsorbents form a fixed or stationary phase and the liquid in which the substance dissolves is called a *mobile phase*. Depending on the nature of the two phases some of the most commonly used chromatographic techniques include *column chromatography*, *paper chromatography* and *thin layer chromatography*.

Column chromatography

Column chromatography uses a solid adsorbent as a stationary phase and a liquid solvent as a mobile phase. Figure 3.19 shows the separation of the components of a mixture by column chromatography. The column is packed with a suitable adsorbent such as silica gel up to about three quarters of the column containing glass wool at the bottom. A solution of the mixture to be separated is poured on top of the silica gel, followed by the liquid solvent as a mobile phase for elution. The less adsorbed components; to the stationary phase runs faster with the solvent than the more adsorbed components hence, the separation of components. These mixture components are collected separately at the bottom of the column.

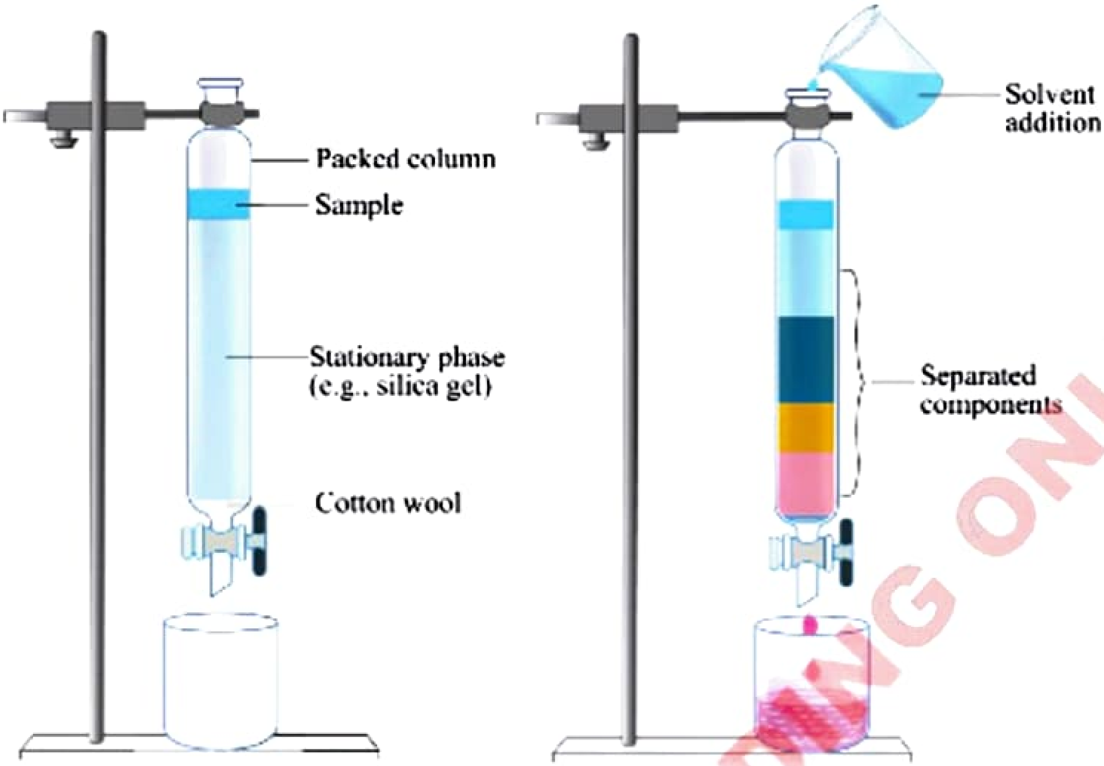


Figure 3.19: *Column chromatography*

Paper chromatography

Paper chromatography uses liquids or solids as the stationary phase and liquid as the mobile phase. It involves the flow of a solvent on a filter paper. The mechanism of paper chromatography is partly partition and partly adsorption. The partly partition comes from the fact that the constituents of the mixture are distributed between the water present in the filter paper (as a stationary phase) and an organic solvent as a mobile phase. The experimental setup for paper chromatography is shown in Figure 3.20.

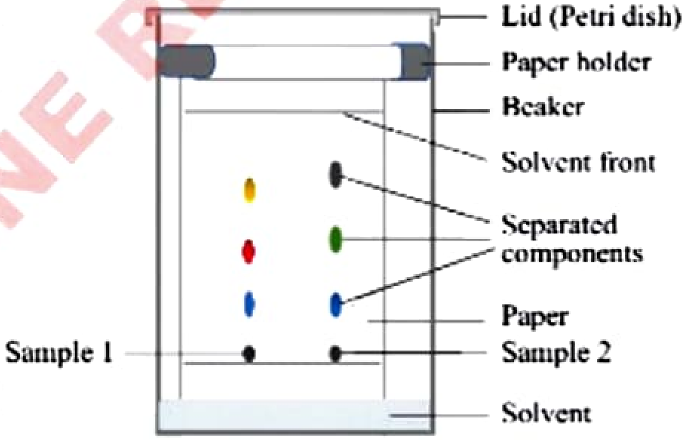


Figure 3.20: *Paper chromatography*

A drop of the mixture of the solution of compounds to be separated is placed near one edge of the filter paper (about 2 cm from the edge) and dried. The paper is dipped into the organic solvent (about 1 cm), leaving a dry spot outside. The organic solvent is sucked up through the capillaries of the paper. As the solvent moves up and reaches the mixture, it removes its components at various speeds, depending on the extent of the adsorption to the stationary phase and polarity relative to the solvent mobile phase. The distance moved by a compound relative to the solvent distance is expressed as R*f*, which is called a *retention factor*.

$$Rf = \frac{\text{Distance travelled by the solute from the original line}}{\text{Distance travelled by the solvent from the original line}} \qquad (3.23)$$

Thin layer chromatography (TLC)

Thin-layer chromatography works in the same way as paper chromatography except that in TLC, a thin layer which is coated with a solid adsorbent material on one side is used.

Confirmatory test for bromide and iodide ions

Partition distribution law serves as a confirmatory test for bromine and iodide ions. To confirm the presence of bromide or iodide in the solution, a solution is treated with chlorine water. If iodide or bromide ions are present, they will be oxidised to iodine and bromine, respectively. When the solution is shaken with trichloromethane (chloroform) and left to stand, two layers are formed with the denser chloroform at the bottom. Iodine or bromine distributes itself between the aqueous and the chloroform layers. Being more soluble in chloroform, iodine or bromine concentrates at the bottom layer, making it violet for iodine and red for bromine.

Task 3.4

Evaluate the methods traditional healers and home remedies use to harness therapeutic properties of medicinal plants to create remedies tailored to specific health conditions.

Exercise 3.4

1. How is chromatography used for the development of drug compounds?
2. Why is the choice of the solvent important in chromatography?
3. How does the distribution law relate to solubility?
4. At 25 °C iodine solution in water contains 0.0516 g/L of iodine in equilibrium with CCl_4 solution containing 4.1280 g/L of iodine. If at 25 °C the water contains 0.410 g/litre of iodine, calculate the solubility of iodine in the CCl_4 solution.

5. The partition coefficient of solute **M** between ethoxyethane and water is 5.0. Calculate the amount of **M** extracted from a solution containing 10 g of **M** in 50 cm^3 of water using 100 cm^3 of ethoxyethane.

6. The partition coefficient for ammonia distributed between the aqueous and chloroform layers is approximately 25. If a 25.00 mL sample of the aqueous ammonia layer requires approximately 24.50 mL of 0.50 mol dm^{-3} sulfuric acid for complete neutralisation, calculate the concentration (mol dm^{-3}) of ammonia in the chloroform layer.

7. An organic compound is two times more soluble in ether than water. Calculate the amount of the compound extracted when 100 mL of aqueous solution containing 1 g is shaken with (a) 100 mL of ether once and (b) two successive quantities of 50 mL of ether each.

8. A particular liquid compound starts decomposing before it is heated to its boiling point under normal pressure. How can this compound be purified?

9. Can the value of R*f* in chromatography be greater than one? Explain.

Revision exercise 3

1. Why is it not advised to use water as a solvent in column chromatography?
2. Write the open structure of the following compounds and explain whether when mixed, they will exhibit positive or negative deviation from Raoult's law:
   (a) Ethanol and acetic acid
   (b) Water and nitric acid
   (c) Acetone and benzene
   (d) Tetrachloromethane and methanol
3. A sample of phenylamine (aniline) $C_6H_5NH_2$ was steam distilled at 98.6 °C and 1 atm. The distillate was found to contain 25.5 g of water and 7.4 g of phenylamine. If the vapour pressure of water at 98.6 °C is 720 Torr, calculate the molar mass of phenylamine.
4. What technique can be used to investigate the existence of coloured components of black ink?

5. An aqueous solution of succinic acid at 15 °C containing 0.07 g in 10 mL is in equilibrium with an ethereal solution, with 0.013 g in 10 mL. The acid has its normal molecular weight in both solvents. What is the concentration

of the ethereal solution which is in equilibrium with an aqueous solution containing 0.024 g in 10 mL?

6. The distribution coefficient of isobutyric acid between ether and water is 3 at 25 °C.
   (a) What amount of isobutyric acid is removed if 4 g of isobutyric acid in 100 mL of water is extracted with 100 mL of ethoxyethane (ether) at 25 °C?
   (b) What would be the effect if two successive 50 mL portions of ether were used to extract isobutyric acid from the aqueous layer?

7. Given that at 20 °C, only 0.24 g of an organic acid **A** dissolves in 100 mL solution, but 2.70 g of the same acid dissolves in 100 mL of ether.
   (a) Determine the partition coefficient.
   (b) Calculate the extraction percentage if 0.12 g of acid is extracted in 100 mL of aqueous solution.
   (c) Find the volume of ether required to extract 85% of 3.00 g of acid A in 100 mL solution.

8. A solution of 6 g of substance **X** in 50 mL of aqueous solution is in equilibrium with a solution of **X** in diethyl ether containing 108 g of **X** in 100 mL at room temperature. Calculate the mass of **X**, which is extracted by shaking 100 mL of an aqueous solution containing 10 g of **X** with (a) 100 mL of ether and (b) twice 50 mL of ether.

9. The solubility of isobutyric acid in water at 25 °C is about one-third of its solubility in diethyl ether; thus, $K_D = 3.0$. Imagine 4.0 g of isobutyric acid is dissolved in a mixture of 35.0 mL of diethyl ether and 100.0 mL of water:
   (a) What is the acid weight in each layer at equilibrium after the first and second extraction?
   (b) Calculate the percentage extraction after the second extraction.

10. At 298 K, an aqueous solution of iodine contains 0.0387×10^{-3} kg dm^{-3} of solution in equilibrium with 3.31×10^{-3} kg dm^{-3} of iodine in carbon tetrachloride. If the solubility of iodine in CCl_4 is 0.0291 kg dm^{-3}, calculate the solubility of iodine in water.

Chapter Four

Energetics

Introduction

Energetics encompasses various principles and laws that govern the transformation, transfer and utilisation of energy in different systems. In this chapter, you will learn about the heat of the reaction, the enthalpy of the reaction, and the application of Hess's law in determining enthalpy changes for chemical reactions. The competencies developed are important in various aspects such as measuring the energy content of food and determining specific enthalpies of fuels, refrigeration and air conditioning.

Think

World with unknown energetics.

4.1 Heat of reaction

Task 4.1

Explore online resources to learn about energetics and its application in food preparation, transport, health care, and environment.

In chemical reactions, energy changes are involved in forming and breaking bonds. The study of chemical processes leading to energy changes is called *energetics*. A branch of chemistry that describes the energy changes that occur during chemical reactions is referred to as *thermochemistry*. The form of energy that is considered here is the heat energy.

Heat is a form of energy that flows between two objects or two parts of an object because of the difference in temperature. Many chemical reactions involve the transfer of heat from the surroundings to the system or vice versa. The amount of heat absorbed or evolved when the reaction goes to completion is called the *heat of the reaction*.

The direction of flow of energy is from a warmer object or part to a cooler one. For example, thermal energy is transferred from a hot object to your hand if you touch the object because the object is warmer than your hand. Similarly, thermal energy is transferred from your hand to a cube of ice if you touch it because ice is cooler than your hand. Heat is a measure of total energy of an object.

A physical property that quantitatively expresses the degree of hotness or coldness of an object is called *temperature*. When substances become warmer, it means that the average kinetic energy of their particles has increased. This kinetic energy causes what you sense as warmth and is quantitatively measured as temperature. The SI unit of temperature is Kelvin (K), but it can also be expressed in degree Celsius (°C).

Temperature is independent of the amount of substance present. For example, both one bucket of water and one cup of water at 50 °C have the same temperature, even though the heat content is different. Unlike temperature, heat content depends on the amount of substance present. A bucket full of water has a large heat content than a cup full of water although they have the same temperature. Heat is expressed in joules (J) or kilojoules (kJ) named after James Prescott Joule (1818–1889), an English Physicist who studied the nature of heat and discovered its relationship to mechanical work.

A joule is a unit of energy which is equal to work done when a force of one Newton acts through a distance of one meter. That is

$$1 \text{ joule (J)} = 1 \text{ N m} = 1 \text{ (kg m s}^{-2}\text{) m} = \frac{1 \text{ kg} \times \text{m}^2}{\text{s}^2}$$

1 kilojoule (kJ) = 1000 joules (J)

The joule is the most commonly used unit of heat (energy). Heat can also be expressed in a unit of calories or kilocalories.

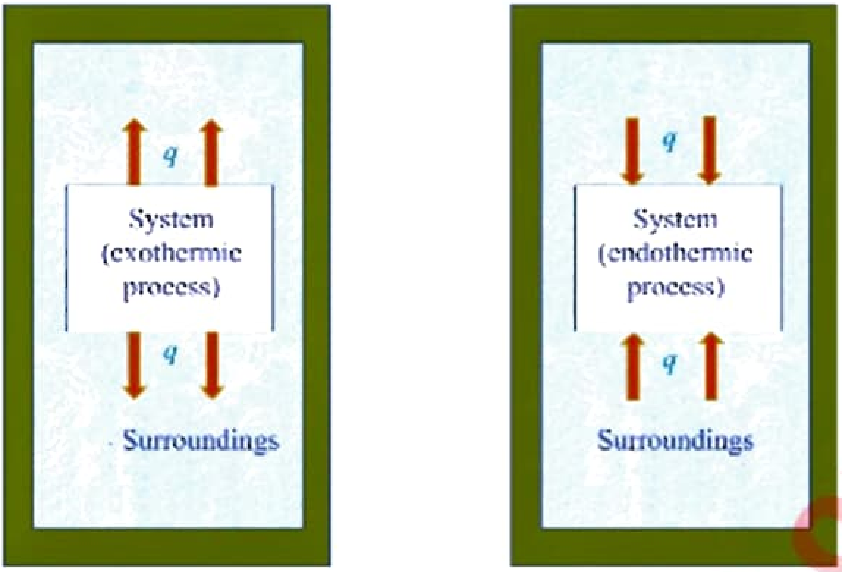
1 calorie (cal) = 4.184 Joules (J)

1000 calories (cal) = 1 kilocalorie (kcal)

1 kilocalorie (kcal) = 4.184 kilojoules (kJ)

Calorie (cal) is the amount of heat required to raise the temperature of 1 gram of water by 1 degree Celsius (1 °C).

As discussed previously, heat flows whenever there is difference in temperature between two parts. For the case of chemical reactions, a system is a collection of matter being studied, and the surroundings refer to everything outside the container. This means that the system and the surroundings are separated by the wall of the container such as beakers and test tubes. If there is heat transfer from the surroundings to the system, heat change is positive, indicating that the surroundings are losing energy and the system is gaining energy. Likewise, if there is a heat transfer from the system to the surroundings, the heat change is negative. In this case, the system is losing energy and the surroundings are gaining energy. The illustration of the energy change between the system and the surroundings is shown in Figure 4.1.



Heat is given out

Heat is absorbed

Figure 4.1: *Energy change between the system and the surroundings*

For exothermic reaction, the system is losing energy, and the temperature of the surroundings increases. For endothermic reaction, the system is gaining energy and therefore the temperature of the surroundings decreases.

4.1.1 Heat capacity and specific heat capacity

When a substance is heated, its temperature increases depending on its heat capacity. *Heat capacity* (C) is the amount of heat required to raise the temperature of a substance by one degree Celsius (1 °C) or one Kelvin (1 K).

The amount of heat required to raise the temperature of a unit mass of a substance by one degree Celsius (1 °C) or one Kelvin (1 K) is called *specific heat capacity* (c). Specific heat capacity tells how much the temperature of an object will increase or decrease by the gain or loss of heat energy.

$$\text{Heat capacity } (C) = \text{mass } (m) \times \text{specific heat capacity } (c) \tag{4.1}$$

The quantity of heat energy (q) can be expressed in terms of mass, heat capacity, specific heat capacity, and a change in temperature, ΔT.

$$q = \text{Heat capacity } (C) \times \text{ change in temperature } (\Delta T) \tag{4.2}$$

Substituting Equation 4.1 in Equation 4.2 gives:

$$q = m \times c \times \Delta T \quad \text{where} \quad \Delta T = T_{\text{final}} - T_{\text{initial}} \tag{4.3}$$

The units of heat capacity are joules per degree Celsius (J/°C) or joules per Kelvin (J/K) while the units of specific heat capacity are joules per kilogram degree Celsius (J/kg°C) or joules per kilogram Kelvin (J/kg K).

Example 4.1

Calculate the amount of heat energy required to increase the temperature of 20 g of nickel from 50 °C to 70 °C given that the specific heat capacity of nickel is equal to 440 J Kg^{-1} °C^{-1}.

Solution

Data given:

Mass of nickel = 20 g, Temperature (T_1) = 50 °C, T_2 = 70 °C

Specific heat capacity of nickel (c) = 440 J kg^{-1} °C^{-1}

$$q = m \times c \times \Delta T$$

$$m = 20\ \text{g} = 0.02\ \text{kg},\ \Delta T = 70\ °\text{C} - 50\ °\text{C} = 20\ °\text{C}$$

$$q = 0.02\ \text{kg} \times 440\ \text{J kg}^{-1}\ °\text{C}^{-1} \times 20\ °\text{C} = 176\ \text{J}$$

Therefore, the heat energy required is 176 J.

Example 4.2

Calculate the heat capacity of 80.0 g of water given that the specific heat capacity of water is 4.48 J g^{-1} °C^{-1}.

Solution

Data given:

Mass of water = 80.0 g

Specific heat capacity of water (c) = 4.18 J/g °C

Heat capacity (C) = mass (m) × specific heat capacity (c)

$$\text{Heat capacity } (C) = 80\ \text{g} \times 4.18\ \text{J g}^{-1}\ °\text{C}^{-1} = 334.4\ \text{J}\ °\text{C}^{-1}$$

Therefore, the heat capacity of 80 g of water is 334.4 J °C^{-1}.

4.1.2 Endothermic and exothermic reactions

Many chemical reactions involve the transfer of heat from the surroundings to the systems or vice versa. The chemical reaction which involves the transfer of heat from the surroundings to the reaction system is called *endothermic reaction*. This means that the reaction is accompanied with the absorption of energy. The chemical reaction which involves the transfer of heat from the reaction system to the surroundings is called *exothermic reaction*. This means that the reaction is accompanied with the evolution of heat. The energy profile diagrams for both endothermic and exothermic reactions are shown in Figure 4.2.

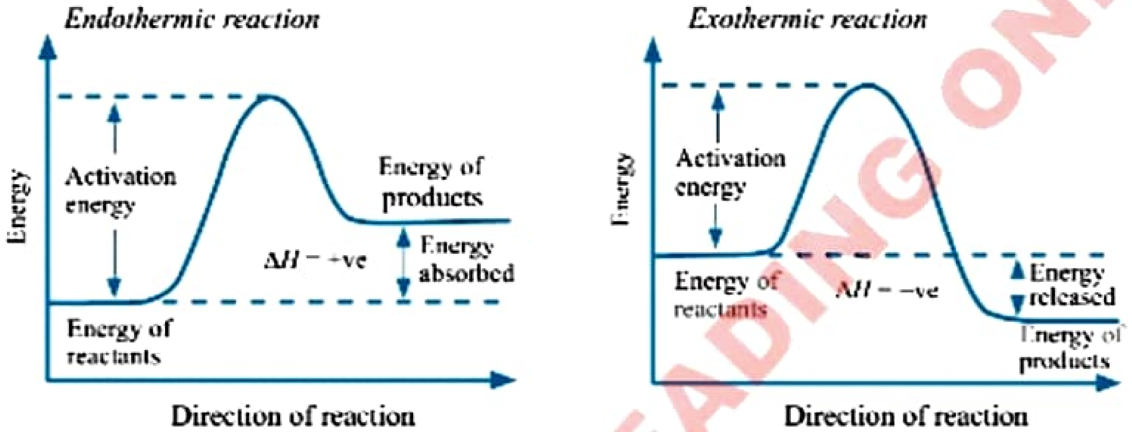


Figure 4.2: *Energy profiles for the endothermic and exothermic reactions*

An endothermic reaction has the products at a higher energy state than the reactants; that is, the internal energy of products is greater than that of the reactants. The change in enthalpy for endothermic reaction is positive ($\Delta H > 0$). An example of endothermic reaction is the dissolution of ammonium nitrate in water to form an aqueous solution of ammonium nitrate.

$$NH_4NO_3(s) \xrightarrow{H_2O(l)} NH_4NO_3(aq) \qquad \Delta H > 0$$

In the exothermic reaction, the products are at a lower energy state than the reactants; that is, the internal energy of the reactants is at greater energy than that of the products. The change in enthalpy for exothermic reaction is negative ($\Delta H < 0$). An example of exothermic reaction is the combustion of methane to form carbon dioxide and water.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H < 0$$

4.2 Enthalpy of reaction

The *heat of reaction* is the amount of heat absorbed or evolved when the reaction goes to completion. The amount of heat absorbed or evolved at constant temperature and pressure is called *enthalpy* (H), and the corresponding amount of heat change during the reaction is called *enthalpy change* (ΔH). Several factors affect the quantity of heat released or absorbed during physical or chemical changes. These include the amounts of reactants or products, the physical states of the reactants and the products, temperature, and pressure. Therefore, in writing a thermochemical equation, the amount of heat change in the reaction or process must be indicated. A *thermochemical equation* is a balanced stoichiometric chemical equation that includes the enthalpy change (ΔH). The equation must indicate the physical states of the reactants and products as solid (s), liquid (l), aqueous (aq), and gas (g), and must be balanced. The following is an example of a thermochemical equation:

$$\mathrm{HNO_3}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{NaNO_3}(aq) + \mathrm{H_2O}(l) \quad \Delta H = -57.2\ \mathrm{kJ\ mol^{-1}}$$

The above thermochemical equation is complete as it is balanced. It shows physical states of the reactants and products as well as the enthalpy change for the reaction.

The heat of reaction can be measured either at constant volume or constant pressure. However, most of the chemical reactions are carried out at constant pressure (atmospheric pressure). The magnitude of changes at constant volume and constant pressure is different. At constant volume, the heat change accompanying a chemical reaction is called *a change in the internal energy* (ΔU) because there is no work done. The enthalpy change accompanying a chemical reaction can be measured accurately and is expressed as follows:

$$\Delta H = H_{\text{products}} - H_{\text{reactants}} \qquad (4.4)$$

It is not possible to measure enthalpy (H) directly, only the enthalpy change (ΔH) can be measured. Since the value of the enthalpy change depends on temperature, pressure, concentration and physical states of the reactants, then the enthalpy changes are stated under standard conditions (that is, gases at 1 atm, solutions at unit concentration, and substances in their standard states).

The notation ΔH° denotes the standard enthalpy change in which the reactants and products are in their standard states. For both endothermic and exothermic reactions, the standard enthalpy change of reaction is symbolised by $\Delta H^\circ_{\text{rxn}}$. The units of $\Delta H^\circ_{\text{rxn}}$ are kilojoules per mole ($\mathrm{kJ\ mol^{-1}}$).

Therefore, the standard enthalpy change is given by:

$$\Delta H^{\circ}_{\text{rxn}} = \Delta H^{\circ}_{\text{products}} - \Delta H^{\circ}_{\text{reactants}}$$

where, Δ – represents change

ΔH° – represents standard enthalpy change

rxn – denotes reaction

The standard state of a substance (solid, liquid or gas) is a pure substance at a pressure of 1 atm and temperature of 25 °C. Therefore, $\Delta H^{\circ}_{\text{rxn}}$ is the standard enthalpy of a reaction at standard conditions. It implies that the reaction takes place at 25 °C and 1 atmospheric pressure.

4.2.1 Types of enthalpy changes of reactions

There are different types of heat or enthalpy changes of reactions ($\Delta H^{\circ}_{\text{rxn}}$) depending on the nature of the reactions. These include: enthalpy of formation (ΔH_{f}), enthalpy of combustion (ΔH_{c}), enthalpy of solution (ΔH_{sol}), enthalpy of neutralisation (ΔH_{n}), enthalpy of fusion (ΔH_{fus}), enthalpy of vaporisation (ΔH_{vap}), enthalpy of sublimation (ΔH_{sub}), enthalpy of transition (ΔH_{t}), enthalpy of dissociation (ΔH_{dis}), enthalpy of dilution (ΔH_{dil}) and enthalpy of atomisation (ΔH_{at}).

Enthalpy of formation (ΔH_{f})

The *enthalpy of formation of a compound* is the enthalpy change that takes place when one mole of a compound is formed from its elements.

For example,

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^{\circ}_{\text{f}} = -285.8\ \text{kJmol}^{-1}$$

The enthalpy change when one mole of a substance is formed from its pure elements in their standard state under standard conditions (1 atm and 25 °C) is called *standard enthalpy of formation* (ΔH°_{f}). The equation used for the standard enthalpy change of formation is

$$\Delta H^{\circ}_{\text{rxn}} = \sum \Delta H^{\circ}_{\text{f(products)}} - \sum \Delta H^{\circ}_{\text{f(reactants)}} \qquad (4.5)$$

Thus, the standard enthalpy change of formation is the sum of the standard enthalpies of formation of the products minus the sum of the standard enthalpies of formation of the reactants.

Note: The enthalpy of formation of elements which naturally occur in their standard state is generally considered to be zero. For example the enthalpy of formation of oxygen (ΔH_f) = 0 kJ mol^{-1}

Example 4.3

Consider a simple chemical equation with the variables A, B, and C representing different compounds:

$$A + B \longrightarrow C$$

Given the standard enthalpy of formation values as

$$\Delta H^{\circ}_{f}(A) = +411 \text{ kJ mol}^{-1}$$

$$\Delta H^{\circ}_{f}(B) = -252 \text{ kJ mol}^{-1}$$

$$\Delta H^{\circ}_{f}(C) = +525 \text{ kJ mol}^{-1}$$

Calculate the standard enthalpy change of the reaction.

Solution

The equation for the standard enthalpy change of formation is written as follows:

$$\Delta H^{\circ}_{rxn} = \Delta H^{\circ}_{f}(C) - \left(\Delta H^{\circ}_{f}(A) + \Delta H^{\circ}_{f}(B)\right)$$

$$\Delta H^{\circ}_{rxn} = (+525 \text{ kJ mol}^{-1}) - \left((411 \text{ kJmol}^{-1}) + (-252 \text{ kJmol}^{-1})\right)$$

$$\Delta H^{\circ}_{rxn} = +525 \text{ kJ mol}^{-1} - 159 \text{ kJ mol}^{-1} = 366 \text{ kJ mol}^{-1}$$

Enthalpy of combustion (ΔH_c)

The *enthalpy of combustion* of a substance is the enthalpy change of a system when one mole of the substance is completely burnt in oxygen.

For example:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_c = -890.4 \text{ kJmol}^{-1}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_c = -393.5 \text{ kJmol}^{-1}$$

The heat of combustion can be used to calculate the heat of formation and the *calorific value* of foods and fuels. The calorific value of a substance is the amount of heat produced in calories (or joules) when one gram of a substance is completely burnt. If the combustion occurs at standard conditions, the heat of combustion is referred to as the *standard enthalpy of combustion* (ΔH_c°).

Example 4.4

The heat of combustion of propane (C_3H_8) is -2220.2 kJ mol^{-1}. If the heats of formation of $CO_2(g)$ and $H_2O(l)$ are -393.5 and -285.8 kJ mol^{-1}, respectively, calculate the standard heat of formation of propane.

Solution

Given the reactions and their corresponding enthalpies:

(i) $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l) \quad \Delta H_c^\circ = -2220.2 \text{ kJmol}^{-1}$

(ii) $C(s) - O_2(g) \longrightarrow CO_2(g) \quad \Delta H_f^\circ = -393.5 \text{ kJmol}^{-1}$

(iii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad \Delta H_f^\circ = -285.8 \text{ kJmol}^{-1}$

The required equation is the formation of propane C_3H_8 from $C(s)$ and $H_2(g)$.

$$3C(s) + 4H_2(g) \longrightarrow C_3H_8(g) \quad \Delta H_f^\circ = ?\text{ kJ mol}^{-1}$$

Therefore, you need to manipulate the above equations in such a way that you get the formation equation of propane.

Propane is formed from 3 moles of $C(s)$; therefore, multiply equation (ii) by 3 and equation (iii) by 4 together with their energies.

$$3C(s) + 3O_2(g) \longrightarrow 3CO_2(g) \quad \Delta H_f^\circ = -1180.5 \text{ kJmol}^{-1}$$

$$4H_2(g) + 2O_2(g) \longrightarrow 4H_2O(l) \quad \Delta H_f^\circ = -1143.2 \text{ kJmol}^{-1}$$

Add these equations to get equation (iv).

(iv) $3C(s) + 4H_2(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l) \quad \Delta H = -2323.7 \text{ kJmol}^{-1}$

Reverse equation (i). Note that if you reverse equation (i), you must also reverse the sign of enthalpy.

$$\text{(v) } 3CO_2(g) + 4H_2O(l) \longrightarrow C_3H_8(g) + 5O_2(g) \qquad \Delta H = +2220.2\ \text{kJmol}^{-1}$$

Combine equations (iv) and (v) and cancel similar atoms, molecules, and compounds appearing on both sides of the equations.

$$3C(s) + 4H_2(g) + \cancel{5O_2}(g) \longrightarrow \cancel{3CO_2}(g) + \cancel{4H_2O}(l) \qquad \Delta H = -2323.7\ \text{kJmol}^{-1}$$

$$\cancel{3CO_2}(g) + \cancel{4H_2O}(l) \longrightarrow C_3H_8(g) + \cancel{5O_2}(g) \qquad \Delta H = +2220.2\ \text{kJmol}^{-1}$$

$$3C(s) + 4H_2(g) \longrightarrow C_3H_8(g) \qquad \Delta H_f^\theta = -103.5\ \text{kJmol}^{-1}$$

Therefore, the heat of formation of propane is $-103.5\ \text{kJmol}^{-1}$.

Enthalpy of solution (ΔH_{sol})

The *enthalpy of solution* is the change in enthalpy when one mole of a substance is dissolved in a large excess of solvent (infinite dilution) such that no further heat change occurs when more solvent is added to the solution. *Infinite dilution* is a condition in which the concentration of a solute in a solvent is extremely low, approaching zero. In this state, the solution contains so much solvent such that adding more solvent brings no significant change in the concentration of the solute. For example, the enthalpies of solution of $NH_4NO_3(s)$ and $NaCl(s)$ when added in water are

$$NH_4NO_3(s) \xrightarrow{H_2O(l)} NH_4^-(aq) + NO_3^-(aq) \qquad \Delta H = +25.7\ \text{kJmol}^{-1}$$

$$NaCl(s) \xrightarrow{H_2O(l)} Na^+(aq) + Cl^-(aq) \qquad \Delta H = +3.9\ \text{kJmol}^{-1}$$

The concept of infinite dilution is included in the enthalpy of solution because if there is still a room for dilution, a further heat change may occur. The energy change in the solution process involves the following steps:

(a) Breaking of solute-solute attractions (endothermic), for example, lattice energy in salts.

(b) Breaking of solvent-solvent attractions (endothermic), for example, hydrogen bonding in water.

(c) Forming solvent–solute attraction (exothermic) in solvation.

The magnitude of the enthalpy of solution is the summation of the energy changes involved in the solute-solute, solvent–solvent and solute–solvent interactions.

The enthalpy changes when one mole of a substance is dissolved in a solvent to form one litre (1 dm^3) of solution at standard conditions (1 atm and 25 °C) is called *standard enthalpy of solution*. The standard enthalpies of the solution of various compounds are shown in Table 4.1.

Table 4.1: *Standard enthalpy changes of solution (ΔH°_{sol}), for selected compounds*

Solution	Standard enthalpy change, ΔH°_{sol} (kJ mol^{-1}) in water at 25 °C
Hydrochloric acid	–74.48
Ammonium nitrate	+25.69
Ammonia	–30.50
Potassium hydroxide	–57.61
Calcium hydroxide	–16.2
Sodium chloride	+3.90
Potassium chloride	+17.2
Acetic acid	–1.51
Sodium hydroxide	–44.51

Activity 4.1

Aim: To determine the enthalpy of solution

Requirements: Beakers, thermometer, stirring rod, distilled water, 2.00 g of each of ammonium nitrate, calcium chloride, sodium hydroxide and sodium chloride

Procedure

1. Measure 50 mL of distilled water into a 100 mL beaker and record its initial temperature (T_1).
2. Add 2.00 g of ammonium nitrate in the same beaker, swirl the mixture, and record the final temperature (T_2).
3. Repeat the procedure for the rest of the sample salts.

Questions

1. What are the temperature changes for each salt?
2. Which dissolution processes are endothermic or exothermic? Explain.
3. What are the heat changes of reactions during the dissolution of the salt samples? Assume that there is no change in the volume of the solution and neglect the heat absorbed by the container. (Specific heat capacity of solution = 4.2 $J\ g^{-1}\ K^{-1}$, density of solution = 1.0 $g\ cm^{-3}$).
4. What are the molar enthalpies of solution for each salt sample?
5. How relevant is this activity to daily domestic activities?

Enthalpy of neutralisation (ΔH_n)

The *enthalpy of neutralisation* is the heat change when solutions of an acid and alkali react to produce one mole of water. The heat change of neutralisation is always measured per mole of water formed and it is always negative because the reaction of an acid and base is accompanied with the evolution of heat. For example:

$$HNO_3(aq) + NaOH(aq) \longrightarrow NaNO_3(aq) + H_2O(l) \qquad \Delta H_n = -57.32\ kJmol^{-1}$$

$$2HNO_3(aq) + Ca(OH)_2(aq) \longrightarrow Ca(NO_3)_2(aq) + 2H_2O(l) \qquad \Delta H_n = -57.32\ kJmol^{-1}$$

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l) \qquad \Delta H_n = -57.24\ kJmol^{-1}$$

$$HCl(aq) + LiOH(aq) \longrightarrow LiCl(aq) + H_2O(l) \qquad \Delta H_n = -57.32\ kJmol^{-1}$$

The enthalpies of neutralisation show that the heat of neutralisation of strong acids and strong bases is almost the same regardless of which acids or bases are used. This observation is explained by considering the general equation for the ionisation of a strong acid (HA) and a strong base (BOH):

$$H^+(aq) + A^-(aq) + B^+(aq) + OH^-(aq) \longrightarrow A^-(aq) + B^+(aq) + H_2O(l)$$

$$\Delta H_n = -57.32\ kJmol^{-1}$$

The ions from the acid and base cancel each other because they are present in both sides of the equation, leaving only $H^+(aq)$ and $OH^-(aq)$ which react to form $H_2O(l)$. As a result, the heat of neutralisation is simply the heat of the formation of water from hydrogen and hydroxyl ions.

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \qquad \Delta H_n = -57.32\ kJmol^{-1}$$

For the case of weak acids or weak bases, the neutralisation process involves the dissociation of weak acid or base in addition to the hydrogen and hydroxyl ions. Therefore, the values of heat of neutralisation differ widely when weak acids or bases are neutralised by strong acids or bases.

For example:

$$HCl(aq) + NH_4OH(aq) \longrightarrow NH_4Cl(aq) + H_2O(l) \qquad \Delta H_n = -51.5\ \text{kJmol}^{-1}$$

$$HCOOH(aq) + NH_4OH(aq) \longrightarrow HCOONH_4(aq) + H_2O(l)$$

$$\Delta H_n = -49.79\ \text{kJmol}^{-1}$$

Activity 4.2

Aim: To determine the enthalpy of neutralisation

Requirements: Beakers, measuring cylinder, thermometer, stirring rod, 0.10 M HCl, and 0.10 NaOH

Procedure

1. Use the thermometer to measure the temperature of the two solutions separately and record as T_1 for the first solution and T_2 for the second solution.
2. Record the average temperature of the two solutions. This is your initial temperature of the solution.
3. Measure 25 mL of 0.10 M NaOH solution into a 100 mL beaker and put a thermometer in it.
4. Measure 25 mL of 0.10 M HCl solution and pour it into the beaker containing NaOH in step 3. Mix the contents and record the maximum temperature. This is your final temperature of the reaction.

Questions

1. What were the temperature changes during the reaction?
2. What is the molar heat of the neutralisation reaction? (Given that the specific heat capacity of the solution = 4.2 J g^{-1} K^{-1} and the density of the solution = 1.0 g cm^{-3}. Neglect the heat loss to the surroundings).

Enthalpy of fusion (ΔH_{fus})

The *enthalpy of fusion* is the enthalpy change when one mole of a solid substance is converted into a liquid state at its melting point. For example, the enthalpy change for the transition from ice to liquid water.

$$\underset{\text{Ice}}{H_2O(s)} \longrightarrow \underset{\text{Water}}{H_2O(l)} \qquad \Delta H_{fus} = +6.0\,\text{kJ mol}^{-1}$$

This enthalpy change is positive, meaning that the transition from ice to liquid water is accompanied with the absorption of 6.0 kJ mol^{-1} of heat. The heat of fusion accounts for the magnitude of intermolecular forces of attraction. The greater the heat of fusion of a substance, the higher the magnitude of intermolecular forces of attraction. The enthalpies of fusion of sodium chloride (NaCl) and magnesium chloride ($MgCl_2$) are +29.0 kJ mol^{-1} and −43.0 kJ mol^{-1}, respectively. These high values of enthalpies of fusion of ionic compounds are due to strong coulombic or electrostatic forces between the constituent ions.

$$NaCl(s) \xrightarrow{\text{melting}} NaCl(l) \qquad \Delta H_{fus} = +29\ \text{kJmol}^{-1}$$

$$MgCl_2(s) \xrightarrow{\text{melting}} MgCl_2(l) \qquad \Delta H_{fus} = +43\ \text{kJmol}^{-1}$$

Enthalpy of vaporisation (ΔH_{vap})

The *enthalpy of vaporisation* is the enthalpy change when one mole of liquid is converted into vapour or gaseous state at its boiling point. A good example is the enthalpy change for the transition from water to steam.

$$\underset{\text{Water}}{H_2O(l)} \longrightarrow \underset{\text{Steam}}{H_2O(g)} \qquad \Delta H = +40.7\ \text{kJ mol}^{-1}$$

This positive enthalpy change means the transition from liquid water to steam is accompanied with the absorption of 40.7 kJ mol^{-1}. of heat. Like the transition from solid to liquid, the heat of vaporisation accounts for the magnitude of intermolecular forces of attractions in liquid. The trend of magnitude of enthalpies of vaporisation is shown as follows:

$$\Delta H_{vap}\,(\text{ionic liquid}) >> \Delta H_{vap}\,(\text{polar liquid}) > \Delta H_{vap}\ (\text{non-polar liquid})$$

Enthalpy of sublimation (ΔH_{sub})

The *enthalpy of sublimation* is the enthalpy change when one mole of a solid is directly converted into a gaseous state or vapour. Example, the enthalpy change for the transition from iodine solid to iodine vapour (gas) is

$$I_2(s) \longrightarrow I_2(g) \qquad \Delta H_{sub} = +62.4\ \text{kJmol}^{-1}$$

The enthalpy of sublimation is the sum of the enthalpies of fusion and vaporisation.

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap} \qquad (4.6)$$

The enthalpies of fusion (ΔH_{fus}), vaporisation (ΔH_{vap}) and sublimation(ΔH_{sub}) are collectively known as enthalpies of transition (ΔH_t).

Enthalpy of dissociation (ΔH_{dis})

The *enthalpy of dissociation* is the enthalpy change when one mole of a bond is broken by homolysis. For example, the dissociation of 1 mole of a gaseous hydrogen chloride molecules into gaseous hydrogen and chlorine atoms requires 432 kJ.

$$HCl(g) \longrightarrow H(g) + Cl(g) \qquad \Delta H_{dis} = +432\ \text{kJmol}^{-1}$$

Enthalpy of atomisation (ΔH_{at})

The *enthalpy of atomisation* is the enthalpy change when one mole of a gaseous substance is decomposed into its atoms in the gas phase. For example, the decomposition of hydrogen gas into its gaseous atoms.

$$H_2(g) \longrightarrow 2H(g) \qquad \Delta H_{at} = +435.4\ \text{kJmol}^{-1}$$

Other examples of atomisation with their corresponding energies are as follows:

$$Cl_2(g) \longrightarrow 2Cl(g) \qquad \Delta H_{at} = +242.0\ \text{kJmol}^{-1}$$

$$I_2(g) \longrightarrow 2I(g) \qquad \Delta H_{at} = +213.2\ \text{kJmol}^{-1}$$

The enthalpy of atomisation of polyatomic molecules like methane (CH_4) is equal to the enthalpy change for the corresponding decomposition reaction.

$$CH_4(g) \longrightarrow C(g) + 4H(g) \qquad \Delta H_{at} = +1665.0\ \text{kJmol}^{-1}$$

Exercise 4.1

1. Why is it important to consider the heat capacity of materials when designing thermal insulation for buildings or containers?
2. When potassium nitrate dissolves in water, the beaker containing the solution gets cooler. Explain whether the dissolution of the salt is an exothermic or endothermic.

3. What can be considered as a "system" and what are the "surroundings" when studying a mixture of chemicals undergoing a reaction?
4. Consider a 2 kg steel frying pan and a 2 g steel pin. Are the heat capacities of these objects different? Explain.
5. The specific heat capacity of water is 4.18 J g^{-1} °C. How many joules of heat must be added to 1 g of water to increase its temperature by 10 degrees Celsius?
6. In one experiment, a student placed 50.0 mL of 1.00 M HCl in a calorimeter and carefully measured its temperature to be 25.5 °C. To this acid, 50.0 mL of 1.00 M NaOH solution whose temperature was also 25.5 °C, was added. The mixture was quickly stirred and the student noticed that the temperature of the mixture inreased to 32.4 °C. What is the molar heat of neutralisation? Assume that the specific heat and density of the solution are the same as that of water, 4.184 J g^{-1} °C^{-1} and 1.00 g/mL, respectively.
7. Explain why you feel cold after entering a cold room.

4.2.2 Measurement of heat of reaction by calorimetry

Calorimetry is a technique of measuring the amount of heat that may be generated or consumed by a reaction. The device used to measure the amount of heat of reaction is called *calorimeter*. This device consists of insulated walls which prevent the exchange of heat between the system and the surroundings. The measurement of heat of reaction is done by enclosing the reactants in the calorimeter and measuring the temperature before and after the reaction. The heat released or absorbed is then determined from the temperature difference. There are different types of calorimeters, but the commonly used ones are *water calorimeter* and *bomb calorimeter*.

Water calorimeter

The water calorimeter uses water as the medium of heat transfer. The apparatus consists of thermally insulated water bath in which a reaction chamber is placed. The thermometer and the stirrer are suspended into water bath through two openings of the lid. A pre-weighed amount of water is poured into the water bath and the initial temperature is recorded. The

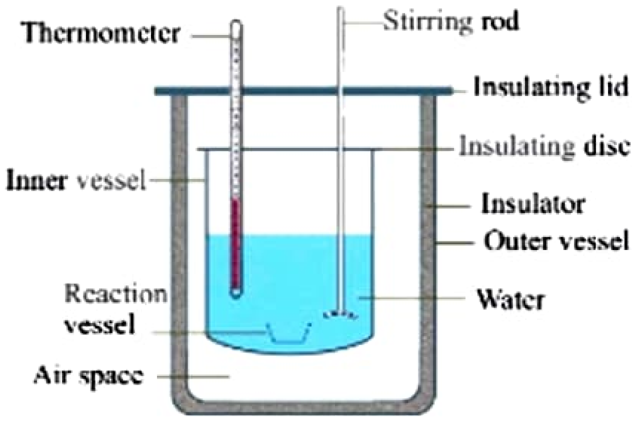


Figure 4.3: *Water calorimeter*

calorimeter and the reactants are left to equilibrate temperature and the reactants are then mixed. The maximum or minimum temperature reached is recorded as the final temperature of the reaction. This is because, the heat released by the reaction is absorbed by water hence its temperature rises, and if the reaction absorbs heat, the temperature of water will decrease. The water calorimeter is illustrated in Figure 4.3. The heat produced or absorbed is calculated from Equation 4.3.

Example 4.5

The temperature of the solution rose by 4.3 °C when 0.20 g of zinc powder was added to 50.00 cm^3 of 0.100 mol dm^{-3} silver nitrate solution. Deduce which reagent was in excess and then calculate the molar enthalpy change (ΔH) of the reaction. Assume that the density of the solution is 1.00 $g\,cm^{-3}$ and the specific heat capacity of the solution is 4.18 ($J\ g^{-1}\ °C^{-1}$). Ignore the heat capacity of the metals and dissolved ions.

Solution

Quantity of heat = mass (g) × specific heat capacity ($J\ g^{-1}\ °C^{-1}$) × change in temperature

Assumption: The volume of water is equal to the volume of silver nitrate solution = 50.00 cm^3

Therefore, the mass of water = volume of solution × density of solution
Thus, the mass of water = $50.00\ cm^3 \times 1\,g\,cm^{-3} = 50.00\,g$
Data given:

Mass of zinc = 0.200 g
$\Delta T = 4.3\ °C$, $c = 4.18\,J\,g^{-1}\ °C^{-1}$
Heat change $(q) = m \times c \times \Delta T = 50.00\,g \times 4.18\,J\,g^{-1}\ °C^{-1} \times 4.3°C = 898.7\,J$

Calculating the molar enthalapy change (ΔH)

$$\text{Amount of } AgNO_3 = \frac{0.1\ mol}{1000\ cm^3} \times 50.00\ cm^3 = 0.005\ mol$$

$$\text{Amount of zinc} = \frac{0.200\ g}{65.38\ g\,mol^{-1}} = 0.0031\ mol$$

$$2AgNO_3(aq) + Zn(s) \longrightarrow Zn(NO_3)_2(aq) + 2Ag(s)$$

$AgNO_3$: Zn
2 mol : 1 mol
0.005 mol : ?

The amount of zinc reacting with 0.005 mol of $AgNO_3$ is

$$\frac{0.005\ \text{mol}\times 1}{2} = 0.0025\ \text{mol}$$

0.005 mol of $AgNO_3$ requires 0.0025 mol of zinc for a complete reaction. Therefore, zinc was in excess because 0.0031 mol of Zn is available. But the temperature change and the enthalpy change are determined by the limiting reactant, which for this case, is the silver nitrate.

$$\text{Therefore, the enthalpy change} = \frac{\text{quantity of heat evolved}}{\text{amount of limiting reactant}}$$

$$\Delta H = \frac{-0.8987\ \text{kJ}}{0.005\ \text{mol}} = -180\ \text{kJ mol}^{-1}$$

The negative sign used on the quantity of heat indicates that there was an evolution of heat during the reaction (exothermic reaction).

Temperature correction during calorimetric measurement

For reactions that occur very fast, accurate measurements of temperature can be easily obtained using a simple calorimeter. For slow reactions, less accurate measurements of temperature are obtained due to loss of temperature to the surroundings. The correction for this temperature loss can be done by plotting the graph of temperature versus time. Figures 4.4 and 4.5 show the temperature versus time curves for exothermic and endothermic reactions, respectively. One reagent is placed in the simple calorimeter and the temperature is recorded up to about 4 minutes which is the time for the equilibration of temperature. The second reagent is then added and the temperature is recorded in intervals until the maximum or minimum temperature is reached depending on the type of the reaction. The recording of temperature is done for several more minutes while stirring the mixture. The temperature versus time curve is plotted from the recorded data. The lines are extrapolated to obtain the maximum or minimum temperature

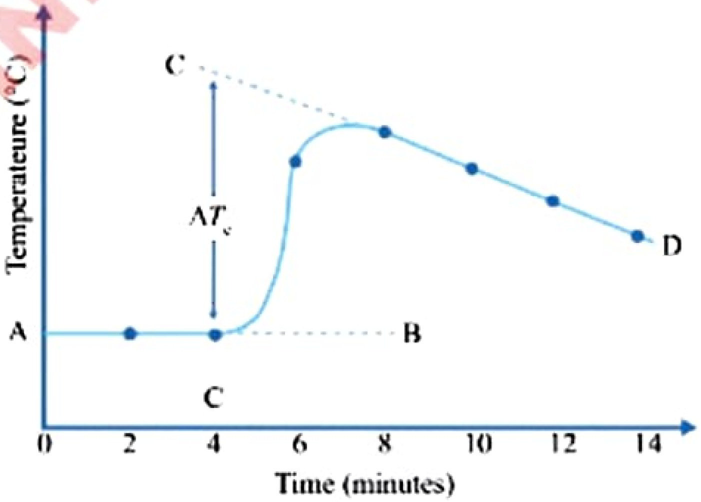


Figure 4.4: *Temperature versus time curve for exothermic reaction*

possible (point C) in the absence of heat exchange between the system and the surroundings.

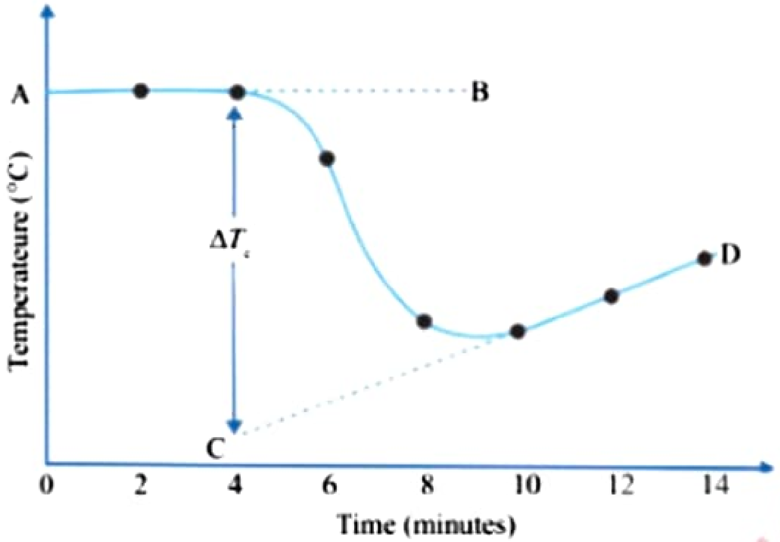


Figure 4.5: *Temperature versus time curve for endothermic reaction*

Bomb calorimeter (constant-volume calorimeter)

A bomb calorimeter is a common type of constant-volume calorimeter which is designed to accurately measure the enthalpy of combustion reactions. The measurement of enthalpy of combustion is very crucial for the determination of standard enthalpies of formation of many new compounds. The bomb calorimeter is illustrated in Figure 4.6. The calorimeter consists of a steel bomb which contains the reactants, a water bath in which the bomb is submerged, a thermometer, a motorised stirrer and ignition wires.

A pre-weighed combustible sample is transfered to the bomb and then filled with oxygen gas. The bomb is then immersed in an insulated water bath which is fitted with motorised stirrer and a thermometer. The calorimeter is left for sometime to allow every component to equilibriate temperature. The initial temperature of the calorimeter is recorded. The sample is ignited by the electrical source and the combustion reaction takes place. As the reaction proceeds, the heat evolved rises the temperature of the

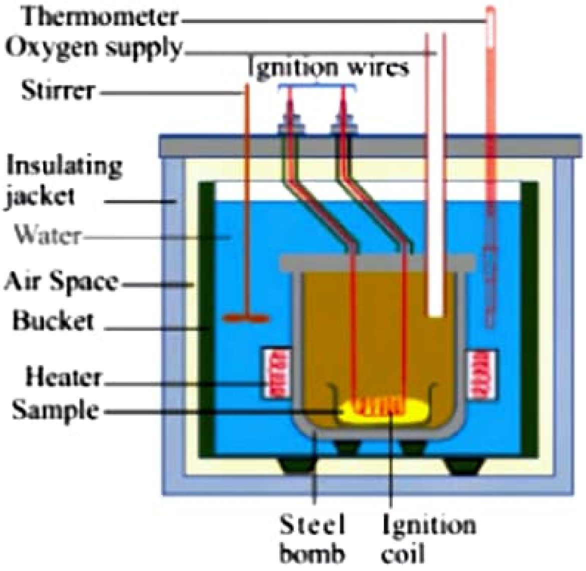


Figure 4.6: *Bomb calorimeter*

system. The final temperature is then recorded. Since the mass of the sample and corresponding heat capacity are known, the measured ΔT is used to calculate the quantity of the heat released.

Activity 4.3

Aim: To determine the enthalpy of combustion of fuel and food samples using calorimetry

Requirements: Fuel samples (e.g., ethanol, propanol, paraffin wax), nuts, potato fries, crackers, bread, calorimeter, thermometer, measuring cylinder, ignition source, water, and stirring rod

Procedure

1. Set up the calorimeter by placing it on a stable surface and insulating it with a lid if available.
2. Fill the calorimeter with a known volume of water and record the initial temperature of the water.
3. Weigh the fuel or food sample to determine its mass, and transfer it into the calorimeter.
4. Ignite the sample using an ignition source and allow it to burn completely.
5. Stir the water gently with the stirring rod to ensure a uniform temperature distribution.
6. Record the maximum temperature reached by the water.
7. Repeat the experiment with the same fuel or food sample multiple times to ensure accuracy of the results.
8. Repeat steps 3 to 7 for all food samples provided.

Questions

1. What is the energy content of each fuel and food sample?
2. Among the food substances investigated, which one is suitable for people with high metabolic rates? Explain.
3. What is the significance of the enthalpy of combustion in understanding the energy content of a substance?

Note: The specific heat capacity of water is 4.2 J/g°C.

Example 4.6

A 1.150 g of sucrose was burnt in a bomb calorimeter. If the temperature increased from 23.42 °C to 27.64 °C, and the heat capacity of the calorimeter was 4.90 kJ °C $^{-1}$, what was the heat of combustion of sucrose ($C_{12}H_{22}O_{11}$) in kilojoules per mole?

Solution

Data given:

Mass of sucrose ($C_{12}H_{22}O_{11}$) = 1.150 g

Initial temperature (T_i) = 23.42 °C

Final temperature, (T_f) = 27.64 °C

Heat capacity of calorimeter = 4.90 kJ °C $^{-1}$

From,

$$q_{\text{calorimeter}} = \text{Heat capacity of colorimeter} \times \text{change in temperature}$$

$$q_{\text{calorimeter}} = C \times \Delta T = 4.90 \text{ kJ} ^\circ\text{C}^{-1} \times (27.64 - 23.42)\ ^\circ\text{C}$$

$$= 4.90 \text{ kJ} ^\circ\text{C}^{-1} \times 4.22\ ^\circ\text{C} = 20.7 \text{ kJ}$$

The heat released in the combustion reaction is equal to the heat gained by the calorimeter.

$$-q_{\text{reaction}} = q_{\text{calorimeter}} \Rightarrow q_{\text{reaction}} = -q_{\text{calorimeter}} = -20.7 \text{ kJ}$$

But the question asks for kJ/mol for combustion of $C_{12}H_{22}O_{11}$:

$$\text{Moles of sucrose} = \frac{\text{mass of sucrose (g)}}{\text{molar mass of sucrose (gmol}^{-1})}$$

$$= \frac{1.150 \text{ g}}{[(12 \times 12) + (1 \times 22) + (16 \times 11)] \text{ g mol}^{1-}} = 0.00336 \text{ mol}$$

$$\text{Heat of combustion} = \frac{-20.7 \text{ kJ}}{0.00336 \text{ mol}} = -6160.7 \text{ kJmol}^{-1}$$

Thus, the heat of combustion of sucrose is $\mathbf{-6160.7 \text{ kJ mol}^{-1}}$.

Exercise 4.2

1. A simple calorimeter is not suitable for the measurement of heat of a reaction that proceeds for a long time. Explain.
2. Analyse the factors which can affect the accuracy of heat measurement in a calorimeter.
3. Compound **A** is burnt in a bomb calorimeter that contains 2.50 litres of water. If the combustion of 0.175 moles of this compound causes the temperature of the water to rise by 45.0 °C, what is the molar heat of combustion of compound **A**? (specific heat capacity of water = 4.184 J g^{-1} $°C^{-1}$).
4. Compound **B** is burnt in a bomb calorimeter that contains 1.50 litres of water. When 50.0 grams of the compound is burnt, the temperature of the water in the calorimeter rises to 35.0 °C. If the heat of combustion of the compound is 2150 kJ mol^{-1}, what is the molar mass of the compound? (specific heat capacity of water = 4.184 J g^{-1} $°C^{-1}$).
5. The molar heat of combustion of compound **C** is 1250 kJ mol^{-1}. If 0.115 moles of this compound were to be burnt in a bomb calorimeter with a reservoir that holds 2.50 L of water, what would be the expected temperature rise?

4.2.3 Hess's law of constant heat summation

Task 4.2

Watch simulations or videos on Hess's law of constant heat summation and summarise its key features.

It is practically difficult to measure the heat for every reaction that takes place in a system. For some reactions, the measurement of heat may not even be feasible. Therefore, the heat of a reaction may be estimated from suitable combinations of compiled standard thermal data, usually in the form of standard heats of formation and heats of combustion. The method of calculating heats of reactions from measured values of heats of formation and combustion is based on the principle known as Hess's law of constant heat summation or simply *Hess's law*.

The basis for the Hess's law

The *Hess's law* is named after a Russian Chemist and Doctor, Germaine Henri Hess (1802–1850), who helped to formulate the early principles of thermochemistry. The law states that the total enthalpy change of a chemical reaction is constant, independent of the reaction path, but depends on the initial and final states of the reactants and products. It was previously discussed that, heat changes in chemical reactions are equal to the change in the internal energy (ΔU) or enthalpy (ΔH), depending on whether the reaction occur at constant volume or pressure. Since ΔU and ΔH are the functions of the state of the system, the heat evolved or absorbed in a reaction depends on the initial and final states of the system and not the way the change takes place. This forms the basis for the law. An illustration of the Hess's law is shown in Figure 4.7.

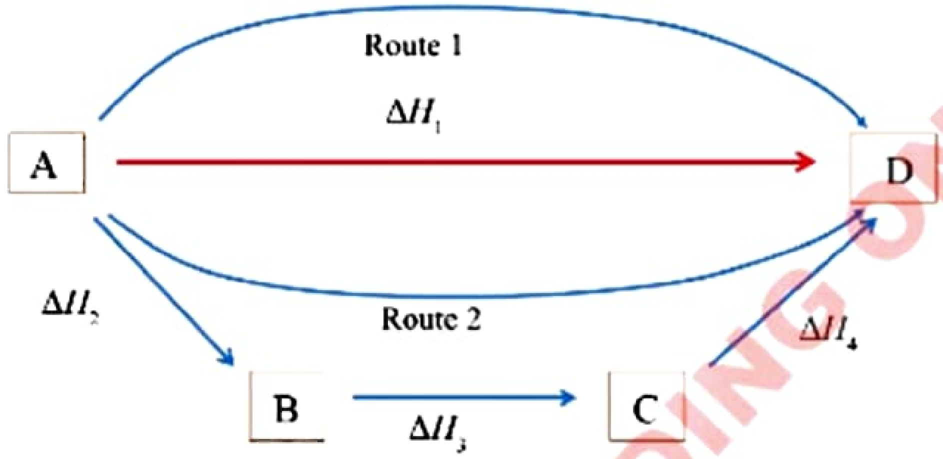


Figure 4.7: *Hess's law of heat summation*

Assume that the reactant **A** is converted into product **D**. This process can take place directly by Route 1 or indirectly by Route 2, through intermediates **B** and **C**. According to Hess's law, the enthalpy change in Route 1, is the same as the enthalpy changes in Route 2. That is

$$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$$

Example 4.7

Consider the formation of sodium hydroxide from metallic sodium which can be achieved via two different routes.

Route 1:

$$2\text{Na}(s) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{Na}_2\text{O}(s) \qquad \Delta H = -418\ \text{kJmol}^{-1}$$

$$\text{Na}_2\text{O}(s) + \text{H}_2\text{O}(l) \longrightarrow 2\text{NaOH}(aq) \qquad \Delta H = -234.3\ \text{kJmol}^{-1}$$

$$\text{Overall}\ 2\text{Na}(s) + \text{H}_2\text{O}(l) + \frac{1}{2}\text{O}_2(g) \longrightarrow 2\text{NaOH}(aq) \quad \Delta H = -652.3\ \text{kJmol}^{-1}$$

Route 2:

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -286.0\ \text{kJmol}^{-1}$$

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g) \qquad \Delta H = -368.2\ \text{kJmol}^{-1}$$

Overall $2Na(s) + H_2O(l) + \frac{1}{2}O_2(g) \longrightarrow 2NaOH(aq) \quad \Delta H = -654.2\ \text{kJmol}^{-1}$

The above results show that the total heat evolved during the formation of NaOH in two different routes is the same (within the experimental error). Therefore, this verifies Hess's law.

Applications of Hess's law

Hess's law is useful in determining the enthalpy changes, such as enthalpy of formation, enthalpy of transition and enthalpy of reaction.

Determination of enthalpy of formation of substances

The heat of the formation of substances, which can otherwise not be obtained experimentally, can be determined using Hess's law. For example, it is very difficult to set an experiment to prepare compounds such as methane or benzene from their constituent elements. Therefore, it is not possible to measure the heat of formation of these compounds directly, but indirectly using Hess's law.

Example 4.8

Calculate the heat of the formation of methane $C(s) + 2H_2(g) \longrightarrow CH_4(g)$ from the following data:

(i) $C(s) + O_2(g) \longrightarrow CO_2 \qquad \Delta H = -393.7\ \text{kJmol}^{-1}$

(ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -286.0\ \text{kJmol}^{-1}$

(iii) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -890.3\ \text{kJmol}^{-1}$

Solution

Required: The equation for the formation of methane (CH_4) from carbon (C) and hydrogen (H_2). Therefore, you need to manipulate the above equations in order to get the formation equation for methane.

Multiply equation (ii) by 2:

$$\text{(iv)}\quad 2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \qquad \Delta H = -572.0\ \text{kJmol}^{-1}$$

Combine equation (i) and equation (iv):

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.7\ \text{kJmol}^{-1}$$

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \qquad \Delta H = -572.0\ \text{kJmol}^{-1}$$

$$\text{(v)}\quad C(s) + 2H_2(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) \qquad \Delta H = -965.7\ \text{kJ mol}^{-1}$$

Reverse equation (iii):

$$\text{(vi)}\quad CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g) \qquad \Delta H = +890.3\ \text{kJ mol}^{-1}$$

Add equation (vi) to equation (v):

$$C(s) + 2H_2(g) + \cancel{2O_2(g)} \longrightarrow \cancel{CO_2(g)} + \cancel{2H_2O(l)} \qquad \Delta H = -965.7\ \text{kJ mol}^{-1}$$

$$\cancel{CO_2(g)} + \cancel{2H_2O(l)} \longrightarrow CH_4(g) + \cancel{2O_2(g)} \qquad \Delta H = +890.3\ \text{kJ mol}^{-1}$$

$$C(s) + 2H_2(g) \longrightarrow CH_4(g) \qquad \Delta H = -75.4\ \text{kJ mol}$$

Thus, the heat of formation of methane (CH_4) is – 74.8 kJ mol $^{-1}$.

Example 4.9

Calculate the heat of formation of ethyl alcohol (C_2H_5OH) if its heat of combustion is 1380.7 kJ mol $^{-1}$, and the heats of formation of $CO_2(g)$ and $H_2O(l)$ are –393.7 kJ mol $^{-1}$ and –286.0 kJ mol $^{-1}$, respectively.

Solution

Data given:

$$\text{(i)}\quad C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H = -1380.7\ \text{kJmol}^{-1}$$

$$\text{(ii)}\quad C(s) + O_2(g) \longrightarrow CO_2 \qquad \Delta H = -393.7\ \text{kJ mol}^{-1}$$

$$\text{(iii)}\quad H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -286.0\ \text{kJ mol}^{-1}$$

Required: The equation for the formation of ethyl alcohol.

$$2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l) \qquad \Delta H = ?\ \text{kJ mol}^{-1}$$

Multiply equation (ii) by 2 and equation (iii) by 3:

(iv) $$2C(s) + 2O_2(g) \longrightarrow 2CO_2(g) \qquad \Delta H = -787.4\ \text{kJ mol}^{-1}$$

(v) $$3H_2(g) + \frac{3}{2}O_2(g) \longrightarrow 3H_2O(l) \qquad \Delta H = -858.0\ \text{kJ mol}^{-1}$$

Combine equation (v) with equation (iv):

$$2C(s) + 2O_2(g) \longrightarrow 2CO_2(g) \qquad \Delta H = -787.4\ \text{kJ mol}^{-1}$$

$$3H_2(g) + \frac{3}{2}O_2(g) \longrightarrow 3H_2O(l) \qquad \Delta H = -858.0\ \text{kJ mol}^{-1}$$

(vi) $$2C(s) + 3H_2(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta H = -1645.4\ \text{kJ mol}^{-1}$$

Reverse equation (i):

(vii) $$2CO_2(g) + 3H_2O(l) \longrightarrow C_2H_5OH(l) + 3O_2(g) \quad \Delta H = +1380.7\ \text{kJ mol}^{-1}$$

Combine equation (vii) with equation (vi):

$$2C(s) + 3H_2(g) + \frac{7}{2}O_2(g) \longrightarrow \cancel{2CO_2(g)} + \cancel{3H_2O(l)} \quad \Delta H = -1645.4\ \text{kJ mol}^{-1}$$

$$\cancel{2CO_2(g)} + \cancel{3H_2O(l)} \longrightarrow C_2H_5OH(l) + 3O_2(g) \quad \Delta H = +1380.7\ \text{kJ mol}^{-1}$$

$$2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l) \qquad \Delta H = -264.7\ \text{kJ mol}^{-1}$$

Thus, the heat of the formation of ethyl alcohol is $-264.7\ \text{kJ mol}^{-1}$.

Activity 4.4

Aim: To determine the enthalpy of formation

Requirements: Beakers, thermometer, stirring rod, 0.40 g magnesium ribbon, 2.00 g magnesium carbonate, and 1.00 M hydrochloric acid

Procedure

1. Measure 60 mL of HCl solution into a 100 mL beaker and record the initial temperature (T_1).

2. Add magnesium ribbon into the beaker with HCl in step 1, swirl the mixture and record the final reaction temperature (T_2).
3. Measure 60 mL of HCl solution into another 100 mL beaker and record the initial temperature (T_3).
4. Add magnesium carbonate into the beaker with HCl in step 3, swirl the mixture, and record the final temperature (T_4).

Questions

1. What is the temperature change after completion of the reaction in step 2?
2. What is the molar enthalpy of formation of magnesium carbonate? (Given that $\Delta H_f\,(CO_2) = -394$ kJ mol^{-1} and $\Delta H_f(H_2O) = -286$ kJ mol^{-1}). Specific heat capacity of solution = 4.2 Jg^{-1}K^{-1} and density of solution = 1 g/cm^3.

Determination of enthalpy of transition

By using Hess's law, the heat of transition, for example, from one allotropic form to another, can be calculated. One example is the transition from monoclinic sulfur to rhombic sulfur. The enthalpy of this transition can be calculated from the heat of combustion of these allotropic forms of sulfur. The required equation is

$$S_{\text{monoclinic}} \longrightarrow S_{\text{rhombic}} \qquad \Delta H = ?$$

Given the enthalpies of combustion:

(i) $S_{\text{rhombic}} + O_2(g) \longrightarrow SO_2(g) \qquad \Delta H = -291.4 \text{ kJ mol}^{-1}$

(ii) $S_{\text{monoclinic}} + O_2(g) \longrightarrow SO_2(g) \qquad \Delta H = -295.4 \text{ kJ mol}^{-1}$

Reverse equation (i):

(iii) $SO_2(g) \longrightarrow S_{\text{rhombic}} + O_2(g) \qquad \Delta H = +291.4 \text{ kJ mol}^{-1}$

Add equation (iii) to equation (ii):

$$S_{\text{monoclinic}} + O_2(g) \longrightarrow SO_2(g) \qquad \Delta H = -295.4 \text{ kJmol}^{-1}$$

$$SO_2(g) \longrightarrow S_{\text{rhombic}} + O_2(g) \qquad \Delta H = +291.4 \text{ kJmol}^{-1}$$

$$S_{\text{monoclinic}} \longrightarrow S_{\text{rhombic}} \qquad \Delta H = -4.0 \text{ kJmol}^{-1}$$

Thus, heat of transition from monoclinic to rhombic sulfur is – 4.0 kJ mol^{-1}.

Determination of enthalpy of reaction (ΔH_{rxn})

The *enthalpy change of reaction* is the amount of energy (or heat) absorbed or released in a chemical reaction. Enthalpies or heat changes of many chemical reactions that are difficult to be measured directly are determined using Hess's Law. For example, Hess's law can be used to determine the enthalpy of dimerisation of nitrogen dioxide (NO_2) as shown in Example 4.10.

Example 4.10

The enthalpy of dimerisation of nitrogen dioxide can be calculated from the enthalpies of combustion. The required chemical equation is as follows:

$$2NO_2(g) \longrightarrow N_2O_4(g) \qquad \Delta H = ?$$

The enthalpies of combustion of nitrogen gas are

$$\text{(i)} \quad N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta H = +67.9\,\text{kJ mol}^{-1}$$

$$\text{(ii)} \quad N_2(g) + 2O_2(g) \longrightarrow N_2O_4(g) \qquad \Delta H = +9.3\,\text{kJ mol}^{-1}$$

Reverse equation (i):

$$\text{(iii)} \quad 2NO_2(g) \longrightarrow N_2(g) + 2O_2(g) \qquad \Delta H = -67.9\,\text{kJmol}^{-1}$$

Combine equation (iii) with equation (ii):

$$\cancel{N_2}(g) + \cancel{2O_2}(g) \longrightarrow N_2O_4(g) \qquad \Delta H = +9.3\ \text{kJ mol}^{-1}$$

$$2NO_2(g) \longrightarrow \cancel{N_2}(g) + \cancel{2O_2}(g) \qquad \Delta H = -67.9\ \text{kJmol}^{-1}$$

$$2NO_2(g) \longrightarrow N_2O_4(g) \qquad \Delta H = -58.6\ \text{kJmol}^{-1}$$

Thus, the enthalpy of dimerisation of nitrogen dioxide is $-58.6\ \text{kJ mol}^{-1}$.

4.2.4 Bond energy

Chemical reactions involve bond breaking and bond forming processes. The formation of a bond between two atoms is accompanied with the release of energy. The same amount of energy is absorbed when the bond between the two atoms is broken. The *bond energy* is the average amount of energy required to break one mole of bonds of a particular type in gaseous covalent molecules. When a chemical reaction occurs, molecular bonds are broken and other bonds are formed to make different molecules. The bonds of two water molecules, for example, are broken to form hydrogen and oxygen.

$$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g) \qquad \Delta H = +481.0\ \text{kJmol}^{-1}$$

This implies that the heat of 481 kJ is absorbed when two moles of water molecules break into two hydrogen molecules and one molecule of oxygen. The same amount of heat is released when two moles of water molecules are formed, that is – 481 kJ.

Bond energies can be used to determine the enthalpy of reaction using thefollowing equation:

$$\Delta H_{rxn} = \sum\Delta H \text{ (bonds broken)} - \sum\Delta H \text{(bonds formed)} \qquad (4.7)$$

Example 4.11

The complete combustion of propane is represented by the following equation:

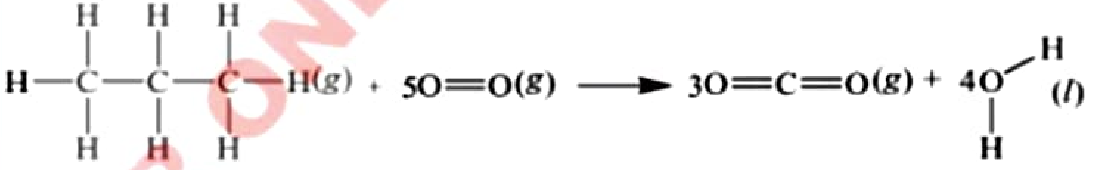
$$CH_3CH_2CH_3(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$$

Calculate the enthalpy of combustion using the following bond energies:

Bond type	Average bond enthalpy (kJ/mol)
C–H	+ 413
C–C	+ 347
O=O	+ 498
C=O	+ 805
H–O	+ 464

Solution

Combustion involves bond breaking and bond formation. Bond breaking involves the absorption of energy (endothermic) and bond formation involves the release of energy (exothermic). The open structures for the reactants and products are



The total endothermic change for bond breaking

$$= 8 \times (C\text{–}H) + 2 \times (C\text{–}C) + 5 \times (O\text{=}O)$$

$$= 8 \times 413 \text{ kJ mol}^{-1} + 2 \times 347 \text{ kJ mol}^{-1} + 5 \times 498 \text{ kJ mol}^{-1} = 6488 \text{ kJ mol}^{-1}$$

The total exothermic change for bond formation

$$= 6 \times (C\text{=}O) + 8 \times (O\text{–}H)$$

$$= (6 \times -805 \text{ kJ mol}^{-1}) + (8 \times -464 \text{ kJ mol}^{-1}) = -8542 \text{ kJ mol}^{-1}$$

A negative sign is used to indicate the release of energy during bond formation. the enthalpy of combustion is the summation of the total endothermic and exothermic enthalpy change.

$$\Delta H_C = \sum \Delta H_{\text{endothermic}} + \sum \Delta H_{\text{exotherme}}$$

$$\Delta H_c = 6488 \text{ kJ mol}^{-1} + (-8542 \text{ kJ mol}^{-1}) = -2054 \text{ kJmol}^{-1}$$

Example 4.12

The bond enthalpies for gaseous H_2 and HCl are 435 kJ mol^{-1} and 431 kJ mol^{-1}, respectively. For the reaction

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \qquad \Delta H = -184 \text{ kJ mol}^{-1}.$$

calculate the bond enthalpy of chlorine.

Solution

Data given:

$$\sum \Delta H \text{ (bonds broken)} = 1 \times 435 \text{ kJmol}^{-1} \text{ (H}-\text{H)} + \text{Cl}-\text{Cl}$$
$$\sum \Delta H \text{ (bonds formed)} = 2 \times 431 \text{ kJmol}^{-1} \text{ (H}-\text{Cl)} = 862 \text{ kJmol}^{-1}$$

$$\Delta H_{rxn} = \sum \Delta H \text{ (bonds broken)} - \sum \Delta H \text{(bonds formed)}$$

$$\Delta H_{rxn} = -184 \text{ kJ mol}^{-1}$$

$$-184 \text{ kJ mol}^{-1} = (435 \text{ kJ mol}^{-1} + \text{Cl}-\text{Cl}) - 862 \text{ kJ mol}^{-1}$$

$$\text{Cl} - \text{Cl} = 862 \text{ kJmol}^{-1} - 184 \text{ kJmol}^{-1} - 435 \text{ kJmol}^{-1} = 243 \text{ kJmol}^{-1}$$

Therefore, the bond enthalpy of chlorine is 243 kJ mol^{-1}.

Exercise 4.3

1. How would Hess's law be affected if enthalpy was not a state function?
2. The standard heats of formation of HCl(g) and HBr(g) are -92.0 kJ mol^{-1} and -36.4 kJ mol^{-1}, respectively. Use this information to calculate $\Delta H°$ for the following reaction:

$$Cl_2(g) + 2HBr(g) \longrightarrow 2HCl(g) + Br_2(g)$$

3. Calculate ΔH for the reaction $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$ from the following data:

$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l) \qquad \Delta H = -1411\,kJ\,mol^{-1}$$

$$C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H = -1560\,kJ\,mol^{-1}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -286\,kJ\,mol^{-1}$$

4. (a) Calculate the standard enthalpy change for the reaction

$$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$$

from the following data:

$\Delta H_f(H_2O_2) = -188\,kJ\,mol^{-1}$

$\Delta H_f(H_2O) = -286\,kJ\,mol^{-1}$

$\Delta H_f(O_2) = 0\,kJ\,mol^{-1}$

(b) State whether the reaction is exothermic or endothermic.

5. The enthalpy of combustion of ethanol and the enthalpies of formation of water and carbon dioxide at 298 K are −1367, −286.0, and −393.7 J mol^{-1}, respectively. Calculate the heat of the formation of ethanol at 298 K.

4.2.5 Born–Haber cycle

Born–Haber cycle is a thermochemical cycle named after two German Physical Chemists, Max Born (1882–1970) and Fritz Haber (1868–1932), who devised it in 1919. The cycle helps to understand and determine the lattice energies of ionic solids. It is the application of Hess's law to the enthalpy of formation of ionic solids at 25 °C. *Lattice energy* is the energy released when 1 mole of an ionic compound is formed from its gaseous ions under a standard state.

The terms ionisation energy, electron affinity, enthalpy of sublimation, and enthalpy of dissociation are important in discussing the Born–Haber cycle.

Sodium chloride, an ionic solid, will be used as an example to discuss the Born–Haber cycle. The formation of one mole sodium chloride crystals from solid sodium and gaseous chlorine is represented by the reaction:

$$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s) \qquad \Delta H_{rxn} = -411\ kJ\ mol^{-1}$$

An illustration of the Born-Haber cycle for the formation of NaCl is shown in Figure 4.8.

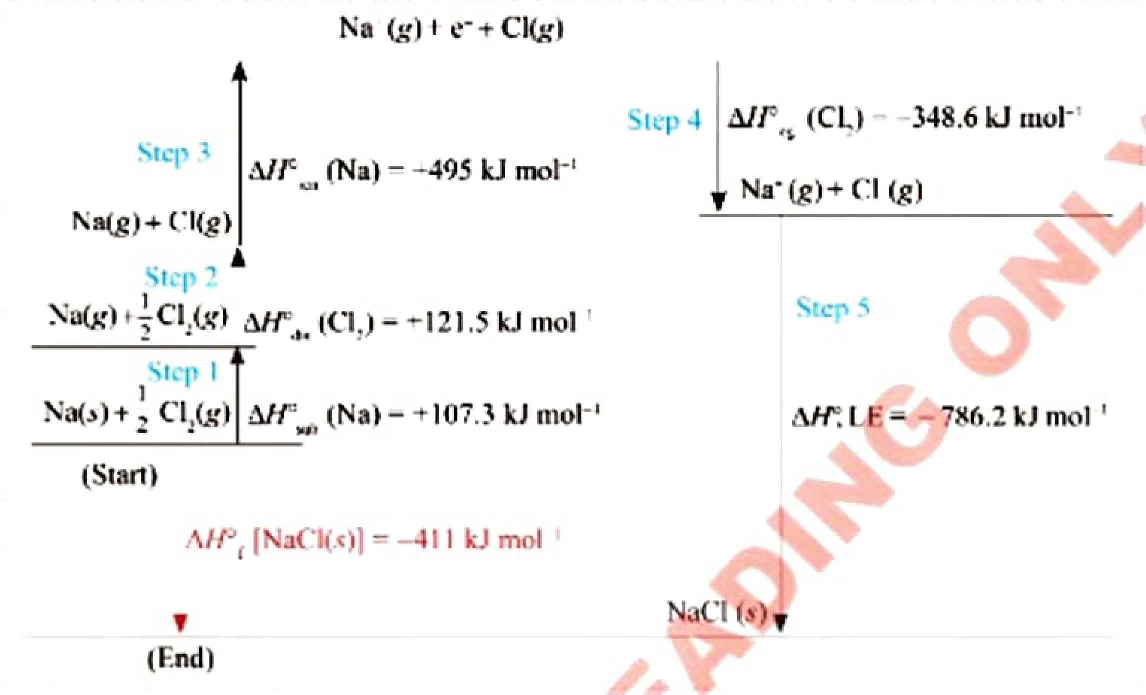


Figure 4.8 *Born–Haber cycle for the formation of sodium chloride*

The overall reaction for the formation of sodium chloride crystal can be considered to occur in a series of steps as discussed below.

Step 1: Sublimation of Na(s)

One mole of solid sodium is converted into gaseous sodium atoms. The energy change is positive because heat must be supplied to convert a solid into a gas.

$$Na(s) \longrightarrow Na(g) \qquad \Delta H^{o}_{sub} = +\ 107.3\ kJ\ mol^{-1}$$

Step2: Dissociation of Cl_2

Gaseous chlorine molecules (Cl_2) dissociate into one mole of gaseous chlorine atoms. During this process, energy must be absorbed in order to break the bonds between chlorine atoms. Therefore, the energy change is positive. Because half a mole of chlorine molecules are being broken, the bond energy is also halved.

$$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g) \qquad \Delta H^{o}_{dis} = \frac{1}{2}\times(+243\,kJ\,mol^{-1}) = 121.5\,kJ\,mol^{-1}$$

Step 3: Ionisation of Na(g)

Gaseous sodium atom is converted to sodium ion by losing an electron. The removal of an electron from an atom is an energy consuming process as the effective nuclear charge must be overcome. Therefore, the energy change is positive.

$$Na(g) \longrightarrow Na^+(g) + e^- \qquad \Delta H^\circ_{ion} = +495\ kJ\ mol^{-1}$$

Step 4: Gain of an electron

One mole of chlorine atoms gain electrons to form chloride ions. The energy released is the electron affinity (EA) of chlorine. The first EA is negative.

$$Cl(g) + e^- \longrightarrow Cl^-(g) \qquad \Delta H^\circ_{eg} = -348.6\ kJ\ mol^{-1}$$

Step 5: Formation of NaCl(s) from $Na^+(g)$ and $Cl^-(g)$

One mole of Na (*g*) combines with one mole of $Cl^-(g)$ to form one mole of NaCl(*s*). The energy released in this process is called *lattice energy* (LE). The process is exothermic because a large amount of heat is released when sodium and chloride ions coalesce to form a crystalline lattice.

$$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s) \qquad \Delta H^\circ, LE, = -786.2\ kJ\ mol^{-1}$$

Lattice energy is determined indirectly through the application of Hess's law provided that ΔH°_f of the product is known. Thus, from the Hess's law of heat summation,

$$\Delta H^\circ_{f(NaCl)} = \Delta H^\circ_{sub} + \Delta H^\circ_{dis} + \Delta H^\circ_{ion} + \Delta H^\circ_{eg} + LE$$

$$LE = \Delta H^\circ_f - (\Delta H^\circ_{sub} + \Delta H^\circ_{dis} + \Delta H^\circ_{ion} + \Delta H^\circ_{eg})$$

Exercise 4.4

1. Draw and label a Born–Haber cycle for magnesium chloride ($MgCl_2$).
2. State whether the following steps in the Born–Haber cycle for the formation of potassium chloride are exothermic or endothermic. Give reasons.
   (a) $\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$
   (b) $Cl(g) + e^- \longrightarrow Cl^-(g)$
   (c) $K(s) \longrightarrow K(g)$
   (d) $K(g) \longrightarrow K^+(g) + e^-$
   (e) $K^+(g) + Cl^-(g) \longrightarrow KCl(s)$
3. Draw and label a Born–Haber cycle for the formation of calcium oxide.

4. Calculate ΔH° for the reaction

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$

from the following data:

(a) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$ $\quad \Delta H^\circ = -180.5 \text{ kJ mol}^{-1}$

(b) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ $\quad \Delta H^\circ = -91.8 \text{ kJ mol}^{-1}$

(c) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$ $\quad \Delta H^\circ = -483.6 \text{ kJ mol}^{-1}$

5. Calculate the heat of a reaction between propene and chlorine to give 1, 2-dichloropropane from the values of bond energies given below.

(a) C–C = 347.5 kJ mol^{-1}
(b) C=C = 615 kJ mol^{-1}
(c) C–H = 413 kJ mol^{-1}
(d) C–Cl = 330.5 kJ mol^{-1}
(e) Cl–Cl = 242.7 kJ mol^{-1}

Revision exercise 4

1. Give the sign of the quantity of heat (*q*) for each of the following processes:
   (a) Steam condenses on a cold window
   (b) Warm milk is placed in a refrigerator
   (c) Ice cream is left on the table

2. Licking a silver spoon that has been dipped in a very hot cup of coffee probably will not burn your tongue. But a spoonful of the same hot coffee dropped on your tongue could leave a blister. Explain.

3. Energetics provides a fundamental framework for understanding the energy changes and heat transfer processes involved in refrigeration and air conditioning systems. Explain.

4. Calcium carbonate decomposes at high temperature to give carbon dioxide and calcium oxide:

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

Given that the enthalpies of formation of calcium carbonate, carbon dioxide and calcium oxide are $-1207 \text{ kJ mol}^{-1}$, -394 kJ mol^{-1}, and -635 kJ mol^{-1}, respectively, determine the enthalpy of reaction.

5. A 150.0 g block of hot iron metal is cooled by placing it in an insulated container with a 50.0 g block of ice at 0.0 °C. After a period of time, the ice melts and when the system reaches an equilibrium, the temperature of the water becomes 78.0 °C. What was the original temperature (in °C) of the metal? The specific heat capacity of liquid water is 4.184 J K^{-1} g^{-1}, the specific heat capacity of solid iron is 0.450 J K^{-1} g^{-1}, and the molar enthalpy of fusion of ice is 6.007 k J^{-1} mol^{-1}.

6. In a coffee-cup calorimeter, 100.0 g of H_2O and 100.0 mL of HCl are mixed. The HCl had an initial temperature of 44.6 °C and the water was originally at 24.6 °C. After mixing them, the temperature of the solution was found to be 31.3 °C.

   (a) Was the reaction exothermic or endothermic? Explain.

   (b) Calculate the amount of heat the water lost or gained.

7. If the water temperature rises to 55.4 °C when 0.315 moles of hexane C_6H_{14} are burnt in a bomb calorimeter containing 5.65 litres of water, what is the molar heat of combustion of hexane? (The specific heat capacity of water is 4.184 $JK^{-1}g^{-1}$).

8. Given the heats of the combustion of ethylene, hydrogen, and ethane are 337.2, 68.3, and 372.8 kcal, respectively, calculate the heat of reaction at 78 °C for the following reaction:

   $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$

Chapter Five

Chemical equilibrium

Introduction

Studying chemical equilibrium provides insights into the behaviour of reactions under varying conditions. In this chapter, you will learn about the reversible reactions, equilibrium constant, factors affecting the chemical equilibrium, and the application of chemical equilibrium in industrial processes. The competencies developed from this topic will increase your ability to foresee the outcome of a chemical reaction under equilibrium given certain conditions and adjust these conditions to obtain a preferred product.

Think

Chemical processes without equilibrium.

5.1 Reversible reactions

Task 5.1

Use online educational resources to explore the concept of chemical equilibrium and identify any examples of chemical equilibrium that are relevant to everyday life or consumer products.

Chemical equilibrium is a fascinating concept in chemistry where a dynamic balance is achieved within a reaction. In this state, the rate of the forward reaction equals the rate of the reverse reaction, resulting in constant concentrations of reactants and products. A chemical reaction in which the reactants interact to form products, which in turn react to give back the reactants, is called *a reversible reaction*. Reversible reactions in a closed vessel reach an equilibrium point in which the concentrations of the reactants and products no longer change. A reversible reaction is denoted by double half headed arrows ($\rightleftharpoons$) pointing in opposite directions of a chemical equation.

An example of a hypothetical reversible reaction in which two gaseous reactants (A and B) interact to give two gaseous products (C and D) in a closed vessel can be represented by the following equation:

$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$

The forward reaction starts with reactants A and B and proceeds to products C and D. The concentrations of A and B decrease while those of C and D increase gradually. After some time, C and D react in a backward direction to form A and B. Since the rate of a chemical reaction is directly proportional to the concentration of the reactants, the initial rate of the forward reaction will be higher than that of the backward reaction. Therefore, as the reaction progress, the rate of the forward reaction decreases and the rate of reverse reaction increases. This process will continue until a state is reached where the rates of forward and backward reactions are equal. At this point, the reaction is said to attain a state of equilibrium. A reversible reaction in which the forward and backward reactions occur at the same rate and the concentrations of the reactants and products do not change with time is called *an equilibrium reaction.*

Consider a chemical reaction between H_2 and I_2 to form HI, and the decomposition of HI to form H_2 and I_2:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

The changes in the rates of the forward and backward reactions are presented in Figure 5.1.

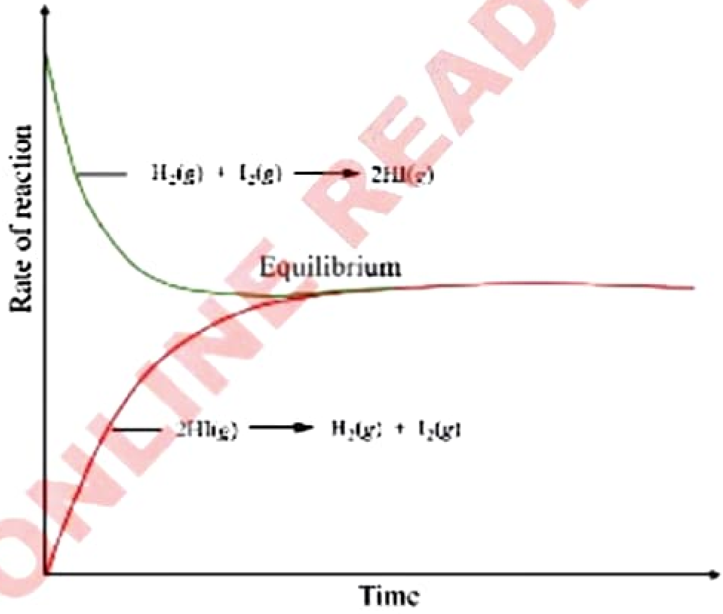


Figure 5.1: *Changes in the rates of the forward and backward reactions*

As shown in Figure 5.1, the state of equilibrium is reached when the forward reaction proceeds at the same rate as the backward reaction. Moreover, it should be noted that the rates of the forward and backward reactions are not zero but equal. Such a state is known as *dynamic equilibrium* because the forward and reverse reactions do not stop but proceed simultaneously at equal rates. As a result, the concentration of the components remains unchanged. One of the examples of dynamic equilibrium is the reaction of sulfur dioxide with oxygen to give sulfur trioxide:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

In this reaction, molecules of SO_2 and O_2 react to yield SO_3. Meanwhile, molecules of SO_3 decompose to give SO_2 and O_2. At equilibrium, all the three types of molecules are present in the reaction mixture and the rate of formation of SO_3 from SO_2 and O_2 is equal to the rate of decomposition of SO_3 to SO_2 and O_2.

5.1.1 Characteristics of chemical equilibria

All chemical equilibria exhibit the following characteristics:

(a) They are characterised by constancy of concentrations. When the chemical equilibrium is established in a closed vessel at constant temperature, the concentrations of the various molecules in the reaction mixture become constant. The reaction mixture at equilibrium is called *equilibrium mixture*, and the concentrations of chemical species at equilibrium are called *equilibrium concentrations*.

(b) They can be initiated from either side of the reaction. The state of equilibrium of a reversible reaction can be approached by starting with either the reactant(s) or the product(s).

(c) Chemical equilibrium cannot be attained in an open vessel. The equilibrium can be established only if the reaction vessel is closed and neither part of the reactants nor of the products enters or escapes the system.

(d) A catalyst does not change the equilibrium point of the chemical reaction. When added to a reaction system, the catalyst alters the rate of both forward and reverse reactions at equal rates.

(e) The value of the equilibrium constant does not depend on the initial concentrations of the reactants. It remains the same when the concentrations of the reacting species are varied over a wide range. However, the equilibrium constants vary with temperature.

5.1.2 The law of mass action

For any chemical reaction to occur, reacting particles must first collide in a proper orientation and with sufficient energy. Thus, not all particles which collide in a reaction vessel will react. Only a fraction of the total number of particles in a reaction vessel which fulfills the stated conditions will react to give products. This fraction is called the *active mass* of the reacting particles. The rate of a chemical reaction is found to be proportional to this mass. The statement that the rate of chemical reaction is proportional to the active mass of the reactants is called the *law of mass action*. In more precise words, the law states that *at constant temperature and presure, the rate of a chemical reaction is directly* *proportional to the product of molar concentrations of the reactants each raised to the power equal to the corresponding stoichiometric coefficient which appear in the balanced chemical equation*. Consider the general chemical reaction of the type:

$$aA + bB \rightleftharpoons cC + dD$$

where A and B are reactants, C and D are products, and a, b, c, and d are their respective stoichiometric coefficients. Mathematically, the law of mass action for the forward reaction is given by $R_1 \propto [A]^a[B]^b$, and for the backward reaction is $R_2 \propto [C]^c[D]^d$ as represented by Equation 5.1, where [ ] represents molar concentrations of individual species, and R_1 and R_2 represent the rates for forward and reverse reactions, respectively.

$$R_1 \propto [A]^a[B]^b,\ R_2 \propto [C]^c[D]^d \tag{5.1}$$

5.2 Equilibrium constant

Consider a reversible reaction represented by the following equation:

$$aA + bB \underset{k_2}{\overset{k_1}{\rightleftharpoons}} cC + dD$$

If [A], [B], [C], and [D] represent the equilibrium concentrations of A, B, C, and D, respectively, applying the law of mass action, the rate of forward reaction is $R_1 = k_1[A]^a[B]^b$. On the other hand, the rate of reverse reaction is given by $R_2 = k_2[C]^c[D]^d$, where k_1 and k_2 are rate constants for the forward and reverse reactions, respectively.

At equilibrium, the rate of forward reaction is equal to the rate of reverse reaction *i.e.* $R_1 = R_2$. Thus,

$$k_1[A]^a[B]^b = k_2[C]^c[D]^d$$

If k_1 is divided by k_2, the following expression is obtained:

$$\frac{k_1}{k_2} = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

At any specific temperature, the ratio $\frac{k_1}{k_2}$ is constant and is called the *equilibrium constant* (*K*). The expression therefore, becomes:

$$K = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \tag{5.2}$$

This gives rise to an *equilibrium law* which states that *if a system is at equilibrium at a given temperature, the ratio of the product of concentration of the products* *raised to their reaction coefficients to the product of concentration of the reactants raised to their reaction coefficients is constant*. This law is universally applicable under any circumstance; however, for reactions that are complete, the results may not be very useful. The equilibrium constant can be expressed in terms of concentration and partial pressures depending on the physical states of the reacting species.

5.2.1 Equilibrium constant in terms of concentration (K_c)

The equilibrium constant can be expressed in terms of concentration as K_c, where c represents molar concentrations. For example, the equilibrium constant in terms of concentration for the reaction

$$aA + bB \rightleftharpoons cC + dD$$

is given by:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad (5.3)$$

In order to obtain an expression for the equilibrium constant in terms of concentrations (K_c) and its numerical value, the following steps should be followed:

(a) Write a balanced chemical equation for the equilibrium reaction.

(b) Place the concentration of products on top of the fraction (numerator) followed by placing the concentration of the reactants on the bottom of the fraction (denominator).

(c) Raise the concentration of the products and the reactants to the power of their respective stoichiometric coefficients.

(d) Compute the value of K_c by substituting the given data.

Note: If any of the reactants or products are present as solid or liquid, their concentrations are equal to one because they are in their pure form and therefore, they are not included in the equilibrium constant expression.

Example 5.1

2.0 mol of gaseous SO_2 and 2.0 mol of gaseous NO_2 were mixed and heated in a 1 dm^3 vessel. After equilibrium was reached, it was found that 1.2 mol of gaseous NO were present. Assume that the reaction is

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g),$$

calculate the value of K_c.

Solution

The equilibrium constant (K_c) is calculated by using equilibrium concentrations. From the reaction equation, the number of moles of SO_2 and NO_2 reacted is equal to the number of moles of SO_3 and NO formed. If the change in equilibrium number of moles is represented by x, then:

	$SO_2(g)$ +	$NO_2(g)$	$\rightleftharpoons$	$SO_3(g)$ +	$NO(g)$
Initial	2 mol	2 mol		0	0
Change	$-x$ mol	$-x$ mol		$+x$ mol	$+x$ mol
At equilibrium	$(2-x)$ mol	$(2-x)$ mol		x mol	x mol

From the question, the number of moles of NO at equilibrium is 1.2, which is also equal to the equilibrium number of moles of SO_3 formed, denoted by x. Conversely, the number of moles of SO_2 and NO_2 at equilibrium can be calculated as follows:

$$SO_2 = 2 - x = 2 - 1.2 = 0.8 \text{ mol}$$

$$NO_2 = 2 - x = 2 - 1.2 = 0.8 \text{ mol}$$

The equilibrium concentrations of the mixture is obtained by dividing the number of moles at equilibrium by the volume of the reaction vessel. That is:

$$[SO_2] = \frac{0.8 \text{ mol}}{1 \text{ dm}^3} = 0.8 \text{ mol dm}^{-3}, \ [NO_2] = \frac{0.8 \text{ mol}}{1 \text{ dm}^3} = 0.8 \text{ mol dm}^{-3}$$

$$[SO_3] = \frac{1.2 \text{ mol}}{1 \text{ dm}^3} = 1.2 \text{ mol dm}^{-3} \quad \text{and}$$

$$[NO] = \frac{1.2 \text{ mol}}{1 \text{ dm}^3} = 1.2 \text{ mol dm}^{-3}$$

Writing equilibrium constant expression and substituting the data gives:

$$K_c = \frac{[SO_3][NO]}{[SO_2][NO_2]} = \frac{1.2 \times 1.2 \ (\text{mol dm}^{-3})^2}{0.8 \times 0.8 \ (\text{mol dm}^{-3})^2} = 2.25$$

Therefore, the value of $K_c = 2.25$.

Example 5.2

A mixture of CO and steam consisting of 0.25 mol of each constituent is placed in a 500 mL flask and the mixture heated up to 900 K. The reaction equation is

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

What is the composition of the equilibrium mixture at this temperature if the K_c for this reaction is 1.56?

Solution

The equilibrium constant expression, $K_c = \frac{[CO_2][H_2]}{[CO][H_2O]}$

The initial concentration of reactants is

$$[CO] = [H_2O] = \frac{0.25\ \text{mol}}{0.5\ \text{dm}^3} = 0.5\ \text{mol dm}^{-3}$$

At equilibrium, the concentrations of CO_2 and H_2 produced are equal. If the change in equilibrium concentration is assumed to be equal to x, then,

	$CO(g)$ +	$H_2O(g)$ $\rightleftharpoons$	$CO_2(g)$ +	$H_2(g)$
Initial	0.5	0.5	0	0
Change	$-x$	$-x$	$+x$	$+x$
At equilibrium	$0.5-x$	$0.5-x$	x	x

Substituting the equilibrium concentrations of the reaction mixture into the equilibrium constant expression, the following is obtained:

$$K_c = 1.56 = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(x)(x)}{(0.5 - x)(0.5 - x)} = \frac{x^2}{(0.5 - x)^2}$$

$$1.56 = \frac{x^2}{(0.5 - x)^2}$$

$$x^2 = 1.56(0.25 - x + x^2)$$

$$x^2 = 0.39 - 1.56x + 1.56x^2$$

$$0.56x^2 - 1.56x + 0.39 = 0$$

Solving the equation by using a quadratic formula for the roots of the general quadratic equation

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$ where, $a = 0.56$, $b = -1.56$ and $c = 0.39$,

the values of x are obtained.

$$x = \frac{1.56 \pm \sqrt{1.56^2 - 4 \times 0.39 \times 0.56}}{2 \times 0.56} = 2.50 \text{ mol dm}^{-3} \text{ or } 0.278 \text{ mol dm}^{-3}$$

Note that only one of the values of x makes sense chemically. The larger value gives negative concentrations at equilibrium (for example, $0.5 \text{ mol dm}^{-3} - 2.50 \text{ mol dm}^{-3} = -2.0 \text{ mol dm}^{-3}$) which has no meaning. Hence, $x_2 = 0.278 \text{ mol dm}^{-3}$ is the only value which will be considered as the right answer. Therefore, concentrations of the components of the reaction mixture at equilibrium are:

$$[CO] = 0.5 - x = 0.5 - 0.278 = 0.222 \text{ mol dm}^{-3}$$

$$[H_2O] = 0.5 - x = 0.5 - 0.278 = 0.222 \text{ mol dm}^{-3}$$

$$[CO_2] = [H_2] = x = 0.278 \text{ mol dm}^{-3}$$

Exercise 5.1

1. Write the equilibrium constant expressions for the following reactions:
   (a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
   (b) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$
2. Nitrogen and oxygen gases combine reversibly at high temperature with absorption of heat to form nitrogen monoxide gas.
   (a) Write a balanced chemical equation for the reaction.
   (b) Write the expression for the equilibrium constant (K_c), for the reaction.
3. Given that the equilibrium constant (K_c), for the reaction in Question 2 at 2680 K and 1 atm is 3.6×10^{-3}, calculate the fraction of the original nitrogen which is used in the reaction mixture if equal volumes of nitrogen and oxygen are mixed and allowed to react until equilibrium is reached.
4. When dinitrogen tetroxide (N_2O_4) dissociates, the following equilibrium is established:

   $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

   (a) State a property which could be measured to follow the progress of this reversible reaction.

(b) Write the equilibrium constant expression (K_c), for this reaction.

(c) When a sample of 0.0370 mol of gaseous dinitrogen tetroxide is allowed to dissociate at 298 K in a container of 1 dm^3, 0.0310 mol of N_2O_4 gas remains in the equilibrium mixture. Complete the table below and use the data to calculate K_c for this reaction. Include units in your calculations.

Reactant-product	N_2O_4	NO_2
Initial number of moles		
Number of moles at equilibrium		

5. Describe examples of reversible reactions that occur naturally in the environment.
6. How is the concept of equilibrium applied in photochromatic lenses?

5.2.2 Equilibrium constant in terms of partial pressure (K_p)

When all reactants and products are gases, the equilibrium constant can be expressed in terms of partial pressure. Assuming that the gases in the system behave ideally, then the ideal gas equation, $PV = nRT$ applies; where P is the pressure of the gas, V is the volume of the gas, n is the number of moles of the gas, R is the universal gas constant, and T is the absolute temperature.

Dividing both sides of the equation by V gives $P = \frac{n}{V}RT$ whereby $\frac{n}{V}$ is the molar concentration (C). Substituting $\frac{n}{V}$ by C, the equation becomes $P = CRT$.

Thus, partial pressure of the gas in the equilibrium mixture is directly proportional to its molar concentration at a given temperature. Therefore, partial pressure can be used in the expression of equilibrium constant instead of concentration.

Consider the gaseous reaction at equilibrium which is represented by the following chemical equation:

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

Applying the law of mass action and substituting partial pressures of the gas components of the equilibrium mixture, Equation 5.4 is obtained.

$$K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b} \qquad (5.4)$$

where P_A, P_B, P_C, and P_D are the partial pressures of individual gases, A, B, C, and D, respectively, in the reaction mixture at equilibrium, and K_p is the equilibrium constant in terms of partial pressures.

Example 5.3

The reaction between H_2 and I_2 to give HI can be represented by the following chemical equation:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

The analysis of the equilibrium mixture of the gases yielded the following results: $P_{H_2} = 2.5 \times 10^{-1}$ atm, $P_{I_2} = 1.6 \times 10^{-1}$ atm and $P_{HI} = 4.0 \times 10^{-1}$ atm. Use this information to accomplish the following:

(a) Write the equilibrium constant expression (K_p) for the reaction.

(b) Calculate the equilibrium constant (K_p) for the reaction.

Solution

(a) By applying the law of mass action, the expression for the equilibrium constant in terms of partial pressure (K_p), is written as follows:

$$K_p = \frac{P_{HI}^2}{P_{H_2} \times P_{I_2}}$$

(b) Substituting the partial pressure values into K_p expression in (a) gives:

$$K_p = \frac{\left(4.0 \times 10^{-1} \text{ atm}\right)^2}{2.5 \times 10^{-1} \text{ atm} \times 1.6 \times 10^{-1} \text{ atm}} = 4$$

Therefore, the equilibrium constant (K_p) for the above reaction is 4.

Exercise 5.2

1. A transparent syringe was filled with a gaseous mixture of N_2O_4 and NO_2 and its tip sealed. If the following equilibrium was established:

$$\underset{\text{Pale yellow}}{N_2O_4(g)} \rightleftharpoons \underset{\text{Dark brown}}{2NO_2(g)}$$

(a) Write the equilibrium constant expression for this reaction in terms of partial pressure.

(b) A 1.0 mol of N_2O_4 was allowed to reach equilibrium at 400 K. At equilibrium, the partial pressure of N_2O_4 was found to be 0.15 atm.

Given that the equilibrium constant (K_p), for this reaction is 48 atm, calculate the partial pressure of NO_2 in the equilibrium mixture.

2. In the vapour phase, sulfur trioxide dissociates as shown in the following chemical equation:

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

   (a) Write the K_p expression for this dissociation reaction.
   (b) At a particular temperature, 75% of sulfur trioxide is dissociated, producing a pressure of 10 atm. Calculate the value of K_p at this temperature and give its units.

3. When silver carbonate is heated in a closed vessel, it decomposes into silver oxide and carbon dioxide as shown in the following chemical equation:

$$Ag_2CO_3(s) \rightleftharpoons Ag_2O(s) + CO_2(g)$$

   At 503 K, the value of K_p for this reaction is 1.5 atm.
   (a) Write the K_p expression for this reaction.
   (b) Calculate the equilibrium pressure of carbon dioxide at 503 K.

4. When nitrosyl chloride gas (NOCl) is heated in a closed vessel, it dissociates reversibly into gaseous nitric oxide (NO) and chlorine (Cl_2) as shown in the following equation:

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

   (a) Write the K_p expression for this reaction.
   (b) If 1.0 mol of nitrosyl chloride gas is placed in a closed container and heated to 823 K, the equilibrium reached contains 78% of nitrosyl chloride and the pressure in the vessel is 5.0 atm. Compute the value of K_p at 823 K.

5. Describe the role of K_p values in controlling the equilibrium composition of gases in industrial processes.

5.2.3 Reaction quotient

In the previous sections, the equilibrium constants, K_c and K_p in terms of equilibrium concentrations and partial pressures, respectively were discussed. For a reaction which is not at equilibrium, the ratio of the product of the concentrations or partial pressures of the products raised to their stoichiometric coefficients to that of the product of the concentrations or partial pressures of the reactants raised to their stoichiometric coefficients can be less or greater than K_c or K_p values at a given temperature. Therefore, it is difficult to tell the direction of equilibrium and the concentrations of the products and reactants in a reaction that is not at equilibrium. The *reaction quotient (Q).* is used for this purpose and it is defined as the ratio of the product of product concentrations to the product of reactant concentrations raised to their respective stoichiometric coefficients when the reaction has not attained equilibrium. It measures the relative amount of products and reactants present in the course of reaction at any instant. Reaction quotients in terms of concentration and partial pressure, Q_c and Q_p are obtained in the same way as the equilibrium constants, K_c and K_p, except that the conditions must be other than equilibrium. They aid in understanding the position of equilibrium by comparing with the equilibrium constants, K_c and K_p.

- If $Q_c > K_c$, it means that more products are present than there would be at equilibrium. The equilibrium will shift to the left to produce more reactants from the excess products.
- If $Q_c < K_c$, it means there are more reactants than would be at equilibrium. The equilibrium shifts to the right to produce more products from the excess reactants.
- If $Q_c = K_c$, it means the reaction has attained equilibrium. Therefore, there is no tendency to form either more products or more reactants.

Example 5.4

Phosphorus pentachloride gas decomposes at 261 °C according to the reaction:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

A container is occupied with these gases at the initial partial pressures of 1.10 atm, 0.44 atm and 9.85 atm for PCl_3, Cl_2 and PCl_5, respectively. If the equilibrium constant, K_p, for the reaction at this temperature is 2.27×10^{-2}, in which direction will a net change occur?

Solution

The Q_p expression for the reaction is:

$$Q_P = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = \frac{1.10\,\text{atm} \times 0.44\,\text{atm}}{9.85\,\text{atm}} = 0.049\,\text{atm}$$

The Q_p is greater than the K_p (0.049 > 0.0227), meaning that there are more products than the reactants, and therefore, the net change is in the reverse direction to form PCl_5 and re-establish equilibrium.

Variation in the forms of the reaction quotient and the equilibrium constant

The values of the reaction quotient (Q) and the equilibrium constant (K) vary depending on how the balanced equation is written. The following are the different forms of expressing Q and K:

(a) If an overall reaction is the sum of two or more reactions, the overall Q and K is the product of the various reaction quotients and equilibrium constants, respectively.

$$Q_{\text{overall}} = Q_1 \times Q_2 \times Q_3 \cdots \qquad K_{\text{overall}} = K_1 \times K_2 \times K_3 \cdots$$

(b) The Q and K for a forward reaction are the reciprocals of the Q and K for the reverse reaction, respectively.

$$Q_{\text{forward}} = \frac{1}{Q_{\text{reverse}}} \text{ and } K_{\text{forward}} = \frac{1}{K_{\text{reverse}}}$$

(c) If all the coefficients of a balanced equation are multiplied by some factor (n), that factor becomes an exponent for relating the Q and K for the reaction.

$$Q' = Q^n \text{ and } K' = K^n$$

Example 5.5

When solid silver is added to a solution containing Ag^+, Fe^{2+} and Fe^{3+} with initial concentrations of 0.40 M, 0.20 M, and 0.60 M, respectively, the following reversible reaction occurs:

$$Ag^+(aq) + Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$$

If the K_c for this reaction is 5.96 at 298 K, calculate the equilibrium concentrations of each ion in the solution.

Solution

Given initial concentration of the species, the reaction quotient Q_c is given by:

$$Q_c = \frac{[Fe^{3+}]}{[Ag^+][Fe^{2+}]} = \frac{0.60\,\text{mol dm}^{-3}}{0.20\,\text{mol dm}^{-3} \times 0.40\,\text{mol dm}^{-3}} = 7.5\,\text{dm}^3\,\text{mol}^{-1}$$

Therefore, the $Q_c = 7.5$ is greater than the $K_c = 5.96$ meaning that the net change is to the left.

Setting the table with the assumption that x represents change in equilibrium concentrations

$$Ag(s) + Fe^{3+}(aq) \rightleftharpoons Ag^{+}(aq) + Fe^{2+}(aq)$$

Initial	0.60	0.40	0.20
Change	$-x$	$+x$	$+x$
Equilibrium	$0.60 - x$	$0.40 + x$	$0.20 + x$

The equilibrium constant for the latter reaction is now an inverse or a reciprocal of the former one. Its expression becomes:

$$K_c' = \frac{1}{K_c} = \frac{[Ag^{+}][Fe^{2+}]}{[Fe^{3+}]}$$

Substituting the equilibrium concentrations and the value of K_c in the expression above gives:

$$K_c' = \frac{1}{5.96} = \frac{(0.40 + x)(0.20 + x)}{0.60 - x}$$

$$0.478 + 3.576x + 5.96x^2 = 0.60 - x$$
$$5.96x^2 + 4.576x - 0.122 = 0$$

Solving for x by using quadratic formula gives $x = -0.79$ mol dm^{-3} or 0.03 mol dm^{-3}. The former value has no chemical meaning and therefore the value of x is taken as 0.03 mol dm^{-3}.

Finding the equilibrium concentrations:

$[Ag^{+}] = 0.20 + x = 0.23$ mol dm^{-3}

$[Fe^{2+}] = 0.40 + x = 0.43$ mol dm^{-3};

$[Fe^{3+}] = 0.60 - x = 0.57$ mol dm^{-3}

5.2.4 The relationship between K_c and K_p

To establish the relationship between equilibrium constants in terms of concentration (K_c), and in terms of partial pressure (K_p), the general reaction of the following type can be considered:

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

As all the reactants and products are gases, the equilibrium constant expression in terms of partial pressures is

$$K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

Assuming that all the gases in the equilibrium mixture are ideal and therefore they obey the ideal gas equation, $PV = nRT$, the partial pressure of each gas in the equilibrium mixture can be calculated using the following relations:

$$P_A = [A]RT,\ P_B = [B]RT,\ P_C = [C]RT \text{ and } P_D = [D]RT$$

Substituting the values of P_A, P_B, P_C, and P_D into Equation 5.4, Equation 5.5 is obtained.

$$K_p = \frac{([C]RT)^c \times ([D]RT)^d}{([A]RT)^a \times ([B]RT)^b} \tag{5.5}$$

Rearranging the terms in Equation 5.5 gives Equation 5.6.

$$K_p = \frac{([C])^c \times ([D])^d \times (RT)^{c+d}}{([A])^a \times ([B])^b \times (RT)^{a+b}} = \frac{([C])^c\ ([D])^d}{([A])^a\ ([B])^b} \times \frac{(RT)^{c+d}}{(RT)^{a+b}} \tag{5.6}$$

From Equation 5.3, $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$, therefore, substituting this into Equation 5.6 gives Equation 5.7.

$$K_p = K_c \times (RT)^{(c+d)-(a+b)} \tag{5.7}$$

The term (c + d) – (a + b) in Equation 5.7 represents the difference between the total number of moles of the products and the reactants in a balanced chemical equation and can be symbolised as Δn. Introducing Δn into Equation 5.7 leads to Equation 5.8.

$$K_p = K_c \times (RT)^{\Delta n} \tag{5.8}$$

When the total number of moles of the products is equal to the total number of moles of the reactants, that is when $\Delta n = 0$, then $K_c = K_p$.

Example 5.6

The reaction between sulfur dioxide and nitrogen dioxide is represented by the following chemical equation:

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

If the K_c for this reaction is 2.25, calculate the value of K_p.

Solution

Apply Equation 5.8, $K_p = K_c \times (RT)^{\Delta n}$. From the balanced chemical equation, the total number of moles of products is equal to the total number of moles of the reactants, thus, $\Delta n = 0$, implying that $K_p = K_c \times (RT)^0 = 2.25$. Therefore, K_p for the reaction is 2.25.

Units of K_c and K_p

As seen from the previous discussions, the equilibrium constant can be expressed in terms of concentrations and partial pressures. Whether expressed in terms of concentration or partial pressure its units will depend on the difference in the total number of moles of the products and reactants which give three possible cases as described hereunder.

Case 1: When the total number of moles of products is equal to the total number of moles of reactants, the values of K_c and K_p have no units. For example, the reaction between nitrogen and oxygen gases to give nitric oxide gas is:

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

The K_p and K_c for this reaction can be expressed as follows:

$$K_p = \frac{P^2_{NO}}{P_{N_2} \times P_{O_2}} \text{ and } K_c = \frac{[NO]^2}{[N_2][O_2]} \qquad \text{(No units)}$$

If the partial pressure is expressed in atm, the units of the equilibrium constant can be derived from its expression as follows:

$$K_p = \frac{(\text{atm})^2}{\text{atm} \times \text{atm}} \qquad \text{(No units)}$$

Similarly, when the concentrations of products and reactants are given in mol dm^{-3}, the K_c units can be computed as follows:

$$K_c = \frac{(\text{mol dm}^{-3})^2}{\text{mol dm}^{-3} \times \text{mol dm}^{-3}} \qquad \text{(No units)}$$

Case 2: When the total number of moles of the products is less than the total number of moles of the reactants, then K_c and K_p have units. Consider the equation for the Haber process.

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

For this reaction, the equilibrium constants K_c and K_p are given by the following expressions:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \text{ and } K_p = \frac{P^2_{NH_3}}{P_{N_2} \times P^3_{H_2}}$$

Inserting the units of concentrations (mol dm^{-3}) and that of partial pressure (atm) in the above K_c and K_p expressions respectively, the K_c and K_p units are obtained.

$$\text{Units of } K_c = \frac{(\text{mol dm}^{-3})^2}{\text{mol dm}^{-3} \times (\text{mol dm}^{-3})^3} = \text{dm}^6 \text{ mol}^{-2}$$

$$K_p = \frac{(\text{atm})^2}{\text{atm} \times (\text{atm})^3} = \text{atm}^{-2}$$

Case 3: When the total number of moles of the products is greater than the total number of moles of the reactants, K_c and K_p as in Case 2, have units. For example, consider the decomposition of phosphorus pentachloride gas.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

For this reaction, the equilibrium constants (K_c and K_p) are expressed as follows:

$$K_c = \frac{[PCl_3] \times [Cl_2]}{[PCl_5]} \text{ and } K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}}$$

Inserting the units of concentration (mol dm^{-3}) and that of partial pressure (atm) in the K_c and K_p expressions respectively, the following units are obtained.

$$\text{For } K_c = \frac{\text{mol dm}^{-3} \times \text{mol dm}^{-3}}{\text{mol dm}^{-3}} = \text{mol dm}^{-3}$$

$$\text{For } K_p = \frac{\text{atm} \times \text{atm}}{\text{atm}} = \text{atm}$$

Note: In all cases, the units for K_c and K_p are obtained by taking the units of concentration or partial pressure raised to the power which is equal to the difference between the total number of moles of the products and the total number of moles of the reactants.

Exercise 5.3

1. At 773 K, the reaction between gaseous nitrogen and hydrogen to form ammonia gas has a $K_c = 6.0 \times 10^{-2}$ dm^6 mol^{-2}. Compute the value of K_p for this reaction.

2. A mixture of nitrogen and hydrogen in a reaction vessel is allowed to attain equilibrium at 753 K. The equilibrium mixture of gases was analysed and found to contain 0.8 mol dm^{-3} H_2, 0.6 mol dm^{-3} N_2 and 0.4 mol dm^{-3} NH_3. Use these data to calculate K_c and K_p given that R is 0.0821 atm dm^3 mol^{-1}K^{-1}.

3. At 1000 K, the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

   reaches equilibrium when the concentrations of the gases in the equilibrium mixture are 0.27 mol dm^{-3} for SO_2, 0.4 mol dm^{-3} for O_2 and 0.33 mol dm^{-3} for SO_3. Calculate the value of equilibrium constant (K_p) at this temperature.

4. The reaction $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$

   was studied at 298 K. The partial pressures of the gases in the equilibrium mixture were found to be 1.2 atm, 0.05 atm and 0.3 atm for NOCl, NO, and Cl_2, respectively. Calculate the equilibrium constant (K_c), for this reaction.

5. How does the reaction quotient help industrial engineers and chemists make decisions about adjusting reaction conditions, such as temperature, pressure, or concentration of reactants and products?

K_c and K_p for systems involving different phases at equilibrium

The previous discussions on K_c and K_p focused only on homogeneous equilibria in which all the components of the reaction are in the same phase. When the components are in different phases, the system reaches *heterogeneous equilibrium*. Experimental results show that the position of a heterogeneous equilibrium does not depend on the amount of pure solids or liquids present in the system. A pure solid or liquid always has the same concentration at a given temperature, that is, the same number of moles per its unit volume. Moreover, since the volume of a solid changes very little with temperature, its concentration also changes very little. For these reasons, the concentration of pure solids is constant and the same argument applies to the concentration of pure liquids which is assumed to be one. Since the concentrations and partial pressures significantly change as the reactants approach equilibrium, the terms for pure liquids and solids from the reaction quotient are eliminated. This is done by incorporating their constant concentrations or partial pressures into a rearranged reaction quotient. Consider the reaction for the decomposition of calcium carbonate.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

The equilibrium constant (*K*) for this reaction is expressed as follows:

$$K = \frac{[CaO][CO_2]}{[CaCO_3]} \tag{5.9}$$

At equilibrium, the $[CaCO_3]$ and $[CaO]$ remain constant. Rearranging Equation 5.9 results in Equation 5.10.

$$K\frac{[CaCO_3]}{[CaO]} = [CO_2] \tag{5.10}$$

But, $K\frac{[CaCO_3]}{[CaO]} =$ constant $= K_c$ because the change in the $[CaCO_3] \approx [CaO] \approx 1$.

Therefore, $K_c = [CO_2]$. Likewise, K_p for this reaction is equal to P_{CO_2}.

The reaction that is represented by the equation

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

has the following equilibrium constant expressions:

$$K_c = \frac{[CO]^2}{[CO_2]} \text{ and } K_p = \frac{P_{CO}^2}{P_{CO_2}}$$

5.3 Factors affecting chemical equilibrium

Task 5.2

Use online resources to explore the Le Chatelier's principle.

One of the remarkable features of equilibrium systems is their ability to return to equilibrium after a change in conditions which were involved in its establishment. For this reason, when a chemical system at equilibrium is subjected to a "disturbance", it regains its equilibrium by undergoing a net reaction that reduces the effect of the "disturbance". The changes in the concentration, pressure, and temperature commonly disturb the equilibrium system.

The general rule that helps to predict the direction in which an equilibrium reaction will move is known as *Le Châtelier's principle*. The Le Châtelier's principle states that, if an external disturbance is applied to a system at equilibrium, the equilibrium shifts in the opposite direction to offset the change. This principle will be used to assess the effect of such changes.

5.3.1 The effect of change in concentration

The effect of concentration on the position of a chemical equilibrium can be demonstrated by the dissolution of potassium dichromate in water as per the reaction:

$$\underset{\text{Orange}}{Cr_2O_7^{2-}(aq)} + H_2O(l) \rightleftharpoons \underset{\text{Yellow}}{2CrO_4^{2-}(aq)} + 2H^+(aq)$$

At the beginning of the reaction, the solution is orange due to the high concentration of $Cr_2O_7^{2-}$. When sodium hydroxide solution is added to this system, the colour of the solution changes from orange to yellow. The disturbance applied to the equilibrium system is an increase in concentration of OH^- (from sodium hydroxide solution). To offset this disturbance, some H^+ will react with the added OH^- and the equilibrium will shift from left to right causing an increase in the concentration of CrO_4^{2-}, hence yellow colour. Conversely, the addition of dilute HCl solution to the system at equilibrium will increase H^+ concentration. To offset this disturbance, some CrO_4^{2-} react with H^+ and hence the equilibrium shifts to the left, making the colour of the solution orange.

Activity 5.1

Aim: To investigate the effect of changes in concentration on the reaction at equilibrium

Requirements: 0.02 M $Fe(NO_3)_3$, 0.02 M KSCN, KSCN crystals, NaH_2PO_4 crystals, distilled water, test tubes with a test tube rack, stirring rod, 100-mL beakers, spatula, droppers and measuring cylinder

Procedure

1. Pour 25 mL of 0.02 M KSCN to a 100-mL beaker and add 25 mL of distilled water. Note the colour of the solution.
2. Add 5 drops of 0.02 M $Fe(NO_3)_3$ to the solution in Step 1. Note the colour of the solution.
3. Pour equal amounts of the solution into four clean and dry test tubes.
4. Label the test tubes A, B, C and D. Test tube A will be a reference that you will use to compare to test tubes B, C, and D.
5. To test tube B, add a scoop of NaH_2PO_4 crystals using a spatula. Note the colour change of the solution.
6. To test tube C, add a scoop of KSCN crystals using a clean and dry spatula. Note the colour change of the solution.

7. To test tube D, add 10 drops of 0.20 M $Fe(NO_3)_3$. Note the colour change of the solution.

Questions

1. What causes the colour changes of the solutions in test tubes B, C, and D? Use balanced equations to support your answer.
2. How does the understanding of the effect of concentration on equilibrium position benefit different fields such as pharmaceuticals, agriculture, or environmental science?

5.3.2 The effect of change in pressure

There are three possible ways to change the pressure of a reaction system involving gaseous components at a given temperature, namely, adding or removing gaseous reactant(s) or product(s) at constant volume, adding an inert gas at constant volume, and changing the volume of the container.

The effect of adding or removing gaseous reactant(s) or product(s) from the equilibrium mixture at constant volume can be explained by considering the ideal gas equation,

$$PV = nRT \text{ or } P = \frac{n}{V}RT$$

Since pressure is directly proportional to the molar concentration (*n*/V) of the gas in the reaction mixture, an increase in pressure is similar to the increase in the concentration of the gas in the reaction mixture. Similarly, a decrease in pressure decreases the concentration of the gas in the reaction mixture. The effect of pressure on the position of equilibrium can be noticed only when there is a change in number of moles between the left hand side (LHS) and the right hand side (RHS) of the reaction. An increase in pressure shifts the position of equilibrium from the side with more number of moles to the side with less number of moles. Conversely, the decrease in pressure shifts the position of the equilibrium from the side with less number of moles to the side with more number of moles.

Consider the formation of carbon monoxide in the steam reforming process:

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

The LHS of this reaction has 2 moles while the RHS has 4 moles. The total number of moles of products is higher than the total number of moles of the reactants. Therefore, the forward reaction is favoured by a decrease in pressure because it proceeds with an increase in volume. The increase in pressure will force the equilibrium to shift to the left to offset the disturbance by decreasing the volume of the reaction mixture. In addition, reducing the volume of the container due to the increase in pressure shifts the equilibrium to the side with fewer number of moles of the gas since fewer moles occupy the smallest volume. Adding an inert gas to the equilibrium mixture will have no effects on the equilibrium position. The inert gas increases the total pressure of the system but does not affect the partial pressure of the reactants or products.

5.3.3 The effect of change in temperature

The effect of temperature on the position of chemical equilibrium depends on the type of reaction, that is whether the reaction is endothermic or exothermic. For endothermic reactions, an increase in temperature favours the forward reaction while a decrease in temperature favours the backward reaction. Conversely, for exothermic reactions, the increase in temperature favours the backward reaction while the decrease in temperature favours the forward reaction. This is according to the van't Hoff's law, i.e., the increase in temperature causes the increase in the rate of endothermic reactions.

An aqueous solution of cobalt(II) chloride acidified with concentrated hydrochloric acid can serve as an example of the effect of temperature on the position of equilibrium. When concentrated hydrochloric acid is added to a pinkish aqueous solution of cobalt(II) chloride, the solution turns blue due to the displacement of the H_2O molecules by the chloride ions:

$$\underset{\text{Pink}}{[Co(H_2O)_6]^{2+}(aq)} + 4Cl^-(aq) \rightleftharpoons \underset{\text{Blue}}{[CoCl_4]^{2-}(aq)} + 6H_2O(l)$$

The temperature of the solution is lowered when concentrated hydrochloric acid is added. This implies that the formation of the complex, $[CoCl_4]^{2-}$, is endothermic. On heating, the equilibrium shifts to the right and therefore, the solution turns blue. Cooling favours the exothermic reaction. That is, the reaction reverses towards formation of $[Co(H_2O)_6]^{2+}$, and the solution turns pinkish.

Activity 5.2

Aim: To investigate the effect of temperature on the rate at which a chemical reaction reaches equilibrium

Requirements: Iron(III) nitrate (70 g), potassium thiocyanate (30 g), 250 mL-volumetric flask, 250 mL-beakers, pipette, refrigerator, water bath, white tile, stopwatch, thermometer and measuring cylinders

Procedure

1. Dissolve each salt to make a 250 mL solution of 1 M, and transfer the solutions into separate beakers.
2. Transfer 40 mL of each solution into two separate beakers and cool them in a refrigerator until the temperature equilibrates to 10 °C.
3. Mix the contents to initiate the reaction and start the stopwatch immediately while stirring the mixture.
4. Record the time taken for the reaction to reach equilibrium (when the resulting colour intensity of the mixture stops changing).
5. Repeat steps 2 to 4, each time altering the temperature to 20, 30, 40, 50, and 60 °C. (In this case use a water bath to warm the contents).
6. Record the time taken for each reaction to reach equilibrium under different temperatures.

Questions

1. What are the reacting ionic species in this experiment? Write a balanced chemical equation.
2. What conclusion can be made on the effect of temperature on the equilibrium under this experiment?
3. What implications do the findings of this activity have to the industrial processes where temperature control is important for optimising reaction rates and yields?

5.3.4 The effect of catalyst

A catalyst alters the rate of a reaction by providing an alternative mechanism of a relatively lower activation energy. The lowering of activation energy affects both the forward and reverse reactions at the same rate. It can therefore be concluded that, the presence of a catalyst neither alters the equilibrium constant nor shifts the position of an equilibrium system.

5.4 Application of Le Châtelier's principle in industrial processes

In industrial processes, chemists and chemical engineers basically strive to choose favourable conditions that maximise yields of the desired products. The synthesis of ammonia by the Haber process and sulfuric acid by the Contact process are among the industrial processes in which Le Châtelier's principle finds application. The chemical equations for the two processes are as follows:

The haber process: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H^{\circ} = -92.4 \text{ kJ mol}^{-1}$

The contact process: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H^\circ = -197$

For the Contact process, the sulfur trioxide gas formed undergoes hydrolysis to form sulfuric acid (H_2SO_4). However, the reaction between sulfur trioxide and water is extremely exothermic such that it vaporises all the acid formed. Therefore, to safely obtain the yield, the sulfur trioxide gas is absorbed in 98% sulfuric acid to form oleum ($H_2S_2O_7$) which undergoes hydrolysis to form concentrated sulfuric acid.

$$SO_3(g) + H_2SO_4(l) \longrightarrow \underset{\text{Oleum}}{H_2S_2O_7(l)}$$

$$H_2S_2O_7(l) + H_2O(l) \longrightarrow 2H_2SO_4(l)$$

In both the Haber and Contact processes, the reactions are reversible, exothermic and proceed with a decrease in volume. For maximum production of ammonia and sulfur trioxide gases, the reactants are made to react at higher pressure and lower temperature. These conditions favour forward reactions. However, the decrease in temperature lowers the rate of reaction which in turn causes a rise in the production cost. To offset this effect, catalysts are used in both cases to speed up the rate of reactions. At the industrial scale, the mass production of ammonia requires a temperature of 500 °C, a pressure of 200 to 1000 atm, and the use of iron with aluminium oxide catalyst. For the maximum conversion of sulfur dioxide to about 95% sulfuric acid, vanadium(V) oxide catalyst, a pressure of 2 atm and a temperature of 450 °C are employed.

Revision exercise 5

1. When 0.4 mol of PCl_5 was heated in a 10.0 dm^3 vessel, it decomposed as shown in the following equation:

   $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

   When the equilibrium was established, the amount of Cl_2 in the vessel was found to be 0.25 mol.

   (a) Calculate the number of moles of PCl_5 and PCl_3 present at equilibrium.

   (b) What are the equilibrium concentrations for all the three components?

   (c) Calculate the equilibrium constant (K) for the decomposition reaction.

2. A 16.0 g sample of sulfur trioxide was placed in an empty container at 800 K where it decomposed as shown in the following chemical reaction:

   $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

   At equilibrium, the total pressure and the density of the gaseous mixture were 3.6 atm and 3.2 g dm^{-3}, respectively. Calculate (K_p) for this reaction.

3. At a particular temperature, the equilibrium constant in terms of concentration, K_c, for the reaction

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

is 3.75. If 0.8 mol of each gas was kept in a 1.0 dm^3 container and allowed to reach equilibrium at that temperature, calculate the concentration of each component in the container.

4. Consider the following reaction:

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g) \quad \Delta H^\circ = -104\ \text{kJ mol}^{-1}$$

Fill the following table by stating how each change will affect the quantity of the reactant, the product, and the equilibrium constant (K) value assuming that the reaction is taking place in a fixed volume of a container. Write "increase", "decrease", or "no change". Give reasons for your choice.

Change	$[H_2]$	$[Br_2]$	$[HBr]$	K value
Some H_2 is added				
Some HBr is added				
Some H_2 is removed				
Some HBr is removed				
Temperature is raised				
Temperature is lowered				
Pressure is increased				

5. Given the reaction:

$$2A(g) \rightleftharpoons B(g) + C(g) \quad \Delta H^\circ = +27\ \text{kJ mol}^{-1} \text{ and } K = 3.2\times10^{-2}$$

Which of the following statements will be true if the temperature is lowered from 378 K to 298 K? Explain your answer.

(a) The value of K will be smaller.
(b) The concentration of A will increase.
(c) The concentration of B will increase.

6. (a) Why is it important to understand the concept of reaction quotient in chemical equilibrium?

(b) The equilibrium constant (K_p) at 698 K for the reaction

$$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$$

is 4.18×10^{-19}. An experiment was conducted by introducing 2 atm of hydrogen bromide, 0.1 atm of hydrogen and 0.1 atm of bromine into a 1.0 dm^3 container and the mixture heated to react at 698 K. Is the reaction at equilibrium? If not, in which direction will it proceed?

7. Hydrogen iodide was found to be 30% dissociated at 1000 K as shown in the following equation:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

Calculate K_c for the reaction at this temperature.

8. Ordinary white phosphorus (P_4) forms a vapour which dissociates into diatomic molecules at high temperature as represented by the following chemical equation:

$$P_4(g) \rightleftharpoons 2P_2(g)$$

When heated to 1100 K, a sample of 0.396 g of white phosphorus formed a vapour having a total pressure of 0.18 atm and a density of 0.132 g dm^{-3}. Use this information to calculate the equilibrium constant (K_p) for the reaction.

9. At 1200 K, a mixture of steam and iron in a closed vessel formed an equilibrium in which the pressure of steam was found to be 15 atm and the total pressure 36.3 atm. Calculate K_p for this reaction at 1200 K if the reaction equation is:

$$3H_2O(g) + 2Fe(s) \rightleftharpoons Fe_2O_3(s) + 3H_2(g)$$

10. The biochemical formation of a disaccharide sugar from two monosaccharides is demonstrated by the following chemical reaction:

fructose + glucose-6-phosphate $\rightleftharpoons$ sucrose-6-phosphate

Given that $K_c = 7.1 \times 10^{-6}$, to what volume should a solution containing 0.050 mol of each monosaccharide be diluted in order to bring about 5% conversion to sucrose-6-phosphate?

11. Nitrosyl bromide (NOBr) is formed by the reaction between nitric oxide (NO), and bromine gas (Br_2) which is represented by the following chemical reaction.

$$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$$

A mixture of the two gases with initial partial pressures of 98.4 atm and 41.3 atm, respectively, were allowed to react and reach equilibrium at 300 K. If at equilibrium the total pressure of the gases was 110.5 atm,

(a) Calculate the value of K_p.

(b) What would the partial pressures of all the species in the equilibrium mixture be if both NO and Br_2 at an initial partial pressure of 0.3 atm were allowed to come to the equilibrium at this temperature?

12. The following equilibrium is set up in solution by dissolving cobalt(II) chloride crystals in water to form pink species ($[Co(H_2O)_6]^{2+}$) and then adding concentrated hydrochloric acid until the solution becomes blue.

$$\underset{\text{Pink}}{[Co(H_2O)_6]^{2+}(aq)} + 4Cl^-(aq) \rightleftharpoons \underset{\text{Blue}}{[CoCl_4]^{2-}(aq)} + 6H_2O(l)$$

(a) Does the reaction cease when the solution becomes blue? Explain.

(b) The forward reaction is endothermic. Explain the colour change observed on cooling the reaction mixture.

(c) Identify one way of reversing the change caused by cooling the reaction.

13. (a) Why is chemical equilibrium described as dynamic?

(b) When a yellow solution of iron(III) chloride ($FeCl_3$) and a colourless solution of potassium thiocyanate (KSCN) were mixed in a test tube, a red colour appeared and the temperature in the reaction mixture is increased. The following equilibrium was established:

$$\underset{\text{Yellow}}{Fe^{3+}(aq)} + SCN^-(aq) \rightleftharpoons \underset{\text{Red}}{[Fe(SCN)]^{2+}(aq)}$$

(i) What is the effect on the Fe^{3+} concentration upon adding KSCN to the equilibrium mixture?

(ii) Does the change in pressure affect this equilibrium? Explain.

(iii) The red colour faded when the test tube containing the equilibrium mixture was placed in an ice-water bath. State whether the value of K_c for this reaction is high or low at the lower temperature. Is the forward reaction exothermic or endothermic? Justify your answer.

14. A student is provided with glassware and other laboratory apparati as well as the following chemicals: potassium dichromate(VI) ($K_2Cr_2O_7 \cdot 2H_2O$), hydrochloric acid (HCl), sodium hydroxide (NaOH), cobalt(II) chloride crystals ($CoCl_2 \cdot 6H_2O$), and deionised water (H_2O).

(a) Describe clearly how the student could use a selection of the chemicals listed above to establish a chemical equilibrium. Write a balanced chemical equation for the equilibrium.

(b) Describe how the student could demonstrate the effect of concentration on the chemical equilibrium stated in 14(a). State the observations expected during the demonstration.

15. Ammonia is formed in the Haber process as shown in the following balanced equation:

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

The percentage of ammonia present at equilibrium under different conditions of temperature (T) and pressure (P) when hydrogen and nitrogen gases were mixed in a 3:1 molar ratio is shown in the following table:

Temperature (K)	573	673	773
Pressure (atm)	Percentage of NH_3 at equilibrium		
10	15	4	1
100	51	25	10
200	63	36	18
1000	92	80	58

(a) From the table, identify the conditions of temperature and pressure at which the highest yield of ammonia is obtained.

(b) Is this reaction endothermic or exothermic? Explain.

(c) Derive the relationship between K_p and K_c for this reaction.

16. The equilibrium constant (K_p) for the reaction

$$CCl_4(g) \rightleftharpoons C(s) + 2Cl_2(g)$$

at 978 K is 0.76 atm. Calculate the initial pressure of carbon tetrachloride that will produce a total equilibrium pressure of 1.2 atm at 978 K.

17. Suppose a chemical reaction reaches equilibrium but doesn't yield the expected product.

(a) How would you analyse the situation to determine possible causes?

(b) What actions would you take to adjust the reaction conditions?

Chapter Six

Ionic equilibria

Introduction

Ionic equilibria explore the balance between ions in aqueous solution and focus on the dynamic nature of the reactions involving ions. In this chapter, you will learn about the ionic equilibria involving acids, bases, and salts, preparation of buffer solutions, determination of the concentration of ionic species in solution through acid-base titrations, and the solubility equilibria. The competencies developed will enable you to manage the pH in products and manipulate the solubility of various substances, thus ensuring the effective functionality of various processes and products.

Think

Absence of ionic equilibria in systems

6.1 Concept of acids and bases

Task 6.1

Use online resources such as educational websites and interactive simulations to study acid, base and salt equilibria.

Chemical substances were originally classified as acids or bases based on their properties in aqueous solutions. However, over time, scientists discovered that some other chemical substances which were initially excluded in the acids and bases family display similar properties when dissolved in water or other solvents. Therefore, the concept of acids and bases has been broadened over time to accommodate all substances that exhibit properties similar to those which were shown by the already classified acids and bases. Arrhenius, Brønsted-Lowry and Lewis made a significant contribution to the current understanding of acids and bases.

6.1.1 Arrhenius concept of acids and bases

In 1884, a Swedish chemist, Svante August Arrhenius, proposed two specific classifications of compounds. He termed them acids and bases depending on the type of ions they produce when dissolved in aqueous solutions. According to Arrhenius, *acids* are defined as substances which produce hydrogen ions (H^+) when dissolved in water. For example, HCl and HNO_3 are Arrhenius acids because they give H^+ as the only positive ions when dissolved in water.

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

$$HNO_3(aq) \longrightarrow H^+(aq) + NO_3^-(aq)$$

The H^- give acids a sour taste, change colour of indicators such as blue litmus paper to red, and cause corrode of some metals.

Arrhenius defined *bases* as substances that produce hydroxide ions (OH^-) when dissolved in water. Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are examples of Arrhenius bases because they ionise in water to release OH^- as the only negatively charged species.

$$KOH(aq) \longrightarrow K^+(aq) + OH^-(aq)$$

$$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$

The OH^- are responsible for the bitter taste, slippery feel and the ability to turn the colour of red litmus paper to blue or phenolphthalein to pink. From the Arrhenius concept, a combination of an acid and a base results in the formation of a water molecule from the H^- of the acid and the OH^- of the base. This leads to the concept of *neutralisation* which is the reaction of an acid and a base to form salt and water only. The Arrhenius theory explains many properties and reactions of acids and bases. For example, the reaction between HCl and NaOH results in a neutral solution containing table salt (NaCl). However, the Arrhenius theory has the following weaknesses:

(a) It is applicable only for acids and bases in aqueous medium implying that the concepts are not valid for acid-base behaviour in the absence of water.

(b) The concept defines acids and bases as substances that contain hydrogen ions (H^+) and hydroxyl ions (OH^-), respectively. However, many compounds act as acids or bases even if they do not contain H^+ or OH^- groups as part of the molecule.

In order to accommodate other acid-base behaviours which the Arrhenius theory failed to account for, another theory developed by Brønsted J. N and Lowry T. M was established.

6.1.2 Brønsted-Lowry concept of acids and bases

In 1923, Brønsted and Lowry independently developed a theory to expand the definition of acids and bases. This theory was known as the *Brønsted-Lowry proton transfer theory*. They suggested that any hydrogen containing species (molecules, cations or anions) which is capable of donating one or more proton(s) to any other substance is called an *acid*. On the other hand any chemical species which is capable of accepting one or more proton(s) from an acid is called *a base*. Therefore, according to Brønsted-Lowry theory, an acid is a proton donor and a base is a proton-acceptor. To accept a proton, a base needs to have a lone pair of electrons to bind the H^+.

Brønsted-Lowry definition of acid and base can be explained by the following example:

$$\underset{\substack{\text{Proton donor}\\ \text{(Acid)}}}{HNO_3(aq)} + \underset{\substack{\text{Proton acceptor}\\ \text{(Base)}}}{H_2O(l)} \longrightarrow \underbrace{H_3O^+(aq) + NO_3^-(aq)}_{\text{Acidic solution}}$$

In aqueous solution, HNO_3 donates a proton to H_2O to form hydroxonium ion (H_3O^+) and nitrate ion (NO_3^-). Thus, H_2O acts as a base because it accepts the donated proton. Similarly, in the next example ammonia (NH_3) acts as a base by accepting a proton when it reacts with water.

$$\underset{\substack{\text{Proton acceptor}\\ \text{(Base)}}}{NH_3(aq)} + \underset{\substack{\text{Proton donor}\\ \text{(Acid)}}}{H_2O(l)} \longrightarrow \underbrace{NH_4^+(aq) + OH^-(aq)}_{\text{Basic solution}}$$

From the two examples, it can be noted that water acts as both an acid and a base by donating and accepting a proton respectively, depending on the strength of the second substance. The substances which show both acidic and basic properties are called *amphoteric substances*.

An important feature of Brønsted-Lowry concept is that the acids and bases are symbiotic. Every acid must form a base on donating its proton, and every base must form an acid on accepting a proton. The symbiotic nature exhibited by acids and bases can be exemplified by the following reaction:

$$\underset{\text{Acid 1}}{HF(aq)} + \underset{\text{Base 2}}{H_2O(l)} \rightleftharpoons \underset{\text{Acid 2}}{H_3O^+(aq)} + \underset{\text{Base 1}}{F^-(aq)}$$

A base that is produced when an acid donates its proton is called the *conjugate base* of the acid. Similarly, the acid that is produced when a base accepts a proton is called the *conjugate acid* of the base. In the above example, F^- is the conjugate base of the acid HF and H_3O^+ is the conjugate acid of the base H_2O. Thus, a conjugate acid differs from its conjugate base by one proton. A pair of an acid and a base which differs from one another by a proton is said to be a *conjugate acid-base pair* as shown in the following reaction.

Acid Base Conjugate base Conjugated acid

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

conjugate acid-base pair

conjugate acid-base pair

Another example of conjugate acid-base pairs is given by the reaction between ammonia and water:

Conjugate acid-base pair

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

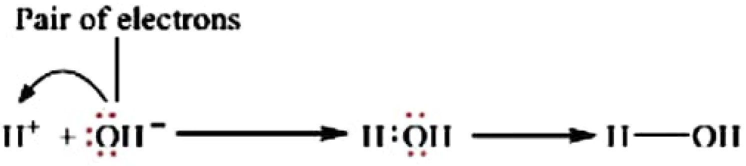
Conjugate acid-base pair

Conjugate bases differ in strength depending on the strength of their conjugate acids. A conjugate base of a strong acid is a weak base whereas a conjugate base of a weak acid is a strong base. The stronger the acid, the weaker its conjugate base and vice versa.

The Brønsted-Lowry concept proved to be better than the Arrhenius concept because it is applicable to aqueous and non-aqueous protic solvent equally well. However, it cannot account for the acidic character of the compounds not containing hydrogen such as oxides of non-metals like CO_2, SO_2, SO_3 as well as $AlCl_3$ and BF_3, and the basic character of compounds such as CaO and Na_2O. Therefore, the need ascended to establish another theory to give explanation on areas where Brønsted-Lowry theory failed. Lewis concept of acids and bases was then established.

6.1.3 Lewis concept of acids and bases

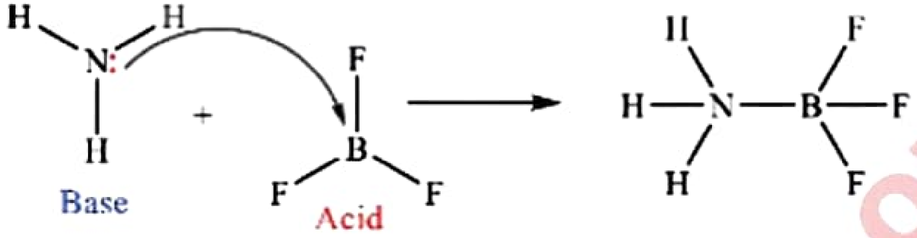
In 1938, Lewis G. N. proposed an alternative theory to describe acids and bases. His theory gave a generalised explanation of acids and bases based on structure and bonding. The theory uses electrons instead of proton transfer and specifically states that an *acid* is a species that accepts an electron pair while a *base* is a species which donates an electron pair. This implies that bases are electron rich while acids are electron deficient. The following example can be used to explain Lewis acid and base reaction.



$$H^+ + :\ddot{\underset{..}{O}}H^- \longrightarrow H:\ddot{\underset{..}{O}}H \longrightarrow H—OH$$

In this case, the OH^- with a pair of electrons is a Lewis base because it has donated its lone pair of electrons to H^+ to form a dative covalent bond in H_2O molecule. On the other hand, H^+ is a Lewis acid because it has accepted a pair of electrons from the base into its vacant orbital.

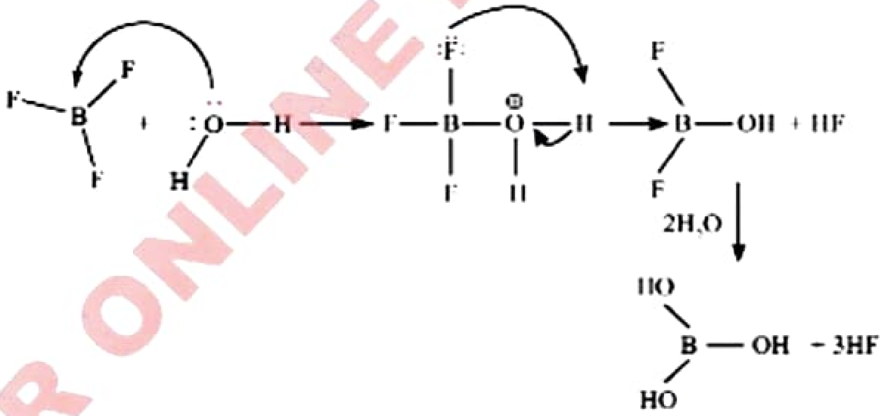
Another Lewis acid base pair is shown in the reaction between NH_3 and BF_3. Under this reaction, NH_3 donates a pair of electrons while BF_3 accepts this pair to form a dative covalent bond:



Based on the Lewis concept of acids and bases, their identification can be done following their features.

(a) Lewis acids include the following:

(i) All molecules possessing an atom with incomplete octet of electrons such as BF_3 and $AlCl_3$ or incomplete doblet such as H^+. For example, when BF_3 reacts with water, B accepts a lone pair of electrons from the water molecule followed by the release of HF. This reaction proceeds in the same way until all the three fluorine atoms of BF_3 are replaced, forming $B(OH)_3$.



(ii) All cations such as Ag^+, Cu^{2+}, Fe^{2+}, and Fe^{3+}. For example, in the reaction between Ag^+ and NH_3, the Ag^+ is accepting electron and it is therefore, a Lewis acid.

$$\underset{\text{Lewis acid}}{Ag^+} + \underset{\text{Lewis base}}{2NH_3} \longrightarrow [Ag(NH_3)_2]$$

Another example of Lewis acid-base reaction is given by the dissolution of $CuSO_4$ crystals in water to form Cu^{2+} and SO_4^{2-}. The produced Cu^{2+} associates with six moles of water, forming a light blue complex $[Cu(H_2O)_6]^{2+}$.

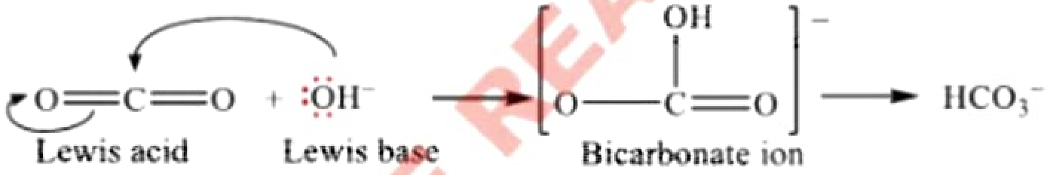
$$Cu^{2+}(aq) + 6H_2O(l) \longrightarrow [Cu(H_2O)_6]^{2+}(aq)$$

In this case, Cu^{2+} and H_2O molecules act as Lewis acid and Lewis base, respectively.

(iii) All molecules in which the central atom can acquire more than eight valence electrons such as $SiCl_4$ and SiF_4. For example, in the following reaction, SiF_4 acts as a Lewis acid because Si accepts electrons from F^-.

$$\underset{\text{Lewis acid}}{SiF_4} + \underset{\text{Lewis base}}{2\ddot{F}^-} \longrightarrow [SiF_6]^{2-}$$

(iv) Molecules with multiple bonds between atoms of different electronegativities such as CO_2 and SO_2. For example, carbondioxide behaves as Lewis acid in the following reaction:



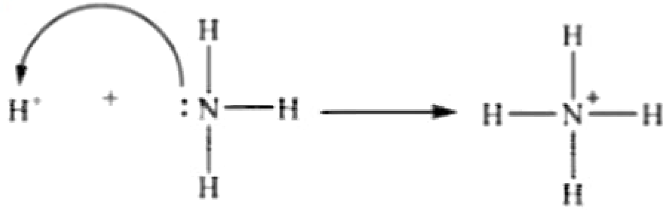
$$O{=}C{=}O + :\ddot{O}H^- \longrightarrow \left[O{-}\overset{\overset{\displaystyle OH}{|}}{C}{=}O\right]^- \longrightarrow HCO_3^-$$

(b) Lewis bases include the following:

(i) All anions like OH^-, CN^-, and CH_3COO^-. For example, OH^- acts as a Lewis base in the following reaction:

$$H\ddot{\underset{..}{O}}:^- + H^+ \longrightarrow H_2\ddot{O}:$$

(ii) All species having lone pairs of electrons such as $\ddot{N}H_3$, $H_2\ddot{\underset{..}{O}}$, $C\ddot{\underset{..}{O}}$, and $R\ddot{N}H_2$.



$$H^+ + :NH_3 \longrightarrow [NH_4]^+$$

Limitations of Lewis concept

(a) According to Lewis, acid-base reactions involve electron transfer. Therefore, they are expected to proceed fast. However, many Lewis acid-base reactions are very slow.

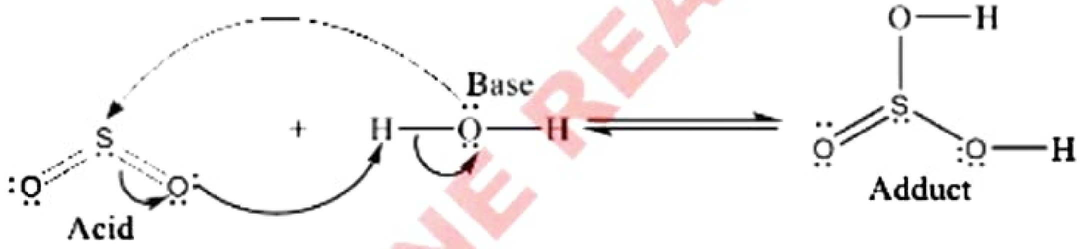
(b) The Lewis acid-base concept failed to account for the relative strength of acids and bases because it is not based on ionisation.

Example 6.1

Sulfur dioxide (SO_2) behaves as a Lewis acid when it reacts with water. Explain.

Solution

Oxygen atom being more electronegative than sulfur, it withdraws electron density from the central S atom and makes it partially positive. The oxygen atom of water molecule donates a lone pair of electrons to the S atom, breaking one of the π–bonds and forming an S–O bond, and a proton is transferred to the oxygen atom. The process can be represented by the following equation:



Exercise 6.1

1. Explain the Lewis concept of acids and bases and show its superiority to Brønsted-Lowry concept.

2. Identify the conjugate acid-base pairs of the following reversible reactions: and give a reason for the pairing.

(a) $H_2SO_4 + H_2O \rightleftharpoons HSO_4^- + H_3O^+$

(b) $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$

3. Dimethylamine ($(CH_3)_2NH$) reacts with HCl to form $(CH_3)_2NH_2Cl$. Write the reaction equation and identify the substance that acts as a Lewis base and a Brønsted-Lowry base.
4. Ammonia is a Lewis base. Explain.

6.2 Ionic equilibria of acids and bases

In the process of ionisation in water, an acid or base is broken into ions. The strength of an acid is determined by the number of moles of H_3O^+ produced for each mole of acid that is ionised. Likewise, the strength of a base is determined by the number of moles of OH^- produced for each mole of a base that is ionised. Acids and bases can therefore be categorised as strong or weak depending on the extent to which they are ionised.

Strong acids and bases ionise completely when dissolved in water. For example, when HF, a strong acid ionises, H^+ is transferred to water resulting in a solution that contains essentially H_3O^+ and F^- only. The ionisation of HF in water is considered to be 100% complete. Similarly, when KOH, a strong base dissolves in water, it ionises to K^+ and OH^- resulting in a solution containing only K^+ and OH^-. It is also considered to be 100% ionised.

Unlike strong acids and bases, weak acids and bases ionise partially to establish equilibrium where most of the original acids or bases remain unionised. Table 6.1a presents a list of some strong and weak acids whereas Table 6.1b presents a list of some strong and weak bases.

Table 6.1 (a): *List of some strong and weak acids*

Strong acids	Weak acids
Hydrochloric acid, HCl	Acetic acid, CH_3COOH
Hydrobromic acid, HBr	Formic acid, HCOOH
Hydroiodic acid, HI	Sulfurous acid, H_2SO_3
Nitric acid, HNO_3	Carbonic acid, H_2CO_3
Perchloric acid, $HClO_4$	Phosphoric acid, H_3PO_4
Sulfuric acid, H_2SO_4	
Hydrofluoric acid, HF	

Table 6.1 (b): *List of some strong and weak bases*

Strong bases	Weak bases
Lithium hydroxide, LiOH	Ammonia,
Sodium Hydroxide, NaOH	Carbonates
Potassium hydroxide, KOH	Hydrogen carbonates
Calcium hydroxide, $Ca(OH)_2$	Aluminium Hydroxide, $Al(OH)_3$
Strontium hydroxide, $Sr(OH)_2$	Ferric hydroxide, $Fe(OH)_3$
Barium hydroxide, $Ba(OH)_2$	Dimethyl amine, $NH(CH_3)_2$

6.2.1 Acid dissociation constant (K_a)

The expression for acid dissociation constant (K_a) can be obtained by considering the following general equation which serves as an example for the ionisation of a weak acid (HA).

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

Applying the law of chemical equilibrium, the ratio of molar concentrations of the reactants and products raised to their corresponding stoichiometric coefficients in a balanced equation is a constant. Thus, for this particular case, the following is obtained.

$$K_c = \frac{[H_3O\ ][A^-]}{[HA][H_2O]}$$

where K_c is the equilibrium constant of an acid.

Since water (H_2O) is present in large quantity compared to the other components of the equilibrium, its concentration does not change significantly. As such, it is considered to remain constant. The product of the two constants ($K_c[H_2O]$) gives another constant (K_a).

$$K_c[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

Substituting K_a in the place of $K_c[H_2O]$, Equation 6.1 is obtained:

$$K_a = \frac{[H_3O^+][A\ ]}{[HA]} \qquad (6.1)$$

Acid ionisation constant (K_a) is associated with weak acids only. The larger the value of K_a, the higher the ionisation of the HA. K_a values can therefore be used to compare strength of acids. An acid with larger K_a value is stronger than the acid with smaller value of K_a. Like any other equilibrium constant, the value of K_a depends on temperature. Table 6.2 shows the K_a values for some monoprotic acids.

Table 6.2: K_a *values of selected monoprotic acids*

Formula	Name	K_a value
C_6H_5OH	Phenol	1.6×10^{-10}
NH_4^+	Ammonium ion	5.6×10^{-10}
HCN	Hydrocyanic acid	6.2×10^{-10}
CH_3COOH	Acetic acid	1.8×10^{-5}
HNO_2	Nitrous acid	4.0×10^{-4}
$HClO_2$	Chlorous acid	1.2×10^{-2}

6.2.2 Base dissociation constant (K_b)

Weak bases ionise partially in water to form basic solutions. In examining the equilibrium system of weak bases, the same procedure is followed as for weak acids in aqueous solutions. Base B dissolves in water by accepting a proton, leaving behind OH^-. This process can be expressed by the following equation:

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

At equilibrium, the equilibrium constant (K_c) expression for this reaction is

$$K_c = \frac{[BH^+]\,[OH^-]}{[B][H_2O]}$$

Based on our earlier reasoning that $[H_2O]$ is treated as constant, $[H_2O]$ is included in the value of K_c to obtain the base ionisation constant (K_b) as shown in Equation 6.2.

$$K_b = \frac{[BH^+][OH^-]}{[B]} \qquad (6.2)$$

The smaller the value of K_b, the weaker the base and vice versa. Table 6.3 shows K_b values of selected bases.

Table 6.3: *K_b values for some weak bases*

Formula	Name	K_b value
CH_3NH_2	Methylamine	4.4×10^{-4}
$CH_3CH_2NH_2$	Ethylamine	5.6×10^{-4}
NH_3	Ammonia	1.8×10^{-5}
C_5H_5N	Pyridine	1.7×10^{-9}
$C_6H_5NH_2$	Aniline	3.8×10^{-10}

Example 6.2

A 0.15 mol dm^{-3} solution of butanoic acid contains 1.5×10^{-3} mol dm^{-3} H_3O^+. What is the K_a of this acid?

Solution

Butanoic acid ionises in aqueous solution as shown in the folloing chemical equation:

$$CH_3CH_2CH_2COOH(aq) + H_2O(l) \rightleftharpoons CH_3CH_2CH_2COO^-(aq) + H_3O^+(aq)$$

For this reaction, the expression for K_a is

$$K_a = \frac{[H_3O^+][CH_3CH_2CH_2COO^-]}{[CH_3CH_2CH_2COOH]}$$

From the equilibrium equation, the number of moles of $CH_3CH_2CH_2COO^-$ and H_3O^+ produced in the process of ionisation is the same. As they are in the same volume, their concentrations are also the same.

Therefore, $[H_3O^+] = [CH_3CH_2CH_2COO^-] = 1.5 \times 10^{-3}$ mol dm^{-3}.

Because the $[CH_3CH_2CH_2COOH]$ at equilibrium is 0.15 mol dm^{-3}, the value of K_a for the above system can be calculated as

$$K_a = \frac{1.5 \times 10^{-3}\ \text{mol dm}^{-3} \times 1.5 \times 10^{-3}\ \text{mol dm}^{-3}}{0.15\ \text{mol dm}^{-3}} = 1.5 \times 10^{-5}\ \text{mol dm}^{-3}$$

Thus, the value of K_a is 1.5×10^{-5} mol dm^{-3}.

Example 6.3

A 0.15 mol dm^{-3} solution of CH_3NH_2 has a K_b value of 4.4×10^{-4} mol dm^{-3}. Calculate [OH^-] of this base.

Solution

Ionisation of CH_3NH_2 in water is given by the following equation:

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3\overset{+}{N}H_3(aq) + OH^-(aq)$$

	CH_3NH_2	$CH_3\overset{+}{N}H_3$	OH^-
Initial (mol dm^{-3})	0.15		
Change	$-x$	$+x$	$+x$
Equilibrium	$0.15 - x$	x	x

At equilibrium, the value of K_b expression is

$$K_b = \frac{[CH_3\overset{+}{N}H_3][OH^-]}{[CH_3NH_2]}$$

Assuming that $[CH_3\overset{+}{N}H_3] = [OH^-] = x$ and given that $[CH_3NH_2] = (0.15 - x)$ mol dm^{-3} ≈ 0.15 mol dm^{-3}, substituting these data into the K_b expression leads to:

$$4.4 \times 10^{-4}\ \text{mol dm}^{-3} = \frac{x^2}{0.15\ \text{mol dm}^{-3}}$$

$$x^2 = 4.4 \times 10^{-4}\ \text{mol dm}^{-3} \times 0.15\ \text{mol dm}^{-3}$$

$$x^2 = 6.60 \times 10^{-5}\ (\text{mol dm}^{-3})^2$$

$$x = \sqrt{6.60 \times 10^{-5}\ (\text{mol dm}^{-3})^2} = 8.12 \times 10^{-3}\ \text{mol dm}^{-3}$$

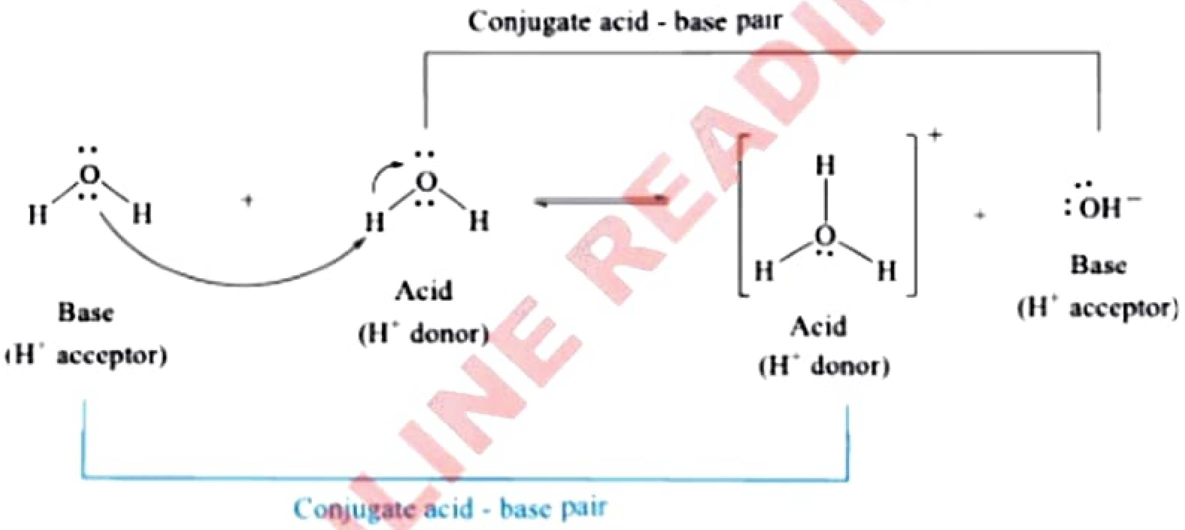
The concentration of OH^- is 8.12×10^{-3} mol dm^{-3}.

6.2.3 Ionic product of water and pH

Task 6.2

Investigate the pH of various fruits and domestic products from your surroundings and classify them as neutral, strong acids, strong bases, weak acids, and weak bases.

In the previous discussion, water was shown to exhibit amphoteric property when it reacts with a base and an acid. In pure water, there is a forward reaction between two water molecules that transfers H^+ from one water molecule to another. One molecule acts as an acid by losing H^+ (proton) and the other water molecule that gains the H^+ acts as a base. The products of the forward reaction are H_3O^+ and OH^-. Since the ionisation of water is a reversible process, the products of the forward reaction react in the reverse reaction to form two water molecules. Thus, an equilibrium is established between the conjugate acid-base pairs of water, a process called *self ionisation of water*.



The equilibrium constant expression for the above ionisation is

$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O][H_2O]}$$

By considering the concentration of pure water to be constant, Equation 6.3 for the ionisation constant of water (K_w) is obtained.

$$K_w = [H_3O^+][OH^-] \qquad (6.3)$$

Experiments have determined that in pure water, the concentrations of H_3O^+ and OH^- at 298 K are 1.0×10^{-7} mol dm^{-3} each. When the $[H_3O^+]$ and $[OH^-]$ are substituted into Equation 6.3, the numerical value of K_w is obtained.

$$K_w = 1.0 \times 10^{-7}\ \text{mol dm}^{-3} \times 1.0 \times 10^{-7}\ \text{mol dm}^{-3} = 1.0 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$$

Therefore, at 298 K, the ionisation constant of water (K_w) is 1.0×10^{-14} mol^2 dm^{-6}. The obtained value of K_w is known as the *ionic product of water*. The value 10^{-14} mol^2 dm^{-6} is a large negative exponent such that its handling is difficult. In aqueous solutions, $[H_3O^+]$ can vary. Thus, for simplicity, the values of $[H_3O^+]$ are expressed in terms of positive numerical system called *pH-scale* which is a negative of the common logarithm of the concentration of such ions. Applying this numerical system to the $[H_3O^+]$ gives pH the negative logarithm of $[H_3O^+]$ or $[H^+]$. Thus,

$$pH = -\log [H_3O^+] \text{ or } pH = -\log [H^+] \qquad (6.4)$$

A pH-scale is used to express other quantities as well. Hydroxide ion concentration and ionic product of water can also be expressed as pOH and pK_w, respectively, as in Equations 6.5 and 6.6.

$$pOH = -\log [OH^-] \qquad (6.5)$$

$$pK_w = -\log K_w \qquad (6.6)$$

It is then possible to take the negative log on both sides of Equation 6.3 and obtain a very useful relationship shown in Equation 6.7.

$$-\log K_w = -\log [H_3O^+] + -\log [OH^-]$$

or

$$pK_w = pH + pOH \qquad (6.7)$$

Thus, at 298 K, the values of pH and pOH are equal to 7 and that of pK_w is equal to 14. The scale can be used to determine acidic or basic strength of an aqueous solution. Acidic strength increases with decrease in pH value whereas the basic strength increases with an increase in pH value.

Example 6.4

Find the pH of the following solutions:

(a) 2.65 g of nitric acid dissolved in water to make 1.0 dm^3 of solution.

(b) 0.28 g of potassium hydroxide dissolved in water to make 1.0 dm^3 of solution.

Solution

(a) Mass of nitric acid = 2.65 g

Molar mass of HNO_3 = 63.0 g mol^{-1}

Volume of the solution = 1.0 dm^3

Then, the amount of HNO_3 in moles (n) dissolved in the solution is

$$n = \frac{\text{mass of nitric acid (g)}}{\text{molar mass of nitric acid (g mol}^{-1})} = \frac{2.65\ \text{g}}{63.0\ \text{g mol}^{-1}} = 0.042\ \text{mol}$$

$$\text{Molar concentration of } HNO_3 = \frac{\text{number of moles (mol)}}{\text{volume of solution (dm}^3)}$$

$$= \frac{0.042\ \text{mol}}{1.0\ \text{dm}^3} = 0.042\ \text{mol dm}^{-3}$$

Since HNO_3 is a strong electrolyte, it ionises completely.

$$HNO_3(aq) \longrightarrow H^+(aq) + NO_3^-(aq)$$

The concentrations of H^+ and NO_3^- are equal to the initial concentration of the ionised HNO_3. Thus,

$[H^+] = [NO_3^-] = 0.042$ mol dm^{-3}.

From

$$\mathbf{pH = -\log[H^+] = -\log 0.042 = 1.4.}$$

Therefore, the pH of this solution is 1.4.

(b) Given:

Mass of potassium hydroxide = 0.28 g

Molar mass of potassium hydroxide = 56 g mol^{-1}

Volume of the solution = 1.0 dm^3

Then, the amount of KOH in moles (n) dissolved in the solution is:

$$n = \frac{\text{mass of potassium hydroxide (g)}}{\text{molar mass of potassium hydroxide (g mol}^{-1})}$$

$$= \frac{0.28\ \text{g}}{56.0\ \text{g mol}^{-1}} = 0.005\ \text{mol}$$

$$\text{The molar concentration of KOH} = \frac{\text{number of moles (mol)}}{\text{volume of solution (dm}^3\text{)}}$$

$$= \frac{0.005\ \text{mol}}{1.0\ \text{dm}^3} = 0.005\ \text{mol dm}^{-3}$$

Since KOH is a strong electrolyte, it ionises completely to give its ions:

$$\text{KOH}(aq) \longrightarrow \text{K}^+(aq) + \text{OH}^-(aq)$$

Then, [KOH] ionised = [OH⁻] produced = 0.005 mol dm⁻³

From $K_w = [\text{OH}^-][\text{H}^+]$,

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]}$$

Then,

$$[\text{H}^+] = \frac{1\times10^{-14}\ \text{mol}^2\ \text{dm}^{-6}}{0.005\ \text{mol dm}^{-3}} = 2\times10^{-12}\ \text{mol dm}^{-3}$$

$$\text{pH} = -\log[\text{H}^+] = -\log\left(2\times10^{-12}\right) = 11.7$$

Therefore, the pH of the solution is 11.7.

From the obtained answers, it can be concluded that strong acids have lower pH values and strong bases have higher pH values. The opposite is the case for weak acids and bases.

Example 6.5

Given that the values of K_w at 291 K and 298 K are $0.64\times10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$ and $1.0\times10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$, respectively. Deduce if the following statements are true or not:

(a) The ionisation of water is an endothermic process.
(b) The pH of water is greater at 298 K than at 291 K.
(c) The [OH⁻] in water at 291 K is $0.8\times10^{-7}\ \text{mol dm}^{-3}$.
(d) Water is only neutral at 298 K.

Solution

(a) K_w value shows the extent to which a solute has ionised into its ions. The greater the value of K_w the higher the extent of its ionisation. Comparing the two values of the K_w given in the question, it can be concluded that with an increase in temperature from 291 K to 298 K, the K_w value of water increases from 0.64×10^{-14} mol^2 dm^{-6} to 1.0×10^{-14} mol^2 dm^{-6} showing that ionisation of water increases with an increase in temperature which is an endothermic process.

(b) From $K_w = [OH^-][H^+]$ and assuming that water has ionised to produce equal concentrations of H^+ and $OH^- = x$, then $K_w = x^2$.

At 291 K, $x = \sqrt{K_{w\,(291\,K)}} = \sqrt{0.64 \times 10^{-14}\ mol^2\ dm^{-6}} = 0.8 \times 10^{-7}$ mol dm^{-3}

Therefore, $[H^+] = 0.8 \times 10^{-7}$ mol dm^{-3}

$pH = -\log[H^+] = -\log(0.8 \times 10^{-7}) = 7.1$

Therefore, the pH of water at 291 K is 7.1.

At 298 K, $x = \sqrt{K_{w\,(298\,K)}} = \sqrt{1.0 \times 10^{-14}\ mol^2\ dm^{-6}} = 1.0 \times 10^{-7}$ mol dm^{-3}

Therefore, $[H^+] = 1.0 \times 10^{-7}$ mol dm^{-3}

From $pH = -\log[H^+] = -\log(1.0 \times 10^{-7}) = 7.0$,

Therefore, the pH of water at 298 K is 7.0.

Comparing the two values, the pH at 291 K is greater than pH at 298 K. Therefore, the statement is not true.

(c) From solution in (b) $[H^+]$ at 291 K is 0.8×10^{-7} mol dm^{-3}. As $[H^+] = [OH^-]$ which is equal to 0.8×10^{-7} mol dm^{-3}, then the statement is true.

(d) From solution in (b), the pH of water was found to be 7 at 298 K. This shows that water is neutral at 298 K. Therefore, the statement is true.

Activity 6.1

Aim: To determine the K_a and K_b values of acetic acid and ammonia solutions

Requirements: 500 mL of 0.1 M acetic acid solution, 500 mL of 0.1 M ammonia solution, distilled water, 100-mL beakers, 50-mL graduated cylinder, stirring rod, and pH meter

Procedure

1. Transfer 50 mL of acetic acid into 5 separate beakers.
2. Measure and record the initial pH of the solution in the first beaker.
3. Dilute the acetic acid solution in the second beaker with 10 mL of distilled water, stir the solution, and then measure the pH again.
4. Repeat step 3, 4, and 5 by adding 20, 30 and 40 mL of distilled water in beakers and record their corresponding pHs.
5. Determine the K_a value for each process.
6. Repeat steps 1 to 5 by using ammonia in place of acetic acid.

Questions

1. What are the concentrations of the acid and base in each dilution?
2. What are the respective K_a and K_b values for the acetic acid and ammonia solutions?
3. How does the dilution affect the K_a and K_b values of each solution?
4. What are the importances of knowing the K_a and K_b values of various acids and bases in daily life?

Exercise 6.2

1. Consider the following ionisation reactions with their ionisation constants:

$$H_2SO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_3^-(aq)\ K_a = 1.2 \times 10^{-2}\ \text{mol dm}^{-3}$$

$$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq)\ K_a = 1.3 \times 10^{-19}\ \text{mol dm}^{-3}$$

Answer the following questions by giving reasons for each:

(a) Identify the stronger acid.

(b) What is the conjugate base of H_2SO_3?

(c) Which acid has weak conjugate base?

(d) Which acid has the stronger conjugate base?

(e) Which acid produces more ions?

2. Aniline ($C_6H_5NH_2$) reacts with water to form $C_6H_5\overset{+}{N}H_3$ and OH^-. Write the equation for the chemical reaction and the base ionisation constant expression for aniline.

3. Calculate the pH of the following:

(a) 0.2 mol dm^{-3} NaOH solution.

(b) A solution containing 25 g of KOH per 1 dm^3.

(c) 1.0×10^{-10} mol dm^{-3} $Ca(OH)_2$ solution.

4. What mass of $HClO_4$ is present in 50 cm^3 of $HClO_4$ solution having a pH of 4.2?
5. pH determination plays a significant role in various aspects of daily life. Explain.

6.3 Buffer solutions

Task 6.3

Use online educational resources to explore the concept of buffer solutions.

The pH of water and most solutions changes drastically when a small amount of acid or base is added. However, some solutions show resistance to pH change when a small amount of either acid or base is added. Aqueous solutions of sodium chloride and ammonium acetate have a pH of 7 at 298 K. An addition of 1.0 cm^3 of 0.1 mol dm^{-3} HCl to 1.0 dm^3 of sodium chloride solution alters the pH to 4. Similarly, the addition of 1.0 cm^3 of 0.1 mol dm^{-3} NaOH solution to 1.0 dm^3 solution of NaCl changes the pH of sodium chloride solution from 7 to 10. However, the addition of the same amount of HCl and NaOH to a neutral solution of ammonium acetate causes no significant change in pH of the solution. From these observations, it can be concluded that certain solutions have a tendency to resist any change in its hydrogen (hydroxonium) ion concentration or pH whenever a small amount of either a strong acid or a strong base is added to it. This property of resisting any change in the pH of a solution is known as *buffer action*. A solution which resists any change of pH when a small amount of either a strong acid or a strong base is added to it is called a *buffer solution.*

6.3.1 Types of buffer solutions

Buffer solutions can be acidic or basic depending on the nature of their mixed components.

Acidic buffers

Generally, acidic buffers can be made by dissolving relatively large amounts of a weak acid and the salt of its conjugate base. Examples include buffers containing acetic acid and sodium acetate, formic acid and sodium formate as well as benzoic acid and sodium benzoate. At 298 K, the pH of acidic buffers is less than 7.

Basic buffers

Basic buffers can be made by dissolving relatively large amounts of a weak base and the salt of its conjugate acid. This is exemplified by buffer containing weak base such as ammonia and the salt of its conjugate acid, ammonium chloride. At 298 K, the pH of the basic buffers is greater than 7.

6.3.2 Preparation of buffer solutions

To prepare either of the two types of the buffer solutions, the following steps must be followed:

(a) Decide on the chemical composition of the buffer by choosing the conjugate acid-base pair.

(b) Calculate the ratio of concentrations of buffer components. This is important because the ability of the buffer to resist the pH change (buffer capacity) is maximum when acid to salt or base to salt ratio is equal to 1. This ratio occurs when there is equal number of moles of acid (or base) and the salt.

(c) Determine the buffer concentration by keeping in mind that the higher the concentration of the components, the greater the buffer capacity. Concentrations of about 0.5 mol dm^{-3} of each component is suitable.

(d) Mix the components to make a solution and adjust the pH by adding a strong acid or strong base while monitoring the pH of the solution with a pH meter.

Activity 6.2

Aim: To prepare an acidic buffer solution with a pH of around 4.75

Requirements: 0.04 M Acetic acid, 3.28 g sodium acetate, distilled water, pH meter or pH indicator paper, beakers, stirring rod

Procedure

1. Measure 500 cm^3 of acetic acid solution into 1000 cm^3-beaker.
2. Weigh out 1.64 g of sodium acetate and dissolve it into the beaker containing acetic acid solution. Stir the solution using a stirring rod to ensure thorough mixing.
3. Measure the pH of the buffer solution using a pH meter or pH indicator paper/strips.
4. If the pH is not within the desired range, make small adjustments by adding more weak acid or salt until the target pH is reached.

Questions

1. What is the significance of selecting a weak acid and its conjugate base with appropriate p*K*a values for the desired pH range?
2. How is the activity relevant to the biological systems and industrial processes?

6.3.3 Determination of pH of buffer solutions

The pH of buffer solutions can be measured by using a pH meter or calculated using the *Henderson-Hasselbalch equation*. The Henderson-Hasselbalch equation for acidic buffer solutions can be derived by considering the ionisation of the weak acid in water.

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

At equilibrium, the equilibrium constant or acid ionisation constant (K_a) of the acid HA is given by:

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

Making $[H_3O^+]$ the subject of the formula leads to:

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

From $pH = -\log[H_3O^+]$, introducing negative logarithm on both sides of the equation gives

$$-\log[H_3O^+] = -\log K_a - \log[HA] + \log[A^-]$$

Rearranging the obtained equation gives:

$$-\log[H_3O^+] = -\log K_a + \log\frac{[A^-]}{[HA]} \qquad (6.8)$$

where $[A^-]$ is the concentration of the salt and [HA] is the concentration of the acid, $-\log[H_3O^+] = pH$ and $-\log K_a = pK_a$. Therefore, Equation 6.8 takes the form of Equation 6.9.

$$\mathbf{pH = pK_a + \log\frac{[Salt]}{[Acid]}} \qquad (6.9)$$

Equation 6.9 is what is known as the Henderson-Hasselbalch equation for acidic buffer solution and it can be used to calculate the pH of acidic buffer solution.

Example 6.6

A buffer solution was made by dissolving 10 g of CH_3COONa in 200 cm^3 of 0.5 mol dm^{-3} CH_3COOH. Assume that the change in volume upon addition of CH_3COONa was negligible. Calculate the pH of acetic acid-sodium acetate buffer solution, given that the ionisation constant (K_a) for acetic acid is 1.7×10^{-3} mol dm^{-3}.

Solution

The reaction for the ionisation of acetic acid in water is

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

Required is the number of moles of the conjugate base (salt) in solution.

Molar mass of CH_3COONa = 82 g mol^{-1}

Mass of the salt = 10 g

Number of moles (n) of CH_3COONa is given by:

$$n = \frac{\text{mass of } CH_3COONa\text{ (g)}}{\text{molar mass of } CH_3COONa\text{ (g mol}^{-1})} = \frac{10\text{ g}}{82\,g\text{ mol}^{-1}} = 0.122\text{ mol}$$

The concentration of the salt will be

$$= \frac{\text{Number of moles of } CH_3COONa\text{ (mol)}}{\text{Volume of the solution (dm}^{-3})} = \frac{0.122\text{ mol}}{0.2\text{ dm}^3} = 0.61\text{ mol dm}^{-3}$$

From the question, the $[CH_3COOH]$ = 0.5 mol dm^{-3}.

Applying the Henderson-Hasselbalch Equation $\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$ and substituting the values of K_a $[CH_3COOH]$ and $[CH_3COONa]$ gives:

$$\mathrm{pH} = -\log(1.7 \text{ x } 10^{-5}) + \log\frac{0.61}{0.5} = 4.77 + 0.09 = 4.86$$

Hence, the pH of this buffer solution is 4.86.

Similarly, the Henderson-Hasselbalch equation for basic buffer solution can be derived by considering the ionisation of a weak base (B) represented by the equation:

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

At equilibrium, the base ionisation constant (K_b) expression for this reaction is

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

Making $[OH^-]$ the subject of the formula leads to:

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

Introducing negative logarithm on both sides of the expression gives:

$$-\log[OH^-] = -\log K_b - \log[B] + \log[BH^+]$$

Rearranging the above equation leads to:

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

But, $-\log[OH^-] = pOH$ and $-\log K_b = pK_b$; therefore, introducing these values into the above equation gives:

$$pOH = pK_b + \log \frac{[BH^+]}{[B]}$$

But,

$$[BH^+] = [\text{Salt}] \text{ and } [B] = [\text{Base}]$$

Therefore,

$$pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \qquad (6.10)$$

From Equation 6.7, $pK_w = pH + pOH$

Making pH the subject of the formula leads to:

$$pH = pK_w - pOH$$

Substituting the value of pOH in Equation 6.10 gives Equation 6.11:

$$pH = pK_w - \left(pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]}\right) \qquad (6.11)$$

Removing the bracket results in equation 6.12.

$$pH = pK_w - pK_b + \log \frac{[\text{Base}]}{[\text{Salt}]} \qquad (6.12)$$

Equation 6.12 is known as *Henderson-Hasselbalch equation* for basic buffer solution and it is used to calculate the pH of basic buffer solutions.

Example 6.7

Calculate the pH of a buffer solution consisting of 0.15 mol dm^{-3} NH_3 and 0.09 mol dm^{-3} NH_4Cl at 298 K, given that the pK_b of ammonia is 4.75.

Solution

From the question, it is given that [salt] = 0.09 mol dm^{-3}, [Base] = 0.15 mol dm^{-3} and pK_b = 4.75. It is also known that pK_w at 298 K is equal to 14. Substituting these values into Equation 6.11 yields the pH.

$$pH = pK_w - pK_b + \log \frac{[Base]}{[Salt]}$$

$$pH = 14 - 4.75 + \log \frac{0.15\ mol\ dm^{-3}}{0.09\ mol\ dm^{-3}}$$

$$pH = 14 - 4.75 + 0.23 = 9.48$$

Therefore, the pH of the basic buffer solution is 9.48.

6.3.4 Mechanism of buffer action

The action of buffer solutions can be explained in terms of *Le Châtelier's principle*. Consider a buffer solution that is made up of acetic acid and its strong salt, sodium acetate. Being a weak acid, acetic acid ionises partially as per the equation:

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

Sodium acetate ionises almost completely to give Na^+ and CH_3COO^-. Initially, we assume that all the CH_3COO^- present in the solution at equilibrium are from the salt (CH_3COONa). When small amounts of acid such as HCl is added to this solution, the added H^+ from HCl will react with CH_3COO^- as represented by the chemical equation:

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

This reaction proceeds until all the added H^+ are removed, and therefore, the pH of the solution remains unchanged. Similarly, if a small amount of strong base such as NaOH is added to the buffer solution, the following reaction occurs:

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

The H^+ present in the equilibrium mixture react with the added OH^- and thus, shift the equilibrium to the right causing further ionisation of CH_3COOH. The reaction proceeds until all added OH^- are removed. Consequently, the pH of the solution remains unchanged. Basic buffers operates in a similar way to resist change in pH. In summary, the presence of significant amounts of a weak acid and its conjugate base makes buffer solutions resist change in pH as small amounts of either a strong acid or a strong base is added. When an acid is added to a buffer solution, the conjugate base present in the solution neutralises the added acid eliminating its effect in the buffer system. In the same way, when a strong base is added to a buffer solution, the weak acid present in the solution neutralises the added base thereby eliminating its effect to the buffer system.

Although the mechanism of absorbing OH^- and H^+ is the same for all buffers, different buffer solutions have different capabilities of resisting pH changes. The capability of a buffer solution to resist pH change is measured as buffer capacity. *Buffer capacity* is the amount of H^+ or OH^- ions a buffer solution can absorb without significant change in pH. The buffer capacity depends on the concentration and ratios of the components of the buffer solution. For example, a buffer that is made up of equal volumes of 1 mol dm^{-3} NH_4OH and 1 mol dm^{-3} NaOH has the same pH as a buffer solution that is made up of equal volumes of 0.1 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} NaOH but the former buffer solution has a larger capacity. This is because, the former buffer is made up of components of high concentration. When a buffer solution performs its role, the concentration of one component increases while that of the other decreases. This causes the ratio of the components to change. Since the ratio of these concentrations determines the pH, the greater the changes in the ratio, the lower the pH changes. The buffer components of similar concentrations will have less pH change when a small amount of an acid or a base is added.

Example 6.8

A buffer solution was made by adding 0.04 mol dm^{-3} CH_3COONa to 1 dm^3 of 0.01 mol dm^{-3} CH_3COOH. What will be the resulting pH if 1 cm^3 of 1 mol dm^{-3} NaOH is added? ($K_a = 1.7 \times 10^{-5}$ mol dm^{-3})?

Solution

From $[CH_3COOH] = 0.01$ mol dm^{-3}

$[CH_3COONa] = 0.04$ mol dm^{-3}

The volume of NaOH added = 1 cm^3

$[NaOH] = 1$ mol dm^{-3}

$$\text{The amount of NaOH added} = \frac{\text{Volume of NaOH added} \times \text{Molarity of NaOH}}{1000}$$

$$= \frac{1\ cm^3 \times 1\,mol}{1000\ cm^3} = 0.001\,mol$$

The addition of 0.001 mol of NaOH to the solution causes the following changes to the buffer components:

$$[CH_3COOH] = 0.01 - 0.001 \cong 0.009\ mol\ dm^{-3} = [Acid]$$

$$[CH_3COO^-] = 0.04 + 0.001 \simeq 0.041\ mol\ dm^{-3} = [Salt]$$

From Equation 6.9,

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

Substituting the values of K_a, [Salt] and [Acid] into the above equation:

$$\text{pH} = -\log 1.7 \times 10^{-5} + \log \frac{0.041}{0.009} = 5.43$$

Therefore, the pH of the resulting solution is 5.43.

6.3.5 Properties of buffer solutions

Buffer solutions have the following properties:

(a) Buffer solutions contain relatively large concentrations of a weak acid or weak base and a conjugate base or conjugate acid, respectively.

(b) When a small amount of H^+ is added to a buffer solution, it is neutralised by the weak base present in the solution as shown below:

$$H^+(aq) + A^-(aq) \longrightarrow HA(aq) \quad \text{or} \quad H^+(aq) + :B(aq) \longrightarrow BH^+(aq)$$

$$\text{e.g., } CH_3COO^-(aq) + H^+(aq) \longrightarrow CH_3COOH(aq) \text{ or}$$

$$H^+(aq) + NH_3(aq) \longrightarrow NH_4^+(aq)$$

(c) When a small amount of OH^- is added to a buffer solution, it is neutralised by the weak acid present in the solution.

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

$$\text{e.g., } OH^-(aq) + CH_3COOH(aq) \longrightarrow H_2O(l) + CH_3COO^-(aq)$$

$$OH^-(aq) + BH^+(aq) \longrightarrow B(aq) + H_2O(l)$$

$$\text{e.g., } OH^-(aq) + NH_4^+(aq) \longrightarrow NH_3(aq) + H_2O(aq)$$

(d) The pH of the buffer solution is determined by the buffering components, HA and A^- or B and BH^+ which are large compared with the amounts of H^+ or OH^- added.

6.3.6 Application of buffer solutions

Buffer solutions play important roles in many industrial processes such as electroplating, manufacturing of dyes, and photographic materials. Many biological and other systems such as saliva, stomach and blood depend on buffer actions to preserve a constant pH. Many household and cosmetic products need to control their pH values. Some instrumental methods like electrophoresis also depend on buffers for effective operations. Not only that but also plants absorb nutrients from the soil at certain pH values which must be maintained.

Exercise 6.3

1. How would you prepare 3.0 dm^3 of a 0.6 mol dm^{-3} acetate buffer solution of pH 5.2? The K_a of acetic acid is 1.75×10^{-5} mol^{-2} dm^{-6}.

2. A weak acid has a K_a value of 1.60×10^{-7} mol^2 dm^{-6}. Calculate the pH of the solution obtained when equimolar concentrations of the acid and its salt are mixed in equal ratio by volume.

3. A Form Six chemistry student intends to prepare 500 cm^3 of a buffer solution with pH of 5 by using sodium acetate and acetic acid. How many grams of sodium acetate should be added to 0.2 mol dm^{-3} of acetic acid?

4. (a) How is the concept of buffer capacity applied in human blood?
   (b) With reasons, identify from the given buffer solutions, the pair which has higher buffer capacity.
      (i) 0.25 mol dm^{-3} CH_3COOH and 0.25 mol dm^{-3} of CH_3COONa.
      (ii) 1.0 mol dm^{-3} CH_3COOH and 1.0 mol dm^{-3} CH_3COONa.
   (c) Which of the two buffers given in (b) will produce a greater pH change when 0.01 M of HCl is added?

6.4 Salt hydrolysis

Salts are ionic compounds. Some salts are soluble while others are insoluble in water. Water soluble salts can be completely soluble, leading to complete ionisation or sparingly soluble resulting in partial ionisation in aqueous solution. Such water soluble salts are assumed to dissociate into their constituent ions which move about independently in solution. Salts can be grouped into four categories depending on the source from which they are made. Some salts are made up of weak acids and weak bases, others from strong acids and strong bases. Also, there are salts which are made up of strong acids and weak bases and those which are made up of weak acids and strong bases. Salts that consist of the cations of strong bases and the anions of strong acids have no effect on H^+ ion produced by ionisation of water when dissolved in it. This means that aqueous solutions of salts such as KCl, NaCl, $NaNO_3$, and KNO_3 are neutral. However, when some salts are dissolved in water, they produce either acidic solutions or basic solutions. This implies that such salts react with water to produce H^+ or OH^- ions. Thus, they cause change in pH of the solution. The reaction of salt with water to form acidic or basic solution is called *salt hydrolysis*.

6.4.1 Behaviour of salts in water

When salt AB dissolves in water, it ionises as shown in the following equation:

$$AB(aq) \longrightarrow A^{n+}(aq) + B^{n-}(aq)$$

where n is the number of charge of the ions.

Therefore, the solution contains only A^{n+}, B^{n-}, and H_2O. In order for the pH of the solution to change, A^{n+} or B^{n-} should react with water by combining with H^+ or OH^-. The reaction will produce either acidic or basic solution depending on which of the two ions (H^+ or OH^-) combine with the anion or cation of the salt. If the ions of the salt have no effect on $[H^+]$ or $[OH^-]$, the solution produced is *neutral*.

Salts that produce basic solutions

Aqueous solution of sodium acetate (CH_3COONa) is basic (pH > 7). To account for this observation, consider the composition of the solution when the salt dissolves in water.

Assume that CH_3COONa dissolves completely, the solution will consist of Na^+, CH_3COO^-, and H_2O only. The Na^+ has neither acidic nor basic properties, and therefore it cannot combine with H^+ or OH^-. The CH_3COO^- is the conjugate base of CH_3COOH, a weak acid. Therefore, it has a significant affinity for a proton and acts as a base. Water is neither a strong enough acid nor a strong enough base to affect H^+. Thus, the pH of this solution will be controlled by the CH_3COO^- which reacts with water according to the reaction:

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

This reaction causes an increase in the $[OH^-]$, making the solution basic. The equilibrium constant expression K_b for this reaction is

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \qquad (6.13)$$

To obtain the K_b value for the acetate ion, you have to find the relationship among K_a, K_b and K_w for a weak acid and its conjugate base by considering the ionisation of acetic acid in water.

Acetic acid ionises in water as follows:

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

The equilibrium constant for the above chemical equation is given by:

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} \qquad (6.14)$$

Multiplying Equation 6.13 by Equation 6.14 gives

$$K_a \times K_b = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} \times \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

Cancelling the like terms in the numerator and denominator results into:

$$K_a \times K_b = [H_3O^+][OH^-]$$

The right-hand side of the above equation is equal to the right-hand side of Equation 6.3 which expresses the value for K_w. Therefore, the product of K_a and K_b can be represented in terms of K_w as

$$K_a \times K_b = K_w \qquad (6.15)$$

By using Equation 6.14 when either K_a or K_b is known, the other constant can be calculated from the known value of K_w.

Note: For any salt whose cation has neutral properties (such as Na^+ or K^+) and whose anion is the conjugate base of a weak acid, the aqueous solution will be basic.

Salts that produce acidic solutions

When solid NH_4Cl is dissolved in water, NH_4^+ and Cl^- are released. The solution produced contains only NH_4^+, Cl^-, and H_2O molecules. As Cl^- have no affinity for H^+ in water, they do not affect the pH of the solution. Therefore, the observed acidic property of the solution is produced by NH_4^+. In water, NH_4^+ behaves as a weak acid by donating a proton to water molecule.

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

This reaction causes an increase in the concentration of H_3O^+ or H^+, hence the pH of the solution. In general, a salt whose cation is the conjugate acid of a weak base reacts with water to produce an acidic solution. Salts that contain highly charged metal ions (highly charged cations) such as Al^{3+} and Fe^{3+} also produce acidic solutions when dissolved in water. Although these cations are not Brønsted-Lowry acids, the high charge on the metal ion polarises the O–H bonds in the coordinated water molecules. This makes the hydrogen atoms in these water molecules more acidic and can readily be attracted by water molecules present in the solution.

$$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq)$$

This causes an increase in $[H_3O^+]$ of the solution, making it acidic.

Salts from weak bases and weak acids

Ammonium cyanide (NH_4CN) is an example of a salt that is made from a weak base NH_3 and weak acid HCN. In water, it ionises to produce NH_4^+ and CN^-. The produced NH_4^+ and CN^- react with water as

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

$$CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$$

The ions H_3O^+ and OH^- react immediately to produce H_2O.

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

The resulting solution can be either acidic, basic or neutral depending on the extent to which NH_4^+ and CN^- have been hydrolysed. If NH_4^+ hydrolyses more than CN^-, the solution will be acidic, and if CN^- hydrolyses more than NH_4^+, the solution will be basic. If both ions hydrolyse at equal extent, the solution will be neutral.

6.4.2 Hydrolysis constant, degree of hydrolysis, and pH of salt solutions

From the preceding sub-section, it is possible to qualitatively predict the nature of the solution which is obtained when a salt of a strong acid and weak base or a salt of a weak acid and strong base is dissolved in water. However, to determine how much acidic or basic the solution has become as a result of hydrolysis of the salt is difficult, especially when the solution is obtained by dissolving a salt of weak acid and weak base. This is because the cations and anions of the salt hydrolyses to furnish H_3O^+ and OH^- in the solution, but to judge which of the two is predominant becomes difficult. To solve this problem, you need to consider quantitative aspect of salts hydrolysis by introducing the concepts of hydrolysis constant, degree of hydrolysis, and pH of the salt solution.

Hydrolysis constant of a salt of weak acid and strong base

Hydrolysis constant of a salt of weak acid and strong base can be derived from the ionisation constant of the corresponding weak acid. Consider the hydrolysis of salt of weak acid and strong base:

	$CH_3COO^-(aq) + H_2O(l)$	$\rightleftharpoons$	$CH_3COOH(aq)$	$+ [OH^-](aq)$
Initial mol dm^{-3}	C		0	0
Change	$-Ch$		$+Ch$	$+Ch$
Equilibrium mol dm^{-3}	$C(1-h)$		Ch	Ch

where C is the molar concentration of the salt (CH_3COONa) and h is the degree of hydrolysis of the salt.

By applying the law of chemical equilibrium, the equilibrium constant (hydrolysis constant, K_h) is given by:

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{(Ch)^2}{C(1-h)} = \frac{Ch^2}{1-h} \tag{6.16}$$

Assuming that the value of h is very small compared to 1, then $1-h$ is approximately equal to 1 and Equation 6.16 can be written as

$$K_h = Ch^2 \tag{6.17}$$

and thus,

$$h = \sqrt{\frac{K_h}{C}} \tag{6.18}$$

To establish the relationship between K_h, K_w, and K_a, consider Equations 6.3, 6.14 and 6.16.

From Equation 6.3, $K_w = [H^+][OH^-]$, implying that $[OH^-] = \frac{K_w}{[H^+]}$ and considering Equation 6.14, $K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$ which can be written in terms of $[CH_3COOH]$ as

$$[CH_3COOH] = \frac{[CH_3COO^-][H^+]}{K_a}$$

Substituting the values of $[OH^-]$ and $[CH_3COOH]$ in Equation 6.16, leads to:

$$K_h = \frac{[CH_3COO^-][H^+]}{K_a} \times \frac{K_w}{[H^+][CH_3COO^-]} = \frac{K_w}{K_a}$$

Therefore,

$$K_h = \frac{K_w}{K_a} \tag{6.19}$$

Equation 6.19 shows that the hydrolysis constant (K_h) of a salt of weak acid and strong base is inversely proportional to the value of K_a of a parent acid. This implies that the weaker the parent acid, the more widespread will be the hydrolysis.

Taking Equation 6.18 as a reference, it can be concluded that there is a relationship between K_h and the degree of hydrolysis (h). The value of K_h in Equation 6.18 can be substituted with Equation 6.19 to obtain Equation 6.20.

$$h = \sqrt{\frac{K_w}{K_a C}} \qquad (6.20)$$

From Equation 6.20, it can be concluded that the degree of hydrolysis of salts of weak acids and strong bases is inversely proportional to the dissociation constant of the parent weak acid and the concentration of the salt. This implies that the degree of hydrolysis decreases with increase in concentration of the salt and the value of dissociation constant (K_a) of the parent weak acid.

Salt hydrolysis results in withdrawal of H^+ or OH^- from water, thus, causing drop or rise in pH of the water. To obtain the equation for quantitative determination of the pH of the salt solution, consider the reaction:

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

From the equation representing hydrolysis of the salt of weak acid and strong base, you have:

$$[OH^-] = Ch \qquad (6.21)$$

Combining Equations 6.3 and 6.21 with rearrangements gives Equation 6.22.

$$Ch = \frac{K_w}{[H^+]} \qquad (6.22)$$

Similarly, when Equation 6.20 is combined with 6.22, Equation 6.23 is obtained.

$$C\sqrt{\frac{K_w}{K_a C}} = \frac{K_w}{[H^+]} \qquad (6.23)$$

Squaring both sides of Equation 6.23 and rearranging it gives Equation 6.24.

$$[H^+] = \sqrt{\frac{K_a \times K_w}{C}} \qquad (6.24)$$

Applying negative logarithm to base 10 on both sides of Equation 6.24, Equation 6.25 is obtained.

$$-\log[H^+] = \frac{1}{2}(-\log K_a + (-\log K_w) + \log C)$$

$$\text{pH} = \frac{1}{2}(\text{p}K_w + \text{p}K_a + \log C) \qquad (6.25)$$

Therefore, the extent to which the salt solution will be acidic or basic upon hydrolysis can be determined by using Equation 6.25. The equation also shows the pH dependence on the K_a and the original concentration of the acid.

Example 6.9

The pH of water at 298 K was found to be 7. After the addition of 41.0 g of a salt of weak acid and strong base ($C_2H_3O_2Na$) into 1 dm^3 of this water, the new pH was recorded indicating that the salt has undergone hydrolysis. Assuming that no changes in volume of water upon the addition of the salt, determine K_h, the degree of hydrolysis and the new pH of water given that the acid dissociation constant (K_a) is 1.8×10^{-5} mol dm^{-3}.

Solution

Given the pH of water (at 298 K) before salt was dissolved to be 7, indicate that $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}

The hydrolysis constant (K_h) for a salt of weak acid and strong base is given by Equation 6.19.

$$K_h = \frac{K_w}{K_a}$$

Substituting the values of K_w and K_a into the K_h equation above, gives:

$$K_h = \frac{1.0\times10^{-14}\ \text{mol}^2\ \text{dm}^{-6}}{1.8\times10^{-5}\ \text{mol dm}^{-3}} = 5.6 \times 10^{-10}\ \text{mol dm}^{-3}$$

Therefore, the hydrolysis constant (K_h) is 5.6×10^{-10} mol dm^{-3}.

Given the mass of hydrolysed salt in 1 dm^3 of water, and calculating the molar mass of the salt from the atomic mass of the elements in the salt, the concentration of the salt is obtained as follows:

$$C = \frac{\text{mass of the solute (g)}}{\text{molar mass of solute (g mol}^{-1}) \times \text{volume of solution (dm}^3)}$$

Substituting the data given, one has the following:

$$C = \frac{41.0\,\text{g}}{82.0\,\text{g mol}^{-1} \times 1\,\text{dm}^{-3}} = 0.5\,\text{mol dm}^{-3}$$

The concentration of salt (C) is 0.5 mol dm^{-3}.

The degree of hydrolysis (h) for salt of this type is calculated by using Equation 6.20.

$$h = \sqrt{\frac{K_w}{K_a C}}$$

Substituting the values of K_w, K_a, and C into this equation gives:

$$h = \sqrt{\frac{1.0 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}}{1.8 \times 10^{-5}\ \text{mol dm}^{-3} \times 0.5\,\text{mol dm}^{-3}}} = 3.33 \times 10^{-5}$$

Therefore, the degree of hydrolysis (h) of the salt is 3.33×10^{-5} or 0.003%.

The pH of a salt of weak acid and strong base can be calculated by using Equation 6.25.

$$\text{pH} = \frac{1}{2}(\text{p}K_w + \text{p}K_a + \log C)$$

Substituting the values of K_a, K_w and C into the above equation gives

$$\text{pH} = \frac{1}{2}\left(-\log 1.0 \times 10^{-14} + -\log 1.8 \times 10^{-5} + \log 0.5\right)$$

$$\text{pH} = \frac{1}{2}(14 + 4.74 - 0.3) = 9.22$$

Therefore, the pH of the solution after hydrolysis of the salt is 9.22.

Hydrolysis constant of a salt of strong acid and weak base

For a salt made from strong acid and weak base, the hydrolysis constant can be obtained by considering the hydrolysis of NH_4Cl (a salt of a weak base, NH_3, and strong acid, HCl). This salt ionises in solution as shown hereunder:

$$NH_4Cl(s) \xrightarrow{H_2O} NH_4^+(aq) + Cl^-(aq)$$

The Cl coming from strong acid do not undergo hydrolysis. Assuming that the cation NH_4^+ undergoes hydrolysis to give h as the amount of ions that goes in the solution, it gives the relation:

	$NH_4^+(aq)$ + $H_2O(l)$ $\rightleftharpoons$	$NH_3(aq)$ +	$H_3O^+(aq)$
Initial Conc.	C	0	0
Change	$-Ch$	$+Ch$	$+Ch$
Equilibrium Conc.	$C(1-h)$	Ch	Ch

Considering initial and equilibrium states, the concentration of NH_4^+ can be taken as C and $C(1-h)$, respectively, and the concentration of NH_3 and H_3O^+ at equilibrium will be Ch mol dm^{-3} each. The hydrolysis constant for the reaction is given by

$$K_h = \frac{[NH_3][H_3O^+]}{[NH_4^+]} \qquad (6.26)$$

When the equilibrium concentrations of the species are substituted into Equation 6.26, the following expression is obtained:

$$K_h = \frac{Ch \times Ch}{C(1-h)} = \frac{Ch^2}{1-h}$$

As the degree of hydrolysis is very small, $1-h$ is approximately equal to 1. Therefore,

$$K_h = \frac{Ch^2}{1} = Ch^2$$

and thus, the degree of hydrolysis takes the form of Equation 6.18.

$$h = \sqrt{\frac{K_h}{C}}$$

K_h can be expressed in terms of K_w and K_b by multiplying Equation 6.26 by $[OH^-]$ in the denominator and numerator to give Equation 6.27:

$$K_h = \left(\frac{[NH_3]}{[NH_4^+][OH^-]}\right)([H_3O^+][OH^-]) \qquad (6.27)$$

But $[H_3O^+][OH^-] = K_w$ and $\frac{[NH_3]}{[NH_4^+][OH^-]} = \frac{1}{K_b}$

substituting K_w and $\frac{1}{K_b}$ into Equation 6.27 gives Equation 6.28:

$$K_h = \frac{1}{K_b} \times K_w = \frac{K_w}{K_b} \qquad (6.28)$$

From this equation, it can be deduced that the values of K_h and K_b are inversely related. The weaker the parent bases, the more extensive will be the hydrolysis.

Combining Equation 6.18 and 6.28 results in the following expression:

$$h = \sqrt{\frac{K_w}{CK_b}} \qquad (6.29)$$

Multiplying both sides of Equation 6.29 by the initial concentration of the salt (C) gives

$$Ch = C\sqrt{\frac{K_w}{CK_b}} = \sqrt{\frac{K_w C^2}{CK_b}} = \sqrt{\frac{K_w C}{K_b}} \qquad (6.30)$$

From the reaction stoichiometry $Ch = [H_3O^+]$, then Equation 6.30 can be written as

$$[H_3O^+] = \sqrt{\frac{K_w C}{K_b}} = \left(\frac{K_w C}{K_b}\right)^{\frac{1}{2}} \qquad (6.31)$$

Introducing negative logarithm on both sides of Equation 6.31 gives Equation 6.32.

$$-\log[\mathrm{H_3O^+}] = \frac{1}{2}\left(-\log K_w - \log C - (-\log K_b)\right) \tag{6.32}$$

But,

$$-\log[\mathrm{H_3O^+}] = \mathrm{pH}; \quad -\log K_w = \mathrm{p}K_w \text{ and } -\log K_b = \mathrm{p}K_b$$

Substituting these values into Equation 6.32 gives Equation 6.33.

$$\mathrm{pH} = \frac{1}{2}(\mathrm{p}K_w - \log C - \mathrm{p}K_b) \tag{6.33}$$

Example 6.10

A salt of NH_4Cl was dissolved in water to make a 0.2 mol dm^{-3} solutions at 298 K. Calculate the hydrolysis constant (K_h) degree of hydrolysis (h) of the salt and pH of the salt solution at this temperature given that the K_b value of NH_4OH at 298 K is 1.8×10^{-5} mol dm^{-3}.

Solution

NH_4Cl is a salt of weak base (NH_4OH) and strong acid (HCl). For such, a salt hydrolysis constant can be calculated by using Equation 6.28.

$$K_h = \frac{K_w}{K_b}$$

Substituting the values of K_w and K_b into Equation 6.28 results into:

$$K_h = \frac{1.0 \times 10^{-14}\ \mathrm{mol^2\,dm^{-6}}}{1.8 \times 10^{-5}\ \mathrm{mol\,dm^{-3}}} = 5.55 \times 10^{-10}\ \mathrm{mol\,dm^{-3}}$$

Therefore, hydrolysis constant of the salt is 5.55×10^{-10} mol dm^{-3}.

The degree of hydrolysis h of a salt of weak base and strong acid can be calculated by using Equation 6.29.

$$h = \sqrt{\frac{K_w}{CK_b}}$$

Substituting the values of K_w, K_b, and C into this equation gives:

$$h = \sqrt{\frac{1.0\times10^{-14}\ \mathrm{mol^2\ dm^{-6}}}{1.8\times10^{-5}\ \mathrm{mol\ dm^{-3}} \times 0.2\ \mathrm{mol\ dm^{-3}}}} = 0.000053 \text{ or } 0.0053\%$$

Therefore, the degree of hydrolysis of the salt is 0.0053%.

The pH of a solution of salt of weak base and strong acid can be calculated using Equation 6.33.

$$\text{pH} = \frac{1}{2}(\text{p}K_w - \log C - \text{p}K_b)$$

$$\text{or}\quad \text{pH} = \frac{1}{2}\left(-\log K_w - \log C - (-\log K_b)\right)$$

Substituting the values of K_w, K_b and C into the above equation gives:

$$\text{pH} = \frac{1}{2}\left((-\log(1.0 \times 10^{-14}\ \text{mol}^2\,\text{dm}^{-6})\right) - \log 0.2 - \left(-\log(1.8 \times 10^{-5}\ \text{mol}\,\text{dm}^{-3})\right)$$

$$\text{pH} = \frac{1}{2}(14 + 0.7 - 4.74) = 4.98$$

Therefore, the pH of NH_4Cl solution is 4.98.

The hydrolysis constant of a salt of weak acid and weak base

Hydrolysis constant of a salt of weak acid and weak base can be deduced by considering the reaction of CH_3COONH_4 with water as represented by the following scheme:

$$\begin{array}{ccccccc} CH_3COO^-(aq) & + & NH_4^+(aq) & + & H_2O(l) \rightleftharpoons & CH_3COOH(aq) & + & NH_4OH(aq) \\ C & & C & & & 0 & & 0 \\ -Ch & & -Ch & & & +Ch & & +Ch \\ C(1-h) & & C(1-h) & & & Ch & & Ch \end{array}$$

The hydrolysis constant for the reaction is given by the expression:

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[NH_4^+][CH_3COO^-]} \qquad (6.34)$$

Multiplying the denominator and numerator of Equation 6.34 by $[H_3O^+]$ and $[OH^-]$ yields Equation 6.35.

$$K_h = \frac{[CH_3COOH]}{[CH_3COO^-][H_3O^-]} \times \frac{[NH_4OH]}{[NH_4^+][OH^-]} \times ([H_3O^+][OH^-]) \quad . \qquad (6.35)$$

But,

$$\frac{[CH_3COOH]}{[CH_3COO^-][H_3O^+]} = \frac{1}{K_a},\ \frac{[NH_4OH]}{[NH_4^+][OH^-]} = \frac{1}{K_b}. \text{ and } [H_3O^-][OH^-] = K_w$$

Substituting the above expressions into Equation 6.35 yields Equation 6.36.

$$K_h = \frac{1}{K_a} \times \frac{1}{K_b} \times K_w = \frac{K_w}{K_a \times K_b} \tag{6.36}$$

Equation 6.36 shows that the hydrolysis constant of the salt of weak acid and weak base is directly proportional to K_w and inversely proportional to K_a and K_b. Thus, a salt of this type hydrolyses more when the values of ionisation constants of the parent acid (K_a) and parent base (K_b) are small. Equation 6.36 helps to establish the relationship between K_w, K_a, K_b, and the hydrolysis constant of salts of weak acid and weak base as follows:

From Equation 6.34,

$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{NH}_4][\text{CH}_3\text{COO}^-]}$$

Recalling the reaction scheme, $[\text{CH}_3\text{COOH}] = [\text{NH}_4\text{OH}] = Ch$ and $[\text{NH}_4^+] = [\text{CH}_3\text{COO}^-] = C(1-h)$ and substituting these values into Equation 6.34 results in Equation 6.37:

$$K_h = \frac{Ch \times Ch}{C(1-h) \times C(1-h)} = \frac{h^2}{(1-h)^2} \tag{6.37}$$

Therefore,

$$\frac{h}{1-h} = \sqrt{K_h} \tag{6.38}$$

As the degree of hydrolysis of the salt of weak base and weak acid is very small compared to 1, 1–h is approximately equal to 1. Hence, Equation 6.38 can be written as

$$\frac{h}{1} = h = \sqrt{K_h} \tag{6.39}$$

Combining Equations 6.36 and 6.39 leads to Equation 6.40.

$$h = \sqrt{\frac{K_w}{K_a \times K_b}} \tag{6.40}$$

Equation 6.40 shows that the degree of hydrolysis of the salt of weak acid and weak base is inversely proportional to K_a and K_b which implies that the weaker the parent acid or base the higher the degree of hydrolysis. In this case, Equation 6.40 can be used to derive the equation used for calculating the pH of the solution of a salt of weak acid and weak base. Hydrolysis of a salt of weak acid and weak base produces parent weak acid and weak base which in turn ionise to give their corresponding ions in the equilibrium mixture. Therefore, K_a value of the parent weak acid and K_b value of the parent weak base should be considered in establishing the equation for calculating pH of the solution of a salt of weak acid and weak base. Considering hydrolysis of CH_3COONH_4 as an example, K_a values of CH_3COOH and K_b value of NH_4OH are used in the derivation of the pH equation.

The K_a and K_b expressions for CH_3COOH and NH_4OH, respectively are as follows:

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} \text{ and } K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

Making $[H_3O^+]$ the subject of the formula from the K_a expression, the following equation is obtained:

$$[H_3O^+] = K_a \frac{[CH_3COOH]}{[CH_3COO^-]}$$

Introducing the equilibrium concentrations of CH_3COOH and CH_3COO^- into the above expression leads to:

$$[H_3O^+] = K_a \frac{Ch}{C(1-h)} = K_a \left(\frac{h}{1-h}\right)$$

But $1 - h \approx 1$, then the above equation can be written as:

$$[H_3O^+] = K_a h$$

Substituting h from Equation 6.40 leads to Equation 6.41.

$$[H_3O^+] = K_a \left(\sqrt{\frac{K_w}{K_a \times K_b}}\right) = \sqrt{\frac{K_w \times K_a^2}{K_a \times K_b}} = \sqrt{\frac{K_w \times K_a}{K_b}}$$

$$[H_3O^+] = \left(\frac{K_w \times K_a}{K_b}\right)^{\frac{1}{2}} \qquad (6.41)$$

Introducing a negative logarithm on both sides of Equation 6.41 results in Equation 6.42.

$$-\log[H_3O^+] = \frac{1}{2}(-\log K_w - \log K_a + \log K_b)$$

$$pH = \frac{1}{2}(pK_w + pK_a - pK_b) \qquad (6.42)$$

From Equation 6.42, it can be deduced that the pH of a solution of a salt of weak acid and weak base does not depend on the concentration of the salt. The solution can be neutral, acidic, or basic depending on the values of K_a and K_b as summarised in Table 6.4.

Table 6.4: *pH dependence of salts of weak acids and bases on K_a and K_b*

Relationship between K_a and K_b	Relationship between K_w and $[H_3O^+]$	pH
$K_a = K_b$	$[H_3O^+] = \sqrt{K_w}$	pH = 7
$K_a > K_b$	$[H_3O^+] > \sqrt{K_w}$	pH < 7
$K_a < K_b$	$[H_3O^+] < \sqrt{K_w}$	pH > 7

Example 6.11

At 298 K, a 0.1 mol dm^{-3} solution of a salt of weak acid and weak base has a pH of 8.0. Calculate the ionisation constant of the parent acid (K_a) if the ionisation constant of the parent weak base (K_b) is 1×10^{-3} mol dm^{-3}. Use the value of K_a to calculate the hydrolysis constant (K_h) and the degree of hydrolysis (h) of the salt.

Solution

From the question, it is given that $K_b = 1 \times 10^{-3}$ mol dm^{-3} and it is known that $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}; therefore, using Equation 6.42 and making pK_a the subject of the formula gives

$$pK_a = 2pH - pK_w + pK_b$$

$$pK_a = 2pH - (-\log K_w) + (-\log K_b)$$

Substituting the values of pH, K_w and K_b into the equation for pK_a results into:

$$pK_a = 2 \times 8 - \left(-\log 1.0 \times 10^{-14}\right) + \left(-\log 1.0 \times 10^{-3}\right)$$

$$pK_a = 16 - 14 + 3 = 5$$

But

$$K_a = \log^{-1}(-pK_a)$$

then,

$$K_a = \log^{-1}(-5) = 1.0 \times 10^{-5}\ \text{mol dm}^{-3}$$

Therefore, the dissociation constant of the parent acid (K_a) is 1.0×10^{-5} mol dm^{-3}. The degree of hydrolysis (h) can be found by using Equation 6.40 as follows:

$$h = \sqrt{\frac{K_w}{K_a \times K_b}}$$

Substituting the values of K_w, K_a, and K_b into the equation above gives

$$h = \sqrt{\frac{1.0\times10^{-14}}{1.0\times10^{-5} \times 1.0\times10^{-3}}} = \sqrt{1.0\times10^{-6}} = 1.0\times10^{-3}$$

Therefore, the degree of hydrolysis of a salt is 1.0×10^{-3} or 0.1%.

The hydrolysis constant of salt is given by Equation 6.39.

$$h = \sqrt{K_h}$$

Upon rearrangement, Equation 6.39 has the form:

$$K_h = h^2$$

Substituting the value of h gives

$$K_h = (1.0\times10^{-3})^2 = 1.0\times10^{-6}$$

Therefore, the hydrolysis constant of the salt, K_h is 1.0×10^{-6}.

Example 6.12

Common salt (NaCl), ammonia sulfate ($(NH_4)_2SO_4$) and sodium hydrogen carbonate (baking powder, $NaHCO_3$) are frequently used in our life. Predict the nature of their aqueous solutions as acidic, basic, or neutral. Give reasons to support your answer.

Solution

When NaCl is dissolved in water, it ionises completely to give Na^+ and Cl^- ions. The resulting solution contains only Na^+, Cl^-, and H_2O molecules.Since Na^+ has no affinity to OH^- and Cl^- has no affinity to H^+, the concentrations of H^+ and OH^- in the solution remain unaffected. Thus, the solution is neutral. Conversely, when $(NH_4)_2SO_4$ is dissolved in water, it ionises to produce NH_4^+ and SO_4^{2-}. The solution therefore contains only NH_4^+, SO_4^{2-}, and H_2O molecules. The SO_4^{2-} being a conjugate base of a strong acid has no affinity to H^+. In this regard, its presence in the solution has no effect on $[H^+]$. However, NH_4^+, a conjugate acid of the weak base, reacts with water molecules according to the chemical reaction:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

This causes an increase in the concentration of H_3O^+; thus, the solution is acidic. Sodium hydrogen carbonate ($NaHCO_3$), dissolves in water to produce Na^+ and HCO_3^-. The solution therefore contains Na^+, HCO_3^- and H_2O molecules. But Na^+

has no affinity to OH^- and H^+. The effect on the pH of the solution is produced by HCO_3^-. This can be explained by the reaction which takes place between HCO_3^- and water as shown in the following chemical reaction:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

The H_2CO_3 is a weak acid; therefore, its conjugate-base HCO_3^- has affinity to H^+ than H_2O which makes it capable of taking away H^+ from water molecule to release OH^-. The reaction increases $[OH^-]$; thus, the solution becomes basic.

Exercise 6.4

1. Write a balanced chemical equation for the hydrolysis of bismuth chloride ($BiCl_3$).
2. Calculate the hydroxyl ion concentration $[OH^-]$, the percentage of hydrolysis, and the pH of a 0.5 mol dm^{-3} solution of sodium acetate given that K_b for CH_3COO^- is 5.6×10^{-10} mol dm^{-3}.
3. The aqueous solution of $CuSO_4$ is acidic while that of KCl is neutral. Explain.
4. Write the ionisation equations for each of the following salts. State whether the cation, anion, or both hydrolyse and whether the salt is acidic, basic, or neutral:
   (a) K_2CO_3 (b) $AlBr_3$ (c) NH_4ClO_4
   (d) $CsNO_3$ (e) $Cr(NO_3)_3$

6.5 Determination of concentration of ions in solution

Determination of concentration of ions in solution is a crucial aspect in enabling the precise measurement of the concentration of specific ions present. Acid-base titrations are some of the methods which can enable the determination of the concentration of ions in solution.

6.5.1 Acid-base titration

The choice of an indicator in acid-base titration depends on the strength of the acid and the base. In a strong acid-strong base titration, a bromothymol blue indicator is used, whereas in weak acid-strong base reactions a phenolphthalein indicator is used. Meanwhile, methyl orange is used for strong acid-weak base reactions. However, there are reactions in which determination and analysis of the amount and concentration of acids or bases are done at two end points. These are called double indicator titrations.

Acid–base titrations using double indicators

In acid-base titrations using double indicators, two different indicators are used to determine the endpoint of the titration. This method allows for increased accuracy and precision, especially when titrating solutions with complex compositions or multiple equivalence points.

Reaction between HCl and Na_2CO_3

Sodium carbonate is a salt of carbonic acid (H_2CO_3), a dibasic acid which dissociates in two steps.

$$H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq) \qquad pK_1 = 6.38$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^-(aq) \qquad pK_2 = 10.32$$

In aqueous solution, Na_2CO_3 hydrolyses as:

$$Na_2CO_3(aq) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2CO_3(aq)$$

Sodium carbonate (Na_2CO_3) reacts with hydrochloric acid (HCl) in two steps. In the first step, one mole of $NaHCO_3$ is produced from one mole of Na_2CO_3 and HCl. In the second step, the sodium bicarbonate formed reacts further with the acid to produce NaCl, CO_2 and water.

$$\text{Step 1: } Na_2CO_3(aq) + HCl(aq) \longrightarrow NaHCO_3(aq) + NaCl(aq)$$

$$\text{Step 2: } NaHCO_3(aq) + HCl(aq) \longrightarrow NaCl(aq) + CO_2(g) + H_2O(l)$$

Assume that 25.00 mL of 0.10 M Na_2CO_3 solution is titrated with 0.10 M HCl solution. By the time 25.00 mL of 0.10 M HCl solution has been added, the reaction is complete. The pH at this point is given by

$$\frac{1}{2}pK_1 + \frac{1}{2}pK_2 = \frac{1}{2}(6.38 + 10.32) = 8.35.$$

Therefore, the first end point can be detected using phenolphthalein indicator. At the completion of the first step, the solution is acidic with a pH of about 3.94, and methyl orange can be used as an indicator. For this titration process, phenolphthalein indicator indicates half way end point of volume of HCl which reacted with sodium carbonate during titration. The other half end point volume of HCl remaining for complete reaction is indicated by methyl orange indicator added to the same solution. The approach for determination of the volume of HCl used when Na_2CO_3 is titrated against HCl using phenolphthalein and methyl orange indicators is demonstrated in Activity 6.3.

Activity 6.3

Aim: To determine the volume of HCl used for the titration with Na_2CO_3 using phenolphthalein and methyl orange indicators

Requirements: Beakers, pipette, burette, retort stand, white tile, conical flasks, 0.05 M Na_2CO_3 solution, 0.10 M HCl solution, methyl orange (MO) indicator, and phenolphthalein (POP) indicator

Procedure

1. Pipette 25.00 mL of Na_2CO_3 solution into a conical flask.
2. Add 2 to 3 drops of phenolphthalein indicator.
3. Put HCl into the burette and take the initial reading.
4. Titrate HCl solution against Na_2CO_3 solution until a colour change is observed and record the first titre value.
5. Add 2 to 3 drops of methyl orange indicator to the same solution in the titration flask and continue titrating until a colour change is observed, then record the second titre value.
6. Repeat steps 1 to 5 to obtain three more readings and record the results in a tabular form as shown in a following table.

Volume of HCl (mL)	Titrations			
	Pilot	1	2	3
Initial burette reading				
Final burette reading after using POP				
Final burette reading after using MO				
Titre volume when POP was used				
Titre volume when MO was used				

Questions

1. What is the average titre value when:
   (a) POP was used?
   (b) MO was used?
2. What is the balanced chemical equation when:
   (a) POP was used as an indicator?
   (b) MO was used as an indicator?

3. What is the total volume of HCl solution used for complete reaction with Na_2CO_3?
4. What is the molarity of sodium carbonate reacted with HCl when POP was added?
5. What is the concentration of the intermediate product in g/L?

Reaction between HCl and a mixture of Na_2CO_3 and NaOH

Determination of the composition of sodium carbonate and sodium hydroxide in a mixture is useful in the analysis of commercial caustic soda. Two methods can be used for this analysis. In the first method the total alkali (carbonate and hydroxide) is determined by titration with standard acid, using methyl orange or other suitable indicators. In the second portion of solution, the carbonate is precipitated with a slight excess of barium chloride solution. The resulting mixture is then titrated with standard acid using phenolphthalein indicator. This titration gives the hydroxide content and by subtracting this from the first titration, the volume of acid required for the carbonate is obtained. The second method utilises two indicators in the same mixture.

It has been stated earlier that the pH of half-neutralised sodium carbonate, that is, at the sodium hydrogen carbonate stage, is about 8.35. The second end point for complete neutralisation is slightly acidic, so a different indicator has to be used. In this case, phenolphthalein and methyl orange indicators are employed. Consider the chemical reaction of the mixture of sodium carbonate and sodium hydroxide with hydrochloric acid given below:

$$Na_2CO_3(aq) + HCl(aq) \longrightarrow NaCl(aq) + NaHCO_3(aq)$$

$$NaHCO_3(aq) + HCl(aq) \longrightarrow NaCl(aq) + CO_2(g) + H_2O(l)$$

$$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

The pH of the solution closer to the equivalence point of the reactions between Na_2CO_3 and HCl, and $NaHCO_3$ and HCl is alkaline, so phenolphthalein indicator is used to indicate the end points of these reactions. On the other hand, the pH of the solution closer to the equivalence point of the reaction between NaOH and HCl is acidic; thus, methyl orange is used to indicate the end point of this reaction. The experimental determination of the percentage composition of sodium carbonate in the mixture can be demonstrated in Activity 6.4.

Activity 6.4

Aim: To determine the percentage composition of sodium carbonate in the mixture

Requirements: Beakers, pipette, burette, retort stand, white tile, conical flasks, a solution containing about 4.94 g of a mixture of sodium carbonate and sodium hydroxide in 1 dm^3 of aqueous solution, 0.10 M pure hydrochloric acid, methyl orange and phenolphthalein indicators

Procedure

1. Pipette 25.00 mL of a solution containing a mixture of Na_2CO_3 and NaOH into a conical flask.
2. Add 2 to 3 drops of phenolphthalein indicator.
3. Fill the burette with HCl solution and take the initial reading.
4. Titrate HCl solution against a solution containing a mixture of Na_2CO_3 and NaOH until a colour change is observed and record the first titre value.
5. Add 2 to 3 drops of methyl orange indicator to the same solution in the titration flask and continue to titrate until a colour change is observed. Record the second titre value.
6. Repeat steps 1 to 5 three times and record the results in tabular form as shown in Table 6.6.

Volume of HCl (mL)	Titrations			
	Pilot	1	2	3
Initial burette reading				
Final burette reading after using POP				
Final burette reading after using MO				
Titre volume when POP was used				
Titre volume when MO was used				

Questions

1. Why should the experimental procedure be repeated for more than once?
2. What volume of HCl reacted completely with Na_2CO_3 in the mixture?
3. What volume of HCl reacted completely with NaOH in the mixture?
4. What is the concentration in g dm^{-3} of Na_2CO_3 and NaOH in the mixture?
5. What is the percentage of Na_2CO_3 in the mixture?

6.6 The concept of solubility

A solute-solvent interaction results in a number of chemical and physical processes that are of interest. When a solute is dissolved in a solvent, three processes which determine whether a substance is soluble, sparingly soluble or insoluble in a solvent (Figure 6.1) occur. One of these processes (Process 1) is the solute expansion caused by interaction between the solute and solvent leading to the separation of solute into its components. Another process (Process 2) which occurs simultaneously with Process 1 is solvent expansion which leads to the creation of a room for the solute components to mix with the solvent. During these processes, the intermolecular forces of attraction between the solvent and solute are overcome. In the third process (Process 3), the expanded solute and solvent interact to form a solution. Figure 6.1 shows the three processes for the formation of solution.

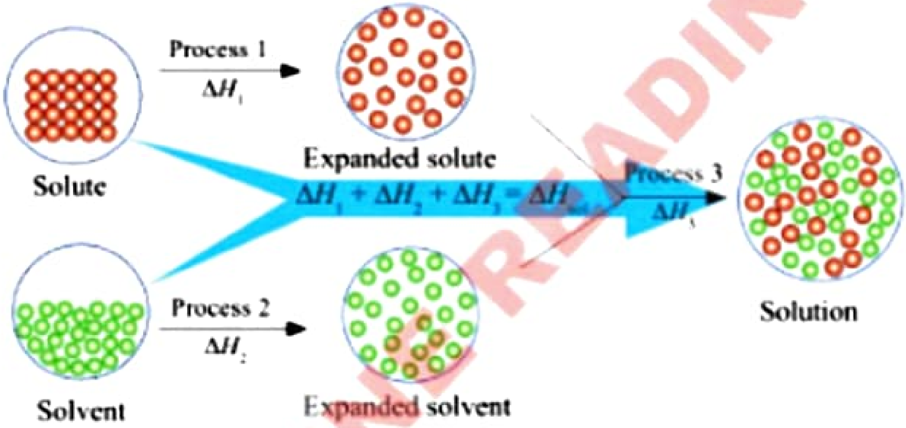


Figure 6.1: *The solution formation process*

Processes 1 and 2 in Figure 6.1 are energy consuming (endothermic) as energy must be supplied to break the intermolecular forces existing between individual solvent and solute molecules, whereas process 3 is the energy releasing process (exothermic). The overall change in energy (enthalpy or heat of solution, ΔH_{sol}) is the sum of enthalpy values:

$$\Delta H_{sol} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

ΔH_{sol} can have a positive or negative sign depending on the difference between the sum of energies in processes 1, 2 and 3. When the value of the enthalpy of solution is negative, energy is released, whereas when the value is positive, energy is absorbed. It is the value of ΔH_{sol} which determines whether a solute is soluble, sparingly soluble or insoluble. Intramolecular and intermolecular attractions within and between a solute and a solvent are other factors for the dissolution of a solute in a solvent. For a solute to dissolve in a solvent, the bond between the solute and the solvent must be stronger than the bond between individual solute or solvent molecules.

A given volume of a solvent has its expansion ability that enables the solute to interact with the solvent. Below the expansion capacity of a solvent, a solute dissolves in a solvent to allow mixing of solute and solvent molecules to form a solution. Above the expansion capacity, the solvent becomes saturated such that it dissolves no more solute.

The extent to which a solute can dissolve in a given amount of solvent is known as *solubility*. Solubility of a solute is expressed as the maximum mass in grams of a solute which can dissolve in 100 g of the solvent to form a saturated solution. It is also expressed as the maximum amount in moles of solute which can dissolve in one kilogram of a solvent to make a saturated solution.

In chemistry, solubility is a qualitative property of substances which is used to classify substances as soluble or insoluble. However, "soluble" or "insoluble" are relative terms as they depend on the conditions to which a chemical substance is subjected. No chemical substance is unconditionally soluble or insoluble. For example, when 50 g of magnesium carbonate ($MgCO_3$) are added to 100 g of water at room temperature, only 0.06 g of the salt dissolves. Since most of $MgCO_3$ remain unchanged, it is said to be insoluble in water. Another example is dissolution of 50 g of hydrated magnesium sulfate ($MgSO_4{\cdot}7H_2O$) in 100 g of water at room temperature. Under these conditions, only 13.6 g of the salt remain unchanged. Since 36.4 g dissolve, $MgSO_4{\cdot}7H_2O$ is regarded as soluble in water. Salts which are considered to be completely insoluble in water are actually not. For example, lead(II) carbonate is regarded as highly insoluble in water but experiments show that 0.000017 g of the salt dissolves in 100 g of water at room temperature. Therefore, the solubility of ionic solid may be considered to be an equilibrium process between solids and ions in solution and is affected by a number of factors. Thus, the most correct definition of *solubility* of a chemical substance is a maximum mass in grams or number of moles of that substance which can dissolve in a known mass of a solvent at a given temperature and pressure.

6.6.1 Factors affecting solubility

Solubility of a solute in any given solvent is affected by several factors such as pressure, nature of solute and solvent, and temperature. Others are purity of solvent (presence of common ions), pH of the solution, and complex ion formation.

(a) *The effects of pressure*

Pressure affects the solubility of gases in liquid solvent but not of dissolved solids. When pressure is applied to a gas that is above the surface of a solvent, the gas will dissolve in the solvent and occupy some of the spaces between the particles of the solvent. When the pressure is decreased, the solubility of the gas is also decreased. This can be demonstrated by opening a bottle of cocacola or any carbonated beverage. The pressure of the gas is lowered when the stopper is removed and the dissolved gas immediately starts leaving the solution as effervescence (fizzing). The quantitative relationship between gas pressure and solubility is expressed by the *Henry's Law* which states that the solubility of a gas in aqueous solution is directly proportional to the partial pressure of the gas above the solution, *i.e.* $C = kP_{gas}$, where C is the gas solubility (mol dm^{-3}), k is Henry's gas constant, and P is the partial pressure of the gas above the gas soulution.

(b) *Nature of solute and solvent*

The amount of the solute in solid form which dissolves in a given amount of a solvent depends on the type or nature of solute and solvent. Solubility is favoured when the solute and solvent have similar properties, i.e., "*like dissolves like*". Thus, polar solvents dissolve polar solutes and non-polar solvents dissolve non-polar solutes. For example, fat-soluble vitamins (A, D, E, and K) cannot dissolve in water and water-soluble vitamin B and C cannot dissolve in fat. This explains why people are advised to frequently take fruits containing vitamin B and C because the body can not store them.

(c) *The effect of temperature*

When solids dissolve in a solvent, a change in their physical state takes place. The process starts by breaking the bonds holding ions or molecules together. This is an *endothermic* process. The separated particles (ions or molecules) are then hydrated to form a solute-solvent bond; the process is *exothermic*. If the heat given off during hydration (dissolving) is greater than the heat required to break the solid apart into its constituent particles, the net reaction for dissolving the solid is exothermic. Hence, solubility is favoured by a decrease in temperature. A good example of a substance whose solubility decreases with an increase in temperature is Ce_2SO_4. Similarly, if the heat given off during dissolution (hydration) is less than the heat required to break apart solid particles, the net dissolving process is endothermic. Hence, the solubility of the solute is favoured by the increase in temperature. This is the most common situation. However, the solubility of gases decreases with the increase in temperature. The higher kinetic energy in gases as the result of increased temperatures causes more motion of molecules which breaks intermolecular bonds and sets them free to escape from the solution.

6.6.2 Equilibrium of sparingly soluble ionic compounds

Sparingly soluble substances have extremely small amounts of ions present in the saturated solution. A solution containing a maximum amount of solute at any fixed temperature and pressure is called a *saturated solution*. A solution is said to be saturated if no more of the solute can dissolve in a solvent. Therefore, a saturated solution cannot dissolve any more solute. Upon adding a small quantity of the solute to a saturated solution, dissolution does not take place and the solute added settles down. When a saturated solution is in contact with the solid solute, there exists a dynamic equilibrium between the solid and the solution phases.

$$\text{Solid substance} \rightleftharpoons \text{Aqueous solution of the substance}$$

Suppose that this equilibrium represents a sparingly soluble ionic compound A_xB_y which dissolves in water in accordance with the following chemical equation:

$$A_xB_y(s) \rightleftharpoons xA^{y+}(aq) + yB^{x-}(aq)$$

At equilibrium, the rate of formation of A^{y+} and B^{x-} is equal to the rate of precipitation of A_xB_y. Assuming that this equilibrium system obeys the law of mass action, the equilibrium constant for the above chemical reaction can be expressed as

$$K_c = \frac{[A^{y+}]^x[B^{x-}]^y}{[A_xB_y]} \tag{6.43}$$

Since A_xB_y is slightly soluble in water, $[A_xB_y]$ does not change significantly and can therefore be considered to remain constant. Thus, $K_c[A_xB_y]$ gives a new constant K_{sp} and Equation 6.43 can be re-written as

$$K_{sp} = [A^{y+}]^x[B^{x-}]^y \tag{6.44}$$

The term K_{sp} in Equation 6.44 is called the solubility product or solubility constant. Generally, *solubility product* (K_{sp}) can be defined as the product of the molar concentration of the ions in their saturated solution each raised to the power equal to the stoichiometric coefficient in the balanced equilibrium equation.

The value of K_{sp} indicates the solubility of an ionic compound in a solvent. The smaller the K_{sp} value, the less soluble the compound is in that solvent and vice versa. However, in using K_{sp} values to compare solubility, you should choose compounds that have similar formula, such as AgCl and ZnS or CaF_2 and $Fe(OH)_2$. Depending on the values of x and y in the ionic compounds, K_{sp} values have different expressions for different ionic compounds.

For the salts of the type AB, that is when $x = y$,

$$K_{sp} = [A^+][B^-] \text{ or } K_{sp} = [A^{2+}][B^{2-}] \qquad (6.45)$$

For a salt of the type AB_y, that is when $x = 1$ and y is any whole number greater than 1,

$$K_{sp} = [A^{y+}][B^-]^y, \text{ where } y = 2, 3, 4, \ldots \qquad (6.46)$$

For salt of the type A_xB, that is $y = 1$ and x is any whole number greater than 1,

$$K_{sp} = [A^+]^x[B^{x-}], \text{ where } x = 2, 3, 4, \ldots \qquad (6.47)$$

The solubility product is a special form of an equilibrium constant. It varies with changes in temperature. Thus, the temperature at which the solubility product is measured must always be indicated. The K_{sp} is not affected by any other factor such as pressure and concentration.

To assign units for the K_{sp} value of any sparingly soluble electrolyte, you need to know the determining factors upon which the units of K_{sp} depend. This can be done by considering the equilibrium which is established in a saturated solution of a substance of a general formula A_xB_y.

It can be deduced that the units of K_{sp} depend on the units of the concentrations of A and B and the coefficients x and y. Since the concentration of the salt and its ions in the saturated solution are usually expressed in mol dm^{-3}, then K_{sp} will have the units of $(\text{mol dm}^{-3})^{x+y}$. This means that the units of solubility products of different electrolytes will differ depending on the solubility product expression.

For example, the dissolution of $BaSO_4$ is represented by the equation:

$$BaSO_4(s) \rightleftharpoons Ba^{2-}(aq) + SO_4^{2-}(aq)$$

The K_{sp} expression for this reaction is

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

The concentration of each ion has the unit of mol dm^{-3}; so, the units for the solubility product will be

$$(\text{mol dm}^{-3})^2 = \text{mol}^2\,\text{dm}^{-6}.$$

Similarly, the dissolution of $Ca_3(PO_4)_2$ is represented by the equation:

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

From this chemical equation, the solubility product for $Ca_3(PO_4)_2$ has the following form:

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$$

The concentration of each ion has the units of mol dm^{-3}; thus, the units for the solubility product will be:

$$(\text{mol dm}^{-3})^5 = \text{mol}^5\ \text{dm}^{-15}.$$

Example 6.13

The molar solubility of the slightly soluble ionic compound A_2B is 5.0×10^{-5} mol dm^{-3} at 298 K. Use this information to calculate the K_{sp} of A_2B.

Solution

A_2B dissolves to form a saturated solution as per the chemical equation:

$$A_2B(s) \rightleftharpoons 2A^+(aq) + B^{2-}(aq)$$

From the stoichiometry, the concentration of A_2B dissolved is equal to half the concentrations of A^+ and is the same as the concentration of B^{2-}. At equilibrium, the solution contains the following:

$$[A^+] = 2 \times 5 \times 10^{-5}\ \text{mol dm}^{-3} = 1.0 \times 10^{-4}\ \text{mol dm}^{-3}$$

$$[B^{2-}] = 5 \times 10^{-5}\ \text{mol dm}^{-3}$$

But, K_{sp} for the chemical reaction is given by the equation:

$$K_{sp} = [A^+]^2[B^{2-}] = (1.0 \times 10^{-4}\ \text{mol dm}^{-3})^2 \times 5 \times 10^{-5}\ \text{mol dm}^{-3}$$

$$= 5.0 \times 10^{-13}\ \text{mol}^3\ \text{dm}^{-9}$$

The solubility product of A_2B at 298 K is 5.0×10^{-13} mol^3 dm^{-9}.

Solubility and solubility product are interdependent quantities. Their quantitative relationship can be used to calculate the amount of solute the solvent can dissolve. It can also be used to calculate the amount of the solute that precipitates out from the saturated solution. For example, for the dissolution of AgCl, the solubility equilibrium is

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

The K_{sp} expression is formulated for ionic species appearing in the equation for the solubility equilibrium. This equation is written for one mole of the slightly soluble solute. The coefficients for the ions in solution are whatever is needed to balance the equation. The coefficients then establish the powers to which the ion concentrations are raised in the K_{sp} expression.

In a saturated solution of AgCl, the $[Ag^+] = [Cl^-] = x$ mol dm^{-3}.

Thus,

$$K_{sp} = [Ag^+][Cl^-] = x^2, \text{ which means that } x = \sqrt{K_{sp}}$$

Therefore, the solubility of AgCl in water can be calculated by using its solubility product. Generally, solubility product (K_{sp}) is a temperature dependent quantity. Each weak electrolyte has its own value of K_{sp} at a given temperature.

Example 6.14

Calculate the molar solubility of AgBr that will dissolve in 1dm^3 of pure water given that the K_{sp} of AgBr is 5.4×10^{-13} mol^2 dm^{-6} at 298 K.

Solution

The equation for dissolution of AgBr in water is:

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$$

The expression for solubility product is given by the equation:

$$K_{sp} = [Ag^+][Br^-]$$

From the solubility equilibrium equation, $[Ag^+] = [Br^-] = x$, thus $K_{sp} = x^2$, and

$$x = \sqrt{K_{sp}} = \sqrt{5.4 \times 10^{-13}\ \text{mol}^2\ \text{dm}^{-6}} = 7.3 \times 10^{-7}\ \text{mol dm}^{-3}$$

Therefore, the molar solubility of AgBr in pure water at 298 K is 7.3×10^{-7} mol dm^{-3}.

Example 6.15

At 298 K, the solubility of $BaCO_3$ in water is 9.0×10^{-5} mol dm^{-3}. Calculate its solubility product.

Solution

The equation for the dissolution of $BaCO_3$ is as follows:

$$BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$$

Thus, $[Ba^{2+}] = [CO_3^{2-}]$.

The expression for solubility product of $BaCO_3$ is presented by the following equation:

$$K_{sp} = [Ba^{2+}][CO_3^{2-}]$$

Since the solubility of $BaCO_3$ is 9.0×10^{-5} mol dm^{-3}, then

$$K_{sp} = \left(9.0 \times 10^{-5}\ \text{mol dm}^{-3}\right)\left(9.0 \times 10^{-5}\ \text{mol dm}^{-3}\right) = 8.1 \times 10^{-9}\ \text{mol}^2\ \text{dm}^{-6}$$

Therefore, the solubility product of $BaCO_3$ is 8.1×10^{-9} mol^2 dm^{-6}.

Example 6.16

A saturated solution of CaF_2 was found to contain 0.0168 g dm^{-3} of CaF_2 at 298 K. Calculate K_{sp} for CaF_2.

Solution

The equation for the dissolution of CaF_2 is presented as

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

The K_{sp} expression for this reaction has the form:

$$K_{sp} = [Ca^{2+}][F^-]^2$$

To calculate K_{sp}, you need to have the molar concentrations of the Ca^{2+} and F^-. Since the molar mass of CaF_2 is 78 g mol^{-1}, the concentration of CaF_2 is given by

$$C = \frac{0.0168\ \text{g dm}^{-3}}{78\ \text{g mol}^{-1}} = 2.15 \times 10^{-4}\ \text{mol dm}^{-3}$$

The equilibrium equation for the dissolution of CaF_2 shows that:

$[Ca^{2+}] = 2.15 \times 10^{-4}$ mol dm^{-3} and

$[F^-] = 2[CaF_2] = 2 \times 2.15 \times 10^{-4}$ mol dm^{-3} $= 4.30 \times 10^{-4}$ mol dm^{-3}

Substituting these values into the expression for K_{sp} gives

$$K_{sp} = (2.15 \times 10^{-4}\ \text{mol dm}^{-3})(4.30 \times 10^{-4}\ \text{mol dm}^{-3})^2 = 4.0 \times 10^{-11}\ \text{mol}^3\ \text{dm}^{-9}$$

Therefore, the K_{sp} of CaF_2 at 298 K is 4.0×10^{-11} mol^3 dm^{-9}.

6.6.3 Factors affecting solubility products

Solubility product is affected by common ions, pH and complex formation.

The effect of common ion

If the solvent in which the solute has to be dissolved contains one of the ions produced by the solute upon dissolution, the amount of the solute that can be dissolved will be less than the amount of the solute dissolved by a pure solvent. *The common ion effect* is the decrease in solubility of a substance due to the presence of a common ion.

If a salt is added to the solvent in which one of its ion is already present, the position of equilibrium shifts to the direction which tends to offset the increase in the concentration of that ion (Le Châtelier's Principle).

Example 6.17

The solubility product of $BaSO_4$ is 1.5×10^{-9} mol² dm⁻⁶. Calculate its solubility in:

(i) Pure water

(ii) 0.1 mol dm^{-3} $BaCl_2$

(iii) Comment on the solubilities of the salt in (i) and (ii)

Solution

The dissolution of $BaSO_4$ is given by the following chemical equation:

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

Therefore, the expression for K_{sp} is:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

(i) Suppose x is the solubility of $BaSO_4$ in mol dm^{-3}. Since $[Ba^{2+}] = [SO_4^{2-}]$, then, K_{sp} expression takes the form:

$$K_{sp} = (x)(x) = x^2 \text{ and thus } x = \sqrt{K_{sp}}$$

$$= \sqrt{1.5 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}} = 3.9 \times 10^{-5} \text{ mol dm}^{-3}$$

Therefore, the solubility of $BaSO_4$ in pure water at 298 K is 3.9×10^{-5} mol dm^{-3}.

(ii) When $BaSO_4$ is dissolved in 0.1 mol dm^{-3} solution of $BaCl_2$ and if y moles of the salt had dissolved at equilibrium,

$$\mathrm{BaSO_4}(s) \rightleftharpoons \underset{\underset{\nwarrow \text{From } \mathrm{BaCl_2}}{y\,+\,0.1}}{\mathrm{Ba^{2+}}(aq)} + \underset{y}{\mathrm{SO_4^{2-}}\ (aq)}$$

Since K_{sp} is very small, y is also very small, then $y + 0.1 \approx 0.1$

Therefore $K_{sp} = [\mathrm{Ba^{2+}}] = 0.1$ and $[\mathrm{SO_4^{2}}] = \mathrm{y}$

$K_{sp} = [\mathrm{Ba^{2+}}][\mathrm{SO_4^{2-}}] = 0.1\ \mathrm{mol\ dm^{-3}} \times y$

Thus, $1.5 \times 10^{-9}\ \mathrm{mol^2\ dm^{-6}} = 0.1\ y\ \mathrm{mol\ dm^{-3}}$

and $y = 1.5 \times 10^{-8}\ \mathrm{mol\ dm^{-3}}$

Hence, the solubility of $\mathrm{BaSO_4}$ in 0.1 M $\mathrm{BaCl_2}$ solution at 298 K is $1.5 \times 10^{-8}\ \mathrm{mol\ dm^{-3}}$.

(iii) Comparing the solubility of $\mathrm{BaSO_4}$ in pure water with that in 0.1 mol $\mathrm{dm^{-3}}$ $\mathrm{BaCl_2}$ solution, it can be seen that the solubility of $\mathrm{BaSO_4}$ has decreased almost 1000 times compared to the solubility in pure water. This decrease in the solubility is caused by the presence of $\mathrm{Ba^{2+}}$ from $\mathrm{BaCl_2}$ which drives the equilibrium to the left, lowering the solubility of $\mathrm{BaSO_4}$.

The effect of pH

If a compound contains anions of a weak acid, the addition of $\mathrm{H_3O^+}$ (from a strong acid) increases its solubility because it shifts the equilibrium to the right hand side of the equation. Consider the reaction represented by the chemical equation:

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

When $\mathrm{H_3O^+}$ is added to the system at equilibrium (pH is lowered), it reacts with a $\mathrm{CO_3^{2-}}$ as shown in the following chemical equation:

$$\mathrm{H_3O^+}\ (aq) + \mathrm{CO_3^{2-}}(aq) \rightleftharpoons \mathrm{HCO_3^-}(aq) + \mathrm{H_2O}(l)$$

This reaction lowers the concentration of $\mathrm{CO_3^{2-}}$ and thus causes the equilibrium to shift to the right, increasing the solubility of $\mathrm{CaCO_3}$.

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

Complex formation

Some sparingly soluble substances are more soluble in the presence of some ions or molecules in the solution due to complex formation. For example:

(i) Lead(II) chloride is sparingly soluble in pure water but soluble in concentrated hydrochloric acid due to the formation of tetrachloroplumbate(II) ion complex.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq) + \underbrace{2Cl^-(aq)}_{\text{from conc. HCl}} \longrightarrow [PbCl_4]^{2-}(aq)$$

The removal of Pb^{2+} by complex formation shifts the equilibrium to the right, causing $PbCl_2$ to dissolve more.

(ii) Copper(II) hydroxide is sparingly soluble in pure water but readily soluble in the presence of concentrated ammonia solution due to the formation of tetraammoniacopper(II) ion complex.

$$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq) + 4NH_3(aq) \longrightarrow [Cu(NH_3)_4]^{2+}(aq)$$

The removal of Cu^{2+} causes the equilibrium to shift to the right. Consequently, more $Cu(OH)_2$ is dissolved.

6.6.4 Ionic products

In Section 6.7.2, the solubility product (K_{sp}) was derived and defined as the ionic product in their saturated solution, each raised to the power equal to the stoichiometric coefficient. In this case, the ions are in contact with the solid substance because the solution is saturated. If the solution is not saturated, the ionic product is not equal to K_{sp} but equal to another value, Q_{sp}.

For example, when a sparingly soluble salt AB dissolves in water, it dissociates according to the reaction:

$$AB(s) \rightleftharpoons A^+(aq) + B^-(aq)$$

At saturation point,

$$K_{sp} = [A^+][B^-] \qquad (6.48)$$

At any condition other than equilibrium, the expression has the form:

$$Q_{sp} = [A^+][B^-] \qquad (6.49)$$

The value of Q_{sp} is called *ionic product*. It is defined as the product of the concentration of the component ions of the sparingly soluble salts, each raised to its power of the stoichiometric coefficients of ions. It follows that if:

$Q_{sp} < K_{sp}$, the solution is unsaturated.

$Q_{sp} = K_{sp}$, the solution is saturated.

$Q_{sp} > K_{sp}$, the solution is supersaturated.

When $Q_{sp} > K_{sp}$, the salt AB will precipitate until the product of $[A^+]$ and $[B^-]$ is equal to the value of K_{sp} at that particular temperature.

Although ionic product and solubility product are similar because both are ionic products, they also differ because the concentrations of ions differ depeding on some conditions. Their differences are given in Table 6.5.

Table 6.5: *Differences between solubility and ionic products*

Solubility product (K_{sp})	Ionic product (Q_{sp})
▶ This is the product of the concentration of ions of sparingly soluble electrolyte, each raised to the power of their stoichiometric coefficients in the balanced chemical equation in a saturated solution.	▶ This is the product of the concentration of ions of sparingly soluble electrolyte, each raised to the power of their stoichiometric coefficients in the balanced chemical equation at any stage of solute dissolution.
▶ At constant temperature, its value is constant for a given electrolyte.	▶ The value keeps changing with concentration at constant temperature.

6.6.5 Prediction of precipitation of electrolytes

The knowledge of whether the solution is saturated, unsaturated or supersaturated is used to predict the precipitation of salts by comparing the values of K_{sp} and Q_{sp}. Suppose a dilute solution of barium chloride is mixed with a very dilute solution of sodium sulfate, how will you know whether precipitation of barium sulfate will occur or not? The solubility product expression for the dissolution reaction of the salt is:

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

Its K_{sp} is given by:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

At 298 K, K_{sp} of $BaSO_4$ is 1.5×10^{-9} mol^2 dm^{-6}. If the product of the concentrations of Ba^{2+} and SO_4^{2-} in the two solutions mixed together exceeds the solubility product, then precipitation occurs until the product of the concentrations has been reduced to the solubility product. If the product of the concentrations of the two species is less than the solubility product, precipitation does not occur. In this case, the equilibrium lies completely to the right. This can be expressed as: if $Q_{sp} > K_{sp}$, precipitation occurs until $Q_{sp} = K_{sp}$, but if $Q_{sp} < K_{sp}$, precipitation does not occur.

Example 6.18

Will the precipitate of silver iodide form if a solution containing 5.8×10^{-10} mol dm^{-3} silver nitrate is mixed with another solution containing 4.6×10^{-7} mol dm^{-3} of sodium iodide? The K_{sp} value for AgI at 298 K is 1.5×10^{-16} mol^2 dm^{-6}.

Solution

The reaction equation for dissolution of AgI is

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$$

Assuming that $AgNO_3$ and NaI dissociate completely as shown in the following equations:

$$AgNO_3(s) \longrightarrow Ag^+(aq) + NO_3^-(aq)$$

$$NaI(s) \longrightarrow Na^+(aq) + I^-(aq)$$

then, the number of moles of silver and iodide ions are equal to the number of moles of their corresponding salts. Therefore, the solutions contain 5.8×10^{-10} mol dm^{-3} of Ag^+ and 4.6×10^{-7} mol dm^{-3} of I^- ions. The expression for the ionic product of silver iodide is

$$Q_{sp} = [Ag^+][I^-]$$

Substituting the values of $[Ag^+]$ and $[I^-]$ into the Q_{sp} expression gives

$$Q_{sp} = 5.8 \times 10^{-10} \text{ mol dm}^{-3} \times 4.6 \times 10^{-7} \text{ mol dm}^{-3} = 2.7 \times 10^{-16} \text{ mol}^2 \text{ dm}^{-6}$$

To decide whether the precipitation of AgI will occur, the K_{sp} and Q_{sp} values should be compared. In this case, the ionic product ($Q_{sp} = 2.7 \times 10^{-16}$ mol^2 dm^{-6}) is greater than the solubility product ($K_{sp} = 1.5 \times 10^{-16}$ mol^2 dm^{-6}); therefore, the precipitation of AgI will occur.

It is important to note that the ability to predict precipitation of a salt using the knowledge of solubility product and ionic product often has a practical value. For example, in industrial and laboratory preparations, the concentrations of ions can be adjusted until the ionic product (Q_{sp}) exceeds the solubility product (K_{sp}) in order to obtain a given compound in the form of a precipitate. This technique is used in analytical chemistry to precipitate sulfides, hydroxides, and carbonates.

Precipitation of sulfides

Certain metals are precipitated as sulfides when hydrogen sulfide is bubbled through the solution. These include group II cations of the qualitative analysis such as Pb^{2+}, Cu^{2+}, Hg^{2+}, Cd^{2+}, Al^{3+} and Sn^{2+} and group IV cations of the qualitative analysis such as Co^{2+}, Ni^{2+}, Mn^{2+}, and Zn^{2+}. Group II sulfides include PbS, CuS and CdS which have very low solubility products. Therefore, they are precipitated even at low concentrations of sulfide ion. Group IV sulfides such as ZnS, MnS, NiS and CoS have relatively higher solubility products; hence, they are precipitated only at higher sulfide ion concentration. For a proper analysis, therefore, experimental conditions must be maintained for selective precipitation of the required metal cations present in the solution. For example, in order for a metal ion (M^{2+}) to be precipitated as a sulfide, the following condition must be fulfilled:

$$[M^{2+}][S^{2-}] > K_{sp}$$

Thus, if $[S^{2-}]$ is low, only those metals whose sulfides have low K_{sp} values will be precipitated. The concentration of S^{2-} ion in solution depends on pH of the solution. This is because hydrogen sulfide is a weak acid which ionises reversibly in aqueous solution as shown in the following reaction:

$$H_2S(g) + 2H_2O(l) \rightleftharpoons 2H_3O^+(aq) + S^{2-}(aq)$$

When an acid is added to the solution, this equilibrium shifts to the left. As a result, the concentration of sulfide ion is lowered. Therefore, group II cations will be selectively precipitated. When the solution is made alkaline, the equilibrium shifts to the right. As a result, the concentration of sulfide ions increases.

Precipitation of hydroxides

In aqueous alkaline condition, group III cations of the qualitative analysis (Fe^{3+}, Al^{3+} and Cr^{3+}) are identified by precipitating their metal hydroxides. To prevent the precipitation of hydroxides of group IV cations (Zn^{2+}, Mn^{2+}, Ni^{2+} and Mg^{2+}), the concentration of OH^- ions should be kept low. This is achieved by first adding sufficient amount of ammonium chloride (NH_4Cl) into the solution before precipitating metal hydroxides using ammonium hydroxide (NH_4OH). NH_4Cl furnishes NH_4^+, which suppresses the ionisation of NH_4OH due to common ion effect, thereby keeping the concentration of OH^- low.

$$NH_4Cl(s) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

$$NH_4OH(s) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

All other metal hydroxides like $Zn(OH)_2$, $Mn(OH)_2$, $Ni(OH)_2$ and $Mg(OH)_2$ have higher solubility products than group III metal hydroxides; hence, they are not precipitated at low OH^- concentration.

Precipitation of carbonates

Group V cations of the qualitative analysis (Ba^{2+}, Sr^{2+}, and Ca^{2+}) are precipitated as carbonates by adding ammonium carbonate ($(NH_4)_2CO_3$) in the presence of ammonium chloride (NH_4Cl) and ammonium hydroxide (NH_4OH). The presence of NH_4Cl suppresses the ionisation of NH_4OH due to common ion effect. This keeps the concentration of OH^- low; thus, it does not permit the precipitation of $Mg(OH)_2$. The NH_4^+ from NH_4Cl also suppress the ionisation of ammonium carbonate, keeping the concentration of CO_3^{2-} low to prevent the precipitation of $MgCO_3$. The concentration of CO_3^{2-}, therefore, is sufficient to cause the precipitation of the carbonates of Ba^{2+}, Sr^{2+}, and Ca^{2+}.

Exercise 6.5

1. Write the K_{sp} expression for dissolution of each of the following compounds:
   (a) Magnesium carbonate
   (b) Iron(II) hydroxide
   (c) Calcium phosphate

2. (a) Lead(II) sulfate ($PbSO_4$) is a key component in lead–acid car batteries. Its solubility in water at 25 °C is 4.25×10^{-3} g/100 cm³ solution. Calculate the K_{sp} of $PbSO_4$.
   (b) When lead(II) fluoride (PbF_2) is shaken with pure water at 25 °C, the solubility is found to be 0.64 g/dm³. Calculate the K_{sp} of PbF_2.

3. Calcium hydroxide (slaked lime) is a major component of mortar, plaster and cement. Solutions of $Ca(OH)_2$ are used in industry as cheap strong base. If the K_{sp} of $Ca(OH)_2$ is 6.5×10^{-6}, calculate the molar solubility of $Ca(OH)_2$ in:
   (a) water
   (b) 0.10 M $Ca(NO_3)_2$

4. Write balanced equations to explain whether addition of H_3O^+ from a strong acid affects the solubility of the following ionic compounds:
   (a) Lead(II) bromide
   (b) Copper(II) hydroxide
   (c) Iron(II) sulfide

5. A solution consists of 0.20 M $MgCl_2$ and 0.10 M $CuCl_2$. Calculate the $[OH^-]$ that would separate the metal ions as their hydroxides. K_{sp} of $Mg(OH)_2$ is 6.3×10^{-10} and K_{sp} of $Cu(OH)_2$ is 2.2×10^{-20}.

6. The solubility of KCl is 3.7 M at 20 °C. Two beakers contain 100 cm^3 of saturated KCl solution. 100 cm^3 of 6.0 M HCl and 12 M HCl are added to the first and second beaker, respectively.
   (a) Calculate the ionic product constant of KCl at 20 °C.
   (b) What mass (if any) of KCl will precipitate from each beaker?

Revision exercise 6

1. Identify an Arrhenius acid and base from the following substances. Give reason(s) for your answer.
   (a) H_3PO_4
   (b) $Mg(OH)_2$
   (c) HBr
   (c) $Fe(OH)_3$

2. Water acts as a Brønsted-Lowry base when it reacts with HNO_3. Write the chemical equation for the reaction and identify the conjugate acid-base pair.

3. Consider the reaction between MnO_4^- and $C_2O_4^{2-}$ in acidic medium which is represented by the chemical reaction:

$$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

   Identify the Lewis acid and the Lewis base in this reaction. Give a reason for your answer.

4. A 655 cm^3 solution of acid HX was made by dissolving 0.250 mol of the acid sample. If the pH of the resulting solution is 3.44, what is the value of dissociation constant (K_a) of acid HX at 298 **K**?

5. A buffer solution of pH 9.0 was made by mixing a certain mass of ammonium chloride with 0.5 dm^3 solution of 1.0 mol dm^{-3} ammonia. Assuming that there is no change in volume upon mixing, calculate the mass of ammonium chloride used to make this buffer solution given that the pK_b of ammonia is 4.75.

6. The ionisation constants of HI, HCOOH, and HCN at 300 K are **5.4 × 10^{-4} mol dm^{-3}**, 1.9 × 10^{-4} mol dm^{-3}, and 5.2 × 10^{-4} mol dm^{-3}, respectively. Calculate the ionisation constants of their corresponding conjugate-base given that K_w at 300 K is 1.0 × 10^{-14} mol dm^{-3}.

7. A buffer solution was made by mixing equal volumes of 0.5 mol dm^{-3} H_2CO_3 and 0.64 mol dm^{-3} K_2CO_3 solutions. What is the pH of the resulting

buffer solution given that the dissociation constant of carbonic acid is 4.7×10^{-11} mol dm^{-3}?

8. Nitrous acid has a K_a of 4.2×10^{-4} mol dm^{-3}. What is the pH of a buffer solution containing 0.2 mol dm^{-3} HNO_2 and 0.2 mol dm^{-3} NO_2^-?

9. (a) When a salt of weak acid and weak base dissolves in water, both the cation and anion of the salt undergo hydrolysis to furnish H^+ and OH^-. However, the resulting solution is not neutral. What determines the pH of the resulting solution?

   (b) A 0.1 mol dm^{-3} solution of acetic acid was titrated with 0.1 mol dm^{-3} solution of sodium hydroxide. Calculate the pH of the solution at the end point given that the dissociation constant of acetic acid (K_a) is 1.0×10^{-5} mol dm^{-3}.

10. (a) Account for the observation that a solution of sodium chloride is neutral while that of sodium fluoride is basic.

    (b) Hydrofluoric acid (HF) is a weak acid with dissociation constant (K_a) of 7.2×10^{-4} mol^2 dm^{-6} at 298 K. If a salt of NaF was dissolved in distilled water to make a 0.3 mol dm^{-3} solution, calculate the pH of the solution, degree of hydrolysis (h) and hydrolysis constant (K_h) of NaF at 298 K.

11. Show whether the following substances are acidic, basic, or neutral when mixed with water: NH_3, CH_3COOLi, and H_3PO_4.

12. The ionisation constant of chloroacetic acid ($ClCH_2COOH$) is 1.5×10^{-4} mol dm^{-3} at 350 K. What will be the pH of 0.2 mol dm^{-3} acid and its 0.5 mol dm^{-3} sodium salt solution?

13. For each of the salts: $(NH_4)_2SO_3$, $Al(NO_2)_3$, and $FePO_4$.
    (a) Write the ionisation equation.
    (b) Write the K_a expression for the cation and K_b expression for the anions.
    (c) State whether each of the salts acts as an acid or a base.

14. Write the K_{sp} expressions with their units for iron(III) sulfide, lead(II) chloride, zinc hydroxide, calcium phosphate and magnesium oxalate.

15. Explain each of the following:
    (a) The solubility of silver chloride in water decreases when dilute hydrochloric acid is added but increases when concentrated hydrochloric acid is added.
    (b) Aqueous ammonium carbonate can precipitate some metals as metal carbonates but the presence of ammonium chloride in the solution often prevents the precipitation.

16. At 298 K, the solubility product (K_{sp}) of calcium carbonate is 4.8×10^{-9} mol^2 dm^{-6}. Calculate its molar solubility in water.

17. The solubility of PbI_2 in water is 0.761 g dm^{-3} at 298 K. Calculate its solubility product given that the molar mass of PbI_2 is 461 g mol^{-1}.

18. The solubility product of barium sulfate in water is 1.8×10^{-10} mol^2 dm^{-6} at 298 K. Calculate its:
    (a) solubility in mol dm^{-3}.
    (b) molar solubility in a solution containing 0.1 mol dm^{-3} Na_2SO_4.

19. If equal volumes of 0.025 mol dm^{-3} of barium nitrate and 0.010 mol dm^{-3} of sodium fluoride are mixed together, will BaF_2 be precipitated? The K_{sp} of BaF_2 is 1.7×10^{-6} mol^3 dm^{-9} at 298 K.

20. The analysis of a solution of PbI_2 gave $[Pb^{2+}] = 0.012$ mol dm^{-3} and $[I^-] = 0.24$ mol dm^{-3}. If at 298 K the K_{sp} value for PbI_2 is 1.39×10^{-8} mol^3 dm^{-9}, show whether the solution is saturated, supersaturated, or unsaturated.

21. At 298 K, the solubility of silver chloride in pure water is 0.00188 g dm^{-3}. What is its K_{sp} given that the molar mass of AgCl is 143.5 g mol^{-1}?

22. What is the molar solubility of Ag_2CrO_4 in water if the value of its solubility product is 1.1×10^{-12} mol^3 dm^{-9} and the molar mass of Ag_2CrO_4 is 332 g mol^{-1}?

23. (a) Calculate the molar solubility of the salt (MF_2) in pure water ignoring the basic properties of F^- given that for MF_2, K_{sp} is 7.9×10^{-10} mol^3 dm^{-9}.
    (b) Calculate the molar solubility of MF_2 in a solution buffered at pH = 2.00 given that the K_a for HF is 7.2×10^{-4} mol^2 dm^{-6}.

24. Calcium oxalate has a solubility of 4.47×10^{-5} mol dm^{-3} in pure water at 298 K. However, it is more soluble in acidified water. How much more soluble is it in 0.1 mol dm^{-3} H^{+} ion solution than in pure water? Ignore the basic properties of CrO_4^{2-} in pure water at 298 K.

25. The solubility product of $Mg(OH)_2$ is 1.2×10^{-11} mol^3 dm^{-9}. Calculate the minimum concentration of OH^- ions which must be added to decrease the concentration of magnesium ion in a solution of $Mg(NO_3)_2$ to less than 1.0×10^{-10} mol dm^{-3}.

26. Justify the statement that although silver chloride has a larger K_{sp} value of 1.6×10^{-10} mol^2 dm^{-6} than silver carbonate with a K_{sp} value of 8.1×10^{-12} mol^3 dm^{-12} , the latter has higher molar solubility than the former.

Chapter Seven

Chemical kinetics

Introduction

Chemical kinetics describes the dynamics and characteristics of a chemical reaction. It helps to control the reaction conditions to obtain products quickly and economically. In this chapter, you will learn about the rate of chemical reactions, rate laws, activation energy, catalysis, reaction mechanisms and the applications of chemical kinetics in real life situations. The competencies developed will enable you to adjust reaction conditions to accelerate desired reactions or slow down undesired ones in both industrial and real-life contexts.

Think

Significance of reaction kinetics in controlling various industrial process

7.1 The rate of chemical reactions

Task 7.1

Use online simulations or any other interactive resources to study the factors which affect the rate of chemical reaction.

Any chemical reaction can be presented as

$$\text{Reactants} \longrightarrow \text{Products}$$

It can be deduced from this equation that in the course of a reaction, reactants are consumed while products are formed. Therefore, the progress of a reaction can be monitored by either measuring the decrease in concentration of the reactants or the increase in concentration of the products. For a simple reaction in which **A** molecules are converted to **B** molecules, the following general equation may be used:

$$\mathrm{A} \longrightarrow \mathrm{B}$$

Initially, only **A** molecules are present. As time passes, the number of molecules of **A** decreases while the number of molecules of **B** increases. Graphically, this reaction can be represented by Figure 7.1.

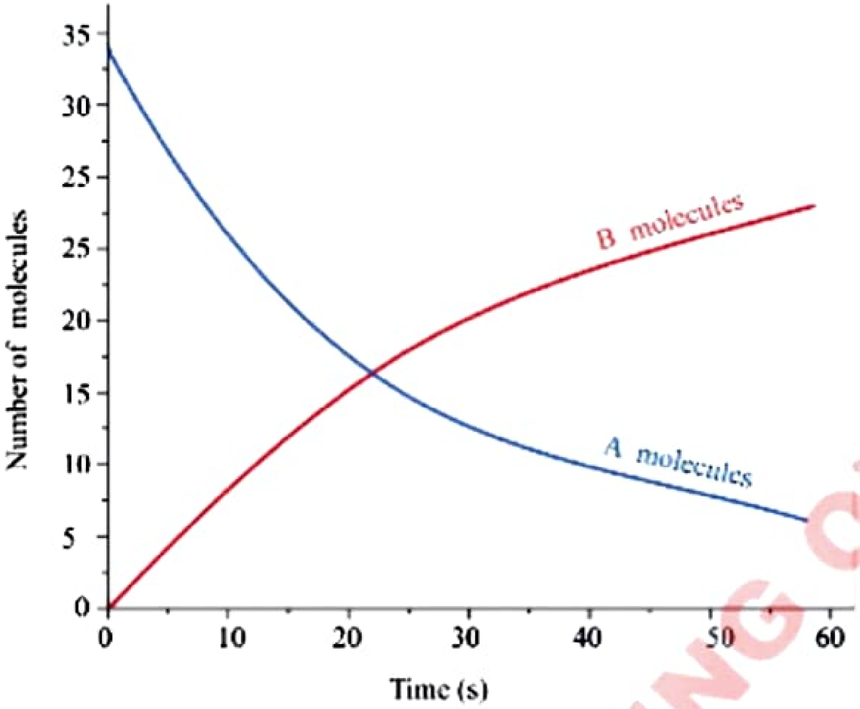


Figure 7.1: *Change in number of molecules of A and B with time*

Practically, the progress of a chemical reaction can be followed by measuring any property which is related to the concentration of the reactant(s) or product(s) at a given time interval, for example, measurement of pressure and volume and change in mass of the system for gaseous reactions. This can also be done by conductivity or pH measurements for reactions involving ions, absorbance measurements for coloured compounds and optical measurements for chiral compounds. In any chemical reaction, the observed change in the concentration of the reactants or products per unit time is referred to as *the rate of the reaction*. Thus, for a simple reaction $A \longrightarrow B$, the rate can be expressed as

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} \text{ or } \text{Rate} = \frac{\Delta[B]}{\Delta t} \qquad (7.1)$$

where Δ[A] and Δ[B] are changes in concentration (molarity) of A and B over a change in time (Δ*t*). Since the concentration of A decreases and the concentration of B increases during the time interval (Δ*t*), A is consumed as B is formed. Therefore, a negative sign in the rate expression stands for the consumption of the reactants while the rate expression in terms of the formation of products is positive. However, in practice, reactants are consumed at the same rate as the products are formed. Therefore,

$$-\frac{\Delta[\text{reactants}]}{\Delta\text{time}} = \frac{\Delta[\text{products}]}{\Delta\text{time}}$$

For more complex reactions, rate expressions have different forms. Consider the reaction represented by the equation 2A →B. The rate at which A decomposes is twice the rate of formation of B. The rate expression is written as

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t} \qquad (7.2)$$

Generally, for a hypothetical reaction,

$$aA + bB \longrightarrow cC + dD$$

the rate is given by:

$$\text{Rate} = -\frac{1}{a}\frac{[A]}{\Delta t} = -\frac{1}{b}\frac{[B]}{\Delta t} = \frac{1}{c}\frac{[C]}{\Delta t} = \frac{1}{d}\frac{[D]}{\Delta t} \qquad (7.3)$$

Example 7.1

Write the rate expression for the following reactions in terms of the disappearance of the reactants and the formation of the products.

(a) $NO_2(g) + CO(g) \rightleftharpoons CO_2(g) + NO(g)$

(b) $S_2O_8^{2-}(aq) + 3I^-(aq) \rightleftharpoons 2SO_4^{2-}(aq) + I_3^-(aq)$

Solution

(a) All stoichiometric coefficients in the equation have the value of 1. Therefore, the rate can be expressed as

$$\text{Rate} = -\frac{\Delta[NO_2]}{\Delta t} = -\frac{\Delta[CO]}{\Delta t} = \frac{\Delta[NO]}{\Delta t} = \frac{\Delta[CO_2]}{\Delta t}$$

(b) Stoichiometric coefficients in equation (b) are 1, 3, 2 and 1 for reactants and products, respectively. Therefore, the rate expression can be written as:

$$\text{Rate} = -\frac{\Delta[S_2O_8^{2-}]}{\Delta t} = -\frac{1}{3}\frac{\Delta[I^-]}{\Delta t} = \frac{1}{2}\frac{\Delta[SO_4^{2-}]}{\Delta t} = \frac{\Delta[I_3^-]}{\Delta t}$$

Example 7.2

For the reaction,

$$4PH_3(g) \longrightarrow P_4(g) + 6H_2(g)$$

at a particular moment, hydrogen gas is being formed at the rate of 0.06 mol dm^{-3} s^{-1}.

(a) At what rate is P_4 being formed?

(b) At what rate is PH_3 being decomposed?

Solution

(a) Considering P_4 and H_2 in the reaction equation in which the coefficients are 1 and 6, respectively, the rate expression has the form:

$$\text{Rate} = \frac{1}{6}\frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[P_4]}{\Delta t}$$

Substituting the value of the rate of formation of hydrogen gas in the rate expression results into:

$$\frac{1}{6}\times 0.06 = \frac{\Delta[P_4]}{\Delta t} = 0.01\ \text{mol dm}^{-3}\text{s}^{-1}$$

P_4 is being formed at the rate of 0.01 mol dm^{-3} s^{-1}.

(b) Considering PH_3 and H_2 in the reaction equation, the corresponding coefficients are 4 and 6, respectively. Substituting these values into the rate expression leads to:

$$\text{Rate} = -\frac{1}{4}\frac{\Delta[PH_3]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2]}{\Delta t}$$

$$\frac{\Delta[PH_3]}{\Delta t} = -\frac{4}{6}\frac{\Delta[H_2]}{\Delta t}$$

$$\frac{\Delta[PH_3]}{\Delta t} = -\frac{4}{6}\times 0.06\ \text{mol dm}^{-3}\ \text{s}^{-1} = -0.04\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

Therefore, PH_3 is reacting at the rate of –0.04 mol dm^{-3} s^{-1}. The negative sign indicates that the concentration of PH_3 is decreasing with time.

7.2 Rate laws

When chemical reactions are considered irreversible, the rate at which they proceed to give products depends on the concentrations of the reactants. The increase in the concentration of reactants increases the rate of the reactions and vice versa. However, for reversible chemical reactions, enough products accumulate after a period of time so that the reverse reaction becomes important. Dealing with the rate of reversible reactions is always challenging. To avoid the complications, this book focuses on the rate of chemical reactions under conditions where the reverse reaction makes negligible contribution.

Consider conditions where the reverse reaction makes no significant contribution. The relationship that exists between the rate of the reaction and the concentration of the reactants can be expressed mathematically. For example, the reaction represented by the equation

$$\mathrm{aA} + \mathrm{bB} \rightleftharpoons \mathrm{cC} + \mathrm{dD}$$

the rate of reaction is expressed as

$$\text{Rate} = k[\mathrm{A}]^n[\mathrm{B}]^m \tag{7.4}$$

Equation 7.4 shows that the reaction rate is directly proportional to the initial concentration of the reactants raised to factors n and m, where n and m can be zero, small integers or simple fractions. Equation 7.4 is called a rate law. Thus, the *rate law* is a mathematical expression which shows how the rate of a chemical reaction depends on the concentration of the reactants. The proportionality constant (k) is called the *rate constant*. The rate law can be used to calculate the reaction rate if the concentration of the reactants and values of n, m, and k are known. The rate law of a given reaction can be obtained experimentally but not from a balanced chemical equation. This is because the values of n and m are not obtained from a chemical equation; although, sometimes they can be equal to the values of the stoichiometric coefficients.

Example 7.3

NO_2 and CO were allowed to react at 488 K and the following data were collected:

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g).$$

Experiment	$[NO_2]_0$ mol dm^{-3} s^{-1}	$[CO]_0$ mol dm^{-3} s^{-1}	Initial rate mol dm^{-3} s^{-1}
1	0.263	0.826	1.44×10^{-5}
2	0.263	0.413	1.44×10^{-5}
3	0.526	0.413	5.76×10^{-5}

Determine the rate law for the reaction.

Solution

Between experiments (1) and (2), the $[NO_2]_o$ is kept constant and that of $[CO]_o$ is halved but there is no effect on the rate of the chemical reaction implying that the rate is independent on $[CO]_o$. Between experiments (2) and (3), $[CO]_o$ is kept constant and $[NO_2]_o$ is doubled. This causes the rate of the chemical reaction to increase by a factor of 4 implying that it depends on the square of $[NO_2]_o$. Therefore, the rate law has the form, $\text{Rate} = k[NO_2]^2$.

7.3 Order of reactions

From Section 7.2, the rate of chemical reaction depends on the concentration of reactants raised to a certain numerical value. The exponent to which the concentration of a reactant is raised to in the rate law is known as the *order of a reaction*. The order of a reaction can be zero, small integers or simple fractions. For a general reaction,

$$aA + bB + eE \longrightarrow \text{Products}$$

the rate law takes the form:

$$\text{Rate} = k[A]^x[B]^y[E]^z \tag{7.5}$$

where, k is called the rate constant, x, y, and z are the orders of reaction with respect to [A], [B] and [E], respectively. The sum of x, y, and z is called the *overall order of reaction*.

Consider a chemical reaction represented by the equation:

$$aA \longrightarrow \text{Products}$$

The rate of the reaction is given by:

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^n$$

For the known values of rate, k and [A], the order of a reaction (n) can be determined and it can be 0, 1 or 2. When $n = 0$, the reaction is said to be a zero order, when $n = 1$ the reaction is first-order and for $n = 2$ the reaction is second-order. In this section, zero, first, and second order reactions are dealt with. Generally, the overall order of reaction is the sum of powers to which the concentration terms of reactants are raised in the rate law equation for a particular chemical reaction.

The orders of reactions are significant in that they tell how the rate of reaction are affected by concentrations of the reactants. This information is crucial for designing and optimising chemical processes in various industries.

7.3.1 Zero-order reactions

Consider a zero-order reaction:

$$\mathrm{A} \longrightarrow \text{Products}$$

$$\text{Rate} = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^n$$

$$\text{Rate} = k[\mathrm{A}]^0 = k \qquad (7.6)$$

It can be deduced from Equation 7.6 that for a zero-order reaction, the rate of chemical reaction is constant (does not vary with increase or decrease in reactant(s) concentration(s)) and it is equal to the rate constant (k).

Since Rate $= -\frac{d[\mathrm{A}]}{dt}$, Equation 7.6 becomes $-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^0$ which gives $-\frac{d[\mathrm{A}]}{dt} = k$. Rearranging and intergrating this equation results into Equation 7.7.

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} d[\mathrm{A}] = \int_0^t -dkt$$

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} d[\mathrm{A}] = -k\int_0^t dt$$

$$[\mathrm{A}]_t - [\mathrm{A}]_0 = -kt$$

$$[\mathrm{A}]_t = -kt + [\mathrm{A}]_0 \qquad (7.7)$$

where $[\mathrm{A}]_t$ = concentration of A at time (t),

k is the rate constant,

t is the time in seconds and $[\mathrm{A}]_0$ is the initial concentration of A.

A plot of $[\mathrm{A}]_t$ (y–axis) against t (x–axis) gives a straight line of slope $-k$ and $[\mathrm{A}]_0$ as y–intercept (Figure 7.2).

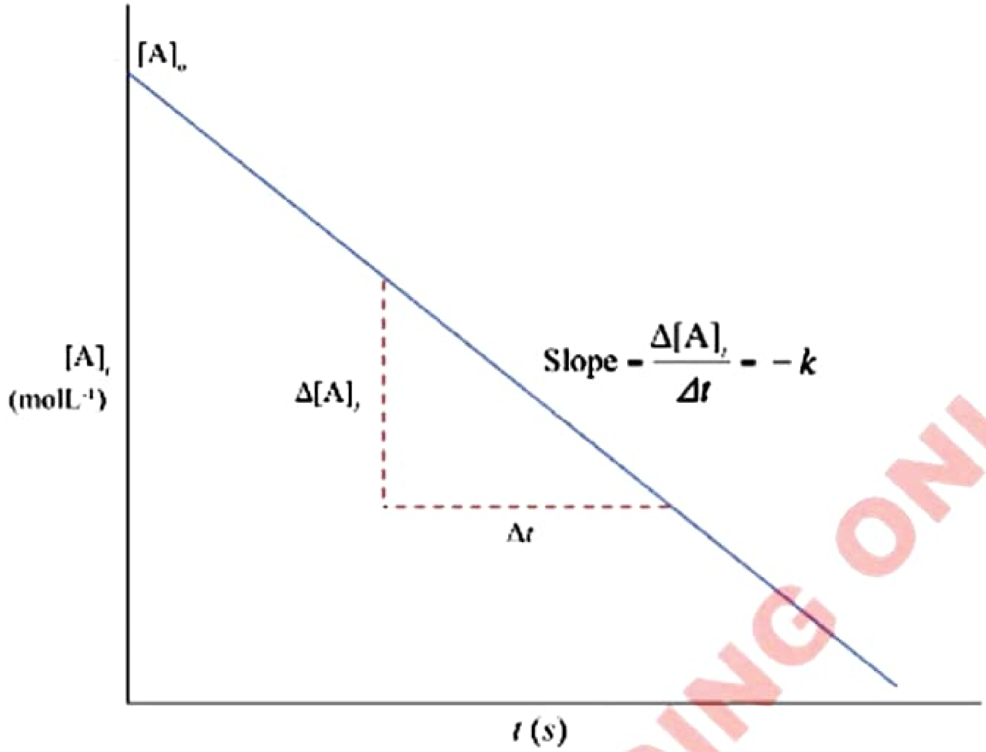


Figure 7.2: *Plot of concentration versus time for a zero-order reaction*

Half-life for zero-order reactions

Figure 7.1 shows that as the chemical reaction proceeds, the concentration of the reactant A decreases. The time at which the concentration of A is half the initial value gives a new measure of a rate of reaction. The time required for the initial concentration of the reactant(s) to decrease to half of its initial concentration is called *half-life* and is often expressed as $t_{1/2}$. The half-life for zero-order reaction can be determined from its integrated rate law (Equation 7.7) where from the definition, half-life, $t_{1/2}$ is obtained when $[A]_t = \frac{[A]_0}{2}$.

Substituting $[A]_t = \frac{[A]_0}{2}$ and $t = t_{1/2}$ in Equation 7.7 gives:

$$\frac{[A]_0}{2} = -kt_{1/2} + [A]_0$$

Rearrangement of this equation results in Equation 7.8.

$$kt_{1/2} = [A]_0 - \frac{[A]_0}{2}$$

$$kt_{1/2} = \frac{[\mathrm{A}]_0}{2}$$

$$t_{1/2} = \frac{[\mathrm{A}]_0}{2k} \qquad (7.8)$$

Equation 7.8 shows that the half-life of the zero-order reaction depends on the initial concentration of the reactant and the rate constant of the reaction.

Units of rate constant for zero-order reactions

The units of k can be derived from an integrated rate law of a particular order of a reaction.

For zero-order reactions,

$$[\mathrm{A}]_t = -kt + [\mathrm{A}]_0$$

$k = \dfrac{[\mathrm{A}]_0 - [\mathrm{A}]_t}{t}$. Since the unit for $\Delta[\mathrm{A}]$ is M and unit for t is s, then units for k are $\dfrac{\mathrm{M}}{\mathrm{s}} = \mathrm{M\,s^{-1}}$

Therefore, the units of the rate constant for zero-order reactions are $\mathrm{M\,s^{-1}}$, *i.e.* $\mathrm{mol\,dm^{-3}\,s^{-1}}$.

Task 7.2

Use online or any other sources to identify zero-order reactions of industrial importance.

Example 7.4

A chemical reaction **A → Products** is a zero-order reaction. Determine:

(a) The rate constant (k) if the concentration of A decreases from 1.4 mol dm^{-3} to 0.7 mol dm^{-3} in100 minutes.

(b) The half-life of substance A if the initial concentration of A is 1.0 mol dm^{-3}.

(c) The new half-life, and compare it with the one calculated in (b) if the initial concentration of A in (b) is increased to 2 mol dm^{-3}.

Solution

(a) The integrated rate law for a zero-order reaction is given by:

$$[\mathrm{A}]_t = -kt + [\mathrm{A}]_o$$

From the question, $[\mathrm{A}]_o = 1.4\ \mathrm{mol\ dm^{-3}}$, $[\mathrm{A}]_t = 0.7\ \mathrm{mol\ dm^{-3}}$, and $t = 100$ min.

Substituting the given values into the integrated rate law results in:

$$0.7\ \mathrm{mol\ dm^{-3}} = -k(100 \times 60)(\mathrm{s}) + 1.4\ \mathrm{mol\ dm^{-3}}$$

$$0.7\ \mathrm{mol\ dm^{-3}} - 1.4\ \mathrm{mol\ dm^{-3}} = -6000\,k\,(\mathrm{s})$$

$$-\frac{0.7\ \mathrm{mol\ dm^{-3}}}{6000\ \mathrm{s}} = -k$$

$$k = 1.17 \times 10^{-4}\ \mathrm{mol\ dm^{-3}\ s^{-1}}$$

Hence, the rate constant (k) for the reaction is $1.17 \times 10^{-4}\ \mathrm{mol\ dm^{-3}\ s^{-1}}$.

Alternatively, the rate constant (k) can be calculated from the zero-order half-life equation. That is, from:

$$t_{\frac{1}{2}} = \frac{[\mathrm{A}]_o}{2k} \Rightarrow k = \frac{[\mathrm{A}]_o}{2t_{\frac{1}{2}}}$$

Since the $[\mathrm{A}]_o$ decreased from $1.4\ \mathrm{mol\ dm^{-3}}$ to $0.7\ \mathrm{mol\ dm^{-3}}$ and the $t_{\frac{1}{2}} = 100$ min, therefore:

$$k = \frac{1.4\ \mathrm{mol\,dm^{-3}}}{2(100 \times 60)\ \mathrm{s}}$$

$$k = 1.17 \times 10^{-4}\ \mathrm{mol\ dm^{-3}\ s^{-1}}$$

(b) The half-life of zero-order reactions as given by Equation 7.8 is $t_{\frac{1}{2}} = \frac{[\mathrm{A}]_o}{2k}$.

From the question, $[\mathrm{A}]_o = 1.0\ \mathrm{mol\ dm^{-3}}$ and the calculations above gave $k = 1.17 \times 10^{-4}\ \mathrm{mol\ dm^{-3}\ s^{-1}}$. Substituting these values in the half-life equation gives:

$$t_{\frac{1}{2}} = \frac{1.0\,\mathrm{mol\,dm^{-3}}}{2 \times 1.17 \times 10^{-4}\,\mathrm{mol\,dm^{-3}\,s^{-1}}} = 4273.5\ \mathrm{s}$$

Therefore, the half-life for this reaction is 4273.5 seconds.

(c) Given the initial concentration of A, $[A]_o = 2.0 \text{ mol dm}^{-3}$ and the rate constant, $k = 1.17 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$, using Equation 7.8, the half-life is given by:

$$t_{\frac{1}{2}} = \frac{2.0 \text{ mol dm}^{-3}}{2 \times 1.17 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}} = 8547 \text{ s}$$

The new half-life of the reaction is 8547 s.

Therefore, doubling the initial concentration of A doubles its half-life as well.

Exercise 7.1

1. The concentrations of R in a chemical reaction, were measured as a function of time and the following data were obtained:

$[R]$ (mol dm^{-3})	1.0	7.5	4	10
Time (s)	4	30	16	40

Comment on the order of the reaction.

2. In a zero-order reaction, for every 10 °C rise in temperature, the rate of the chemical reaction doubles. What will the rate of the chemical reaction be when the temperature is increased from 10 °C to 90 °C?

3. Explain the significance of zero-order reactions in the following aspects:
   - (a) Drug delivery systems
   - (b) Chemical manufacturing processes
   - (c) Environmental remediation
   - (d) Corrosion protection

4. A household bleaching agent reacts when it comes into contact with stains on clothing or surfaces. The bleaching agent breaks down slowly over time regardless of the concentration of the stain or the amount of bleaching agent applied. How would you explain the mechanism behind the bleaching process in this scenario?

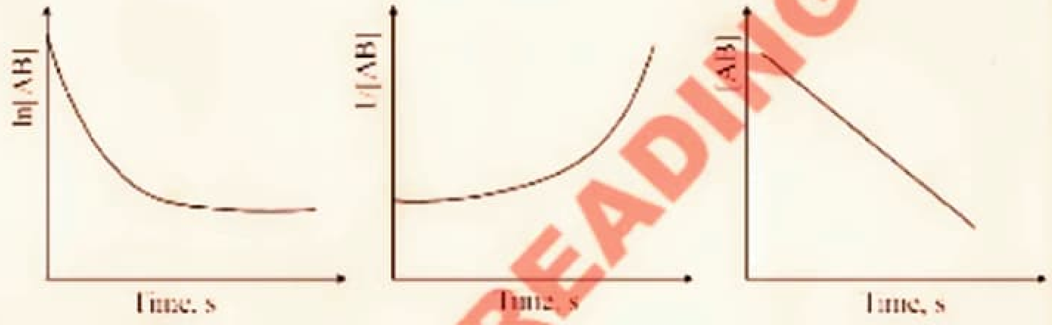
5. A 500 mg pharmaceutical formulation contains a drug that degrades via a zero-order reaction with a rate constant of 5 mg $L^{-1} h^{-1}$. How long will it take for its concentration to fall to 250 mg in the patient's body?

6. You are tasked to investigate the decomposition rate of a chemical compound X which is known to undergo a zero-order reaction.
   (a) Describe an experimental setup you would use to determine the rate law for this reaction.
   (b) What measurements would you take?
   (c) How would you vary the initial concentration of X?

7. A trial and error method was used to determine the order of a certain chemical reaction represented by the following chemical equation:

$$AB(g) \longrightarrow A(g) + B(g)$$

The concentrations of AB remaining in the reaction mixture were obtained at regular time intervals and were used to plot the graphs of ln[AB] vs time, $^1/_{[AB]}$ vs time, and [AB] vs time as shown below:



(a) (b) (c)

Use the graphs to deduce the order of the reaction.

7.3.2 First-order reactions

For the first-order chemical reaction of the form:

$$aA \longrightarrow \text{Products}$$

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^1 \quad (7.9)$$

Equation 7.9 can be rearranged into Equation 7.10.

$$\frac{d[A]}{[A]} = -kdt \quad (7.10)$$

Integrating Equation 7.10 from $[A]_o$ to $[A]_t$ and from $t = 0$ to time t, Equation 7.11 is obtained.

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k\int_0^t dt$$

$$\ln\Big[A\Big]_{[A]_0}^{[A]_t} = -kt_0^t$$

$$\ln[A]_t = -kt + \ln[A]_0 \qquad (7.11)$$

For the first-order reaction, a plot of $[A]_t$ against time gives a curve and a plot of $\ln[A]_t$ against time gives a straight line (Figure 7.3).

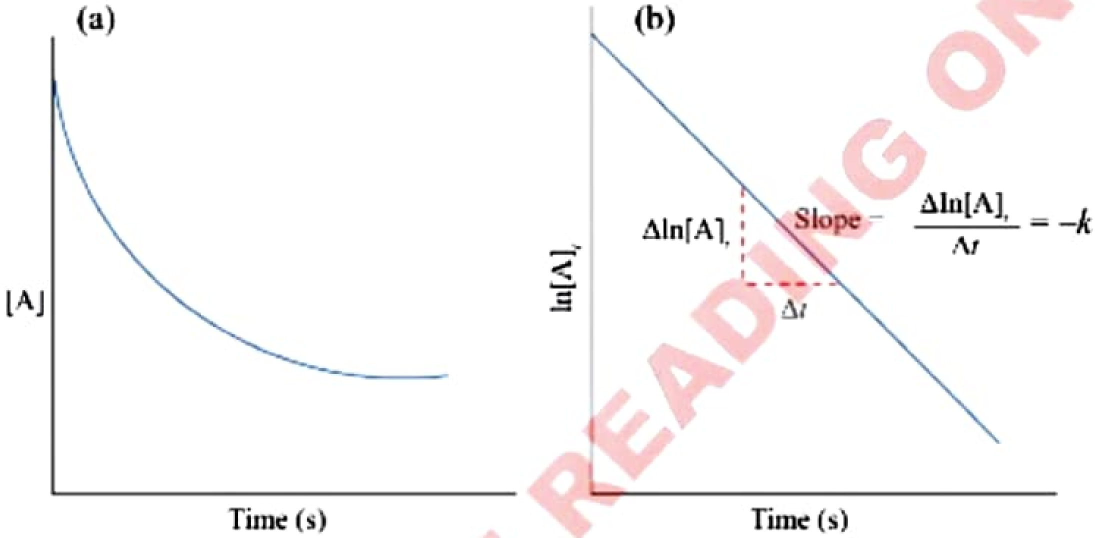


Figure 7.3: *Graph of (a) $[A]_t$ versus time and (b) ln $[A]_t$ versus time for the first-order reaction*

An example of the first-order reaction is the decomposition of dinitrogen pentoxide.

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

Let the data for the reaction be as shown in Table 7.1.

Table 7.1 *Rate of decomposition of gaseous N_2O_5*

Experiment	$[N_2O_5]_0$, mol dm^{-3}	Initial Rate, mol dm^{-3} s^{-1}
1	0.075	8.90×10^{-4}
2	0.190	2.26×10^{-3}
3	0.275	3.26×10^{-3}
4	0.410	4.85×10^{-3}

Assuming that the rate law for this reaction is Rate $= k[N_2O_5]^x$, the value of x can be calculated by making the following considerations:

For experiment 1,

$$\text{Rate}_1 = k[N_2O_5]^x.$$

Substituting the data obtained in Experiment 1 in the rate law, the following is obtained:

$$8.9 \times 10^{-4} = k(0.075)^x$$

For experiment 2,

$$\text{Rate}_2 = k[N_2O_5]^x.$$

Substituting the data obtained in Experiment 2 in the equation results into:

$$2.26 \times 10^{-3} = k(0.19)^x$$

Dividing R_2 by R_1 leads to:

$$\frac{2.26 \times 10^{-3}}{8.9 \times 10^{-4}} = \frac{k(0.190)^x}{k(0.075)^x}$$

$$2.5^1 = 2.5^x \Rightarrow x = 1$$

Since the rate of this reaction depends on the concentration of N_2O_5 raised to the first power, the order of the reaction is 1. Thus, the rate law for this reaction is

$$\text{Rate} = \frac{-d[N_2O_5]}{dt} = k[N_2O_5]$$

This means that if the concentration of N_2O_5 in the reaction vessel is doubled, the rate of production of NO_2 and O_2 will also double.

Half-life for first-order reactions

The expression for the half-life of the first-order reaction can be obtained from its integrated rate law. Thus, from the integrated rate law, $\ln[A]_t = -kt + \ln[A]_o$, the half-life, $t_{1/2}$ is reached when $[A]_t = \frac{1}{2}[A]_o$.

Then, $\ln\frac{[A]_o}{2} = -kt_{\frac{1}{2}} + \ln[A]_o$

$$kt_{\frac{1}{2}} = \ln[A]_o - \ln\frac{[A]_o}{2}$$

$$kt_{\frac{1}{2}} = \ln\left([A]_0 \div \frac{[A]_0}{2}\right)$$

$$kt_{\frac{1}{2}} = \ln\left([A]_0 \times \frac{2}{[A]_0}\right)$$

$$kt_{\frac{1}{2}} = \ln 2 = 0.693$$

$$t_{\frac{1}{2}} = \frac{0.693}{k} \tag{7.12}$$

It can therefore be deduced from Equation 7.12 that for first-order reactions, the half-life is independent of the initial concentration of the reactant.

Units of rate constant for first-order reactions

The rate constant for the first-order reactions has different units compared to the units of zero-order reactions and can be derived from the intergrated rate law. Consider the integrated rate law for the first-order reaction.

$$\ln[A]_t = -kt + \ln[A]_0$$

$$kt = \ln[A]_0 - \ln[A]_t$$

Applying logarithmic laws to the above equation gives:

$k = \dfrac{\ln \dfrac{[A]_0}{[A]_t}}{t}$. Since the unit of t is s then the unit of the rate constant (k) for the first-order reactions is s^{-1}.

Example 7.5

A radioactive phosphorous (^{32}P) has a decay constant of 0.048 per day. Use a trial and error method to determine the order of the reaction if its half-life is 14.44 days and the initial concentration is 0.5 mol dm^{-3}.

Solution

Assume that phosphorous-32 decays following either zero or the first-order reaction. Thus, trial half-lives can be computed and compared with the one given in the question as follows:

Order	Half-life equation	Rate constant	$[P]_o$, M	Calculated half-life
0	$t_{\frac{1}{2}} = \frac{[P]_o}{2k}$	0.048 day^{-1}	0.5	5.21 days
1	$t_{\frac{1}{2}} = \frac{0.693}{k}$	0.048 day^{-1}	0.5	14.44 days

From the obtained results, the calculated half-life value which gives the answer similar to the one given in the question is the one computed using half-life equation of the first-order. Thus, it can be concluded that the radioactive decay of phosphorous-32 is the first-order.

Exercise 7.2

1. A household cleaning product undergoes decomposition in a container due to exposure to light. The decomposition follows first-order kinetics with a half-life of 24 hours. If the initial concentration of the cleaning agent is 0.2 M, what will be the concentration after 3 days?

2. The half-life of a pollutant that undergoes first-order decay doesn't depend on its initial concentration. What is its implication for environmental management?

3. A particular drug has a decay rate constant of $1.07 \times 10^{-6}\,s^{-1}$. If a patient is given a 400 mg dose of the drug, how much of the drug will remain in the patient's body after 12 hours? Comment on your answer.

4. The reaction represented by the equation

   $$(CH_3)_3CBr(aq) + H_2O(l) \longrightarrow (CH_3)_3COH(aq) + H^+(aq) + Br^-(aq)$$

   has the rate law, Rate = $k[(CH_3)_3CBr]^1[H_2O]^0$.

   (a) What happens to the initial rate if the water concentration is tripled?

   (b) What happens to the initial rate if the concentration of $(CH_3)_3CBr$ is halved?

5. The first-order reaction is 90% complete in 428 minutes.

   (a) Calculate the first and second half-lives for this reaction.

   (b) How long does it take to complete 80% of the reaction?

6. For the first order reaction,

$$B \longrightarrow \text{Products}$$

the half-life was observed to be 20.0 seconds for an experiment in which the initial concentration of B ($[B]_o$) was 0.05 mol dm^{-3}. Calculate the concentration of B at

(a) 50 seconds

(b) 30 seconds

7.3.3 Second-order reactions

Chemical reactions whose reactants are raised to an overall power of two form second-order. These reactions can be a single reactant changing into products or two reactants changing into products. The rate law for the two cases can be deduced from the equations below.

$$aA \longrightarrow \text{Products}$$

$\text{Rate} = k[A]^x$ where $x = 2$

or

$$aA + bB \longrightarrow \text{Products}$$

$\text{Rate} = k[A]^y[B]^z$ where $y = z = 1$ and the overall order of the reaction is 2.

The type of second-order reaction involving two different reacting molecules, A and B, is too complex to discuss at this level. Therefore, the discussion will consider the simplest type which involves only one kind of reactant molecule. Thus, for a reaction,

$$aA \longrightarrow \text{Products}$$

the rate is expressed by Equation 7.13.

$$\text{Rate} = -\frac{d[A]}{dt} \qquad (7.13)$$

The rate law for a second-order reaction is given by Equation 7.14.

$$\text{Rate} = k[A]^2 \qquad (7.14)$$

Combining Equations 7.13 and 7.14 gives Equation 7.15.

$$-\frac{d[A]}{dt} = k[A]^2 \qquad (7.15)$$

Rearranging Equation 7.15 results in Equation 7.16.

$$\frac{d[A]}{[A]^2} = -k dt \qquad (7.16)$$

Integrating Equation 7.16 from $[A]_o$ to $[A]_t$ for the case of concentration and from 0 to t for the case of time gives:

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = -\int_0^t k\,dt$$

$$-\left[\frac{1}{[A]}\right]_{[A]_o}^{[A]_t} = k(t)_o^t$$

$$-\frac{1}{[A]_t} + \frac{1}{[A]_o} = -k(t-0)$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt \tag{7.17}$$

A plot of $\frac{1}{[A]_t}$ against t gives a straight line (Figure 7.4) with slope equal to k and y–intercept equal to $\frac{1}{[A]_o}$.

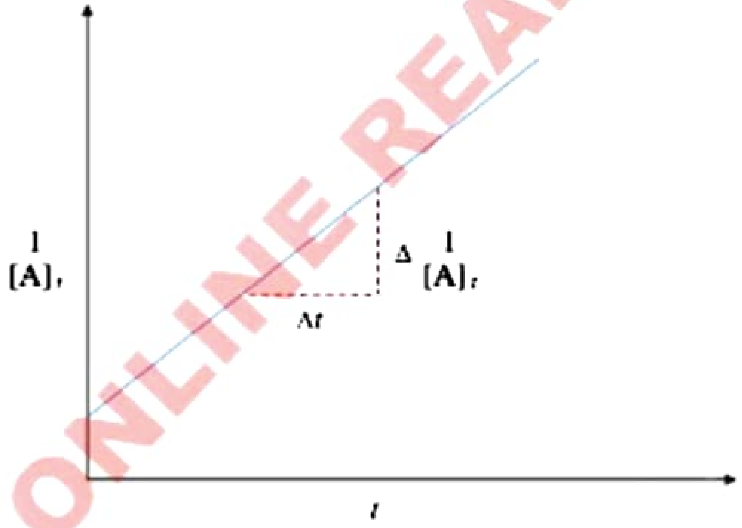


Figure 7.4: *Plot of* $\frac{1}{[A]_t}$ *against* t *for the second order reaction*

Half-life for second-order reactions

The half-life for the second-order reaction is calculated from its integrated rate law (Equation 7.17). By setting $[A]_t = \frac{[A]_o}{2}$ in Equation 7.17, Equation 7.18 for the half-life of the second-order reaction is obtained.

$$\frac{1}{\left(\frac{[A]_0}{2}\right)} = kt_{\frac{1}{2}} + \frac{1}{[A]_0}$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{\frac{1}{2}}$$

$$\frac{1}{[A]_0} = kt_{\frac{1}{2}}$$

$$t_{\frac{1}{2}} = \frac{1}{k[A]_0} \tag{7.18}$$

From Equation 7.18, the half–life of the second–order reaction is inversely proportional to the initial concentration of the reactants. The smaller the initial concentration of the reactants, the higher the half-life and vice versa.

Units of rate constant for second–order reactions

The units of the rate constant for a second–order reaction can be obtained from its intergrated rate law given in Equation 7.17 as follows:

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$\frac{\frac{1}{[A]_t} - \frac{1}{[A]_0}}{t} = k$$

$$\frac{\frac{1}{\text{mol dm}^{-3}}}{\text{s}} = k = \text{M}^{-1}\ \text{s}^{-1}$$

Hence, the units of the rate constant for the second-order reaction are $\text{M}^{-1}\ \text{s}^{-1}$.

Example 7.6

The following chemical reaction was carried out at a constant temperature:

$$4A(g) - 3B(g) \longrightarrow 2C(g)$$

The data obtained when A and B were allowed to react at the same temperature are:

Experiment	$[A]_0$, M	$[B]_0$, M	Initial rate, M s^{-1}
1	0.100	0.100	5.000
2	0.300	0.100	45.00
3	0.100	0.200	10.00
4	0.300	0.200	90.00

Calculate the order of the reaction with respect to [A].

Solution

Assuming that the rate law for the reaction is given by Rate = $k[A]^m[B]^n$ and considering experiment 1 and 2, the ratio of R_2 to R_1 can be written as:

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[A]_2^m[B]_2^n}{k[A]_1^m[B]_1^n} = \left(\frac{[A]_2}{[A]_1}\right)^m \times \left(\frac{[B]_2}{[B]_1}\right)^n$$

Substituting the values of Rate 2, Rate 1 and the corresponding initial concentrations of A and B leads to:

$$\frac{45}{5} = \left(\frac{3}{1}\right)^m \times \left(\frac{0.1}{0.1}\right)^n$$

$$9 = (3)^m$$

$$3^2 = (3)^m$$

$$m = 2$$

Therefore, the reaction is second-order with respect to [A].

The integrated rate laws corresponding to zero-order, first-order and second-order reactions with a single reactant are summarised in Table 7.2.

Table 7.2: *Summary of the rate laws for reactions with a single reactant of different orders*

Description	**Order of a reaction**		
	Zero	First	Second
Rate law	Rate = k	Rate = $k[A]$	Rate = $k[A]^2$
Integrated rate law	$[A]_t = -kt + [A]_o$	$\ln[A]_t = -kt + \ln[A]_o$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$
Straight line plot	$[A]_t$ versus t	$\ln[A]_t$ versus t	$\frac{1}{[A]_t}$ versus t
Relationship of rate constant to the slope of the straight line	slope = $-k$	slope = $-k$	slope = k
Half-life	$t_{\frac{1}{2}} = \frac{[A]_o}{2k}$	$t_{\frac{1}{2}} = \frac{0.693}{k}$	$t_{\frac{1}{2}} = \frac{1}{k[A]_o}$
Units of k	M s ^{1}	s ^{1}	M ^{1} s ^{1}

Exercise 7.3

1. The reaction rate of the following second-order reaction is $0.005\ \text{mol dm}^{-3}\text{s}^{-1}$.

   $$A + B \longrightarrow \text{Products}$$

   If the reaction is first-order with respect to both A and B and the concentrations of A and B are 0.15 mol dm ^{3} and 0.1 mol dm ^{3}, respectively,

   (a) write the rate law for this reaction.

   (b) calculate the rate constant for this reaction.

2. The rate law for the reaction $2NOBr(g) \longrightarrow 2NO(g) + Br_2(g)$ at a certain temperature is

   $$\text{Rate} = -\frac{\Delta[NOBr]}{\Delta t} = k[NOBr]^2$$

   (a) If the half-life for this reaction is 0.2 s when the initial concentration of NOBr is 9.0 mol dm^{-3}, calculate the value of k.

(b) How long would it take for the concentration of NOBr to fall to 1 mol dm^{-3}?

3. Some of the unfriendly environmental substances decay by second-order reactions. Explain the practical consequences of such substances to the environment.

4. A contaminated soil site is undergoing remediation by introducing a chemical agent that reacts with the pollutant via a second-order reaction. The rate constant for the reaction is 0.001 $M^{-1}day^{-1}$. If the initial concentration of the pollutant in the soil is 10 mg/kg, how long will it take for the pollutant concentration in the soil to decrease to half of its original value?

5. After collecting data on initial concentrations and reaction rates of a reaction which is believed to be second order, describe how you would analyse the data to determine the rate law of the reaction.

6. The reaction,

   $$aA \longrightarrow \text{Products}$$

   has $[A]_o = 5$ mol dm^{-3} and $k = 1.0 \times 10^{-2}$ (assuming that the units of k are appropriate for the second-order reaction). Calculate [A] after 60 seconds of the reaction.

7.4 Experimental determination of rate laws

The rate law for a chemical reaction which involves only one reactant can be determined experimentally by changing the concentrations of the reactant and measuring the initial rates of the reaction. The obtained initial rates and the new concentrations are compared with the previous initial rates and concentrations. For example, if the reaction is first-order with respect to reactant A, doubling the concentration of A will double the rate of the reaction. Moreover, if the reaction is second-order with respect to A, then the rate is proportional to $[A]^2$ and doubling the concentration of A will cause the rate to increase by a factor of 4.

For reactions involving more than one reactant, a different approach is needed to determine the rate law. One commonly used method is to maintain the concentration of one reactant constant while altering the concentration of the second reactant. This method allows for a systematic study of the reactions rate and provides valuable insights into the reactions mechanism.

Consider the reaction:

$$A - B \longrightarrow \text{Products}$$

When $[A]_0 = 0.001$ mol dm^{-3} and $[B]_0 = 1$ mol dm^{-3}, as the reaction proceeds, the concentration of A decreases significantly whereas that of B remains approximately constant. Under this condition, where [B] is much larger than [A], it can be assumed that throughout the reaction, $[B]_t = [B]_0$. Therefore, considering $k[B]^m = k'$, the rate law Rate = $k[A]^n[B]^m$ has the form Rate = $k'[A]^n$ which implies that under this condition, the rate is determined by the concentration of A. From this rate law, the order of the reaction with respect to A can be determined. Similarly, when $[A]_0 = 1$ mol dm^{-3} and $[B]_0 = 0.001$ mol dm^{-3}, the rate of reaction will depend on the concentration of B as the concentration of A is considered to remain approximately constant. Considering $k[A]^n = k''$, the rate law Rate = $k[A]^n[B]^m$ has the form Rate = $k''[B]^m$, which implies that under this condition, the rate of the reaction depends on the concentration of B and its order of reaction can be determined. For instance, hydrogen peroxide reacts with iodide ions in an acidic medium to form iodine. The iodine produced then reacts with thiosulfate ions as indicated in the following reactions:

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \longrightarrow I_2(aq) + 2H_2O(aq)$$

$$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

The initial rate of oxidation of iodide ions by hydrogen peroxide in an acidic solution is found by measuring the time taken to liberate sufficient iodine to react with the thiosulfate ions present and then produce a blue colour with a starch solution. The rate law for the reaction can be written as rate = $k[H_2O_2]^a[H^+]^b[I^-]^c$. By varying the concentration of each reactant independently, the orders of reaction a, b and c can be determined.

Activity 7.1

Aim: To determine the order of reaction for the reaction between $Na_2S_2O_3$, KI and H_2O_2 using a graphical method

Requirements: Beakers, 10-mL measuring cylinder, burette, conical flasks, stopwatch, A 0.10 M hydrogen peroxide, 0.25 M H_2SO_4, 0.05 M sodium thiosulfate, 0.30 M KI, starch solution, and distilled water

Procedure

1. Measure 10 mL of H_2O_2 solution, 25 mL of H_2SO_4 solution, and 5 mL of $Na_2S_2O_3$ solution into a 100 mL beaker.
2. Add approximately 1 mL of starch solution.
3. Measure 5 mL of KI solution into another beaker and add 20 mL of distilled water. Label this mixture A.
4. Add mixture A to the first beaker and start a stopwatch/clock. Swirl the content to mix thoroughly. Tabulate the time taken for the blue colour to appear.
5. Repeat steps 1 to 4, but this time using mixture A with the composition as indicated in the following table:

	Composition	
	KI, mL	Water, mL
Mixture A	10	15
	15	10
	20	5
	25	0

Questions

1. What is the graphical relationship between log 1/t and log volume of KI?
2. What is the order of the reaction with respect to KI?

An example for the determination of the rate law, order of reaction and rate constant, *k* is given in Example 7.7.

Example 7.7

Consider the results of the following set of experiments when studying the rate of a reaction of nitric oxide with hydrogen at 1553 K.

$$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$$

Experiment	$[NO]_0$, mol dm^{-3}	$[H_2]_0$, mol dm^{-3}	Initial Rate, mol dm^{-3} s^{-1}
1	5.0×10^{-3}	2.0×10^{-3}	1.3×10^{-5}
2	1.0×10^{-2}	2.0×10^{-3}	5.2×10^{-5}
3	1.0×10^{-2}	4.0×10^{-3}	1.0×10^{-4}

Use the data obtained to determine the order of the reaction with respect to NO and H_2. Deduce the rate law and calculate the rate constant.

Solution

From experiments 1 and 2, when the concentration of hydrogen is kept constant, doubling concentration of NO from 5.0×10^{-3} to 1.0×10^{-2} mol dm^{-3} leads to quadrupling of the rate. The reaction is therefore second-order with respect to [NO].

Similarly, from experiments 2 and 3, when the concentration of NO is kept constant, doubling $[H_2]$ from 2.0×10^{-3} to 4.0×10^{-3} mol dm^{-3} doubles the rate. The reaction is therefore first-order with respect to $[H_2]$.

Thus, Rate $\alpha\ [NO]^2[H_2] = k[NO]^2[H_2]$. Therefore, the rate law has the form:

$$\text{Rate} = k[NO]^2[H_2]$$

Using the above rate law and data obtained in experiment 1, the rate constant can be calculated as

$$1.3\times10^{-5}\ \text{mol dm}^{-3}\text{s}^{-1} = k\left(5.0\times10^{-3}\ \text{mol dm}^{-3}\right)^2\left(2.0\times10^{-3}\ \text{mol dm}^{-3}\right)$$

Solving for k gives:

$$k = \frac{1.3\times10^{-5}\ \text{mol dm}^{-3}\text{s}^{-1}}{\left(5.0\times10^{-3}\ \text{mol dm}^{-3}\right)^2\left(2.0\times10^{-3}\ \text{mol dm}^{-3}\right)} = 260\ \text{dm}^6\ \text{mol}^{-2}\ \text{s}^{-1}$$

Therefore, the rate constant (k) for the reaction is 260 dm^6 mol^{-2} s^{-1}.

Note that for this kind of questions, you have to calculate the rate constants from all the experimental data provided and finally determine the average value of the rate constant.

Activity 7.2

Aim: To determine the order of reaction for the reaction between $Na_2S_2O_3$ and HCl by isolation method

Requirements: Beakers, pipettes, burettes, conical flasks, measuring cylinder, a piece of white paper marked "+", stop watch, 0.15 M sodium thiosulfate, 0.10 M hydrochloric acid, and distilled water

Procedure

1. Place a 250-mL beaker on top of the "+" mark on the white paper.
2. Measure 50 mL of sodium thiosulfate using a measuring cylinder into the beaker placed on the marked paper.
3. Using another measuring cylinder, measure 50 mL of hydrochloric acid. Add the measured acid into the beaker containing sodium thiosulfate and immediately start the stopwatch.
4. In a tabular form, record the time taken for the precipitation to obscure the mark "+" on the piece of white paper.
5. Repeat the procedure by using other concentrations as shown in the following table:

Exp.	Volume of $Na_2S_2O_3$, mL	Volume of H_2O, mL	Volume of HCl, mL
1.	50	0.00	50.00
2.	40	10.00	50.00
3.	30	20.00	50.00
4.	20	30.00	50.00

Questions

1. What reaction occurred in this experiment? Show it by ionic equation.

2. Given that the volumes of individual solutions are directly proportional to their concentrations, what is the reaction order with respect to sodium thiosulfate?
3. What causes the disappearance of the mark on the white paper?

Exercise 7.4

1. Consider the results of the following set of experiments used in studying the rate of the chemical reaction.

$$A + B \longrightarrow \text{Products}$$

Experiment	$[A]_0$, mol dm^{-3}	$[B]_0$, mol dm^{-3}	Initial rate, mol dm^{-3} s^{-1}
1	0.24	0.12	2.00
2	0.12	0.12	0.50
3	0.24	0.06	1.00

(a) Determine the rate law.

(b) Calculate the rate constant (*k*).

(c) Calculate the reaction rate when [A] is 0.014 mol dm^{-3} and [B] is 1.350 mol dm^{-3}.

2. The experimental data in the table below were collected for the decomposition reaction:

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

Experiments	$[SO_2Cl_2]_0$, mol dm^{-3}	Initial rate, mol dm^{-3} s^{-1}
1	0.01	2.2×10^{-7}
2	0.02	4.4×10^{-7}
3	0.03	6.6×10^{-7}

Determine the rate law for this reaction.

3. The data in the table below were collected for the reaction:

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

[HI], mol dm^{-3}	Time, s
0.1000	0
0.0751	50
0.0558	100
0.0457	150
0.0387	200
0.0336	250
0.0296	300

(a) Plot a graph of [HI] in mol dm^{-3} versus time in seconds and calculate the rate of the reaction at 120 seconds.

(b) On your graph in (a), sketch the change in the concentration of hydrogen gas over time.

7.5 Factors affecting the rate of chemical reactions

Task 7.3

Use online resources to establish the causes of early food stuff spoilage when kept at room temperature rather than when refrigerated.

The rate of chemical reactions is influenced by the nature of chemical substances and other factors such as concentration, pressure, temperature, surface area, catalyst and light. The following sub-sections discuss the effects of these factors on the rate of chemical reaction.

7.5.1 Concentration of the reactants

From the expression of the rate law, the rate of a reaction is proportional to the concentration of reactants. It is also qualitatively agreed that for a chemical reaction to occur, reacting particles (molecules) must first come into contact or collide. Based on these two arguments, it can be concluded that there is a greater chance that molecules will collide more in a system where particles (molecules) are in higher concentration than in a system where they are less concentrated. The effect of the concentration on the reaction rate can be demonstrated by the reaction between sodium thiosulfate, $Na_2S_2O_3$ and potassium iodide (KI) in an acidic solution (Activity 7.3).

Activity 7.3

Aim: To determine the effect of reactant(s) concentration on the rate of reaction

Requirements: Beakers, pipette, stopwatch, 0.1 M $Na_2S_2O_3$, 0.2 M KI and 1.0 M H_2SO_4 solutions, distilled H_2O, starch solution, dropper and two 10-mL measuring cylinder

Procedure

1. Measure 10 cm^3 of 0.1 mol dm^{-3} $Na_2S_2O_3$ solution into a 100 cm^3 beaker. Add 10 cm^3 of 1.0 M H_2SO_4 solution and two drops of starch solution in the same beaker.
2. Measure 10 cm^3 of 0.2 mol dm^{-3} KI solution.
3. Pour the KI solution into the beaker containing a mixture of $Na_2S_2O_3$, starch solution and sulfuric acid and immediately start the stopwatch. Record the time it takes for the blue-black colour to appear. This will help in determining the reaction rate.
4. Repeat steps 1 to 3, but this time with decreasing the concentration of $Na_2S_2O_3$ solution by measuring 5 cm^3 of the 0.1 mol dm^{-3} $Na_2S_2O_3$ solution, and adding distilled water to make 10 cm^3.

Questions

1. Which solution of $Na_2S_2O_3$ reacts faster? Give reason(s).
2. Why does the blue-black colour appear? Explain with the aid of chemical equations.
3. Which reaction can be considered as the rate-determining step?

7.5.2 Temperature

Temperature is important for many life processes such as combustion, cooking, rusting, and all biological processes. The effect of temperature can be explained in terms of the average kinetic energy of the reacting particles. Increasing the temperature of the system increases the average kinetic energy of the constituent particles. As the average kinetic energy increases, the particles move faster and collide more frequently per unit time. It is worth noting that the temperature (in kelvin) is proportional to the kinetic energy of the particles in a substance. Therefore, the reaction rates of all reactions increase with increasing temperature. Similarly, the reaction rates of virtually all reactions decrease with temperature. For example, refrigeration of food retards the rate of growth of bacteria in food by decreasing the reaction rate of biochemical reactions that enable bacteria to reproduce.

The collision model qualitatively explains the observation that an increase in temperature increases the rate of chemical reaction. However, it is found that the reaction rate is much smaller than the calculated collision frequency in a given reaction vessel. This implies that only a small fraction of the collision produces a reaction. Svante Arrhenius proposed the existence of a threshold energy which the reacting particles must acquire for a chemical reaction to take place. This energy barrier is called the *activation energy* (E_a) and is defined as the minimum energy required for reactants to start forming products. As stated previously, chemical reactions occur when this energy barrier is attained because the energy is needed to break the bonds of the reactants for the product(s) to be formed. Within a molecule, energy is stored as potential energy and is released when molecules (reacting particles) rearrange into products. Particles with small kinetic energy will not have enough energy to break the bonds; so, no reaction will occur. This idea can easily be understood by considering the decomposition of NOBr molecules in the gas phase.

$$2NOBr(g) \longrightarrow 2NO(g) + Br_2(g)$$

For this reaction to occur, NOBr must acquire enough energy to form an activated complex at the transition state. At this point, the activated molecules possess high energy, making them less stable and easily convertible into products. The NO–Br bonds break down, followed by one Br–Br bond formation. Breaking the N–Br bond in O–N–Br requires a considerable amount of energy (243 kJ mol^{-1}), which must be supplied to the system. The progress of the above reaction is summarised in Figure 7.5.

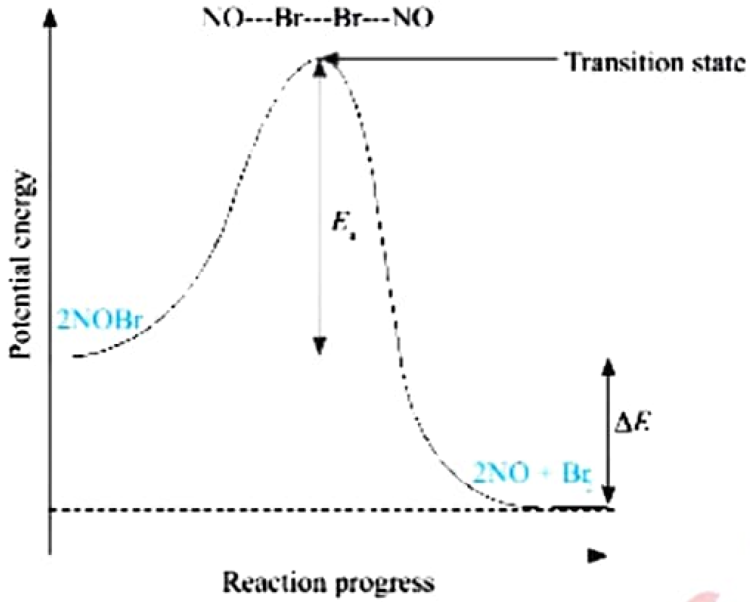


Figure 7.5: *Change in potential energy as a function of time for the decomposition of NOBr*

Kinetic nature of the reacting substances

Arrhenius postulated that the number of collisions having energy equal to or greater than the activation energy is given by the expression:

$$k = z\,e^{-E_A/RT}$$

where k is the number of collisions per second with at least the activation energy, z is the collision frequency (total number of collisions per second), E_A is the activation energy, R is the universal gas constant, T is the Kelvin temperature, and the factor $e^{-E_A/RT}$ is a fraction of collisions with sufficient energy to produce a reaction. However, experimental evidences shows that the observed reaction rate is considerably smaller than the rate of collisions with enough energy to disrupt the bonds of the reacting molecules to form products. This observation implies that some collisions might have the required energy but not produce a reaction. Another factor known as proper orientation of reacting particles during collisions was proposed to account for this observation. Some collision orientations can lead to reactions while others cannot. Therefore, a factor to allow for collisions with proper molecular orientations was agreed to be included. Considering these two factors, Arrhenius obtained an expression shown in Equation 7.19.

$$k = zp\,e^{-E_A/RT} \qquad (7.19)$$

where p is the steric factor which reflects the fraction of collisions with effective orientations. This expression in most cases is written in the form:

$$k = Ae^{-E_a/RT} \qquad (7.20)$$

Equation 7.20 is called the *Arrhenius Equation* where A which replaces zp is the pre-exponential factor or frequency factor for the chemical reaction. From Equation 7.20, it can be deduced that the rate constant is directly proportional to A (collision frequency). The minus sign associated with the exponent $^{-E_a/RT}$ implies the rate constant decreases with increasing activation energy and increases with temperature.

Introducing the natural logarithm on both sides of Equation 7.20 yields Equation 7.21.

$$\ln k = -\frac{E_a}{RT} + \ln A \qquad (7.21)$$

Equation 7.21 is a linear equation of the form $y = mx + c$. It can be deduced that for a reaction whose rate constant obeys the Arrhenius equation, a plot of ln k against $\frac{1}{T}$ gives a straight line. The values of the slope and the y– intercept can be used to determine the E_a and A of the reaction, respectively.

Therefore, from Equation 7.21, slope $= -\frac{E_a}{R}$ which leads to:

$$E_a = -R \times \text{slope} \qquad (7.22)$$

Experimentally, activation energy (E_a) of a reaction can be determined by measuring the rate constant (k) at several temperatures and then plotting ln (k) versus $\frac{1}{T}$.

At temperature (T_1) and rate constant (k_1) Equation 7.21 has the following form:

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \qquad (7.23(a))$$

At temperature (T_2) and rate constant (k_2) Equation 7.21 has the form:

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A \qquad (7.23(b))$$

Subtracting Equation 7.23 (a) from Equation 7.23 (b) gives:

$$\ln k_2 - \ln k_1 = -\frac{E_a}{RT_2} + \frac{E_a}{RT_1}$$

$$\ln\left(\frac{k_2}{k_1}\right)=\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \tag{7.24}$$

Therefore, the values k_1 and k_2 measured at temperatures T_1 and T_2 can be used to calculate E_a using $R = 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}$.

Example 7.8

The reactants CO and Cl_2 in the following reactions have the same concentration.

$$CO(g) + Cl_2(g) \longrightarrow COCl_2(g)$$

If the reaction rate at 250 °C is 1.5×10^3 times as fast as the rate of the same reaction at 150 °C, calculate the activation energy of this reaction $(R = 8.314\ \text{Jmol}^{-1}\text{K}^{-1})$.

Solution

Given $k_1 = \text{k}$, $T_1 = 150 + 273\ \text{K}$, $k_2 = 1.5 \times 10^3\ \text{k}$, $T_2 = 250 + 273 = 523\ \text{K}$

Rearranging Equation 7.24 by making E_a the subject of the formula gives

$$E_a = R\left(\frac{T_2 \times T_1}{T_2 - T_1}\right)\ln\left(\frac{k_2}{k_1}\right)$$

Substituting the values into the above equation leads to

$$E_a = 8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}\left(\frac{523\,\text{K} \times 423\,\text{K}}{523\,\text{K} - 423\,\text{K}}\right)\ln\left(\frac{1.5 \times 10^3\,\text{k}}{\text{k}}\right)$$

$$E_a = 8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1} \times 2212.3\,\text{K} \times \ln(1.5 \times 10^3) = 134.5\ \text{kJmol}^{-1}$$

Therefore, the activation energy of the reaction is 134.5 kJ mol^{-1}.

Example 7.9

The variation of the rate constants with temperature for the first-order reaction

$$2N_2O_5(g) \longrightarrow 2N_2O_4(g) + O_2(g)$$

is shown in the following table:

Temperature (T), K	Rate constant (k), s^{-1}
298	1.74×10^{-5}
308	6.60×10^{-5}
318	2.51×10^{-4}
328	7.59×10^{-4}
338	2.40×10^{-3}

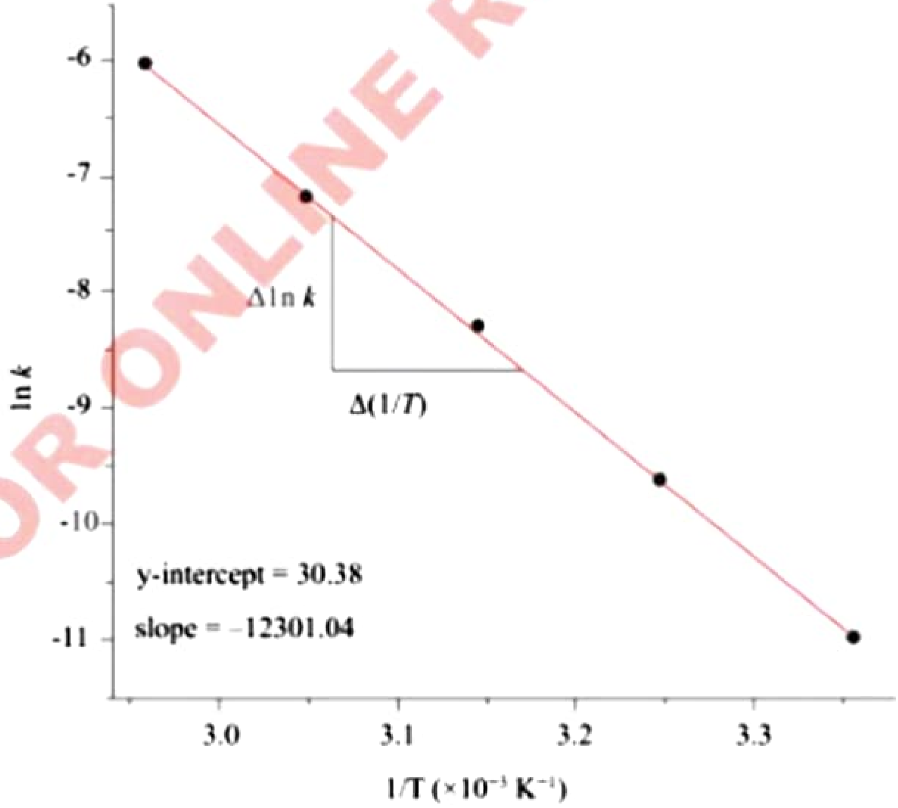
Determine the activation energy of the reaction graphically.

Solution

From the data above, values of $\frac{1}{T}$ and ln$k$ are calculated.

Temperature (T), K	Rate constant (k), s^{-1}	$\frac{1}{T}$ ($\times 10^{-3}$ K^{-1})	ln$k$
298	1.74×10^{-5}	3.36	−10.96
308	6.60×10^{-5}	3.25	−9.62
318	2.51×10^{-4}	3.14	−8.29
328	7.59×10^{-4}	3.05	−7.18
338	2.40×10^{-3}	2.96	−6.03

Plot a graph of ln$k$ against $\frac{1}{T}$ and determine its slope.



The analysis of the graph gives a slope = −12301.04 K. Using the slope and Equation 7.22 results in:

$$E_a = 8.314\,\text{J mol}^{-1}\,\text{K}^{-1} \times 12301.04\ \text{K} = 1.023 \times 10^5\ \text{Jmol}^{-1}$$

Therefore, the activation energy of the reaction is 102.3 kJ mol^{-1}.

Activity 7.4

Aim: To determine the activation energy of the reaction

Requirements: Beakers, two measuring cylinders of 10 mL, boiling tubes, conical flasks, Bunsen burner, thermometer, stopwatch, 0.02 M $KMnO_4$, and 0.05 M oxalic acid in 0.50 M H_2SO_4

Procedure

1. Put about 250 mL of water into a 300 mL beaker and warm it. Use this as a water bath.
2. Measure 10 mL of $KMnO_4$ solution and 10 mL of acidified oxalic acid and put them into separate boiling tubes.
3. Put a thermometer into a boiling tube containing an oxalic acid solution and heat the boiling tubes in a water bath. Allow the content to warm at 50 °C.
4. Pour the hot solutions of $KMnO_4$ and acidified oxalic acid into a 100 mL beaker and immediately start a stopwatch. Record the time taken for the purple colour to disappear.
5. Repeat the experiment at 60 °C, 70 °C and 80 °C temperatures.
6. Record your results in a tabular form.

Questions

1. What is the graphical relationship between log t (s) and 1/T (K^{-1})?
2. What is the activation energy of the reaction?
3. What chemical reaction decolourised the purple colour?

Exercise 7.5

1. The rate constant, k, of a reaction is 5.2×10^{-2} at 298 K and the activation energy is 20.0 kJ mol^{-1}. Calculate the value of k, at 318 K, given $R = 8.314\ \text{J mol}^{-1}\,\text{K}^{-1}$.

2. Describe how activation energy influences the rate of chemical reactions and the likelihood of reactions occurrence.

3. In a certain temperature dependence study of the rate of the gaseous phase chemical reaction, the following data were obtained:

Temperature (T), K	Rate constant (k), $dm^3\ mol^{-1}\ s^{-1}$
190	1.08×10^9
200	2.14×10^9
210	4.30×10^9
220	8.57×10^9
230	1.70×10^{10}

Calculate the activation energy of the reaction.

4. A particular reaction has an activation energy of 50 $kJ\ mol^{-1}$. When the temperature of the reaction is raised by 20 °C, the rate constant increases by a factor of 6.5. Calculate the initial and final temperatures.

7.5.3 Surface area

In heterogeneous reactions, the rate of the chemical reaction depends on the surface area of solid reactants. The greater the surface area, the higher the rate of a chemical reaction. For instance, finely divided calcium carbonate reacts more quickly with hydrochloric acid than calcium carbonate chips. This is because powdered calcium carbonate offers a larger surface area to the reacting acid. In other words, by increasing the surface area of the reactant, the rate of reaction increases due to the increased contact surface area between individual particles.

Activity 7.5

Aim: To investigate the effect of surface area on the rate of reaction

Requirements: Pieces of chalk, mortar and pestle (or any tool for grinding), stopwatch or timer, beakers, 2 M hydrochloric acid solution, measuring cylinder, and stirring rod

Procedure:

1. Take two pieces of chalks of the same mass.
2. Grind one piece of chalk into a fine powder.

3. Pour 20 mL of hydrochloric acid solution into two separate beakers. Label the beakers as 'A' and 'B', respectively.

4. Add the ground piece of chalk in beaker 'A' and an intact piece of chalk into beaker 'B'. Start the stopwatch as soon as you add the chalks (ground or intact) into the beakers containing HCl.

Questions

1. What trend did you observe in the rate of reaction between the ground pieces of chalk and the intact chalks?

2. In what real-world scenarios or industries might this experiment findings apply?

7.5.4 Pressure

When pressure is applied to reactants in solid or liquid state, no significant change in the rate of the reaction is observed. This is because solid and liquid reactants are incompressible. On the other hand, a change in pressure shows a significant change in the rate of reaction in which reactants are in gaseous form. This observation can be explained by using the collision model. When pressure is increased, the volume of gaseous reaction mixture decreases resulting in increasing chances of the gases molecules to collide. Figure 7.6 shows the effect of increasing pressure from P_1 to P_2.

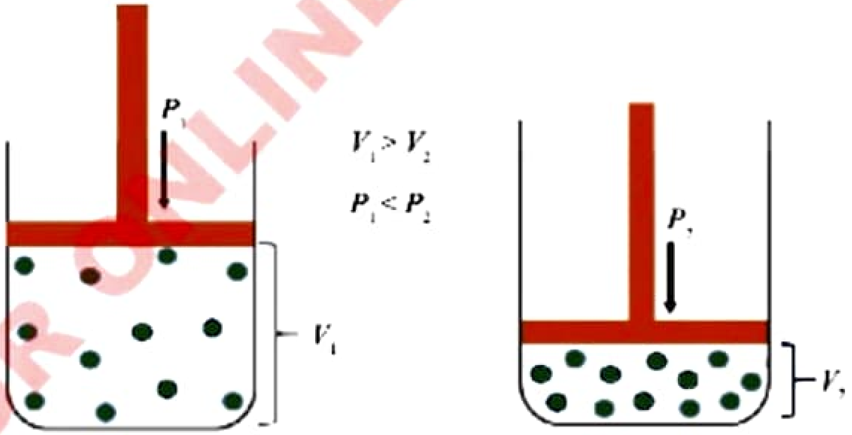


Figure 7.6: *Effect of changing pressure on the volume of the gas mixture*

7.5.5 Catalysts

Some reactions usually take a long time to go to completion, so they are economically not viable in the industrial production of substances. Such reactions may require monitoring their rates by controlling either the concentration of the reactants or the temperature to which a chemical reaction is subjected. Dealing with concentration and temperature in controlling the rates of chemical reactions is not without limitations. These include the imprecise concentration of reactants or the introduction of unwanted reactions that may emanate from the temperature. To avoid these effects, catalysts are the best choice for controlling the rate of chemical reactions. A *catalyst* is defined as a chemical substance that alters the rate of a chemical reaction but remains chemically unchanged at the end of the reaction.

Examples of reactions in which catalysts have a role include the decomposition of H_2O_2 in the presence of KI or the decomposition of solid $KClO_3$ in the presence of solid manganese(IV) oxide. In the first case, H_2O_2 decomposes relatively lowly rate in the absence of I^- ions. The addition of KI to the H_2O_2 solution at pH 7 increases the rate of the decomposition reaction to produce water and oxygen.

$$2H_2O_2(aq) \xrightarrow{I^-} 2H_2O(l) + O_2(g)$$

At the end of the reaction, the added KI remains qualitatively unchanged. Similarly, the rate of thermal decomposition of $KClO_3$ is increased when manganese(IV) oxide powder is added.

$$2KClO_3(s) \xrightarrow[\Delta]{MnO_2} 2KCl(s) + 3O_2(g)$$

Like in the first case, at the end of the chemical reaction the quality of MnO_2 also remains unchanged.

The mechanism of a catalytic process

The role of catalysts in chemical reactions is to offer an alternative route towards the formation of products through an elementary reaction with the lowest activation energy. Figure 7.7 shows a reaction profile for a catalysed and uncatalysed pathways of the same reaction.

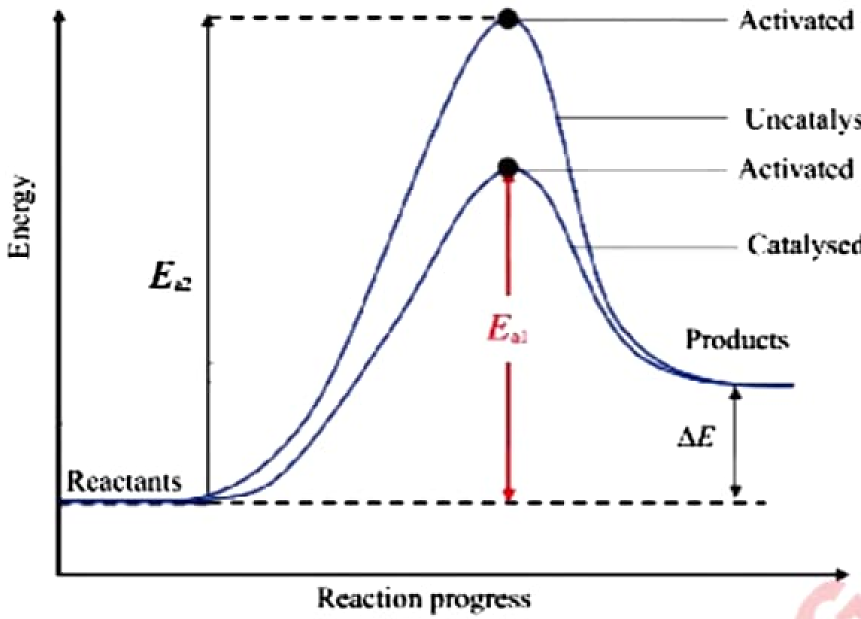


Figure 7.7: *Reaction profile for catalysed and uncatalysed pathways*

In Figure 7.7, the activated complex of a catalysed pathway is formed at lower activation energy (E_{a1}) compared to that of the uncatalysed reaction (E_{a2}). The catalyst favoured the reaction in an elementary step with the lower activation energy, hence a shorter time is taken for the reaction to complete.

Types of catalysis

Catalysis is classified based on the phase of a catalyst with respect to the phase(s) of the reactants. In this criterion, catalysis can either be homogeneous or heterogeneous. In *homogeneous catalysis*, a reactant and a catalyst are in the same phase. That is to say, if the reactant is in the gaseous phase, the catalyst must also be in gaseous phase for a catalytic process to be classified as homogeneous. An example of homogeneous catalysis is the reaction between ethyl acetate and water to form acetic acid and ethanol in the presence of hydrochloric acid as a catalyst. In the presence of HCl solution, the rate is faster than in its absence.

$$CH_3COOC_2H_5(l) + H_2O(l) \xrightleftharpoons{H^+} CH_3COOH(l) + C_2H_5OH(l)$$

Unlike homogeneous catalysis, *heterogeneous catalysis* involves reactants and catalyst which are in different phases. That is to say, when a reactant is in the liquid phase, a catalyst can be in the solid phase or vice versa. An example of heterogeneous catalysis is in the Haber process for ammonia production. The production of ammonia from hydrogen and nitrogen gases can be increased by decreasing the temperature. However, the reaction becomes too slow for the process to be economically feasible. Therefore, the reaction is catalysed by a solid phase iron with aluminium oxide.

$$N_2(g) + 3H_2(g) \xrightleftharpoons{Fe,\ Al_2O_3} 2NH_3(g)$$

Enzyme catalysis

Chemical processes which occur in living systems are catalysed by biological catalysts which are called *enzymes*. Almost every biologically important reaction is assisted by a specific enzyme. As the human body is designed to operate at an almost constant temperature of 37 °C, many biochemical reactions would have been too slow at this temperature without these enzymes. An example of enzyme catalysis is the reaction between carbon dioxide and water catalysed by carbonic anhydrase.

$$CO_2(g) + H_2O(l) \xrightleftharpoons[]{\substack{\text{carbonic}\\ \text{anhydrase}}} HCO_3^-(aq) + H^+(aq)$$

This reaction is important as it removes the CO_2 formed in the cell during metabolism.

Activity 7.6

Aim: To investigate the effect of a catalyst on the rate of reaction

Requirements: Hydrogen peroxide (H_2O_2) solution, potassium iodide (KI) solution, manganese(IV) oxide (MnO_2) powder, yeast, beakers, stopwatch or timer, and measuring cylinder

Procedure

1. Pour equal volumes of hydrogen peroxide solution (20 mL) into two separate beakers.
2. Add a small amount of manganese(IV) oxide (MnO_2) powder to one of the beakers as catalyst.
3. Start the stopwatch when the MnO_2 is added to the H_2O_2 solution.
4. Record the time taken for the appearance of any observable changes in the two beakers.
5. Repeat steps 1−4 for each catalyst given.

Questions

1. Did you observe any differences in the reaction rate between the solution with the catalyst and the solution without the catalyst? If so, which catalyst is the best?
2. How are the findings from this activity applicable to environmental remediation?

7.5.6 Light

Not all chemical reactions are affected by light except a few that usually form free radicals. Photochemical reactions are influenced by light. The photosynthesis process serves as an example of those reactions. Light activates some of the reactant molecules producing free radicals. Often, when a molecule absorbs a photon, the resulting excited state is much more chemically reactive than the molecule in its ground state. When photons of light strike the reactant molecules, it provides the necessary activation energy and enables the reaction to proceed at a faster rate.

Activity 7.7

Aim: To investigate the effect of light on the rate of reaction

Requirements: 2 M NaCl solution, 1 M $AgNO_3$ solution, test tubes, test tube rack, measuring cylinder and dropper

Procedure

1. To approximate 10 mL NaCl solution in a test tube, add a few drops of $AgNO_3$ solution.
2. Divide the precipitate formed into two parts in separate test tubes.
3. Put one of the test tubes into a dark environment and the other under the sunshine or any other light source.

Questions

1. What trend did you observe in the photochemical reaction rate under the two conditions?
2. In what real-world applications might the findings of this experiment be relevant?

Exercise 7.6

1. The reaction of dilute hydrochloric acid with magnesium ribbon is fairly slow whereas the reaction with the same mass of magnesium powder can be extremely vigorous. Explain.

2. Reflect on the role of catalysts in environmental remediation processes such as catalytic converters in automobiles. How do catalysts help reduce harmful emissions?

3. The disproportionation of H_2O_2 into H_2O and O_2 has an enthalpy of reaction of -98.2 kJ mol^{-1} and an activation energy barrier of 75.0 kJ mol^{-1}. Iodide ions act as a catalyst for the reaction with an activation energy barrier of 56.0 kJ mol^{-1}. The enzyme catalase is also a catalyst for this reaction, and its pathway has an activation barrier of 23.0 kJ mol^{-1}. Draw a labelled potential energy diagram for this process both with and without the catalysts.

4. The activation energy for a particular biochemical reaction is 42.0 kJ mol^{-1}. In the presence of an enzyme at 298 K, the rate constant for the reaction increases by a factor of 2.0×10^3 compared with uncatalysed reaction. Assuming that the collision frequency factor (A) is the same for both cases, calculate the activation energy for the catalysed reaction.

5. Consider the following chemical reaction with $\Delta H = +364$ kJ mol^{-1}.

   $$2NO(g) + H_2(g) \longrightarrow N_2O(g) + H_2O(g)$$

   What will the effect of increasing the reaction temperature be on the rate of this reaction?

6. Sucrose can be hydrolysed to produce two glucose molecules according to the reaction below.

   $$C_{12}H_{22}O_{11}(aq) + H_2O(l) \longrightarrow 2C_6H_{12}O_6(aq)$$

   The reaction rate is much faster if an acid is added to the reactants. Explain the role of the acid.

7.6 Reaction mechanisms

Reaction equations are symbolic presentation of chemical reactions which specify only the origin and destination of the reaction process. They do not actually tell much about how the reaction takes place. Most chemical reactions occur by a series of steps known as *elementary steps*. Therefore, reaction equations represent the sum of several elementary steps. A series of steps through which a certain chemical reaction passes to form products is called *reaction mechanism*.

Consider the reaction between NO and Br_2 to form NOBr. A proposed mechanism for this reaction is as follows:

$$\text{Step 1} \qquad NO(g) + NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g)$$

$$\text{Step 2} \qquad N_2O_2(g) + Br_2(g) \xrightarrow{k_2} 2NOBr(g)$$

Steps 1 and 2 are elementary steps. The net chemical equation which represents the overall reaction is given by the sum of the elementary steps.

$$\left.\begin{aligned} &\text{Step 1} \qquad NO(g) + NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \cancel{N_2O_2}(g) \\ &\text{Step 2} \qquad \cancel{N_2O_2}(g) + Br_2(g) \xrightarrow{k_2} 2NOBr(g) \end{aligned}\right\} +$$

The overall reaction is

$$2NO(g) + Br_2(g) \longrightarrow 2NOBr(g)$$

The sum of the elementary steps must give the accepted overall balanced equation for the reaction. Species such as N_2O_2 in the above example are called intermediates because they appear in the mechanism of the reaction but not in the overall balanced chemical equation. Intermediates are formed in an early elementary step and consumed in a later elementary step. They are neither reactants nor products but species which are formed and consumed in the course of the reaction to form products. By looking at the preceding example of the reaction mechanism, it can be deduced that two molecules are involved in the reaction in each of the two elementary steps. In step 1, two NO molecules are involved, and in step 2, N_2O_2 and Br_2 are involved. An elementary step in which two molecules are involved is referred to as a *bimolecular reaction*.

Elementary reactions involving one or three molecules (species) are called *unimolecular* and *termolecular*, respectively. The number of molecules reacting in an elementary step is called the *molecularity* of a reaction. When the rate laws for unimolecular, bimolecular and termolecular reactions are observed, they correspond to their reaction orders, respectively. For example, the rate law is always second-order for a bimolecular reaction. This is either of the form $k[A]^2$ for a step with a single reactant or $k[A][B]$ for a step involving two reactants. Generally, it can be concluded that a unimolecular elementary step is always first-order, a bimolecular elementary step is always second-order and a termolecular elementary step is always third-order.

If chemical reactions occur in a series of steps and if each step has its own rate, then it can be concluded that the step that proceeds at the slowest rate is that one which controls the overall reaction rate. An example of this is the rapid pouring of water through a funnel into a container. The water collects in the container at a rate essentially determined by the size of the funnel opening and not by the rate of pouring water into the funnel. The slowest step in the sequence of steps leading to product formation is called the *rate-determining step*. Thus, the rate-determining step gives the rate law for the overall process. The rate law expression that is obtained from the rate-determining step must agree with the experimentally determined rate law.

Note: Overall order of reaction should not be confused with molecularity. A reaction which is first-order overall may involve a number of bimolecular and unimolecular steps.

Exercise 7.7

1. For the chemical reaction

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

the experimentally determined rate law is:

Rate = $k[NO_2]^2$.

Show that the expression is consistent with the following reaction mechanism:

Step 1 $2NO_2(g) \rightleftharpoons N_2O_4(g)$ Slow

Step 2 $N_2O_4(g) \rightleftharpoons NO(g) + NO_3(g)$ Fast

Step 3 $NO_3(g) + CO(g) \rightleftharpoons NO_2(g) + CO_2(g)$ Fast

2. The chemical reaction

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

exhibits the following reaction mechanism:

$2NO(g) + 2O_2(g) \rightleftharpoons 2NO_3(g)$ Slow

$2NO_3(g) + NO_2(g) \longrightarrow 3NO_2(g) + O_2(g)$ Fast

Deduce its rate law.

3. With an example, how can the rate law of the elementary reaction be determined?

Revision exercise 7

1. The decomposition of a particular insecticide in water follows first-order kinetics with a rate constant of 1.45 year^{-1} at 277 K. A certain amount of this insecticide has been found in fish organs at a concentration of 5.0×10^{-5} g kg^{-1} of fish stored at the same temperature. Assume that the average temperature of the lake is 285 K.

   (a) Calculate the insecticide concentration after two years of storage.

   (b) How long will it take for the insecticide concentration to drop by 4.9×10^{-5} g kg^{-1}?

2. The decomposition of dimethyl ether $(CH_3)_2O$ at 783 K is a first-order process with a rate constant of $6.8 \times 10^{-4}\ \text{s}^{-1}$. If the initial pressure of $(CH_3)_2O$ is 135 atm, calculate its partial pressure after 1420 s.

   $$H_3C{-}O{-}CH_3(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

3. How does the half-life of a substance influence its handling, storage and disposal?

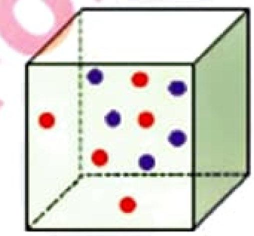
4. A particular drug with a half-life of 360 seconds is eliminated in the body via the first order reaction. How long will it take for the level of the drug in the body to fall to one-eighth of its original value?

5. Think about a scenario where a catalyst significantly speeds up a chemical reaction in your daily life. Describe the situation and explain how the catalyst works to increase its reaction rate.

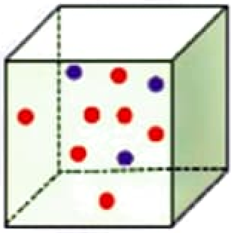
6. Consider the reaction

   $$A + B \longrightarrow C$$

   for which rate = $k[A][B]^2$. Each box below represents a reaction mixture in which A and B are shown as red and purple spheres, respectively. Rank these mixtures in the order of the increasing rate of the reaction.



1



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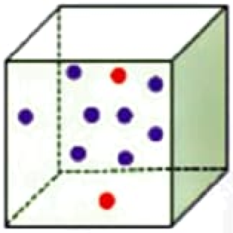


3

7. (a) Suggest any three methods you can use to determine the order of the reaction.

(b) In the Contact process, the oxidation of SO_2 to SO_3 is presented as follows:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

What is the relationship between the production rate of SO_3 and the consumption rate of O_2?

8. Ammonia (NH_3) decomposes to yield N_2 and H_2 according to the following chemical equation:

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

This reaction was studied on two surfaces of a catalyst and the following results were obtained:

Surface	Activation energy (E_a), kJ mol^{-1}
W	163
Os	197

Without the catalyst, the decomposition of NH_3 has an activation energy of 335 kJ mol^{-1}.

(a) Which surface is the best heterogeneous catalyst for the decomposition of ammonia? Give reasons.

(b) How often does the reaction occur at 298 K on the W surface compared with the reaction without a catalyst? Assume that the frequency factor (A) is the same for each reaction.

9. (a) Describe two requirements which must be met for a mechanism of a chemical reaction to be plausible.

(b) The rate law for the reaction

$$2BrO_3^-(aq) + 5SO_3^{2-}(aq) + 2H^+(aq) \longrightarrow Br_2(g) + 5SO_4^{2-}(aq) + H_2O(l)$$

is $\text{Rate} = k[BrO_3^-][SO_3^{2-}][H^+]$.

The first step in the proposed mechanism for the reaction is

$$SO_3^{2-}(aq) + H^+(aq) \longrightarrow HSO_3^-(aq) + H_2O(l) \qquad \text{(Fast)}$$

The second elementary reaction is the rate determining step. Write the possible second step for the mechanism.

10. Ethyl chloride decomposes on heating to give HCl and C_2H_4 according to the following reaction:

$$CH_3CH_2Cl(g) \longrightarrow HCl(g) + C_2H_4(g)$$

The decomposition rate of ethyl chloride was studied at 923 K and the following data were obtained.

Experiment	$[CH_3CH_2Cl]_0$, mol dm^{-3}	Initial Rate, mol dm^{-3} s^{-1}
1	0.010	1.6×10^{-8}
2	0.015	2.4×10^{-8}
3	0.030	4.8×10^{-8}
4	0.040	6.4×10^{-8}

(a) Use the data to calculate the rate constant and order of the reaction.

(b) If a sample of ethyl chloride with an initial concentration of 0.02 mol dm^{-3} is heated at 923 K, what is the concentration of ethyl chloride after 10 h and how long would it take for the concentration of ethyl chloride to decrease to 0.005 mol dm^{-3}?

11. The half-life for the first-order decomposition of nitramide

$$NH_2NO_2(aq) \longrightarrow N_2O(g) + H_2O(l)$$

is 124 min at 288 K. If 165 cm^3 of a 0.2 mol dm^{-3} NH_2NO_2 solution is allowed to decompose, how long must the reaction proceed to yield 50.0 cm^3 of N_2O collected over water at 288 K and a barometric pressure of 750 Torr? (The vapour pressure of water is 12.9 Torr).

12. (a) In a particular experiment for determining the rate constant at different temperatures, different rate constant values, k, were obtained. A plot of ln$k$ versus $1/T$ resulted in a straight line with a slope of -1.10×10^4 K and y-intercept of 33.3. Assume that k has units of s^{-1}. Determine the

activation energy (E_a) and the collision frequency factor (A) for this reaction.

(b) The following data were obtained from three reactions:

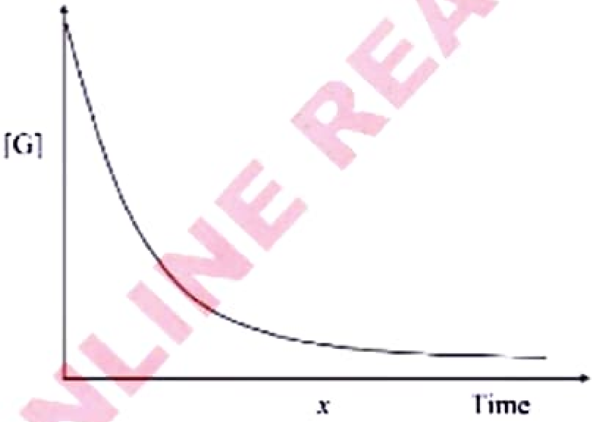
Reaction	ΔE, kJ mol^{-1}	E_a, kJ mol^{-1}
1	−10	+25
2	−10	+50
3	−50	+50

(i) For each case, sketch a rough energy profile diagram.

(ii) Assuming that the frequency factor (A) is the same for all the three reactions, determine which reaction will have the greatest rate at 298 K.

13. For the reaction

$G(g) \longrightarrow E(g)$, a plot of [G] versus time gives the following graph:



(a) How can the reaction rate at time x be determined?

(b) Plot the graph of [E] versus time.

Chapter Eight

Electrochemistry

Introduction

Electrochemistry offers a promising field of chemistry with a range of applications in various areas, such as the manufacture of storage batteries, extraction and purification of metals in the mining industry, and coating of metals for durability and appearance. In this chapter, you will learn about the electrochemical cells, electrode potential, and application of electrochemistry in real life situations. The competencies developed are vital for developing and improving various technologies in batteries, fuel cells, electrochemical sensors, corrosion protection systems, electroplating processes, and electrolytic production of metals and chemicals.

Think

A world without electrochemistry

8.1 Electrochemical cells

Task 8.1

Use online resources to explain various industries and scientific disciplines that apply the knowledge of electrochemistry.

Electrochemical cells are fundamental devices that convert chemical energy into electrical energy or vice versa through reduction-oxidation (redox) reactions. The cells allow the flow of electrons during the redox reactions to produce electrical energy or drive non-spontaneous chemical processes. Understanding the principles behind electrochemical cells is crucial for advancing fields that involve redox reactions. These include renewable energy generation, battery technology, and electrochemical sensors.

8.1.1 Types of electrochemical cells

Task 8.2

Watch online videos that show electrochemical cells and describe their basic working principle. Share your findings with your colleagues.

Electrochemical cells are classified into galvanic (voltaic) cells and electrolytic cells based on the general thermodynamic nature of the reaction (i.e. spontaneous or non-spontaneous). Galvanic cells spontaneously generate electrical energy from the chemical reactions occurring within them. The terms galvanic and voltaic are often used interchangeably to describe the same type of cell, emphasising the dual legacy of Luigi Galvani and Alessandro Volta in developing electrochemical cells. Electrolytic cells use external electrical energy to drive non-spontaneous redox reactions allowing for processes such as electroplating, electrolysis and chemical synthesis. Both galvanic and electrolytic cells have two electrodes called the anode and cathode where the redox reactions take place. The oxidation half-reaction takes place at the anode and the reduction half-reaction takes place at the cathode. In a galvanic cell, the anode is negative because of the electrons resulting from the oxidation reaction, and the cathode is positive. For an electrolytic cell, the anode is positive as it attracts negatively charged ions from the solution whereas the cathode is negative and attracts positive ions.

Differences between galvanic and electrolytic cells

Although the two types of electrochemical cells share some similarities, they also have distinct differences in their operation. Table 8.1 summarises the main differences between galvanic and electrolytic cells.

Table 8.1: *The differences between galvanic and electrolytic cells*

S/N	Galvanic cell	Electrolytic cell
1	Converts chemical energy to electrical energy	Converts electrical to chemical energy
2	Operates under spontaneous conditions	Operates under non-spontaneous conditions
3	The anode carries negative sign while the cathode has a positive sign	The anode has a positive sign while the cathode has a negative sign
4	$E^{\circ}_{\text{cell}} > 0$ while $\Delta G^{\circ} < 0$	The $E^{\circ}_{\text{cell}} < 0$ while $\Delta G^{\circ} > 0$
5	Electrons flow from the anode to the cathode in external circuit	Electrons enter the circuit through the cathode and leave by the anode.

8.1.2 The salt-bridge

Redox reactions involve the transfer of electrons from the reducing agent to an oxidising agent. The reactions can either take place in the same solution or between two solutions kept separately. The separated half-cells are connected with an external wire that allows the flow of electrons from the reducing agent to the oxidising agent. In this arrangement, conventionally the oxidation half-cell (anode) is placed on the left-hand side and the reduction half-cell (cathode) is placed on the right-hand side (Figure 8.1).

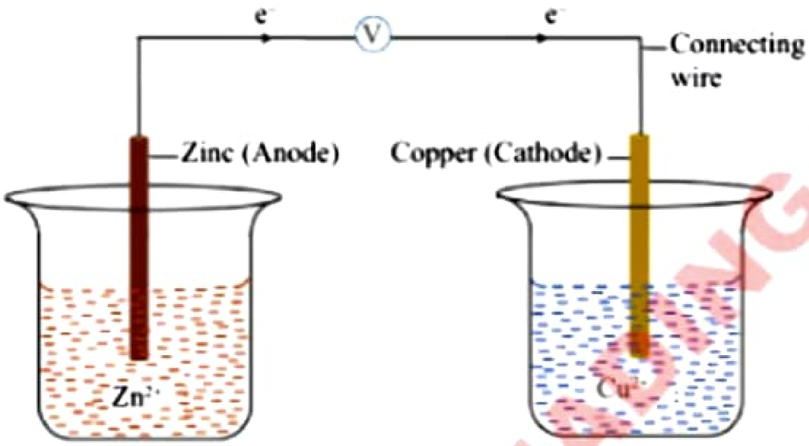


Figure 8.1: *Oxidising and reducing agent of the two compartments of electrochemical cell*

When the two half-cells are connected as in Figure 8.1, current flows for a short time and then ceases. This is because the flow of electrons from zinc electrode to copper electrode results into the build-up of charge in the two compartments. That is to say there is accumulation of Zn^{2+} in the anode compartment. To sustain the flow of electrons under these conditions, a great amount of energy which is practically not feasible is required, . This problem can be solved by connecting the two solutions with a salt-bridge as shown in Figure 8.2. A *salt-bridge* is a U-shaped tube filled with a concentrated solution of an inert electrolyte sealed by cotton plugs. The contents of the U-tube (normally solutions of KCl, Na_2SO_4, KNO_3 or NH_4NO_3) are called inert electrolytes because they do not undergo any chemical change or participate directly in the electrochemical process occuring within the cell. Therefore, the salt bridge completes the circuit and allows ions to flow without extensive mixing of the solutions.

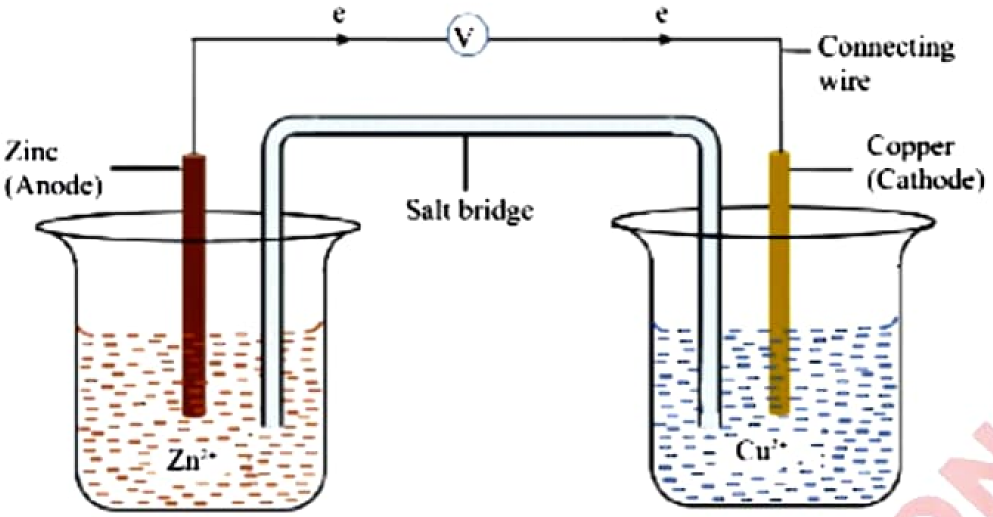


Figure 8.2: *Electrochemical cell made up of copper and zinc half cells connected with a salt bridge*

Figure 8.2 is a special type of galvanic cell called the *Daniell cell* named in favour of the British chemist, John Frederick Daniell (1770-1845). The cell consists of a zinc electrode on the anode immersed in a zinc sulfate solution and a copper electrode at the cathode immersed in a copper(II) sulfate solution.

From the standard reduction potential values, zinc has a greater tendency of losing electrons than copper. Therefore, the copper electrode will withdraw electrons from the zinc electrode, and the following half-reactions will take place at the electrodes.

At zinc electrode $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

At copper electrode $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Overall redox reaction $Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$

In a galvanic cell, there is a constant flow of electrons, resulting in a generation of electricity. An electric current flows from the anode to the cathode because of the existing difference in electrode potentials between the electrodes which act as the driving force of the electric current. This difference in potential is measured by a voltmeter. The reading on the voltmeter indicates the cell voltage which is also known as *cell electromotive force* (*emf*) or *cell potential*. When a galvanic cell operates spontaneously, its cell potential is positive, ($E_{cell} > 0$).

Activity 8.1

Aim: To construct a Daniell cell

Requirements: Zinc strip, copper strip, zinc sulfate solution (about 1 M), copper(II) sulfate solution (about 1 M), potassium nitrate solution (about 2 M), glass beakers, salt bridge or porous barrier e.g. soaked paper towel, voltmeter and connecting wires with crocodile clips

Procedure

1. Fill one beaker with zinc sulfate solution and the other with copper(II) sulfate solution.
2. Place the zinc strip in the zinc sulfate solution and the copper strip in the copper(II) sulfate solution.
3. Connect the zinc sulfate solution and the copper sulfate solution using a salt bridge or porous barrier, ensuring that the salt bridge does not touch the respective electrodes as shown in Figure 8.2.
4. Connect the zinc strip to the negative terminal and the copper strip to the positive terminal of the voltmeter using connecting wires with the crocodile clips.
5. Record the reading on the voltmeter regulary to observe any changes over time.

Questions

1. What are the observations at each electrode during the operation of the Daniell cell?
2. How does the Daniell cell generate electrical energy?
3. What will happen to the Daniell cell if the salt bridge is removed?

8.2 Electrode potential

When a metal is dipped into the solution containing its ions, a potential difference is developed between the surface of the metal and the solution. This potential is known as electrode potential which is a measure of the tendency of the metal to provide electrons.

The electrode immersed in a solution containing its ions as in Figure 8.3 constitutes a half-cell. Each half-cell has its own electrode potential or half-cell potential. To measure electrode potential or half-cell potential in each case, a second electrode is needed. A voltmeter has to be connected to the external circuit across the two electrodes. The reading on the voltmeter will be the sum of the electrode potentials of the two electrodes. Therefore, in order to obtain the electrode potential of a particular half-cell, a reference electrode with known potential is used.

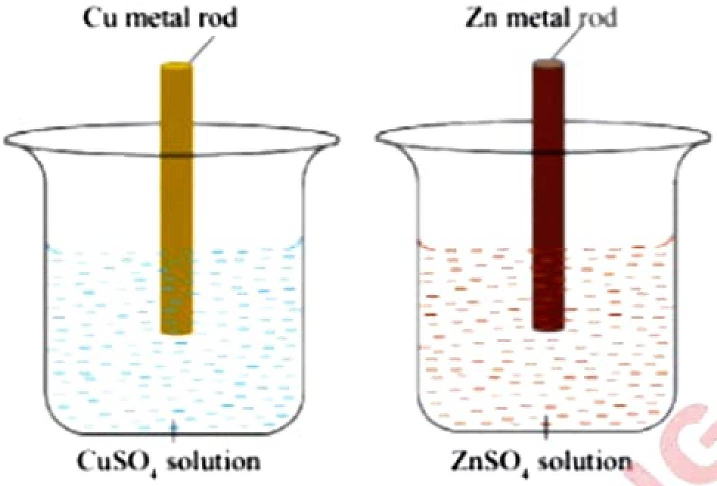


Figure 8.3: *Copper and zinc electrodes in their respective solutions*

The hydrogen electrode has been chosen as the standard electrode against which electrode potentials of other elements can be measured. The electrode potential for the hydrogen electrode is arbitrarily assigned a value of 0.00 V. Hence, when a standard hydrogen electrode is connected to copper electrode (Figure 8.4), the reading on the voltmeter is assumed to be the potential of the copper electrode. The standard hydrogen electrode consists of platinum foil immersed in a 1.0 M solution of H^+, a hydrogen gas at 1 atmosphere pressure bubled over the platinum foil, and a temperature of the electrolyte of 25°C.

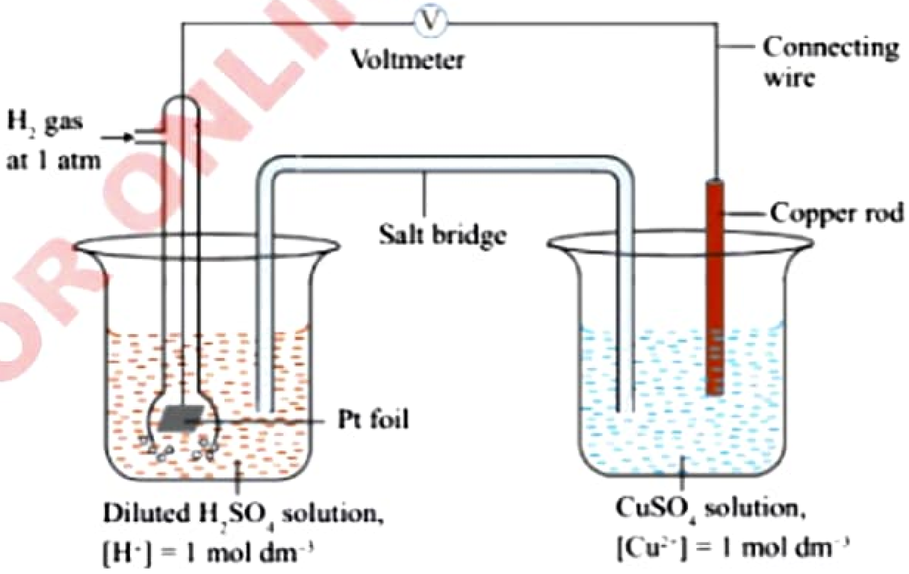


Figure 8.4: *Setup for the measurement of the electrode potential of copper*

The electrode potential of an element measured against standard hydrogen electrode as a reference electrode and ions of the element which equals to 1 mol dm^{-3} at standard conditions is called *standard electrode potential*, (E°). During this measurement, the hydrogen electrode is the anode and the metal is the cathode. The redox reactions occuring in the electrochemical cell during the measurement of electrode potential of copper (Figure 8.4) are:

At the anode: $H_2(g) \longrightarrow 2H^+(aq) + 2e^-$ (Oxidation) $E^\circ = 0.00$ V

At the cathode: $Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$ (Reduction) $E^\circ = 0.34$ V

The overall redox reaction equation is

$$H_2(g) + Cu^{2+}(aq) \longrightarrow 2H^+(aq) + Cu(s) \qquad E^\circ = 0.34 \text{ V}$$

The hydrogen gas is oxidised and the Cu^{2+} is reduced. Therefore, the potential difference which is measured by the voltmeter is the driving force for the reduction process of Cu^{2+}. This is called a reduction potential of the element. If it is measured under standard conditions, it is called *standard reduction potential*.

Each element has its own value of standard reduction potential. When the values of the standard reduction potentials of elements are arranged from negative to positive values, the obtained series is called an *electrochemical series*. The most negative values are placed at the top of the electrochemical series and the most positive at the bottom (Table 8.2).

Table 8.2: *Electrochemical series of elements*

Increasing reducing strength

Half reaction	E° (V)
$Li^{+}(aq) + e^{-} \longrightarrow Li(s)$	-3.05
$K^{+}(aq) + e^{-} \longrightarrow K(s)$	-2.92
$Ca^{2+}(aq) + 2e^{-} \longrightarrow Ca(s)$	-2.76
$Na^{+}(aq) + e^{-} \longrightarrow Na(s)$	-2.71
$Mg^{2+}(aq) + 2e^{-} \longrightarrow Mg(s)$	-2.37
$Al^{3+}(aq) + 3e^{-} \longrightarrow Al(s)$	-1.66
$Mn^{2+}(aq) + 2e^{-} \longrightarrow Mn(s)$	-1.18
$Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn(s)$	-0.76
$Cr^{3+}(aq) + 3e^{-} \longrightarrow Cr(s)$	-0.73
$Fe^{2+}(aq) + 2e^{-} \longrightarrow Fe(s)$	-0.44
$Cd^{2+}(aq) + 2e^{-} \longrightarrow Cd(s)$	-0.40
$Ni^{2+}(aq) + 2e^{-} \longrightarrow Ni(s)$	-0.23
$Sn^{2+}(aq) + 2e^{-} \longrightarrow Sn(s)$	-0.14
$Pb^{2+}(aq) + 2e^{-} \longrightarrow Pb(s)$	-0.126
$Fe^{3+}(aq) + 3e^{-} \longrightarrow Fe(s)$	-0.04
$2H^{+}(aq) + 2e^{-} \longrightarrow H_2(g)$	0.00
$Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$	+0.34
$I_2(g) + 2e^{-} \longrightarrow 2I^{-}(aq)$	+0.54
$Fe^{3+}(aq) + e^{-} \longrightarrow Fe^{2+}(aq)$	+0.77
$Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)$	+0.80
$Hg^{2+}(aq) + 2e^{-} \longrightarrow Hg(s)$	+0.89
$Br_2(g) + 2e^{-} \longrightarrow 2Br^{-}(aq)$	+1.07
$O_2(g) + 4H^{+}(aq) + 4e^{-} \longrightarrow 2H_2O(l)$	+1.23
$Cl_2(g) + 2e^{-} \longrightarrow 2Cl^{-}(aq)$	+1.36
$Au^{3+}(aq) + 3e^{-} \longrightarrow Au(s)$	+1.50
$MnO_4^{-}(aq) + 8H^{+}(aq) + 5e^{-} \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$F_2(g) + 2e^{-} \longrightarrow 2F^{-}(aq)$	+2.87

Increasing oxidising strength

8.2.1 Applications of electrochemical series

The relative position of a metal in the electrochemical series is a useful technique in predicting its reducing or oxidising ability. Metals with positive electrode potentials have higher tendency to accept electrons and therefore, are better oxidising agents, $M^+ + e^- \rightarrow M$. However, metals with negative electrode potentials have greater tendency to lose electrons and therefore, are better reducing agents, $M \rightarrow M^+ + e^-$. This entails that the metals with higher electrode potential (more positive) will be reduced by the metals with lower electrode potential (less positive) in the electrochemical series. The following points are important regarding electrochemical series of elements:

(a) *Predicting the oxidising or reducing ability of a metal*

The electrode potentials arranged in order of increasing $E^\circ_{\text{electrode}}$ values, place the oxidising agents in increasing order of their ability to attract electrons. Thus:

(i) The more positive the value of $E^\circ_{\text{electrode}}$, the better the oxidising ability of the ion, element or compound.

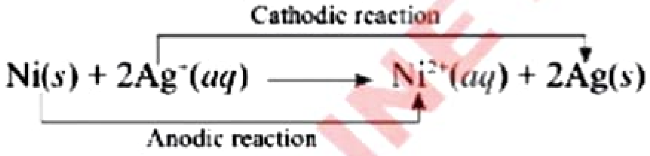
(ii) The more negative the value of $E^\circ_{\text{electrode}}$, the better the reducing ability of the ion, element or compound.

(iii) Any substance in the series will spontaneously reduce any other substance lower than it in the series.

(b) *Predicting cell emf*

The standard *emf* of a cell is obtained as the difference between the E° values of the cathode and the anode electrodes which is given by: $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

For example, predict the *emf* of the reaction:



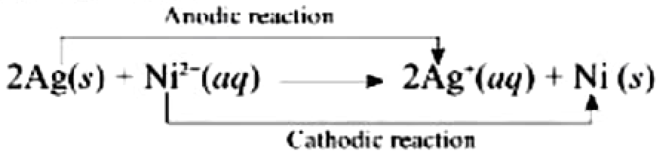
$$\text{Ni}(s) + 2\text{Ag}^+(aq) \longrightarrow \text{Ni}^{2+}(aq) + 2\text{Ag}(s)$$

From E° values in Table 8.2, $E^\circ_{\text{cathode}} = +0.80\ \text{V}$ and $E^\circ_{\text{anode}} = -0.23\ \text{V}$

Therefore $E^\circ_{\text{cell}} = +0.80\ \text{V} - (-0.23\ \text{V}) = +1.03\ \text{V}$

(c) *Predicting the feasibility of a reaction*

The electrochemical series can be used to predict whether a redox reaction will occur or not, *i.e.*, reaction feasibility. This is done by calculating the net *emf* of the cell. If E°_{cell} is positive, the reaction is feasible and when E°_{cell} is negative, the redox reaction is not feasible. For example, predict whether the following reaction is feasible:



$$2\text{Ag}(s) + \text{Ni}^{2+}(aq) \longrightarrow 2\text{Ag}^+(aq) + \text{Ni}(s)$$

From Table 8.2, $E^{\circ}_{\text{cathode}} = -0.23\ \text{V}$ and $E^{\circ}_{\text{anode}} = +0.80\ \text{V}$

Therefore, $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = -0.23\ \text{V} - 0.80\ \text{V} = -1.03\ \text{V}$
Since the standard cell potential is negative, then the reaction is not feasible.

(d) *Predicting the preferential displacement of metal from its salt solution*

As stated previously, metals lower in the electrochemical series are stronger oxidising agents. Contrarily, metals at the top of the series are strong reducing agents and they are oxidised to their ions. For instance, zinc which is found higher in the series is oxidised to Zn^{2+} while copper which is located lower in the series is produced by reduction of Cu^{2+}. In this process, the following half reactions occur:

Anode reaction: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e$

Cathode reaction: $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$

Therefore, when zinc is placed in $CuSO_4$ solution, copper metal is precipitated. Generally, it can be said that a metal higher in the series can precipitate the metal lower in the series. So, silver metal cannot precipitate nickel from aqueous solution since silver metal is lower in the series and is a strong oxidising agent.

(e) *Predicting the preferential displacement of hydrogen from a dilute acid solution*

Metals found above hydrogen in the electrochemical series are stronger reducing agents than hydrogen and can reduce H^{+} to H_2. However, metals found below hydrogen in the series are weaker reducing agents than hydrogen and therefore cannot convert H^{+} to H_2. This justifies, for example, why Zn reacts with dilute sulfuric acid to liberate hydrogen gas while copper does not react with dilute sulfuric acid.

8.2.2 Standard cell potential

The measured potential of a voltaic cell is affected by factors like changes in concentration, temperature, pressure, and energy loss. Therefore, in order to compare the output of different cells, a standard cell potential has to be considered. The *standard cell potential* is the potential of the cell measured at standard conditions (temperature of 298 K, concentrations of the reactants and products are 1 mol dm^{-3} and 1 atm pressure for gases). Just as each part of a half-reaction contributes to the overall reaction, the potential of each half- cell also makes up a part of the overall standard cell potential.

Focusing on the Daniel cell (Figure 8.2), the electrons flow spontaneously from the zinc electrode (anode) toward the copper electrode (cathode) because zinc is a stronger reducing agent than copper. Therefore, to obtain a positive E°_{cell}, E°_{zinc} is subtracted from E°_{copper}. That is,

$$E^\circ_{cell} = E^\circ_{copper} - E^\circ_{zinc}$$

Generally, the standard cell potential is the difference between the standard electrode potential of the cathode (reduction half-cell) and the standard electrode potential of the anode (oxidation half-cell). Thus,

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} \qquad (8.1)$$

8.2.3 Cell diagram or cell notation

Instead of writing a full chemical equation of a redox reaction, a cell diagram or cell notation can be used. A cell diagram is a shorthand notation used to represent electrochemical cells and their reactions. It provides a concise and standardised way to represent the components and conditions of a cell.

For the cell shown in Figure 8.2, if the concentrations of Zn^{2+} and Cu^{2+} are 1 M, the cell diagram is

$$Zn(s)/Zn^{2+}(aq)(1\,M)\,//\,Cu^{2+}(aq)(1\,M)/Cu(s)$$

In the cell diagram, the single vertical line represents phase boundary between the solution and the electrode and double vertical lines represent salt bridge. Conventionally, cell diagrams are written by using the following rules:

(a) The anode is written on the left hand side of the salt bridge and the cathode on the right hand side.

(b) The anodic half-cell is represented by writing the metal first followed by a single vertical line and then metal ions present, for example, $Zn(s)/Zn^{2+}(aq)$.

(c) The magnitude of the concentration in mol dm^{-3} of the solution in which the anode electrode is dipped is written in brackets after the oxidation half reaction in a cell diagram, for example, $Zn(s)/Zn^{2+}(aq)$ (1 mol dm^{-3}).

(d) The cathodic half-cell is represented by first writing the metal ion of the electrolyte in solution, and then the metal. The metal ion and the metal are separated by a single vertical line, for example, $Cu^{2+}(aq)/Cu(s)$.

(e) The molar concentration or activity of the solution is written in brackets after the formula of the ion just like in the anodic cell, for example, $Cu^{2+}(aq)(1\,M)/Cu(s)$.

Note that when the reactants or products of the same phase are more than one, they are separated by a semicolon as demonstrated in the cathodic reaction of the following cell diagram:

$$Fe(s)/Fe^{2+}(aq)(1\ M)//MnO_4^-(aq)(1\ M);\ Mn^{2+}(aq)(1\ M);\ H^+(aq)(1\ M)/H_2,\ Pt$$

Example 8.1

Calculate the standard *emf* of the cells formed by the following combination of half cells:

(a) Zinc and copper half cells are considered

(b) Copper and silver half cells are considered

Solution

In galvanic cells, a half-cell with more positive or less negative electrode potential acts as a cathode while that having less positive or more negative electrode potential acts as an anode. Based on these facts:

(a) When zinc and copper half-cells are considered,

$$E^o_{\text{Anode}} = E^o_{Zn/Zn^{2+}},\ E^o_{\text{Cathode}} = E^o_{Cu^{2+}/Cu}$$

$$E^o_{\text{cell}} = E^o_{Cu^{2+}/Cu} - E^o_{Zn^{2+}/Zn}$$

Substituting the values of $E^o_{Zn^{2+}/Zn}$ and $E^o_{Cu/Cu^{2+}}$ into the equation, gives:

$$E^o_{\text{cell}} = 0.34\ V - (-0.76\ V) = 1.1\ V$$

Therefore, the standard emf in this cell is 1.1V.

(b) When copper and silver half-cells are considered,

$$E^o_{\text{Cathode}} = E^o_{Ag^+/Ag},\ E^o_{\text{Anode}} = E^o_{Cu/Cu^{2+}}$$

$$E^o_{\text{cell}} = E^o_{Ag^+/Ag} - E^o_{Cu^{2+}/Cu}$$

Substituting the given values of $E^o_{Ag^+/Ag}$ and $E^o_{Cu/Cu^{2+}}$

$$E^o_{\text{cell}} = 0.8\ V - 0.34\ V = 0.46\ V$$

Therefore, the standard *emf* in this case is 0.46 V.

8.3 The dependence of cell potential on concentration

For any galvanic cell, when temperature and pressure of gases are not in standard conditions, the *emf* of the galvanic cell differs from its standard *emf* value. It can be less or greater than its standard cell potential. To understand this phenomenon, consider the following reversible redox reaction:

$$Mg(s) + Pb^{2+}(aq) \rightleftharpoons Mg^{2+}(aq) + Pb(s)$$

Under standard conditions, this cell has standard cell potential of 2.24 V. Applying the *Le Châteliers Principle*, an increase in the concentration of Pb^{2+} will favour the forward reaction that results into an increase in the driving force of the electrons and the corresponding increase in the cell potential. At the same time, an increase in the concentration of the product, Mg^{2+} will favour the backward reaction, thus, decreasing the cell potential. The maximum cell potential is obtained when there is no current flow. When the current flows, the cell discharges and the concentrations change; as a result, the E_{cell} also changes. The following equations are examples which distinguish the cell potential at standard and non-standard conditions:

$$\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(1.0\ \mathrm{M}) \longrightarrow \mathrm{Zn}^{2+}(1.0\ \mathrm{M}) + \mathrm{Cu}(s) \qquad E^{\circ}_{cell} = 1.103\ \mathrm{V}$$

$$\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(0.075\ \mathrm{M}) \longrightarrow \mathrm{Zn}^{2+}(1.5\ \mathrm{M}) + \mathrm{Cu}(s) \qquad E^{\circ}_{cell} = 1.064\ \mathrm{V}$$

Any galvanic cell will spontaneously discharge until it reaches equilibrium, a point at which the reaction quotient becomes equal to the equilibrium constant. That is, $Q = K$ and $E_{cell} = 0$. At this point, a cell or battery is said to be dead. A *dead battery* is the one in which its cell reaction has reached equilibrium. At this state, there is no more driving force to push electrons through the external wire.

8.3.1 Relationship between free energy and cell potential

In galvanic cells, chemical energy is converted to electrical energy. The electrical energy that is generated as the result of the chemical reaction is equal to the product of the *emf* of the cell and the total charge that passes through the electrochemical cell. Thus,

Electrical energy (J) = maximum cell potential (V) × total electrical charge (C)

However, the total charge is obtained by multiplying the number of moles, (n), of electrons that pass through the circuit by the electrical charge contained in 1 mol of electrons. Thus;

$$\text{Total electrical charge} = nF$$

Substituting the value of total electrical charge into the electrical energy equation under standard states leads to:

$$\text{Electrical energy} = -E^{\circ}_{cell} \times nF$$

The negative sign on the right-hand side of the equation indicates that the system works on the surroundings. In accordance with Gibbs, the energy released by a chemical reaction and which is used to perform a certain work is called *Gibbs free energy*, (*G*). This energy is equal to the difference in free energies between the final and initial stages of the reaction. The change in the Gibbs free energy like the change in electrode potential is the driving force of the reaction. The electrical energy is therefore equivalent to the change in the Gibbs free energy, (ΔG), and under standard states it is given by:

$$\Delta G^\circ = -nFE^\circ \tag{8.2}$$

The free energy of the system at the initial stage is

$$G_i = -RT\ln Q \tag{8.3}$$

and at the final or equilibrium stage it is

$$G_f = -RT\ln K \tag{8.4}$$

where Q and K represent reaction quotient and equilibrium constant, respectively.

Subtracting Equation 8.3 from Equation 8.4, ΔG is obtained as follows:

$$\Delta G = G_f - G_i = RT\ln Q - RT\ln K$$

$$\Delta G = RT(\ln Q - \ln K) \tag{8.5}$$

The change in Gibbs free energy in the electrochemical cell system represents the maximum amount of useful work (energy) that can be obtained from a redox reaction (Equation 8.2). When the initial state is at standard conditions, $\Delta G = \Delta G^\circ$ and $Q = 1$, Equation 8.5 will take the form:

$$\Delta G^\circ = RT\ln 1 - RT\ln K \text{ or}$$

$$\Delta G^\circ = -RT\ln K \tag{8.6}$$

Substituting Equation 8.6 into Equation 8.5 leads to:

$$\Delta G = \Delta G^\circ + RT\ln Q \tag{8.7}$$

where ΔG is change in Gibbs free energy, ΔG° is change in standard Gibbs free energy, R is universal gas constant, T is Kelvin temperature, and Q is the reaction quotient.

From Equation 8.2, $\Delta G^\circ = -n\text{F}E^\circ$ and $\Delta G = -n\text{F}E$. Substituting these values into Equation 8.7 leads to:

$$-n\text{F}E = -n\text{F}E^\circ + RT\ln Q \tag{8.8}$$

Dividing each side of the equation by $-n$F gives:

$$E = E^\circ - \frac{RT}{n\text{F}}\ln Q \tag{8.9}$$

where R, T, and F are constant with their values equal to 8.314 J $\text{mol}^{-1}\,\text{K}^{-1}$, 298 K and 96500 C mol^{-1}, respectively. Equation 8.9 is known as the *Nernst Equation*. Substituting the values of the constant terms and changing natural logarithm to common logarithm, Equation 8.9 has the form:

$$E = E^{\circ} - \frac{0.0591}{n} \log Q \qquad (8.10)$$

The Nernst Equation can be used to determine the *emf* of a cell at any given concentrations of the components in the redox reaction. For the electrode reaction,

$$M^{n+}(aq) + ne^{-} \longrightarrow M(s)$$

the electrode potential at any concentration measured with respect to standard hydrogen electrode potential is:

$$E_{(M^{n+}/M)} = E^{\circ}_{(M^{n+}/M)} - \frac{0.0591}{n} \log \frac{[M]}{[M^{n+}]} \qquad (8.11)$$

For the electrode reaction,

$$Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$$

Equation 8.11 will have the form:

$$E_{(Cu^{2+}/Cu)} = E^{\circ}_{(Cu^{2+}/Cu)} - \frac{0.0591}{2} \log \frac{[Cu]}{[Cu^{2+}]}$$

The concentration of the solid reactant is taken as unit; therefore, for Cu^{2+}/Cu, Equation 8.11 can be written as:

$$E_{(Cu^{2+}/Cu)} = E^{\circ}_{(Cu^{2+}/Cu)} - \frac{0.0591}{2} \log \frac{1}{[Cu^{2+}]}$$

Generally,

$$E_{half-cell} = E^{\circ}_{half-cell} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]} \qquad (8.12)$$

Considering a Daniell cell, the electrode potentials of the half-cells are:

$$E_{(Cu^{2+}/Cu)} = E^{\circ}_{(Cu^{2+}/Cu)} - \frac{0.0591}{2} \log \frac{1}{[Cu^{2+}]}$$

$$E_{(Zn^{2+}/Zn)} = E^{\circ}_{(Zn^{2+}/Zn)} - \frac{0.0591}{2} \log \frac{1}{[Zn^{2+}]}$$

Substituting the equations of $E_{(Cu^{2+}/Cu)}$ and $E_{(Zn^{2+}/Zn)}$ into Equation 8.1 and rearranging the obtained equation gives:

$$E_{(Cu^{2+}/Cu)} = \left(E^\circ_{(Cu^{2+}/Cu)} - \frac{0.0591}{2}\log\frac{1}{[Cu^{2+}]}\right) - \left(E^\circ_{(Zn^{2+}/Zn)} - \frac{0.0591}{2}\log\frac{1}{[Zn^{2+}]}\right)$$

$$E_{cell} = (E^\circ_{(Cu^{2+}/Cu)} - E^\circ_{(Zn^{2+}/Zn)}) + \frac{0.0591}{2}\left(\log\frac{1}{[Zn^{2+}]} - \log\frac{1}{[Cu^{2+}]}\right)$$

$$E_{cell} = \Delta E^\circ + \frac{0.0591}{2}\log\frac{[Cu^{2+}]}{[Zn^{2+}]} \qquad (8.13)$$

Therefore, the Nernst Equation can generally be written as

$$E_{cell} = \Delta E^\circ + \frac{0.0591}{n}\log\frac{[\text{reduced species}]}{[\text{oxidised species}]} \qquad (8.14)$$

Equation 8.14 shows that for an electrochemical cell in which usually ΔE° and n are constants, the E_{cell} depends only on the concentration of the components taking part in the redox reaction.

Example 8.2

An electrochemical cell is constructed based on the following redox reaction:

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

If the concentrations of copper and zinc are 5.0 mol dm^{-3} and 0.05 mol dm^{-3}, respectively, calculate the *emf* of this cell at 298 K given that:

$E^\circ_{Cu^{2+}/Cu} = 0.34$ V and $E^\circ_{Zn^{2+}/Zn} = -0.76$ V.

Solution

From the redox reaction,

Zn^{2+} is the oxidised species, Cu^{2+} is the reduced species and the number of electrons involved in the reaction, $(n) = 2$. The standard *emf* of the cell is given by:

$$E^\circ_{Cell} = E^\circ_{Cu^{2+}/Cu} - E^\circ_{Zn/Zn^{2+}}$$

Substituting the values of $E^\circ_{Zn/Zn^{2+}}$ and $E^\circ_{Cu^{2+}/Cu}$ into the equation, gives:

$$E_{cell} = 0.34\text{ V} - (-0.76\text{ V}) = 1.10\text{ V}$$

Applying the Nernst Equation,

$$E_{cell} = \Delta E^\circ + \frac{0.0591}{n}\log\frac{[\text{reduced species}]}{[\text{oxidised species}]}$$

and substituting the values of ΔE°_{cell}, n, [oxidised species] and [reduced species] into the equation, results into:

$$E_{cell} = 1.10\,V + \left(\frac{0.0591}{2}\log\left(\frac{5\,M}{0.05\,M}\right)\right)V$$

$$E_{cell} = 1.10\,V + \left(\frac{0.0591}{2}\log 100\right)V$$

$$E_{cell} = 1.10\,V + \frac{0.0591}{2}V \times 2 = 1.10\,V + 0.0591\,V = 1.16\,V$$

Therefore, the *emf* of the cell (E_{cell}) is 1.16 V

Example 8.3

Calculate the voltage produced by the cell

$Sn(s)/Sn^{2+}(aq)$ (1.7 M)//$Ag^{+}(aq)$ (0.15 M)/$Ag(s)$ at 298 K.

Given $E^{o}Sn^{2+}/Sn = -0.14V$, $E^{o}Ag^{+}/Ag = 0.80V$

Solution

From the Nernst Equation,

$$E_{cell} = \Delta E^{o} + \frac{0.0591}{n}\log\frac{[\text{reduced species}]}{[\text{oxidised species}]}$$

Calculate the value of ΔE^{o}.

$Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^{-}$	$E^{o} = 0.14\,V$
$2Ag^{+}(aq) + 2e^{-} \longrightarrow 2Ag(s)$	$E^{o} = 0.80\,V$
$2Ag^{+}(aq) + Sn(s) \longrightarrow 2Ag(s) + Sn^{2+}(aq)$	$E^{o} = 0.94\,V$

Substituting the values in the Nernst Equation,

$$E_{cell} = \Delta E^{o} + \frac{0.0591}{n}\log\frac{[Ag^{+}]^{2}}{[Sn^{2+}]}$$

$$E_{cell} = 0.94 + \frac{0.0591}{2}\log\left(\frac{(0.15)^{2}}{1.7}\right) = 0.88\,V$$

Therefore, the voltage produced by the cell is 0.88 V.

Exercise 8.1

1. Given the standard electrode potential values of the following half-cells:

   $Ag^{+}(aq)/Ag(s)$ $E^\circ = 0.80$ V

   $Zn^{2+}(aq)/Zn(s)$ $E^\circ = -0.76$ V

   (a) Write the balanced half-equations and the overall cell reaction.

   (b) Calculate the standard *emf* of the cell.

   (c) Write the conventional cell diagram (cell notation).

2. Use the Nernst equation to calculate the reduction potential of the following half-cell reactions at 298 K.

   (a) $Cu(s)/Cu^{2+}(aq)$ (0.1 mol dm^{-3})

   (b) $Cu(s)/Cu^{2+}(aq)$ (1.5×10^{-5} mol dm^{-3})

3. (a) Use the data from Table 8.2 and any other knowledge to account for the following observations:

   (i) Pale blue solution of copper(II) sulfate disappears when iron rod is dipped in it.

   (ii) It is improper to use nickel spatula to stir a solution of copper(II) sulfate.

   (b) Use the Nernst equation to calculate the pressure of H_2 gas that will be required to make the *emf* of the hydrogen electrode equal to zero in a solution of 1 mol dm^{-3} at 298 K.

4. Given the following chemical equations:

   (a) $2Br^{-}(aq) + Sn^{2+}(aq) \longrightarrow Br_2(l) + Sn(s)$

   (b) $Cu^{+}(aq) + Fe^{3+}(aq) \longrightarrow Cu^{2+}(aq) + Fe^{2+}(aq)$

   Using data in Table 8.2, predict the spontaneity of the reactions in aqueous solutions at 298 K(E° for $Cu^{2+}/Cu^{+1} = 0.16$ V).

8.3.2 Equilibrium constants for redox reactions in electrochemical cells

In the preceding sections, a discusion was made on the dependence of the cell potential on the electrode potentials, the concentrations of ions, and the Gibbs free energy of the solution. It was also mentioned that apart from these factors, the potential of the cell also depends on the equilibrium constant of the cell. When the cell has established equilibrium, the cell potential ($E_{cell} = 0$) and the

the reaction quotient ($Q = K$). When these values are substituted into the Nernst Equation (Equation 8.10), it leads to:

$$0 = E^{\circ}_{cell} - \frac{0.0591}{n}\log K$$

Making K the subject of the formula gives:

$$K = \log^{-1}\left(\frac{nE^{\circ}_{cell}}{0.0591}\right) \qquad (8.15)$$

Equation 8.15 is used to calculate equilibrium constants of redox reactions in electrochemical cells.

Example 8.4

Calculate the equilibrium constant (K), for the following reaction at 298 K.

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) \qquad \Delta E^{\circ}_{cell} = 1.10\ V$$

Solution

The balanced cell reaction indicates that 2 moles of electrons, n, were involved in the reaction.

Substituting the value of n and E°_{cell} in Equation 8.15 results into:

$$K = \log^{-1}\left(\frac{2 \times 1.1}{0.0591}\right) = 1.68 \times 10^{37}$$

Therefore, the equilibrium constant (K) is 1.68×10^{37}.

Example 8.5

Calculate the equilibrium constant (K) of the cell $Mg(s)/Mg^{2+}(aq)//Al^{3+}(aq)/Al(s)$.

Solution

The overall cell reaction is:

$$3Mg(s) + 2Al^{3+}(aq) \rightleftharpoons 3Mg^{2+}(aq) + 2Al(s)$$

The standard cell potential, E°_{cell} is:

$$E^{\circ}_{cell} = -1.66\ V - (-2.37\ V) = 0.71\ V$$

The number of electrons involved in the reaction, $n = 6$

Substituting the values of E°_{cell} and n into Equation 8.15,

$$K = \log^{-1}\left(\frac{nE^\circ_{\text{cell}}}{0.0591}\right)$$

$$K = \log^{-1}\left(\frac{6 \times 0.71}{0.0591}\right) = 1.2 \times 10^{72}$$

Therefore, the equilibrium constant for the cell is 1.21×10^{72}.

Exercise 8.2

1. The half-cells at 298 K have the following reduction potentials:

   $Ni^{2+}(aq)/Ni(s) = -0.26$ V

   $Co^{2+}(aq)/Co(s) = -0.28$ V

   Use the given data to:

   (a) write the half–equation of each electrode and identify the electrode which is reduced or the one being oxidised.

   (b) write the overall redox reaction.

   (c) calculate the equilibrium constant (K) of the reaction.

2. How does the choice of electrolyte affect the performance and suitability of an electrochemical cell for a given application?

3. Compute the equilibrium constant (K) for the following reaction:

   $$Zn(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + H_2(g)$$

4. Calculate the equilibrium constant at 298 K for the following electrochemical cell: Given that $E^\circ Cu^{2+}/Cu = 0.34V$ $E^\circ Ag^+/Ag = 0.8$

   $$Cu(s)/Cu^{2+}(aq)\ (1\ \text{mol dm}^{-3})//Ag^+(aq)\ (1\ \text{mol dm}^{-3})/Ag(s)$$

5. At 298 K, the equilibrium constant (K) for the reaction:

   $$Sr(s) + Mg^{2+}(aq) \rightleftharpoons Sr^{2+}(aq) + Mg(s)$$

   is 2.69×10^{12}. Calculate E° for a cell made up of Sr/Sr^{2+} and Mg/Mg^{2+} half-cells.

6. An electrochemical cell is made up of Pb^{2+}/Pb and $Pt/H^+/H_2$ half-cells. The $[Pb^{2+}]$ is 0.1 mol dm^{-3}, $[H^+]$ is 0.05 mol dm^{-3}, and pressure of hydrogen is 1.0 atm.

   (a) Write the cell diagram for the spontaneous reaction.

   (b) Calculate the *emf* of the cell given that $E^o_{H^+/H_2} = 0$ V and $E^o_{Pb^{2+}/Pb} = -0.13$ V.

8.4 Ionisation of electrolytes in solutions

When electrolytes are dissolved in water, they dissociate into their constituent ions. The ions released in the solution are responsible for the flow of charges as they carry them from one place to another. Different substances have different degrees of dissociation in water; some electrolytes ionise completely while others ionise partially. Based on the degree of ionisation, electrolytes can be classified into strong and weak electrolytes. *Strong electrolytes* ionise completely when dissolved in water to form free ions. Examples of strong electrolytes are soluble salts like $BaCl_2$, strong acids like HCl, HNO_3 and H_2SO_4, and strong bases such as NaOH and KOH. On the other hand, *weak electrolytes* dissociate partially to produce relatively few ions when dissolved in water. An example of a weak electrolyte is CH_3COOH.

The extent to which an electrolyte has dissociated in aqueous solution is known as the *degree of dissociation*. Weak electrolytes form an interesting field of chemistry called the dissociation of weak electrolyes. It is of interest to know the percentage of ions of a weak electrolyte that has dissociated since the free ions participate in chemical reactions. Generally, the degree of dissociation or ionisation is the fraction of the electrolyte which has dissociated into ions in aqueous solution. For example, if an electrolyte is 50% dissociated, its degree of dissociation is 0.5. The degree of dissociation is represented by a symbol α. The dissociation of an electrolyte results in an increase in the number of dissolved particles in the solution. The ratio of the number of particles produced as the result of dissociation to the number of particles before dissociation gives what is known as the *van't Hoff's Factor* (*i*), which is denoted by:

$$i = \frac{\text{Number of particles after dissociation}}{\text{Number of particles before dissociation}}$$

The number of particles after dissociation refers to the actual number of particles produced by dissociation/ionisation.

$$i = \frac{\text{Actual number of particles produced by ionisation}}{\text{Number of particles without ionisation}}$$

Assuming that 1 mol of an electrolyte is capable of producing v ions on complete ionisation and its degree of ionisation is α, then the total number of particles in the solution is equal to the number of unionised particles ($1-\alpha$) plus the number of ions produced by the process of ionisation (αv) *i.e* total number of particles $= 1 - \alpha + \alpha v$.

Applying the van't Hoff's relationship and making α the subject of the formula, Equation 8.16 is obtained.

$$i = \frac{1-\alpha+\alpha v}{1}$$

$$i - 1 = \alpha v - \alpha = \alpha(v-1)$$

Therefore,

$$\alpha = \frac{i-1}{v-1} \qquad (8.16)$$

where α is the degree of dissociation of the electrolyte in the solution,

i is the van't Hoff's Factor, and

v is the number of ions an electrolyte is capable of producing on complete ionisation.

Equation 8.16 can be used to calculate the degree of ionisation of a weak electrolyte.

Example 8.6

What will be the degree of dissociation of $Mg(NO_3)_2$ solution if the van't Hoff's factor is 2.74?

Solution

In aqueous solution, $Mg(NO_3)_2$ ionises as follows:

$$\mathrm{Mg(NO_3)_2}(aq) \longrightarrow \mathrm{Mg^{2+}}(aq) + 2\mathrm{NO_3^-}(aq)$$

From the above chemical equation, $v = 3$

Given that $i = 2.74$, the degree of ionisation of $Mg(NO_3)_2$ is calculated by using Equation 8.16,

$$\alpha = \frac{i-1}{v-1}$$

Substituting the values of i and v in the equation gives:

$$\alpha = \frac{2.74 - 1}{3 - 1} = \frac{1.74}{2} = 0.87$$

Therefore, the degree of ionisation of $Mg(NO_3)_2$ is 0.87 or 87%.

Exercise 8.3

1. The van't Hoff's Factor (*i*) for a 0.1 mol dm^{-3} $Al_2(SO_4)_3$ solution is 4.2. Calculate the degree of ionisation of the electrolyte.
2. Aqueous solution of 0.004 mol dm^{-3} of sodium sulfate and 0.01 mol dm^{-3} of glucose is isotonic. Calculate the percentage of ionisation of Na_2SO_4.
3. Calculate the degree of ionisation of the following compounds given that $i = 5$ for both compounds.
   (a) $M_3(PO_4)_2$
   (b) $K_4Fe(CN)_6$
4. Assuming that the compounds, $NaNO_3$ and H_2SO_4 have $\alpha = 100\%$, calculate the van't Hoff factor for each compound.

8.4.1 Conductivity of electrolytes in solutions

The important characteristic of electrolytes is their ability to conduct electricity. They conduct electricity because they possess mobile charge carriers (ions). The property of electrolytic solution which indicates the extent to which it conducts electricity is known as *conductance*. Its numerical value is equal to the reciprocal of resistance (*R*), to the flow of electricity through the solution and it is denoted by the symbol *G*. The mathematical expression of conductance is given by Equation 8.17. The unit for conductance is siemens (symbol S), i.e., $S = \Omega^{-1}$.

$$G = \frac{1}{R} \tag{8.17}$$

The conductance of the electrolytic solution is directly proportional to the surface area (*A*) of the electrodes and inversely proportional to the distance (*l*), between the two electrodes. Thus,

$$G \propto \frac{A}{l}$$

Introducing the constant of proportionality (κ) to the expression above gives:

$$G = \kappa \frac{A}{l} \tag{8.18}$$

Rearranging Equation 8.18 gives $\kappa = G\frac{l}{A}$

where $\frac{l}{A}$ is the cell constant and κ is the specific conductance or conductivity. *Specific conductance* (conductivity) indicates how well an electrolyte conducts electricity. The electrolytic conductivity depends on the concentration of the electrolyte; therefore, to compare conductivity of various electrolytic solutions, their molar conductivity have to be considered. The relationship between conductivity and molar conductivity is given by:

$$\Lambda_m = \frac{\kappa}{C} \tag{8.19}$$

where C = concentration of electrolyte

Λ_m = molar conductivity

The value of molar conductivity (Λ_m), is equivalent to the conductance caused by all the ions in a volume of solution in m^3 containing 1 mol of electrolyte with the electrodes being 1 m apart and of unit surface area.

Example 8.7

A 0.40 mol dm^{-3} solution of sodium chloride has an electrolytic conductivity of 4.96×10^{-2} Scm^{-1} at 298 K. Compute the molar conductivity for this solution.

Solution

Substituting the data into Equation 8.19, gives:

$$\Lambda_m = \frac{4.96 \times 10^{-2}\ S\ cm^{-1}}{0.40\ mol\,dm^{-3}} = 1.24 \times 10^{-1}\ Scm^{-1}\ dm^{3}\ mol^{-1}$$

Since 1 $dm^3 = 10^3$ cm^3.

Therefore, the molar conductivity of the solution is 1.24×10^2 S cm^2 mol^{-1}.

Example 8.8

Calculate the molar conductivity of 0.02 mol dm^{-3} KCl at 298 K if its specific conductivity is $2.78 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$.

Solution

Given $\kappa = 2.78 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ and the concentration (C) of KCl = 0.02 mol dm^{-3} or 0.02mol/1000cm^3, Applying Equation 7.22 and substituting the value of κ and C leads to:

$$\Lambda_m = \frac{\kappa\left(cm^{-1}\ \Omega^{-1}\right)}{C\,(mol\ cm^{-3})} = \frac{2.78 \times 10^{-3}\ \Omega^{-1}\ cm^{-1} \times 1000}{0.02\ mol\ cm^{-3}} = 139\ cm^2\ mol^{-1}\ \Omega^{-1}$$

Therefore, the molar conductivity of KCl solution is 139 $cm^2\ mol^{-1}\ \Omega^{-1}$.

Molar conductivity increases with the decrease in concentration of electrolyte in the solution (Equation 8.19). The data on Table 8.3 and Figure 8.5 show how the molar conductivities of strong and weak electrolytes vary with concentration.

Table 8.3: *Dependence of molar conductivity of electrolytes on concentration*

Concentration mol dm^{-3}	Molar conductivity, Λ_m (S cm^2 mol^{-1})	
	Strong electrolyte/HCl	Weak electrolyte/CH_3COOH
1.0	333	-
0.1	391	5
0.01	413	16
0.001	421	91
0.0001	426	391

From Table 8.3, a sharp increase in molar conductivity of weak electrolyte at low concentration which is approaching infinite dilution is observed. This is because at infinite dilution, weak electrolytes ionise more to give maximum number of ions. For strong electrolytes, the increase in molar conductivity upon dilution is not very significant because the electrolytes ionise completely. So, diluting the solution does not change the number of ions in it.

As stated before, dilution causes an increase in the degree of ionisation as well as molar conductivity of a weak electrolyte. In this regard, the molar conductivity and the degree of ionisation at any given temperature are directly related. That is:

$$\Lambda_m \propto \alpha \text{ or } \Lambda_m = k\alpha \tag{8.20}$$

where k is the proportionality constant called the molar conductivity of a weak electrolyte at infinite dilution, (Λ_m^∞.) Substituting k with Λ_m^∞ in Equation 8.20 gives:

$$\Lambda_m = \Lambda_m^\infty \alpha \tag{8.21}$$

From Equation 8.21, the degree of ionisation, α is given by:

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\infty} \tag{8.22}$$

It is not possible to determine the molar conductivity of weak electrolyte by extrapolation method because the graph of molar conductivity versus concentration is not linear (Figure 8.5).

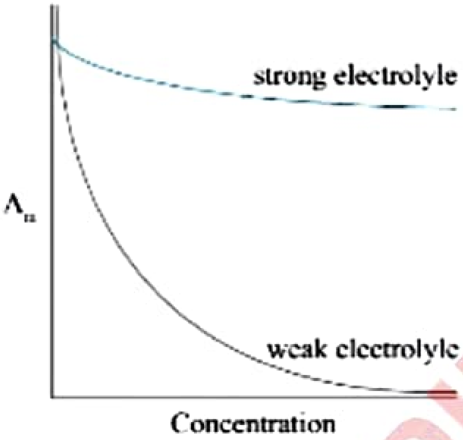


Figure 8.5: *Molar conductivity versus concentration*

In 1875, *Kohlrausch* developed a law called the *law of independent ionic mobilities*. The law states that the molar conductivity of an electrolyte at its infinite dilution is the sum of the individual conductivities of the ions present in the solution. Mathematically, the law can be expressed as

$$\Lambda_m^\infty = \Lambda_{cation}^\infty + \Lambda_{anion}^\infty$$

For example, for the electrolyte CH_3COONa,

$$\Lambda_{CH_3COONa}^\infty = \Lambda_{CH_3COO^-}^\infty + \Lambda_{Na^+}^\infty$$

This relationship can be used to calculate molar conductivity of any weak electrolyte by using known values of molar conductivity of suitable strong electrolytes.

Example 8.9

How can you determine the molar conductivity of acetic acid at infinite dilution if you are given molar conductivities of sodium chloride, hydrochloric acid and sodium ethanoate at infinite dilution?

Solution

If for any electrolyte, $\Lambda_{Electrolyte}^\infty = \Lambda_{Cation}^\infty + \Lambda_{Anion}^\infty$, then for the given three electrolytes, the following equations are obtained.

$$\Lambda^\infty_{NaCl} = \Lambda^\infty_{Na^+} + \Lambda^\infty_{Cl^-} \qquad \text{(i)}$$

$$\Lambda^\infty_{HCl} = \Lambda^\infty_{H^+} + \Lambda^\infty_{Cl^-} \qquad \text{(ii)}$$

$$\Lambda^\infty_{CH_3COONa} = \Lambda^\infty_{CH_3COO^-} + \Lambda^\infty_{Na^+} \qquad \text{(iii)}$$

Adding Equation (ii) and (iii) and subtracting Equation (i), one gets the following:

$$\Lambda^\infty_{HCl} + \Lambda^\infty_{CH_3COONa} - \Lambda^\infty_{NaCl} = \Lambda^\infty_{CH_3COO^-} + \Lambda^\infty_{Na^+} + \Lambda^\infty_{H^+} + \Lambda^\infty_{Cl^-} - \Lambda^\infty_{Na^+} - \Lambda^\infty_{Cl^-}$$

$$\Lambda^\infty_{HCl} + \Lambda^\infty_{CH_3COONa} - \Lambda^\infty_{NaCl} = \Lambda^\infty_{CH_3COO^-} + \Lambda^\infty_{H^+}$$

But,

$$\Lambda^\infty_{CH_3COO^-} + \Lambda^\infty_{H^+} = \Lambda^\infty_{CH_3COOH}$$

Hence,

$$\Lambda^\infty_{CH_3COOH} = \Lambda^\infty_{CH_3COONa} + \Lambda^\infty_{HCl} - \Lambda^\infty_{NaCl}$$

Therefore, it can be concluded that having molar conductivities of strong electrolytes of suitable combination, it is possible to calculate the molar conductivity of a weak electrolyte.

8.4.2 Ostwald dilution law

The effect of dilution on the ionisation of weak electrolytes was also investigated by Ostwald. He considered the ionisation of an electrolyte AB to produce A^+ and B^-. The equilibrium between the ions and the unionised molecules can be represented by the equation:

$$AB(aq) \rightleftharpoons A^+(aq) + B^-(aq)$$

If C is taken to be the initial concentration of AB in mol dm^{-3}, and α as its degree of ionisation, then, the changes in quantities of each species is as follows:

	$AB(aq)$	$\rightleftharpoons$	$A^+(aq)$	+	$B^-(aq)$
Initial	C		0		0
Change	$-\alpha C$		$+\alpha C$		$+\alpha C$
At equilibrium	$C(1-\alpha)$		αC		αC

The equilibrium constant (*K*), is given by:

$$K = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \qquad (8.23)$$

For weak electrolytes, α is very small and therefore, the term $1-\alpha \approx 1$. Hence,

$$K = C\alpha^2 \text{ or } \alpha = \sqrt{\frac{K}{C}} = \sqrt{KV} \qquad (8.24)$$

where $V = \frac{1}{C}$, the volume of the solution in litres containing 1 mol of the solute.

It follows from Equation 8.24 that, if the concentration of electrolytes decreases, the degree of ionisation (α) increases. This relationship is called the *Ostwald dilution law* which states that at constant temperature, the degree of ionisation or dissociation is inversely proportional to the square root of the concentration and directly proportional to the square root of dilution. The Ostwald dilution law is only applicable on solutions of weak electrolytes.

Example 8.10

The molar conductivity at infinite dilution and molar conductivity of 0.1 mol dm^{-3} CH_3COOH are 3.88×10^{-2} S m^2 mol^{-1} and 5.2×10^{-4} S m^2 mol^{-1}, respectively. Calculate the degree of ionisation (α) of CH_3COOH.

Solution

Given,

$$\Lambda_m^\infty = 3.88 \times 10^{-2}\ \text{S m}^2\ \text{mol}^{-1} \text{ and } \Lambda_m = 5.2 \times 10^{-4}\ \text{S m}^2\ \text{mol}^{-1}$$

from

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\infty}$$

$$= \frac{5.2 \times 10^{-4}\ \text{S m}^2\ \text{mol}^{-1}}{3.88 \times 10^{-2}\ \text{S m}^2\ \text{mol}^{-1}} = 0.013$$

The degree of ionisation of the CH_3COOH is 0.013 or 1.3%.

Exercise 8.4

1. Calculate the molar conductivity of a 2.0 mol dm^{-3} KCl solution at 298 K, if its specific conductivity is $2.68 \times 10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}$.
2. A conductance cell filled with 0.02 M KCl solution at 298 K, showed a resistance of 165 Ω and a specific conductance (conductivity) of $2.77 \times 10^{-3}\ \Omega^{-1}\text{cm}^{-1}$. The same cell containing 0.01 molar solution of NaCl gave an electrical resistance of 384 Ω. Calculate the molar conductivity of NaCl solution.

3. Calculate the molar conductivity of ethanoic acid at infinite dilution given that the molar conductivities of HCl, NaCl, and CH_3COONa at infinite dilution are $4.26\times10^{-2}\,m^2\,\Omega^{-1}mol^{-1}$, $1.26\times10^{-2}\,m^2\,\Omega^{-1}\,mol^{-1}$, and $9.10\times10^{-3}m^2\Omega^{-1}mol^{-1}$, respectively.

4. The ionisation constant of phenol is 1.0×10^{-10} mol dm^{-3}. What is the concentration of phenoxide ion in 0.05 mol dm^{-3} of phenol solution?

5. The first ionisation constant of hydrogen sulfide (H_2S) is 9.1×10^{-8} mol dm^{-3}. Calculate the concentration of HS^- assuming the concentration of $[H_2S]$ is 0.1 mol dm^{-3}.

6. The K_a of 0.05 mol dm^{-3} solution of ethanoic acid (CH_3COOH) is $1.85\times10^{-5}mol\,dm^{-3}$. Calculate the concentration of H^+ in this solution.

8.5 Applications of electrochemistry in industries and real-life situations

Electrochemistry has numerous applications in various industries and real-life scenarios, ranging from extraction of metals and electroplating to corrosion inhibition and batteries productions.

8.5.1 Electrolytic extraction of metals

Metals such as lithium, potassium, magnesium, calcium, and aluminium have high negative reduction potentials. Due to their strong reducing properties, no specific reducing agents can effectively reduce them. Consequently, the extraction of these metals is accomplished through electrolysis.

8.5.2 Purification of metals

Metals like copper and silver can be obtained in high purity through electrolytic process. The impure metal is made an anode during electrolysis in which the pure metal will be deposited on the cathode. The electrolyte is the salt solution of the respective metal.

8.5.3 Electroplating

The electrical deposition of a metal on another metal is called *electroplating*. The purpose of electroplating is to protect the plated metal from corrosion or rusting and improve its appearance. The most commonly used metals in electroplating include gold, silver, chromium, nickel, tin, copper and palladium. Electroplating is used to make ornaments such as rings, earrings, bangles and wrist watches to appear as if they were made of gold or silver. Steel parts of cars, bicycles and some tools appear shiny because they are electroplated with chromium. During the electroplating process, the anode is usually made of the metal to be used for plating while the cathode is the object to be electroplated. The electrolyte used should be a salt solution of the electroplating metal. In the course of electrolytic process, the plating metal dissolves in the electrolyte and transfers to the cathode where it is deposited.

Activity 8.2

Aim: To demonstrate the process of electroplating a metal object with copper

Requirements: Copper sulfate ($CuSO_4$) powder, distilled water, copper electrodes, metal objects to be plated (e.g., door key made of iron, iron nails, zinc-coated screws, or brass keys), DC power supply, connecting wires, crocodile clips, glass or plastic beakers, stirring rod, clean cloth and sandpaper or steel wool

Procedure

1. In a container, dissolve 10 g of copper sulfate in 250 mL of distilled water. Stir well until all the copper sulfate is dissolved.
2. Clean the metal objects thoroughly using sandpaper or steel wool to remove any dirt or grease from the surface. Rinse them with distilled water and dry them with a clean cloth.
3. Connect the copper plate to the positive terminal of the power supply using a crocodile clip and the cleaned metal object to be plated onto the negative terminal of the battery (cathode).
4. Submerge the electrodes and metal objects into the copper sulfate solution, making sure they are fully immersed but not touching each other.
5. Turn on the power supply and allow the current to flow for about 15–20 minutes and observe what is happening on the electrodes.
6. Turn off the power supply and carefully remove the metal objects from the solution. Rinse the plated objects with distilled water to remove any excess electrolyte and allow the plated objects to air dry.

Questions

1. What changes are observed on the metal objects after the electroplating process?
2. What is the function of the solution in electroplating?
3. How does the process of electroplating apply in everyday life and industries?

8.5.4 Corrosion inhibition

The term *corrosion* refers to the wearing of metals by an electrochemical process. Rust on iron, tarnish on silver and the green patina formed on copper and brass are few examples of corrosion. Corrosion is an undesirable process because it enormously damages things like buildings, bridges, pipelines, ships, and cars. Corrosion is a redox reaction that takes place between a metal, water, and the gases in the air. Some metals are readily attacked by corrosion while others show a remarkable resistance to corrosion. Metals of group one such as sodium, potassium, rubidium, and caesium are very reactive. When they are exposed to air, they tarnish rapidly and others like rubidium and caesium catch fire. The oxide layers formed on their surfaces are weak and can be easily attacked by gases and moisture of the atmosphere to allow further reaction (corrosion).

Unlike group one elements, metals like aluminium, lead, and zinc tarnish at a relatively low rate to form a layer of oxide on their surface, which is hard, non-porous, impermeable and difficult to crack. The oxide of iron is not strong enough to prevent the metal from being attacked by corrosion. In the presence of air and moisture, iron serves as the anode. Therefore, it undergoes oxidation to iron(II).

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$$

The electrons that are released move through the iron and reduce atmospheric oxygen at the cathode, which is another region of the same metal surface.

$$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$$

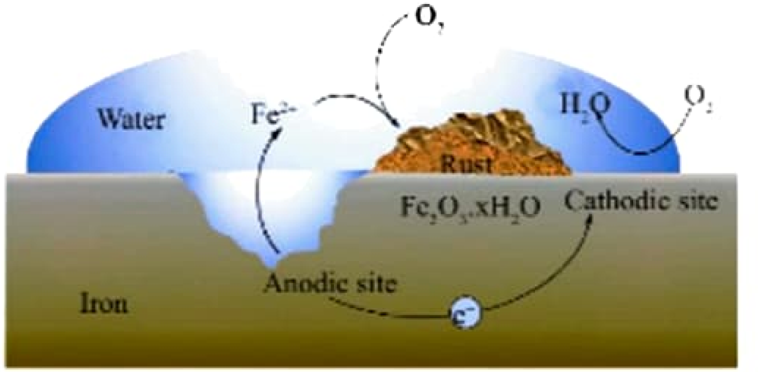
The overall process is represented by the overall redox reaction:

$$2Fe(s) + O_2(g) + 2H_2O(l) \longrightarrow 2Fe^{2+}(aq) + 4OH^-(aq)$$

The Fe^{2+} which are formed at the anode are further oxidised by oxygen as follows:

$$4Fe^{2+}(aq) + O_2(g) + (4+2x)H_2O(l) \longrightarrow 2Fe_2O_3{\bullet}xH_2O(s) + 8H^+(aq)$$

The hydrated form of iron(III) oxide is what is known as rust. Analysis of the reaction equations representing corrosion of iron leads to the conclusion that corrosion is a redox reaction which takes place on the surface of the metal whereby one region of the same metal acts as the cathode and the other as the anode (Figure 8.6).



$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$ $\quad$ $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$

Figure 8.6: *Process of rust formation*

Metals are used in all areas of human economic activities. If corrosion is not controlled, deterioration of metals may bring a negative impact to the economic development of nations. Because of this, prevention of metal corrosion becomes inevitable. Various techniques have been devised to protect metals from corrosion. These include coating, passivation, alloying, and cathodic protection.

Coating

The electrochemical nature of the rusting of iron explains the importance of moisture in corrosion. Moisture must be present to act as an electrolyte between anodic and cathodic regions. When there is no moisture, the circuit is incomplete and therefore no reaction occurs and hence corrosion is impaired. Prevention of corrosion by coating is based on this principle where the metal surface is coated with a layer of paint or another metal. For example, iron is commonly coated with tin, zinc, paints like red-oxide, and organic polymers. However, coating is not permanent it can become weak or worn out after sometime and can fail to prevent the metal from being attacked by corrosion.

Passivation

The surface of iron or any other metal can be made inactive by a process called *passivation*. When iron is treated with a strong oxidising agent such as concentrated HNO_3, a thin layer of oxide is formed on the surface of the metal. The metal surface becomes passive. The metal is therefore said to be passivated. However, the developed resistance against corrosion is temporary.

Alloying

Mixing of one metal with one or more other metals in a specified proportion is called *alloying*. Brass, steel and stanless steel are examples of alloys. The tendency of metals to oxidise is greatly reduced when they are alloyed with certain other metals. For example, stainless steel is resistant to corrosion because nickel and chromium form oxide coating that changes steel's reduction potential to one characteristic of the noble metals. However, alloying is expensive.

Cathodic protection

Cathodic protection is a method most often used to protect steel in buried fuel tanks and pipelines. In this process, the tanks or pipelines are connected to an active metal such as magnesium by a wire. If the pipeline or tank is made of iron, electrons will be furnished by magnesium because it is a better reducing agent than iron. This will keep iron away from being oxidised. As the oxidation goes on, magnesium anode wears and so must be replaced periodically. Similarly, iron coated with zinc is protected by coating but at the same time is protected by cathodic protection. From Table 8.2 of the standard electrode potentials, it is seen that zinc is readily oxidised than iron. Therefore, iron coated with zinc (galvanised) acts as the cathode and zinc acts as the anode. In normal atmospheric exposure, zinc will lose electrons in preference to iron. Therefore, iron will remain unattacked.

8.5.5 Batteries production

Task 8.3

Use any search engine or other sources to identify the production of electrochemical cells.

Electrochemical cells have numerous applications across various industries and sectors due to their ability to convert chemical energy into electrical energy or electrical energy into chemical energy. The principle behind the operation of the electrochemical cells is very important in the manufacture of batteries. A *battery* is a device that is designed to store chemical energy for later release as electricity. Batteries may consist of a single voltaic cell as in a flashlight cell or may consist of two or more voltaic cells joined in series to increase the total voltage as in an automobile battery. Although the principle of operating a battery is similar to that of electrochemical cells, batteries are of advantage because they are self-contained as no auxiliary components such as salt bridges are needed. Types of batteries include primary batteries (primary cells), secondary batteries (secondary cells), and fuel cells.

Primary batteries

Primary batteries are electrochemical cells that generate electrical energy through irreversible chemical reactions. When the reactants have been converted to products, no more electricity is produced and the battery is said to be dead.

Primary cells cannot be recharged and once their chemical reactants are consumed, they are discarded. Examples of common primary batteries are dry cell batteries and alkaline batteries.

Dry cell battery

Dry cell also known as the *Leclanché* cell was inverted by a French engineer, Georges Leclanché, to overcome the difficulty of electrolyte solution leaking out of the Daniell cell. In the dry cell (Figure 8.7) commonly known as zinc-carbon batteries, oxidation occurs at a zinc anode and reduction at an inert carbon electrode. The electrolyte is made of a paste of MnO_2, $ZnCl_2$, NH_4Cl and carbon black. This type of cell produces a voltage of about 1.5 V and is used in portable electronic devices such as radios, flashlights, remote controls, toys and watches.

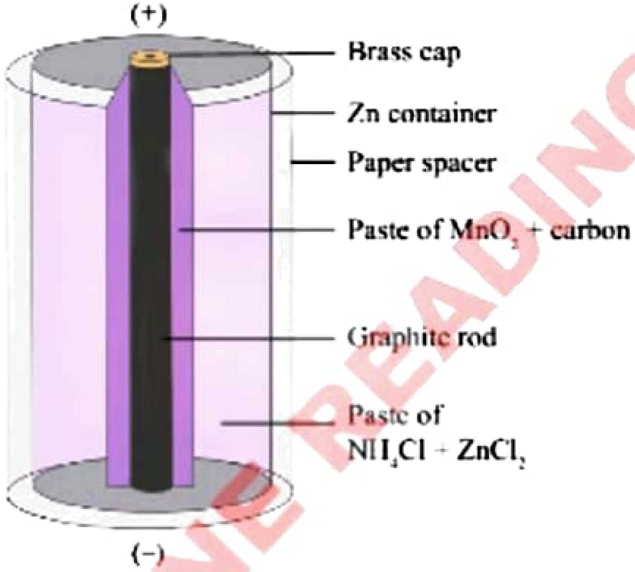


Figure 8.7: *Cross section of a dry cell*

The anode half reaction of the dry cell is

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$

The cathode half reaction involves reduction of MnO_2 to Mn_2O_3 and the reaction of NH_4^+ with OH^- ions to produce NH_3.

$$2MnO_2(s) + H_2O(l) + 2e^- \longrightarrow Mn_2O_3(s) + 2OH^-(aq)$$

The produced OH^- ions react with the NH_4^+ from NH_4Cl to produce NH_3 gas.

$$2NH_4^+(aq) + 2OH^-(aq) \longrightarrow 2NH_3(g) + 2H_2O(l)$$

Overall:

$$Zn(s) + 2NH_4^+(aq) + 2MnO_2(s) \longrightarrow Zn^{2+}(aq) + 2NH_3(g) + Mn_2O_3(s) + H_2O(l)$$

If the produced NH_3 gas is allowed to build up at the cathode, it will disrupt the flow of the current. The condition is prevented by a reaction between Zn^{2+} and the NH_3 gas to form the complex ion $[Zn(NH_3)_2]^{2+}$ which crystallizes as the chloride salt.

$$Zn^{2+}(aq) + 2NH_3(g) + 2Cl^-(aq) \longrightarrow [Zn(NH_3)_2]Cl_2(s)$$

The portability, low maintenance, safety, affordability and versatility of dry cell batteries make them a popular choice for powering a wide range of devices and applications in everyday life. However, their single-use nature, limited capacity and environmental impact hinder their use for a particular application. The limited capacity in producing electrical energy is because only a small portion of the MnO_2 near the cathode undergoes reduction and only a fraction of the zinc cathode is consumed during cell discharge. In addition, when the current is drawn rapidly from the cell, NH_3 builds up on the electrode leading to the drop down of the voltage. Furthermore, the acidic nature of the electrolytes due to the presence of NH_4Cl causes the zinc metal to dissolve slowly. This led to the development of the superior form of Leclanché cell called the alkaline cell battery.

Alkaline cell battery

The development of alkaline batteries came in the 1950s by Lewis Urry, a Canadian chemical engineer, as a better alternative to the zinc-carbon batteries that were commonly used at the time. Alkaline batteries are a type of dry cell battery that uses an alkaline electrolyte typically KOH in a place of NH_4Cl to generate electrical energy through chemical reactions (Figure 8.8).

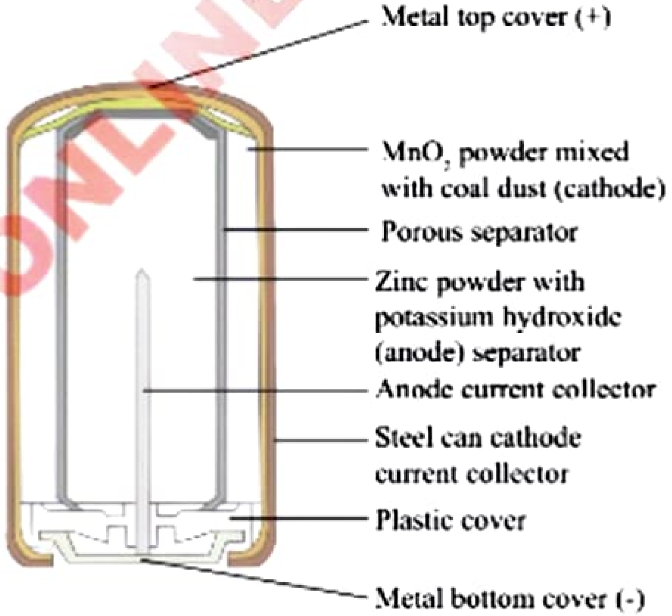


Figure 8.8: *Cross section of an alkaline battery*

The anode of the alkaline battery is typically composed of powdered zinc which serves as the active material. During discharge, zinc undergoes oxidation, releasing electrons to the external circuit. The cathode is composed of powdered manganese dioxide mixed with graphite. MnO_2 serves as the active material for reduction during battery discharge. The half-cell reactions involved are

Anode: $Zn(s) + OH^-(aq) \longrightarrow Zn(OH)_2(s) + 2e^-$

Cathode: $2MnO_2(s) + H_2O(l) + 2e^- \longrightarrow Mn_2O_3(s) + 2OH^-(aq)$

Overall: $Zn(s) + 2MnO_2(s) + H_2O(l) \longrightarrow Mn_2O_3(s) + Zn(OH)_2(s)$

Alkaline batteries have higher energy output compared to zinc-carbon dry cells. The zinc electrode does not dissolve in the basic medium as it does in acidic medium. When the current is drawn, alkaline batteries have a capacity of maintaining the voltage. For long term storage of the battery, it is advisable to remove them from the devices because alkaline batteries have a tendency of leaking the potassium hydroxide. A leakage of potassium hydroxide electrolyte and battery rupture are enhanced when the non-rechargeable alkaline batteries are recharged.

Secondary cells

Secondary cells, also known as rechargeable batteries, are electrochemical cells that can be recharged multiple times by reversing the chemical reactions that occur during discharge. Unlike primary cells which are single-use and cannot be recharged, secondary cells can be reused after being depleted by replenishing their chemical reactants through an external electrical source. Common examples of secondary cells are lead-acid storage battery, nickel-cadmium (NiCd) batteries and lithium-ion (Li-ion) batteries.

Lead-acid storage battery

A lead-acid battery is a type of secondary cell (rechargeable battery) that is widely used for various applications including automotive starting, lighting and ignition systems, backup power supplies, and renewable energy storage. It consists of six identical electrochemical cells joined together in series. Each cell contains a lead plate at the anode and a cathode made of lead dioxide (PbO_2). Aqueous solution of sulfuric acid serves as the electrolyte hence the name lead-acid battery (Figure 8.9).

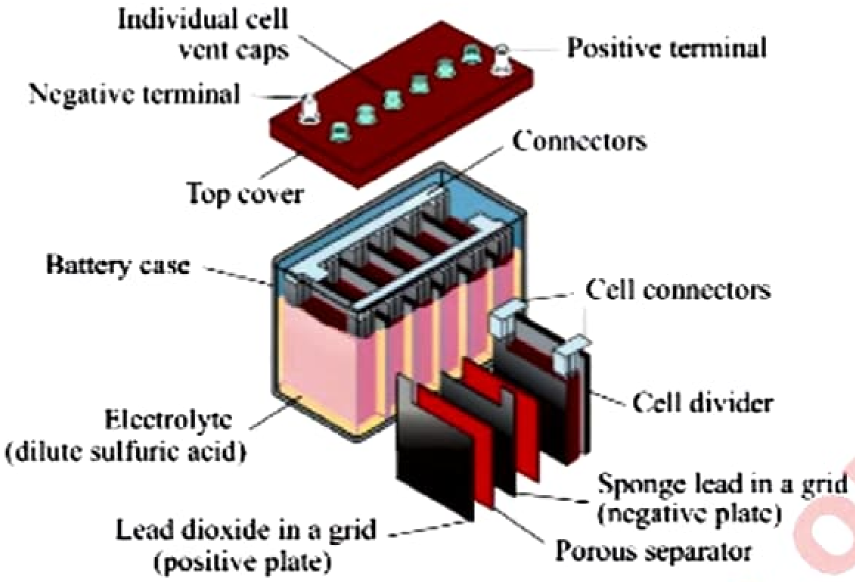


Figure 8.9: *Cross section of a lead-acid battery*

The redox reactions involved in the lead-acid battery are

$$\text{Anode: } Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$$

$$\text{Cathode: } PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e \longrightarrow PbSO_4(s) + 2H_2O(l)$$

$$\text{Overall: } Pb(s) + PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

As the batteries are continuously in use, there will reach a time when the electrodes become coated with the formed $PbSO_4$ and the electrolyte becomes diluted with the water formed during the redox reactions. When this happens, the battery can no longer produce current and therefore it has to be recharged by applying an external voltage. Recharging the battery non spontaneously reverses the electrode reactions to produce the starting materials in the cell.

Lead-acid batteries are cost-effective and can be charged quickly compared to some other types of rechargeable batteries. However, lead-acid batteries have a limited number of charging and discharging cycles compared to some other types of rechargeable batteries. Over time, the performance of lead-acid batteries may degrade, resulting in reduced capacity and shorter service life.

Nickel-cadmium battery

The nickel-cadmium (NiCd) battery is a type of rechargeable battery that has been widely used for various applications due to its reliability, durability, and relatively low cost. The positive electrode of a NiCd battery consists of a cadmium (Cd) plate or grid that is coated with cadmium hydroxide ($Cd(OH)_2$) as the active material. The negative electrode is typically made of nickel (Ni) and is coated with nickel oxide hydroxide ($NiO(OH)_2$) as the active material. A separator often made of porous material is used to keep the positive and negative electrodes apart while allowing the flow of ions during charging and discharging. The electrolyte used in NiCd batteries is a solution of potassium hydroxide (Figure 8.10).

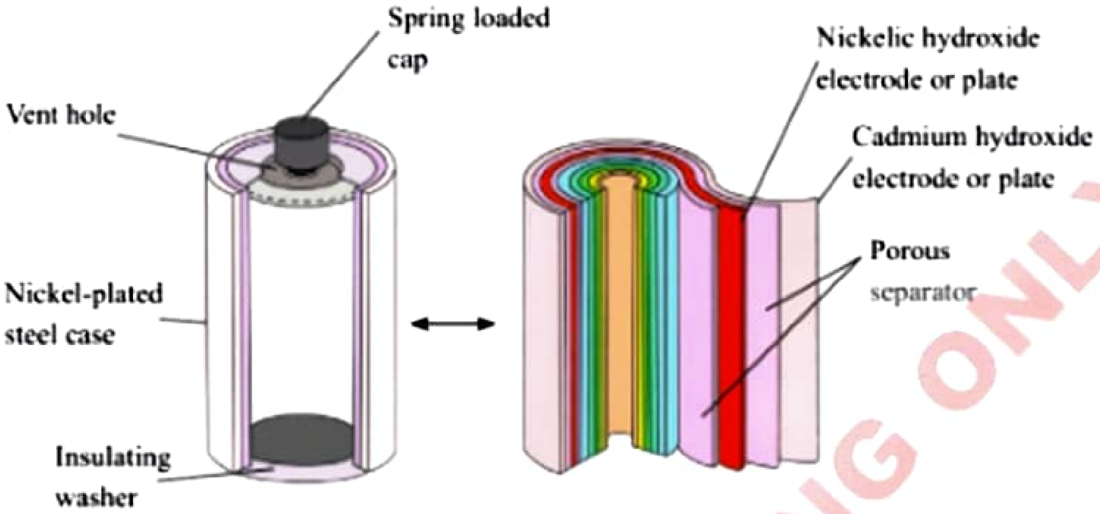


Figure 8.10: *Cross section of a nickel-cadmium battery*

During discharge, the electrode reactions are

Anode: $Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^-$

Cathode: $2NiO(OH)(s) + 2H_2O(l) + 2e^- \longrightarrow 2Ni(OH)_2(s) + 2OH^-(aq)$

Overall: $Cd(s) + 2NiO(OH)(s) + 2H_2O(l) \longrightarrow Cd(OH)_2(s) + 2Ni(OH)_2(s)$

When charging, the reactions are reversed as follows:

Anode: $Cd(OH)_2(s) + 2e^- \longrightarrow Cd(s) + 2OH^-(aq)$

Cathode: $2Ni(OH)_2(s) + 2OH^-(aq) \longrightarrow 2NiO(OH)(s) + 2H_2O(l) + 2e^-$

Overall: $Cd(OH)_2(s) + 2Ni(OH)_2(s) \longrightarrow Cd(s) + 2NiO(OH)(s) + 2H_2O(l)$

Despite the high discharge rates and the wide operating temperature range of NiCd cells, their popularity has declined in recent years due to the environmental concerns associated with cadmium and nickel upon improper disposal.

Lithium-ion (Li-ion) batteries

Lithium-ion batteries utilise lithium ions as the charge carriers between the cathode and anode electrodes. Lithium-ion batteries are typically composed of multiple cells connected in series or parallel to achieve the desired voltage and capacity. Each cell consists of a cathode, an anode and a separator soaked in an electrolyte solution such as a mixture of ethylene carbonate, dimethyl carbonate along with a lithium salt such as lithium hexafluoro phosphate. The cathode material consists of lithium metal oxides such as lithium cobalt oxide ($LiCoO_2$), lithium iron phosphate ($LiFePO_4$), or lithium manganese cobalt oxide ($LiNiMnCoO_2$). The anode material is made of lithium-graphite. The entire assembly is enclosed in a protective casing as shown in Figure 8.11.

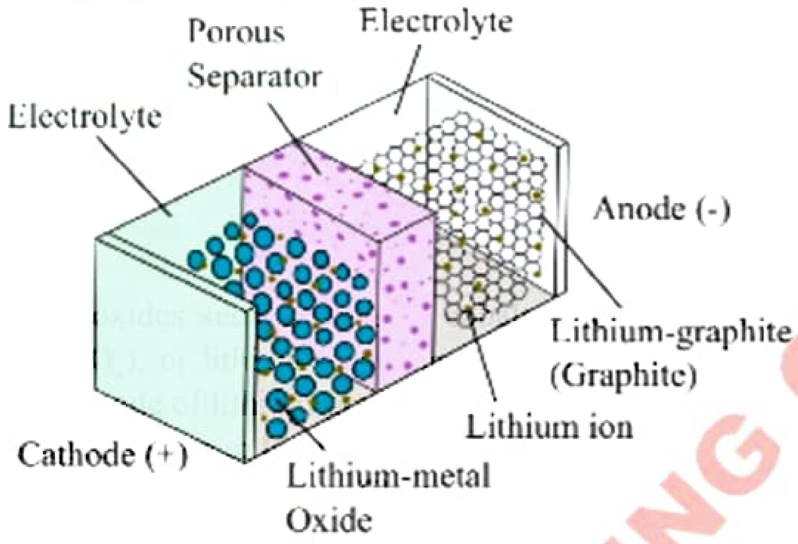


Figure 8.11: *Parts of a lithium-ion battery*

During discharge, lithium ions migrate from the anode to the cathode through the electrolyte, while electrons flow through the external circuit, generating electrical current. The redox reactions involved are

Anode: $LiC_6(s) \longrightarrow 6C(s) + Li^+(aq) + e^-$

Cathode: $CoO_2(s) + Li^+(aq) + e^- \longrightarrow LiCoO_2(s)$

Overall: $LiC_6(s) + CoO_2(s) \longrightarrow 6C(s) + LiCoO_2(s)$

The reverse occurs during charging with lithium ions moving back to the negative electrode and electrons being stored in the anode.

Anode: $6C(s) + Li^+(aq) + e^- \longrightarrow LiC_5(s)$

Cathode: $LiCoO_2(s) \longrightarrow CoO_2(s) + Li^+(aq) + e^-$

Overall: $6C(s) + LiCoO_2(s) \longrightarrow LiC_6(s) + CoO_2(s)$

Lithium-ion batteries can withstand hundreds to thousands of charging and discharging cycles, depending on the specific chemistry and usage conditions, making them suitable for long-term use in powering many devices including smartphones, laptops and electric vehicles. However, lithium-ion batteries are expensive to manufacture compared to some other types of rechargeable batteries primarily due to the cost of raw materials such as lithium and cobalt. Despite the limitations, lithium-ion batteries remain one of the most widely used and versatile rechargeable battery technologies.

Fuel cells

Task 8.4

Use online resources to gather information on fuel cell technology and prepare a presentation covering the types, working mechanisms, applications, advantages and their associated challenges.

Fuel cells differ from other energy storage cells as the reactants are continuously fed and products removed to allow continuous flow of electricity. The cells operate on the principle of electrochemical reactions between a fuel and an oxidant (typically oxygen from the air) at separate electrodes. The fuel undergoes oxidation at the anode while the oxidant undergoes reduction at the cathode. The flow of electrons through an external circuit generates electrical energy. Common fuels used in fuel cells include hydrogen, methanol, natural gas and hydrogen-rich fuels obtained from renewable sources. The electrolyte materials in fuel cell may include proton-conducting polymers, ceramic oxides and molten salts depending on the type of a fuel cell. A hydrogen fuel cell shown in Figure 8.12 is an example of a fuel cell that uses hydrogen gas as the fuel. The cell involves the oxidation of hydrogen fed at the anode catalyst and the reduction of oxygen at the cathode catalyst.

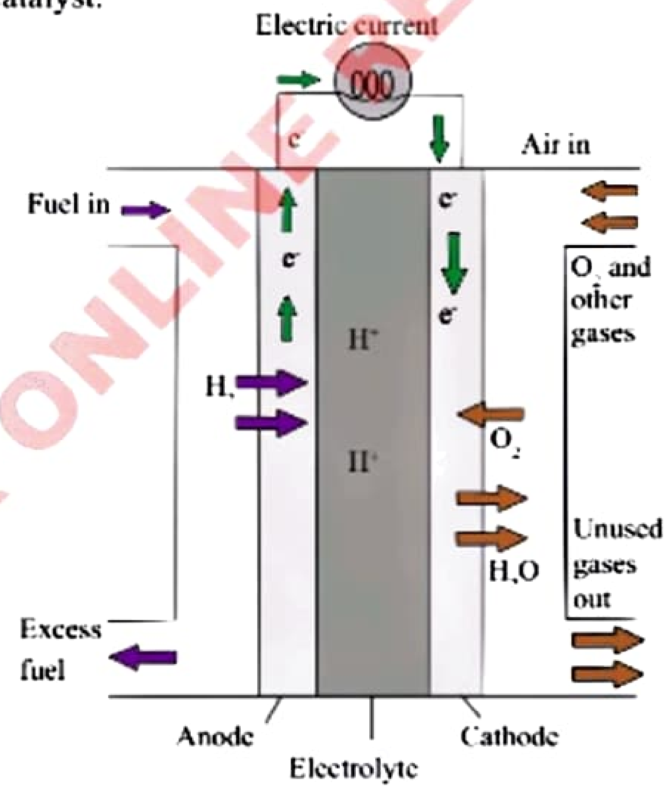


Figure 8.12: *Hydrogen fuel cell*

At the cathode electrode, oxygen from the air accepts electrons and combines with the cations from the anode to form water. The redox reactions involved are:

Anode: $2H_2(g) \longrightarrow 4H^+(aq) + 4e^-$

Cathode: $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$

Overall: $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

In order to increase the voltages and power outputs of fuel cells, several fuel cells are arranged in series or parallel configurations to produce a fuel cell stack or fuel cell system. In addition, connecting fuel cells in parallel increases the current capacity of the system useful for applications that require a large amount of electrical current such as cars and generators.

Revision exercise 8

1. A conductance cell filled with 0.02 mol dm^{-3} solution of KCl at 298 K showed a resistance of 120 Ω and conductivity of $2.77 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$. The same cell containing 0.005 mol dm^{-3} solution of NaCl gave an electrical resistance of 340 Ω. Calculate the molar conductivity of the solutions.
2. A 0.125 mol dm^{-3} solution of dichloroethanoic acid has a conductivity of $2.38 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$. Calculate the degree of ionisation of dichloroethanoic acid if its molar conductivity at infinite dilution is 0.273 S cm^2 mol^{-1}.
3. What are the safety considerations when handling rechargeable batteries, and how are they comparable to non-rechargeable batteries in terms of safety?
4. How is the understanding of electrolytic conductivity relevant when comparing different types of batteries for use in everyday devices?
5. A conductivity cell with 0.1 mol dm^{-3} of KCl solution has a resistance of 100 Ω and a conductivity of 1.29 S m^{-1}. If the resistance of the same cell when filled with 0.02 mol dm^{-3} KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 mol dm^{-3} KCl solution.
6. Calculate the *emf* of the cell with the following redox reaction:

   $Ni(s) + 2Ag^+(0.002\ M) \longrightarrow Ni^{2+}(0.16\ M) + 2Ag(s)$

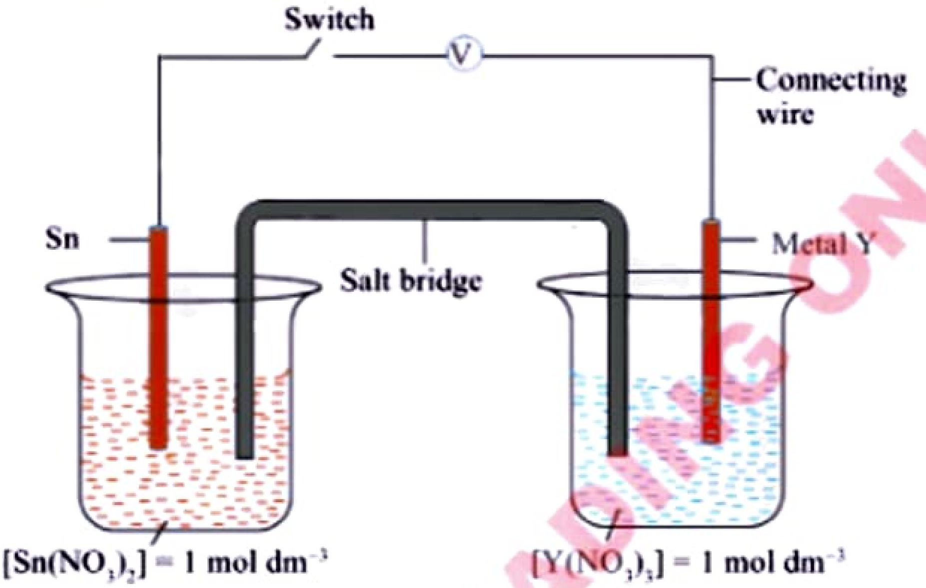
   Given $E^\circ Ag^+/Ag = 0.8V$ $E^\circ Ni^{2+}/Ni = -0.23V$
7. Use the given standard reduction potentials to calculate the equilibrium constant for the following reaction at 25 °C:

$$3I_2 + 2Al \longrightarrow 6I^- + 2Al^{3+}$$

$$I_2 + 2e^- \longrightarrow 2I^- \qquad E^\circ = +0.54\,V$$

$$Al^{3+} + 3e^- \longrightarrow Al \qquad E^\circ = -1.66\,V$$

8. An electrochemical cell is constructed with an open switch as shown in the following figure.



A strip of Sn and that of an unknown metal Y are used as electrodes. When the switch is closed, the mass of the Sn electrode increases. The reduction half reactions are:

$$Y^{3+}(aq) + 3e^- \longrightarrow Y(s) \qquad E^\circ = x$$

$$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s) \qquad E^\circ = -0.14V$$

From the figure:

(a) label the anode and cathode and justify your answer.

(b) draw an arrow indicating the direction of the current when the switch is closed.

(c) if the reaction standard cell potential is 0.60 V, calculate the standard electrode potential in volts for the $Y^{3+}(aq)/Y(s)$ electrode.

(d) identify metal Y.

(e) write the balanced redox reaction for the cell.

(f) if the concentrations of Sn^{2+} is changed from 1.0 mol dm^{-3} to 4 mol dm^{-3} and that of Y^{3+} from 1.0 mol dm^{-3} to 0.1 mol dm^{-3},

   (i) determine the cell potential.

   (ii) compare the calculated cell potential and the standard cell potential based on the answer in (i) above. Justify your answer.

9. **In hydrogen-oxygen fuel cell, the energy is produced by the net chemical reaction:**

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

   (a) **When the fuel cell operates at 298 K and 1.0 atm for 4680 s, 0.0746 mol of O_2 gas are consumed. Determine the volume of hydrogen gas consumed for that period.**

   (b) **If the fuel cell operates under acidic medium,**

      (i) **write its half-reactions.**

      (ii) **determine its standard cell potential.**

10. **The standard cell potential and the cell potential for a voltaic cell containing cadmium and nickel at 25 °C are +0.17 V and +0.24 V, respectively. Find the concentration of cadmium in the solution given that the concentration of nickel(II) is 1 mol dm^{-3}.**

11. **Given the Galvanic cell with the reaction:**

$$2MnO_4^-(aq) + 10Br^-(aq) + 16H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5Br_2(l) + 8H_2O(l)$$

If the concentrations of the chemical species are $[MnO_4^-] = 0.01$ mol dm^{-3}, $[Br^-] = 0.01$ mol dm^{-3}, $[Mn^{2+}] = 0.15$ mol dm^{-3}, and $[H^+] = 1$ mol dm^{-3}, calculate its cell potential at 298 K.

12. **A metal bridge is suffering from corrosion due to exposure to saltwater. Propose electrochemical methods to prevent or slow down the corrosion process.**

13. **Explain the environmental advantages associated with adopting the fuel cells technology over other cell technologies.**

Project work

Select an area of your interest related to Chemistry, then design and conduct a project

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Answers to numerical exercises

Chapter One

Exercise 1.1

1. 499.05 mL
3. 3041.5 L
5. 0.16 g/L
6. 9 L
8. 55.9 mL

Exercise 1.2

1. 4.89 atm
2. P_{He} = 1.2 atm; P_{Ar} = 2.8 atm
4. 0.92 atm
5. 406 K or 133 °C
7. (a) Perfume B due to smaller molecular mass (205) hence has high speed
   (b) 12.95 seconds
8. 64 g/mol

Exercise 1.3

5. 2:1
8. 59.03
9. 170.9 g/mol

Revision exercise 1

1. 0.19 L
3. 529.95 dm^3
5. 588 balloons
6. 189.7 Torr
7. 11.89 L
8. 11.66 L
9. (a) P_{CO_2} = 0.118 atm and, P_{Ne} =1.01 atm (b) P_T = 1.128 atm
10. 1.57 atm
11. They will meet at 59.44 cm from the side of NH_3 or 40.56 cm from the side of HCl.
13. 4.69 times that of CO_2

Chapter Two

Exercise 2.1

2. (a) 30.31 Torr (b) 1.51 Torr

3. 48 g/mol

4. S_8

5. 342.78 g/mol

Exercise 2.2

1. 101.15 °C

3. NaCl will have high boiling point of 100.9 °C than sucrose of 100.3°C

4. 39.3 g/mol

Exercise 2.3

1. 211.86 g/mol

3. 5333.3 g

4. 333.3 g or 0.333 kg

5. $\Delta T_f = 2.25$ °C, Freezing point = −2.25 °C

6. 4.97 °C

Exercise 2.4

3. 59342.58 g/mol

4. 65116.17 g/mol

5. 0.287 mol/L

6. 54.1 g/L

7. $i = 1.9$

Revision exercise 2

4. 23.7 Torr

5. Freezing point = −7.79 °C

6. (a) 0.44 *m* (b) $K_b = 3.32$ °C/*m*

7. 222.89 g/mol $InCl_3$

8. (a) 4.39 *m*, (b) 2.195 moles (c) 395.49 g

9. 1.16 *m*

10. α = 8%

11. 3.28 mol/L

12. 35.8 °C

13. (a) $\Delta T_f = -0.35$ °C (b) 100.096 °C (c) 444.27 atm

Chapter Three

Exercise 3.3

4. 16% nitrobenzene; 84% water

5. 157.07 g/mol

6. 27%

7. 84.7%

Exercise 3.4

4. 32.8 g/L **5.** 9.1 g **6.** 0.04 mol/dm^3

7. (a) 0.67 g (b) 0.75 g

Revision exercise 3

3. 94.02 g/mol **5.** 4.46×10^{-3} g/L

6. (a) 1st extraction = 3 g (b) two portions extraction = 3.36 g

7. (a) $K_D = 11.25$ (b) 50% (c) 50.37 mL

8. $K_D = 9$, (a) 9 g (b) 9.67 g

9. (a) In the 1st extraction, 2.05 g in diethyl ether; 1.95 g in water. In the 2nd extraction, 1 g in diethyl ether; 0.95g in water

(b) 76.25%

10. 3.4×10^{-4} g/dm^3

Chapter Four

Exercise 4.1

5. 41.8 J **6.** −57684 J/mol or −57.684 kJ/mol

Exercise 4.2

3. -2.69×10^3 kJ/mol **4.** 489.4 g/mol **5.** 13.74 °C

Exercise 4.3

2. −111.2 kJ/mol **3.** −137 kJ/mol **4.** −196 kJ/mol

5. −277.5 kJ/mol

Exercise 4.4

4. − 1628.2 kJ/mol **5.** −150.6 kJ/mol

Revision exercise 4

4. +178 kJ/mol **5.** 566.7 °C **6.** (b) −2761.44 J

7. −4157.57 kJ/mol **8.** −32.7 kcal

Chapter Five

Exercise 5.1

3. 0.03
4. (c) 4.65×10^{-3} mol dm^{-3}

Exercise 5.2

1. (b) 2.68 atm
2. (b) 24.48 atm
3. (b) 1.5 atm
4. (b) 0.037 atm

Exercise 5.3

1. 1.49×10^{-5} atm^{-2}
2. $K_c = 0.52$ dm^6 mol^{-2}, $K_p = 1.36 \times 10^{-4}$ atm^{-2}
3. $K_p = 0.0455$ atm^{-1}
4. $K_c = 46974$ dm^3 mol^{-1}

Revision exercise 5

1. (a) 0.15 mol, 0.25 mol
   (b) $PCl_5 = 0.015$ mol dm^{-3}, $PCl_3 = 0.025$ mol dm^{-3}, $Cl_2 = 0.025$ mol dm^{-3}
   (c) $K_c = 0.042$ mol dm^{-3}
2. $K_p = 7.9$ atm
3. $[NO_2] = [SO_2] = 0.54$, $[SO_3] = [NO] = 1.06$
7. $K_c = 4.6 \times 10^{-2}$
8. $K_p = 2.3$ atm
9. $K_p = 2.86$
10. 640 µL
11. (a) $K_p = 0.18$ atm^{-1}
    (b) $P_{NO} = 0.12$ atm, $P_{Br} = 0.21$ atm, $P_{NOBr} = 0.18$ atm
16. 1.0 atm.

Chapter Six

Exercise 6.2

3. (a) pH = 13.3 (b) pH = 13.6 (c) pH = 4.3
4. 3.17×10^{-4} g

Exercise 6.3

1. 0.649 moles of acid should be added

2. pH = 6.8   3. 14.76 g of sodium acetate

Exercise 6.4

2. pH = 9.224, $[OH^-] = 1.67 \times 10^{-5}$ mol dm^{-3}, $h = 0.6\%$.

Exercise 6.5

2. (a) 1.96×10^{-8} (b) 2.814×10^{-8} mol^3 dm^{-9}
3. (a) 1.18×10^{-2} M   (b) 4.01×10^{-3} M
5. 5.6×10^{-5} mol dm^{-3}
6. (a) 3.69   (b) 1 g

Revision exercise 6

4. $K_a = 3.45 \times 10^{-7}$ mol dm^{-3}
5. 48. 68 g
6. $K_{b(F^-)} = 2.0 \times 10^{-11}$, $K_{b(HCOO^-)} = 5.26 \times 10^{-11}$ and $K_{b(CN^-)} = 1.92 \times 10^{-11}$
7. pH = 10.22
8. pH = 3.38
9. (b) pH = 8.31
10. (b) pH = 9.88, $K_h = 1.39 \times 10^{-11}$, $h = 0.05$
12. pH = 4.22
16. 6.91×10^{-5} mol/dm^3
17. 1.8×10^{-8} mol^3 dm^{-9}
18. (a) 1.34×10^{-3} mol/dm^3 (b) 1.8×10^{-9} mol/dm^3
19. Yes, $Q_{sp} > K_{sp}$
20. Super saturated since Q_{sp} $(2.76 \times 10^{-5}) > K_{sp}$ (1.39×10^{-8})
21. 1.72×10^{-10} mol^2 dm^{-6}
22. 6.49×10^{-5} mol dm^{-3}
23. (a) 5.816×10^{-4} mol dm^{-3} (b) 7.24×10^{-4} mol dm^{-3}
24. 0.05 mol dm^{-3}

25. 0.3464 mol dm^{-3}

26. 1.27×10^{-4} mol dm^{-3} (Ag_2CO_3) > 1.26×10^{-5} mol dm^{-3} (AgCl)

Chapter Seven

Exercise 7.1

2. 256 times **5.** 50 hours

Exercise 7.2

1. 0.025 M

3. 381.37 mg

5. (a) 128.8 min, 128.8 min ($t_{1/2}$ is always constant for the 1st order reaction)

(b) 299.2 min

6. (a) 8.842×10^{-3} mol dm^{-3} (b) 1.768×10^{-2} mol dm^{-3}

Exercise 7.3

1. (a) Rate = $k[A][B]$ (b) 0.33 dm^3 mol^{-1} s^{-1}

2. (a) 0.56 dm^3 $mol^{-1}s^{-1}$ (b) 1.59 s

4. $t_{1/2}$ = 100 days

6. 1.25 mol dm^{-3}

Exercise 7.4

1. (a) Rate = $k[A]^2[B]$ (b) 289.4 dm^6 mol^{-2} s^{-1} (c) 0.08 mol dm^{-3} s^{-1}

2. Rate = $k[SO_2Cl_2]$

4. (b) Rate ≃ 2.22×10^{-4} mol dm^{-3} s^{-1}

Exercise 7.5

1. 8.31×10^{-2}

3. $E_a = 25.4$ kJ mol^{-1}

4. Lower and higher temperatures are 244 K and 264 K, respectively.

Exercise 7.6

4. 23.2 kJ mol^{-1}

Revision exercise 7

1. (a) 2.76×10^{-6} g kg^{-1} (b) 2.7 years
2. 51 atm
4. $t = 1080.2$ s
8. (b) 1.4×10^{30} times
10. (a) First-order, $k = 1.6 \times 10^{-6} s^{-1}$ (b) 0.019 mol dm^{-3}, 240.7 h
11. 11.8 min
12. (a) $E_a = 91.4$ kJ mol^{-1}, $A = 2.9 \times 10^{14}$

Chapter Eight

Exercise 8.1

1. (b) 1.56 V
2. (a) 0.37 V (b) 0.49 V
3. (b) 1 atm
4. (a) Non-spontaneous ($E = -1.20$ V)
   (b) Spontaneous ($E = +0.62$ V)

Exercise 8.2

1. (c) 4.75
3. 5.24×10^{25}
4. 3.69×10^{15}
5. 0.37 V
6. (b) 0.08 V

Exercise 8.3

1. 80% or 0.8
2. 75% or 0.75
3. (a) 100% or 1.0 (b) 100% or 1.0
4. $i = 2$ and $i = 3$, respectively

Exercise 8.4

1. 1.34 $\text{cm}^2\ \Omega^{-1}\ \text{mol}^{-1}$
2. 119 $\text{cm}^2\ \Omega^{-1}\ \text{mol}^{-1}$
3. $3.91 \times 10^{-2}\ \text{m}^2\ \Omega^{-1}\ \text{mol}^{-1}$
4. 2.24×10^{-6} mol dm^{-3}
5. 9.54×10^{-5} mol dm^{-3}
6. 9.62×10^{-4} mol dm^{-3}

Revision exercise 8

1. $\Lambda_{m(KCl)} = 138.5\ \text{cm}^2\ \Omega^{-1}\ \text{mol}^{-1}$, $\Lambda_{m(NaCl)} = 195.6\ \text{cm}^2\ \Omega^{-1}\ \text{mol}^{-1}$
2. 70% or 0.7
5. $0.25\ \Omega^{-1}\ \text{m}^{-1}$, $0.012\ \Omega^{-1}\ \text{m}^2\ \text{mol}^{-1}$
6. 0.974 V
7. $K = \infty$
8. (c) –0.74 V (f) (i) 0.64 V
9. (a) 3.34 dm^3 (b) (ii) $E^\circ = 1.23$ V
10. 4.32×10^{-3} mol dm^{-3}
11. 0.313 V

Appendix

Appendix 1 Table of some fundamental physical constants

Constant	Symbol	Value
Avogadro's number	N_A	6.02×10^{23} mol^{-1}
Charge of electron/proton	e	1.60×10^{-19} C
Faraday constant	F	9.65×10^{4} C mol^{-1}
Mass of a neutron	m_n	1.673×10^{-27} kg
Mass of a proton	m_p	1.673×10^{-27} kg
Mass of an electron	m_e	9.11×10^{-31} kg
Molar volume of ideal gas at S.T.P	V_m	2.24×10^{-2} m^3 mol^{-1}
Planck's constant	h	6.625×10^{34} Js
Rydberg constant	R	1.097×10^{7} m^{-1}
Speed of light	c	3×10^{8} m s^{-1}
Universal gas constant	R	8.314 J mol^{-1} K^{-1}
		0.0821 L atm mol^{-1} K^{-1}

Appendix 2 Some conversion factors

1 cal	=	4.184 J		
1 kcal	=	10^3 cal		
1 Å	=	10^{-8} cm	=	10^{-10} m
1 L	=	1 dm^3	=	10^{-3} m^3
	=	1000 cm^3	=	1000 mL
1 nm	=	10^{-9} m		
1 eq	=	10^{-3} meq		
1 atm	=	1.01325×10^5 N m^{-2}		
	=	1.01325 bar		
	=	1.01325×10^5 Pa		
	=	760 Torr		
	=	760 Torr		
1 J	=	1 kg m^2 S^{-1} = 1Nm		
1 N	=	1 kg m S^{-2}		
1 Pa	=	1 kg m^{-1} S^{-2} = 1Nm^{-2}		

Appendix 3 Table of elements showing atomic numbers and atomic masses

Name of the element	Symbol	Atomic number	Atomic mass	Name of the element	Symbol	Atomic number	Atomic mass
Actinium	Ac	89	227	Mendelevium	Md	101	258
Aluminium	Al	13	26.9815	Mercury	Hg	80	200.59
Americium	Am	95	243	Molybdenum	Mo	42	95.94
Antimony	Sb	51	121.75	Moscovium	Mc	115	289
Argon	Ar	18	39.948	Neodymium	Nd	60	144
Arsenic	As	33	74.9216	Neon	Ne	10	20.183
Astatine	At	85	210	Neptunium	NP	93	237
Barium	Ba	56	137.34	Nickel	Ni	28	58.71
Berkelium	Bk	97	247	Nihonium	Nh	113	286
Beryllium	Be	4	9.0122	Niobium	Nb	41	93
Bismuth	Bi	83	208.980	Nitrogen	N	7	14.0467
Bohrium	Bh	107	264	Nobelium	No	102	259
Boron	B	5	10.811	Oganesson	Og	118	294
Bromine	Br	35	79.909	Osmium	Os	76	190
Cadmium	Cd	48	112.40	Oxygen	O	8	15.9994
Caesium	Cs	55	132.905	Palladium	Pd	46	106.4
Calcium	Ca	20	40.08	Phosphorus	P	15	30.9734
Californium	Cf	98	251	Platinum	Pt	78	195.09
Carbon	C	6	12.01115	Plutonium	Pu	94	242
Cerium	Ce	58	140.40	Polonium	Po	84	209
Chlorine	Cl	17	35.453	Potassium	K	19	39.102
Chromium	Cr	24	51.996	Praseodymium	Pr	59	141
Cobalt	Co	27	58.9332	Promethium	Pm	61	145
Copernicium	Cn	112	285	Protactinium	Pa	91	231
Copper	Cu	29	63.54	Radium	Ra	88	226
Curium	Cm	96	247	Radon	Rn	86	222
Darmstadtium	Ds	110	281	Rhenium	Re	75	186
Dubnium	Db	105	262	Rhodium	Rh	45	102.905
Dysprosium	Dy	66	162.50	Roentgenium	Rg	111	280
Einsteinium	Es	99	252	Rubidium	Rb	37	85.47
Erbium	Er	68	167.26	Ruthenium	Ru	44	101
Europium	Eu	63	151.96	Rutherfordium	Rf	104	261
Fermium	Fm	100	257	Samarium	Sm	62	150
Flerovium	Fl	114	289	Scandium	Sc	21	44.946
Fluorine	F	9	18.9984	Seaborgium	Sg	106	269
Francium	Fr	87	223	Selenium	Se	34	78.96
Gadolinium	Gd	64	157.25	Silicon	Si	14	28.086
Gallium	Ga	31	69.72	Silver	Ag	47	107.870

Name of the element	Symbol	Atomic number	Atomic mass	Name of the element	Symbol	Atomic number	Atomic mass
Germanium	Ge	32	72.64	Sodium	Na	11	22.9898
Gold	Au	79	196.967	Strontium	Sr	38	87.62
Hafnium	Hf	72	178.49	Sulfur	S	16	32.064
Hassium	Hs	108	277	Tantalum	Ta	73	181
Helium	He	2	4.0026	Technetium	Tc	43	98
Holmium	Ho	67	164.930	Tellurium	Te	52	127.604
Hydrogen	H	1	1.00797	Tennessine	Ts	117	294
Indium	In	49	114.82	Terbium	Tb	65	159
Iodine	I	53	126.904	Thallium	Tl	81	204.37
Iridium	Ir	77	192.2	Thorium	Th	90	232.038
Iron	Fe	26	55.847	Thulium	Tm	69	169
Krypton	Kr	36	83.80	Tin	Sn	50	118.71
Lanthanum	La	57	138.91	Titanium	Ti	22	48.867
Lawrencium	Lr	103	262	Tungsten	W	74	183.85
Lead	Pb	82	207.19	Uranium	U	92	238.03
Lithium	Li	3	6.939	Vanadium	V	23	50.942
Livermorium	Lv	116	393	Xenon	Xe	54	131.30
Lutetium	Lu	71	174.97	Ytterbium	Yb	70	173
Magnesium	Mg	12	24.312	Yttrium	Y	39	89
Manganese	Mn	25	54.9380	Zinc	Zn	30	65.38
Meitnerium	Mt	109	268	Zirconium	Zr	40	91

Glossary

Acid dissociation constant	An equilibrium constant of a weak acid which is expressed as the ratio of the product of the ionic concentration of the acid radical and the concentration of hydrogen ions raised to their stoichiometric coefficients to the concentration of undissociated molecule at constant temperature
Acid-base indicators	Substances which possess different colours at different hydrogen ion concentrations or pH of solution
Amphoteric substances	Substances which show both acidic and basic properties
Analyte	A substance whose chemical constituents are being identified and measured
Anode	An electrode at which oxidation reaction occurs
Aqueous solution	A solution in which water is a solvent
Azeotropic mixture	A mixture of liquids that boils at constant temperature, behaves like a pure liquid and exhibits the same composition in the liquid phase in the vapour phase
Bimolecular reaction	An elementary step in which two molecules are involved
Boiling point	The temperature at which the vapour pressure of a substance is equal to the atmospheric pressure
Boiling point elevation	The difference between the boiling point of a solution and that of pure solvent
Bond energy	The average amount of energy which is required to break one mole of bonds of a particular type in gaseous covalent molecules
Born Haber cycle	The splitting of the overall energy terms into several cyclic steps of energy changes required to form an ionic crystal

Boyle's law	At constant temperature, the volume of a fixed mass of a gas is inversely proportional to its pressure
Buffer solution	A solution which resists a change in pH when a small amount of either a strong acid or strong base is added to it
Calorimeter	A device that is used to measure the quantity of heat
Calorimetry	The method of determining heat of reaction by using a calorimeter
Catalyst	A chemical substance that alters the rate of a chemical reaction but remains chemically unchanged at the end of the reaction
Cathode	An electrode to which a reduction reaction takes place
Cell constant	The ratio of the cell's electrode separation to the cross section area of the cell's electrode
Charles' law	At constant pressure, the volume of a fixed mass of a gas is directly proportional to the absolute temperature
Chemical kinetics	The study of reaction rates and their mechanisms
Chromatography	A technique which is used to separate the components of a mixture due to their differences in the affinity between the two phases (a mobile phase and stationary phase)
Colligative properties	The properties of solutions that depend on the number of solute particles dissolved and not on the nature of solute particles
Column chromatography	A separation technique which uses a solid adsorbent as a stationary phase and a liquid solvent as a mobile phase
Combined gas law	For a fixed mass of a gas, the volume is directly proportional to the absolute temperature and inversely proportional to the pressure

Concentration cell	A galvanic cell in which a solution of the same nature is used with two half-cells of different concentrations
Conductance	The reciprocal of the resistance of a conductor with respect to the solution of an electrolyte
Corrosion	A gradual destruction of metal by electrochemical reactions when exposed to the environment
Critical solution temperature	The temperature at which the two liquid layers merge into one another to form one layer
Cryoscopic constant	The ratio of the depression of the freezing point of a solvent caused by dissolving a solute to the molality of the solution or is the quantity of the freezing point depressed when one mole of a solute is dissolved in one kilogram of the solvent
Dead battery	One in which its cell reaction has reached equilibrium and there is no more driving force for electric current
Degree of dissociation	The extent to which an electrolyte has dissociated in aqueous solution
Diffusion	A net movement of atoms or molecules from the region of high concentration to the region of low concentration
Distillation	A method of separating and purifying liquid mixtures into their individual components based on their differences in boiling point
Distribution or partition law	The ratio of the concentrations of solute X distributed between two immiscible liquids (1 and 2) at constant temperature
Dynamic equilibrium	A reversible reaction in which the forward and backward reactions are at equal rates
Ebullioscopic constant	The amount of temperature elevated when one mole of a solute is dissolved in one kilogram of a solvent
Effusion	The process by which gas molecules escape from their container through a tiny hole into an evacuated space

Electrochemical series	The arrangement of the elements in order of their standard electrode potentials
Electrochemistry	A branch of chemistry that deals with the interconversion of chemical and electrical energies
Elementary reaction (step)	A single reaction step in the overall reaction mechanism
End point	An indication of completeness of the titration reaction revealed by a sudden colour change of an indicator
Enthalpy	The amount of heat absorbed or evolved at constant temperature and pressure
Enthalpy change	The heat change at constant pressure accompanying the reaction
Enthalpy of atomisation	The heat or enthalpy change when one mole of gaseous substance is decomposed into its atoms in the gas phase
Enthalpy of combustion	The enthalpy changes of a system when one mole of the substance is completely burnt in air or oxygen
Enthalpy of formation	Enthalpy change when one mole of a compound is formed from its constituent elements in their standard states
Enthalpy of fusion	Enthalpy change when one mole of a solid substance is converted into a liquid state at its melting point
Enthalpy of neutralisation	The heat or enthalpy change when solutions of an acid and alkali react together to produce one mole of water
Enthalpy of solution	The heat or enthalpy change when one mole of a substance is dissolved in excess amount of solvent such that no further heat change occurs when more solvent is added to the solution
Enthalpy of sublimation	The heat or enthalpy change when one mole of a solid is directly converted into a gaseous state or vapour below its melting point without passing through a liquid state

Enthalpy of vaporisation	The heat or enthalpy change when one mole of liquid is converted into vapour or gaseous state at its boiling point
Equilibrium concentrations	The amounts of reactants and products present at equilibrium in a reversible reaction
Equilibrium reaction	A reversible reaction whereby the forward and backward reactions occur at the same rate
Equivalence point	A point at which the amount of a titrant added is enough to neutralise an analyte during titration
Exothermic reaction	A chemical reaction which involves the transfer of heat from the reaction system to the surroundings
Fractional distillation	A method for carrying out several simple distillations in one apparatus resulting in high yields of pure liquid components with minimum loss
Half-life	The time required for the initial concentration of the reactant(s) to decrease to a half
Heat	A transfer of thermal energy as a result of a temperature difference
Heat capacity	The amount of heat required to raise the temperature of a substance by one degree Celsius (1 °C) or one Kelvin (1 K)
Hess's law	If reactions can be converted into products by a series of reactions, the sum of the heats of these reactions is equal to the heat of reaction for direct conversion from reactants to products
Heterogeneous catalysis	A catalytic reaction in which the reactants and the catalyst are in different phases
Homogenous catalysis	A catalytic reaction in which the reactants and the catalyst are in the same phase
Ideal gas	The one which obeys the gas equation $PV = nRT$ at all pressures and temperatures
Ideal gas equation	The volume of a given amount of a gas is directly proportional to the number of moles of

	the gas, temperature and inversely proportional to the pressure
Ideal solution	A solution that is made from completely miscible liquids whose intermolecular forces are the same as the intermolecular forces between the liquids involved in forming the solution and obeys the Raoult's Law at any concentration
Immiscible liquids	Liquids which when mixed together in any proportions form two separate phases
Indicator	The substance which changes its colour according to pH change in the solution
Indicator error	The difference between the theoretical end point and the actual end point
Internal energy	Total energy attributed to the particles of matter and their interactions within a system
Ionic product	The product of the ionic concentrations in moles per litre each raised to its stoichiometric coefficient for a sparingly soluble salt
Ionisation energy	The energy which is required to remove completely one mole of electrons from one mole of gaseous atoms or ions
Isotonic solutions	Are solutions with the same osmotic pressures across a semi-permeable membrane
Kohlrausch's law	The molar conductivity of an electrolyte at infinite dilution equals the sum of the individual molar conductivities of the anions and cations
Lattice energy	The energy released during the formation of one mole of a crystal from its constituent ions at standard conditions or the energy required to separate one mole of an ionic solid into gaseous ions at standard conditions
Law of mass action	The rate of chemical reaction is proportional to the active mass of the reacting substances
Le Châtelier's principle	If a system is in equilibrium, any change imposed on the system tends to shift the equilibrium so as to nullify the effect of the imposed change

Lowering of vapour pressure	The difference between vapour pressure of pure solvent and the vapour pressure of the solution
Miscible liquids	Liquids which dissolve completely in one another in all proportions to form a homogeneous solution
Molality	The number of moles of a solute dissolved in 1 kg of a solvent
Molar conductivity	The specific conductivity of an electrolyte divided by the molar concentration of the electrolyte
Molar gas volume	The volume occupied by one mole of any gas at standard temperature and pressure
Mole fraction	The ratio of the number of moles of a given component in a mixture to the total number of moles in the mixture
Molecularity of the reaction	The number of molecules (species) reacting in an elementary step
Non-ideal solution	A solution that is made from completely miscible liquids whose intermolecular forces of attractions are different from the intermolecular forces of the liquid components that form the solution
Order of the reaction	The exponent to which the concentration of a reactant is raised to in the rate law equation
Osmosis	The process whereby solvent molecules move from a region of dilute solution to a region of concentrated solution through a semipermeable membrane
Osmotic pressure	The pressure applied on the side of a solution to stop the net flow of the solvent into the solution through semi-permeable membrane
Oxidation	The electron loss by a substance or increase in oxidation state of a substance or addition of oxygen to a substance or removal of hydrogen from a substance

Oxidation state	The number of electrons gained, shared or lost by an atom during combination with other atoms
Oxidising agent	A specie that causes oxidation but itself becomes reduced
Paper chromatography	A separation technique which uses liquids in both stationary and mobile phases and involves a flow of a solvent on a filter paper
Partially miscible liquids	Are liquids which dissolve in one another to a limited extent
pH	A negative logarithm of concentration of hydrogen ions
Raoult's Law	The vapour pressure of a solvent above a solution ($P_{solvent}$) is equal to the vapour pressure of pure solvent times the mole fraction of the solvent ($\chi_{solvent}$)
Rate constant	A constant which gives the relationship between the rate of reaction and concentrations of the reactants
Rate determining step	The slowest step in a series of steps of the reaction mechanism from which the rate law is determined
Rate law	A mathematical expression which shows the dependence of the rate of chemical reaction on the concentration of the reactants
Reaction mechanism	A series of steps through which a certain chemical reaction passes to form products
Reaction quotient	Is the ratio of the product of product concentrations to those of the reactants raised to their respective stoichiometric coefficients when the reaction has attained or not attained equilibrium
Real gas	A gas that does not have the properties assigned to an ideal gas. Its molecules have a finite size and there are forces between them

Redox reactions	Reactions which involve simultaneous oxidation and reduction of chemical species
Redox titration	The determination of the concentration of an analyte from the sample through redox reaction by measuring volumes of the analyte and titrant
Reducing agents	A specie that causes reduction but itself becomes oxidised in the reaction
Reduction	The electron gain by a substance or decrease in oxidation state of a substance or removal of oxygen from a substance or addition of hydrogen to a substance
Relative lowering of vapour pressure	The ratio of the lowering of vapour pressure to the vapour pressure of pure solvent
Reversible reaction	A chemical reaction that can be made to reverse direction by just an infinitesimal change
Salt hydrolysis	The reaction of salt with water to form either an acidic or a basic solution
Self-indicator	A reactant which acts as an indicator due to its colour change at the end of the reaction
Solubility	The maximum quantity in grams or moles that can dissolve to form one litre of a saturated solution
Solubility product	The product of the concentration of ions in moles per litre raised to their stoichiometric coefficient for a saturated sparingly soluble salt solution
Specific conductivity	The reciprocal of the resistivity of a conductor with respect to the solution of an electrolyte
Specific heat capacity	The amount of heat required to raise the temperature of a unit mass of a substance by one degree Celsius (1 °C) or one Kelvin (1 K)
Standard cell potential	The potential difference of the cell measured at standard conditions

Standard electrode potential	The potential difference of an element measured against hydrogen as a reference electrode when the concentrations of H^- and ions of that element are equal to one mole per litre at standard conditions
Standard enthalpy of combustion	The heat or enthalpy change of a system when one mole of the substance is completely burnt in oxygen at standard conditions
Standard enthalpy of formation	The heat or enthalpy change when one mole of a substance is formed from its pure elements in their standard state under standard conditions (1 atm and 25 °C)
Standard enthalpy of neutralisation	The heat energy released when one mole of hydrogen ions reacts with one mole of hydroxide ions to form one mole of water at standard temperature and pressure
Standard enthalpy of solution	The amount of heat absorbed or released during the dissolution of one mole of a substance to form one litre of a solution at standard temperature and pressure
Steam distillation	A process whereby the steam is passed through impure liquid which is immiscible with water; and in the presence of steam, the liquid compound is made volatile and distils with steam
Sublimation energy	The amount of energy required to change one mole of solid substance at constant pressure directly into a gaseous state without passing through a liquid state
Thermochemistry	A branch of chemistry that describes the energy changes that occur during chemical reactions
Unimolecular reaction	An elementary step in which one molecule of reactants is involved in the reaction
van't Hoff – Avogadro's law	Two solutions with equal concentrations of different solutes exert the same osmotic pressure at the same temperature

van't Hoff – Boyle's law	The osmotic pressure (π) of a dilute solution is directly proportional to its molar concentration (M) or inversely proportional to the volume of the solution, provided that temperatures remain constant
van't Hoff-Charles' law	The osmotic pressure of a dilute solution is directly proportional to the absolute temperature provided that the concentration remains constant
van't Hoff's factor	The ratio of number of particles produced as the result of dissociation to the number of non-dissociated particles
van't Hoff's law of osmotic pressure	The magnitude of osmotic pressure is proportional to the number of solute particles present in a given volume of solution
Vapour density	The ratio between the mass of a certain volume of the gas to the mass of the same volume of hydrogen gas at the same temperature and pressure
Volumetric analysis	The determination of the concentration of an analyte (unknown substance) in a solution by measuring volumes

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