CHEMISTRY

FOR

ASSOCIATE NURSING PROGRAM

STUDENT'S BOOK

Senior 6

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FOREWORD

Dear Student,

Rwanda Basic Education Board is honoured to present to you this Chemistry Textbook for Senior Six for Associate Nursing program which serves as a guide to competence-based teaching and learning to ensure consistency and coherence in the learning of Chemistry subject.

The Rwandan educational philosophy is to ensure that you achieve full potential at every level of education which will prepare you to be well integrated in society and exploit employment opportunities. The government of Rwanda emphasizes the importance of aligning teaching and learning materials with the syllabus to facilitate your learning process.

Many factors influence what you learn, how well you learn and the competences you acquire.

Those factors include the instructional materials available among others. Special attention was paid to the activities that facilitate the learning process in which you can develop your ideas and make new discoveries during concrete activities carried out individually or with peers.

In competence-based curriculum, learning is considered as a process of active building and developing knowledge and meanings by the learner where concepts are mainly introduced by an activity, a situation or a scenario that helps the learner to construct knowledge, develop skills and acquire positive attitudes and values. For effective use of this textbook, your role is to:

Work on given activities including application activities which lead to the development of skills;

Share relevant information with other learners through presentations, discussions, group

work and other active learning techniques such as role play, case studies, investigation and research in the library, from the internet or from your community;

Participate and take responsibility for your own learning;

Draw conclusions based on the findings from the learning activities.

I wish to sincerely extend my appreciation to the people who contributed towards the development of this book, the Ministry of Health, Human Resource for Health Secretariat (HRHS), University of Rwanda, School of Nursing and Midwifery, Higher Learning Institutions and Rwanda Basic Education Board.

Special gratitude goes to University faculty, Nurses, Midwives, Teachers, illustrators, designers, HRH Secretariat Staff and REB Staff who diligently worked to successful completion of this book.

Dr.Nelson MBARUSHIMANA
Director General, Rwanda Basic Education Board

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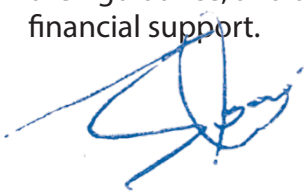

Joan MURUNGI,
Head of Curriculum, Teaching and Learning Resources Department / REB

ACRONYMS AND ABBREVIATIONS

IUPAC: International Union of Pure and Applied Chemistry

REB: Rwanda Basic Education Board

REMA: Rwanda Environmental Management Authority

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UNIT 1

PROPERTIES AND USES OF TRANSITION METALS

UNIT 1: PROPERTIES AND USES OF TRANSITION METALS

Key Unit Competence:

Explain the properties and uses of transition metals.

Learning objectives

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

- Discuss qualitatively the properties of transition elements;
- Explain the principle of ligand exchange;
- State the rules of naming complex ions and stereoisomers;
- Describe reactions of transition metals;
- State the uses of transition metals;
- Relate the electronic configurations to special properties of transition metals;
- Predict the shape of the complex compounds of transition metal cations;
- Perform the confirmatory tests for transition metal ions.

Introductory Activity

The following pictures show how some elements play a big role in our daily lives.

Observe these objects carefully.

A	B	C	D
E	F	G	J

Most of the metals in the periodic table belong in the d-block of transition metals. They are hard and strong, and many of them are very familiar to us. For instance, zinc

is in brass instruments like trumpets and tubas. Have you ever heard of the element "scandium" before? But you have interacted with it if you have ever ridden a bicycle.

1.1. Definition and electronic configuration of transition metals.

Activity 1.1

1. Write the electronic configuration of the following atoms and ions:
   a. Ca(Z=20) b. Ca^{2+} c. Na(Z=11) d. Na^{+}
2. Referring to the portion of periodic table in this book,
   a. Write the electronic configuration of the elements from Sc to Zn.
   b. Point out any difference between the electronic configuration of the above elements and that of other elements in s and p blocks
3. Define the term transition metal.

According to IUPAC system, a transition metal is "an element whose atom has a partially filled d sub-shell, or which can give rise to cations with an incomplete d-orbitrals".

Transition metals are located between groups 1& 2 (s-block) and group 13 (p-block) on the periodic table. The elements are also called d-block elements because their valence electrons are in d-orbitals.

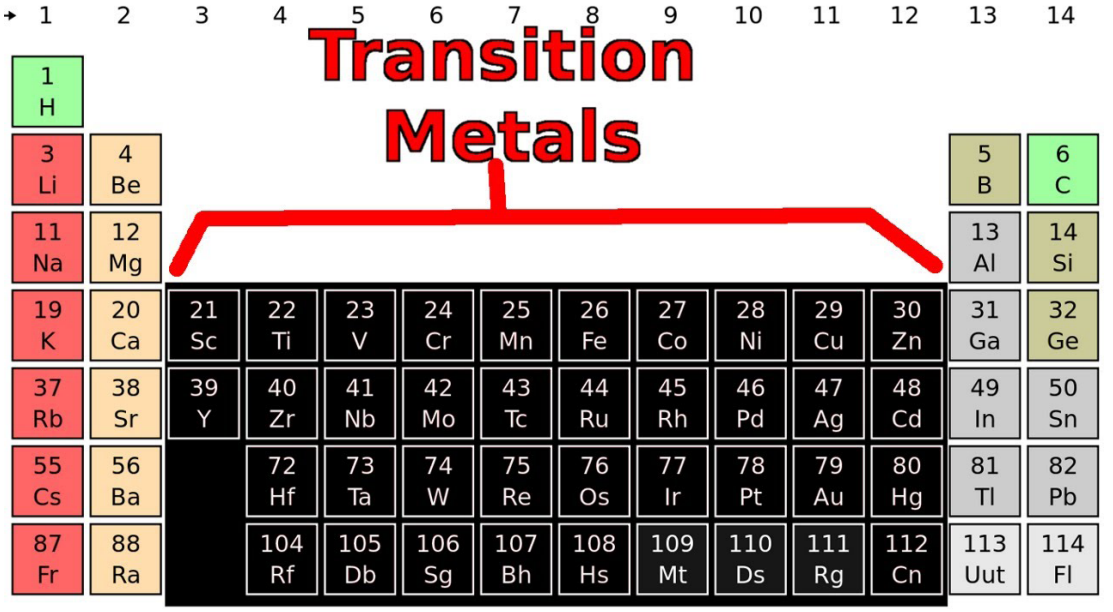


Figure 1.1: Portion of periodic table with transition metals in the middle

The properties of transition elements are between the highly reactive metallic elements of the s-block which generally form ionic compounds and the less reactive elements of the p-block which form covalent compounds. Transition metals form ionic compounds as well as covalent compounds.

The first 3 rows, i.e. period 4, period 5 and period 6, are called first transition series, second transition series and third transition series respectively. The metals of the first series are all hard and dense, good conductors of heat and electricity.

This block is known as the transition metals because some of their properties show a gradual change between the active metals in s-block and p-block where non-metals are found.

Electronic configuration is the arrangement of electrons in orbitals around the nucleus. The electronic structure of the first transition series is shown in the table below:

Element	Atomic number	Electronic configuration	Noble gas configuration	**Electron in box diagram**
Scandium (Sc)	21	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$	$[Ar]4s^2 3d^1$	
Titanium (Ti)	22	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$	$[Ar]4s^2 3d^2$	
Vanadium (V)	23	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$	$[Ar]4s^2 3d^3$	
Chromium (Cr)	24	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$	$[Ar]4s^1 3d^5$	
Manganese (Mn)	25	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$	$[Ar]4s^2 3d^5$	
Iron (Fe)	26	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$	$[Ar]4s^2 3d^6$	
Cobalt (Co)	27	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$	$[Ar]4s^2 3d^7$	
Nickel (Ni)	28	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$	$[Ar]4s^2 3d^8$	
Copper (Cu)	29	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$	$[Ar]4s^1 3d^{10}$	
Zinc (Zn)	30	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$	$[Ar]4s^2 3d^{10}$	

Figure 1.2: Electronic configuration of the first transition series

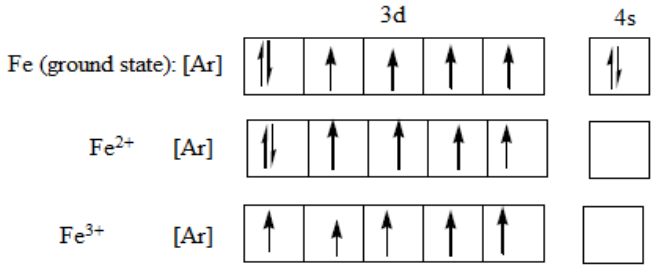
When building electronic structure of transition metals, 4s orbital is filled before 3d orbitals.

The transition elements are stable when their d-orbitals are filled (d^{10}) or when their d-orbitals are half filled (d^5).This explains the electronic structure of copper, [Ar] $4s^1 3d^{10}$ instead of [Ar] $4s^2 3d^9$. The same applies for Cr: [Ar] $4s^1 3d^5$ and not [Ar] $4s^2 3d^4$.

In order to attain that stability an electron can jump from 4s orbital to 3d orbital because those two orbitals are close in energy.

This also explains why Fe^{2+} with $3d^6$ is easily oxidized to Fe^{3+} with $3d^5$ and Mn^{2+} with $3d^5$ is resistant to oxidation to Mn^{3+} with $3d^4$.

Transition metals form ions by losing electrons first from the 4s sub-shell rather than the 3d sub-shell. Hence electronic configuration of Fe, Fe^{2+} and Fe^{3+} are the following:



The 4s electrons are removed before 3d electrons. This is because the 3d electrons are inner while the 4s electrons are outer therefore the outer electrons (4s) have to be removed before the inner electrons.

Checking up 1.1

1. Explain the difference between the electronic configuration of transition elements and that of main group elements.
2. Why d-block metals are so called transition metals?

1.2. Properties of the transition metals

1.2.1. Melting and boiling points

Activity 1.2 (a)

Experiment: Investigation of the melting point of transition metals compared with s-block elements

Materials: Potassium or Rubidium metal and copper or iron metal, pair of tongs, spatulas, bunsen burner and match box.

Procedure:

1. Take a half filled spatula of
   a. Potassium (K) or Sodium (Na), Rb, or Cs
   b. Iron turnings or very small piece of copper sheet (which can fit on a spatula)
2. Heat both spatulas on the Bunsen burner flame
3. Write down the observations
4. What can you conclude about your findings?

The melting points and the molar enthalpies of fusion of the transition metals are both high in comparison to main group elements. Most of the transition metals have melting points above 1000 °C; mercury is liquid at room temperature.

This is due to the high number of valence electrons that increases the electrostatic attraction force between those electrons and the metallic cations, hence increasing the strength of the metallic bond and the melting point.

Table 1.1: Melting and boiling points of the 1st series of Transition Metals

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
MP/^{0}C	1400	1677	1917	1903	1244	1539	1495	1455	1083	420
BP/^{0}C	2477	3277	3377	2642	2041	2887	2877	2837	2582	908

Checking up 1.2 (a)

Compare and comment on the melting points of transition metals and those of s-block metals.

1.2.2. Densities and atomic/metallic radii

Activity 1.2 (b)

Procedure for practical:

1. a. Take a magnesium ribbon and a copper foil of the same size (if possible you may use their turnings)
   b. You weigh those two samples using an electronic balance and record their masses
2. a. Take aluminum foil and copper foil of the same size (if possible you may use their turnings)
   b. You weigh those two samples using an electronic balance. Record their masses
3. Comment on your observations by explaining why their masses are different and yet they have the same size.
4. Use the internet or any book or even this one to interpret the data given about metallic radii of the first series transition metals. From your research, compare metallic radii of transition metals and those of main group elements.

The transition elements are much denser than the s-block elements and show in general a gradual increase in density from left to right in a period as you can see below from scandium to copper. This trend in density can be explained by a decrease in metallic radii coupled with the relative increase in atomic mass

Table 1.2: Density (g cm $^{-3}$) of the first transition series

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1

Table1.3: Metallic radii of the first transition series

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
164	147	135	129	137	126	125	125	128	137

Checking up 1.2 (b)

The metallic radius of vanadium is smaller than that of titanium. Explain this statement.

1.2.3. Ionization energies

Activity 1.2 (c)

Use this book or any other source (textbook or search engine) to interpret/ analyze the summary about ionization energies of the transition metals (first series). From your findings, compare

a. Ionization energies of those transition metals.

b. Ionization energies of transition metals and those of main group elements

The ionization energy of transition metals is related to the energies of its d orbitals, its ease of oxidation, and its basicity.In simplest terms, the greater the ionization energy of a metal, the harder it is to pull an electron from it.

As the number of protons increases across a period (or row) from left to right of the periodic table, the first ionization energies of the transition-metal elements are relatively the same, while that for the main-group elements increases.

In moving across the series of metals from scandium to zinc, a small change in the values of the first and second ionization energies is observed. This is due to the build-up of electrons in the immediately underlying d-sub-shells that efficiently shields the 4s electrons from the nucleus and minimizing the increase in effective nuclear charge from element to element.

Table 1.4: First, second and third ionization energies of 1st Series Transition metals /kJ mol^{-1}

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
1st I.E	631	656	650	653	717	762	758	736	745	906
2nd I.E	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
3rd I.E	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829

The figure 1.3 below shows the first ionisation energies for transition metals of 1st, 2nd and 3rd rows (series).

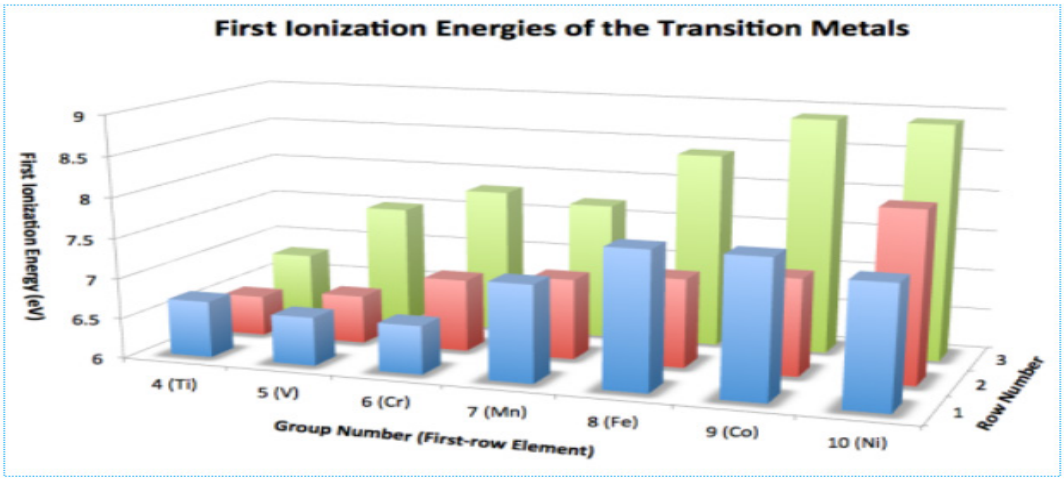


Figure 1.3: First Ionisation Energies of the transition elements.

In general, ionization energy increases as we move from left to right across the period. Notable dips occur at row 1, group 10 (Ni) and row 3, group 7 (Re).

Checking up 1.2 (c)

Briefly explain the following observations:

a. The first ionization energy of cobalt is only slightly larger than the first ionization energy of iron.

b. The third ionization energy of iron is much lower than the 3rd ionization energy of Mn.

1.2.4. Transition elements have variable oxidation states

Activity 1.2 (d)

Use this book or any other source (textbook or search engine) to

a. Explain the term oxidation number

b. Compare the oxidation numbers of transition metals (first series) and those of main group elements.

c. Analyze the stability of ions formed by transition metals (first series).

Oxidation state is a number assigned to an element in chemical combination which represents the number of electrons lost or gained.The transition elements from

Titanium to Copper all form ions with two or more oxidation states. In most cases, this is the result of losing the two electrons of 4s orbital and electeons in 3d orbitals. The 4s electrons are lost first because they are in the highest energy level. However, because the 3d and 4s energy level are so close in energy, the 3d electrons can also be lost when an atom forms a stable ion. The common oxidation states shown by the first transition series are:

Table 1.5: The oxidation states shown by the transition metals (series)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3	+2 +3 **+4**	+2 +3 +4 **+5**	+2 +3 +4 +5 **+6**	**+2** +3 **+4** +5 +6 **+7**	+2 **+3** +4 +6	**+2** **+3** +4	**+2** +3 +4	+1 **+2**	+2

- The common stable oxidation states for those transition metals with variable oxidation states are bolded and underlined.
- The oxidation state corresponding to a full or half-filled d-orbital is energetically stable. For example, Fe^{3+} is more stable than $Fe^{2+}$and Mn^{2+} is more stable than Mn^{3+}.
- However, in most compounds and solutions, copper exist as Cu^{2+} ion rather than Cu^{+} ion. Meaning that the former is more stable than the latter. The explanation of this is beyond this level.

Checking up 1.2 (d)

Which gaseous ion is more stable, Mn^{2+} or Mn^{3+}? Explain why ?

1.2.5. Most transition metals and their compounds have high ability of being catalyst

Activity 1.2 (e)

Experiment 1: Preparation of oxygen using hydrogen peroxide, H_2O_2, without a catalyst

a. Put 10 mL of H_2O_2 in a conical flask (Pyrex preferably)

b. Write down the observation, if any.

Experiment 2: Preparation of oxygen using hydrogen peroxide, H_2O_2, in presence of a transition metal compound, MnO_2.

a. Put 10 mL of H_2O_2 in a conical flask (Pyrex preferably)

b. Put a very small amount of MnO_2 in the conical flask

c. Write down the observation, if any.

Question:

What is the role of MnO_2 in the above experiment?

Compare the rate of the formation of oxygen gas in the two experiments.

A catalyst is a substance that can speed up (positive catalyst) or that can slow down (negative catalyst) the rate of reaction and is found unchanged at the end of the reaction. But generally the term catalyst is used for the substance that helps in accelerating the rate of the reaction. A catalyst that speeds up the reaction provides another pathway with lower activation energy.

In some catalytic process, transition metal ions undergo changes in their oxidation states but are regenerated at the end of the reaction.

The reasons for transition metals to work as catalysts:

- Presence of empty d orbitals which enable transition metal ions (or atoms) to form temporary bonds with reactant molecules at the surface of a catalyst and weakens the bond in the reactant molecules
- Variable oxidation states which allow them to work as catalysts in the reactions involving the transfer of electrons

Table 1.6: Reactions catalysed by transition metals

Transition elements	Substance used as a catalyst	Reaction catalyzed
Ti	$TiCl_3/Al_2(C_2H_5)_6$	Polymerization of ethene into polythene
V	V_2O_5 or vanadate (VO_3^-)	$2SO_2 + O_2 \longleftrightarrow 2\ SO_3$
Fe	Fe or Fe_2O_3	$N_2 + 3H_2 \longleftrightarrow 2NH_3$ Haber process
Ni	Ni	$RCH{=}CH_2 + H_2 \longrightarrow RCH_2CH_3$ Hardening of vegetable oil (E.g.: Manufacture of margarine)
Cu	Cu or CuO	$CH_3CH_2OH + ½O_2 \longrightarrow CH_3CHO + H_2O$ Oxidation of ethanol to ethanal
Pt	Pt	$2\ SO_2 + O_2 \longleftrightarrow 2\ SO_3$ Contact process
Pt	Pt	$4NH_3 + 5\ O_2 \longrightarrow 4NO + 6\ H_20$ Manufacture of nitric acid from ammonia

Checking up 1.2 (e)

Explain why s-block metals and their compounds are not used as catalysts

1.2.6. Most transition metal ions are paramagnetic

Activity 1.2(f)

Given the following materials:

1. Organize yourselves into groups to identify the objects shown in the pictures above.
2. Using a magnet, classify the above materials into two groups as shown in the table below.

   Objects attracted by a magnet

   Objects not attracted by a magnet
3. Research, using any relevant source (textbook or internet), to identify in which metal the objects **A** to **E** are made
4. Research to know why some objects are attracted by a magnet while others are not

Paramagnetism is a property of substances to be attracted in a magnetic field. Substances which are not attracted (i.e slightly repelled) in a magnetic field are said to be diamagnetic. Transition metal ions show paramagnetism because of the presence of unpaired electrons in their 3d arbitrals.

The greater the number of unpaired electrons, the stronger the paramagnetism; that is the reason why:

- Fe^{3+} is more paramagnetic than Fe^{2+} because Fe^{3+} has five unpaired electrons while Fe^{2+} has four unpaired.
- Sc^{3+} and Zn^{2+} are not paramagnetic, they are diamagnetic because they do not have unpaired electrons.

Other examples of paramagnetic substances are: Cr, Mn, $CuSO_4$, Fe, Co, Ni, Pt.

Examples of diamagnetic substances are: Zn, Cu^+, Au^+, TiO_2.

Checking up 1.2 (f)

Predict whether the following substances are paramagnetic or not. Explain

a. $CuSO_4$
b. Co
c. Ca
d. Cr

1.2.7. Formation of alloys

Activity 1.2 (g)

Observe the trophies or other objects made in the materials below and compare their appearances with the elements from which they are derived.

a. Bronze with copper
b. Stainless steel with iron
c. Pewter and copper

You can use the internet, books (including this one) or any other relevant source to find the figures of the above objects, the elements they are made from and their uses.

An alloy is a Homogeneous solid mixture (solid solution) made by combining two or more elements where at least one is a metal.

Importance of alloying:

- Increase of the strength of a metal,
- Resistance to corrosion,
- Gives to the metal a good appearance

Generally, alloys are needed and used to improve the quality of the required material. For example, *brass* (alloy of zinc and copper) is much stronger than either pure copper or pure zinc. Pure gold is too soft to be used in some applications.

Table 1.7: The properties and uses of some common alloys formed by transition metals (first series)

ALLOY	COLOUR	COMPOSITION	PROPERTIES	USES
Bronze	Chocolate brown	90 % copper 10 % tin	Hard and strong Does not corrode easily Has shiny surface	To build statues and monuments In the making of medals, swords and artistic materials.
Brass	Yellow	70 % copper 30 % zinc	Harder than copper	In the making of musical instruments and kitchenware.
Steel	Blue, grey, etc	99 % iron 1 % carbon	Hard and strong	In the construction of building and bridges. In the building of the body of cars and railway tracks.
Stainless steel	Ranges of colors, including blue, black, bronze, gold, green, red/ violet	74 % iron 8 % carbon 18 % chromium	Shiny Strong Does not rust	To make cutlery and surgical instruments.
Duralumin	Metallic colour	93 % aluminium 3 % copper 3 % magnesium 1 % manganese	Light Strong	To make the body of airplanes and bullet trains.

Pewter	Grey	96 % tin 3 % copper 1 % antimony	Luster Shiny Strong	In the making of souvenirs.

Checking up 1.2 (g)

1. Explain why alloys are said to be solid solutions.
2. Give the importance of alloying

1.2.8. Formation of complex ions

Activity 1.2 (h)

Use this book or any other source (library textbook or internet) to analyze and discuss on the following. You have to take note on what to be presented to share with your colleagues and teacher.

a. What is a ligand?
b. State the types of ligands
c. The geometry of complexes

A complex or coordination compound is a chemical species made of a central metal (cation or neutral) bonded to other chemical species called ligands by coordination or dative bonds. A complex may be neutral, positively or negatively charged.

Transition metals form complexes because of:

- Their small and highly charged ions,
- The presence of vacant (empty) d-orbitals which can accommodate lone pair of electrons donated by other groups (ligands)

The general formula of a complex is: $[ML_n]^y$

Where:

- M-metal ion or atom
- L-Ligand
- n-the number of ligands surrounding the metal
- y-the charge of the complex; $[ML_n]$ indicates a neutral complex.

-Coordination number of a complex: is the number of coordinate bonds on the central metal in a complex.

-Ligand: It is a species (anion or a molecule) that is bonded to a central metal ion or atom in a complex. A ligand should have at least one lone pair of electrons to form a coordinate bond.

Ligands are classified depending on the number of sites at which one molecule of a ligand is coordinated to the central metallic atom; the ligands are classified as monodentate (or unidentate), and polydentate (or multidentate) ligands

a. Monodentate ligands

The ligands which have only one donor atom or are coordinated through one electron pair are called monodentate ligands because they have only one tooth with which to attach themselves to the central cation or atom. Such ligands are coordinated to the central metal at one site or by one metal-ligand bond only. These ligands may be neutral molecules or in anionic form.

The table below provides examples of some monodentate ligands.

Table 1.8: some monodentate ligands

Ligand symbol	Ligand name
$H_2\ddot{O}$:	Aqua/aquo
:NH_3	Ammine
CO	Carbonyl
F^-	Fluoro
Cl^-	Chloro
NO_2^-	Nitro (coordination through n-atom)
NH_2^-	Amido

Ligands that can use different sites to coordinate to the central metal are called "ambidentate": e.g. CN^- and NC^-(see table above).

Notice that a ligand with a donor atom that possesses 2 lone pairs of electrons, such as $H_2\ddot{O}$:, is not bidentate, since it cannot use both lone pairs simultaneously to bind to the metal because of the steric effect.

b. Polydentate ligands

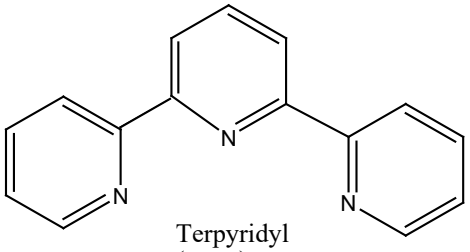
These may be bidentate, tridentate, tetradentate, pentadentate, and hexadentate ligands if the number of donor atoms present in one molecule of the ligand attached with the central metallic atom is 2, 3, 4, 5, and 6 respectively. Thus one molecule of these ligands is coordinated to the central metallic atom at 2, 3, 4, 5, and 6 sites respectively. In other words, we can say that one molecule of these ligands makes 2,

3, 4, 5, and 6 *metal-ligand coordinate bonds* respectively.

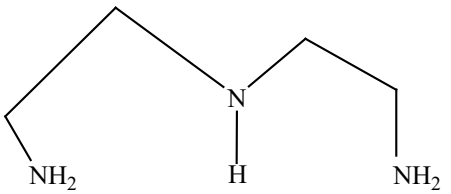
- Bidentate:

Ethylenediammine

- Tridentate

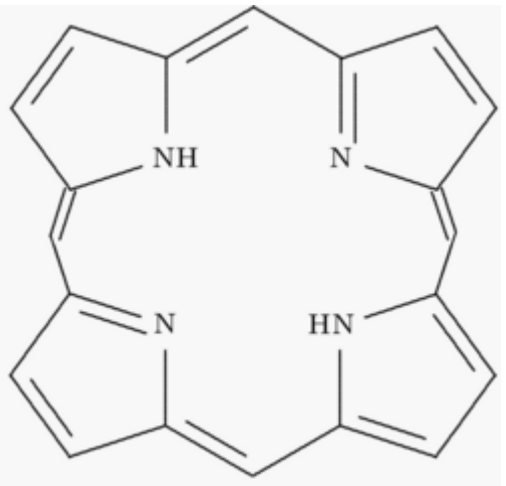


Terpyridyl
(terpy)



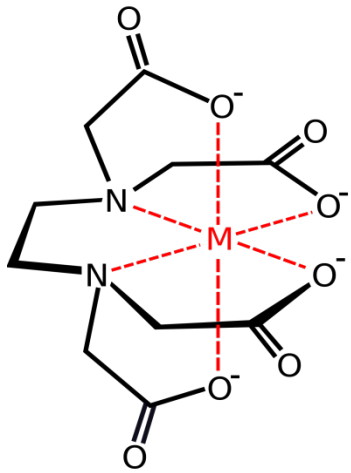
Bisethylenediammine
(tris)

- Tetradentate



- Hexadentate

The structure shows that it has two neutral N- atoms and four negatively charged O^- atoms as its donor atoms which can form coordinate bonds with a transition metal ion.

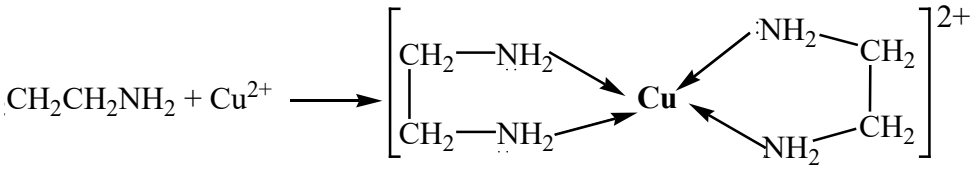


The complex ions which form between polydentate ligands and cations are known as chelates or chelated complexes.

In general, polydentate ligands form more stable complexes than monodentate ligands. The stability of complex is much enhanced by chelation. A polydentate ligand can hold the central cation more strongly.

Examples of complexes:

- Copper (II) ions have a coordination number of four in most of its complexes $[Cu(H_2O)_4]^{2+}$, $[Cu(NH_3)_4]^{2+}$, $[CuCl_4]^{2+}$, $[Cu(NH_2\text{-}(CH_2)_2\text{-}NH_2)_2]^{2+}$, …



- Most of ions have coordination number of 6.

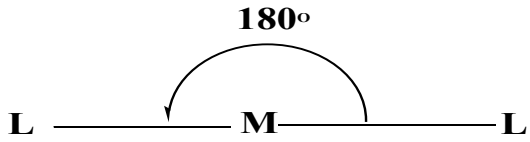
  $[Cr(H_2O)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$, $[Cr(H_2O)_4Cl_2]^{-}$, …
- Very few ions have a coordination number of 2: $[Ag(NH_3)_2]^{+}$, $[Ag(CN)_2]^{-}$, $[CuCl_2]^{-}$, …

Geometry of complexes

Complexes have a variety of geometries or shapes, but the most common geometries are the following:

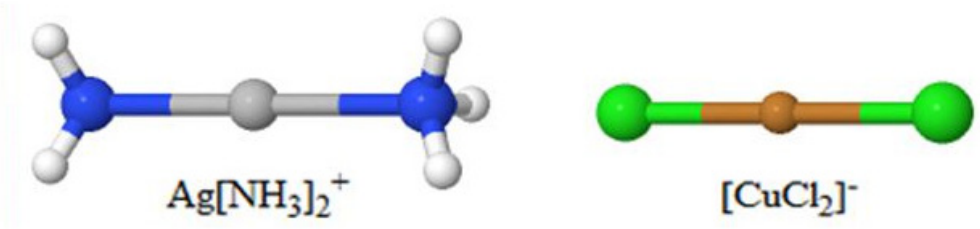
- Complexes with coordination number 2 adopt a linear shape. Example: $[Ag(NH_3]_2^{+}$: $[H_3N\text{-}Ag\text{-}NH_3]^{+}$

The complexes having coordination number of 2 are **linear** since minimises ligand repulsion.



Cu^+, Ag^+ and Au^+ form such complexes

Examples: $[Cu(CN)]_2^-$, $[Cu(NH_3)]_2^+$, $[Hg(CN)]_2^-$, $[CuCl_2]^-$

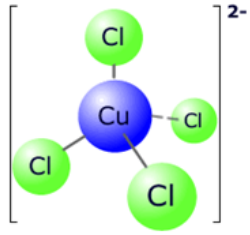


- Complexes with coordination number 4 generall adopt a tetrahedral shape. But few of them can form a square planar shape.

Examples:

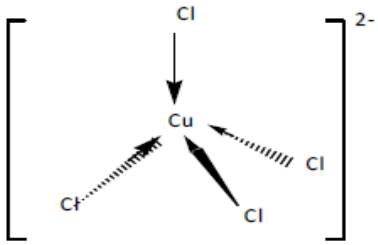
$[Zn(NH_3)_4]^{2+}$, $[NiCl_4]^{2-}$ and some few others adopt a *square planar shapes*, examples: $[Cu(NH_3)4]^{2+}$, $[Ni(CN)_4]^{2-}$,$[CuCl_4]^{2-}$,$[CoCl_4]^{2-}$,…

The square plannar geometry is characteristic of transition metal ions with eight d electrons in the valence shell, such as platinum(II)and gold(III).

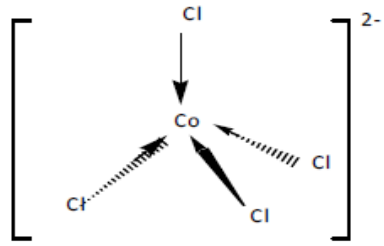


tetrachlorocuprate (II) ion

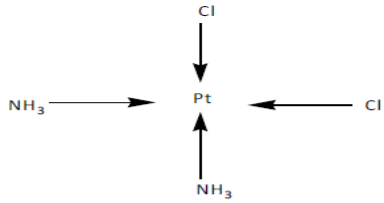
Copper (II) and cobalt (II) ions have four chloride ions bonded to them rather than six, because the chloride ions are too big to fit any more around the central metal ion.



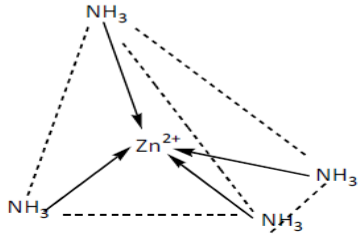
$[CuCl_4]^{2-}$



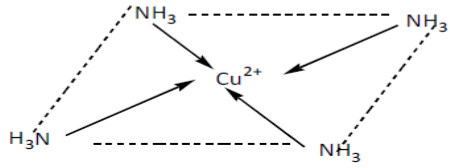
$[CoCl_4]^{2-}$



$Pt(NH_3)_2Cl_2$



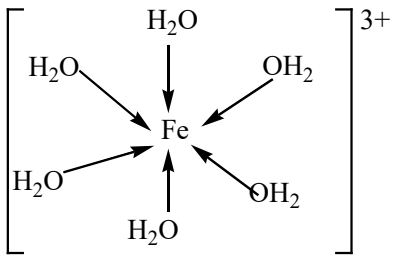
Tetrahedral structure



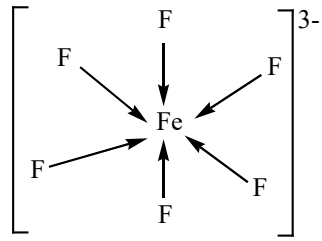
Square planar structure

- Complexes with coordination number 6 adopt an octahedral shape. Example: $[Cr(NH_3)_6]^{3+}$.

These ions have four of the ligands in one plane, with the fifth one above the plane, and the sixth one below the plane.



$[Fe(H_2O)_6]^{3+}$



$[AlF_6]^{3-}$

Checking up 1.2 (h)

1. What do you understand by :
   a. Coordination number.
   b. Ligand.
2. Give the main types of ligands and give an example for each
3. Say if the following statement is correct or wrong and justify: The coordination number equals the number of ligands bonded to the central metal.

1.2.9. Many transition metal ions and their compounds are coloured

Activity 1.2 (i)

Experiment 1: Identification of transition metal ions using their colours

Apparatus: Test tubes, droppers, spatula, test tube holders.

Chemicals: NaCl, $CaCl_2$, $FeSO_4$, $Fe_2(SO_4)_3$, $KMnO_4$, $K_2Cr_2O_7$, distilled water, $Cr_2(SO_4)_3$.

1. What are the colours of the compounds above?
2. Determine the oxidation states of each metal in the above compounds?
3. a. Take an endful spatula of each product given above and put each in a test tube.
   b. Put 10 mL of distilled water in each test tube.
   c. Write down the colours of solutions formed and conclude.

Experiment 2: Investigation of ligand exchange reactions involving copper (II) ions, Cu^{2+}

Apparatus: Test tubes, droppers, spatula, test tube holders.

Chemicals: Copper (II) sulphate, concentrated hydrochloric acid, concentrated ammonia solution and distilled water.

Procedure:

1. Use a spatula to place a small amount of anhydrous copper (II) sulphate in a test tube.
2. Add 10 drops of distilled water to the anhydrous copper (II) sulphate and shake
3. To the test tube in step 2, add concentrated ammonia solution drop by drop while shaking the test tube until there is no further change. Record all observations.
4. Repeat steps 1 and 2
5. To the test tube from step 4, add concentrated hydrochloric acid drop by drop while shaking until there is no further change. Record all observations.

Points for discussion:

1. What happens when anhydrous copper (II) sulphate is dissolved in water?
2. Describe what is observed when concentrated ammonia is added dropwise to an aqueous solution of copper (II) sulphate.Write balanced equations for each observation if possible
3. Describe what happens when concentrated hydrochloric acid is added to an aqueous solution of copper (II) sulphate. Write balanced equation(s) for the observation(s) made.
4. State any other possible observation(s) for this experiment.

The formation of colored ions by transition elements is associated with the presence of incompletely filled 3d orbitals.

Ion (aq)	Colour	Outer 3d electrons
Sc^{3+}	Colourless	$3d^0$
Ti^{3+}	Purple	$3d^1$
V^{3+}	Green	$3d^2$
Cr^{3+}	Green	$3d^3$
Mn^{2+}	Pink	$3d^5$
Fe^{2+}	Green	$3d^6$

Co^{2+}	Pink	$3d^7$
Ni^{2+}	Green	$3d^8$
Cu^{2+}	Blue	$3d^9$
Zn^{2+}	Colourless	$3d^{10}$

This property has its origin in the excitation of d electrons from lower energy d-orbitals to higher energy. In fact, when the central metal is surrounded by ligands, these cause d orbitals to be split into groups of higher and lower energy orbitals. When electrons fill d-orbitals, they fill first of all the lower energy orbitals; if there is free space in higher energy d-orbitals, an electron can be excited from lower energy d-orbitals to higher energy d-orbitals by absorbing a portion of light corresponding to a given colour, the remaining color light is the white light minus the absorbed colour.

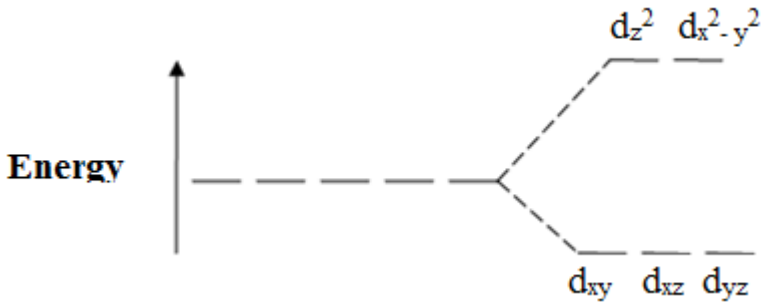


Figure 1.4: d-orbital split into two groups of different energies in an octahedral complex

When a coloured object is hit by white light, the object absorbs some colour and the colour transmitted or reflected by the object is the colour which has not been absorbed. The observed colour is called complementary colour.

When a metal cation has full d-orbitals, such as Cu^{+}or Zn^{2+}or no electron in d orbital, such as Sc^{3+}.

Table1.9: Complementarities of colors observed and absorbed when light is emitted

Observed/transmitted colour	Absorbed/complementary colour
White	No absorption of light
Black	Total absorption of light
Greenish yellow	Violet
Yellow	Blue
Red	Blue-green

Violet	Yellow-green
Dark blue	Yellow
Blue	Orange
Green	Red

The colour of a particular transition metal ion depends upon two factors:

- The nature of the ligand

Example: The color of hydrated copper (II) ion $[Cu(H_2O)_4]^{2+}$, is pale blue but on addition of sufficient ammonia, it turns to deep blue.

$$[Cu(H_2O)_4]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) \quad 4H_2O(aq)$$

Pale blue **Deep blue**

Also on the addition of sufficient concentrated hydrochloric acid the pale blue solution turns to yellowish brown.

$$[Cu(H_2O)_4]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 4H_2O(aq)$$

Pale blue **Yellow brown**

•The oxidation state of the metal ion

Example: $Cr^{2+}(aq)$ is blue but $Cr^{3+}(aq)$ is green

The principle of ligand exchange

Complexing reactions involve competitions between different ligands for central metal. A more powerful ligand displaces a less powerful ligand from a complex. During the process there is a change in colour.

Here below is a list of some ligands in increasing order of strength.

$O_2^{2-} < I^- < Br^- < S^{2-} < SCN^-$ (S–bonded) $< Cl^- < N_3^- < F^- < NCO^- < OH^- < C_2O_4^{2-} \approx H_2O < NCS^-$ (N–bonded) $< CH_3CN < NH_3 <$ en (ethylenediammine)$< NO_2^- < PPh_3 < CN^- <$ CO

The above series are called the spectrochemical series and shows that cynide ion and carbon monoxide are very strong ligands

The stability of a complex ion is measured by its stability constant. The higher the stability constant of a complex, the more stable is the complex.

Checking up 1.2 (i)

Predict whether each of the following ion forms coloured compounds and explain your reasoning: Fe^{2+}, Mn^{7+}, K^+

1.3. The anomalous properties of Zinc and Scandium

Activity 1.3

From the information you have learnt about the properties of transition metals,

Suggest the difference between the properties of Zn and Sc and other transition metals. You can consult different sources (books or internet) to provide enough information

On the basis of the properties of transition metals, zinc and scandium are not considered as typical transition metals even though they are members of the d-block.

Zinc:

- It has a complete d-orbital.
- Zinc forms only the colourless Zn^{2+} ion, isoelectronic with the Ga^{3+}ion, with 10 electrons in the 3d subshell.
- Zinc and its compounds are not paramagnetic

Scandium*:*

- Has one oxidation state,+3
- Sc forms only the colourless Sc^{3+}ion, isoelectronic with the Ca^{2+} ion, with no electrons in the 3d subshell.
- Its compounds are diamagnetic
- It forms compounds containing ions with a completely empty 3d subshell.

Checking up 1.3

Give any one property by which Zn differs from Sc

1.4. Naming of complex ions and isomerism in of transition metal complexes

1.4.1. Naming of complex ions

Activity 1.4 (a):

1. Name the following molecules and explain the basis /principle used to name them.

   a. $CaBr_2$

   b. CCl_4

   c. SF_6

2. Analyze the IUPAC rules for naming complex ions in the summary in this book or using any other source (textbook or search engine) and apply them by naming the following:

   a. $[CuCl_4]^{2-}$

   b. $[Cu(H_2O)_6]^{2+}$

   c. $[Cr(NH_3)_3(H_2O)_3]Cl_3$

   d. $[Pt(NH_3)_2Cl_2]$

   e. $(NH_4)_2[Ni(C_2O_4)_2(H_2O)_2]$

Naming molecules requires the knowledge of certain rules, such as how to name cations, anions, where to start from when both a cation and an anion are combined in an ionic molecule or when two non metals are combined in a covalent molecule.

Like other compounds, complex compounds/ions are named by following a set of rules. You are familiar with some of them and the new ones can be understood and applied easily.

1. In simple metal compounds, the metal is named first then the anion.

Example: $CaCl_2$: calcium chloride

2. In naming the complex:

   a. Name the ligands first, in alphabetical order, then the metal atom or cation, followed by its oxidation state written between brackets as Roman number, though the metal atom or cation is written before the ligands in the chemical formula.

Example: $[CuBr_4]^{2-}$: Tetrabromocuprate (II) ion

The names of some common ligands are listed in the table below:

Table 1.10: Names of common ligands

Anionic Ligands	Names	Neutral Ligands	Names
Br^-	bromo	NH_3	ammine
F^-	fluoro	H_2O	Aqua/aquo
O^{2-}	oxo	NO	Nitrosyl
OH^-	Hydroxo	CO	Carbonyl
CN^-	cyano	O_2	dioxygen
$C_2O_4^{2-}$	oxalato	N_2	dinitrogen
CO_3^{2-}	carbonato	C_5H_5N	pyridine
CH_3COO^-	Acetato	$H_2NCH_2CH_2NH_2$	ethylenediamine

b. Greek prefixes are used to indicate the number of each type of ligand in the complex:

The numerical greek prefixes are listed in the following table:

Table 1.11: Greek numerical prefixes

Number	Prefix	Number	Prefix	Number	Prefix
1	Mono	**5**	penta (pentakis)	**9**	nona
2	di (bis)	**6**	hexa (hexakis)	**10**	deca
3	tri (tris)	**7**	hepta	**11**	undeca
4	tetra (tetrakis)	**8**	octa	**12**	dodeca

c. After naming the ligands, name the central metal.

- If the complex bears a positive charge (cationic complex), the metal is named by its usual name.

Example*:* Cu: Copper Pt: Platinum

If the complex bears a negative charge (anionic complex), the name of the metal ends with the suffix –ate

Example*:* Co in a complex anion is called cobaltate and Pt is called platinate.

For some metals, the Latin names are used in the complex anions e.g. Fe is called ferrate (not ironate). See table below:

Table 1.12: Latin names of some transition metals in anionic complexes

Name of Metal	Name in an Anionic Complex
Iron	Ferrate
Copper	Cuprate
Lead	Plumbate
Silver	Argentate
Gold	Aurate
Tin	Stannate

1. For historic reasons, some coordination compounds are called by their common names.

Example: $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ are named ferricyanide and ferrocyanide respectively, and $Fe(CO)_5$ is called iron carbonyl.

2. To name a neutral complex molecule, follow the rules of naming a complex cation. Example: $[Cr(NH_3)_3Cl_3]$: triamminetrichlorochromium (III)

You can have a compound where both the cation and the anion are complex ions. Notice how the name of the metal differs even though they are the same metal ions. Remember: Name the cation before the anion.

Example: $[Ag(NH_3)_2][Ag(CN)_2]$ is diamminesilver(I)dicyanoargentate(I)

Note that:

- The names are written as a one word: Tetraamminecopper (II), not Tetraammine copper (II).
- Complex ions formula is written between square brackets and the charge of the ion as superscript outside the brackets: $[Cu(NH_3)_4]^{2+}$. When oppositely charged ions approach the complex ion, a neutral molecule can be obtained:

$[Cu(NH_3)_4]^{2+}2Cl^-$ or simply, $[Cu(NH_3)_4]Cl_2$: tetraamminecopper(II)chloride.

The ions outside the square brackets are known as "counter ions".

Checking Up 1.4 (a):

1. Complete the table below using the names of the given metals when they are in anionic complexes

Element	Name in an anionic complex
Ti	
V	
Cr	
Mn	
Co	
Zn	
Hg	
B	
Al	
Ge	

2. Give the systematic names for the following complex ions/compounds:

   a. $[Cr(NH_3)_3(H_2O)_3]^{3+}$

   b. $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$

   c. $K_4[Fe(CN)_6]$

   d. $Fe(CO)_5$

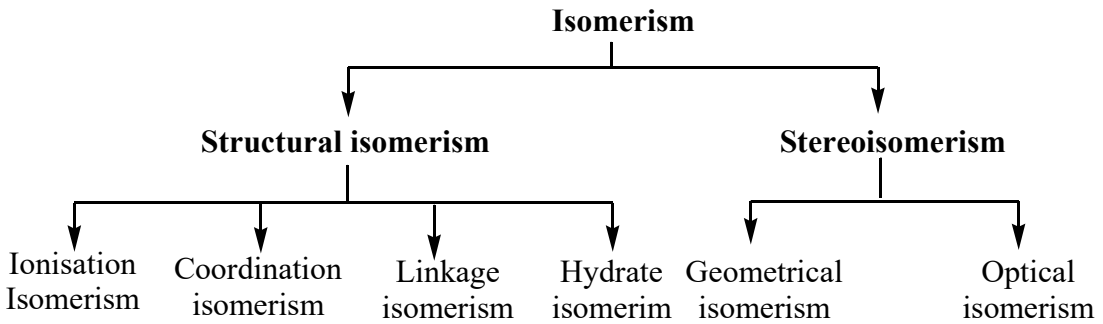
1.4.2. Isomerism in complexes

Activity 1.4 (b):

1. Discuss on the following questions:
   a. What do you understand by the term "isomerism"?
   b. Give examples of molecules that can exist as isomers and explain their isomerism
2. Read and discuss the summary below to understand how complex ions/ compounds exhibit isomers
3. Present your findings to your colleagues and teacher to share your understanding.

Isomers are chemical species that have the same molecular formulal, but different molecular structures or different arrangements of atoms or groups of atoms in space. Isomerism among transition metal complexes arises as a result of different arrangements of their constituent ligands around the metal.

The diagram below shows the different categories of isomerism in transition metal complexes.



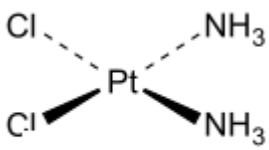
In this unit, we are specifically concerned with 'stereoisomerism' which gives rise to isomers known as "stereoisomers". Stereoisomers have the same structural formulal but different arrangements of ligands in space.

They are classified in two categories: geometrical isomers and optical isomers.

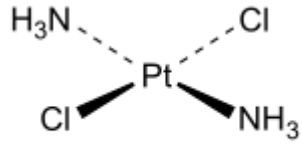
1. Geometrical isomers

Coordination complexes, with two different ligands in the cis and trans positions from a ligand of interest, form isomers.

For example, the square planar, diammine dichloroplatinum (II) $Pt(NH_3)_2Cl_2$),can be presented as follows:

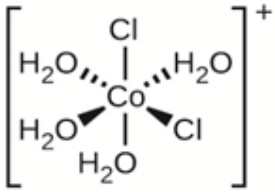


Cisplatin

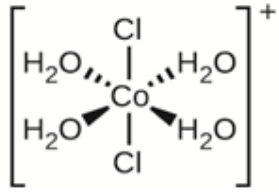


Transplatin

The octahedral $[Co(H_2O)_4Cl_2]^+$ ion can also have geometrical isomers.



Violet, cis- form



Green, trans- form

Different geometrical isomers are different chemical compounds. They exhibit different properties, even though they have the same formula. For example, the two isomers of $[Co(H_2O)_4Cl_2]NO_3$ differ in color; the *cis* form is violet, and the *trans* form is green. Furthermore, these isomers have different dipole moments, solubilities and reactivities.

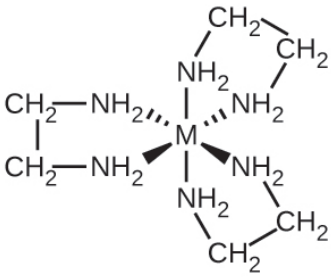
2. Optical isomers (enantiomers)

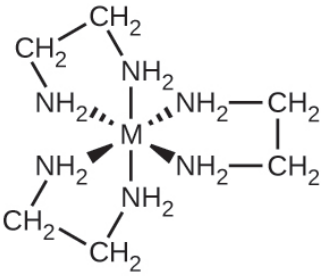
Optical isomers are non-superimposable mirror images of each other. A classic example of this is your two hands (left and right); hold them face-to-face: one is the mirror image of the other. Now try to superimpose them one over another: they are non-superimposable (only the middle fingers superimpose one over the other. Chemical compounds that behave like the hands are called "chiral", in reference to the Greek word for hands.

Optical isomers are very important in organic and biochemistry because living systems often incorporate one specific optical isomer and not the other.

Unlike geometric isomers, optical isomers have identical physical properties (boiling point, polarity, solubility, etc.). Optical isomers differ only in the way they affect polarized light and how they react with other optical isomers.

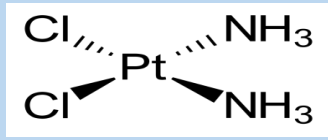
1. For coordination complexes, many coordination compounds such as $[M(en)_3]^{n+}$ [in which M^{n+} is a central metal ion such as iron(III) or cobalt(II)] form enantiomers, as shown in figure below.These two isomers will react differently with other optical isomers. For example, DNA helices are optical isomers, and the form that occurs in nature (right-handed DNA) will bind to only one isomer of $[M(en)_3]^{n+}$ and not the other.





Checking up 1.4 (b):

1. The geometric isomer of $[Pt(NH_3)_2Cl_2]$ is shown in the figure below. Draw the other geometric isomer and give its full name.



2. Draw the ion trans-diaqua-trans-dibromo-trans-dichlorocobaltate (II).
3. Sketch the arrangement of bonds in the complexes
   a. Hexaaquacobalt(III) ion
   b. Hexacyanoferrate (III) ion
   c. Diamminesilver (I) ion
   d. The complex compound tetracarbonylnickel (0).
4. The compound $[NiCl_2(NH_3)_2]$ has cis-trans isomers. These have a complex non-ionic structure.
   a. Does $[NiCl_2(NH_3)_2]$ have a tetrahedral or a square-planar structure? Explain your answer.
   b. Draw the cis and trans isomers for $[NiCl_2(NH_3)_2]$.
5. Early in the 20th century, the German scientist Werner succeeded in clarifying the situation concerning the five compounds of $PtCl_4$ and ammonia. The properties of these compounds are listed in the table below.

Compound	Empirical formula	ions in the empirical formula	No. of Cl- ions in the empirical formula
A	$PtCl_4 \cdot 6NH_3$	Five	Four
B	$PtCl_4 \cdot 5NH_3$	Four	Three
C	$PtCl_4 \cdot 4NH_3$	Three	Two
D	$PtCl_4 \cdot 3NH_3$	Two	One
E	$PtCl_4 \cdot 2NH_3$	Zero	Zero

a. What is the oxidation state of Pt in each of the compounds A-E?

b. The co-ordination number of Pt in each compound is six. Write a right formula for each of the five compounds. Show the complex ion and the other ions and/or molecules present.

c. Each of the compounds forms an octahedral complex ion. Draw the structures for the complex ions in A, B, C, and D.

d. Which of the complex ions in (c) have isomers?

1.5. The Chemistry of individual transition metals

Activity 1.5

Using the library and internet or other textbooks, make your own research and make presentation of the results of your research:

1. On how each of the transition metals (first series) reacts with each of the following substances
   a. Oxygen
   b. Water
   c. Hydrochloric acid
   d. Sodium hydroxide
   e. Chlorine
2. On the uses and their corresponding properties for each of the above transition metals.

1.5.1. Scandium

Scandium is a silvery-white solid. It melts at 1539 °C and boils at 2748 °C. Its density is about 3.0.

1. Chemical reactions

a. Reaction of scandium with air

Scandium tarnishes in air, and burns readily, forming scandium (III) oxide, Sc_2O_3.

$$4\ Sc(s) + 3\ O_2(g) \longrightarrow 2\ Sc_2O_3(s)$$

b. Reaction of scandium with water

When finely divided, or heated, scandium dissolves in water, forming Sc (III) hydroxide and hydrogen gas, H_2.

$$2\ Sc(s) + 6\ H_2O(l) \longrightarrow 2\ Sc(OH)_3(aq) + 3\ H_2(g)$$

c. Reaction of scandium with acids

Scandium dissolves readily in dilute hydrochloric acid, forming Sc(III) ions and hydrogen gas, H_2.

$$2\ Sc(s) + 6\ HCl(aq) \longrightarrow 2\ Sc^{3+}(aq) + 6\ Cl^{-}(aq) + 3\ H_2(g)$$

d. Reaction of scandium with halogens

Scandium reacts with the halogens, forming the corresponding Sc(III) halides

$$2\ Sc(s) + 3\ F_2(g) \longrightarrow 2\ ScF_3(s)$$
$$2\ Sc(s) + 3\ Cl_2(g) \longrightarrow 2\ ScCl_3(s)$$
$$2\ Sc(s) + 3\ Br_2(g) \longrightarrow 2\ ScBr_3(s)$$
$$2\ Sc(s) + 3\ I_2(g) \longrightarrow 2\ ScI_3(s)$$

2. Uses

- Scandium has as low density (2.99 g/cm^3) as aluminium (2.7 g/cm^3) but a much higher melting point.
- An aluminium-scandium alloy has been used in fighter planes, high-end bicycle frames and baseball bats.
- Scandium iodide is added to mercury vapour lamps to produce a highly efficient light source resembling sunlight. These lamps help TV cameras to reproduce colour well when filming indoors or at night-time.

1.5.2. Titanium

Titanium is a gray, solid with a density of about 4.50. It melts at 1667 °C and boils at 3285 °C.

1. Chemical reactions

a. Reaction of titanium with air

Titanium does not react with air under normal conditions. If brought to burn, titanium will react with both oxygen, O_2, and nitrogen, N_2.

$$Ti(s) + O_2(g) \longrightarrow TiO_2(s)\ [white]$$
$$2\ Ti(s) + N_2(g) \longrightarrow 2\ TiN(s)$$

b. Reaction of titanium with water

Titanium does not react with water, under normal conditions. If the water is heated to steam, it will react with titanium, forming titanium(IV) oxide, TiO_2, and hydrogen, H_2

$$Ti(s) + 2\ H_2O(g) \longrightarrow TiO_2(s)\ [white] + 2\ H_2(g)$$

c. Reaction of titanium with acids

Titanium does not react with most acids, under normal conditions. It will react with hot hydrochloric acid, and it reacts with HF, forming Ti(III) complexes and hydrogen gas, H_2.

$$2\ Ti(s) + 12\ HCl(aq) \longrightarrow 2\ Ti[Cl_6]^{3-}(aq) + 3\ H_2(g) + 6\ H^+(aq)$$
$$2\ Ti(s) + 12\ HF(aq) \longrightarrow 2\ [TiF_6]^{3-}(aq) + 3\ H_2(g) + 6\ H^+(aq)$$

d. Reaction of titanium with bases

Titanium does not appear to react with alkalis, under normal conditions, even when heated.

e. Reaction of titanium with halogens

Titanium reacts with halogens, when heated, forming the corresponding titanium(IV) halides

$$Ti(s) + 2\ F_2(g) \longrightarrow TiF_4(s)\ [white]$$
$$Ti(s) + 2\ Cl_2(g) \longrightarrow TiCl_4(s)\ [colourless]$$
$$Ti(s) + 2\ Br_2(g) \longrightarrow TiBr_4(s)\ [orange]$$
$$Ti(s) + 2\ I_2(g) \longrightarrow TiI_4(s)\ [dark\ brown]$$

2. Uses

- Titanium is as strong as steel but much less dense. It is therefore important as an alloying agent with many metals including aluminium, molybdenum and iron. These alloys are mainly used in aircraft, spacecraft and missiles because

of their low density and ability to withstand extremes of temperature. They are also used in golf clubs, laptops, bicycles and crutches.

- Power plant condensers use titanium pipes because of their resistance to corrosion. Because titanium has excellent resistance to corrosion in seawater, it is used in desalination plants and to protect the hulls of ships, submarines and other structures exposed to seawater.
- Titanium metal connects well with bone, so it has found surgical applications such as in joint replacements (especially hip joints) and tooth implants.
- The largest use of titanium is in the form of titanium (IV) oxide. It is extensively used as a pigment in house paint, artists' paint, plastics, enamels and paper. It is a bright white pigment with excellent covering power. It is also a good reflector of infrared radiation and so is used in solar observatories where heat causes poor visibility.

1.5.3. Vanadium

Vanadium is a grey, solid with a density of about 6.11. It melts at 1915 °C and boils at 3350 °C. It is insoluble in water at room temperature.

1. Chemical reactions

a. Reaction of vanadium with air

Vanadium metal reacts with excess oxygen, O_2, upon heating to form vanadium (V) oxide, V_2O_5. When prepared in this way, V_2O_5 is sometimes contaminated by other vanadium oxides.

$4V(s) + 5\ O_2(g) \longrightarrow 2\ V_2O_5(s)$ [yellow-orange]

b. Reaction of vanadium with water

Vanadium does not react with water, under normal conditions.

c. Reaction of vanadium with bases

Vanadium metal is resistant to attack by molten alkali.
In strong alkaline solutions (pH > 13), Vanadium (V) exists as colourless orthovanadate ions, VO_4^{3-}.

d. Reaction of vanadium with halogens

Vanadium reacts with fluorine, F_2, when heated, forming vanadium (V) fluoride

$2\ V(s) + 5\ F_2(g) \longrightarrow 2\ VF_5(l)$ [colourless]

2. Uses

- About 80% of the vanadium produced is used as a steel additive. Vanadium-steel alloys are very tough and are used for spanners, armour plate, axles, piston rods and crankshafts. Less than 1% of vanadium, and as little chromium, makes steel shock resistant and vibration resistant. Vanadium alloys are used in nuclear reactors because of vanadium's low neutron-absorbing properties.
- Vanadium (V) oxide is used as a pigment for ceramics and glass, as a catalyst and in producing superconducting magnets.

1.5.4. Chromium

Chromium is a silver gray metal with density of about 7.14. It melts at 1900 °C and boils at 2690 °C. Chromium is insoluble in water at room temperature.

1. Chemical reactions

a. Reaction of chromium with air

Chromium metal does not react with air at room temperature. Heated clean chromium is oxidized superficially in air to green solid, chromium (II) oxide.

$$4\ Cr(s) + 3\ O_2(g) \longrightarrow 2\ Cr_2O_3(s)$$

b. Reaction of chromium with water

Normally, Chromium metal does not react with water at room temperature. When red hot, it reacts with steam to form chromium (II) oxide.

$$2\ Cr(s) + 3H_2O(g) \rightarrow 2\ Cr_2O_3(s) + H_2(g)$$

c. Reaction of chromium with acids

Metallic chromium dissolves in dilute hydrochloric acid forming Cr(II) and hydrogen gas, H_2. In aqueous solution, Cr(II) is present as the complex ion $[Cr(OH_2)_6]^{2+}$.

$$Cr(s) + 2\ HCl(aq) \longrightarrow Cr^{2+}(aq) + 2\ Cl^{-}(aq) + H_2(g)$$

Similar results are seen for sulphuric acid but pure samples of chromium may be resistant to attack.

Chromium metal is not dissolved by nitric acid, HNO_3 but is passivated instead.

d. Reaction of chromium with hydroxide ions

Chromium dissolves rapidly in hot concentrated aqueous alkali forming a blue solution containing chromium (II) ion and hydrogen gas is evolved.

$$Cr(s) + 2\ OH^{-}(aq) + 2\ H_2O(l) \longrightarrow [Cr(OH)_4]^{2-}(aq) + H_2(g)$$

e. Reaction of chromium with halogens

Chromium reacts directly with fluorine, F_2, at 400°C and 200-300 atmospheres to form chromium (VI) fluoride, CrF_6.

$Cr(s) + 3\ F_2(g) \longrightarrow CrF_6(s)$ [yellow]

Under milder conditions, chromium (V) fluoride, CrF_5, is formed.

$2\ Cr(s) + 5\ F_2(g) \longrightarrow 2\ CrF_5(s)$ [red]

Under milder conditions, chromium metal reacts with the halogens to form chromium tri halides or chromium (III) halides:

$2\ Cr(s) + 3\ F_2(g) \longrightarrow 2\ CrF_3(s)$ [green]
$2\ Cr(s) + 3\ Cl_2(g) \longrightarrow 2\ CrCl_3(s)$ [red-violet]
$2\ Cr(s) + 3\ Br_2(g) \longrightarrow 2\ CrBr_3(s)$ [very dark green]
$2\ Cr(s) + 3\ I_2(g) \longrightarrow 2\ CrI_3(s)$ [very dark green]

2. Uses

- Chromium is used to harden steel, to manufacture stainless steel (resists to corrosion) and to produce several alloys.
- Chromium plating can be used to give a polished mirror finish to steel. Chromium-plated car and lorry parts, such as bumpers, were once very common. It is also possible to chromium plate plastics, which are often used in bathroom fittings.
- About 90% of all leather is tanned using chromium. However, the waste effluent is toxic so alternatives are being investigated.
- Chromium compounds are used as industrial catalysts and pigments (in bright green, yellow, red and orange colours). Rubies get their red colour from chromium, and glass treated with chromium has an emerald green colour.
- Chromium (IV) oxide is used in magnetic tapes for sound/video recording.
- Chromium is used in the control of cholesterol and help insulin sugar control in blood.

1.5.5. Manganese

Manganese is a grey-white solid with a slightly red colour. Its density is about 7.44 °C. Manganese melts at 1244 °C and boils at 2060 °C. It is insoluble in water but soluble in diluted acids, at room temperature.

1. Chemical reactions

a. Reaction of manganese with air

Manganese is not very reactive with air. The surface of manganese lumps oxidizes a little. Finely divided manganese metal burns in air. In oxygen the oxide Mn_3O_4 is formed and in nitrogen the nitride Mn_3N_2 is formed.

$$3\ Mn(s) + 2\ O_2(g) \longrightarrow Mn_3O_4(s)$$
$$3\ Mn(s) + N_2(g) \longrightarrow Mn_3N_2(s)$$

b. Reaction of manganese with water

Manganese reacts slowly with water to form manganese (IV) oxide:

$$Mn(s) + 2\ H_2O(l) \rightleftharpoons MnO_2(s) + 4\ H^+(aq) + 4\ e^-$$

c. Reaction of manganese with acids

Manganese dissolves readily in dilute sulphuric acid, forming a colorless solution of Mn(II) ions and hydrogen gas, H_2.

$$Mn(s) + H_2SO_4(aq) \longrightarrow Mn^{2+}(aq) + SO_4^{2-}(aq) + H_2(g)$$

d. Reaction of manganese with halogens

Manganese reacts with the halogens, forming the corresponding manganese (II) halides. For fluoride, manganese (III) fluoride is also formed.

$$Mn(s) + F_2(g) \longrightarrow MnF_2(s)$$
$$2\ Mn(s) + 3\ F_2(g) \longrightarrow 2\ MnF_3(s)$$
$$Mn(s) + Cl_2(g) \longrightarrow MnCl_2(s)$$
$$Mn(s) + Br_2(g) \longrightarrow MnBr_2(s)$$
$$Mn(s) + I_2(g) \longrightarrow MnI_2(s)$$

2. Uses

- Manganese is too brittle to be of much use as a pure metal. It is mainly used in alloys, such as steel. Steel contains about 1% manganese, to increase the strength and also improve workability and resistance to wear. Manganese steel contains about 13% manganese. This is extremely strong and is used for railway tracks, safes, rifle barrels and prison bars.
- Drinks cans are made of an alloy of aluminium with 1.5% manganese, to improve resistance to corrosion. With aluminium, antimony and copper it forms highly magnetic alloys.
- Manganese (IV) oxide is used as a catalyst, a rubber additive and to decolourise glass that is coloured green by iron impurities. Manganese (IV) oxide is a powerful oxidising agent and is used in quantitative analysis. It is also used to make Fertilizers and ceramics.
- Manganese sulphate is used to make a fungicide.

1.5.6. Iron

Iron is a grey to black, odourless metal with density 7.874. It melts at 1535 °C and boils at 2750 °C.

1. Chemical reactions

a. Reaction of iron with air

Iron reacts with oxygen, O_2, forming Fe (II) and Fe(III) oxides. The oxide layer does not passivate the surface. Finely divided iron, e.g. powder or iron wool, can burn:

$4\ Fe(s) + 3\ O_2(g) \longrightarrow 2\ Fe_2O_3(s)$ rust (but this reaction requires also the presence of water)

$3\ Fe(s) + 2\ O_2(g) \longrightarrow Fe_3O_4(s)$ (this is a mixture of iron oxides: Fe_2O_3 and FeO)

b. Reaction of iron with water

Air-free ***water*** has little effect upon ***iron*** metal. However, ***iron*** metal reacts in moist air by oxidation to give a hydrated ***iron*** oxide. This does not protect the ***iron*** surface to further ***reaction*** since it flakes off, exposing more ***iron*** metal to oxidation. This process is called rusting.

c. Reaction of iron with acids

Iron metal dissolves readily in dilute sulphuric acid in the absence of oxygen forming Fe(II) ions and H_2. In aqueous solution Fe(II) is present as the complex $[Fe(H_2O)_6]^{2+}$.

$Fe(s) + H_2SO_4(aq) \longrightarrow Fe^{2+}(aq) + SO_4^{2-}(aq) + H_2(g)$

If oxygen is present, some of the Fe(II) oxidizes to Fe(III).

$3\ Fe(s) + 4\ H_2SO_4(aq) \longrightarrow Fe^{2+}(aq) + 2\ Fe^{3+}(aq) + 4\ SO_4^{2-}(aq) + 4\ H_2(g)$

Concentrated nitric acid, HNO_3, reacts on the surface of iron and passivates the surface (makes it unreactive).

d. Reaction of iron with halogens

Iron reacts with excess of the halogens, F_2, Cl_2, and Br_2, to form Fe(III) halides.

$2\ Fe(s) + 3\ F_2(g) \longrightarrow 2\ FeF_3(s)$ [white]

$2\ Fe(s) + 3\ Cl_2(g) \longrightarrow 2\ FeCl_3(s)$ [dark brown]

$2\ Fe(s) + 3\ Br_2(l) \longrightarrow 2\ FeBr_3(s)$ [reddish brown]

For I_2, Fe is only oxidized to Fe(II)

$Fe(s) + I_2(s) \longrightarrow FeI_2(s)$ (grey)

2. Uses

- Iron is an enigma – it rusts easily, yet it is the most important of all metals. 90% of all metal that is refined today is iron. Most is used to manufacture steel, used in civil engineering (reinforced concrete, girders etc) and in manufacturing.
- Alloy steels are carbon steels with other additives such as nickel, chromium, vanadium, tungsten and manganese. These are stronger and tougher than carbon steels and have a huge variety of applications including bridges, electricity pylons, bicycle chains, cutting tools and rifle barrels.
- Stainless steel is very resistant to corrosion. It contains at least 10.5% chromium. Other metals such as nickel, molybdenum, titanium and copper are added to enhance its strength and workability. It is used in architecture, bearings, cutlery, surgical instruments and jewellery.
- Cast iron contains 3–5% carbon. It is used for pipes, valves and pumps. It is not as tough as steel but it is cheaper.
- Magnets can be made of iron and its alloys and compounds.
- Iron catalysts are used in the Haber process for producing ammonia, and in the Fischer–Tropsch process for converting syngas (hydrogen and carbon monoxide) into liquid fuels.
- Iron plays an important role in the transfer of oxygen by hemoglobin. Each hemoglobin binds four iron atoms. Iron in hemoglobin binds with oxygen as it passes through the blood vessels in the lungs and releases it in the tissues.

1.5.7. Cobalt

Cobalt is a dark grey metal with a density of 8.90. It is insoluble in water at room temperature.

1. Chemical reactions

a. Reaction of cobalt with air

Cobalt does not react readily with air. Upon heating the oxide Co_3O_4 is formed, and if the reaction is carried out above 900°C, the result is cobalt (II) oxide, CoO.

$$3\ Co(s) + 4\ O_2(g) \longrightarrow 2\ Co_3O_4(s)$$
$$2\ Co(s) + O_2(g) \longrightarrow 2\ CoO(s)$$

Cobalt does not react directly with nitrogen, N_2.

b. Reaction of cobalt with water

Cold water has little effect upon cobalt metal. The reaction between red hot cobalt metal and steam produces cobalt (II) oxide, CoO.

$$2\ Co(s) + 2\ H_2O(g) \longrightarrow 2\ CoO(s) + H_2(g)$$

c. Reaction of cobalt with acids

Cobalt metal dissolves slowly in dilute sulphuric acid to form solutions containing the hydrated Co(II) ion together with hydrogen gas, H_2. The actual occurrence of Co (II) in aqueous solution is as the complex ion $[Co(OH_2)_6]^{2+}$.

$Co(s) + H_2SO_4(aq) \longrightarrow Co^{2+}(aq) + SO_4^{2-}(aq) + H_2(g)$

It also dissolves in dilute nitric acid to form cobalt (II) nitrate and oxides of nitrogen.

$Co(s) + HNO_3(dil.) \longrightarrow Co^{2+}(aq) + NO_x(g) + H_2O(l)$

(where NO_x stands for any oxide of nitrogen, i.e, NO, NO_2, …)

Concentrated nitric acid renders it passive due to the formation of oxide layer Co_3O_4 which is insoluble in the acid.

d. Reaction of cobalt with halogens

Metallic cobalt reacts with halogens, forming cobalt (II) halides.

$Co(s) + Br_2(l) \longrightarrow CoBr_2(s)$ [green]
$Co(s) + Cl_2(g) \longrightarrow CoCl_2(s)$ [blue]
$Co(s) + I_2(s) \longrightarrow CoI_2(s)$ [blue-black]

2. Uses

- Cobalt, like iron, can be magnetized and so is used to make magnets. It is alloyed with aluminium and nickel to make particularly powerful magnets.
- Other alloys of cobalt are used in jet turbines and gas turbine generators at high temperature.
- Cobalt metal is sometimes used in electroplating because of its attractive appearance, hardness and resistance to corrosion.
- Cobalt salts have been used for centuries to produce brilliant blue colours in paint, porcelain, glass, pottery and enamels.
- Cobalt is an essential trace element and found at the centre of the vitamin B_{12} (cobalmin, $C_{63}H_{88}CoN_{14}O_{14}P$). It contains a cobalt(III) ion and is necessary for the prevention of pernicious anaemia and the formation of red blood corpuscles, but it is involved in many other functions too.

1.5.8. Nickel

Nickel is a grey solid metal with density of about 8.9. It melts at 1455 °C and boils at 2920 °C.

1. Chemical reactions

a. Reaction of nickel with air

Nickel does not react with oxygen, O_2, at room temperature, under normal conditions.

Finely divided nickel can burn in oxygen, forming nickel (II) oxide, NiO.

$$2\ Ni(s) + O_2(g) \xrightarrow{\Delta} 2\ NiO(s)$$

b. Reaction of nickel with water

Nickel metal does not react with water under normal conditions. Nickel (II) ion complexes with water under acidic and neutral conditions forming a *light green hexaqua nickel ion:* $[Ni(H_2O)_6]^{2+}{}_{(aq)}$

In basic condition, nickel hydroxide precipitates:

$$[Ni(H_2O)_6]^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \longrightarrow Ni(OH)_2(s) + 6H_2O(l)$$

light green

c. Reaction of nickel with acids

Nickel metal dissolves slowly in dilute sulphuric acid to form the hydrated Ni(II) ion and hydrogen, H_2.

$$Ni(s) + H_2SO_4(aq) \longrightarrow Ni^{2+}(aq) + SO_4{}^{2-}(aq) + H_2(g)$$

The strongly oxidizing concentrated nitric acid, HNO_3, reacts on the surface of nickel and passivates the surface.

d. Reaction of nickel with hydroxide ions

Metallic nickel does not react with aqueous sodium hydroxide.

e. Reaction of nickel with halogens

Nickel reacts slowly with halogens, forming the corresponding dihalides.

$$Ni(s) + Cl_2(g) \longrightarrow NiCl_2(s)\ [yellow]$$
$$Ni(s) + Br_2(g) \longrightarrow NiBr_2(s)\ [yellow]$$
$$Ni(s) + I_2(g) \longrightarrow NiI_2(s)\ [black]$$

2. Uses

- Nickel resists corrosion and is used to plate other metals to protect them. It is, however, mainly used in making alloys such as stainless steel. Nichrome is an alloy of nickel and chromium with small amounts of silicon, manganese and iron. It resists corrosion, even when red hot, so is used in toasters and electric ovens. A copper-nickel alloy is commonly used in desalination plants, which convert seawater into fresh water. Nickel steel is used for armour plating. Other alloys of nickel are used in boat propeller shafts and turbine blades.
- Nickel is used in batteries, including rechargeable nickel-cadmium batteries and nickel-metal hydride batteries used in hybrid vehicles.
- Nickel has a long history of being used in coins. The US five-cent piece (known as a 'nickel') is 25% nickel and 75% copper.

- Finely divided nickel is used as a catalyst for hydrogenating vegetable oils. Adding nickel to glass gives it a green colour.

1.5.9. Copper

Copper is a light pink to red (shiny-reddish) metal of density 8.95 g/cm^3. It melts at 1083 °C and boils at 2570 °C.

1. Chemical reactions

a. Reaction of copper with air

Copper metal is stable in air under normal conditions. When heated until red hot, copper metal and oxygen react to form Cu_2O.

$$4\ Cu(s) + O_2(g) \longrightarrow 2\ Cu_2O(s)$$

b. Reaction of copper with water

Copper does not react with water in all conditions.

c. Reaction of copper with acids

Copper is not dissolved by non-oxidizing dilute acids such as dilute H_2SO_4 and HCl to produce hydrogen gas. This is why it is called a 'noble metal'. Other noble metals include gold, silver and platinum.

But copper metal dissolves in dilute and concentrated nitric acid, HNO_3 to form copper (II) nitrate and oxides of nitrogen. Here nitric acid acts as an oxidising agent.

$$3\ Cu(s) + 8\ HNO_3(dil.) \longrightarrow 3\ Cu(NO_3)_2(aq) + 2\ NO(g) + 4\ H_2O(l)$$

blue colour

$$Cu(s) + 4\ HNO_3(conc.) \longrightarrow Cu(NO_3)_2\ (aq) + 2\ NO_2(g) + 2\ H_2O(l)$$

brown

It also reacts with hot concentrated sulphuric acid to form copper (II) sulfate, sulphur dioxide gas and water. But normally, sulphuric acid is not an oxidising acid!

$$Cu(s) + H_2SO_4(aq) \longrightarrow Cu^{2+}(aq) + SO_4^{2-}(aq) + SO_2(g) + H_2O(g)$$

d. Reaction of copper with halogens

Metallic copper metal reacts with the halogens forming corresponding dihalides.

$Cu(s) + F_2(g) \longrightarrow CuF_2(s)$ white if anhydrous, but green if hydrated
$Cu(s) + Cl_2(g) \longrightarrow CuCl_2(s)$ yellow-brown if anhydrous, blue-green if hydrated
$Cu(s) + Br_2(g) \longrightarrow CuBr_2(s)$ black

2. Uses

- Historically, copper was the first metal to be worked by people. The discovery that it could be hardened with a little tin to form the alloy bronze gave the name to the Bronze Age.
- Traditionally it has been one of the metals used to make coins, along with silver and gold. However, it is the most common of the three and therefore the least valued. All US coins are now copper alloys, and gun metals also contain copper.
- Most copper is used in electrical equipment such as wiring and motors. This is because it conducts both heat and electricity very well, and can be drawn into wires. It also has uses in construction (for example roofing and plumbing), and industrial machinery (such as heat exchangers).
- Copper sulphate is used widely as an agricultural poison and as an algaecide in water purification.
- Copper compounds, such as Fehling's solution, are used in chemical tests for sugar detection.
- Copper helps in storing iron, is involved in production of pigments for colouring hair, skin and eyes.

1.5.10. Zinc

Zinc is a grey solid with a density of 7.14 g/cm^3. It melts at 419.5 ^{o}C and boils at 907 ^{o}C.

1. Chemical reactions

a. Reaction of zinc with air

Zinc reacts with oxygen in moist air. The metal burns in air with a blue-green flame to form zinc (II) oxide, a material that goes from white to yellow on prolonged heating.

$$2\ Zn(s) + O_2(g) \longrightarrow 2\ ZnO(s)\ [white]$$

b. Reaction of zinc with water

Zinc is unaffected with cold water. However, elemental zinc will reduce steam at high temperatures:

$$Zn(s) + H_2O(g) \longrightarrow ZnO(s) + H_2(g)$$

c. Reaction of zinc with acids

Zinc metal dissolves slowly in dilute sulphuric acid to form Zn(II) ions and hydrogen, H_2. In aqueous solution the Zn (II) ion is present as the complex ion $[Zn(H_2O)_6]^{2+}$.

$$Zn(s) + H_2SO_4(aq) \longrightarrow Zn^{2+}(aq) + SO_4^{2-}(aq) + H_2(g)$$

When zinc reacts with oxidizing acids like HNO_3, no hydrogen gas is evolved.

$$Zn(s) + 4\ HNO_3(aq) \longrightarrow Zn(NO_3)_2(aq) + 2\ NO_2(g) + 2\ H_2O(l)$$

d. Reaction of zinc with hydroxide ions

In hot aqueous alkali, powdered zinc dissolves with effervescence:

$$Zn(s) + 2\ OH^-(aq) + H_2O(l) \longrightarrow [Zn(OH)_4]^{2-}(aq) + H_2(g)$$

e. Reaction of zinc with halogens

Zinc will react with gaseous bromine, Br_2, and iodine, I_2.

$$Zn(s) + Br_2(g) \longrightarrow ZnBr_2(s)\ [white]$$
$$Zn(s) + I_2(g) \longrightarrow ZnI_2(s)\ [white]$$

2. Uses

- Mostly, zinc is used to galvanise other metals, such as ironsheets (amabati), to prevent corrosion. Galvanised steel is used for car bodies, street lamp posts, safety barriers and suspension bridges. Many houses in Rwanda are covered by galvanized iron sheets (amabati).
- Large quantities of zinc are used to produce die-castings, which are important in the automobile, electrical and hardware industries.
- Zinc is also used in alloys such as brass, nickel silver and aluminium solder.
- Zinc oxide is widely used in the manufacture of many products such as paints, rubber, cosmetics, pharmaceuticals, plastics, inks, soaps, batteries, textiles and electrical equipment. Zinc sulphide is used in making luminous paints, fluorescent lights and x-ray screens.
- It is a component of insulin.

Checking up 1.5

1. State what is observed and write an equation, for the reaction that would take place when

   a. Copper is added to hot concentrated sulphuric acid.

   b. Chromium is dissolved rapidly in hot concentrated aqueous alkali

   c. Nickel (II) ions complexes react with water under acidic and neutral conditions.

   d. Powdered zinc is dissolved in hot aqueous alkali.

2. State at least one property that makes that:

   a. An aluminum - scandium alloy be used in fighter planes, high-end bicycle frames and baseball bats.

   b. Many alloys of titanium with aluminium, molybdenum and iron be mainly used in aircraft, spacecraft and missiles.

   c. Vanadium-steel alloys be used for armour plate, axles, piston rods and crankshafts.

   d. Alternatives of tanning leather using chromium be investigated.

   e. Manganese steel be used for railway tracks, safes, rifle barrels and prison bars.

   f. Iron be considered as an enigma.

   g. Cobalt be necessary for the prevention of pernicious anaemia and the formation of red blood corpuscles.

   h. Nichrome be used in toasters and electric ovens.

   i. Most copper be used in electrical equipment such as wiring and motors.

   j. Galvanised steel be used for car bodies, street lamp posts, safety barriers and suspension bridges.

Assignment

Question 3 is given to you as an assignment. You can use any source to carry out research in order to gain and provide relevant information to be presented comfortably.

3. The following figures show objects made in different transition metals. Observe them and complete the table with the main transition metal which forms the objects, its two important properties and other two uses (apart from that shown by the figure).

	Object	Transition metal	Properties	Other uses
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				

1.6. Identification of transition metal ions

Activity 1.6

Given a substance Y which contains one cation (from transition metal) and one anion, identify the cation and anion in Y. Carry out the following tests on Y , record your observations and deductions in the table below. Identify any gas evolves.

Tests	Observations	Deductions
a) Note Appearance of **Y**		
b) To one spatula of **Y** in a test tube add a few drops of diluted nitric acid or diluted sulphuric acid		
c) Heat one spatula end-full of **Y** in a dry test tube until there is no further change		
d) Put one spatula of **Y** in a test tube and add about 6cm^3 of water and shake. Divide the solution into two portions.		
(i) To the first solution add diluted NaOH drop wise until in excess		
(ii) To the 2nd portion, add ammonia solution drop wise until in excess		

- The cation in **Y is .....**
- The anion in **Y** is **.....**
- Write the ionic equations for the reactions in test (i) and test (ii) .....

Different transition metals have different colors. Also, different charges, or cations of one transition metal can give different colors. Another factor is the nature of the ligand. The same cations of a transition metal can produce a different color depending on the ligand it binds to.

Many compounds containing transition metals have certain characteristic colours and thus, by observing a compound, we can not identify it.

- Appearance or colour of different solid compounds containing transition metals

Table 1.13: Colours of different solid compounds containing transition metals (first series)

Cations	Colour
Copper (II)	Green or Blue
Iron (III)	Yellow/Brown or reddish/brown
Iron (II)	Green
Chromium (III)	Green or violet
Cobalt (II)	Purple or red
Manganese (II)	Very pale pink
Nickel (II)	Bright green
Zinc (II)	White

- **Colours of aqueous solutions of some transition metal ions**

In aqueous solutions where water molecules are the ligands, the colours of some metal ions observed are listed in the table below:

Table 1.14: Colours of different aqueous solutions containing some transition metals (first series)

Colour of the aqueous solution	Deduction
Green solution	Fe^{2+}, Cr^{3+}, Ni^{2+}
Yellow or Brown	Fe^{3+}
Colorless	SC^{3+}, Cu^{+}, Ti^{4+}, Zn^{2+} or Mn^{2+}
Blue	Cu^{2+}
Pink or red	Co^{2+}

- **Action of heat on solid compounds containing transition metal ions**

Table 1.15: Colours of different solid compounds containing transition metals (first series) due to action of heat.

Observation	Deduction
Pink turns Blue black	Co^{2+}
Yellow turns reddish brown	Fe^{3+}
Violet turns Green	Cr^{3+}
Green turns yellow	Ni^{2+}
Blue turns white and white turns black	Cu^{2+}
Green turns yellow and yellow turns red or black	Fe^{2+}

Note: On heating the following temporary colour changes may also occur:

Observation	Deduction
Yellow (**when hot**) and White (**When cold**)	Zn^{2+}
Black (**when hot**) and Reddish/brown (**When cold**)	Fe^{2+}

- **Effect of aqueous sodium hydroxide and aqueous ammonia on solutions containing transition metal ions**

The hydroxides of transition metals are precipitated from solutions of the metal ions by the addition of hydroxide ions or ammonia. The colour of the precipitate can often be used to identify the metal present. The precipitates formed are gelatinous and often coloured and some form soluble complex ions with excess ammonia.

a. To about 1cm³ of the solution containing the positive ion (cation), add 2M aqueous sodium hydroxide dropwise until in excess

A white precipitate formed, soluble in excess to form a colorless solution	Zn^{2+} probably present $Zn^{2+}(aq) + 2OH^-(aq) \longrightarrow Zn(OH)_2(s)$ $Zn(OH)_2(s) + 2OH^-(aq) \longrightarrow [Zn(OH)_4]^{2-}(aq)$
A pale blue precipitate formed, insoluble in excess	Cu^{2+} present $Cu^{2+}(aq) + 2OH^-(aq) \longrightarrow Cu(OH)_2(s)$
A dirty green precipitate formed, insoluble in excess and turns brown on standing due to aerial oxidation	Fe^{2+} present $Fe^{2+}(aq) + 2OH^-(aq) \longrightarrow Fe(OH)_2(s)$ $4Fe(OH)_2(s) + O_2(g) + 2H_2O(l) \longrightarrow 4Fe(OH)_3(s)$

A rust-brown precipitate formed, insoluble in excess	Fe^{3+} present $Fe^{3+}(aq) + 3OH^-(aq) \longrightarrow Fe(OH)_3(s)$
A white precipitate formed, insoluble in excess and rapidly turns brown on standing due to aerial oxidation	Mn^{2+} present $Mn^{2+}(aq) + 2OH^-(aq) \longrightarrow Mn(OH)_2(s)$ $2Mn(OH)_2(s) + O_2(g) \longrightarrow 2MnO_2xH_2O(s)$
A green precipitate formed, soluble in excess to give a green solution	Cr^{3+} present $Cr^{3+}(aq) + 3OH^-(aq) \longrightarrow Cr(OH)_3(s)$ $Cr(OH)_3(s) + OH^-(aq) \longrightarrow [Cr(OH)_4]^-(aq)$
A green precipitate formed, insoluble in excess	Ni^{2+} present $Ni^{2+}(aq) + 2OH^-(aq) \longrightarrow Ni(OH)_2(s)$
A blue precipitate formed, insoluble in excess and turns pink on standing	Co^{2+} present $Co^{2+}(aq) + 2OH^-(aq) \longrightarrow Co(OH)_2(s)$

b. To about 1cm³ of the solution containing the positive ion (cation), add 2M aqueous ammonia dropwise until in excess

A white precipitate formed, soluble in excess to form a colorless solution	Zn^{2+} present $Zn^{2+}(aq) + 2OH^-(aq) \longrightarrow Zn(OH)_2(s)$ $Zn(OH)_2(s) + 4NH_3(aq) \longrightarrow [Zn(NH_3)_4]^{2+}(aq) + 2OH^-(aq)$
A blue precipitate formed, soluble in excess to form a deep blue solution	Cu^{2+} present $Cu^{2+}(aq) + 2OH^-(aq) \longrightarrow Cu(OH)_2(s)$ $Cu(OH)_2(s) + 4NH_3(aq) \longrightarrow [Cu(NH_3)_4]^{2+}(aq) + 2OH^-(aq)$
A dirty green precipitate formed, insoluble in excess and turns brown on standing due to aerial oxidation	Fe^{2+} present $Fe^{2+}(aq) + 2OH^-(aq) \longrightarrow Fe(OH)_2(s)$ $4Fe(OH)_2(s) + O_2(g) + 2H_2O(l) \longrightarrow 4Fe(OH)_3(s)$
A rust-brown precipitate formed, insoluble in excess	Fe^{3+} present $Fe^{3+}(aq) + 3OH^-(aq) \longrightarrow Fe(OH)_3(s)$

A white precipitate formed, insoluble in excess and rapidly turns brown on standing due to aerial oxidation	Mn^{2+} present $Mn^{2+}(aq) + 2OH^-(aq) \longrightarrow Mn(OH)_2(s)$ $2Mn(OH)_2(s) + O_2(g) \longrightarrow 2MnO_2xH_2O(s)$
A grey-green precipitate formed, soluble in excess to give a green solution	Cr^{3+} present $Cr^{3+}(aq) + 3OH^-(aq) \longrightarrow Cr(OH)_3(s)$ $Cr(OH)_3(s) + 6NH_3(aq) \longrightarrow [Cr(NH_3)_6]^{3+}(aq) + 3OH^-(aq)$
A green precipitate formed, soluble in excess to form a blue solution	Ni^{2+} present $Ni^{2+}(aq) + 2OH^-(aq) \longrightarrow Ni(OH)_2(s)$ $Ni(OH)_2(s) + 6NH_3(aq) \longrightarrow [Ni(NH_3)_6]^{2+}(aq) + 2OH^-(aq)$
A blue precipitate insoluble in excess is formed	Co^{2+} present $Co^{2+}(aq) + 2OH^-(aq) \longrightarrow Co(OH)_2(s)$

- **Confirmatory tests for some transition metal ions**

Confirmatory tests are the tests required to confirm the analysis. Generally, a confirmatory test is used after other tests have been carried out to isolate/identify the ion in order to confirm the ion without any dought

a. Zinc ions

i. Addition of little solid ammonium chloride followed by disodium hydrogen phosphate solution to a solution of zinc ions gives a white precipitate. The precipitate dissolves in excess ammonia or dilute mineral acids.

ii. Addition of potassium ferrocyanide solution to a solution of zinc ions gives a white precipitate.

$$Zn^{2+}(aq) + [Zn(CN)_6]^-(aq) \longrightarrow Zn_2[Fe(CN)_6](s)$$

b. Chromium ions

To a solution of chromium (III) ions, add excess aqueous sodium hydroxide followed by little hydrogen peroxide and boil the resultant mixture. A yellow solution of a chromate is formed.

$$2Cr^{3+}(aq) + 10\ OH\text{-}(aq) + 3H_2O_2(aq) \rightarrow 2CrO_4^{2-}(aq) + 8H_2O(l)$$

Treatment of the yellow solution with:

i. Lead (II) ethanoate or Lead(II)nitrate solution gives a yellow precipitate of Lead(II) chromate. $Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow PbCrO_4(s)$

ii. Barium nitrate (or chloride) solution gives a yellow precipitate of barium chromate.

$$Pb^{2+}(aq) + CrO_4^{2-}(aq) \longrightarrow PbCrO_4(s)$$

iii. Silver nitrate gives a brick red precipitate of silver chromate

$$2Ag^{+}(aq) + CrO_4^{2-}(aq) \longrightarrow Ag_2CrO_4(s)$$

iv. A little alcohol (for example, butan-1-ol) and dilute sulphuric acid , a blue color is formed in the alcohol layer. The blue color is due to unstable CrO_5.

c. Manganese (II) ions

To the solution of manganese (II) ions, add little concentrated nitric acid followed by little solid lead(IV) oxide or solid sodium bismuthate(V) and boil the mixture. A purple solution is formed due to MnO_4^- ion.

$$2Mn^{2+}(aq) + 5BiO_3^-(aq) + 14H^+(aq) \longrightarrow 2MnO_4^-(aq) + 5Bi^{3+}(aq) + 7H_2O(l)$$

$$2Mn^{2+}(aq) + 5PbO_2(s) + 4H^+(aq) \longrightarrow 2MnO_4^-(aq) + 5Pb^{2+}(aq) + 2H_2O(l)$$

d. Iron (II) ions

i. Addition of potassium hexacyanoferrate (III) solution to a solution of iron (II) ions gives a dark blue precipitate .

ii. Addition of few drops of concentrated nitric acid to a solution of iron (II) ions gives a yellowish solution due to iron (III) ions formed. The solution gives positive test for iron (III) ions.

e. Iron(III) ions

i. Addition of potassium hexacyanoferrate (II) solution to a solution of iron(III) ions gives a dark blue precipitate

ii. Addition of potassium thiocyanate or ammonium thiocyanate solution to a solution of iron (III) ions gives a blood red coloration.

f. Cobalt (II) ions

Addition of potassium thiocyanate or ammonium thiocyanate solution to a solution of cobalt(II) ions gives a blue colored product of potassium cobalt(II) tetrathiocyanate.

$$Co^{2+}(aq) + 4KSCN(aq) \longrightarrow KCo(SCN)_4(aq) + 2K^+(aq)$$

g. Nickel (II) ions

i. **Addition of potassium cyanide solution give**s a yellow-green precipitate of Nickel(II) cyanide. The precipitate dissolves in excess reagent to form a dark yellow solution tetracyanonickel (II) ion.

$$Ni^{2+}(aq) + 2CN^{-}(aq) \longrightarrow Ni(CN)_2(s)$$

$$Ni(CN)_2(s) + 2CN^{-}(aq) \longrightarrow [Ni(CN)_4]^{2-}(aq)$$

ii. Addition of aqueous ammonia followed by 2 to 3 drops of dimethylglyoxime solution to a solution of nickel (II) ions gives a red precipitate. The formation of this precipitate may sometimes require that the solution mixture would be warmed.

h. Copper (II) ions

In addition to use of aqueous ammonia, the copper(II) ions can be confirmed by addition of the following reagents to an aqueous solution of copper(II) ions:

i. **Potassium iodide solution:** A white precipitate of copper (I) iodide stained brown with free iodine.

$$2Cu^{2+}(aq) + 4I^{-}(aq) \longrightarrow Cu_2I_2(s) + I_2(aq)$$

Brown color fades on addition of sodium thiosulphate solution due to the reaction below:

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$$

ii. **Potassium hexacyanoferrate (II) solution:** A brown precipitate is formed.

$$2Cu^{2+}(aq) + [Fe(CN)_6]^{4-}(aq) \longrightarrow Cu_2Fe(CN)_6(s)$$

iii. **Potassium (or ammonium) cyanide solution:** A yellow precipitate is formed. The precipitate rapidly turns white.

$$Cu^{2+}(aq) + 2CN^{-}(aq) \longrightarrow Cu(CN)_2(s)$$

$2Cu(CN)_2(S) \longrightarrow 2CuCN(S) + C_2N_2(g)$ (cyanogen is a colouless and toxic gas)

Checking up 1.6 (a)

Given a substance K which contains one cation and one anion, carry out the following tests on K and record your observations and deductions in the table below. Identify any gas evolved.

Tests	Observations	Deductions
a) Note appearance of K		
b) Put one spatula end-full of K in a dry test tube and heat it strongly		
c) To a spatula end-full of K in a test tube add a few drops of concentrated sulphuric acid then heat the mixture		
d) Dissolve about one spatula end-full of K in about 5 cm3 of water and divide the solution into four portions		
(i) To the 1st portion add dilute sodium hydroxide solution dropwise until in excess and heat the mixture		
(ii) To the 2nd portion, add ammonia solution dropwise until in excess		
(iii) To the 3rd portion add a few drops (2 or 3 drops) of potassium hexacyanoferrate(II) solution		
(iv) To the 4th portion add a few drops of lead(II) nitrate solution and warm the mixture		

- The cation present in the compound K is ……
- The anion present in the compound K is ……

Checking up 1.6 (b)

You are provided with substance D which contains one cation and one anion. You are required to identify the cation and anion in D. Carry out the following tests, record your observations and deductions in the table below. Identify any gas evolved.

Tests	Observations	Deductions
1) Note appearance of D		
2) Put one spatula end-full of D in a test tube and heat it strongly until there is no further change		
3) Dissolve one spatula of D in about 10 cm3of water and divide the resultant solution into five parts.		
a) To the 1st part is added sodium hydroxide solution drop wise until in excess		
b) To the second part is added dilute sodium hydroxide solution dropwise until in excess followed by 1cm^3 of 10% hydrogen peroxide solution and the resultant mixture boiled and later cooled. the resultant solution is then divided into three portions		
i) To the 1st portion is added silver nitrate solution dropwise until no further change takes place.		
ii) To the second portion is added a drop of barium chloride solution		
iii) To the 3rd portion is added a few drops of hydrochloric acid.		
d) To the fourth part was added a few drops of lead (II) nitrate solution.		
e) To the last part was carried a test of one's own choice. Test: To the last portion is added a few drops of barium nitrate followed by 1 cm^3 of dilute nitric acid.		

- The cation in D is .....
- The anion in D is .....

Checking up 1.6 (c)

Aqueous sodium hydroxide is added separately to solutions of salts of the transition metals **A, B** and **C.** Identify **A**, **B** and **C** from the following observations.

A: The white precipitate which appears is soluble in an excess of aqueous sodium hydroxide and also in aqueous ammonia.

B: The blue precipitate which appears is insoluble in an excess of aqueous sodium hydroxide but dissolves in aqueous ammonia to form a deep blue solution.

C: The green precipitate which appears is insoluble in an excess of aqueous sodium hydroxide and also in aqueous ammonia.

END UNIT ASSESSMENT

a. Multiple choice questions: Write the Roman number corresponding to the correct answer.

1. Which of the following elements is not a transition metal?
   i. Copper
   ii. Nickel
   iii. Iron
   iv. Magnesium
2. Which of the following complexes is linear?
   i. $[Ag(NH_3)_2]^+$
   ii. $[CoCl_4]^{2-}$
   iii. $[Pt(NH_3)_2Cl_2]$
   iv. $[CuCl_4]^{2-}$
3. Which of the following ions does not form coloured solutions?
   i. Cu^+
   ii. Mn^{2+}
   iii. Cr^{3+}
   iv. Co^{2+}
4. Which of the following reactions of Cu^{2+} is an example of a chelation reaction?
   i. $[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow [Cu(H_2O)_4(OH)_2] + 2H_2O$
   ii. $[Cu(H_2O)_6]^{2+} + CO_3^{2-} \longrightarrow CuCO_3 + 6H_2O$
   iii. $[Cu(H_2O)_6]^{2+} + EDTA^{4-} \longrightarrow [CuEDTA]^{2-} + 6H_2O$
   iv. $[Cu(H_2O)_6]^{2+} + 2NH_3 \longrightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^+$

5. Which of the following complexes forms both geometric and optical isomers?

   i. $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$

   ii. $[Ni(H_2O)_4(OH)_2]$

   iii. $[Ni(NH_2CH_2CH_2NH_2)_2Cl_2]$

   iv. $[NiCl_4]^{2-}$

6. Which of the following properties is not a characteristic of transition metal ions

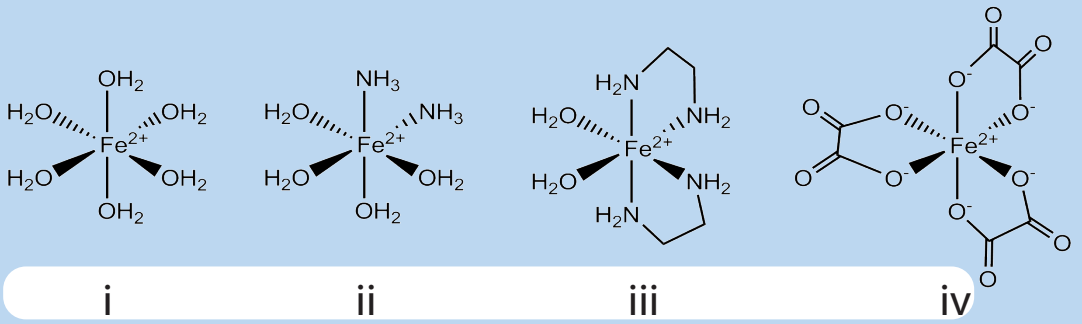
   i. Variable oxidation states

   ii. Form coloured solutions

   iii. Act as catalysts

   iv. Are diamagnetic

7. Which complex ion shows optical isomerism and geometrical isomerism?



i ii iii iv

8. All the following complex ions contain metal ions. Overall charges are not shown.

   Which complex ion has no overall charge?

The charge of the central metal ion is given in brackets next to the formula of the complex

   i. $[CuCl_4]$ (+2)

   ii. $[Cu(OH)_2(H_2O)_4]$ (+2)

   iii. $[Al(H_2O)_6]$ (+3)

9. Which atom(s) among the following transition elements have only 1 electron in 4s orbital? Chromium
   i. Chromium
   ii. Cobalt
   ii. Scandium
   iv. Zinc

b. Open Questions

1. Complete the following table:

Coordination Compound	Complex Ion	Ligands	Counter Ion	Coordination Number	Oxidation State
$[Co(H_2O)_6]Cl_3$			Cl^-		
	$[Fe(CN)_6]^{3-}$		K^+		
$[Cu(NH_3)_4]SO_4$					

2. What is the characteristic of electron configurations of transition metals?
3. Which electrons, 3d or 4s, have the lowest ionization energies in a transition metal?
4. a. Name any three transition metals that are essential to the biological system.

   b. Why do you think transition metals form coordination compounds that have covalent bonds?
5. Name the following coordination compounds using systematic nomenclature.
   a. $[Co(H_2O)_6]Cl_2$
   b. $[Cr(NH_3)_6](NO_3)_3$
   c. $K_4[Fe(CN)_6]$
   d. $Na[Au(CN)_4]$
   e. $[Co(H_2O)_2(en)_2]Cl_3$
6. a. (i) What is meant by the term co-ordinate bond?
   (ii) Explain why co-ordinate bonds can be formed between transition metal ions and water molecules.

   b. What name is given to any ligand that can form two co-ordinate bonds to one metal ion? Give an example of such a ligand.

7. In order to determine the concentration of a solution of cobalt(II) chloride, a 25.0 cm^3 sample was titrated with a 0.0168 M solution of $EDTA^{4-}$; 36.2 cm^3 were required to reach the end-point. The reaction occurring in the titration is:

$$[Co(H_2O)_6]^{2+} + EDTA^{4-} \longrightarrow [Co(EDTA)]^{2-} + 6\ H_2O$$

   a. What type of ligand is $EDTA^{4-}$?

   b. Calculate the molar concentration of the cobalt (II) chloride solution.

8. The ethanedioate (oxalate) ion, $C_2O_4^{2-}$, acts as a bidentate ligand. This ligand forms an octahedral complex with iron (III) ions.

   a. Deduce the formula of this complex and draw its structure showing all the coordinate bonds present.

   b. Give the name of a naturally-occurring in human body complex compound which contains iron.

   c. What is the important function of this complex compound?

9. The compound $[Co(NH_3)_4Cl_2]Cl$ contains both chloride ions and ammonia molecules as ligands.

   a. State why chloride ions and ammonia molecules can behave as ligands.

   b. What is the oxidation state and the co-ordination number of cobalt in this complex compound?

10. a. Suggest why the compound $[Co(NH_3)_6]Cl_3$ has a different colour from that of $[Co(NH_3)_4Cl_2]Cl$.

    b. Name and give the formula of an ammonia complex used to distinguish between aldehydes and ketones.

11. Chloride ions form the tetrahedral complex ion $[AlCl_4]^-$ but fluoride ions form the octahedral complex ion $[AlF_6]^{3-}$. Suggest a reason for this difference.

UNIT 2

EXTRACTION OF METALS

UNIT 2: EXTRACTION OF METALS

Key Unit Competence

To be able to: Relate the properties of metals to their methods of extraction and uses and suggest preventive measures to dangers associated with their extraction.

Learning objectives

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

- Describe the extraction of copper, iron, sodium, tantalum, zinc, wolfram and aluminium;
- Outline and explain the uses of copper, iron, tantalum, zinc, wolfram, and tin ore (cassiterite);
- Explain the issues associated with the extraction of metals and preventive measures;
- Relate the properties of metals to their methods of extraction.

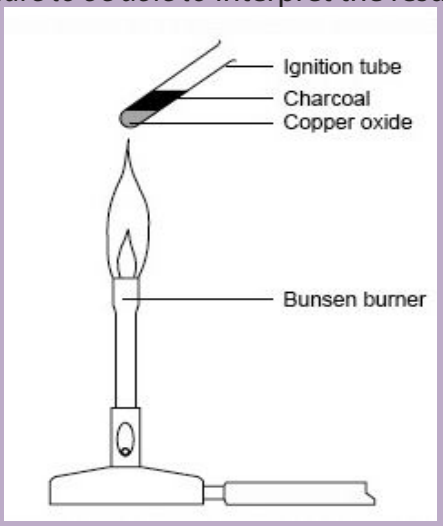
Introductory activity

1. a. Do you know any metal and mineral extracted in Rwanda?

   b. If yes, name them

   c. Give the applications of those metal and mineral .

2. Most of the metals are found in nature, not as pure metals, but as compounds, i.e. combined with other chemical elements. Such metals are extracted from their compounds using chemical reactions. The following setup shows one example *of a laboratory chemical reaction. Analyse it and follow the procedure to be able to* interpret the results.



Procedure

1. Transfer one spatula measure of copper (II) oxide to a hard-glass test-tube.
2. Carefully add one spatula of charcoal powder on top of the copper (II) oxide without any mixing.
3. Strongly heat these two layers for 5 minutes in a Bunsen flame.
4. Allow the tube to cool and then look closely at where the two powders meet in the test tube.

Questions

1. Describe the solid copper (II) oxide before heating.
2. Name the gas formed in the reaction.
3. Describe the solid remaining after heating.
4. Name the solid formed in the reaction.
5. Write the word and symbol equations for the reactions.
6. What does this reaction tell you about the relative reactivities of carbon and copper?
7. Explain why this reaction is a redox reaction.

The chemical substances in the earth's crust obtained by mining are called minerals in which are source of metal economically needed, are called **"Ore".** The unwanted impurities present in ore are called **gangue.** A native metal is any metal that is found in its metallic form, either pure or alloyed, in nature (example: Gold). The entire process of extraction of metal from its ore is called **metallurgy.**

Many metals are found in the Earth's crust as ores. An ore is usually a compound of the metal mixed with impurities. An ore is any naturally-occurring source of a metal that you can economically extract the metal from. Most metals exist in nature as compounds, usually oxides or sulphides.

Sulphide ores cannot be converted directly into the metal. Instead they must be converted to the oxide. This is achieved by roasting them in air. **Roasting** involves heating of ore in presence of air below melting point of metal in reverberatory furnace.

Reverberatory furnace, in zinc, copper, tin and nickel production, is a furnace used for smelting or refining in which the fuel is not in direct contact with the ore but heats it by a flame blown over it from another chamber. In steel making, this process, now largely obsolete, is called the **open-hearth process.**

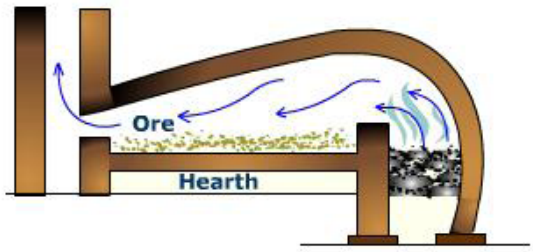


Figure 2.1: Reverberatory furnace

In this process, volatile impurities escape leaving behind metal oxide and sulphur dioxide (metal sulphide is converted to metal oxide).

$$2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2$$

$$2\,PbS + 3\,O_2 \longrightarrow 2\,PbO + 2\,SO_2$$

$$2\,Cu_2S + 3\,O_2 \longrightarrow 2\,Cu_2O + 2\,SO_2$$

This process causes problems because of the large quantity of sulphur dioxide produced. Sulphur dioxide is one of the principal causes of ***acid rain;*** hence SO_2 is one of the air pollutants.

However if the sulphur dioxide can be collected before being released into the atmosphere, it can be used to make sulphuric acid.

Metals in their compounds are in oxidized form, i.e. have lost electron(s) and bear a positive charge. In order to get them as metals, they need to gain electrons: this process or reaction of gaining electrons is called "**reduction**". Reduction of metals can be carried out using a chemical reducing agent such as carbon (coke, charcoal) or electricity.

When the mineral is dug up, a method must be used to separate the metal from the rest of the ore. This is called **extraction of the metal.**

2.1. Relating the properties of metals to their methods of extraction

Activity 2.1

Make a research (in books or internet) in order to:

1. Find different methods of extraction of metals referring to the reactivity.
2. Explain why the ores have to be concentrated and different ways that can be used.

2.1.1. Methods of metal extraction according to their properties

A number of methods are used to extract metals from their ores. The best method to use depends on a number of factors. These factors are based on the properties of the metal.

The main factor here is the reactivity of the metal (the position it takes in the reactivity series). Let us use the following questioning method to clarify these factors.

- Will the method successfully extract the metal? This depends on the reactivity of the metal.
- How much do the reactants cost? Raw materials vary widely in cost.
- What purity is needed, and are the purification methods expensive? Some metals are not useful unless very pure, others are useful impure.
- How much energy does the process use? High temperatures and electrolysis use a lot of energy.
- How efficiently, and in what quantities, can the metal be made? Continuous processes are more efficient than batch processes.
- Are there any environmental considerations? Some processes produce a lot of pollutants.

Different methods of metal extraction will be considered in this unit. Some examples are given below:

- **Reduction of metal oxides with carbon**

Carbon (as coke or charcoal) is cheap. It not only acts as a reducing agent, but it also acts as the fuel to provide heat for the process. However, in some cases (for example with aluminium) the temperature needed for carbon reduction is too high to be economic - so a different method has to be used. Carbon may also be left in the metal as an impurity. Sometimes this can be removed afterwards (for example, in the extraction of iron); sometimes it cannot (for example in producing titanium), and a different method would have to be used in cases like this.

- **Electrolysis of the metal ore**

This method is used to extract metals which are difficult to reduce by chemical agents. These metals include aluminium or metals which are difficult to reduce such as Group 1 and 2 metals.

Reduction of the metal oxide with hydrogen

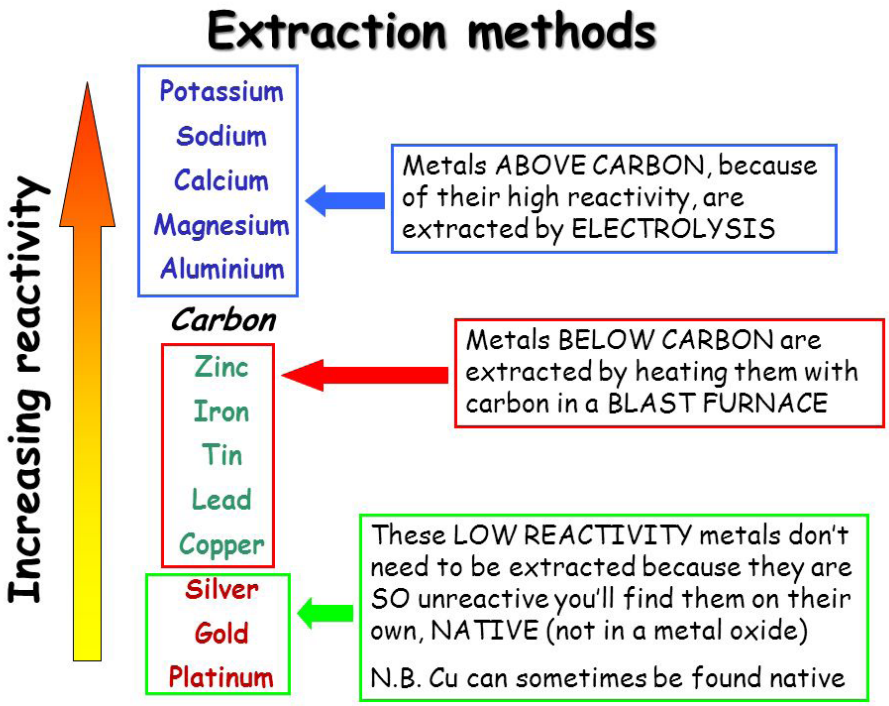
- Hydrogen can be used as a reducing agent, it is also used in purification of copper.

This is the main method for the extraction of tungsten from its oxide.

Sustainable use of natural resources: As these extraction processes are expensive and the supply of ore is not infinite, it is essential to recycle the metals as much as possible. Recycling of metals is one way of conservation and sustainable use of natural resources.

Metallurgical operations are sources of pollution, water and air pollution. Measures

must be taken to eliminate or at least to minimise that kind of pollution.



(Source: http://slideplayer.com/slide/8328520/)

2.1.2. Concentrating the ore

Concentrating the ore is also called **"Dressing"** or **"Benefaction of ore".** The ore from which the metal will be extracted has to be prepared before extraction. Concentrating the ore is getting rid of as much of the unwanted rocky material as possible before the ore is converted into the metal. This simply means **"Removal of gangue from ore"**. This may be done by chemical or physical means.

- **By physical processes**

Physical operations use physical techniques that do not change the chemical nature of the minerals; these techniques are based on physical properties such as: density, magnetic properties, etc… In many cases, it is possible to separate the metal compound from unwanted rocky material by physical means.

- **Mechanical sorting (Hand picking):** this involves use of hands to pick the gangue and breaking away the gangue using a hammer.
- **Magnetic separation:** the ore is crushed and a very strong magnet is used to sort out magnetic materials from non-magnetic materials. This method is for example used to separate wolframite from cassiterite where cassiterite being non-magnetic is not attracted by the magnet.
- **Washing:** the ores are usually denser than the gangue, which may be washed

away in a stream of water on an inclined table. Examples of ores separated in this way are galena and limestone; cassiterite from silicates.

- **Froth flotation method:** this process is important in treating many sulphide ores like galena, zinc blende (zinc sulphide), copper pyrites, etc. Separation is based on different abilities of mineral and gangue particles to be moistened by water. During this process, the ore is first powdered and fed into a large concentration tank containing water and a suitable oil (frothing agents).

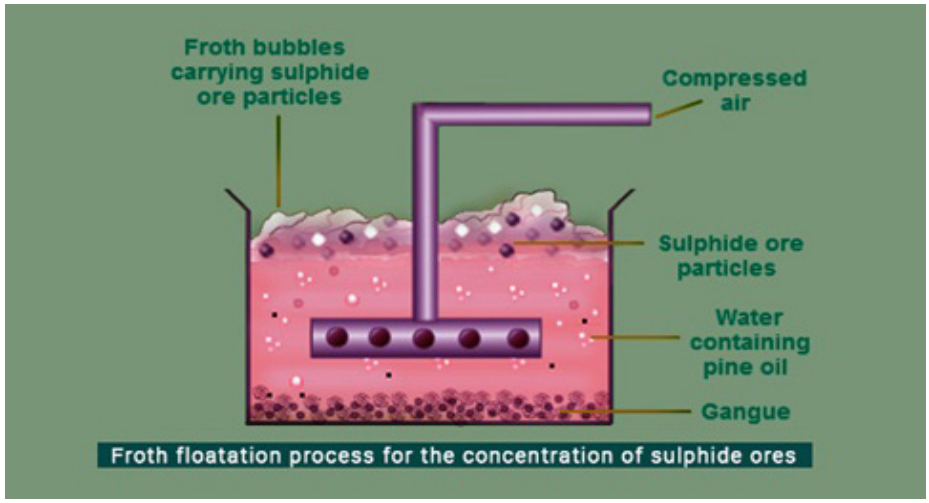


Figure 2.2 : Froth floatation process for the concentration of sulphide ores

(Source: https://blog.byjus.com/extraction-of-zinc/)

The mixture is agitated by blowing air through at a high pressure. The sulphide ores rise to the surface in the froth while the gangue sinks to the bottom. The froth is skimmed off the surface, and an acid is added to break up the froth. The concentrated ore is filtered and dried.

- **By chemical processes.**

For example, pure aluminium oxide is obtained from bauxite by a process involving a reaction with sodium hydroxide solution. Some copper ores can be converted into copper (II) sulphate solution by leaving the crushed ore in contact with dilute sulphuric acid for a long time and then copper can be extracted from the copper (II) sulphate solution.

- **Leaching with aqueous solvents:** in this method the finely powdered ore is treated with a suitable reagent that dissolves the ore but not impurities, for example:
  1. Bauxite is crushed and digested with sodium hydroxide solution
  2. Zinc ores can be leached with dilute sulphuric acid and electrolysed
- **Roasting in air and Calcination:** Here the ore is powdered and roasted in air to drive off the water (for the hydrated ores) and other volatile substances. For example,

Sulphides release sulphur dioxide gas:

$$2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$$

- **Calcination:** It is a process heating the ore strongly either in limited supply of air ih the absence in air

$$ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$$

- **Smelting** is the process by which a metal is obtained, either as the element or as a simple compound, from its oxide ore by heating beyond the melting point, ordinarily in the presence of reducing agents, such as coke.

$$CuO + C \rightarrow Cu + CO$$

Checking up 2.1

1. What is an ore?
2. What is the difference between an ore and a mineral?
3. Are ores a finite resource?
4. Are ores renewable?
5. When is carbon used for extraction?
6. Name a metal that could be extracted from its ore using carbon.
7. When is electrolysis used for extraction?
8. What do you understand with dressing of ore, smelting, froth flotation and gangue?
9. Name two metals that can only be extracted by electrolysis.
10. Suggest a reason why iron is extracted using carbon rather than by electrolysis.
11. State three factors which determine the choice of reduction method used for the extraction of metals from their ores.
12. Complete with the following words: iron, extracted, crust, gold, native, elemental, reduced

"Metals come from the Earth's …….. Some metals like ……. are very unreactive and are found as ……. in their ……state. Metals such as zinc, lead and ……are found combined with oxygen in compounds. These metals can be …… using chemical reactions. The metal oxides are ……as oxygen is removed from the compound".

13. Why most of metals are produced by reduction method ?

2.2. Methods of extraction of Copper

Activity 2.2

Use the search engine and the library:

1. To find out the name of the two main ores of Copper.
2. To describe the full process which metal is extracted from its ores.
3. To demonstrate how copper is useful in our daily life.

We are going to deal with the extraction of copper from its ores, its purification by electrolysis, and some of its uses.

2.2.1. Extracting copper from its ores

There are two main copper ore types of interest, **copper oxide ores** and **copper sulphide ores.** Both ore types can be economically mined, however, the most common source of copper ore is the sulphide ore mineral ***chalcopyrite*** also known as ***copper pyrites***, which accounts for about 50 percent of copper production.

Table 2.1: Some main ores of copper

Mineral	Formula	% copper when pure
Cuprite	Cu_2O	88.8
Chalcocite	Cu_2S	79.8
Bornite	$2Cu_2S•CuS.FeS$	63.3
Malachite	$CuCO_3•Cu(OH)_2$	58
Azurite	$Cu_3(CO_3)_2(OH)_2$	55
Chalcopyrite	$CuFeS_2$	35

The ores typically contain low percentages of copper and have to be concentrated by, for example, froth flotation before processing.

The method used to extract copper from its ores depends on the nature of the ore. Sulphide ores such as chalcopyrite are converted to copper by a different method from silicate, carbonate or sulphate ores. Copper, Cu, is mainly extracted from the ore chalcopyrite, $CuFeS_2$, in a ***three stage*** process.

- In the ***first stage,*** chalcopyrite is heated with silicon dioxide and oxygen

  $2\ CuFeS_2 + 2\ SiO_2 + 4\ O_2 \rightarrow Cu_2S + 2\ FeSiO_3 + 3\ SO_2$

- In the ***second stage***, the copper (I) sulphide is roasted with oxygen at a high temperature in a reverberatory furnace giving copper (II) oxide.

  $Cu_2S + 2\ O_2 \rightarrow 2\ CuO + SO_2$

- In the third stage, the copper (II) oxide is reduced by heating with carbon.

  $CuO + C \rightarrow Cu + CO$

The end product of this is called blister copper - a porous brittle form of copper, about 98 - 99.5% pure.

2.2.2. Purification of copper

When copper is made from sulphide ores by the first method above, it is impure. The blister copper is first treated to remove any remaining sulphur (trapped as bubbles of sulphur dioxide in the copper - hence "blister copper") and then cast into anodes for refining using electrolysis (electrolytic refining). The purification uses an electrolyte of copper (II) sulphate solution, impure copper anodes, and strips of high purity copper for the cathodes.

The diagram shows a very simplified view of a cell.

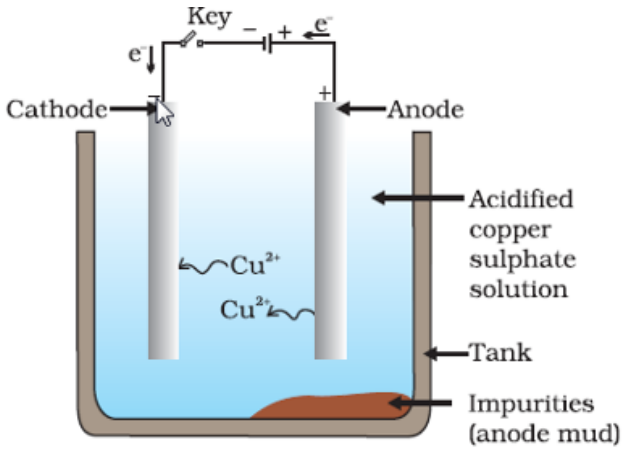


Figure 2.3: Electrolyitic purification of copper using $CuSO_4$ electrolyte.

- At the cathode, a reduction reaction takes place; copper (II) ions are deposited as pure copper: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
- At the anode, an oxidation reaction takes place; impure copper goes into solution as copper (II) ions: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

For every copper ion that is deposited at the cathode, in principle another one goes into solution at the anode. The concentration of the solution should stay the same.

All that happens is that there is a transfer of copper from the anode to the cathode. The cathode gets bigger as more and more pure copper is deposited; the anode gradually disappears.

In practice, it is not quite as simple as that because of the impurities involved.

What happens to the impurities?

- Any metal in the impure anode which is below copper in the electrochemical series (reactivity series) does not go into solution as ions. It stays as a metal and falls to the bottom of the cell as **"anode sludge"** together with any unreactive material left over from the ore. The anode sludge may contain valuable metals such as silver and gold.
- Metals above copper in the electrochemical series (like zinc) will form ions at the anode and go into solution. However, they will not get discharged at the cathode provided their concentration does not get too high.

Extracting copper from other ores

Copper can be extracted from non-sulphide ores by a different process involving three separate stages:

Step 1: Reaction of the ore (over quite a long time and on a huge scale) with a dilute acid such as dilute sulphuric acid to produce a very dilute copper (II) sulphate solution.

Step 2: *Concentration of the copper (II) sulphate solution by solvent extraction.*

The very dilute solution is brought into contact with a relatively small amount of an organic solvent containing a substance which will bind with copper (II) ions so that they are removed from the dilute solution. The solvent must not mix with water. Copper (II) ions are removed again from the organic solvent by reaction with fresh sulphuric acid, producing a much more concentrated copper (II) sulphate solution than before.

Step 3: *Electrolysis of the new solution.* Copper (II) ions are deposited as copper on the cathode. The anodes for this process were traditionally lead-based alloys, but newer methods use titanium or stainless steel. The cathode is either a strip of very pure copper or stainless steel.

Checking up 2.2

1. Based on the knowledge you have on unit 1, give 3 uses of copper.
2. Describe the process by which copper is extracted from chalcopyrite, $CuFeS_2$
3. Give any difference between the extraction of copper from chalcopyrite and from cuprite.

2.3. Methods of extraction of Iron

Activity 2.3

Using your own research, use the available resources (chemistry books, notebooks, internet...) to make a succinct summary of:

1. The main ores of iron.
2. The full process involved in the blast furnace while the iron is being extracted (Include the diagram, the raw materials introduced and the role of each and the equations of the main reactions occurring).
3. The main different forms of iron, its properties and their respective uses.

The common ores of iron are iron oxides, and these can be reduced to iron by heating them with carbon in the form of coke. Coke is produced by heating coal in the absence of air. Coke is cheap and provides both the reducing agent for the reaction and also the heat source - as you will see below.

2.3.1. Iron ores

The most commonly used iron ores are haematite, Fe_2O_3, and magnetite, Fe_3O_4. The other examples of iron ores are: Limonite ($Fe_2O_3 \cdot 3H_2O$), Iron pyrites (FeS_2) and Siderite ($FeCO_3$).

2.3.2. The heat source

The air is blown into the bottom of the giant chimney called **a blast furnace.**

The blast furnace is about 30 metres high and lined with fireproof bricks. This furnace is heated using the hot waste gases from the top. Heat energy is valuable, and it is important not to waste any.

The coke (essentially impure carbon) burns in the blast of hot air to form carbon dioxide - a strongly exothermic reaction. This reaction is the main source of heat in the furnace.

$$C + O_2 \rightarrow CO_2$$

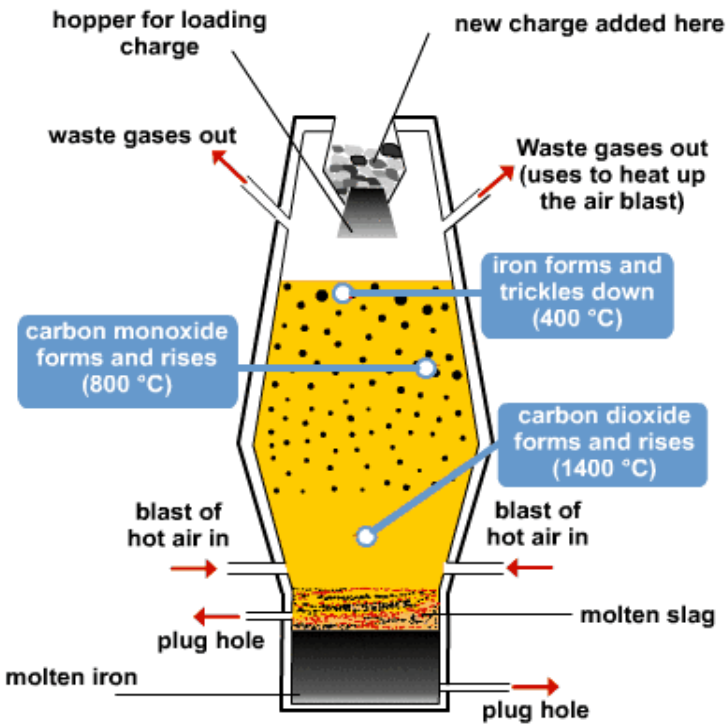


Figure 2.4: Blast furnace for the preparation of iron

2.3.3. Extraction

Three substances are needed to enable extraction of iron from its ore. The combined mixture is called the **"charge":**

- Iron ore
- Limestone (calcium carbonate).
- Coke - mainly carbon.

The charge is placed into the blast furnace. Hot air is blasted through the bottom. Several reactions take place before the iron is finally produced. This is a continuous process that needs a high temperature. The high temperature is produced by burning the carbon in a blast of hot air.

Oxygen in the air reacts with coke to give carbon dioxide.

$$C(s) + O_2(g) \rightarrow CO_{2(g)}$$

Limestone (calcium carbonate) is added to the blast furnace to remove sandy impurities (SiO_2). The limestone breaks down to form carbon dioxide.

$$CaCO_{3(s)} \rightarrow CaO(s) + CO_{2(g)}$$

Carbon dioxide produced (both from carbon and from calcium carbonate) reacts with more coke to produce carbon monoxide.

$$CO_{2\,(g)} + C(s) \rightarrow 2CO(g)$$

2.3.4. The reduction of the ore

The Fe_2O_3 is reduced by both carbon (C) and carbon monoxide (CO) as shown by the equations below.

$$Fe_2O_{3(s)} + 3\,C_{(s)} \rightarrow 2\,Fe_{(l)} + 3\,CO_{(g)}$$

$$Fe_2O_{3(s)} + 3\,CO_{(g)} \rightarrow 2\,Fe_{(l)} + 3\,CO_{2(g)}$$

The limestone reacts with the sand to form slag (calcium silicate)

$$CaO(s) + SiO_{2(s)} \rightarrow CaSiO_3\,(l)$$

Both the slag and iron are drained from the bottom of the furnace.

The calcium silicate melts and runs down through the furnace to form a layer on top of the molten iron. It can be tapped off from time to time as slag.

The slag is mainly used in the construction industry (to build roads, to make breeze blocks, as **"slag cement"** - a final ground slag which can be used in cement, often mixed with Portland cement…)

The iron whilst molten is poured into moulds and left to solidify - this is called cast iron.

In Rwanda tradition, iron was produced from an iron ore (heamatite, Fe_2O_3, and magnetite, Fe_3O_4) called **ubutare** ,by traditional smelters called **abacuzi,** they used charcoal as reducing agent. Then from that, they were able to produce traditional tools such hoes, machets, arrows, etc…..

2.3.5. Different forms of iron

- **Pig iron** (Cast iron after removing some impurities), an alloy of iron that contains 2 to 4 percent carbon, along with varying amounts of silicon and manganese and traces of impurities such as sulphur and phosphorus.
- It is made by reducing iron ore in a blast furnace.
- It has a low tensile strength
- It is used in making gates, pipes, lamp posts where high strength is not needed.
- **Wrought iron** is a soft, ductile, fibrous variety that is produced from a semi-

fused mass of relatively pure iron globules (haematite) partially surrounded by slag. It usually contains less than 0.1 percent carbon and 1 or 2 percent slag.

- It is purer than cast iron.
- It is fibrous and tough
- It can be welded (joined by hammering when red hot)
- It is malleable and ductile
- It is used for making sheets, wire and nails.
- Steel is an alloy of iron, carbon, manganese, nickel and vanadium.

2.3.6. Alloys of iron and their uses

ALLOY	Iron mixed with	Special properties	Uses
Stainless steel	Chromium and nickel	Resists corrosion	Cutlery, cooking utensils, kitchen sinks, industrial equipment for food and drink processing
Titanium steel	Titanium	Withstands high temperatures	Gas turbines, spacecraft
Manganese steel	Manganese	Very hard	Rock-breaking machinery, some railway track (e.g. points), military helmets

Checking up 2.3

1. Iron is extracted using the Blast Furnace
   a. What is introduced into the top of the blast furnace?
   b. What is the source of heat used in the blast furnace? Write the involved equation
   c. What is the main reducing agent and how is it produced? (give an equation)
   d. How is the iron oxide reduced by this reducing agent? (give an equation)
   e. What is the other reducing agent and how does it reduce the iron oxide?
      (give an equation)
2. The blast furnace is a continuous process. What does this mean and why is it advantageous?

2.4. Methods of extraction of tin

Activity 2.4

Make a research using the appropriate books and internet to:

1. Find out the main tin ore and state 2 regions in Rwanda where it is mined.
2. Describe the process taken to extract tin from its principal ore.
3. State three properties and uses of tin.

The principal tin ore is mainly made of tin and oxygen and is ***cassiterite*** *(gasegereti in Kinyarwanda)*. The main component of cassiterite is tin (IV) oxide or tin dioxide, SnO_2.

From long time ago, cassiterite has been one of Rwandan exported products. It is extracted in some regions such as: Rutongo, Rwinkwavu, Gatumba, etc…

2.4.1. Extraction of tin from cassiterite

Extraction of tin from cassiterite is done into the following steps.

- **Washing:** Here the minerals dug from the site must be washed to remove the soil/earth accompanying the mineral.

- **Concentration:** The crushed cassiterite is concentrated by gravity separation and the magnetic impurities like wolframite [$(Mn,Fe)WO_4$], etc, are separated from cassiterite by magnetic separators.
- **Roasting:** The tin ore is roasted in air to remove other impurities, such as arsenic and sulphur as volatile oxides. Iron compounds, which might be present as impurities are removed by electromagnetic separation and iron pyrites change to their oxides and sulphates.
- **Leaching and washing:** The roasted ore is treated with water and the soluble $CuSO_4$ or $FeSO_4$ are washed away from the main ore. Further lighter ferric oxide is washed away leaving behind heavier ore particles known as black tin containing 60 to 70 % SnO_2.
- **Smelting:** The tin metal is extracted from its ore by carbon reduction. The concentrated ore is mixed with coke/charcoal and heated in a furnace.

$$SnO_2 + 2\,C \rightarrow Sn + 2\,CO$$

In the furnace, there are other impurities such as silica (SiO_2). This one is removed using limestone. Limestone is added in the furnace and undergoes the thermal decomposition giving calcium oxide. Calcium oxide then reacts with SiO_2 to form calcium silicate which has a relatively low melting point.

$$\mathbf{CaCO_3 \xrightarrow{\Delta} CaO + CO_2}$$

$$\mathbf{CaO + SiO_2 \rightarrow CaSiO_3}$$

Molten tin is drawn into blocks. It contains 99.5 % of tin metal and is called ***block tin*.**

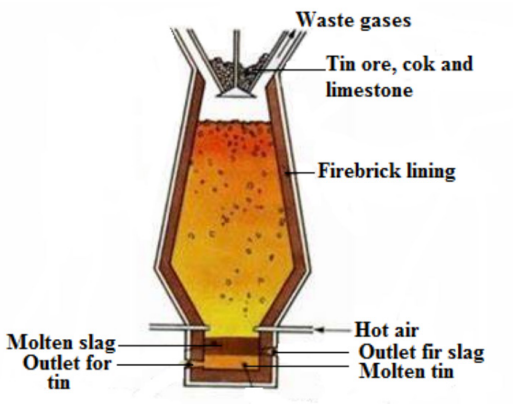


Figure 2.5: The furnace for extraction of Tin

(Source: http://onelearningsolution.blogspot.com/2015/02/33-reactivity-series-of-metals-and-its.html)

- **Refining of tin:** The tin obtained is purified. It is separated from copper, iron and any other element present as impurities by either thermal (liquation) -heating beyond its melting point of 232°C, and running off the molten tin, leaving behind any less fusible impurities - or by electrolytic means.

Purer tin is obtained by the electrolysis of aqueous solution of tin (II) chloride, $SnCl_2$ - the impure tin is made anode, while the cathode is pure tin. The electrolyte may also consist of tin sulphate containing a small amount of hydrofluorosilicic acid (H_2SiF_6) and sulphuric acid.

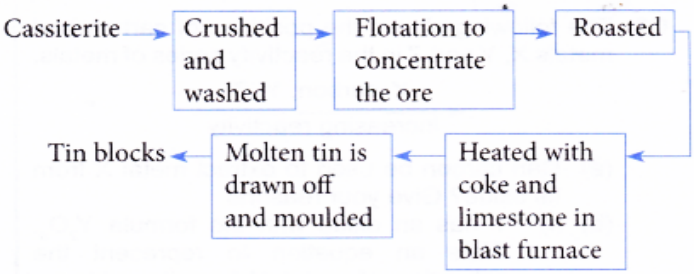


Figure 2.6: Steps in the Extraction of tin

2.4.2. Uses of tin

- Tin is used to plate iron to prevent it from rusting and as alloys such as bronze (tin and copper) and solder (tin and lead). This silvery, malleable p-block metal is not easily oxidized in air and is used to coat other metals to prevent corrosion. In modern times tin is used in many alloys.
- Another large application for tin is corrosion-resistant tin plating of steel.
- Because of its low toxicity, tin-plated metal is also used for food packaging, giving the name to tin cans, which are made mostly of steel.
- Due to its resistance to atmospheric corrosion and low melting point, it can be used to make sheet glass.

Checking up 2.4

1. Name the main ore of tin.
2. Explain the extraction of tin from tin oxide.
3. Tin metal is obtained by removing oxygen from the metal oxide. What name do we give to this chemical reaction?
4. Explain why tin is said to be very useful.

2.5. Methods of extraction of Zinc

Activity 2.5

Use the library or other search engine to

1. Find out the main ores of zinc.
2. Describe all steps followed to obtain the purified zinc from its sulphide ore.
3. Demonstrate how zinc is so useful.

The main ore of zinc is zinc blende, ZnS which is contaminated with lead sulphide. Another example of zinc ore is calamine ($ZnCO_3$).

Zinc is extracted from zinc blende in various steps such as concentration, roasting, smelting and purification which are given below in details.

a. Process of concentration

The first process in the extraction of zinc is the concentration. This process involves the implementation of froth flotation method for the extraction of zinc ores from zinc blende.

Zinc blende is mixed up in a large tank consisting of a mixture of pine oil and water. Later compressed air is passed through this combination. The froth containing the concentrated zinc sulphide ores settles on the surface leaving behind the impurities in water.

b. Process of roasting

The concentrated ore is then treated at 900°C in the presence of excess air, on the base of a reverberatory furnace. This process of heating is called roasting. During this process, zinc oxide is obtained from the zinc sulphide ore. The equation for this process is:

$$2\ ZnS + 3\ O_2 \rightarrow 2\ ZnO + 2\ SO_2$$

c. Process of smelting

Here, the mixture of zinc oxide and coke is heated in the presence of carbon to obtain zinc. This is a reduction of zinc. The involved equation is:

$$2ZnO + C \rightarrow 2Zn + CO_2$$

The process is employed in a vertical container. In this whole process, the zinc oxide and coke are mixed in the ratio 2:1 and in the form of a compressed mixture. This mixture is introduced into the furnace and is heated inside at a temperature of about 1400 °C. Zinc is obtained in the form of vapors which later condenses in the condenser which gives out molten zinc called spelter zinc (impure zinc).

d. Purification process

This is the last step of the entire process of zinc extraction. The molten zinc obtained from the previous process contains some impurities. Hence the process of the removal of these impurities is called Purification. This process can be done in two ways as given below.

- **Fractional distillation**

This is very useful for low boiling metals like zinc and mercury. The impure metals is evaporated to obtain the pure metal as distillate.

- **Electrolysis process**

Electrolysis is one method of removing impurities from the zinc spelter. The method uses a zinc rod which acts as a cathode, while the impure zinc serves as an anode. $ZnSO_4$ and dilute H_2SO_4 are mixed up and used as an electrolyte.

The current is passed through the electrolyte; Zinc is deposited on the cathode leaving the impurities in the electrolyte solution.

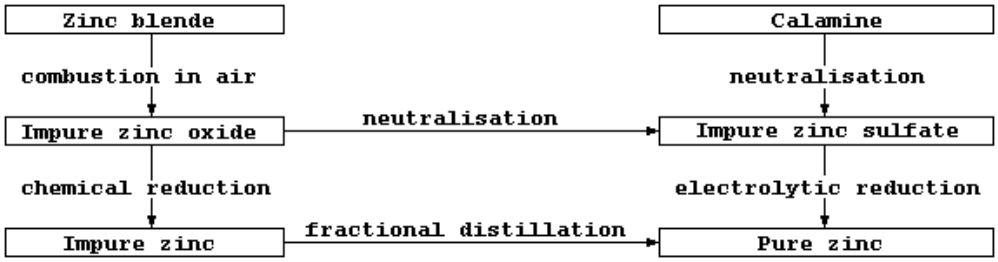


Figure 2.7: Different ways of zinc purification

Checking up 2.5

1. State two uses of zinc (refer to unit 1)
2. Describe the extraction of zinc from zinc oxide.
3. Zinc is extracted by removing oxygen from zinc oxide.
   a. What name is given to a reaction in which oxygen is removed from a substance?
   b. Explain how oxygen can be removed from zinc oxide to make zinc.
4. Describe different methods by which the impurities in zinc extracted can be removed.

2.6. Methods of extraction of Sodium

Activity 2.6

You are requested to use all resources about sodium (books, internet, textbooks).

1. Discuss on the importance of sodium and its compounds in Chemistry and in everyday life.
2. Sodium metal does not occur in Free State in nature. Explain why
3. Use the available resources to describe the way this valuable metal can be obtained at large scale (include the mining process, separation methods from its compounds, reaction equations where necessary, the main drawbacks that can be encountered during this process and the way to overcome them).

On industrial scale sodium metal is extracted by **"Down's Process".** Down's Process is based on the electrolysis of fused salt (NaCl). This compound is found all around the world, dissolved in sea water. It is also mined from the ore called **rock salt,** which is made up mainly of sodium chloride (NaCl).

2.6.1. Extraction using Down's Cell

The salt is found mixed with insoluble impurities of sand and bits of rock. Once the dissolved rock salt has been filtered, we are left with a solution of sodium chloride in water. You might think that this could be electrolysed to extract the sodium. However, because sodium is more reactive than the hydrogen in the water, hydrogen would be produced at the cathode instead of sodium. Instead, sodium chloride is crystallized out of the solution and melted. The molten sodium chloride is then electrolysed to extract the sodium metal. This is carried out in a Down's cell as shown in figure below.

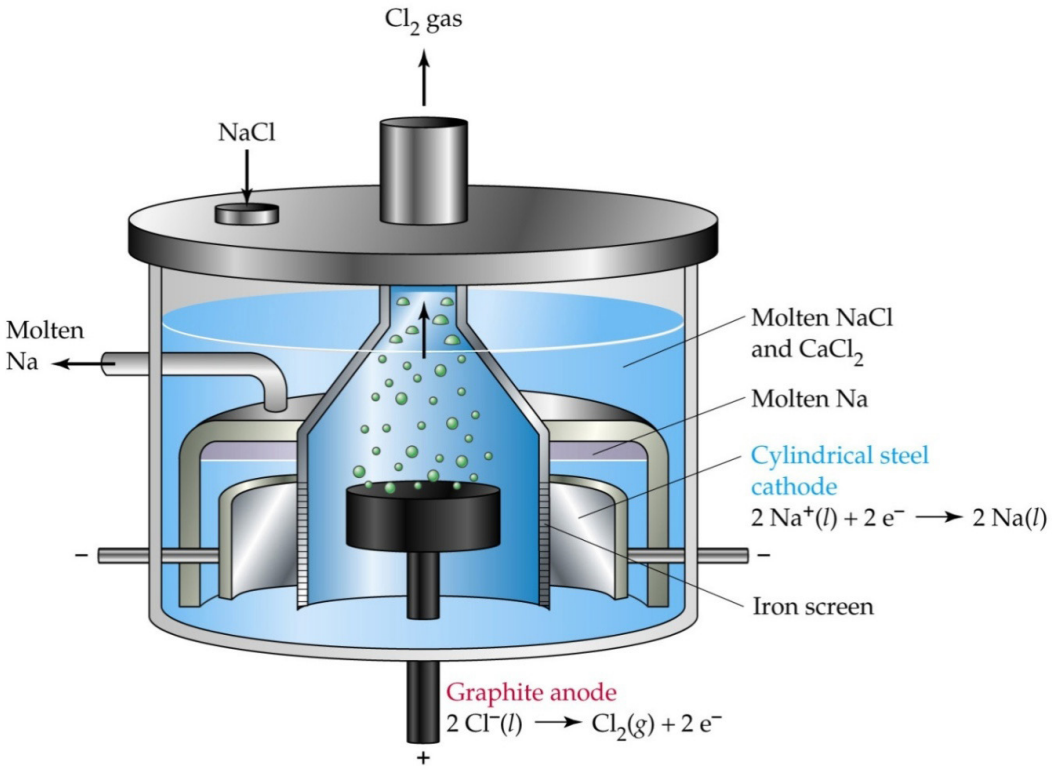


Figure 2.8: Structure of a Down's cell

(Source:http://chem1180.blogspot.com/2010/11/199-1911-electrolysis-of-molten-salts.html)

- Down's cell consists of a container of steel.
- Inside of the tank is lined with firebricks.
- Anode is a graphite rod which projects centrally up through the base of the cell.
- Cathode is a ring of iron, which surrounds the anode.
- The anode and cathode are separated from each other by a cylindrical steel gauze diaphragm (iron screen) so that Na and Cl_2 are kept apart.
- A bell-like hood is immersed in electrolyte over the anode.

When an electric current is passed through the molten mixture of NaCl and $CaCl_2$, NaCl decomposes into Na^+ and Cl^- ion. Na^+ ions migrate towards cathode while Cl^- ions towards the anode. The molten sodium collects in the cathode compartment where it rises to the top and is tapped off by a pipe. Chlorine is collected at the anode.

During electrolysis, calcium is also obtained at cathode but sodium and calcium are separated from each other due to the difference in density. Density of Na is 0.67 g cm^{-3} and the density of Ca is 2.54 g cm^{-3} i.e.much higher than that of Na. That is why they do not mix with each other.

2.6.2. Problems with Down's method

Down's Cell NaCl is a poor conductor in its solid form, but fusing it allows for conduction of electric current by mobile ions. However, in its liquid form, its melting point is at about 800°C, a point at which a "metallic fog" will form between the electrolyte (NaCl) and the metallic sodium (Na) being formed and this is impossible to separate.

2.6.3. Steps to overcome this difficulty

In order to overcome this difficulty instead of only NaCl, a mixture of NaCl and $CaCl_2$ is electrolyzed in Down's cell. The melting point of this mixture is 600 °C. At 600 °C, no metallic fog is formed. The composition of the charge in Down's Cell is NaCl = 42 % and $CaCl_2$ = 58 %

2.6.4. Uses of sodium

- Molten sodium is used as a coolant in some types of nuclear reactor. Its high thermal conductivity and low melting temperature and the fact that its boiling temperature is much higher than that of water make sodium suitable for this purpose.
- Sodium wire is used in electrical circuits for special applications. It is very flexible and has a high electrical conductivity. The wire is coated with plastics to exclude moisture.
- Sodium vapour lamps are used for street lighting; the yellow light.
- Sodium amalgam and sodium tetrahydridoborate, $NaBH_4$, are used as reducing agents.
- Sodium is also a component of sodium chloride (NaCl), a very important compound found everywhere in the living environment; particularly as cooking and table salt.
- Other uses are: to improve the structure of certain alloys; in soap, in combination with fatty acids, to purify molten metals, etc.
- In countries that experience very cold winter, NaCl is spread on the roads to de-ice the roads.

Checking up 2.6

1. Why is sodium not extracted by carbon reduction process? What is the method used?
2. What difficulties arise in the extraction of sodium from its ore?
3. Choose the suitable answer. In sodium extraction, fused (molten) NaCl is used rather than the dissolved (aqueous) NaCl because:

a. Obtaining molten NaCl is easy than obtaining aqueous NaCl.

b. In molten NaCl, the ions are free to move and not in aqueous NaCl.

c. Molten sodium NaCl is an electrolyte and not the aqueous NaCl.

d. Electrolysis of molten NaCl gives Na metal at the cathode but that of aqueous NaCl gives H_2 gas.

2.7. Methods of extraction of Aluminium

Activity 2.7

Research in library textbook or search engine about aluminium and its extraction and make a good summary containing the following:

1. The main ores of aluminium.
2. Why aluminium extraction is suitable to be done by electrolytic method rather than reduction with carbon.
3. The way the main ore is purified to have the pure aluminium oxide
4. The process by which aluminium is extracted from the purified ore by electrolytic method (include the diagram, reaction equations at electrodes and the way to solve some difficulties which may arise during this extraction process)
5. The properties of aluminium which makes it to be very important in our daily uses and the uses of aluminium.

The main ore of aluminium is called bauxite ($Al_2O_3.2H_2O$). Other examples of ores are: Cryolite ($Na_3\ AlF_6$), Feldspar ($KAlSiO_3O_8$) and Mica [$KAlSiO_{10}\ (OH)_2$].

Bauxite is purified to yield a white powder, aluminium oxide, from which aluminium can be extracted. Aluminium is too high in the electrochemical series (reactivity series) to extract it from its ore using carbon reduction. The temperatures needed are too high to be economic. Instead, it is extracted by electrolysis as follows.

2.7.1. Purifiying the bauxite (The Bayer Process)

The bauxite (red-brown solid) - hydrated aluminium oxide mixed with impurities - is extracted from the earth-crust. The extracted aluminium oxide (bauxite) is then treated with alkali; this separates insoluble impurities from aluminium which forms soluble complex ion $Al(OH)_4^-$.

a. Reaction with sodium hydroxide solution

Crushed bauxite is treated with moderately concentrated sodium hydroxide solution. The concentration, temperature and pressure used depend on the source of the bauxite and exactly what form of aluminium oxide it contains. Temperatures are typically from 140 °C to 240 °C; pressures can be up to about 35 atmospheres. High pressures are necessary to keep the water in the sodium hydroxide solution liquid at temperatures above 100 °C. The higher the temperature, the higher the pressure needed.

With hot concentrated sodium hydroxide solution, aluminium oxide reacts to give a solution of sodium tetrahydroxoaluminate (sodium aluminate).

$$Al_2O_3 + 2\ NaOH + 3\ H_2O \rightarrow 2\ NaAl(OH)_4$$

The impurities in the bauxite remain as solids. For example, the other metal oxides present tend not to react with the sodium hydroxide solution and so remain unchanged. Some of the silicon dioxide reacts, but goes on to form a sodium aluminosilicate which precipitates out.

Silica (SiO_2) also dissolves in sodium hydroxide to form soluble sodium trioxosilicate (IV), Na_2SiO_3.

$$SiO_2 + 2\ NaOH \rightarrow Na_2SiO_3 + H_2O$$

The impurities are filtered out and the filtrate contains sodium tetrahydroxoaluminate (III) and sodium trioxosilicate (IV) only.

b. Precipitation of aluminium hydroxide

CO_2 is bubbled through the filtrate containing sodium tetrahydroxoaluminate (III) and sodium trioxosilicate (IV). At this stage the solution may be seeded with freshly precipitated aluminium hydroxide.

$$NaAl(OH)_4(aq) + CO_2(g) \rightarrow NaHCO_3(aq) + Al(OH)_3(s)$$

c. Formation of pure aluminium oxide

Aluminium oxide (sometimes known as **alumina**) is made by heating (decomposition) the aluminium hydroxide to a temperature of about 1100 – 1200 °C.

$$2\ Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O$$

2.7.2. Extraction of the aluminium from purified bauxite by electrolysis (Hall-Heroult Process)

Alumina (purified bauxite) is then transported to huge tanks. The tanks are lined with graphite that acts as the cathode. Also blocks of graphite hang in the middle of the iron (steel) tank, and acts as anodes.

The alumina is mixed with cryolite, Na_3AlF_6 and this lowers the melting point of the mixture - Cryolite is another aluminium ore, but is rare and expensive, and most of it is now synthesized.

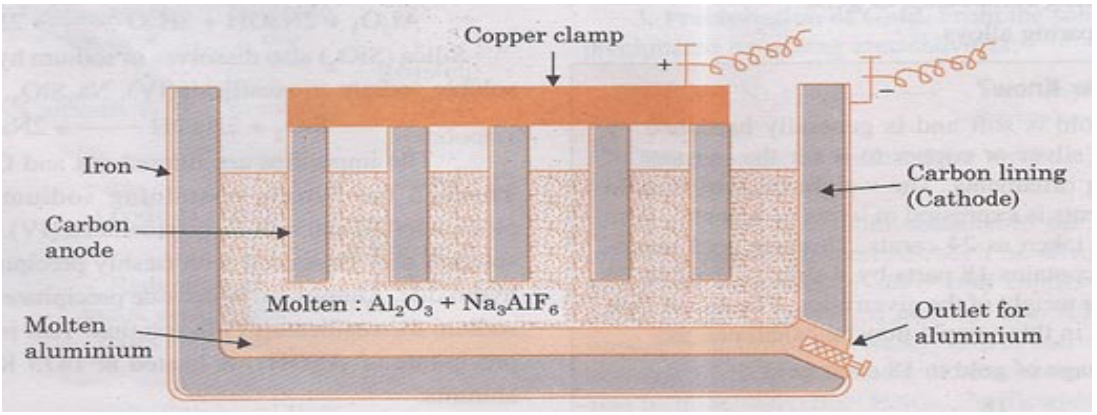


Figure 2.9: Electrolytic cell for production of aluminium

The electrode equations are as follows:

- At the cathode: Here the aluminium ions capture electrons to become atoms again:

  $Al^{3+} + 3e^- \rightarrow Al$

- At the anode: The oxide ions lose electrons to become oxygen molecules, O_2:

  $2\ O^{2-} \rightarrow O_2 + 4e^-$

The positive electrode burns away as the carbon reacts with the oxygen produced there.

$$C + O_2 \rightarrow CO_2$$

Since during electrolysis, the carbon electrodes get consumed, they have to be replaced periodically. For each kg of aluminium about 0.5 kg carbon is burnt away.

2.7.3. Uses of aluminium

- It is a good conductor of electricity. Since it is not as good conductor as copper, thicker cables of aluminium are used for transmission of electricity.
- Aluminium forms many useful alloys e.g., magnalium (Al and Mg), duralumin (Al, Cu, Mg and Mn). Aluminium alloys are used in aircraft and other transportation vehicles because of its low density.

- It is used as jewellery because it is a shiny metal, it has a good appearance.
- Resists corrosion because of the strong thin layer of aluminium oxide on its surface. This layer can be strengthened further by anodising the aluminium.
- It is used for making window frames.
- Aluminium foil is used for wrapping cigarettes, food, etc because it reflects light.
- Drink cans because it is not toxic.
- Aluminium utensils are extensively used for household purposes.
- Aluminium is used to produce metals such as chromium and manganese from their ores (aluminothermic process).

$$Cr_2O_3 + 2\ Al \rightarrow Al_2O_3 + 2\ Cr$$

$$3\ MnO_2 + 4\ Al \rightarrow 2\ Al_2O_3 + 3\ Mn$$

2.7.4. Recycling of aluminium

Aluminum is one of the most recycled materials in the world. This is due to high cost of new aluminium that involves high cost of electricity needed to produce aluminium. Recycled aluminium cost less in production and constitutes another way of sustainable management of our natural resources.

- The consumer throws aluminium cans and foil into a recycle bin.
- The aluminium is then collected and taken to a treatment plant.
- In the treatment plant the aluminium is sorted and cleaned ready for reprocessing.
- It then goes through a re-melt process and turns into molten aluminium, this removes the coatings and inks that may be present on the aluminium.
- The aluminium is then made into large blocks called ingots.
- The ingots are sent to mills where they are rolled out, this gives the aluminium greater flexibility and strength.
- This is then made into aluminium products such as cans, chocolate wrapping and ready meal packaging.
- In as little as 6 weeks, the recycled aluminium products are then sent back to the shops ready to be used again.

Checking up 2.7

Consider the electrolytic extraction of aluminium.

1. How is aluminium ore called?
2. Explain why cryolithe is added to aluminium oxide
3. Describe the process by which the ore of aluminium is purified.
4. Write half-equations for the reactions at each electrode, and write an overall equation for the reaction.
5. State what each electrode is made of.
6. Explain why
   a. The anodes need to be regularly replaced.
   b. The electrolysis of aluminium oxide is expensive.
   c. Aluminium is recycled.
7. Give three uses of aluminium and the properties responsible for each use.

2.8. Methods of extraction of Wolfram (Tungsten)

Activity 2.8

1. Visit the nearby mining sites of wolfram and make a field report.
2. Research using internet and some books and make a summary about the following:
   a. The ores of wolfram.
   b. Where in Rwanda do we find wolfram?
   c. How wolfram extraction differs from that of zinc in terms of reduction.
   d. Full description of the extraction process of tungsten from its ore.
   e. The main uses of tungsten.

Tungsten ore is a rock from which the element tungsten can be economically extracted. The ore minerals of tungsten include wolframite [(Fe, Mn)WO_4], scheelite ($CaWO_4$) and ferberite ($FeWO_4$).

Tungsten is a dull silver-colored metal with the highest melting point (3410 °C) of any pure metal. Also known as Wolfram, from which the element takes its symbol, W, tungsten is more resistant to fracturing than diamond and is much harder than steel. It is unique in being a refractory metal - its strength and ability to withstand high temperatures - that make it ideal for many commercial and industrial applications.

Most tungsten ores contain less than 1.5% WO_3 and frequently only a few tenths of a percent. On the other hand, ore concentrates traded internationally require 65-75% WO_3. Therefore, a very high amount of gangue material must be separated. This is why ore dressing plants are always located in close proximity to the mine to save transportation costs.

2.8.1. Processing

Modern processing methods dissolve scheelite and wolframite concentrates by an alkaline pressure digestion, using either a soda ash (Na_2CO_3) or a concentrated NaOH solution. The sodium tungstate solution obtained is purified by precipitation and filtration, before it is converted into an ammonium tungstate solution. This stage is carried out exclusively by solvent extraction or ion exchange resins. Finally, high purity Ammonium paratungstate (APT) is obtained by crystallization.

Wolframite concentrates can also be smelted directly with charcoal or coke in an electric arc furnace to produce ferrotungsten (FeW) which is used as alloying material in steel production. Pure scheelite concentrate may also be added directly to molten steel.

Once tungsten ore has been processed and separated, the chemical form, ammonium paratungstate (APT), is produced.

2.8.2. The extraction process

APT can be heated with hydrogen to form tungsten oxide (WO_3) or will react with carbon at temperatures above 1050°C to produce tungsten metal. Pure tungsten cannot be obtained by reducing tungsten (VI) oxide using carbon, because it reacts with carbon to make tungsten carbide. Instead, the reducing agent is hydrogen.

Powdered tungsten (VI) oxide is heated to temperatures in the range 550 - 850°C in a stream of hydrogen.

$$WO_3 + 3\,H_2 \longrightarrow W + 3\,H_2O$$

An excess of hydrogen is used, and this carries away the steam produced during the reaction. The hydrogen is dried and recycled.

Great care obviously has to be taken to keep the whole system free of air to avoid explosion risks with the hydrogen at these high temperatures.

2.8.3. Advantages and disadvantages of the process

a. Advantages:

- It produces very pure tungsten
- Hydrogen is a cheap reagent

b. Disadvantages:

- The energy cost are high
- Using a flammable gas such as hydrogen at high temperatures is very dangerous

2.8.4. Uses

- Tungsten is mostly used in light bulb filaments which heat up to 2000°C, when many other metals would vaporise, particularly at the pressures found inside light bulbs. This is because it has a very high melting point.
- Tungsten has the highest melting point of all metals and is alloyed with other metals to strengthen them. Tungsten and its alloys are used in many high-temperature applications, such as arc-welding electrodes and heating elements in high-temperature furnaces.
- Tungsten carbide (WC) is extremely hard and is very important to the metal-working, mining and petroleum industries. It is made by mixing tungsten powder and carbon powder and heating to 2200°C. It makes excellent cutting and drilling tools, including a new 'painless' dental drill which spins at ultra-high speeds.
- Calcium and magnesium tungstates are widely used in fluorescent lighting. Tungsten mill products are either tungsten metal products, such as lighting filaments, electrodes, electrical and electronic contacts, wires, sheets, rods etc or tungsten alloys.
- Due to tungsten's ability to keep its shape at high temperatures, tungsten filaments are now also used in a variety of household applications, including lamps, floodlights, heating elements in electrical furnaces, microwave ovens, x-ray tubes and cathode-ray tubes (CRTs) in computer monitors and television sets.
- The metal tolerance to intense heat also makes it ideal for thermocouples and electrical contacts in electric arc furnaces and welding equipment.
- Applications that require a concentrated mass, or weight, such as counterweights, fishing sinkers, and darts often use tungsten because of its high density (19.3 g/cm^3).

Checking up 2.8

1. Nowadays, there is a special reduction method used to extract Tungsten from its ores.

   a. State 2 main ores of tungsten.

   b. Write the balanced equation of the reduction reaction of tungsten (II) oxide.

2. Suggest the reason why ore concentrating plants are always located in close proximity to the mine.

3. Give 2 widely known physical properties of tungsten and the uses associated to these properties.

2.9. Methods of extraction of tantalum

Activity 2.9

1. Visit the nearby mining sites of tantalum and make a field report.

2. The picture below shows the miners at work in Rwanda. The metal being extracted here is very important in modern area. According to Merchant and Consulting Ltd (2018), Rwanda is the world's largest producer of this metal which is called "tantalum".

Research using any relevant source of information about tantalum:

a. To find out the physical properties of tantalum metal and its main uses.

b. To make a description of the extraction of tantalum from its main ore tantalite.

Tantalum is a hard, heavy, shiny, grayish-blue metal that is very stable, almost impervious (impermeable) to air, water and all but a few acids. It has the third highest melting point of all elements (over 3000 °C), and its primary use is in capacitors for electronic applications, and for vacuum furnace parts.

It is classified as a "refractory" metal, which means it can sustain high temperatures and resist corrosion. It is a good conductor of heat and electricity, which makes it useful in various electronics. Pure tantalum can be drawn into fine wire filament, which is used to evaporate other metals.

2.9.1. Where tantalum is found

Tantalum is found in hard rock deposits such as granites, carbonites and pegmatites (igneous rock that consists of coarse granite). The chief tantalum ores are tantalite [$(Fe, Mn)(Ta, Nb)_2O_6$], which also contains iron, manganese and niobium (former name is columbium), and samarskite, which contains seven metals. Another ore which contains tantalum and niobium is pyrochlore. In Rwanda tantalum is found with niobium in mineral known as coltan (colomb-tantalite).

Tantalum is an important component in many modern technologies, and is used in capacitors for everything from computers to mobile phones.

Despite its importance in the world today, tantalum mining takes place in very few countries and mining it is difficult. Only four countries produced tantalum in 2016, and most was mined in the Democratic Republic of Congo (DRC). Rwanda, Brazil and China were the other top countries for tantalum mining in that year. Sites are being identified for future development, and existing sites are being evaluated for expansion.

2.9.2. How tantalum is mined

Tantalum comes from the processing and refining of tantalite. Tantalite is the common name for any mineral ore containing tantalum. Most tantalum mines are open pit; some are underground.

The process of mining tantalum involves blasting, crushing and transporting the resulting ore to begin the process of freeing the tantalum. Before transportation, the ore is concentrated at or near the mine site, to increase the percentage (by weight) of tantalum oxide and niobium. The material is concentrated through wet gravity techniques, gravity, electrostatic and electromagnetic processes.

2.9.3. How tantalum is processed

The tantalum concentrate is transported to the processor for chemical processing. The concentrate is then treated with a mixture of hydrofluoric and sulphuric acids at high temperatures. This causes the tantalum and niobium to dissolve as fluorides.

Numerous impurities are also dissolved. Other elements, such as silicon, iron, manganese, titanium, zirconium, uranium and thorium, are generally present and processed for other uses.

The concentrate is broken down into a slurry (A slurry is a watery mixture of insoluble matter such as mud, lime, or plaster of Paris). The slurry is filtered and further processed by solvent extraction. Using methyl isobutyl ketone (MIBK), or liquid ion exchange using an amine extract in kerosenes, produces highly purified solutions of tantalum and niobium. In this way, the tantalum oxide is obtained which is finally reduced with molten sodium to produce tantalum metal in powder form.

It can then be compacted (as it is for capacitors) to final shape, or may be melted (and refined) in an electron beam furnace.

2.9.4. Uses for tantalum

- Tantalum is used to make electrolytic conductors, aircraft engines, vacuum furnace parts, nuclear reactors and missile parts.
- Tantalum is unaffected by body fluids, and is non-irritating, which makes it useful for surgical appliances.
- It is common in the production of cell phones, personal computers, igniter chips in car air bags, cutting tools, drill bits, teeth for excavators, bullets and heat shields.
- Because the metal is an electrical conductor, it is useful in many consumer electronics, such as microprocessors for plasma televisions.

Checking up 2.9

In pairs, answer the following questions:

1. Where tantalum is found in Rwanda?
2. How tantalum is mined.
3. How tantalum is processed
4. Give 3 uses of tantalum.
5. What is the role of methyl isobutyl ketone (MIBK) in tantalum processing?

2.10. Dangers associated with extraction of metals

Activity 2.10

If you have ever visited a mining site, remember all the processes involved and suggest all possible common dangers associated with the extraction of metals.

The following are some of the dangers associated with metals extraction. Especially, these hazards are found in smelting and refining and in addition mining.

1. Injuries

Metal extraction industry has a higher rate of injuries than most other industries. Sources of these injuries include: splattering and spills of molten metaland slag resulting in burns; gas explosions and explosions from contact of molten metal with water; collisions with moving vehicles; falls of heavy objects; falls from a height,slipping and tripping injuries from obstruction of floors and passageways.

Precautions

Adequate training, appropriate personal protective equipment (PPE) [for example, hard hats, safety shoes, work gloves and protective clothing]; good storage, housekeeping and equipment maintenance; traffic rules for moving equipment (including defined routes and an effective signal and warning system); and a fall protection programme.

2. Heat illnesses

Heat stress illnesses such as heat stroke are a common hazard, primarily due to infrared radiation from furnaces and molten metal. This is especially a problem when strenuous work must be done in hot environments.

Prevention of heat illnesses

Water screens or air curtains in front of furnaces, spot cooling, enclosed air-conditioned booths, heat-protective clothing and air-cooled suits, allowing sufficient time for acclimatization, work breaks in cool areas and an adequate supply of beverages for frequent drinking.

3. Pollutions

Mining operations are major contributors to the pollution of our environment such as: air pollution, water pollution, degradation of landscape, etc.

Exposure to a wide variety of hazardous dusts, fumes, gases and other chemicals can occur during smelting and refining operations. Crushing and grinding ore in particular can result in high exposures to silica and toxic metal dusts (containing lead, arsenic and cadmium, for example). There can also be dust exposures during furnace maintenance operations. During smelting operations, metal fumes can be a major problem especially risk of developing respiratory system illness. In metallurgical operations, the carbon dioxide released has more dangers especially the global warming because it is a greenhouse gas. Acid gases released in atmosphere such as SO_2, SO_3, NO_x are sources of acid rains.

Control

Dust and fume emissions can be controlled by enclosure, automation of processes, local and dilution exhaust ventilation, wetting down of materials, reduced handling of materials and other process changes. Where these are not adequate, respiratory protection would be needed.

Many smelting operations involve the production of large amounts of sulphur dioxide from sulphide ores and carbon monoxide from combustion processes. Dilution and local exhaust ventilation (LEV) are essential.

Sulphuric acid is produced as a by-product of smelting operations and is used in electrolytic refining and leaching of metals. Exposure can occur both to the liquid and to sulphuric acid mists. Skin and eye protection and LEV are needed.

The extraction of some metals can have special dangers. Examples include fluorides in aluminium smelting, arsenic in copper, etc. These processes require their own special precautions

Other dangers

- Glare and infrared radiation from furnaces and molten metal can cause eye damage including cataracts. Proper goggles and face shields should be worn. High levels of infrared radiation may also cause skin burns unless protective clothing is worn.
- High noise levels from crushing and grinding ore, gas discharge blowers and high-power electric furnaces can cause hearing loss. If the source of the noise cannot be enclosed or isolated, then hearing protectors should be worn. A hearing conservation program including audiometric testing and training should be instituted.
- Electrical hazards can occur during electrolytic processes. Precautions include proper electrical maintenance with lockout/tagout procedures; insulated gloves, clothing and tools; and ground fault circuit interrupters where needed.
- Manual lifting and handling of materials can cause back and upper extremity injuries. Mechanical lifting aids and proper training in lifting methods can reduce this problem.

CASE OF RWANDA

According to Rwanda Environment Management Authority (REMA), mining activities often impact significantly on the environment. For instance, sand collecting and quarrying are already shown some significant environmental impacts, including resource depletion, energy consumption, waste generation and emissions of air pollutants. The dangers to human life and health associated with mining include the displacement of people, land use changes, dust and noise pollution.

In fact, the preparation of ores which uses a lot of water constitutes a major pollutant of stream water in Rwanda. For example, the waters draining the mining sectors of Rutongo and Gatumba pollute the rivers of Nyabarongo and Nyabugogo by sediments of clay and sand which they transport over long distances. It is this considerable mineral load which partly gives them the brown colour that is characteristic of the rivers in Rwanda. Mining and quarrying produce massive rejects which appear in nature in the form of enormous lots of earth and rocks. Erosion from rain water transports the mineral residue towards the valleys where streams are filled and covered by the residue which may be toxic to biodiversity.

Checking up 2.10

1. State 5 sources of injuries associated with the extractions of metals
2. Give 3 ways you can prevent from heat illnesses.
3. Describe 2 ways you can control the dangers associated with the chemicals in extraction of metals.
4. Suggest a way of protecting mining workers against the risk of lung disease due to dust at their working place?

2.11. Preventive measures associated with metal extractions

Activity 2.11

We already know that there are many dangers associated with the extraction of metals.

Recommend measures that must be taken to prevent from these dangers (risks).

Effort should be made by mining componies or planned for the future, to eliminate or minimize the environmental problems associated with metal extractions include:

1. The potential sources of air contaminants should be enclosed and isolated.
2. Brief, for any operation related to metal extraction, measures must be adopted to protect the workers in particular and the environment in general by:

   - Elimination or reduction of air polluting gases.
   - Avoiding water and soil pollution.
   - Protect the landscape.
   - Using cleaner production techniques i.e Minimize sources of pollution and use of energy.

3. Adopt technology that minimizes wastes produced through process-reengineering/recycling

Checking up 2.11

1. In extraction of metals, the best and least costly preventive measures are those taken at the planning stage of a new process of extraction. Explain the main aspects that should be taken into account.
2. what are the main sources of pollution in metallurgy?

END UNIT ASSESSMENT

1. Which metal is extracted from Bauxite?
   a. Tin
   b. Tantalum
   c. Copper
   d. Aluminum
2. Brass is
   a. An Element
   b. A Compound
   c. A Mixture
   d. An Alloy
3. Bronze is an alloy of
   a. Copper and Zinc
   b. Lead and Copper
   c. Copper and Tin
   d. Barium, Zinc and Iron
4. Which of the following metals is often found in pure state?
   a. Copper
   b. Iron
   c. Gold
   d. Aluminum
5. Which metal is extracted from Haematite?
   a. Tin
   b. Iron
   c. Manganese
   d. Cadmium
6. Rocks rich in metals with economic value are known as
   a. Metalloids
   b. Ores
   c. Allotropes
   d. Slag
7. An alloy is a
   a. Compound of three elements
   b. Homogeneus mixture of two or more metals
   c. Heterogeneous mixture
   d. Element in impure form

8. If a metal ore is called "pyrites" then it most probably has
   a. Chlorine
   b. Oxygen
   c. Sulphur
   d. Nitrogen

9. Often to prevent corrosion, metals are galvanized by covering them with a layer of
   a. Copper
   b. Sodium
   c. Zinc
   d. Tin

10. What is not true about Tantalum?
   a. It is classified as a "refractory" metal
   b. Tantalum oxide is reduced with molten sodium to produce tantalum metal in powder form.
   c. Its ore minerals include scheelite
   d. It is found in hard rock deposits such as granites, carbonites and pegmatites

11. Complete with the terms applied in the Extraction of iron from haematite in industry (Blast Furnace).

   a. Raw materials: _____

   A mixture of _____, _____ and _____ is added at the top of the furnace. _____ air is blown into the furnace from the bottom. A chain of chemical reactions occur:

   b. Carbon reacts with oxygen in air to form _____.

      Equation: _____

   c. The hot carbon dioxide rises in the furnace and is reduced by _____ to form _____. Equation: _____

   d. Carbon monoxide is a _____ agent. It _____ iron(III) oxide in haematite to form hot molten _____.

      Equation: _____
      The hot molten iron is then rum out from the bottom of the furnace.

   e. The formula of limestone: _____

      Limestone breaks up into_____ and_____ when heated.

Equation: _____

f. Calcium oxide helps to remove _____ (the impurities) to form a liquid '_____'. Equation: _____

12. a. By giving reagents and conditions, state three different methods of extracting metals starting from their oxides. In each case, write equation(s) to illustrate the extraction of an appropriate metal.

b. i. Why are metals more usually extracted from their oxides rather than from any other compound?

ii. State two environmental problems associated with the extraction of metals from their oxides or sulphides and give the chemical responsible for each problem.

13. a. Give the ores of iron.

b. Explain the extraction of iron from its ores.

14. a. Give 2 or 3 uses of aluminium, copper, zinc, and iron.

b. Give two reasons why the extraction of aluminium is expensive.

15. Tungsten is prepared in a pure form by high temperature reduction of tungsten (VI) oxide with hydrogen.

a. Construct an equation for this reaction.

b. Suggest why carbon is not used as the reducing agent.

c. Suggest one advantage (other than purity of the product) and one disadvantage of using hydrogen as the reducing agent on an industrial scale.

16. Zinc and copper are extracted in the same way as iron (in blast furnace) but exist as their sulphide ores.

a. How is the sulphide ore converted into an oxide and what is the problem with this process? (give an equation)

b. Why can aluminium not be extracted in this way?

c. Why can tungsten not be extracted in this way?

17. Copper is a widely used metal. The main ore of copper contains copper sulphide. Copper can be extracted from copper sulfide in a three stage process.

a. In the first stage of extraction the copper sulfide is heated in air.

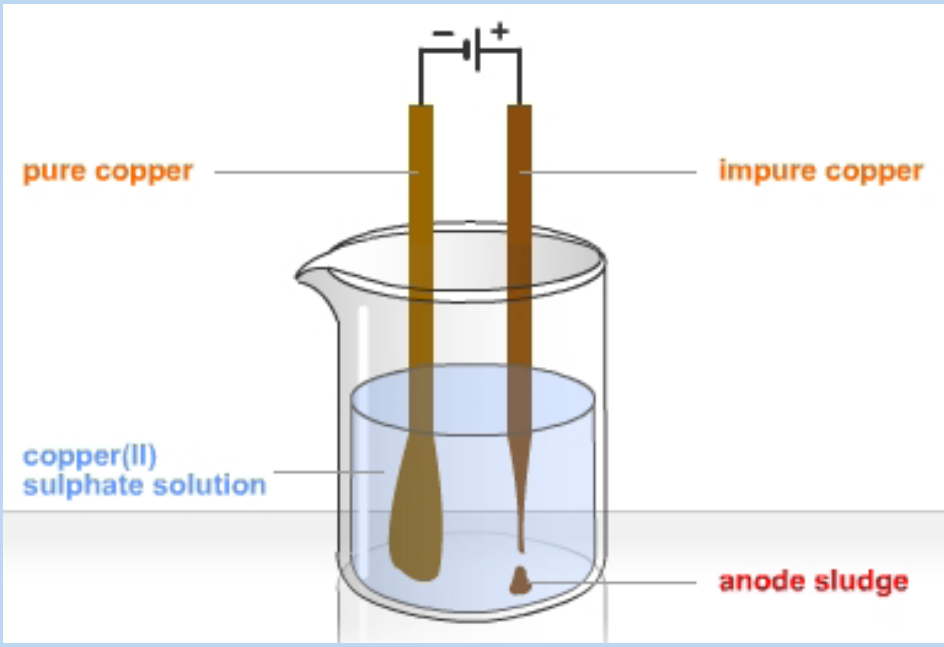
i. Balance the symbol equation for the reaction.

$Cu_2S + O_2 \rightarrow CuO + SO_2$

ii. Explain why there would be an environmental problem if the gas from this reaction were allowed to escape into the atmosphere.

b. In the second stage copper oxide, CuO, is reduced using carbon. Describe and explain what happens during this reaction.

c. During the third stage the copper can be purified as shown in the diagram.



i. What is the name of the type of process used for this purification?

ii. Give one use of purified copper.

d. Copper-rich ores are running out. New ways of extracting copper from low grade ores are being researched. Recycling of copper may be better than extracting copper from its ores. Explain why.

UNIT 3

NPK AS COMPONENTS OF FERTILIZERS

UNIT 3: NPK AS COMPONENTS OF FERTILIZERS

Key Unit Competency:

To be able to analyze the components of quality Fertilizers and their benefits, effects of misuse and dangers associated with the substandard fertilizers.

Learning objectives

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

- State the major constituents of fertilizers;
- Identify the characteristics of good fertilizer;
- Briefly describe the manufacture of fertilizers;
- State the advantages and disadvantages of using fertilizers;
- Interpret the labels on the fertilizer containers;
- Classify the fertilizers in terms of composition.

Introductory Activity

A plot of land has been divided into two parts and in both irish potatoes have been cultivated by two cultivators.

One of them harvested 2000 kg of irish potatoes of big size and the other harvested 50kg of irish potatoes of small size.

Given that on both plots of land, the following work has been done at the same time

- Cultivation,
- planting
- Hoeing (or weeding)
- Harvesting

Suggest reason(s) which caused the difference in the harvest.

The total population in Rwanda was estimated at 11.3 million people in 2016, according to the latest census figures. Looking back, in the year of 1960, Rwanda had a population of 2.9 million people. Rwanda's population will shoot to 18.2 million people by 2050 at an average growth rate of 2.3 %, the United Nations Population Fund (UNFPA) has projected. These statistics show that the population of Rwanda is going on increasing but as we know the area of Rwanda is not increasing. That is why Fertilizers and other agricultural techniques are needed for the population of Rwanda to be capable of feeding itself and even feed some other population in the region.

3.1. Types of Fertilizers

Activity 3.1

1. a. What is the role of fertilizers
   b. Name any examples of Fertilizers you have ever heard
2. Using this book or any other book or internet, read and analyse the content about the types of fertilizers and make a summary to be presented to the class.

A fertilizer is any material, organic or inorganic, that is used to supply nutrients to the soil.

There exist types of Fertilizers:

1. Natural Fertilizers(or organic Fertilizers)
2. Artificial Fertilizers (or chemical Fertilizers)

3.1.1. Natural Fertilizers

The name organic fertilizer refers to materials used as fertilizer that occur regularly in nature, usually as a by-product or end product of a naturally occurring process. They are made from remains of dead plants, wastes from animals or they can be minerals. Examples include manures and minerals. Manure is an organic material that is used to fertilize land.

1. Farmyard manure: animal manure that consists of feces
2. Green manure: is a term used to describe specific plant or crop varieties that are grown and turned into the soil to improve its overall quality.
3. Compost manure: is organic matter that has been decomposed and recycled as a fertilizer and soil amendment.
4. Minerals: Mineral mined powdered limestone, rock phosphate and sodium nitrate, are inorganic compounds which are energetically intensive to harvest and are approved for usage in organic agriculture in minimal amount.

3.1.2. Artificial Fertilizers

They are fertilizers which are chemically synthesized which contain one or more of the major elements required by plants for good growth.

Examples**:** Urea**,** N.P.K, ammonium dihydrogen phosphate, $NH_4(H_2PO_4)$,…

Table 3.1: Differences between natural and artificial fertilizers

Natural	Artificial
1. It is a natural substance. It is obtained by decomposition of animal wastes such as dung (gobar) of cattle, buffaloes and plant residues.	1. It is a human made substance. It is an inorganic salt or an organic compound.
2. It contains small amounts of essential plant nutrients such as nitrogen, phosphorus and potassium.	2. They are very rich in plant nutrients such as nitrogen, phosphorus and potassium.
3. It adds a great amount of organic matter in the form of humus in the soil.	3. It does not add any humus to the soil.
4. Nutrients present in the natural fertilizer are absorbed slowly by the crop plants since manure is not soluble in water. Nutrients exist locked inside the organic compounds of humus.	4. Being soluble in water, a artificial fertilizer is readily absorbed by the crop plants.
5. It is not nutrient specific and it tends to remove the general deficiency of the soil.	5. It is nutrient specific. It can provide specifically nitrogen, phosphorus and potassium to the soil according to the need.
6. It is voluminous and bulky so it is inconvenient to store, transport, handle and apply to the crop.	6. It is compact and concentrated so it is easy to store, transport and apply to the crop.
7. It is cheap and is prepared in rural homes or fields.	7. It is costly and is prepared in factories.
8.It is environment friendly	8. Risk of environmental pollution

Checking up 3.1

Give the two main types of Fertilizers and discuss the pros and cons of using one or another type of fertilizer.

3.2. Components of a fertilizer

Activity 3.2

1. Name any nutrients you know that plants need in order to grow
2. Using this book, any other books or internet do a research and find out
   a. The types of nutrients and give any three nutrients in each category that plants need for their growth and classify the nutrients depending on how plants need them
   b. Any two roles for each nutrients for the plant growth.

First it is important to understand that all industrial Fertilizers, by convention, regardless of type and specific use, have something called a NPK ratio.The NPK ratio will be prominently labeled on the package and indicates the percentage of major (or primary) nutrients the fertilizer contains. Example: Urea is a fertilizer with an NPKratio of 46-00-00.

The nutrients of plants are classified into three types namely:

- Major nutrients
- Secondary nutrients
- Micronutrients

3.2.1. The major nutrients

The major nutrients for soil are nitrogen (N), phosphorus (P), and potassium (K). These major nutrients usually are lacking or insuffiscient in the soil because plants consume these nutrients in large amounts for their growth and survival.

The letter N represents the actual nitrogen content in the fertilizer by percentage mass while P and K represent the amount of oxide in the form of phosphorus (V) oxide (P_2O_5) and potassium oxide (K_2O) respectively.

Example:

- If a fertilizer is labelled **17-17-17**, it means that the fertilizer contains17% by mass N, 17% by mass P_2O_5 and 17% by mass K_2O.
- If fertilizer is labelled 10-20-20, it means that the fertilizer contains 10% by mass N, 20% by mass P_2O_5 and 20% by mass K_2O.

Role of nutrients N, P, K

Nutrients	Role
Nitrogen (N)	• Stimulates the overall plant growth • In synthesis of proteins • In synthesis of chlorophyll • Early feeding of corn
Phosphorus (P)	• Promotes early growth, as well as early maturity of plants • Promotes growth of healthy roots and flowering and helps in the formation of high-yielding seeds • Increases the resistance of the plants to frost and disease
Potassium (K)	• Regulates the structure in leaves that allows CO_2 to enter the leaf, and oxygen and water to exit • It helps the production of sugars • Formation of fruits and flowers

If a fourth number is included on the label of a fertilizer, it indicates the sulphur content. That fertilizer is NPK**S.**

3.2.2. Secondary nutrients

Now, in the category of secondary nutrients, are calcium (Ca), magnesium (Mg), and Sulphur (S). As, these nutrients are generally enough in the soil, so fertilization is not always needed. Also, large amounts of Calcium are added when lime is applied to acidic soils. In fact, Sulphur is usually found in sufficient amounts from the slow decomposition of soil.

3.2.3. Micronutrients

In fact, micronutrients are those elements essential for plant growth which are needed but in only very small (micro) quantities. These elements are even called minor elements or trace elements. The common micro nutrients are boron (B), copper (Cu), iron (Fe), chlorine (Cl), manganese (Mn), molybdenum (Mo) and zinc (Zn). In fact, recycling organic matter such as grass clippings and tree leaves is an excellent way of providing micro nutrients to growing plants.

Table 3.2: Characteristics of some common artificial Fertilizers

Name	Chemical formula	Composition of essential elements	Comments
Ammonium sulphate	$(NH_4)_2SO_4$	21%N	Crystalline salt soluble in H_2O easily tends to acidify the soil, leached from the soil, applied as top dressing (an application of manure or fertilizer to the surface layer of soil or a lawn)
Calcium ammonium nitrate	$(NH_4 NO_3 + CaCO_3)$	25-26%N	Half N in nitrate and the other half in the ammonium form, highly hygroscopic, generally applied as top-dressing
Urea	$CO(NH_2)_2$	45-46%N	White crystalline material, soluble in water, produces both NH_4^+ and NO_3^- in the soil, pellets coated –hence releases N slowly

Checking up 3.2

1. How did commercial fertilizer come to be used?
2. Among the major nutrients of plants, which one is responsible for
   a. Promoting the growth of roots (e.g. Irish potatoes)
   b. The production of sugars
3. A NPK fertilizer is labelled 13-13-13. Interpret this labelling.

3.3. The manufacture of Fertilizers

Activity 3.3

1. Write reactions for the formation of the following compounds
   a. Ammonium sulphate
   b. Potassium sulphate
   c. Ammonium nitrate
   d. Urea
   e. Ammonium phosphate
2. Using this book or any other book or internet, read and analyse the content about the manufacture of the following Fertilizers and make a summary to be presented to the class;

   Ammonium sulphate, potassium sulphate, ammonium nitrate, urea, and phosphates
3. Rwanda has a resources that can be used to produce an industrial fertilizer; name that resource

1. Ammonium Sulphate [$(NH_4)_2SO_4$]

Ammonium sulphate is the most important commercial ammonium salt. It contains 24-25%NH_3.

Manufacture

a. The manufacture of ammonium sulphate is done by reacting ammonia gas with concentrated (60%) sulphuric acid:

$2\,NH_3\,(g) + H_2SO_4\,(aq) \rightarrow \mathbf{(NH_4)_2SO_4}(s)$

b. The manufacture of ammonium sulphate can also be done by reacting calcium sulphate (gypsum) with ammonium carbonate:

Step 1: $2NH_3+H_2O+CO_2 \rightarrow (NH_4)_2CO_3$

Step 2: $(NH_4)_2CO_3(aq)+CaSO_4(aq) \rightarrow (NH_4)_2SO_4(aq)+CaCO_3(s)$

The insoluble $CaCO_3$ is filtered off and the filtrate is concentrated to crystallization.

2. Potassium Sulphate (K_2SO_4)

It occurs in large quantities in salts like schoenite ($K_2SO_4.MgSO_4.6H_2O$) and ***kainite*** ($K_2SO_4.MgSO_4.MgCl_2.6H_2O$)

Manufacture

1. When a saturated solution of kainite is allowed to cool, $K_2SO_4.MgSO_4.6H_2O$ crystallizes out:

   $K_2SO_4.MgSO_4.MgCl_2.6H_2O \rightarrow K_2SO_4.MgSO_4.6H_2O + MgCl_2$

   The $K_2SO_4.MgSO_4.6H_2O$ found is treated with a solution of KCl(sylvine) and concentrated, sparingly soluble K_2SO_4 crystallizes out.

   $K_2SO_4.MgSO_4.6H_2O + KCl \rightarrow K_2SO_4 + MgCl_2.6H_2O$

2. It can also be made by heating potassium chloride with concentrated sulphuric acid:

   $2KCl(s) + H_2SO_4(conc.) \rightarrow K_2SO_4(s) + 2HCl(g)$

HCl, being volatile, evaporates and potassium sulphate is left.

3. Ammonium Nitrate (NH_4NO_3)

Laboratory Preparation

Ammonium nitrate is made by action of concentrated nitric acid on ammonia gas or $(NH_4)_2CO_3$

$NH_3 + HNO_3 \rightarrow NH_4NO_3$ or $(NH_4)_2CO_3 + 2\ HNO_3 \rightarrow 2NH_4NO_3 + H_2O + CO_2$

Manufacture

The manufacture of ammonium nitrate is done by:

a. Passing NH_3 gas into 60% HNO_3

b. By double decompositionof $NaNO_3$ and $(NH_4)_2SO_4$ in solution

$(NH_4)_2SO_4(aq) + 2NaNO_3(aq) \rightarrow 2NH_4NO_3(aq) + Na_2SO_4$(least soluble)

Na_2SO_4, being least soluble at the temperature of hot solution, crystallizes out first and NH_4NO_3 is obtained by evaporation.

- Ammonium nitrate is sold as a mixture of calcium carbonate and ammonium nitrate

  ($NH_4\ NO_3$ and $CaCO_3$): Calcium ammonium nitrate (nitro-chalk).
- It melts at 169.5°C.
- It is used in making explosives like amatol and ammonal and therefore not easily stored.

4. Urea or carbamide (H_2N-CO-NH_2)

Urea is an organic compound used as a fertilizer. It is the most important nitrogenous

fertilizer. Urea is a crystalline solid which melts at 133 °C. The solid readily dissolves in water

Laboratory Preparation

- In 1828, a German chemistWöhler synthesized urea.Before that synthesis, urea was derived from urine.The synthesis of urea is considered as the starting point of modern organic chemistry**.** Wöhler synthesized urea by boiling aqueous solution of ammonium cyanate which is a typical inorganic compound **(Wöhler synthesis**).

  $NH_4^+CNO^-_{(aq)} \xrightarrow{Heat} \mathbf{H_2N\text{-}CO\text{-}NH_2}$(Urea)

- Urea can also be prepared by reacting ammonia with carbonyl chloride.

  $Cl\text{-}CO\text{-}Cl + 4NH_3 \rightarrow \mathbf{(H_2N\text{-}CO\text{-}NH_2)}+2NH_4Cl$

The manufacture of urea

The manufacture of urea consists of the following steps.

- Crude naphtha obtained from oil refineries is subjected to partial combustion in specially designed burners to get a mixture of H_2 and CO.
  Crude naphtha $\rightarrow$ CO $+H_2$
- The mixture of H_2 and CO obtained is made to react with steam in presence of Fe, Cr or Co (catalyst), where CO is oxidized to CO_2 and H_2 remains as such.
  $CO + H_2O \rightarrow CO_2 + H_2$

CO_2 is separated from H_2 by washing with H_2O under pressure or by the treatment with $KHCO_3$ solution.

- H_2 separated from the mixture,$(CO + H_2)$ is mixed with N_2, the mixture containing H_2 and N_2 is passed over heated (temperature = 450-500 ^{0}C), finely divided iron (catalyst) containing Al_2O_3 (promotor) under 200-1000 atmospheres where NH_3 is obtained (Haber process for the preparation of ammonia):
  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
- Now NH_3 obtained as above is allowed to react with gaseous CO_2 under 200 atm pressure where unstable ammonium carbamate ($H_2NCOONH_4$) is obtained. ($H_2NCOONH_4$) being unstable, decomposes to give urea:
  $2NH_3 + CO_2 \rightarrow [H_2NCOONH_4] \rightarrow H_2NCONH_2$ (Urea)$+ H_2O$

5. Phosphate Fertilizers (or P- type Fertilizers)

These Fertilizers supply only phosphorus as a major nutrient to the soil. Phosphates naturally occur as phosphate (V): phosphorite $[Ca_3(PO_4)_2]$ and apatite $[3Ca_3(PO_4)_2 \cdot CaF_2]$ which are sparingly soluble in water and hence are not able to supply phosphorus to the plants. These minerals are, therefore, converted into soluble materials, by reacting them with sulphuric acid, or phosphoric acid or nitric acid.

Calcium phosphate, $Ca_3(PO_4)_2$, commonly known as rock phosphate is widely used in the manufacture of Fertilizers such as superphosphates, triple superphosphates and nitrophosphates.

a. Calcium Dihydrogen Phosphate Sulphate, $Ca(H_2PO_4)_2 \cdot 2CaSO_4 \cdot 2H_2O$

This compound is also called **superphosphate of lime** or **calcium superphosphate** and is a mixture of $Ca(H_2PO_4)_2 \cdot H_2O$ and two molecules of gypsum, $CaSO_4 \cdot 2H_2O$.

Manufacture

It is manufactured by treating calcium phosphate, $Ca_3(PO_4)_2$, from for example bone ash with sulphuric acid.

$Ca_3(PO_4)_2 + 2H_2SO_4 + 5H_2O \rightarrow [Ca(H_2PO_4)_2 \cdot H_2O + 2(CaSO_4 \cdot 2H_2O)]$ (superphosphate of lime)

$Ca(H_2PO_4)_2 \cdot H_2O$ contains 45-60% available phosphorus as P_2O_5.

$Ca(H_2PO_4)_2(aq) \cdot 2CaSO_4 \cdot 2H_2O$ is a compound containing 16-20% of P_2O_5 depending on the purity of the phosphate rock used in its manufacture.

b. Calcium dihydrogen phosphate, $Ca(H_2PO_4)_2 \cdot H_2O$

This compound is prepared in laboratory by dissolving $Ca_3(PO_4)_2$ or $Ca(HPO_4)$ in aqueous solution of H_3PO_4 and evaporating the resulting solution.

$Ca_3(PO_4)_2 + 4H_3PO_4 \rightarrow 3Ca(H_2PO_4)_2$

Or $CaHPO_4 + H_3PO_4 \rightarrow Ca(H_2PO_4)_2$

Manufacture

Triple superphosphate, $Ca(H_2PO_4)_2$, is manufactured by dissolving slaked lime, $Ca(OH)_2$ or limestone($CaCO_3$) in H_3PO_4 and crystallizing the resultant solution.

$Ca(OH)_2 + 2H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + H_2O$,

$CaCO_3 + 2H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + H_2O + CO_2$

$Ca(H_2PO_4)_2 \cdot H_2O$ contains 45-60% of P_2O_5

c. Calcium dihydrogen phosphate nitrate, $Ca(H_2PO_4)_2.2Ca(NO_3)$ (Double salt)

This compound is also called calcium superphosphate nitrate or nitrophosphate and it is a salt containing one molecule of $Ca(H_2PO_4)_2$ and two molecules of 2 $Ca(NO_3)_2$

$Ca_3(PO_4)_2 + 4HNO_3 \rightarrow Ca(H_2PO_4)_2 + 2Ca(NO_3)_2$ (Nitrophosphate)

d. Diammonium hydrogen phosphate , $(NH_4)_2(HPO_4)$,DAP

Diammonium hydrogen phosphate is prepared by neutralizing phosphoric (V) acid by excess ammonia. This fertilizer supplies both phosphorus and nitrogen to the soil.

$3\ NH_3(excess) + H_3PO_4(aq) \rightarrow (NH_4)_2(HPO_4)$

Depending on the nature of the essential elements that a fertilizer can supply to the soil, the Fertilizers have been classified into the following groups:

- **Nitrogenous Fertilizers: N-type Fertilizers**

These Fertilizers supply only nitrogen as a major nutrient to the soil. Examples: ammonium sulphate, urea, sodium nitrate (also called chile saltpeter or chile nitre).

- **Phosphorus Fertilizers: P-type Fertilizers**

Are Fertilizers which supply phosphorus as a major nutrient to the soil. Examples: Calcium dihydrogen phosphate, $Ca(H_2PO_4)_2 \cdot H_2O$, phosphate slag, $Ca_3(PO_4)_2 \cdot CaSiO_3$

- **Potassium Fertilizers: (K-type Fertilizers)**

These Fertilizers supply only potassium as a major nutrient to the soil. Examples: potassium chloride, potassium sulphate.

- **Mixed Fertilizers**

Mixed fertilizers are those which can supply more than one essential element to the soil. Depending on the nature of the essential element supplied by the fertilizer, mixed Fertilizers can be classified into the following groups:

- NP Fertilizers:These Fertilizers supply two essential elements, nitrogen and phosphorus, to the plant.Examples:
- Ammonium dihydrogen phosphate, $(NH_4)(H_2PO_4)$,(also called dihydrogen ammoniated phosphate or ammophos).
- Calcium dihydrogen phosphate nitrate, $Ca(H_2PO_4)_2 \cdot 2Ca(NO_3)_2$,(also called calcium superphosphate nitrate or nitrophosphate).

- PK Fertilizers: It is a mixture of two compounds; one containing phosphorus and the other containing potassium. For example, a mixture of $H_2PO_4)_2 \cdot H_2O$, and K_2SO_4.
- KN fertilizer.Example: KNO_3
- NPK Fertilizers: These are Fertilizers that contain %N, %P as P_2O_5 and %K as K_2O

Example: A mixture of $(NH_4)_2SO_4$ (N-type fertilizer),$(H_2PO_4)_2.H_2O$(P-type fertilizer), and K_2SO_4(K-type fertilizer).

The Fertilizers listed above are subdivided in two categories:

a. **Straight or single Fertilizers:** Those which supply a single element

Example: Ammoniumnitrate: It supplies **N**

b. Compound or complex Fertilizers: Those which supply two or more elements.

Examples:

Fertilizer	Element supplied
Di-ammonium phosphate(DAP)	N and P
Potassium nitrate(PN)	K and N

- If a fertilizer contains all the three primary nutrients, it is said to be complete.
- If a fertilizer lacks one or two primary nutrients, it is said to be incomplete.

Characteristics of a good fertilizer

A good fertilizer should have the following characteristics:

- It should contain the required nutrients, in such a form that they can be assimilated by the plants.
- It should be cheap.
- It should be soluble in water.
- It should be stable, so that it may be available for a long time for the growing plant.
- It should not be injurious to the plants.
- It should be able to correct the acidity of the soil.
- Not pollutant

Checking up 3.3

1. Complete the following table

Fertilizer	Raw materials	Reaction (s) involvwd
Ammonium sulphate		
Urea, or carbamide (H_2N-CO-NH_2)		

2. Apart from being used as source of energy, discuss what other application(s) Kivu methane gas can be used for.

3.4. Disadvantages of the use of organic and inorganic Fertilizers

Activity 3.4
"The use of fertilizers is a harm to humanity", yes or not. Explain

3.4.1. Organic Fertilizers

The use of organic fertilizer may have many advantages but also it may have some disadvantages

a. Advantages

1. The manures add organic matter (called humus) to the soil which restores the soil texture for better retention of water and for aeration of soil. For example, organic matter present in the manures increases the water holding capacity in sandy soils and drainage in clay soil.
2. The organic matter of manures provides food for the soil organisms (decomposers such as bacteria, fungi, etc.) which help in making nutrients available to plants.
3. Nutrient release: slow and consistent at a natural rate that plants are able to use. No danger of over concentration of any element, since microbes must break down the material.
4. Trace minerals: typically present in a broad range, providing more balanced nutrition to the plant.
5. They will not burn: safe for all plants with no danger of burning due to salt concentration.
6. Long lasting: does not leach out since the organic matter binds to the soil particles where the roots have access to it.
7. Fewer applications required: once a healthy soil condition is reached, it is easier to maintain that level with less work
8. Controlled growth: does not over-stimulate to exceptional growth which can cause problems and more work.

b. Disadvantages

1. Many organic products produce inconsistent results.
2. The level of nutrients present in organic fertilizer is often low.
3. The time of their preparation is too long.
4. Eutrophication

3.4.2. Inorganic Fertilizers

The use of inorganic fertilizers may have many advantages but also it may have some disadvantages

a. Advantages

1. Chemical Fertilizers are made with synthetic ingredients designed to stimulate plant growth.
2. Commercial chemical Fertilizers have the advantage of predictability and reliability
3. Formulations are blended with accuracy and you can buy different blends for different types of plants; commercial formulated Fertilizers allow you to know exactly which nutrients you're giving your plants, rather than guessing at the composition of organic formulas

b. Disadvantages

1. They can burn plants
2. They require a specific timetable of application and watering because of fast release of nutrients
3. Groundwater
   - Increased nitrate levels increase the risks of blue baby syndrome, a rare form of anaemia which affects babies below 6 months of age. The cause is the oxidation by nitrite ions of Fe^{2+} in haemoglobin to Fe^{3+}. The oxidized hemoglobin cannot bind oxygen, and the baby turns blue from lack of oxygen. Conditions in the digestive tracks of young children are more favourable to the bacteria which reduce nitrates to nitrites than those in adults.
   - Another hazard of chemical Fertilizers is that carcinogenic nitrosoamines (yellow oil substance) may be formed in the human digestive track by the conversion of nitrate into nitrite. The nitrite produced in the stomach it combines with HCl to produce nitrous acid. Nitrous acid can react with any secondary amine in foods to form nitrosoamines and the reaction of nitrite with amino acids.
4. Repeated use or excess use of the same fertilizer producing acidic ions (NH_4^+). Example of such a fertilizer is $(NH_4)_2SO_4$.
5. Repeated use or excess use of the same fertilizer producing basic ions. Example of such a fertilizer is $CaCO_3$.
6. Warm temperatures and high rain fall: Cations such as Ca^{++}, Mg^{++}, K^+ which are essential to living organisms, are leached (dissolved) from the soil profile, leaving behind more stable materials rich in Fe and Al oxides. This natural weathering process makes soils acid.

Other causes of acid soils include:

- Man-made processes also contribute significantly to soil acidity. For example, Sulphur dioxide (SO_2) and nitrogen oxides (NOx) released primarily by industrial activities react with water to form acid rain, which acidifies soils, particularly forest soils with.

- Organic acids from plants during decomposition;
- CO_2 from root respiration and microbial respiration.

Effects of acid soil

- Major effects of extremes in pH levels include gaps in nutrient availability and the presence of high concentrations of minerals that are harmful to plants. In very alkaline soil, certain micronutrients such as zinc and copper become chemically unavailable to plants. In very acidic soil, macronutrients such as calcium, magnesium and phosphorous are not absorbed while others reach toxic levels,
- Acid soil, particularly in the subsurface, will also restrict root access to water and nutrients.
- In addition to affecting how nutrients are dispensed to growing plants, pH levels also influence microorganism activity that contributes to the decomposition of organic materials. A neutral pH is ideal for microbial action that produces chemical changes in soil, making nitrogen, sulfur and phosphorus more available. A pH that is either too high or too low may also interfere with the effectiveness of pesticides by changing their basic composition or weakening their ability to kill unwanted insects.

Plant growth and most soil processes, including nutrient availability and microbial activity, are favoured by a soil pH range of 5.5 – 8. Example: The optimal pH range for most plants is between 5.5 and 7.0. The optimal pH range for some plants is between is given in the table below.

Crop	pH
Avocado	6.0-6.5
Macadamia	5.0-6.5
Pineapple	4.7-5.7
Sugarcane	6.0-7.0

For soils the pH should be maintained at above 5.5 in the topsoil and 4.8 in the subsurface.

Eutrophication

The undesirable overgrowth of vegetation caused by high concentration of plants nutrients (Nitrogen and Phosphorous) in bodies of water (lakes, rivers,...)

As consequence, water plants (e.g: water hyacinth: amarebe) grow more vigorously and this prevents the sun light from reaching the water and stops photosynthesis of aquatic plants which provide oxygen in the water to animals needed then animals die, deposits of organic matter on the bottom of the lake build up.

When lake water is enriched with nutrients (e.g.: nitrates and phosphates), algal flourish, and produce an algae bloom, a green scum with an unpleasant smell. When algal die they are decomposed by aerobic bacteria. When the oxygen content falls too low to support aerobic bacteria, anaerobic bacteria take over. They convert the dead matter into unpleasant-smelling decay products and debris which falls to the bottom. Gradually, a layer of dead plant material builds up on the bottom of the lake. The lowering of the oxygen concentration leads to the death of aquatic animals (fish, crabs,…….)

Figure 3.1: Eutrophication of a water body

Checking up 3.4

1. Ammonia itself can be used as a fertilizer but has some disadvantages. Explain the disadvantages of using ammonia as a fertilizer.
2. Give any two advantages of the use of
   a. Natural Fertilizers
   b. Artificial Fertilizers
3. Give any two causes of acid soils

3.5. Dangers of the use of substandard Fertilizers

Activity 3.5

Using books or internet find out the dangers of substandard fertilizers

Sub-standard fertilizer means any fertilizer which does not conform to the required NPK ratio.

Example: A fertilizer may be labelled 16-00-00, while the real NPK ratio is for example 25-00-00, 10-00-05, etc

Using these Fertilizers can lead to:

- Soil pollution (basic soil or acidic soil) due to accumulation of ions which are acidic or basic

- Poor growth of plants
- Poor harvest
- Eutrophication
- Fertilizer burn: leaf scorch resulting from over-fertilization, usually referring to excess nitrogen salts. Fertilizer burn is the result of desiccation of plant tissues due to osmotic stress, creating a state of hypertonicity.

In order to reduce the effects of substandard fertilizers different measure can be taken;

- Standardization of the fertilizer before use
- Production of fertilizers in Rwanda, as this will help us to choose good minerals (where necessary) in producing fertilizers
- Use of chemical fertilizers with coated pellets so that nutrients are released slowly
- Regular watering

Checking up 3.5

1. Give any three dangers of substandard Fertilizers.
2. What can be done to avoid or minimize those dangers?

Experiment

Determination of the percentage by mass of N in $(NH_4)_2SO_4$

You provided with the following

1. A Solution prepared by mixing 5.0 g of a sample of ammonium sulphate fertilizer which were warmed with sodium hydroxide and the ammonia evolved was absorbed in 100 cm^3 of 0.5$moldm^{-3}$ sulphuric acid

2. 1M sodium hydroxide

Procedure

a. Fill the burette with solution of sodium hydroxide

b. Pipette 20 cm^3 of solutions of the prepared solution in (1), in conical flask. Add 2-3 drops of methyl orange indicator.

c. Titrate this solution with sodium hydroxide from the burette until the indicator changes colour (indicator changes from pink to yellow).

d. Record the results in the table.

Volume of pipette used: ……cm^3

Titration number			
Final burette reading (cm^3)			
Initial burette reading (cm^3)			
Volume of sodium hydroxide used (cm^3)			

Questions

1. Title values: …….
2. Calculate the average volume of sodium hydroxide used:
3. Write the equation for the reaction between
   a. Sodium hydroxide and sulphuric acid:
   b. Ammonium sulphate and sodium hydroxide
   c. Ammonia and sulphuric acid

4. Calculate
    a. Moles of base that reacted with excess sulphuric acid
    b. Moles of excess sulphuric acid
    c. Total moles of the added sulphuric acid
    d. Moles of sulphuric acid that reacted with ammonia
    e. Mole of ammonia produced by the fertilizer
    f. Moles of $(NH_4)_2SO_4$
    g. Mass of $(NH_4)_2SO_4$
    h. Mass of N in the fertilizer
    i. Percentage of N in the fertilizer

PROJECT WORK

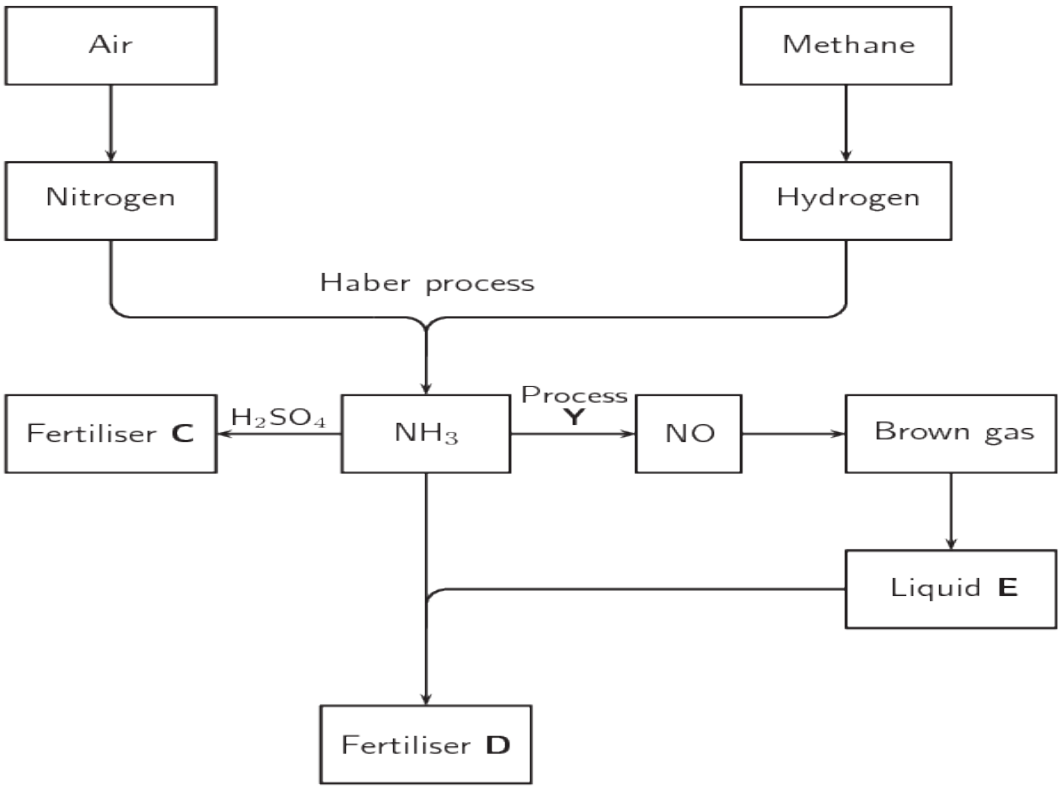
Design a project of making compost manure and test its impact using a control experiment and write a report.

END UNIT ASSESSMENT

1. If nitrogen is the main element of Fertilizers then Fertilizers are classified as
   a. Structural Fertilizers
   b. Non-structural Fertilizers
   c. Nitrogen Fertilizers
   d. Respiratory Fertilizers
2. Increased ratio of chemical nutrients in ecosystem is classified as
   a. Triplication
   b. Eutrophication
   c. Crystallization
   d. Distillation
3. Greenhouse gas which can be emitted from storage of nitrogen based Fertilizers is
   a. Nitrous oxide
   b. Nitric oxide
   c. Oxygen
   d. Hydroxide

4. Organic Fertilizers can be derived from
   a. Animal materials
   b. Carbon materials
   c. Plant materials
   e. Both (a) and (c)
5. Find by calculation, which is the best source of nitrogen: Sodium nitrate, ammonium nitrate, ammonium sulphate or urea (CH_4N_2O).
6. The chemical plant for manufacturing ammonia is often on the same site as plants manufacturing nitric acid and Fertilizers.
   a. What advantages will this have for the manufacturing company?
   b. Describe two important ways in which it is possible to reduce the environmental impact of such plants on the surrounding area.
7. Sulphuric acid reacts with ammonia to give ammonium sulphate
   a. Write the balanced equation for that reaction
   b. What property of ammonia is shown in this reaction?
   c. Calculate the maximum mass of ammonium sulphate that can be obtained from 100 g of ammonia. [Ar: H, 1.0;N, 14.0; O, 16.0;S, 32.1)
   d. State the large scale use of ammonium sulphate.
8. A laboratory method of finding the percentage of ammonia in a fertilizer involves boiling the fertilizer with an excess of aqueous sodium hydroxide until no more ammonia is given off. The excess of sodium hydroxide is found by titration with standard hydrochloric acid.
   a. Write an equation for the reaction between ammonium ions and hydroxide ions to give ammonia
   b. Say how you could test for ammonia gas.

9. The flow diagram below shows the main steps in the industrial preparation of two important solid Fertilizers.



a. How can Fertilizers play a role in increasing the soil's ability to produce crops?
b. Are the processes illustrated by the flow diagram above that of organic or inorganic Fertilizers? Give a reason for your answer.
c. Write down the balanced chemical equation for the formation of the brown gas.
d. Write down the name of process Y.
e. Write down the chemical formula of liquid E.
f. Write down the chemical formulae of Fertilizers C and D respectively

10. Discuss the advantages and disadvantages of the use of organic and inorganic Fertilizers

11. Identify the effects of misusing Fertilizers and the dangers of substandard fertilizers

UNIT 4

BENZENE

UNIT 4: BENZENE

Key Unit Competence:

To be able to relate the chemistry and uses of benzene to its nature and structure

Learning objectives

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

- State the physical properties of benzene;
- Describe the uses of benzene;
- Outline the preparations of benzene;
- Describe the chemical properties of benzene;
- State the conditions required for different reactions;
- Relate the conditions for the reactions of benzene to its chemical stability;
- Illutrate the mechanism of electrophilic substitutions on benzene.

Introductory Activity

From your prior studies in organic chemistry, it is known that carbon is tetravalent while hydrogen is monovalent and compounds constituted by the two elements are known as 'hydrocarbons'. The structures and chemistry of the hydrocarbons reflects to their uses as fuels and starting materials for many substances important in life such as pharmaceutical drugs, solvents, packaging materials, clothes and so on. In this activity you need to follow instructions given to explain how the structure of a substance determines its chemical properties and uses.

1. Write down the molecular formulae for these five hydrocarbons
   a. A molecule with 6 carbon atoms and 14 hydrogen atoms
   b. A molecule with 6 carbon atoms and 12 hydrogen atoms
   c. A molecule with 6 carbon atoms and 10 hydrogen atoms
   d. A molecule of 6 carbon atoms with 8 hydrogen atoms
   e. A molecule of 6 carbon atoms with 6 hydrogen atoms
2. From the molecules in 1) above, choose molecule(s) that fit(s) in the description provided, and then draw its (their) structural formula (e).
   a. Unsaturated hydrocarbon (s) that decolorize (s) bromine water and alkaline potassium manganate (VII)
   b. Saturated hydrocarbon (s)
   c. Hydrocarbon (s) with empirical formula of CH
   d. Unsaturated hydrocarbon (s) which do (es) not decolorize bromine water and potassium manganate (VII).

e. Unsaturated hydrocarbon (s) that form(s) a white precipitate when treated with ammoniacal silver nitrate and forms a reddish-brown precipitate when treated with ammoniacal copper (I) chloride.

3. It is known that unsaturated hydrocarbons decolourise both bromine water and alkaline potassium manganate (VII). Explain any assumption you can suggest about the compound in question 2.d)

Some or all people are unique in their living attitudes and values. But being unique does not mean to be isolated from others as people need each other in order to complement and build a strong nation.

This is true for benzene. From the above activity question 3 you may have been stuck while discussing on why this unsaturated compound has properties that are different from other unsaturated hydrocarbons provided within the same activity. But this does not mean that it is quite different from them. It will share some properties with others but exhibit its identity or its unique properties from others.

In this unit, you will discover what makes benzene resistant towards some reactants and its importance will be highlighted.

4.1. Structure of benzene

Activity 4.1

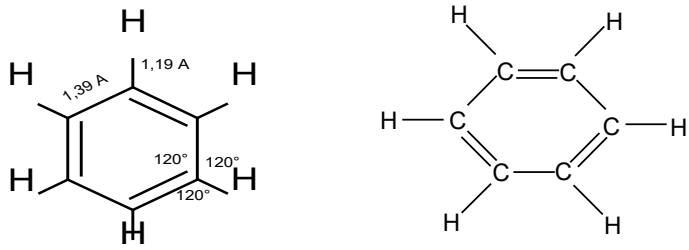
- Research in books or search engine about the structure of benzene.
- Read and make a summary on the historical development of benzene's structure.

Michael Faraday was the first to isolate benzene from coal. Benzene was found to have the molecular formula of C_6H_6. However, its structural formula posed a problem for many years.

For example, you can work out the structures of compounds whose molecular formula is C_6H_6 and see how many you can find.

The structure of benzene must be only one, in which all the six hydrogen atoms occupy equivalent positions. This was discovered by *Friedrich August Kékulé Von Stradonitz* while daydreaming of a snake seizing its own tail. From this, he proposed a ring structure of six carbon atoms with double bonds alternating with single bonds.

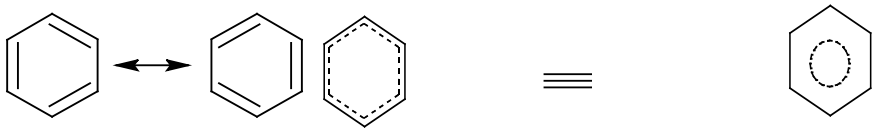
Furthermore, X-ray diffraction studies, first carried out by Kathleen Lonsdale, showed that benzene is planar and all its C-C bonds are of the same length (0.139 nm which is intermediate of C-C single bond and C=C double bond in alkenes) and bond angles of the same size (120°).



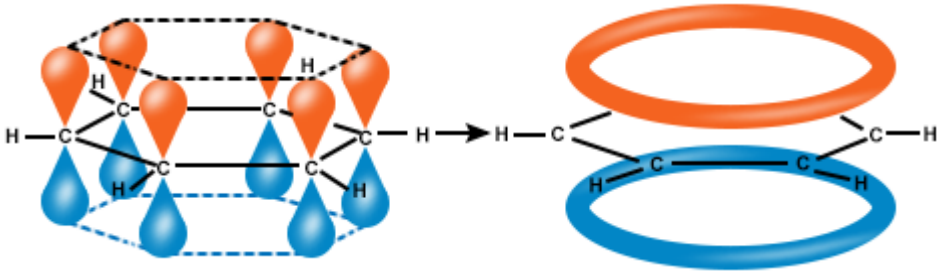
By comparing benzene with alkenes, the following points are noticed:

- Benzene fixes 3 moles of hydrogen, thus it has 3 double bonds,
- Benzene does not decolourise bromine water or acidified potassium manganate (VII) and does not turn green the acidified potassium dichromate,
- Benzene does not react with water and hydracids under normal conditions.

From the above points it can be easily noticed that benzene is not quite an alkene, due to its double bonds which do not occupy fixed positions. This change of positions of the double bonds is referred to as 'resonance'.



The sp^2 hybridized orbitals of carbon is involved in sigma bond formation with other two carbon atoms and one hydrogen atom to make a hexagonal ring. The remaining unhybrid p-orbital is involved in side-ways overlapping with a neighbor carbon atom to form a pi-bond. Since there is an equal probability of making the pi-bond with either neighbor carbon atom, pi-electron remains delocalized over six carbon atoms of the ring.



Checking up 4.1

Discuss and provide appropriate answers for the following questions:

1. a. Benzene has the molecular formula C_6H_6. Draw the Kekulé structure for this showing all the atoms.
   b. Draw the skeletal structure showing the way the Kekulé structure is normally drawn.
2. How does the structure of benzene differ from the cyclohexane structure?
3. Describe the Structure and Bonding of Benzene

4.2. Physical properties, uses and toxicity of benzene

Activity 4.2

- Using the same resources (books or internet) as in activity 4.1, make a research about the main points that should be talked about while discussing the physical properties of any substance.
- Then, make a summary to be presented about properties, uses and toxicity of benzene.

Benzene has the following physical properties:

- Benzene is a colourless volatile liquid with an aromatic (pleasant/sweet) smell.
- Benzene boils at 80.1 °C
- Benzene melts at 5.5°C.
- Like other aromatic hydrocarbons (arenes) benzene is insoluble in water.
- It is less dense than water (specific gravity or relative density is 0.88).

Benzene has many uses:

It has been used by chemists since 1800 because it is a *good solvent for other organic compounds*. Benzene itself is an excellent solvent for certain elements, such as sulphur, phosphorus, and iodine. It is found in crude oil. It is used to make plastics, resins, synthetic fibers, rubber, lubricants, dyes, detergents, drugs and pesticides.

Benzene is *highly toxic* and is said to be ***carcinogenic***.

A person exposed for long time to benzene (even at low levels), can develop anaemia and leukaemia.

Benzene is formed in both natural and synthetic processes. Natural sources of benzene include volcanoes and forest fires. It is a component of crude oil, petrol and cigarette smoke.

Figure 4.1: Benzene is a component of compact discs and explosives

Checking up 4.2

1. Benzene is flammable and carcinogenic. What do you understand by the term "carcinogenic"?
2. What advice can you give to your friend who smokes?

4.3. Preparation of benzene

Activity 4.3

- Some of the reaction of all alkanes and alkynes discussed in senior five lead to the formation of benzene. Use the following examples to describe how each of the following conversions can be carried out
  1. From $CH \equiv CH$ to C_6H_6
  2. C_6H_6 from n-hexane
  3. Ethanol to C_6H_6

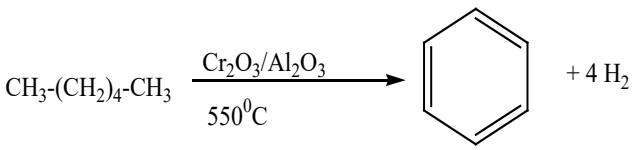
- To add other methods used to prepare benzene and to be able to describe them, use the same sources (books/search engines) as in previous activities to discuss about all the methods that can be used to obtain benzene.
- Take a note to share with others.

All the raw materials provided in the activity above are from the topics covered in senior five, so hopefully you performed them very well. The methods used for preparing benzene are based on reduction reaction and decomposition reaction and even addition reaction.

1. Industrial preparation (on large scale)

a. From petroleum oils: By catalytic reformation of petroleum products

By fractional distillation followed by reforming. Fraction of naphtha is heated over $Cr_2O_3 - Al_2O_3$ at 500-550°C and 15atm pressure (aromatisation).

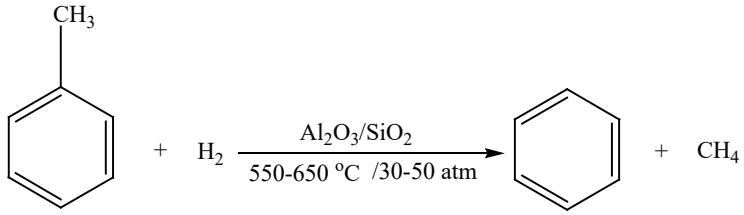


When platinum is used at 15 atm pressure at 500°C, the process is called 'platforming'.

b. By converting methylbenzene into benzene

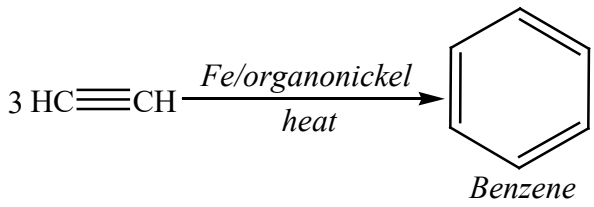
Methylbenzene is much less commercially valuable than benzene. The methyl group can be removed from the ring by a process known as "demethylation".

The methylbenzene is mixed with hydrogen at a temperature of between 550 and 650°C, and a pressure between 30 and 50 atmospheres, with a mixture of silicon dioxide and aluminium oxide as catalyst.



c. From ethyne

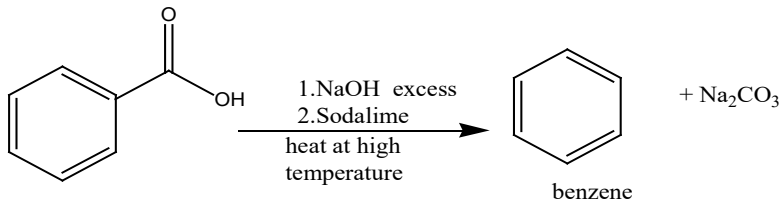
When ethyne is heated in the presence of iron as catalyst or organo-Nickel, it undergoes cyclization.



2. Laboratory preparation

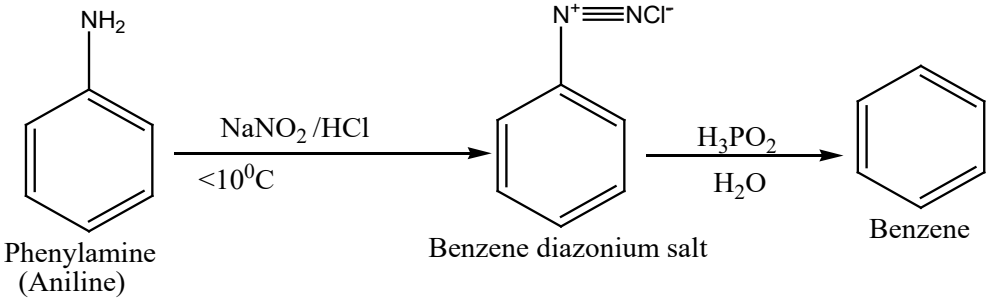
a. From benzoic acid

In this method benzoic acid is *heated with soda lime*.

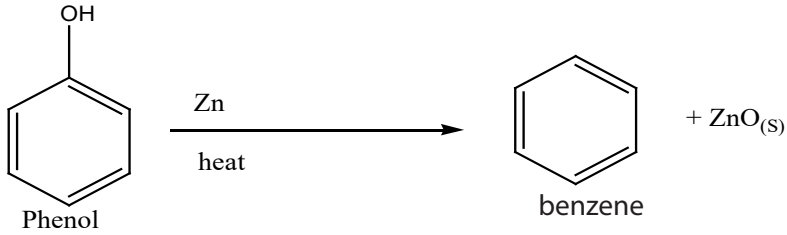


b. From benzenediazonium salt

In this method, the benzenediazonium salt formed by reacting phenylamine with sodium nitrite and a mineral acid is treated with hypophosphorus acid (H_3PO_2) and water.

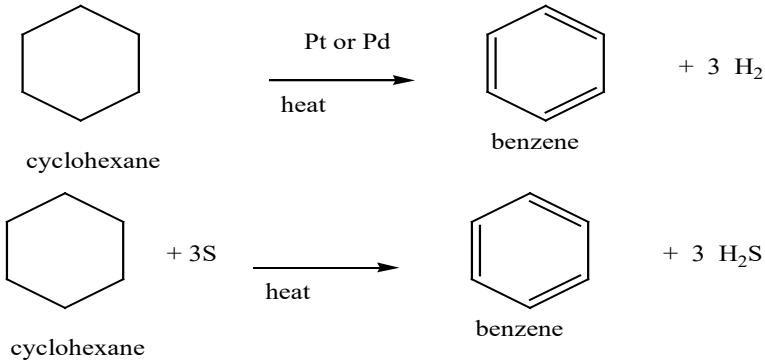


c. From phenol by heating phenol with zinc dust.



d. From cyclohexane

When cyclohexane is heated with Palladium or Platinum as catalyst and with sulfur, it undergoes *dehydrogenation* forming benzene. When cyclohexane is heated with sulphur, benzene is also produced.



Checking up 4.3

Discuss and describe how you can obtain benzene starting with inorganic reagents, showing necessary conditions at every step.

4.4. Chemical stability of benzene

Activity 4.4

In chemical energetics (senior five), you learnt many forms of enthalpy changes that take place when various reactions take place. In this activity, you have to use some of the concepts of these enthalpy changes in order to understand the stability of benzene. By following instructions provided as questions and using the following data:

Enthalpy change of atomization of carbon, C(s):	+715 kJ (mol of C atoms)$^{-1}$
Enthalpy change of atomization of hydrogen, H_2(g):	+218 kJ mol^{-1}
Bond energy of C=C (average):	610 kJ mol^{-1}
Bond energy of C-C (average):	346 kJ mol^{-1}
Bond energy of C-H (average):	413 kJ mol^{-1}

Discuss and work out the enthalpy change of formation of benzene by the following stages.

1. Calculate the energy needed to produce
   a. Six moles of gaseous carbon atoms from C(s)
   b. Six moles of gaseous hydrogen atoms from H_2(g)
2. Calculate the energy released when
   a. Three moles of C-C bonds are formed from gaseous atoms
   b. Three moles of C=C bonds are formed from gaseous atoms
   c. Six moles of C-H bonds are formed from gaseous atoms.
3. Use your answers to [1] and [2] to calculate the total energy change when a mole of gaseous benzene is formed from its elements.
4. Compare your answer with experimental value of +82 kJ mol^{-1}.
5. Now, use the available resources (books or internet) to find out what you can present about the stability of benzene.

Benzene is an aromatic compound with molecular formula of C_6H_6. It is a planar hexagonal ring with three pi-bonds in an alternate manner.

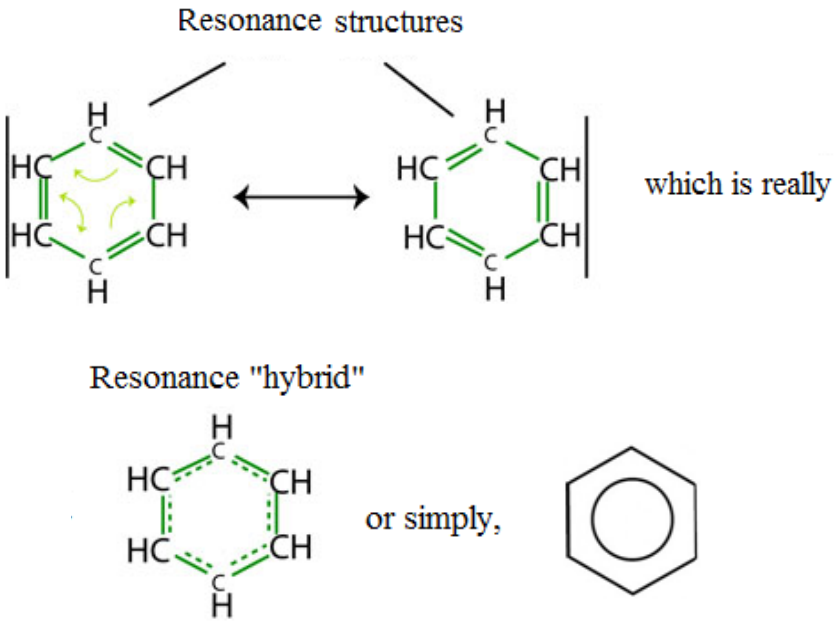
The delocalization of pi-electrons in benzene molecule provides extra stability which is known as 'aromaticity'. Due to this aromaticity, benzene is more stable than expected as compared to aliphatic alkenes or the cyclic alkenes with three double bonds. Thus, it does not undergo addition reaction like alkenes do. In other words, benzene is less reactive than alkenes for addition reactions as this type of reactions

can be responsible for loss of aromaticity (or resonance or stability). Benzene reacts preferably through substitution reactions in which one of its bonded H-atoms is replaced by an electrophile.

Benzene is not the only aromatic molecule known (it is the smallest aromatic molecule, others include naphthalene, anthracite,…). Thus, for a molecule to be aromatic, it has to fulfill the following criteria:

- It must be cyclic and flat
- It must be conjugated (i.e, all atoms around the ring must be able to participate in pi-bonding through resonance)
- It must have pi-delocalised electrons (4n + 2), where n (number of benzene rings), n= 0,1,2,3,4,5,6. This is known as Huckel's rule.

The stability of benzene can be explained on the basis of resonance in the molecule. There are two possible resonance structures (or forms) of benzene molecule that are in equilibrium. Thus, an approaching reagent (such as bromine for instance) can not be attracted to a double bond before the structures changes. The resonance hybrid of benzene molecule is represented with a circle at the center of hexagonal ring of carbon atoms as shown below:

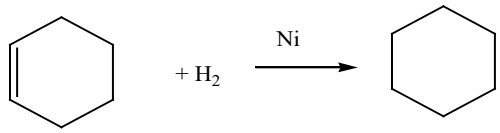


Another measurement of stability of benzene is the tendency of benzene to undergo electrophilic substitution reactions rather than electrophilic addition reactions as alkenes. The regular-hexagonal planar ring of benzene is attributed to resonance stabilization of this conjugated cyclic alkene. Two resonance structure of benzene is responsible for the extra stability of molecule. The presence of the p electron cloud

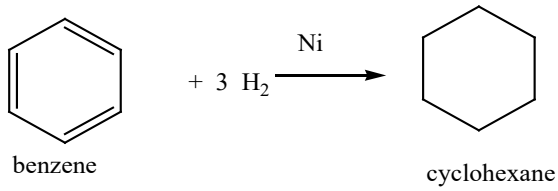
makes a negative zone that could be attacked by electrophilic reagents, by giving electrophilic substitution reactions.

Thermochemical data show that benzene does not have true double bonds. The theoretical heat of formation of gaseous benzene, taking into consideration 3 double bonds, is +252 kJ/mol while experimental value is +82 kJ/mol, therefore the true structure is more stable by 170 kJ/mol than cyclohexa-1,3,5-triene (Kekulé structure).

The enthalpy of hydrogenation of cyclohexane is -120 kJ/mol.



Therefore, since Kekulé (cyclohexa-1,3,5-triene) structure has 3 double bonds, the expected heat of hydrogenation is 3 times i.e. 3 x (-120) kJ/mol = -360 kJ/mol.



However the experimental enthalpy of hydrogenation of benzene is only -208 kJ/mol! Therefore benzene is more stable by 152 kJ/mol than it would be if it was cyclohexa-1,3,5-triene. This stabilization energy is called delocalisation energy or resonance energy.

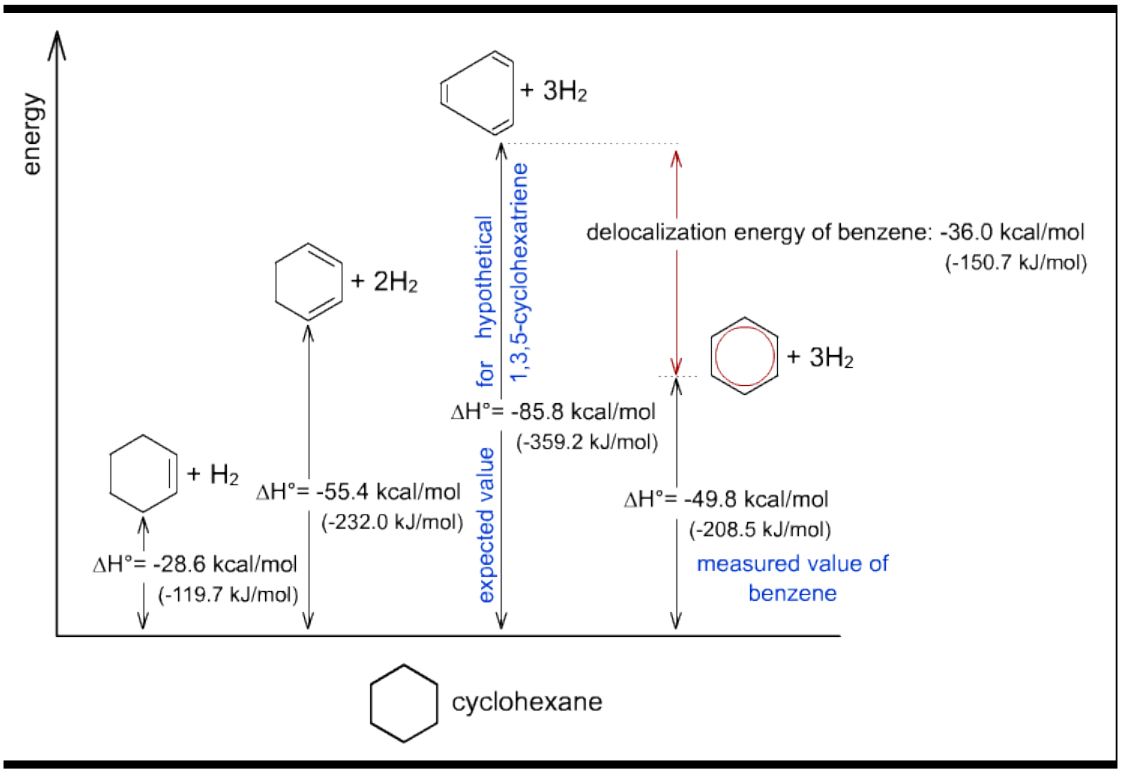


Figure 4.2: comparison between enthalpy change of hydrogenation of benzene and that of cyclohexene

The ones with the shorter black solid lines are the ones which are most stable.

This is an enthalpy diagram so/ I would have thought that the ones which have the biggest enthalpy change (i.e the ones with the longest solid black lines) are the ones which require more energy to change them into cyclohexane and so are the ones which are more stable

Note: Because of this extra stability, benzene:

- Does not undergo reactions with halogens and halogen acids which are characteristic of alkene,
- Does not react with water in the presence of H^+ and does not react with acidified $KMnO_4$
- Cannot be represented by these structures because of its inertness,
- CH_2=C=CH-CH=C=CH_2 nor $CH_3 - C \equiv C - C \equiv C - CH_3$
- Under drastic conditions, it however reacts with Cl_2 or Br_2 in the presence of ultraviolet light/light or halogen carrier,
- Reacts so fast with oxygen, by producing yellow luminous flame which is sooty.

Checking up 4.4

Refer to your results from the ***activity 4.4*** to discuss and conclude on this:

Do your results support that real benzene is more or less stable than the Kekule structure? Explain your answer.

4.5. Reactions of Benzene

Activity 4.5

From the previous topics discussed in this unit, you have found that benzene has some uniqueness from aliphatic unsaturated compounds.

Use the same resources to find out

- How benzene reacts and
- Its reactions with different substances and their respective mechanisms

As seen in the previous discussions, since benzene contains carbon-carbon double bonds, it might be expected to undergo electrophilic addition reactions readily as it is the case for alkenes. This is not the case, however, and benzene does not decolourise bromine water. Neither does it readily undergo any other addition reactions.

The reason for this is that the delocalized system in benzene is stable, and addition reactions would break up this delocalization and lead to the formation of the products which are less stable than benzene itself. Benzene thus tends to undergo electrophilic substitution reactions rather than addition reactions.

4.5.1. Electrophilic aromatic substitution reactions

Aromatic compounds undergo substitution reactions with electrophiles in which one or more hydrogens of the benzene ring are substituted.

Since the reagents and conditions employed in these reactions are electrophilic, these reactions are commonly referred to as "Electrophilic Aromatic Substitution". The catalysts and co-reagents serve to generate the strong electrophilic species needed to perform the initial step of the substitution.

Many substitution reactions of benzene have been observed and the five most useful are listed below.

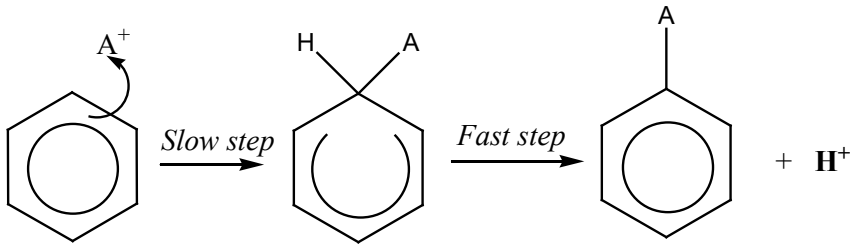
The specific electrophile in each type of reaction is listed in the right hand column.

Reaction Type	Typical Equation
Halogenation:	$C_6H_6 + Cl_2 \xrightarrow[FeCl_3 \text{ catalyst}]{r.t} C_6H_5Cl + HCl$ Chlorobenzene
Nitration:	$C_6H_6 + HNO_3 \xrightarrow[H_2SO_4 \text{ catalyst}]{heat} C_6H_5NO_2 + H_2O$ Nitrobenzene
Sulfonation:	$C_6H_6 + H_2SO_4 + SO_3 \xrightarrow{heat} C_6H_5SO_3H + H_2O$ Benzenesulfonic acid
Friedel-Crafts Alkylation:	$C_6H_6 + R\text{-}Cl \xrightarrow[AlCl_3 \text{ catalyst}]{heat} C_6H_5\text{-}R + HCl$ An Arene
Friedel-Crafts Acylation:	$C_6H_6 + RCOCl \xrightarrow[AlCl_3 \text{ catalyst}]{heat} C_6H_5COR + HCl$ An Aryl Ketone

Mechanism for electrophilic substitution reactions of benzene

All electrophilic substitution reactions of benzene follow the same mechanism. After the formation of the electrophile, a two-step mechanism has been proposed for these electrophilic substitution reactions.

In the first, slow or rate-determining step the electrophile forms a sigma-bond to the benzene ring, generating a positively charged benzenonium intermediate. In the second, fast step, a proton is removed from this intermediate, yielding a substituted benzene ring.



Unstable intermediate

Briefly, electrophilic aromatic substitution reaction is realised in 3 steps:

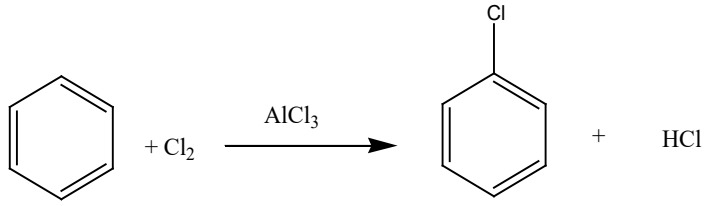
1. Electrophile formation
2. Attack of the ring by electrophiles
3. Deprotonation = loss of H^+

1. Halogenation

Benzene reacts with chlorine or bromine in the presence of a catalyst, replacing one of the hydrogen atoms on the ring by a chlorine or bromine atom.

- The reactions happen at room temperature.
- The catalyst has to be a Lewis acid known as "halogen carrier". The most commonly used catalysts are: aluminium (or iron) chloride, $AlCl_3$/ $FeCl_3$ or aluminium (or iron) bromide, $AlBr_3$/ $FeBr_3$ if you are reacting benzene with bromine.
  Example: The reaction with chlorine (Chlorination)

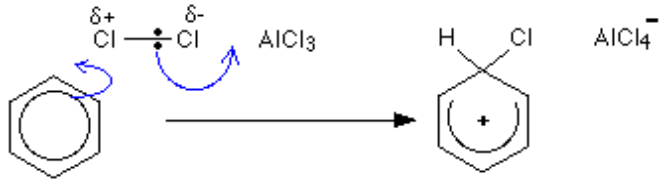
  The reaction between benzene and chlorine in the presence of either aluminium chloride or iron gives chlorobenzene.



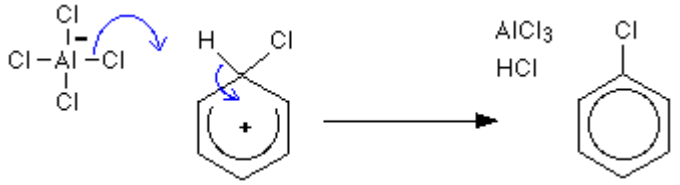
Or $C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$

Mechanism:

Step one:



Step two:

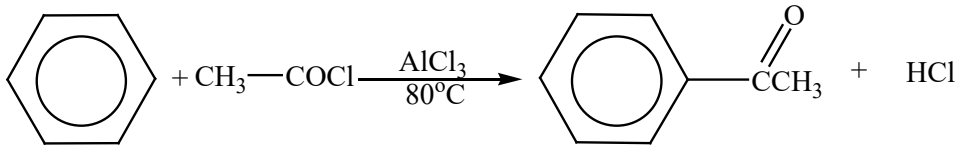


2. Friedel-craft-acylation

Acylation involves substituting an acyl group, RCO-, into a benzene ring.

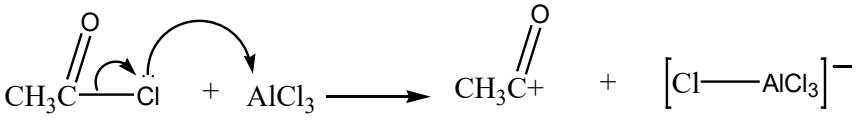
The most reactive substance containing an acyl group is an acyl chloride (also is known as an acid chloride). These have the general formula of RCOCl.

When ethanoyl chloride (CH_3COCl) reacts with benzene under the presence of $AlCl_3$, phenylethanone is produced (C_6H_5-$COCH_3$) at 80°C.

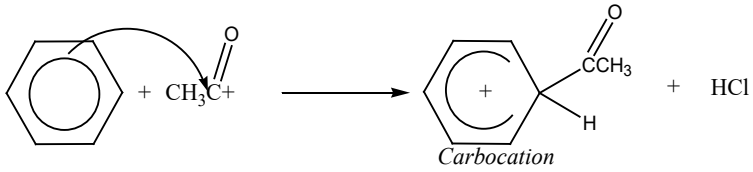


The mechanism for acylation

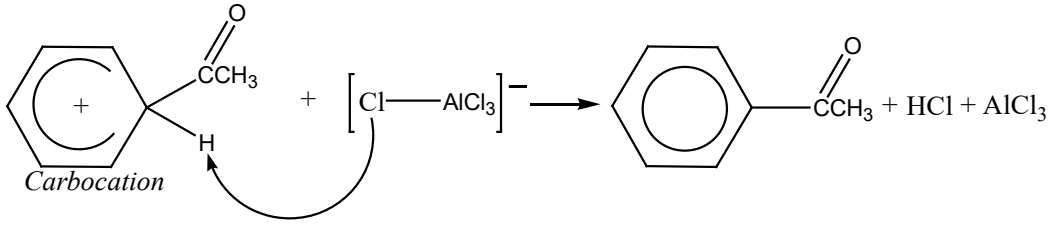
Step 1: Formation of electrophile by heterolytic fission.



Step 2: Electrophile attacking the benzene ring to form carbocation



Step 3: Proton is lost from the unstable carbocation formed earlier



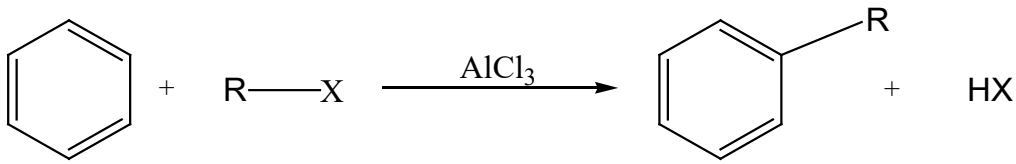
Note: An acid anhydride such as ethanoic anhydride, CH_3CO-O-$COCH_3$ can also be used for acylation purposes.

3. Friedel-Crafts Alkylation

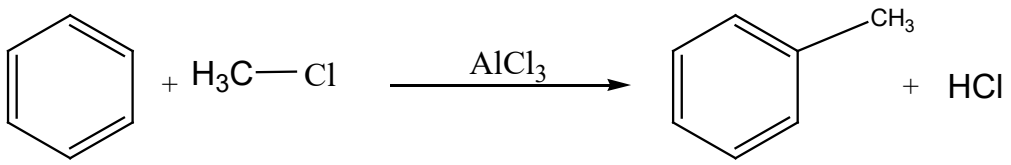
This reaction involves substituting an alkyl group into a benzene ring. Hydrogen on the ring is replaced by a group like methyl or ethyl and so on.

a. Using haloalkanes

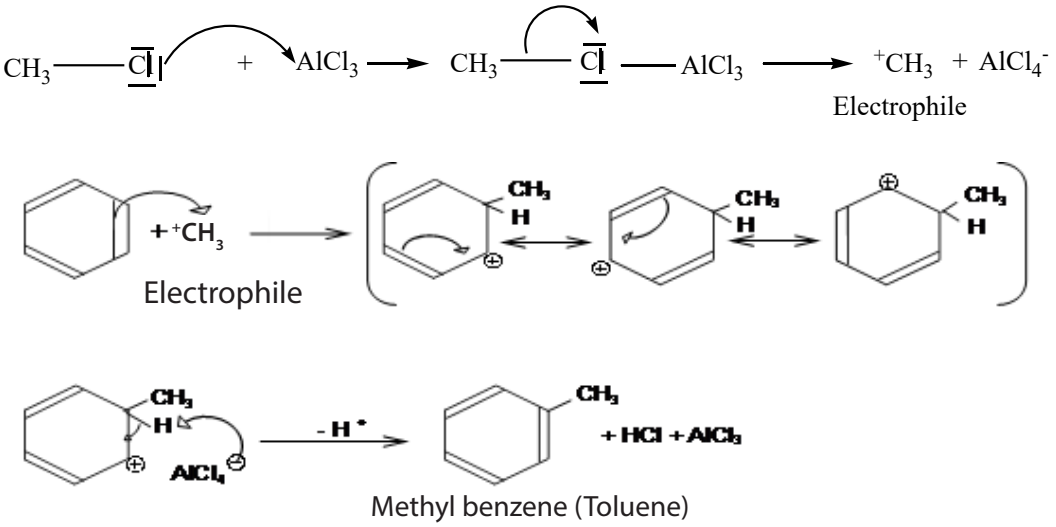
Benzene reacts with chloroalkanes in the presence of anhydrous $AlCl_3$ or $FeCl_3$ as a catalyst under reflux at 50°C to form alkylbenzenes



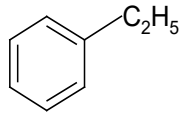
Example:



Mechanism:



If chloroethane (C_2H_5Cl) is used, then ethylbenzene ($C_6H_5C_2H_5$) is formed.

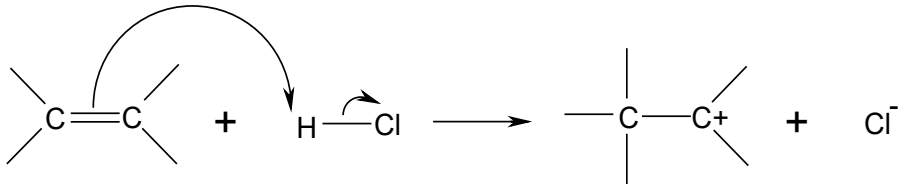


b. Using alkenes

Alkylbenzenes other than methylbenzene can be formed by reacting benzene with alkenes in the presence of HCl and $AlCl_3$, under reflux at temperatures below 50°C.

Mechanism:

Step 1: The alkene reacts with the HCl in the same way as in electrophilic addition reactions:



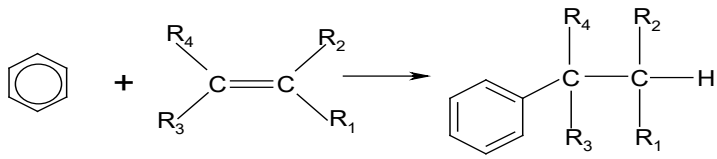
The carbocation behaves as the electrophile.

Step 2 and Step 3 proceed in the same way as in the alkylation reaction described above.

The overall reaction can be written as follows:

$$C_6H_6 + R_1R_2C{=}CR_1R_2 \rightarrow C_6H_5CR_1R_2CR_3R_4$$

It can also be written as follows:



The $AlCl_3$ and the HCl act as catalysts.

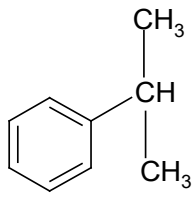
If ethene is used, the main product is ethylbenzene.

Unsymmetrical alkenes can give two possible carbocations when HCl is added. In such cases two different products are possible. In most cases one carbocation is produced in greater quantities than the other. Thus, a major product and a minor product are formed.

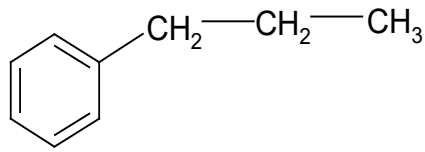
Example: Propene can react with HCl to give two possible carbocations:

more stable or less stable

The more stable cation gives the major product, methylethylbenzene (or isopropylbenzene).



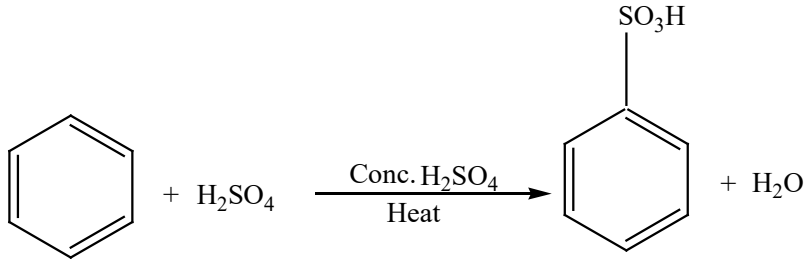
The less stable cation gives the minor product, propylbenzene.



4. Sulphonation

Sulphonation involves replacing one of the hydrogens on a benzene ring by the sulphonic acid group, $-SO_3H$. There are two equivalent ways of sulphonating benzene:

- Heat benzene under reflux with concentrated sulphuric acid for several hours.
- Warm benzene under reflux at 40°C with fuming sulphuric acid, **$H_2S_2O_7$,** for 20 to 30 minutes.

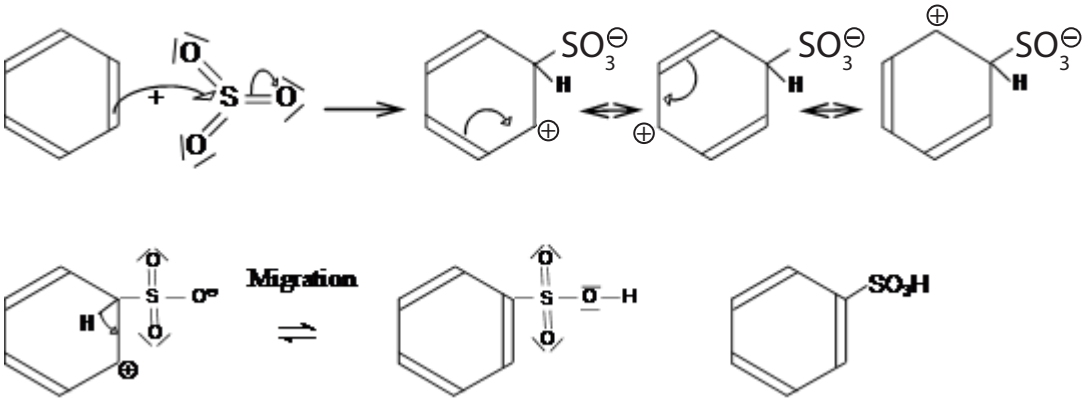


$$C_6H_6 + H_2SO_4 \rightarrow C_6H_5SO_3H + H_2O$$

The product is ***benzenesulphonic acid***.

Mechanism:

$$2\,H_2SO_4 \rightarrow SO_3 + H_3O^+ + HSO_4^-$$



5. Nitration

Nitration happens when one (or more) of the hydrogen atoms on the benzene ring is replaced by a nitro group, $-NO_2$.

Benzene is treated with a 50:50 mixture of concentrated nitric acid and concentrated sulphuric acid at a temperature not exceeding 50°C. The mixture is held at this temperature for about half an hour. Yellow oily nitrobenzene is formed.

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$$

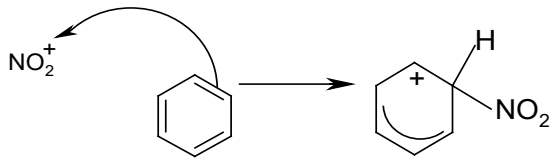
The concentrated sulphuric acid is acting as a catalyst and so is not written into the equations.

Mechanism:

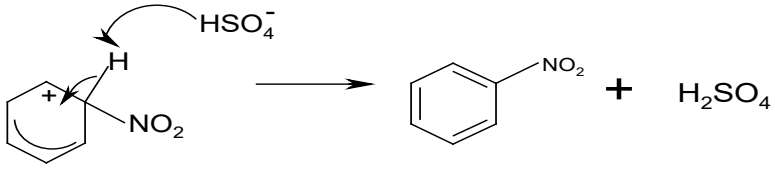
Step 1: Nitric acid is a less strong acid than sulphuric acid, and acts as a *base as the electrophile* is formed.

$$H_2SO_4 + HNO_3 \rightarrow H_2O + NO_2^+ + HSO_4^-$$

Step 2: The NO_2^+ is the electrophile and attacks the delocalised ring, breaking it temporarily:



Step 3: The delocalised system then reforms itself by pulling in the electrons from the C-H bond. The H^+ recombines with the HSO_4^- to form H_2SO_4.



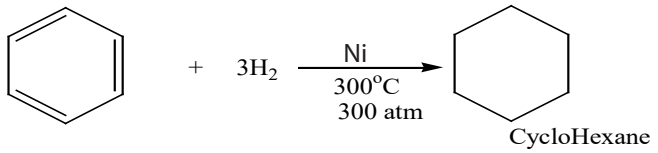
The overall reaction is $\mathbf{C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O}$

The sulphuric acid behaves as a catalyst. The product is known as nitrobenzene.

4.5.2. Some addition reactions and combustion reaction

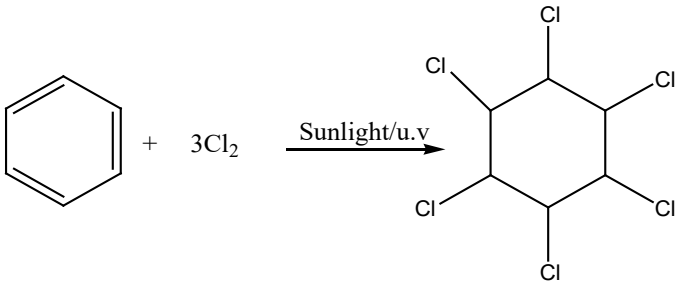
The benzene ring can undergo addition reaction under drastic conditions, breaking down its resonance.

1. Hydrogenation



CycloHexane

2. Addition of chlorine



Hexachloro cycloHexane
(it is used as an insecticide and is very unstable)

3. Combustion reaction

As other hydrocarbons, benzene burns in air forming carbon dioxide (or carbon monoxide in a limited supply of air) and water.

$C_6H_6(l) + 15/2\ O_2(g) \rightarrow 6\ CO_2(g) + 3\ H_2O(l)$ or $C_6H_6(l) + 9/2O_2(g) \rightarrow 6\ CO(g) + 3\ H_2O(l)$

Checking up 4.5

Discuss and find out the answers for the following questions:

Benzene can be nitrated to form nitrobenzene, $C_6H_5NO_2$.

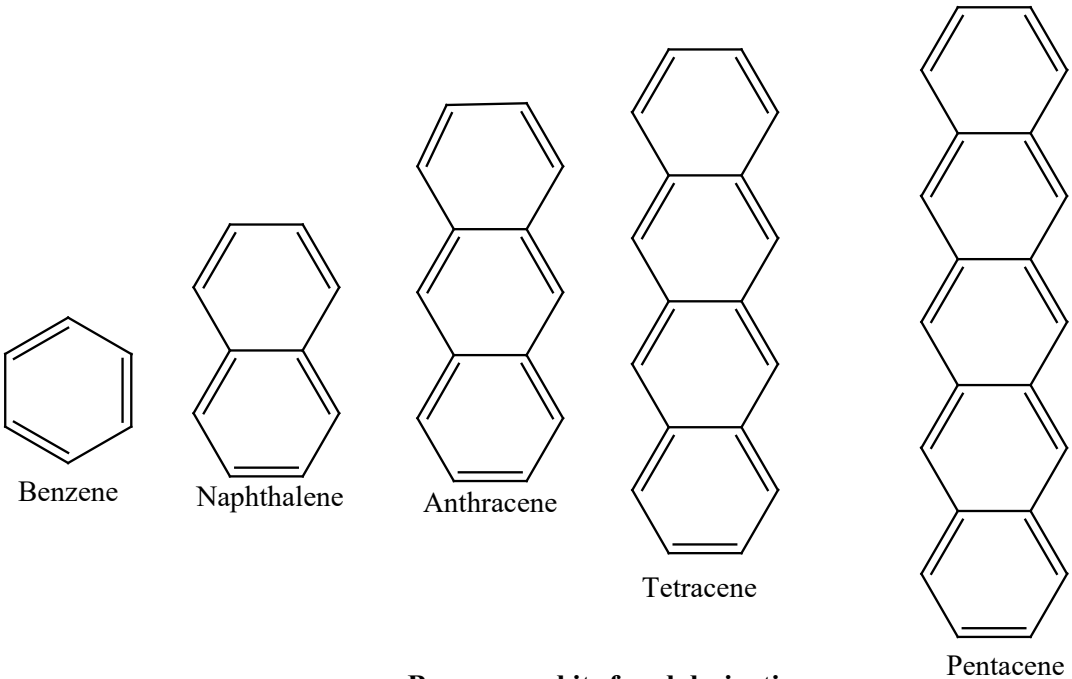
a. Draw the structural formula for benzene and give its empirical formula
b. State the reagents needed for the nitration of benzene
c. An electrophile is formed during the nitration of benzene
   i. What is the formula of this electrophile?
   ii. Write an equation for the production of the electrophile
   iii. Use curly arrows to show the mechanism for the nitration of benzene

4.6. Nomenclature and positional isomerism in derivatives of benzene

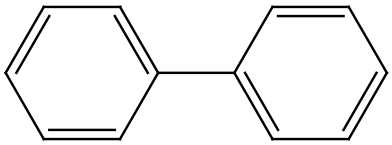
Activity 4.6

1. Name the following molecules:
   a. $CH_3CH_2CH(CH_3)CH_3$
   b. $ClCH_2CH_2CHOHCH_3$
   c. $CH_3CH(C_6H_5)CH_2CH_2CH_3$
   d. $C_6H_5NO_2$
   e. C_6H_4ClBr
2. Discuss about rules for naming aromatic compounds in this book or any other source (textbook or internet). Then, make a summary to be presented.

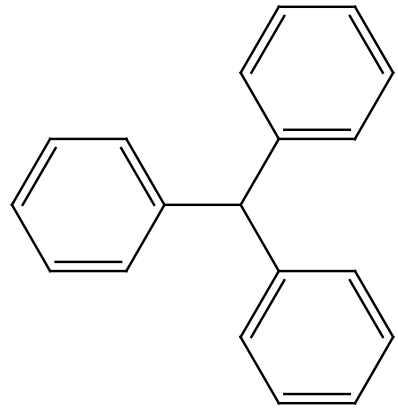
As you have seen from the previous lessons of this unit, benzene and its derivatives are referred to as *aromatic compounds*. The following diagram provides the structures of some aromatic compounds starting with benzene with one ring and then others with more than one ring and their respective names:



Benzene and its fused derivatives



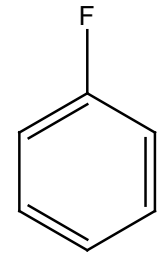
Biphenyl



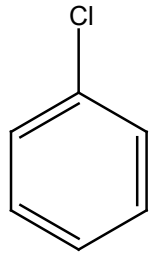
Triphenylmethane

Benzene derivatives, as seen, are obtained by replacing one or more hydrogen atoms on benzene ring with other substituent groups. According to the systematic nomenclature, the naming of benzene derivatives is purely based on the substitution part.

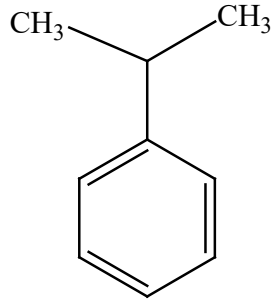
- The IUPAC system of naming mono substituted benzene derivatives uses the name of the substituent as prefix to benzene. Examples: fluorobenzene, chlorobenzene, isopropylbenzene and ethylbenzene, and so on.



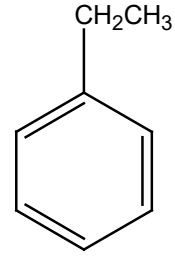
Fluorobenzene



Chlorobenzene

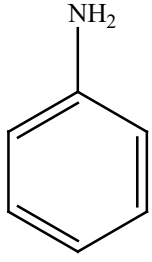


Isopropylbenzene

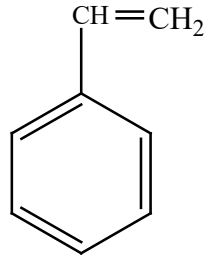


Ethylbenzene

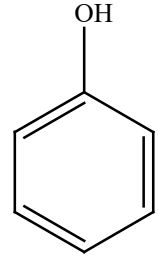
Some benzene derivatives have their traditional or popular names such as the following**:**



Aniline

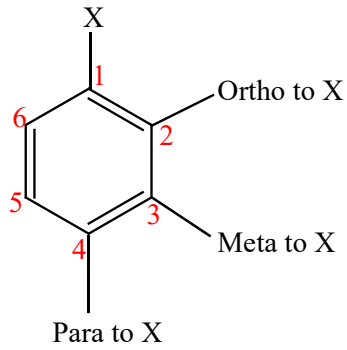


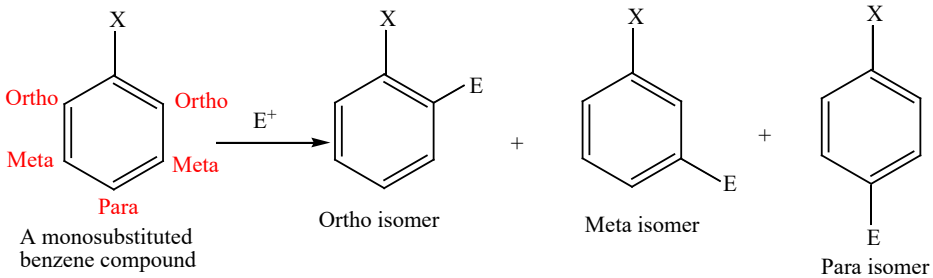
Styrene



Phenol

- Di-substituted benzene derivatives with the prefixes "Ortho- or o-" for substituent groups on adjacent carbons (e.g, C_1 and C_2) in benzene ring. "Meta- or m-" for substituents separated by one carbon atom (e.g, C_1 and C_3). "Para- or p-" for substituent groups on carbons on opposite sides of ring (e.g, C_1 and C_4). The positions on the benzene ring are as follows:

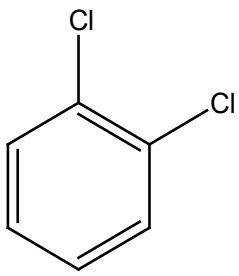




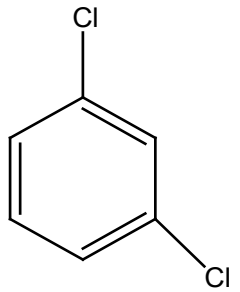
Benzene derivatives consisting of two substituents attached to the ring could be distinguished among three positional isomers (ortho- , meta- and para- isomers).

These are named either by numbers or by using non numerical prefixes (ortho, meta and para).

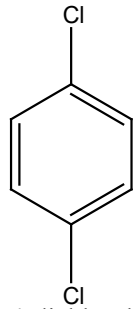
Notice that there are 2 identical ortho positions (2, 6), and 2 identical meta positions (3,5).



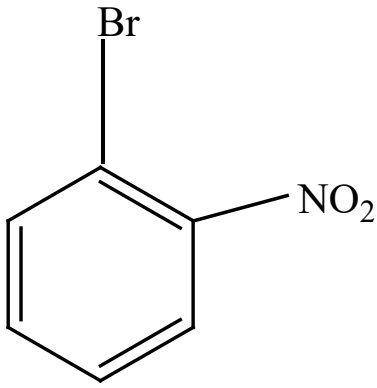
1,2-dichlorobenzene
or ortho-dichlorobenzene



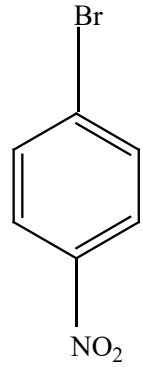
1,3-dichlorobenzene
or meta-dichlorobenzene



1,4-dichlorobenzene
or para-dichlorobenzene

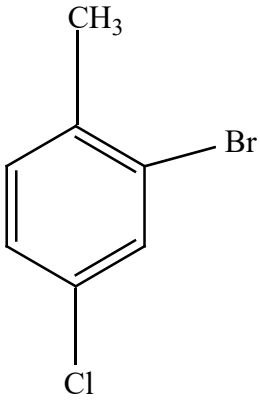


1-Bromo-2-nitrobenzene
o-Bromonitrobenzene

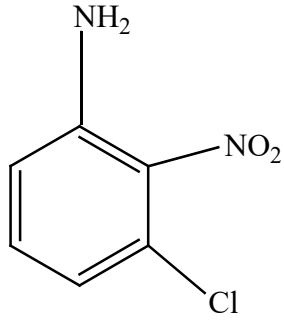


1-Bromo-4-nitrobenzene
p-Bromonitrobenzene

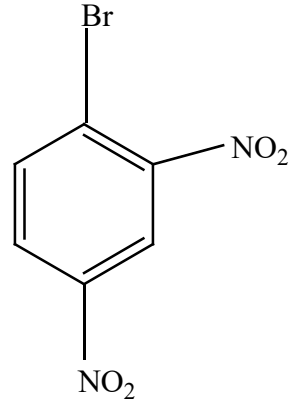
- When there is presence of more than two groups, ring substituent's positions are indicated with specific numbers. The ring thus gets numbered in a specific way in order to obtain the lowest number possible for these carbon atoms having substituents.



2-Bromo-4-chloro-methylbenzene



3-Chloro-2-nitroaminobenzene



1-Bromo-2,4-dinitro-benzene

- Some benzene derivatives are named by using their common names (or commercial names).

Table 4.1: Common and IUPAC names of some benzene derivatives

Substituent of benzene	Common name	IUPAC name
-CN	Benzonitrile	Benzenecarbonitrile
-OH	Phenol	Benzenol.
$-CH_3$	Toluene	Methyl benzene
-COOH	Benzoic acid	Benzene carboxylic acid
$-C_2H_2$	Styrene	vinyl benzene
$-OCH_3$	Anisole	Methoxy benzene
$-NH_2$	Aniline	Benzenamine
$-SO_3H$	Benzenesulphonic acid	
-CHO	Benzaldehyde	Benzenecarbaldehyde

Checking up 4.6

Discuss and provide appropriate answers to the following questions:

1. You are provided with $C_6H_4Br_2$. Give three different structural formulae of isomers of $C_6H_4Br_2$ and name them.
2. Provide all the structures and names of compounds having the same molecular formula as $C_6H_5NO_3$.

END UNIT ASSESSMENT

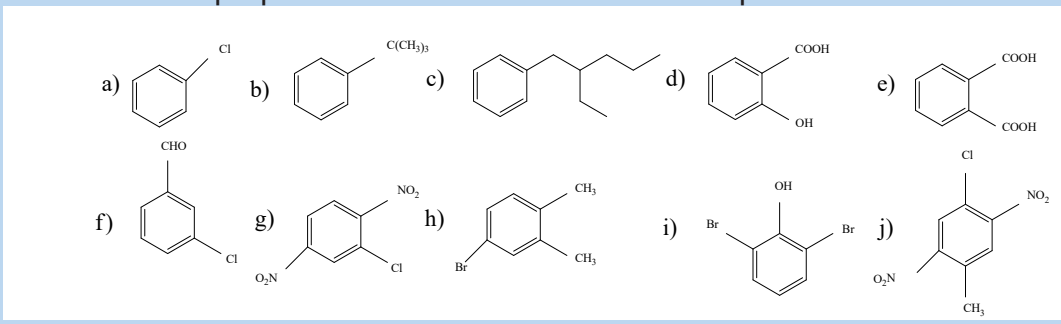
I. MULTIPLE CHOICE QUESTIONS: Write the letter corresponding to the right answer.

1. Which of the following features is not characteristic of aromatic compounds?
   a. They are planar.
   b. They are cyclic
   c. They contain an odd number of pairs of pi electrons.
   d. The ring atoms must be carbon atoms.
   e. They have an uninterrupted cloud of delocalized pi electrons.
2. What is the hybridization of the ring atoms in an aromatic compound?
   a. s
   b. sp^3
   c. sp
   d. p
   e. sp^2
3. What kind of catalyst is essential for halogenation of aromatic compounds with Cl_2 or Br_2?
   a. A Lewis acid
   b. Light
   c. A Lewis base
   d. A Brönsted acid
   e. A Brönsted base
   f. Arrhenius acid
4. Why do aromatic compounds undergo electrophilic substitution rather than electrophilic addition?
   a. Formation of the substituted benzene is highly exergonic.
   b. Aromatic compounds are not very stable.
   c. The addition product is much less stable than the substitution product, since it is non-aromatic.
   d. Aromatic compounds are not nucleophiles.
5. Resonance forms are in equilibrium with each other. State true or false
   a. True
   b. False

6. Identify the incorrect statement regarding aromaticity
   a. It is the extra stability possessed by a molecule
   b. p-orbitals must be planar and overlap
   c. Cyclic delocalization takes place
   d. It does not follow Huckel's rule
7. Aromatic rings do not have resonance structures. State true or false
   a. False
   b. True
8. Select the incorrect statement:
   a. A resonance may sometimes cause sp3 atoms to become sp2 hybridized
   b. Delocalizing one lone pair causes aromaticity
   c. One lone pair will be counted as two pi electrons according to Huckel's equation
   d. Two sigma bonds make up a double bond

II. OPEN QUESTIONS

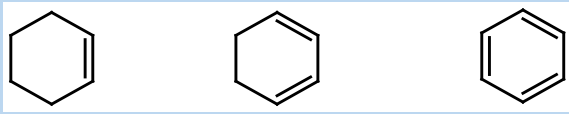
1. Give the proper IUPAC name for each of the compounds shown below.



2. Draw the structure corresponding to each of the following IUPAC names.
   a. Ortho-bromopropylbenzene
   b. 2, 3, 5-trinitrophenol
   c. 1-fluoro-2, 4- dinitrobenzene
   d. (1-bromoethyl) benzene
   e. 2-methyl-6-phenylheptane
   f. 1-Bromo-2,4-diethylbenzene

g. 4-aminobenzenesulfonic acid
h. Benzaldehyde
i. Benzyl bromide
j. Vinyl benzene

3. Give four reasons for unusual stability of benzene.
4. Compare the stability of cyclohexene, 1, 3-cyclohexadiene, and benzene based on heat of hydrogenation.



5. What type of reactions benzene and benzene derivatives typically undergo? Provide at least two examples.
6. a. Bromine reacts with benzene in the presence of a suitable catalyst.

   i. Give the name or formula of a suitable catalyst for this reaction.
   ii. State the general name of this type of catalyst.
   iii. Write a balanced equation for this reaction.
   iv. State the name of the product obtained.
   v. The reaction between bromine and benzene is an electrophilic substitution reaction. Outline the likely mechanism for this reaction. Show clearly all the curly arrows as well as the structures of the intermediate and the products.

   b. Bromine reacts much more readily with cyclohexene than it does with benzene.
   The reaction with cyclohexene does not need a catalyst.

   i. Describe with the aid of diagrams, the bonding in cyclohexene and benzene.
   ii. Use your answer to explain why bromine reacts much more readily with cyclohexene than it does with benzene.

7. The nitration of benzene is an important industrial reaction.
   a. State the conditions required for the nitration of benzene using nitric acid.
   b. Write a balanced equation for the nitration of benzene.
   c. i. Outline the mechanism for the nitration of benzene.
   ii. Explain what curly arrow means in this type of mechanism.
   iii. Give the name of the NO_2^+ ion and state its function in the mechanism of nitration of benzene.

UNIT 5

DERIVATIVES OF BENZENE

UNIT 5: DERIVATIVES OF BENZENE

Key Unit Competency

The learner should be able to relate aromatic ketones, aldehydes, carboxylic acids and amines to their chemical activity.

Learning objectives

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

- Explain the effects of substituent groups on the benzene ring;
- Give systematic names of aromatic compounds;
- Describe the preparation and reactions of phenol, benzoic acid, benzaldehyde, phenyl ethanone and phenylamine;
- State the uses of phenols;
- Describe the reactions of phenol, aromatic carbonyl compounds and carboxylic acids;
- Describe chemical properties of phenylamines;
- Explain the azo-coupling reactions of phenylamine in manufacture of dyes and indicators;
- Test and compare th acidity of phenol with alcohols and carboxylic acids;
- Test for the presence of phenol in a given solution;
- Compare and contrast the alkalinity of phenylamines with aliphatic amines and ammonia.;
- Perform experiments on the reactions of phenol and phenylamine

Introductory Activity

Observe carefully the following pictures and answer the questions below:

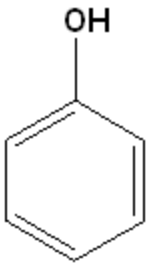
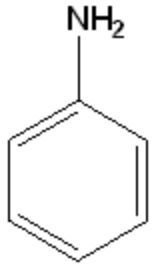
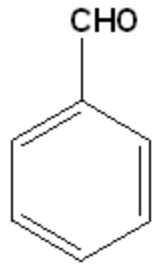
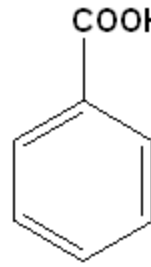
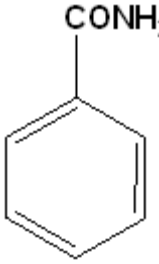
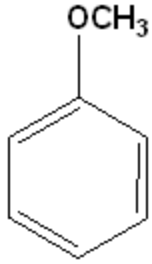
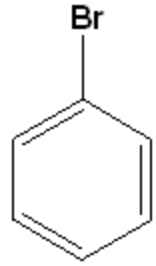
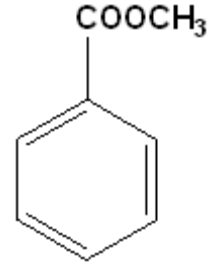
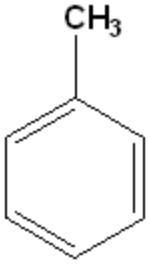
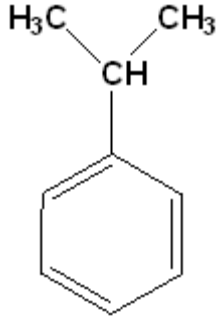
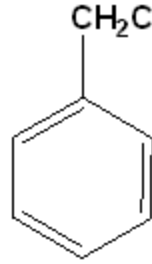
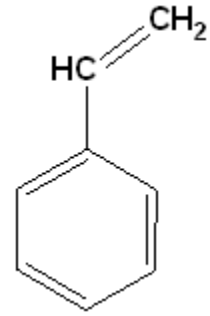
Aspirin	Phenolphthalein
Detergent	Quinine
DDT	Dettol

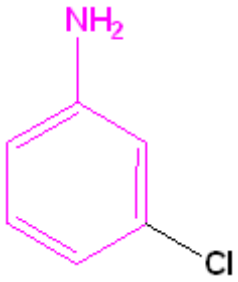
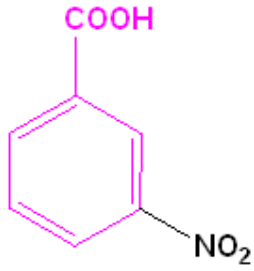
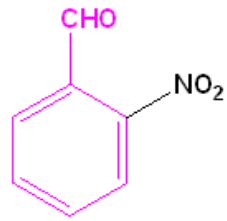
1. State the uses of the above substances
2. Make a research (in books or internet) and then suggest the chemical formulae of the above substances
3. Identify the similarities, if any, in their formulae.
4. Suggest other similar compounds.

The simplest and most important member of aromatic hydrocarbons is benzene (C_6H_6). The benzene ring is particular because of its stability and certain properties.

Many important chemical compounds are derived from benzene by replacing one or more of its hydrogen atoms with another functional group. It is a typical compound from which many of compounds of common properties derive.

Some examples of derivatives of benzene are given below:

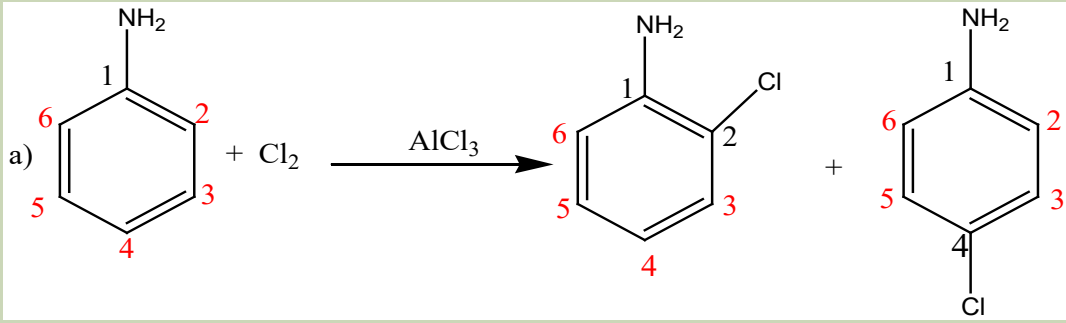
				
Phenol (Hydroxybenzene)	Aniline (Aminobenzene)	Benzaldehyde	Benzoic Acid	
				
Benzamide	Anisole	Bromobenzene	Methylbenzoate	
				
Toluene (Methylbenzene)	Cumene (Isopropylbenzene)	Ethylbenzene	Styrene (Vinylbenzene)	

			
Toluene is the parent name	Aniline is the parent name	Benzoic acid is the parent name	Benzaldehyde is the parent name
2-Bromotoluene	3-Chloroaniline	3-Nitrobenzoic acid	2-Nitrobenzaldehyde
o-Bromotoluene	m-Chloroaniline	m-Nitrobenzoic acid	o-Nitrobenzaldehyde

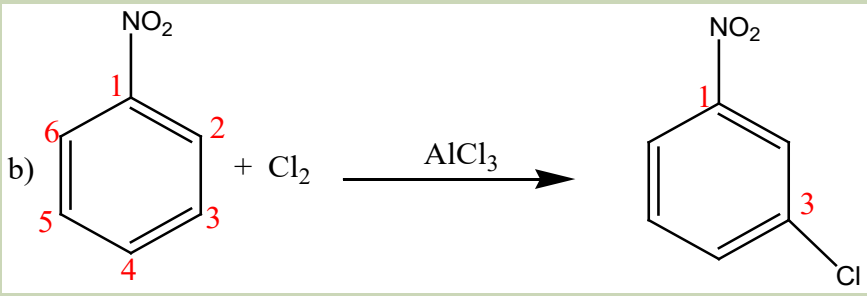
5.1. Effect of substituent groups on the benzene ring

Activity 5.1

When aminobenzene reacts with chlorine in the presence of Lewis acid such as $AlCl_3$ or $FeCl_3$, two major products shown below are produced:



When nitrobenzene, reacts with chlorine in the presence of Lewis acid such as $AlCl_3$ or $FeCl_3$, only one major product shown below is produced:



After comparing the two reactions, it was found that aniline is more reactive than nitrobenzene with chlorine respectively.

Using different books or internet make a research and find out why:

1. Aminobenzene is more reactive than nitrobenzene towards chlorine and all other electrophiles.
2. In reaction (a) the second substituent is oriented in ortho and para positions.
3. In reaction (b) the second substituent is oriented in only meta position.
4. In your research, find other substituents attached to benzene ring which orient second substituent in ortho and para positions; find other substituents attached to benzene ring which orient second substituent in meta positions.

The nature of a substituent already present in the benzene ring, not only determines the position of the next incoming group but also influences the rate of the second substitution reaction compared to the rate of substitution in benzene itself.

A substituent might increase the rate of the second substitution, i.e. make the ring more reactive relative to benzene. Another group if present in benzene ring could decrease the rate of further substitution, i.e. make the ring less reactive compared to benzene.

Groups already on the ring affect both the rate of the reaction and the site of attack. We say, therefore, that substituent groups affect both reactivity and orientation in electrophilic aromatic substitutions.

5.1.1. Deactivating and activating substituents

We can divide substituent groups into two classes according to their influence on the reactivity of the ring. The substituents which cause the compounds to undergo second substitution faster than benzene are called Activating Substituents (electron-releasing groups); they increase the electronic density on the benzene ring.On the other side, substituents which retard the rate of further substitution are referred to as Deactivating Substituents (electron-withdrawing groups); they decrease the electronic density on the benzene ring.

Examples

Activating Substituents (Activators)	Deactivating Substituents (Deactivators)
$-NH_2$, - NHR, - NR_2, - OH, - NHCOR, -OR, -R, -Ar, $-CH=CR_2$ (Alkenyl),	-CN, $-SO_3H$, $-CO_2H$, $-CO_2R$, -CHO, -COR, $-NO_2$, $-CF_3$, $-CCl_3$, -F, -Cl, -Br, -I

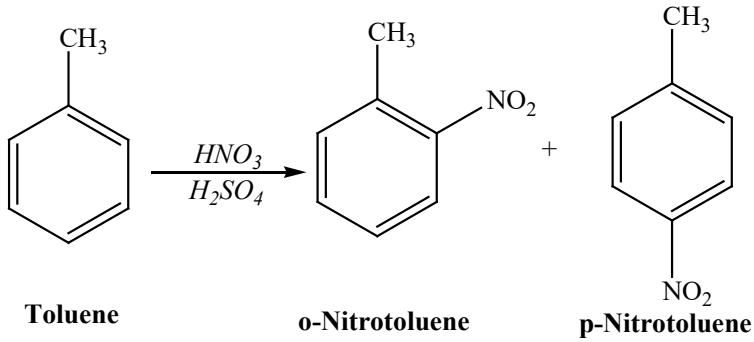
5.1.2. Directing the incoming substituents

During the formation of monosubstituted products in benzene, the electrophile can be attached at any position on the benzene ring. But, when the monosubstituted product is to be converted into disubstituted one, the existing substituent present in the ring directs the incoming group to a particular position. This is referred to as directive influence of the group. Depending on their directive influence, various groups (substituents) can be divided into two categories:

- Ortho and Para Directors
- Meta Directors

a. Ortho and para directors

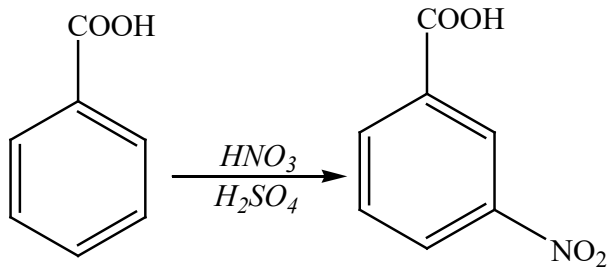
These direct the new substituents to enter the ring primarily in Ortho and Para positions to themselves. These groups increase the electron density at the ring. Thus the reactivity of benzene ring towards electrophilic substitution reactions increases. For example if we carry out nitration of toluene, the mixture of ortho and paranitrotoluenes is formed.



Toluene **o-Nitrotoluene** **p-Nitrotoluene**

b. Meta directors

These direct the new substituents to enter the ring primarily in Meta position to themselves. For example, the nitration of benzoic acid produces m-nitrobenzene.



Benzoic acid **m-Nitrobenzoic acid**

These groups withdraw the electrons from benzene ring through resonance effect, reducing the electron density at the benzene ring. They decrease the reactivity of benzene ring towards electrophilic substitution reaction and make it less susceptible to the electrophilic attack.

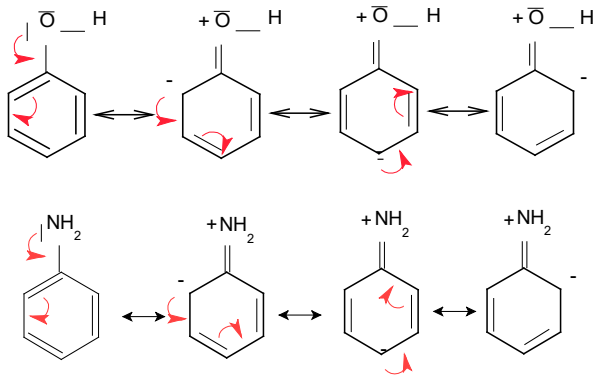
It has been found experimentally that in general ortho-para directing substituents activate the benzene ring and thus enhance the rate of reaction with electrophiles. On the contrary, the meta directing substituents deactivate the ring and retard the rate of reaction as compared to unsubstituted benzene.

- **Why activating substituents (Activators) have ortho and para directing properties?**

When the substituent present in the ring, has one or more lone pairs of electrons on the atom attached to the ring, it interacts with pi-electron system of the ring and it acts as electron donor (electron-donating substituent).

The presence of an electron-donating group such as –OH or -NH_2 causes further electrophilic substitution in ortho-para positions and also activates the ring to electrophilic attack.

Let us take the example of phenol (C_6H_5-OH) and aniline (C_6H_5-NH_2) which have available electron pairs on the atom directly attached to benzene ring. Thus phenol and aniline exhibit resonance and can be represented as hybrid of the following forms:



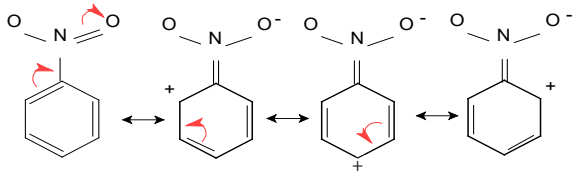
In the above two examples, positions 2 and 4 are relatively richer in electrons than position 3 and this makes them susceptible to electrophilic attack. The electrophile would attack the ring preferentially at ortho and para positions where the electron density relatively is greater as compared to the meta positions. The second electrophile will be directed where sites are negatively charged, i.e ortho and para positions.

From the above considerations, we conclude that all groups which are electron-donating are ortho-para directing and facilitate electrophilic substitution in the benzene ring.

- **Why Deactivating Substituents (Deactivators) have meta-directing properties?**

When the substituent has at least one strongly electronegative atom and a multiple bond in conjugation with benzene ring, the substituent acts as electron- withdrawing substituent.

Consider the nitrobenzene which contains $-NO_2$ is able to exist as the following resonance forms:



In the above example, it may be noted that resonance causes the decrease of electron density in the ring of nitrobenzene, and specifically at the ortho and para positions.

In general, the electron withdrawing substituents decrease the electron density of benzene ring and thereby act as deactivators and meta-directors.

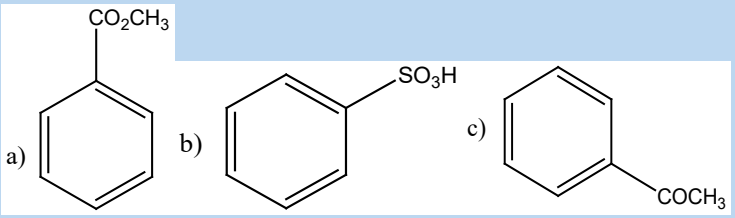
- **Anomalous Behaviour of Halogen Substituents**

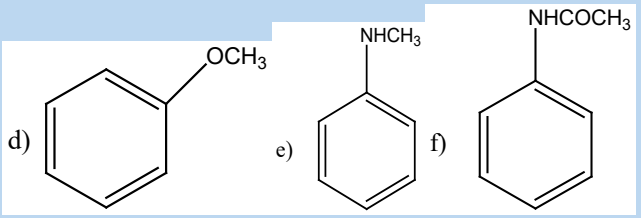
The resonance effect enables the halogen substituents to act as ortho and para director. It is also expected to activate the ring to electrophilic attack, but on the contrary it is a ring deactivator. This is attributed to the very high electronegativity of the halogens due to which they withdraw electrons so strongly that they deactivate the benzene ring.

While the resonance effect accounts for the ability of halogen to donate electrons to ortho and para positions, the combination of the two effects makes the halogenated benzene deactivated.

Checking up 5.1

1. Explain how the following substituents attached to benzene ring are going to direct further substitutions.

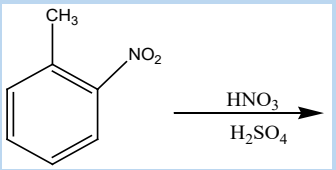




2. Classify the following as ortho, para orienting and meta orienting substituents:

   Methyl, nitro, cyano, methoxyl.

3. Explain the following statement: Chlorine is deactivating, yet it is ortho and para-directing in electrophilic aromatic substitution reactions.
4. Predict the major product for the following reaction:



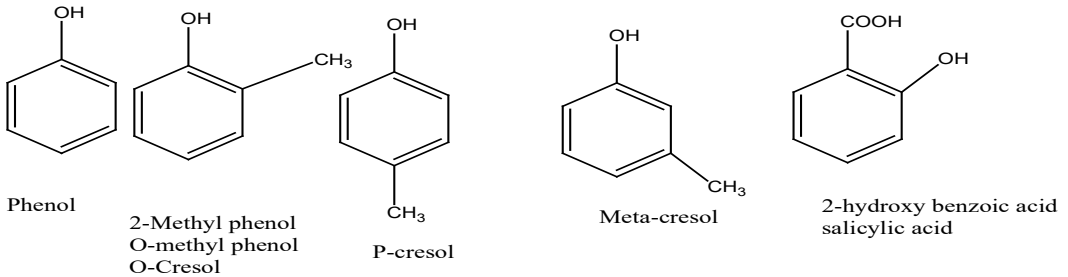
5.2. Phenol

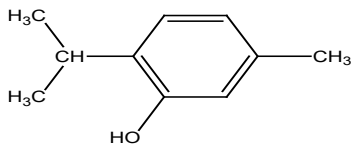
Activity 5.2 (a)

Aspirin, phenolphthalein indicator, Dettol, and other many compounds like dyes are produced from a substance containing only one hydroxyl (-OH) group attached to benzene ring. Make a research and find out:

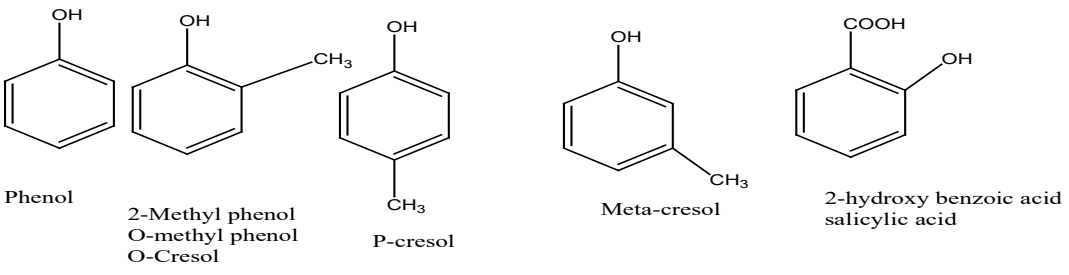
1. The structural formula of this substance,
2. The systematic and common name of the above substance,
3. The physical and chemical properties,
4. The uses of that very important substance.

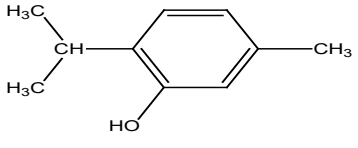
The phenols are organic compounds with one or more **−OH−OH** groups directly attached to a carbon atom in a benzene ring. The following are examples of phenols:





2-Isopropyl 5-Methyl phenol
Thymol

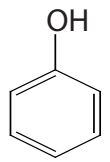




2-Isopropyl 5-Methyl phenol
Thymol

Phenols occupy an important position in the modern synthetic organic chemistry for the preparation of dyes, antioxidants, phenolic resins and certain pharmaceutical products.

The most important member in this family is phenol (hydroxybenzene):



Phenol (hydroxybenzene) is a colorless crystalline solid which melts at 43°C and boils at 182°C. On exposure to air or light, it becomes coloured due to oxidation.

Phenol is soluble in organic solvents and slightly soluble in water at room temperature, but infinitely soluble above 66 °C.

Phenol exhibits intermolecular hydrogen bonding and this makes its melting point higher than that of hydrocarbons of comparable molecular mass.

5.2.1. Sources and preparations of phenol

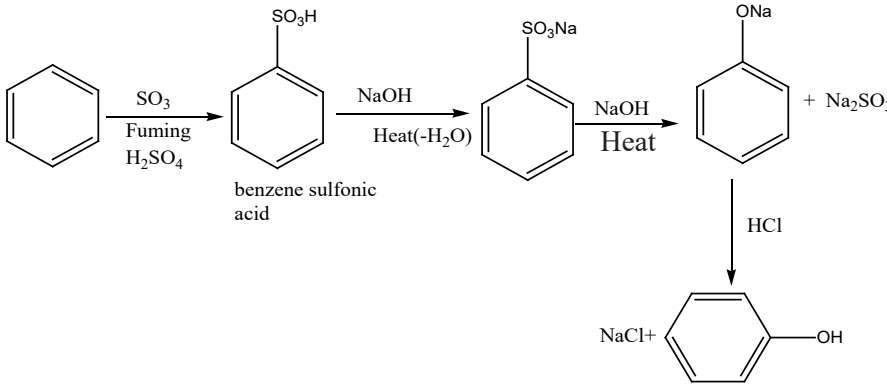
Phenols are common in nature; examples include tyrosine, one of the standard amino acids found in most proteins. Many of the more complex phenols used as flavourings and aromas are obtained from essential oils of plants. Other phenols obtained from plants include thymol, isolated from thyme, and eugenol, isolated from cloves.

Phenol, the cresols (methylphenols), and other simple alkylated phenols can be obtained from the distillation of coal tar or crude petroleum.

Phenol can be prepared:

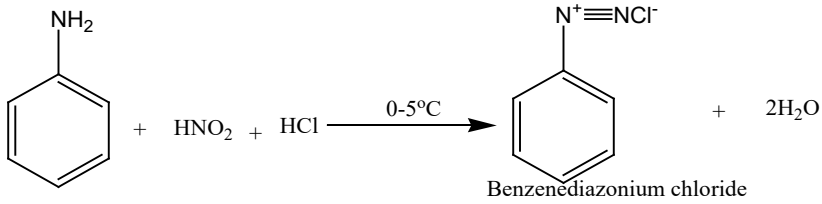
a. From benzenesulfonic acid

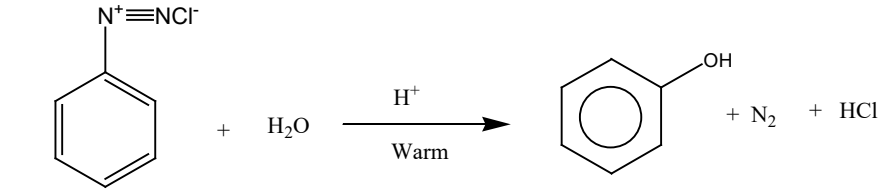
In this method, benzenesulphonic acid obtained from sulphonation of benzene reacts with sodium hydroxide to produce phenol.



b. From aniline via diazonium salts

On warming a diazonium salt solution with diluted acid, phenol is obtained.

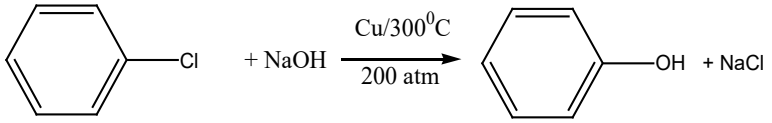




Benzenediazonium chloride

c. From aromatic halides

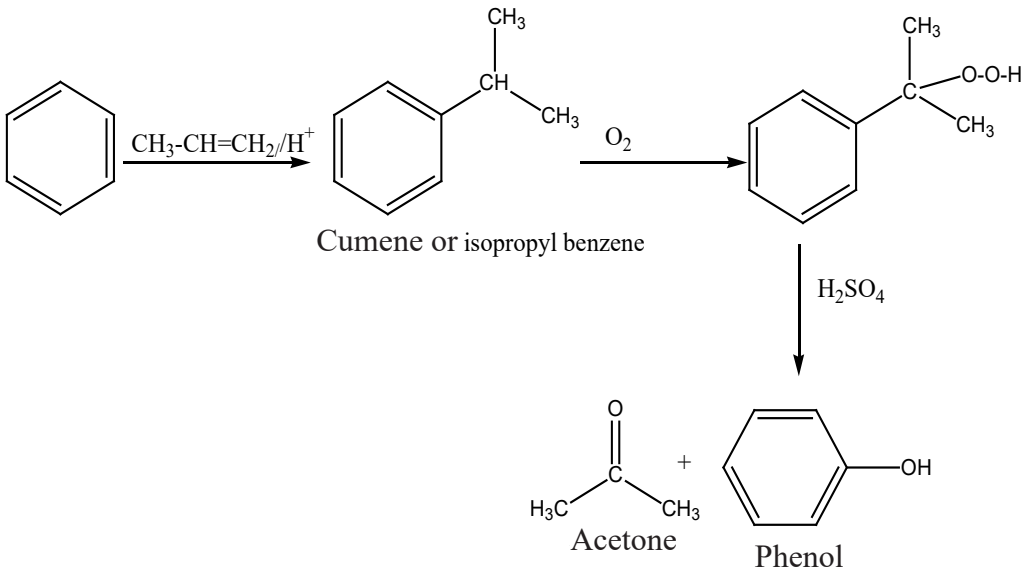
Phenol can be prepared by heating aromatic halides with caustic soda at temperature of 300^{0}C and pressure of about 200 atmospheres in the presence of copper as catalyst.



phenol

d. By cumene process

Isopropyl benzene or cumene is treated with air and concentrated H_2SO_4.



Cumene or isopropyl benzene

Acetone

Phenol

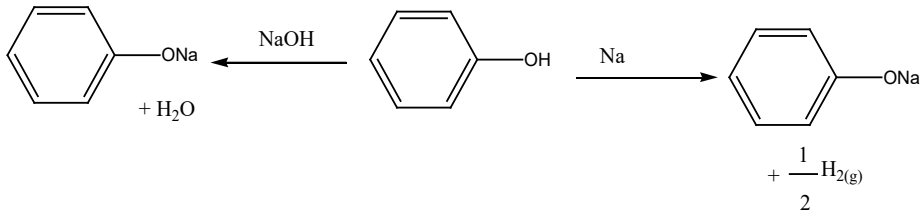
Activity 5.2 (b)

- Dissolve 5g of phenol in 20 mL of distilled water and put that aqueous solution in the beaker number 1,
- Put 20ml of ethanol in the second beaker,
- Put 20ml of ethanoic acid in the third beaker,

Put a blue litmus paper in each beaker and note down your observations then make a research in order to be able to explain your observations.

The O-H bond is weaker in phenol than in alcohol. This is because the lone pair of electrons on the oxygen atom becomes associated with delocalized electrons of the ring. Because of this partial double bond develops between carbon and oxygen with the result that C-O bond is strengthened and the O-H weakened as the electronic density is displaced towards the ring. This gives to phenol a more acidic nature than alcohols.

Therefore, phenol is more acidic than phenylmethanol and ethanol or cyclohexanol and this explains why phenol and not cyclohexanol nor phenylmethanol is soluble in sodium hydroxide solution. Because of this acidic property, phenol unlike alcohols reacts with alkali metal and sodium hydroxide or potassium hydroxide solution. Alcohols are not acidic enough to react with sodium hydroxide or potassium hydroxide solution but react only with alkali metal.



Note: Phenol is a weaker acid it does not react with sodium carbonate or sodium hydrogen carbonate unlike carboxylic acids. The reaction with sodium carbonate or sodium hydrogen carbonate is also used to distinguish a carboxylic acid like benzoic acid from a phenol. Carboxylic acids give effervescence (liberate CO_2) with sodium carbonate or sodium hydrogen carbonate while phenols do not.

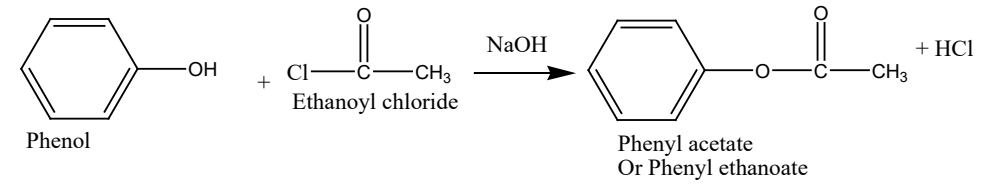
5.2.3. Reactions of phenols

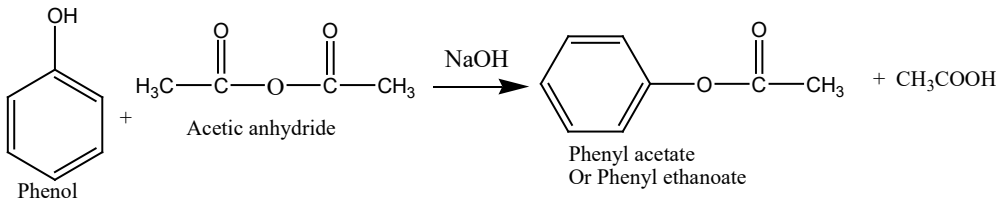
The reactions of phenol are of two types:

- Reactions in which the O-H is broken;
- Those involving the aromatic ring (Electrophilic substitution reactions).

a. Esterification

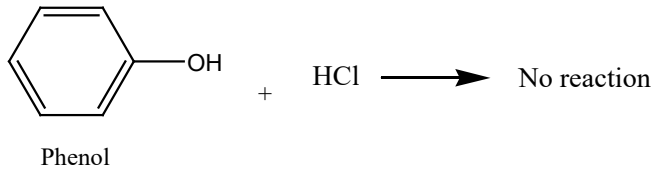
Phenols are weaker nucleophiles compared to alcohols because their lone pairs of electrons are partially delocalized over the benzene ring; that is why they do not form esters by direct reaction with carboxylic acids. However, the phenoxide ion ($C_6H_5O^-$) is a better nucleophile and it reacts with acid derivatives such as acid chloride or acid anhydride, which are themselves more reactive than the parent acid:



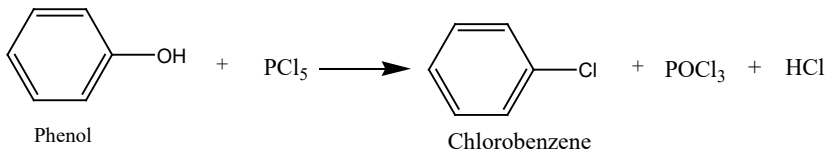


b. Replacement of OH by Halogens

Unlike alcohols, phenolic OH cannot be replaced by halogen by reaction with hydrogen halides.



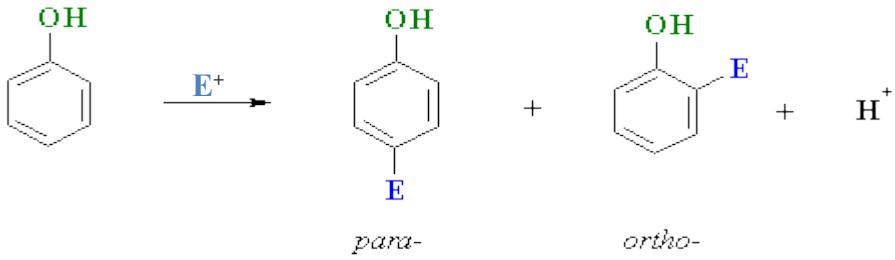
However, PCl_5 or PBr_5 reacts with phenol to form aryl halide:



c. Electrophilic substitution reactions of phenol

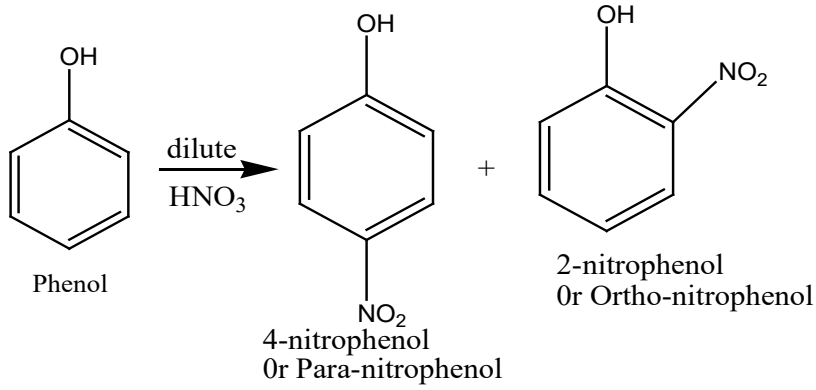
These reactions involve the replacement of hydrogen atoms at Para and Ortho positions of the ring, since the –OH is a para and ortho directing. The hydroxyl group increases the availability of electrons in the aromatic ring especially at para and ortho positions.

Because of this ring activation, phenols react more readily with electrophiles than benzene itself.

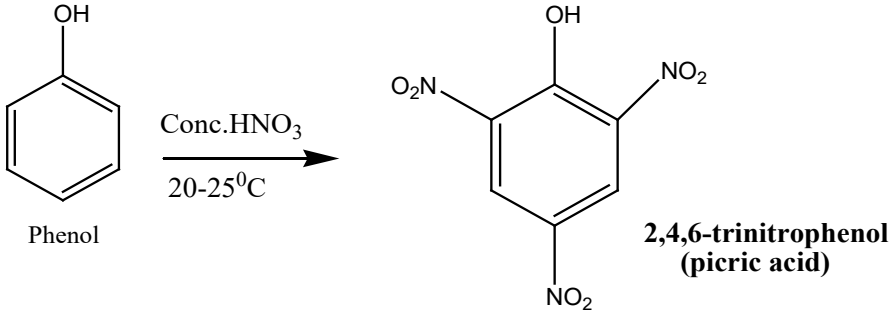


i. Nitration

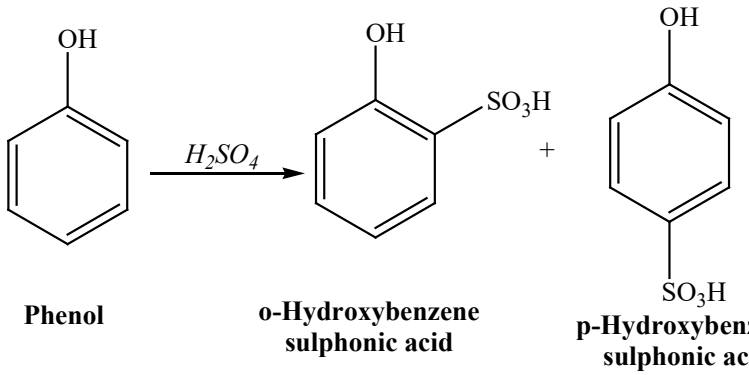
At room temperature, phenol reacts with dilute nitric acid to yield a mixture of 2-nitrophenol and 4-nitrophenol:



With concentrated nitric acid, phenol forms a yellow crystalline solid known as 2,4,6-trinitrophenol (picric acid) widely used in the manufacture of explosives and in solution as a yellow dye.



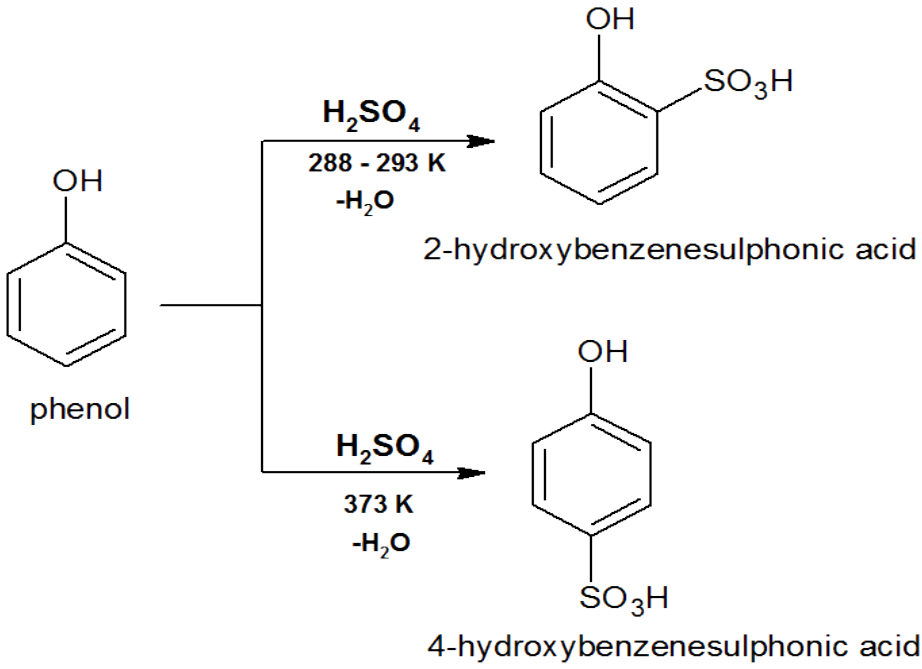
ii. Sulphonation



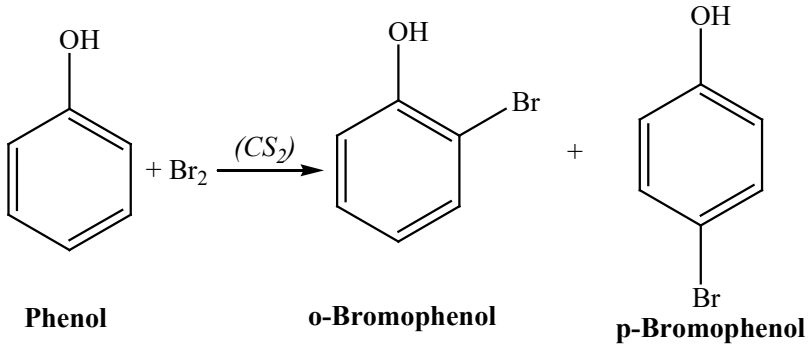
Phenol

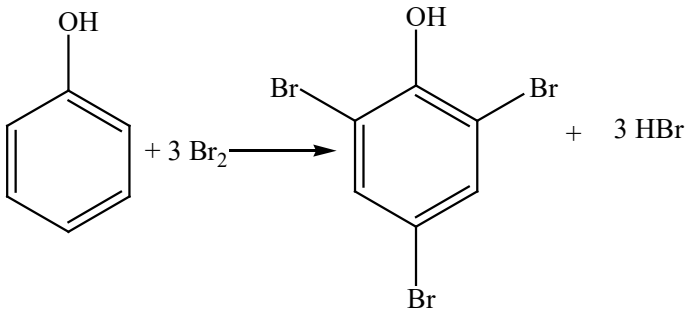
o-Hydroxybenzene sulphonic acid

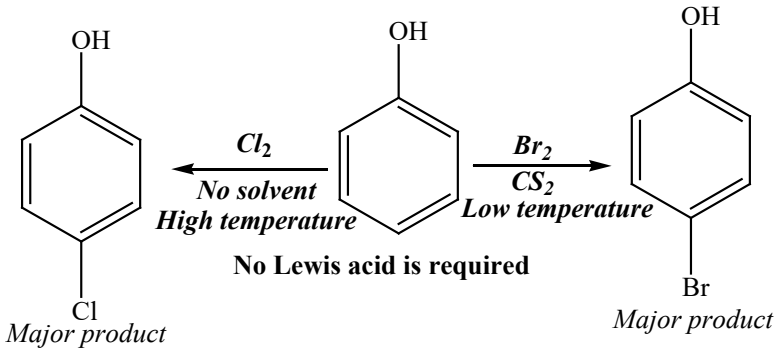
p-Hydroxybenzene sulphonic acid

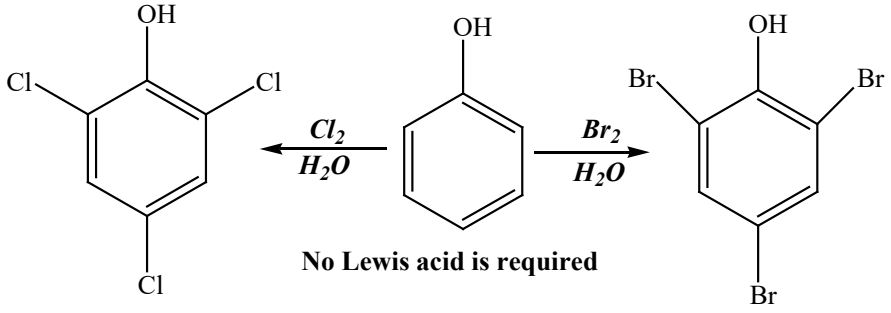


iii. Halogenation

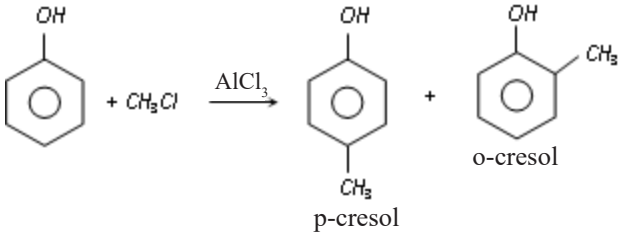






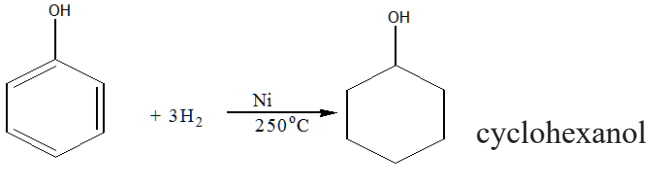


iv. Alkylation



$\Delta H = -12Kcal$

v. Hydrogenation



cyclohexanol

vi. Reduction

Phenol can be reduced by heating molten phenol with zinc dust (powdered zinc) to produce benzene.

$$C_6H_5OH(l) + Zn(s) \xrightarrow{400^oC} C_6H_{6(l)} + ZnO(s)$$

5.2.4. Test and uses of phenol

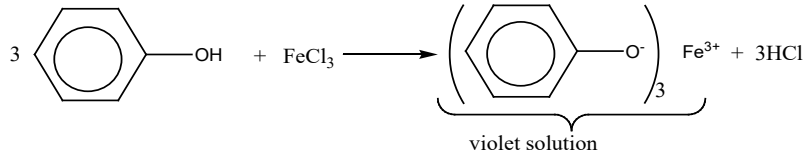
Activity 5.2 (c)

Put 5 mL of phenol in a test tube and add drop by drop bromine water. Write your observations and use books or internet for interpretation of your observations. Research other ways of testing the presence of phenol.

a. Chemical tests of phenol

i. Reaction with $FeCl_3$

Phenol, unlike alcohols, reacts with aqueous neutral ferric chloride (iron (III) chloride) to form colored complexes. The product is mainly of violet color. This reaction is used to distinguish phenol from tertiary alcohol since formation of violet product with $FeCl_3$ confirms phenol.

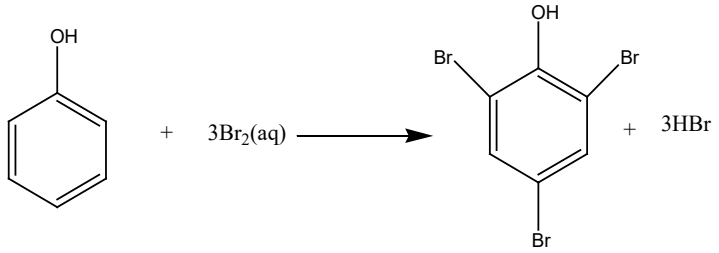


$$C_6H_5OH(l) + FeCl_3(aq) \longrightarrow C_6H_5O^-FeCl_2^+ + HCl$$

Violet complex

ii. Reaction with bromine water

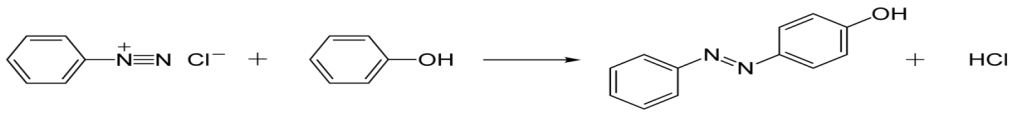
Add dropwise bromine water to aqueous solution of phenol, the white precipitate of 2,4,6-tribromophenol is formed



White precipitate

iii. Coupling with diazonium ions

Add dropwise solution of benzene diazonium chloride to aqueous solution of phenol, orange precipitate is formed.



b. Uses of phenol

i. The major use of phenol is its conversion to plastics or related materials. Phenol condenses with aldehydes to form phenol-aldehyde derivatives which are useful plastics for example phenol-methanal plastic (Bakelite).

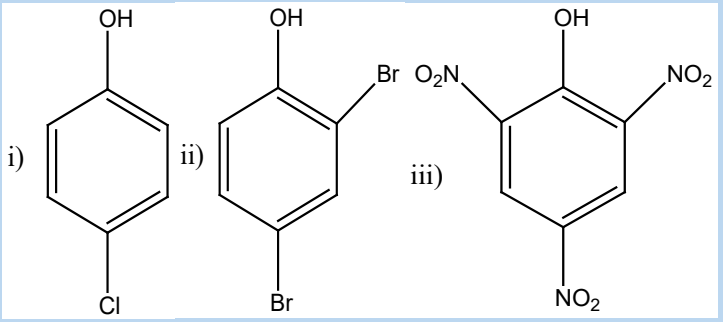
ii. Phenol is used in the manufacture of picric acid (used as a yellow dye) and other azo dyes when phenol reacts with amines.

iii. Phenol is a starting material for the manufacture of explosives
iv. Phenol is a starting material for the manufacture of weed killers (example: 2,4-dichlorophenoxyethanoic acid known as 2,4-D).
v. Phenol is used in the manufacture of phenolphthalein indicator ($C_{20}H_{14}O_4$).
vi. Phenol is also used in the manufacture of antiseptics (example: 2,4-dichloro-3,5-dimethylphenol which is present in "Dettol")
vii. Phenol is used as an oral anesthetic/analgesic in the treatment of throat infections.

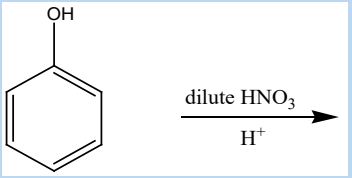
Checking up 5.2

1. Explain the following observations:
   a. Phenol is a stronger acid than phenylmethanol
   b. Phenoxide ion is a weaker base than ethoxide ion
   c. 4-nitrophenol is less volatile than 2-nitrophenol

2. Name the following compounds:



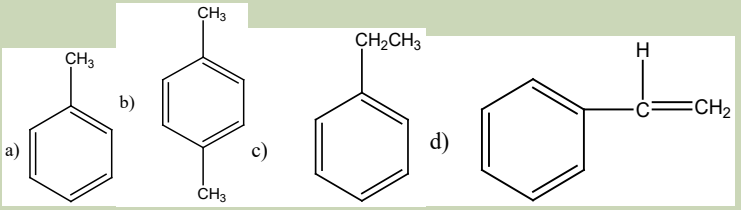
3. Predict the major product of the following reaction:



5.3. Aromatic hydrocarbons

Activity 5.3

Observe the following structures and make research then give their names, their reactivity, their preparations and uses.



An aromatic hydrocarbon or arene (or sometimes aryl hydrocarbon)is a hydrocarbon with sigma bonds and delocalized pi electrons between carbon atoms forming a circle. In contrast, aliphatic hydrocarbons lack this delocalization.

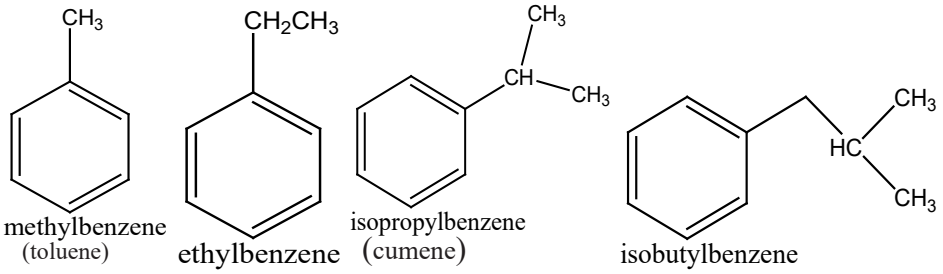
5.3.1. Structure and nomenclature of aromatic hydrocarbons

The trivial name of the parent monocyclic arene is benzene. The other members of this class are to a large extent assigned the systematic IUPAC names. However IUPAC have adopted the trivial names of lower arenes particularly, which have become popular by long usage. This has been done for brevity and convenience. Thus methylbenzene is invariably named as Toluene.

a. Structure and nomenclature of aromatic alkanes

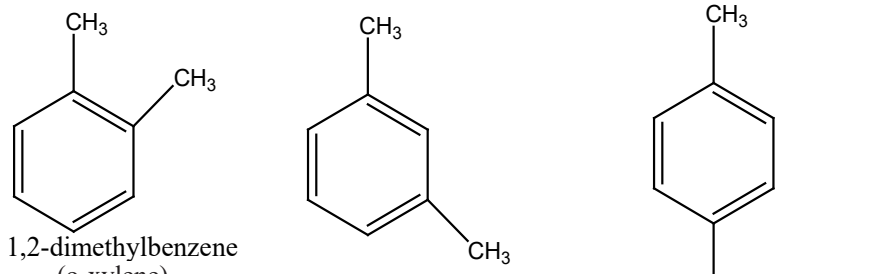
In the IUPAC system, arenes of this class are named in straight forward manner as substituted-benzenes.

For example,



methylbenzene (toluene) | ethylbenzene | isopropylbenzene (cumene) | isobutylbenzene

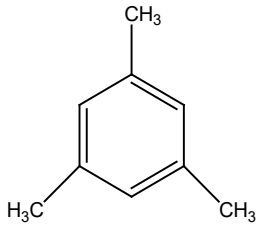
When there are two substituents on the benzene ring, then positions are indicated by numbers, or by the prefixes ***ortho (o-)***, ***meta (m-)*** and ***para (p-)***. Thus the isomeric dimethylbenzenes are named as:



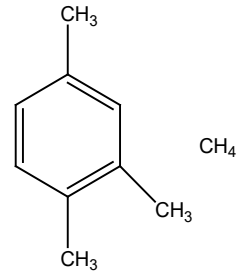
1,2-dimethylbenzene (o-xylene) | 1,3-dimethylbenzene (m-xylene) | 1,4-dimethylbenzene (p-xylene)

If there are three or more substituent groups present on the ring, the arenes are preferably designated by IUPAC names. One of the groups is written at the top

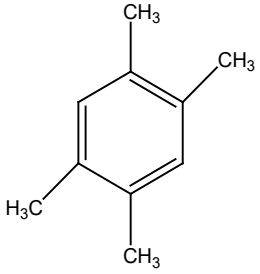
position of the hexagon, which becomes number 1. The six carbon atoms of the benzene are then numbered from 1 to 6 around the ring so that the substituents groups get the lower numbers. The substituent groups are preferably named in the alphabetical order. Thus,



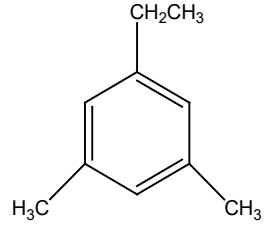
1,3,5-trimethylbenzene
(Mesitylene)



1,2,4-trimethylbenzene
NOT 1,3,4-trimethylbenzene



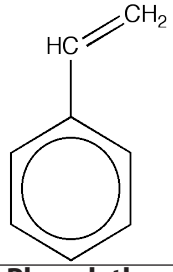
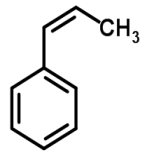
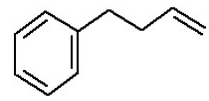
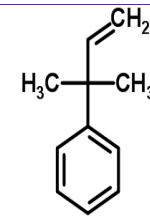
1,2,4,5-tetramethylbenzene
NOT 1,3,4,6-tetramethylbenzene



1-ethyl-3,5-dimethylbenzene

Note: The hydrocarbon group left after the removal of a hydrogen atom of the benzene itself is called phenyl group (C_6H_5-). The group left after the removal of a hydrogen atom of the CH_3- group of toluene is called benzyl (C_6H_5-CH_2-).

b. Structure and nomenclature of some aromatic alkenes

Struc-ture				
Name	**Phenylethene**	**Phenylpropene**	**4-Phenyl-but-1-ene**	**3-Methyl-3-phenyl-1-butene**

5.3.2. Reactions of alkylbenzenes

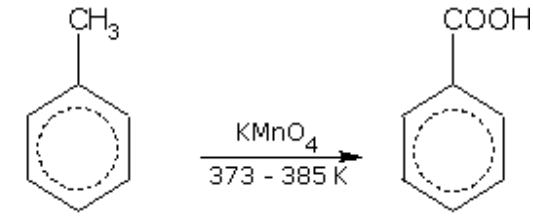
Alkylbenzenes involve two parts of their structures in chemical reactions:

- The side chain which can be oxidized by strong oxidizing agents like $KMnO_4$ and $Na_2Cr_2O_7$
- The benzene ring which can take place in electrophilic substitution. In electrophilic substitution alkylbenzenes react more strongly than benzene itself since the alkyl groups donate electrons. Alkyl groups are ortho and para directing.

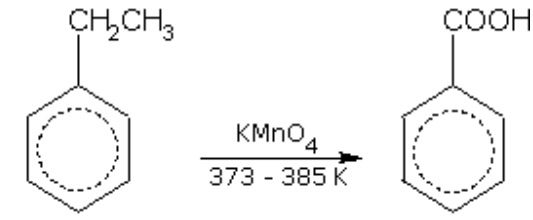
a. Oxidation of the side chain

When alkylbenzenes are oxidized by powerful oxidizing agents (such as hot acidified or alkaline $KMnO_4$ and $Na_2Cr_2O_7$), the entire side chain, regardless of length, are oxidized to benzoic acid.

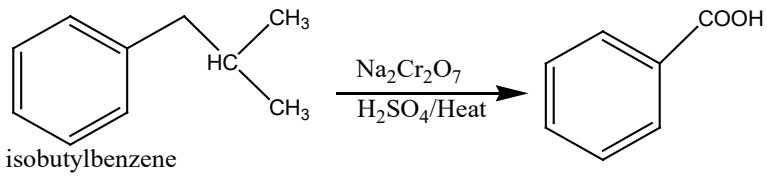
For example,



Toluene Benzoic acid

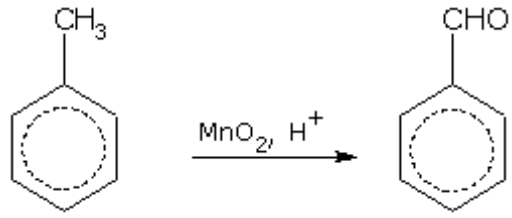


Phenylethane Benzoic acid



isobutylbenzene

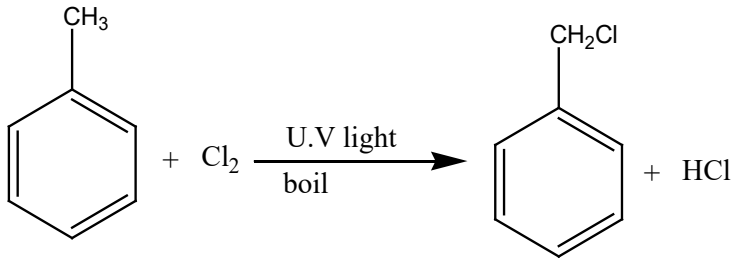
With weak oxidising agents such as acidic manganese dioxide (MnO_2) or chromylchloride (CrO_2Cl_2), the side chain is oxidised to aldehyde (-CHO) group.



Toluene benzaldehyde

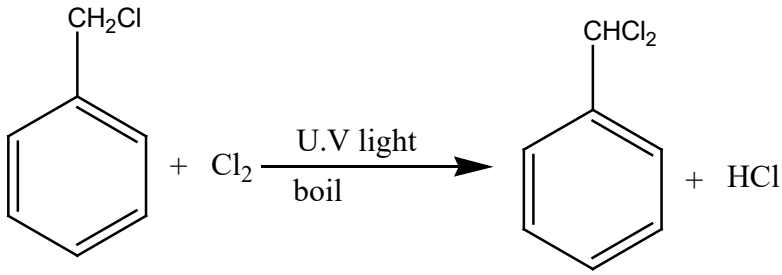
b. Radical substitution

Radical substitution takes place in three steps as for aliphatic alkanes: initiation, propagation and termination. The side chain substitution of hydrogen atom (s) occurs when chlorine or bromine is bubbled through boiling alkylbenzene in the presence of ultraviolet light or strong sunlight.

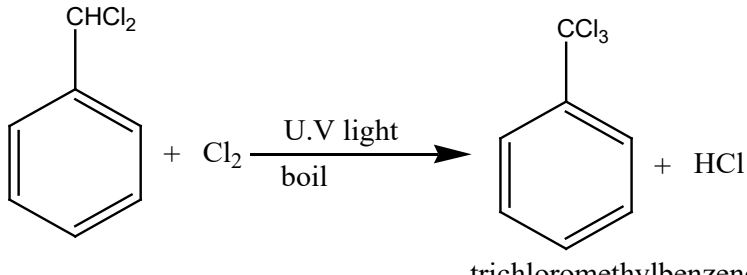


Benzyl chloride
or Chloromethylbenzene

Note that the above reaction may continue until all hydrogen atoms are replaced by halogen atoms.



dichloromethylbenzene



trichloromethylbenzene

Note: Bromine gives similar products under similar conditions.

Checking up 5.3

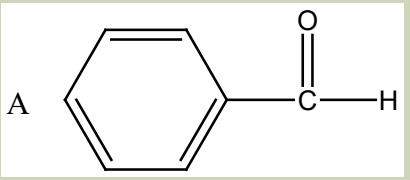
How can you prepare:

ortho-xylene (1,2-dimethyl benzene) and para-xylene (1,4-dimethyl benzene) from benzene.

5.4. Aromatic carbonyl compounds

Activity 5.4

Observe the following structures and make research then give their names, reactivity, preparations and uses.

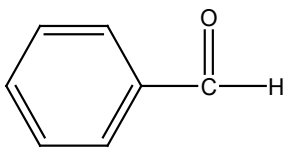


The compounds with carbonyl group attached to the benzene ring are known as aromatic aldehydes and aromatic ketones.

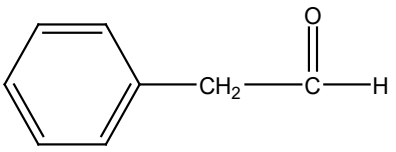
5.4.1. Structure and nomenclature of aromatic carbonyl compounds

a. Aromatic Aldehydes

These carbonyl compounds contain a phenyl group in their structures. Aromatic aldehydes are of two types: (a) those in which the aldehyde group (CHO) is directly attached to a carbon of the aromatic ring; and (b) those in which the aldehyde group (CHO) is directly attached to a carbon of the side chain. Aldehydes of type (a) are called aromatic aldehydes, while those of type (b) are best regarded as aryl-substituted aliphatic aldehydes.

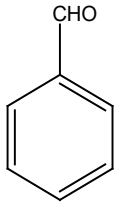


Aromatic aldehyde

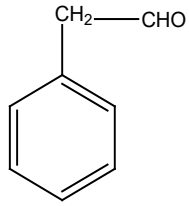


aryl-substituted aliphatic aldehyde

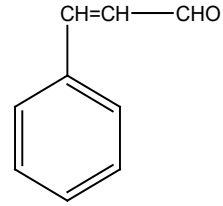
Benzaldehyde is a typical aromatic aldehyde, while phenylacetaldehyde and cinnamic aldehyde are to be designated as aryl-substituted aliphatic aldehydes.



Benzaldehyde

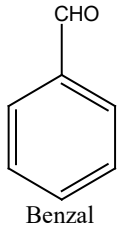


Phenylacetaldehyde

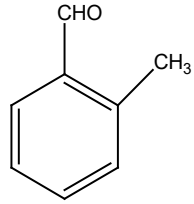


Cinnamic aldehyde

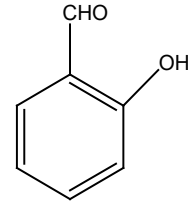
The IUPAC name of an aromatic aldehyde is derived by dropping the ending –ene of the name of the parent hydrocarbon and appending the suffix –al. Thus,



Benzal

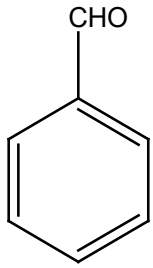


2-methylbenzal

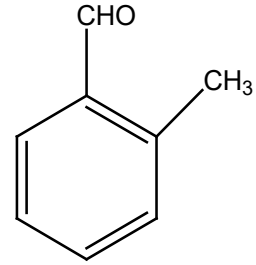


2-hydroxybenzal

Aromatic aldehydes are generally called by their common names which are derived from the names of the corresponding carboxylic acid by replacing the –ic or –oic acid by –aldehyde. Thus the name benzaldehyde is derived from benzoic acid; ortho-tolualdehyde is derived from ortho-toluic acid, and salicylaldehyde from salicylic acd.



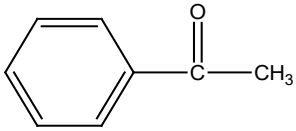
Benzaldehyde
(Benzal)



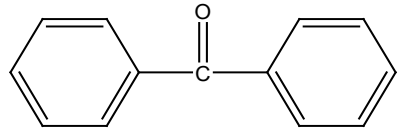
ortho-tolualdehyde
(2-methylbenzal)

b. Aromatic ketones

Ketones containing the carbonyl group attached to a benzene ring are named phenones. The individual name of such a ketone is derived by adding phenone to the stem formed by removing –ic from the name of the corresponding acid.



Acetophenone
(Methylphenylketone)



Benzophenone
(diphenylketone)

The common names of aromatic ketones are obtained as usual by naming the alkyl or aryl groups attached to the carbonyl group, followed by the word ketone. These are given in the brackets above.

5.4.2. Preparation of aromatic carbonyl compounds

a. Preparation of aromatic aldehydes

Benzaldehyde is the simplest member in this family and it may be prepared by the following methods which are applicable to aromatic aldehydes in general.

Benzaldehyde can be prepared using different methods. However, the main method is oxidation of methylbenzene. The methods of preparation include:

i) $C_6H_5CH_3 \xrightarrow[\text{Heat}]{MnO_2/H_2SO_4} C_6H_5CHO$

ii) $C_6H_5CH_3 + 2Cl_2 \xrightarrow{\text{U.V light}} C_6H_5CHCl_2 + 2HCl$

$C_6H_5CHCl_2 \xrightarrow[\text{Reflux}]{H_2O/OH^-} C_6H_5CHO$

iii) $C_6H_5CH_3 + O_2 \xrightarrow[\text{Heat}]{V_2O_5} C_6H_5CHO + H_2O$

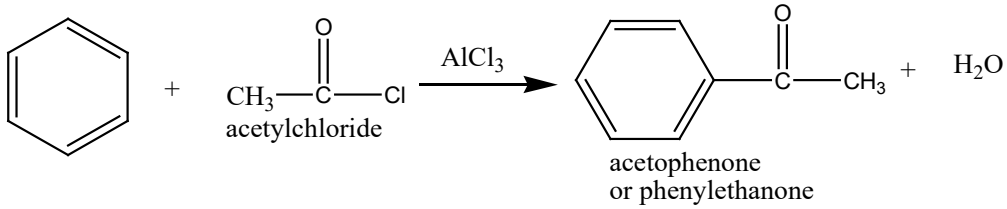
iv) $C_6H_5COCl + H_2 \xrightarrow{Pd\text{-}BaSO_4} C_6H_5CHO + HCl$

b. Preparation of aromatic ketones

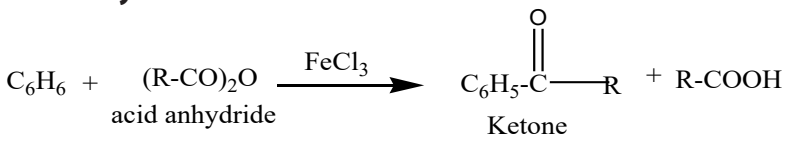
Although aromatic ketones may be prepared by any of the methods used for aliphatic ketones, they are generally prepared by Friedel-Crafts reaction between an aromatic hydrocarbon and acylchloride or acid anhydride. The benzene is treated with acylchloride or acid anhydride in the presence of a halogen carrier.

- **From acylchloride**

$C_6H_6 + \underset{\text{Acylchloride}}{R\text{-}COCl} \xrightarrow{AlCl_3} \underset{\text{Ketone}}{C_6H_5\text{-}C(=O)\text{-}R} + HCl$



- **From acid anhydride**



5.4.3. Reactions of aromatic carbonyl compounds

The most typical reactions of the carbonyl groups are nucleophilic addition. In the carbon-oxygen double bond of the carbonyl group, oxygen is more electronegative than carbon, hence it has a strong tendency to pull electrons towards itself. This makes the carbon-oxygen double bond highly polar.

The partially positive carbon atom can be attacked by nucleophiles. During the reaction, the carbon-oxygen bond gets broken and the net effect is that the carbonyl group undergoes addition reaction.

The carbonyl group of aromatic aldehydes and ketones withdraws electrons from the benzene ring by inductive effect and resonance effect. Hence this group deactivates the benzene ring towards electrophilic substitution. The presence of the carbonyl group directs the substitution in meta-position. The electrophilic substitution of aromatic aldehydes and ketones is more difficult than electrophilic substitution of non substituted benzene.

a. Reactions of aromatic aldehydes

Aromatic aldehydes present the same properties as aliphatic aldehydes. They give a positive test with ***Brady's reagent*** (2, 4- Dinitrophenyl Hydrazine; observation: yellow or orange precipitate), with ***Fehling solution*** (observation: red solution brown precipitate), with ***Tollen's reagent*** (observation: silver mirror) and with ***Schiff reagent*** (pink colour will be observed).

Benzaldehyde is the typical and the simplest of aromatic aldehyde and will be used for illustrating the properties of this class of aromatic aldehydes. Benzaldehyde undergoes chemical reactions involving the side chain and benzene ring.

i. Benzaldehyde is not oxidized as readily as aliphatic aldehydes of oxidizing agents. While it reduces ammoniacal silver nitrate forming a silver mirror, it does not reduce Fehling's solution. Nevertheless, benzaldehyde undergoes

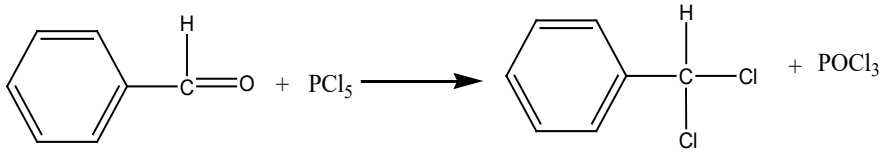
oxidation by atmospheric oxygen at ordinary temperature to form benzoic acid. This process known as autoxidation is catalyzed by light.

$$2C_6H_5CHO + O_2 \xrightarrow{h\nu} 2C_6H_5COOH$$

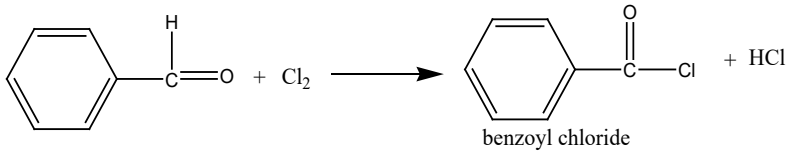
ii. When benzaldehyde is reduced with zinc and hydrochloric acid, benzylalcohol is produced:

$$C_6H_5CHO \xrightarrow[Zn/HCl]{[H]} C_6H_5CH_2OH$$

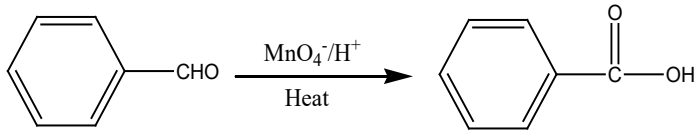
iii. Benzaldehyde reacts with phosphorous pentachloride to form the gem-dihalide:



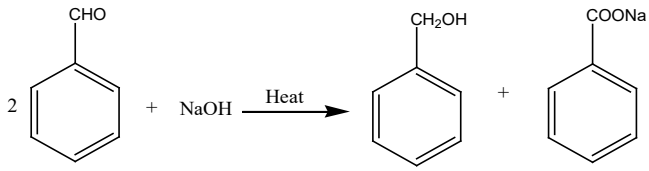
iv. The aldehyde group attached directly to the benzene ring is deactivating and hence chlorine does not substitute hydrogen in the ring in the absence of a catalyst. Instead, the chlorine substitutes hydrogen of the aldehyde group and benzoyl chloride is formed.

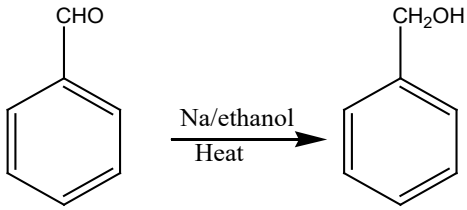


v.



vi. Benzaldehyde on treatment with concentrated sodium hydroxide solution gives benzyl alcohol and sodium benzoate this reaction is called Cannizzaro reaction:





viii. Benzaldehyde undergoes nitration, sulphonation and halogenation. The substitution takes place in the meta-position to the group CHO.

Note: Benzaldehyde condenses with hydroxylamine (NH_2OH) and phenylhydrazine ($C_6H_5NHNH_2$) to form benzaldoxime and phenylhydrazone respectively. Similarly, benzaldehyde reacts with hydrazine and semicarbazide to give hydrazine and semicarbazone respectively.

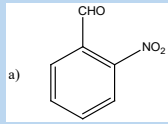
Benzaldehyde is used for flavouring foods, scenting soaps, in the manufacturing of perfumes, in the preparation of dyes and in the synthesis of antibiotics.

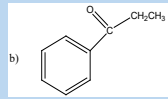
b. Reactions of aromatic ketones

The reactivity of the carbonyl group in aromatic ketones is not greatly affected by the aryl groups attached to it. In consequence, they undergo the same general reactions as aliphatic ketones. However, they do not form the bisulphite compound, and in addition give the usual substitution reactions in the aromatic ring.

Checking up 5.4

1. Assign the systematic names of the following compounds:



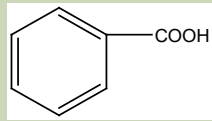


2. Discuss the methods of preparation of benzaldehyde as a representative of the aromatic aldehydes.

5.5. Aromatic carboxylic acids

Activity 5.5

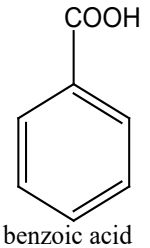
Observe the following structure and make research then give its name, reactivity, preparation and uses.



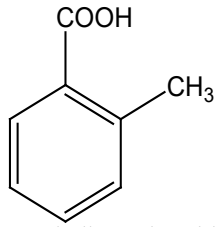
Aromatic acids contain one or more carboxyl groups (–COOH) attached directly to the benzene ring. The acids in which the –COOH group is attached to the side-chain group may be regarded as aryl-substituted aliphatic acids. However, there are no characteristics differences in the behavior of the ring and side-chain acids. The term "aromatic acids" includes both classes of compounds.

5.5.1. Structure and nomenclature of aromatic carboxylic acids

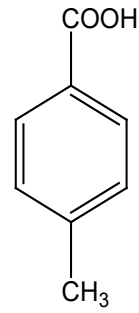
Aromatic carboxylic acids are called by their common names or after the name of the parent hydrocarbon. Thus:



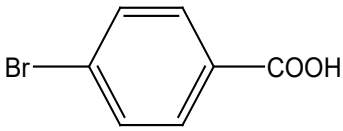
benzoic acid
(benzenecarboxylic acid)



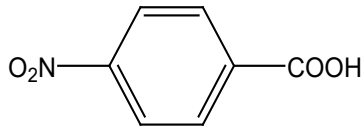
o-methylbenzoic acid
(2-methylbenzenecarboxylic acid)
(o-toluic aci)



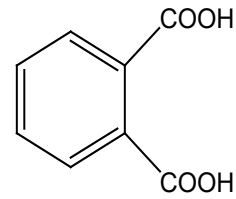
p-methylbenzoic acid
(4-methylbenzenecarboxylic acid)
(p-toluic aci)



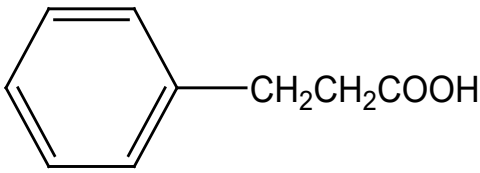
4-bromobenzoic acid



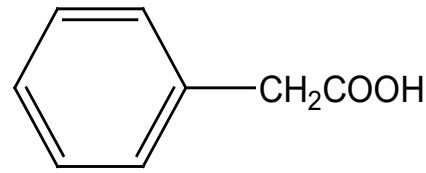
4-nitrobenzoic acid



benzene-1,2-dicarboxylic
acid (phthalic acid)



3-phenylpropanoic acid

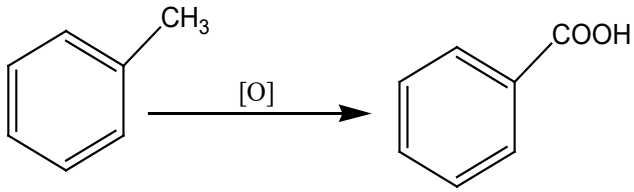


2-phenylethanoic acid

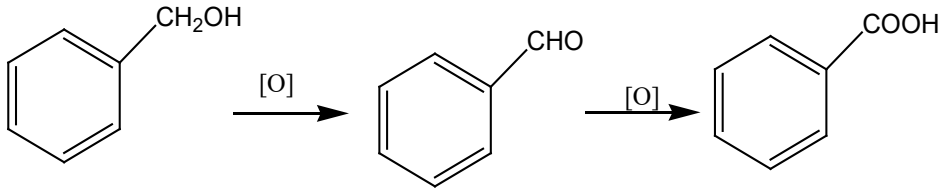
5.5.2. Preparation of aromatic carboxylic acids

Aromatic acids can be prepared by the same general methods which are available for aliphatic acids. In addition they may be obtained by oxidation of aromatic hydrocarbons having a side-chain.

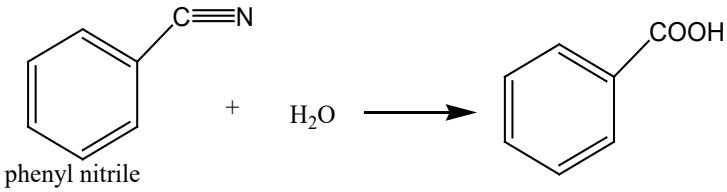
a. Oxidation of alkylbenzenes



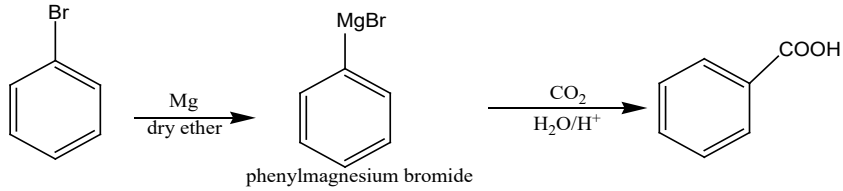
b. Oxidation of primary alcohols and aldehydes



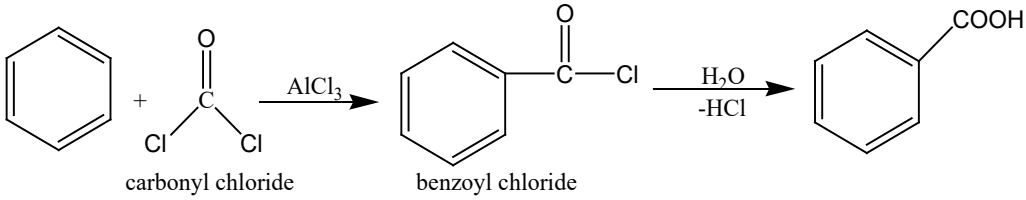
c. Hydrolysis of nitriles:



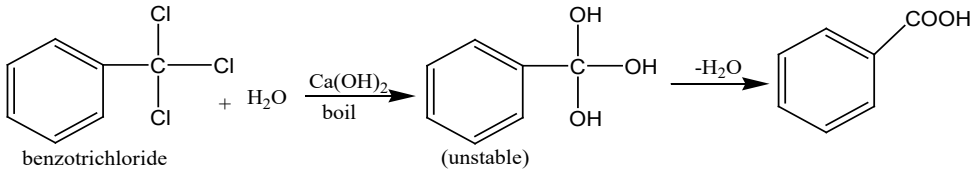
d. Carbonation of Grignard reagents:



e. Friedel-Crafts reaction:



f. Hydrolysis of trichlomethyl group on benzene ring:



5.5.3. Reactions of aromatic carboxylic acids

Aromatic acids are white crystalline solids, having higher melting points than aliphatic acids. They are slightly soluble in cold water but dissolve readily in hot water to form a colorless solution and on cooling, the acids recrystallise.

Aromatic carboxylic acids with unsubstituted benzene ring are slightly stronger acids than the aliphatic acids. Thus benzoic acid is stronger acid than acetic acid.

For the most part, the reactions of aromatic carboxylic acids are identical with those of aliphatic acids, the more important differences being in their rates.

Benzoic acid, the simplest aromatic carboxylic acid is more acidic than phenol since it can react with Na_2CO_3 or $NaHCO_3$ to liberate carbon dioxide gas. Its reactivity is attributed to its two parts: the carboxylic acid groupand the benzene ring.

a. Side chain reactions

i. Benzoic acid dissolves in water to form acidic solution which turns blue litmus paper into red.

$$C_6H_5COOH + H_2O \rightleftharpoons C_6H_5COO^- + H_3O^+$$

ii. Like aliphatic acids, aromatic carboxylic acids also form salts:

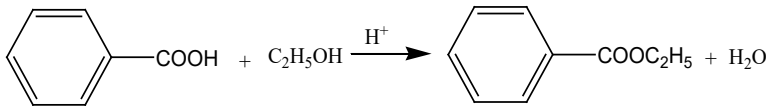
$$C_6H_5COOH + NaOH \rightarrow C_6H_5COONa + H_2O$$

$$2C_6H_5COOH + Na_2CO_3 \rightarrow 2C_6H_5COONa + CO_2 + H_2O$$

$$C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + H_2O + CO_2$$

$$2C_6H_5COOH + Na \rightarrow 2\,C_6H_5COONa + H_2$$

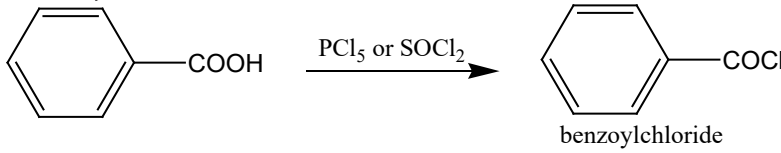
iii. Esterification: Aromatic acids having no substituent in the ortho-position to COOH group, are readily converted into esters by direct reaction with alcohols in the presence of mineral acids (HCl or H_2SO_4) as catalyst. If, however, an ortho substituent is present, the rate of esterification is considerably reduced. When both ortho positions are occupied, esterification does not occur at all.



Ethylbenzoate

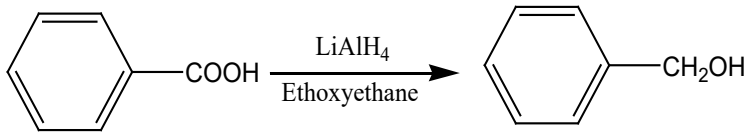
iv. Acid halides: Aromatic acids, like the aliphatic acids, are converted to

corresponding acid halides by heating with phosphorous pentachloride or with thionyl chloride.



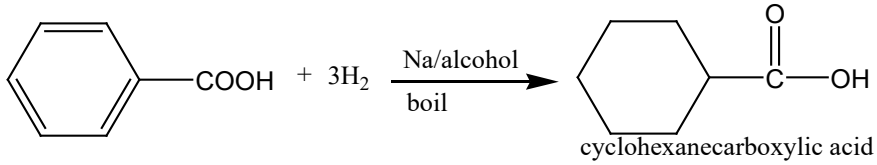
benzoylchloride

v. Benzyl alcohols: Aromatic acids on reduction in the presence of lithium aluminium hydride and ethoxyethane conditions give benzyl alcohols.



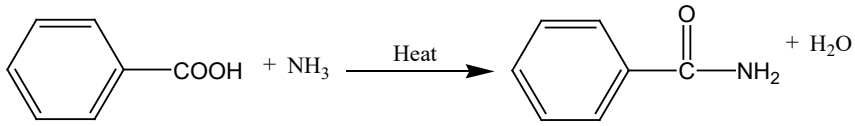
vi. Reduction: Ordinary reducing agents, like hydrogen and metal catalyst or sodium and alcohol, do not reduce the carboxyl group and rather reduce the aromatic ring. Thus benzoic acid when reduced with sodium and boiling alcohol is converted to cyclohexane carboxylic acid.

Remember here, in organic chemistry, that reduction of an organic compound means increase the hydrogen content in its molecule.



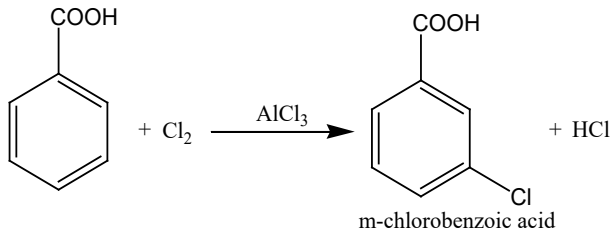
cyclohexanecarboxylic acid

vii. Aromatic acids form ammonium carboxylates which on heating give acid amides.



b. Benzene ring reactions

Aromatic acids undergo electrophilic substitution reactions in the benzene ring. The COOH group is meta-director and the substitution takes place less readily than in the parent hydrocarbon ring. For example,



m-chlorobenzoic acid

5.5.4 Uses benzoic acid and its derivatives

- Benzoic acid is used in medicine, in the dye industry for making aniline blue.
- Sodium benzoate being less toxic is used for preserving food products such as tomato ketchup and fruit juices.

Checking up 5.5

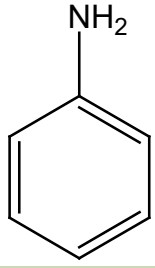
Show how ethylchloride can be used to produce benzoic acid indicating suitable reagents and conditions.

5.6. Aromatic amines

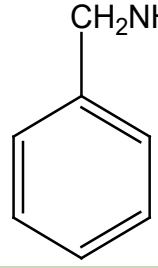
Activity 5.6

Observe the following structures and make research, then give their names and focus on the reactivity, preparations and uses of substances A and B.

A:



B:



The amino derivatives of the aromatic hydrocarbons are of two types:

a. Aromatic amines or aryl amines in which the $-NH_2$ group (or substituted $-NH_2$ group) is attached directly to a carbon of the benzene ring.

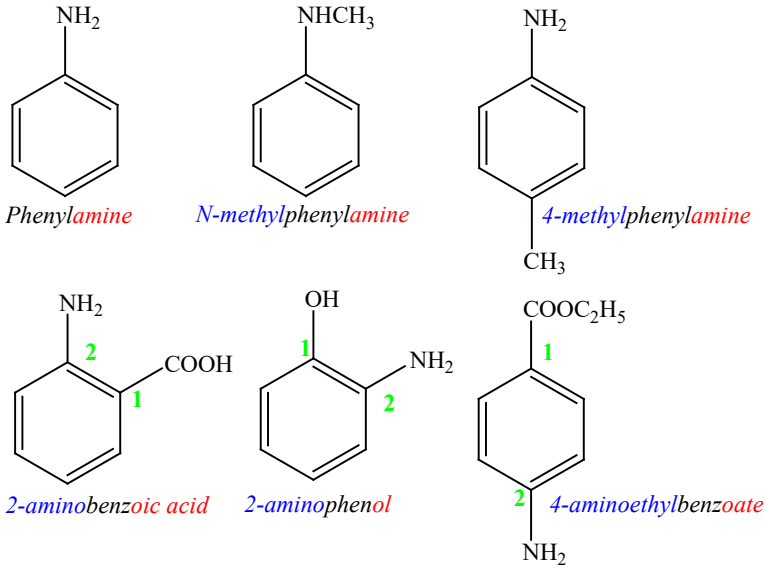
b. Aryl-alkyl or aralkyl amines in which the $-NH_2$ group is attached to a carbon of the side-chain.

Like the aliphatic amines, the aromatic amines may also be divided into primary, secondary and tertiary amines.

5.6.1. Structure and nomenclature of aromatic amines

In systematic naming, the numbering of carbon depends on the whole structure of the aromatic compound and the nature of the group attached to the benzene ring. In general, when more than one group are attached to the benzene ring, some groups are given priority as functional group.

Here is a simple list for guidance on precedence (priority) of groups: COOH > COO^- > COOR >COCl> $CONH_2$ > CN > CHO > COR > OH >NH_2 which means that from the list given, the amino is the least important, whereas the carboxylic acid group is the most important.

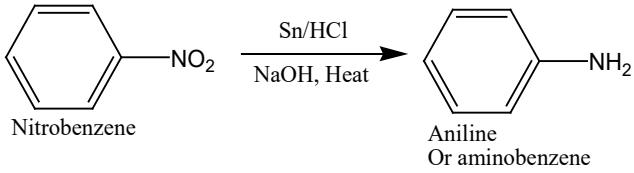


4-aminoethylbenzoate

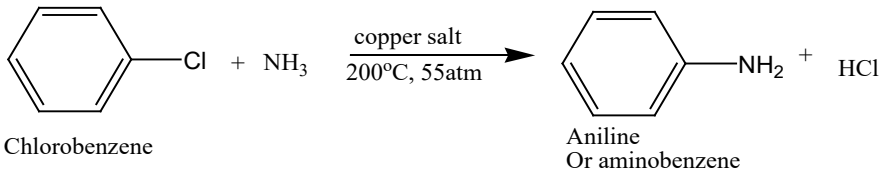
5.6.2. Preparation of Phenylamine and uses of its derivatives

a. Preparation of phenylamine

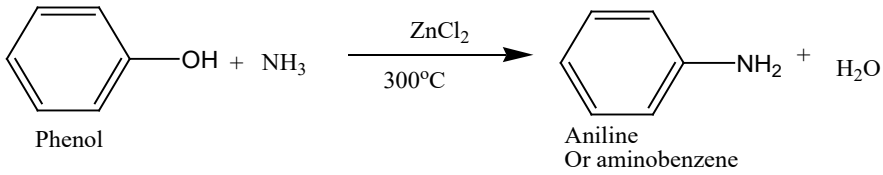
i. Phenylamine, like other arylamines, can be prepared by the reduction of nitro compounds.
The nitro compounds are treated with granulated tin, zinc or iron and HCl.



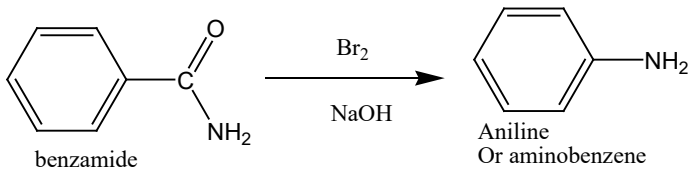
ii. Phenylamine can also be prepared by the addition of ammonia to chlorobenzene using copper (II) salts as catalyst at high temperature and high pressure.



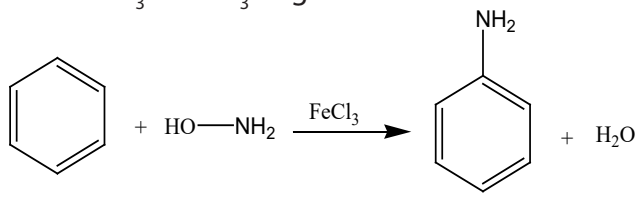
iii. Phenols react with ammonia in the presence of zinc chloride at about 300 °C to form the corresponding amines.



iv. Like primary aliphatic amines, primary aromatic amines can be obtained by the degradation of aryl amides with bromine in alkaline solution (Hofmann Degradation).



v. Aromatic hydrocarbons react directly with hydroxylamine in the presence of catalyst like $FeCl_3$ or $AlCl_3$ to give monoamines.



b. Uses of aniline and its derivatives

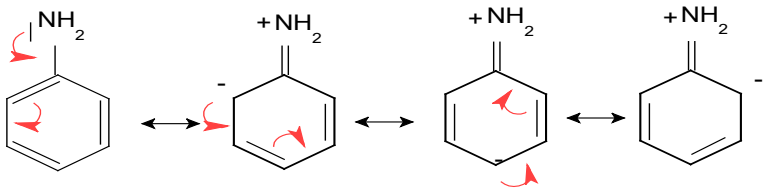
Derivatives of phenylamine or aniline are known as "Anilines". These are employed in various fields of science and everyday life as given below:

i. Anilines are used in the rubber industry for the processing of rubber material such as car tyres, balloons, gloves, etc.
ii. It is used as a dyeing agent in the manufacture of clothes such as jeans, etc
iii. It is employed in the production of drugs such as Paracetamol, Tylenol, Acetaminophen.
iv. It is used as a pesticide and fungicides in the agricultural industry.
v. It is utilized in the manufacture of polyurethane, which is in turn used in the making of plastics.

5.6.3. Alkalinity of phenylamine

Amines, both aliphatic and aromatic are basic. They are soluble in water. Phenylamine is weaker base than ammonia and aliphatic amines because the non-bonded electrons on the nitrogen atom are delocalized into the pi-system of the benzene ring. This makes the lone pair of electrons less available for reaction with a proton.

The delocalization of the lone pair of electrons on the nitrogen atom in phenylamine can be represented by the following resonance forms:



Thus aniline structure is greatly resonance stabilized.

5.6.4. Reactions of phenylamine

Aniline, also called phenylamine or aminobenze ($C_6H_5NH_2$), is a colorless oily liquid, slightly soluble in water and soluble in organic solvents. It turns brown on exposure to sunlight.

The aromatic amines in general give all the reactions of the amine group of aliphatic amines. However, the reactivity of the amine group is modified by delocalization of the non-bonded electrons on nitrogen atom into the pi-system of the aromatic ring.

a. Reaction of aniline with water (H_2O)

$$C_6H_5\text{-}NH_2 + H_2O \rightleftharpoons \underset{\text{anilinium ion}}{C_6H_5\text{-}NH_3^+} + OH^-$$

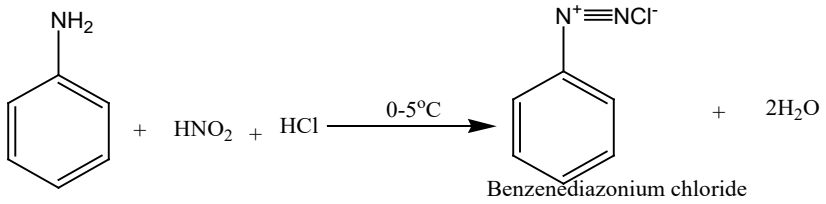
b. Reaction of aniline with hydrochloric acid (HCl)

Aniline is able to react with acids to produce salts. Phenylamine reacts with mineral acids to form phenylammonium chloride.

$$C_6H_5\text{-}NH_2 + HCl \longrightarrow C_6H_5\text{-}NH_3^+Cl^-$$

c. Reaction of aniline with nitrous acid (HNO_2)

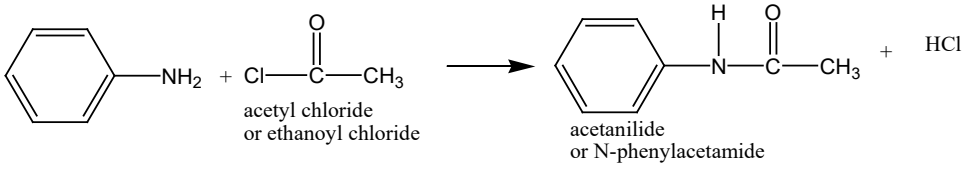
This is a very important reaction in the manufacture of dyes. The starting material is an aromatic amine such as phenylamine.

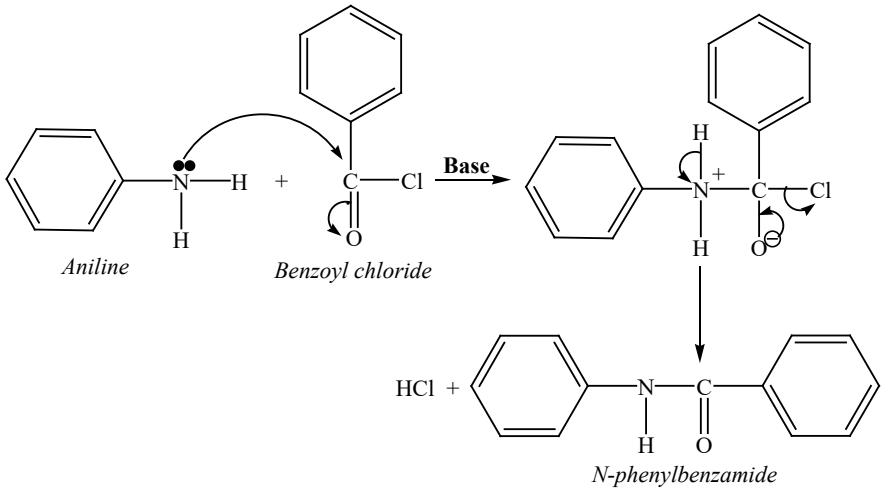


This reaction is called diazotization

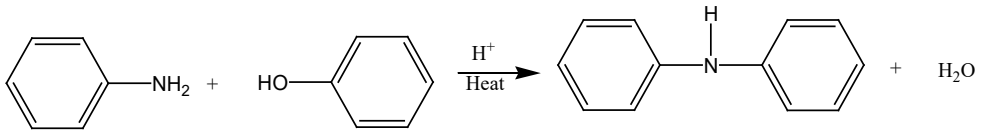
d. Reaction of aniline with ethanoyl chloride and benzoyl chloride

Phenylamine undergoes acylation to produce substituted amides.



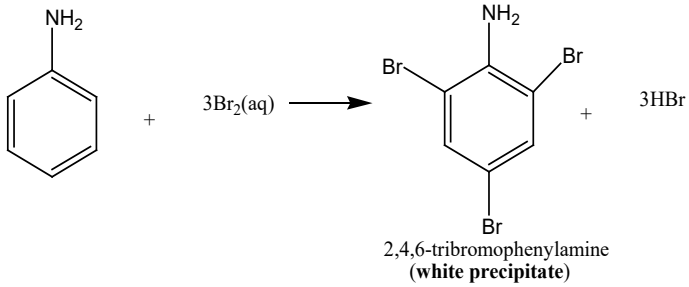


e. Reaction of aniline with phenol

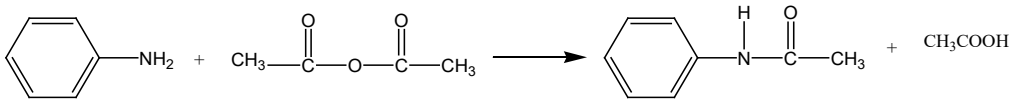


f. Reaction of aniline with halogens

The presence of amino group activates the ring and directs the incoming electrophiles to ortho and para positions. For example, addition of bromine water to phenylamine, results in formation of immediate white precipitate of 2,4,6-tribromophenylamine.



g. Reaction of aniline with acid anhydride

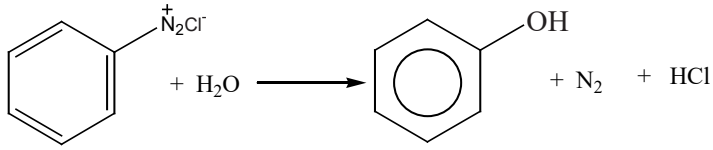


5.6.5. Reactions of diazonium salts

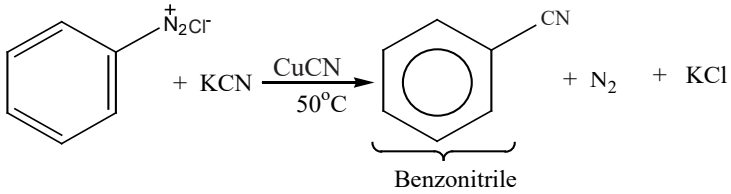
Aromatic amines when treated with nitrous acid in cold mineral acid solution, give a very important class of compounds known as aryldiazonium salts. For example, aniline reacts with nitrous acid in hydrochloric acid solution at 0-5^{0}C to form a solution of benzenediazonium chloride. The reaction producing these salts is referred to as Diazotization.

Diazonium salts give two types of reactions: (a) those in which the $-N_2X$ (where X is any anion, such as Cl^-, Br^-, NO_3^-, etc) is replaced by another univalent atom or group, with the liberation of nitrogen gas; (b) those in which the two nitrogen atoms are retained.

a. Diazonium salts with water



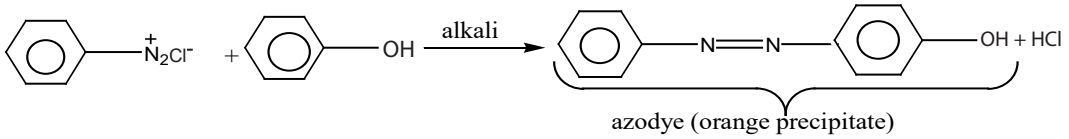
b. Diazonium salts with KCN



c. Coupling reactions

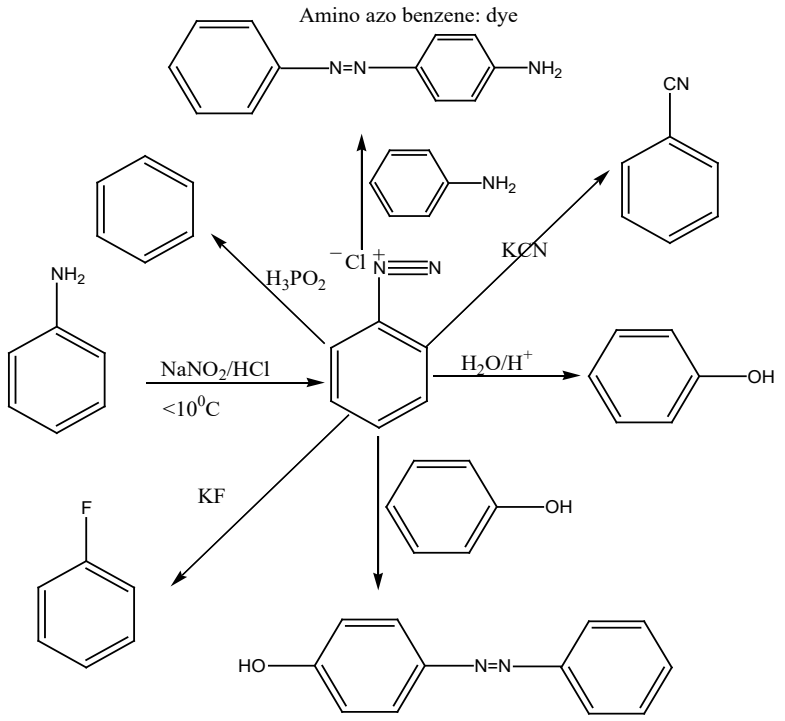
Diazonium salts act as electrophiles and react with highly activated benzene rings (like phenols and aromatic amines) to form brightly colored compounds called azo-compounds with the general formula: Ar-N=N-Ar, -N=N- is a linkage called azo linkage and responsible for the colour of the dye. These reactions are referred to as

coupling reactions and they proceed via electrophilic substitution mechanism.



A large number of benzene derivatives can be synthesized via diazonium salts. This will be illustrated by taking example of benzenediazonium chloride.

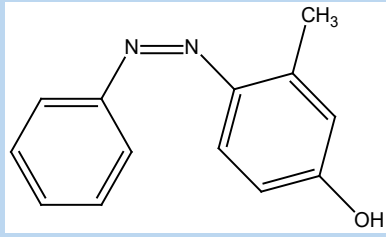
Reactions of benzenediazonium chloride are summarized in the following scheme:



Azo dyes: Coupling reaction

Checking up 5.6

1. Starting from benzene, outline how a sample of phenylamine can be made. Give equations and all essential reagents and conditions.
2. The azo dye shown below is made by a reaction between a diazonium ion and another arene.



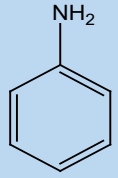
   a. Give a balanced equation to show the formation of the diazonium ion from phenylamine.

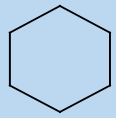
   b. What conditions would be needed for this reaction to occur?

   c. Identify the compound with which the diazonium ion joins to form the azo dye.

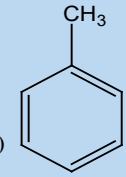
END UNIT ASSESSMENT

1. Which of the following compounds are not aromatic?

a) 

b) 

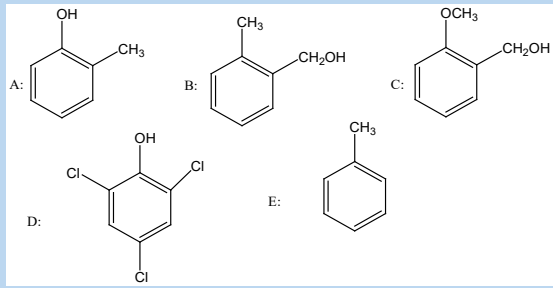
c)

d) 

e) $CH_3CH_2CH_2CH_2CH_2CH_3$

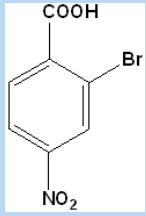
f) C_6H_5Cl

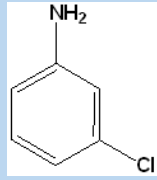
2. Which of the following structures are phenols and which are alcohols?

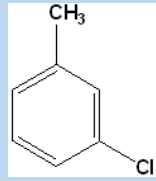


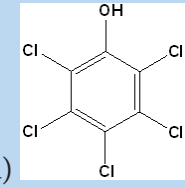
3. a. What would you expect to see when bromine is added to aqueous phenol?
   b. Why does bromine react more readily with phenol than with benzene?
   c. Give three uses of phenol.

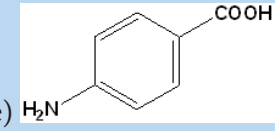
4. Write the IUPAC names of the following structures:

a) 

b) 

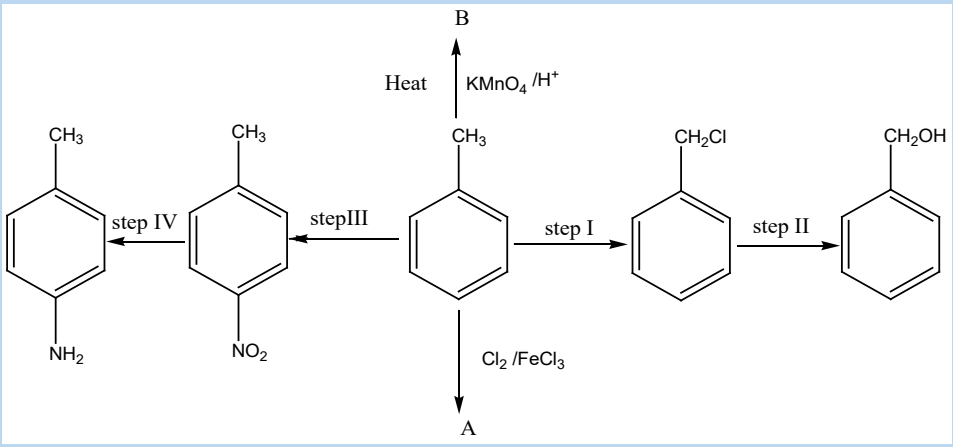
c) 

d) 

e) 

5. Write equations indicating the reagent and condition to show how the following conversions can be done:
   a. Benzene to 2-hydroxybenzoic acid (salicylic acid)
   b. Aniline to 3-bromophenol
   c. Benzene to paranitrobenzoic acid

6. The scheme below shows some reactions starting with methylbenzene



a. Give the reagents and conditions used to carry out reactions in the steps below

   i. Step I
   ii. Step II
   iii. Step III

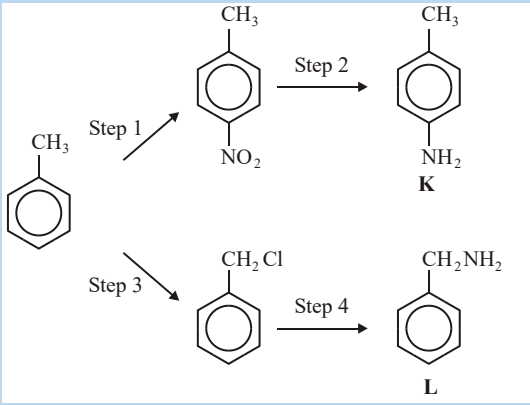
b. What type of reaction is involved in step IV?

c. Give the structural formula and name of compounds A and B

d. What is the name of the mechanism involved in

   i. Step I
   ii. Step II

7. The following reaction scheme shows the formation of two amines, K and L, from methylbenzene.



a. i. Give the reagents needed to carry out Step 1.

ii. Name and outline a mechanism for step 1.

b. Give the suitable reagent or combination of reagents for Step 2.

c. i. Give the reagent for Step 4 and state the condition to ensure that the primary amine is the major product.

ii. Name and outline a mechanism for Step 4.

d. Explain why amine K is a weaker base than ammonia.

e. Draw the structure of the organic compound formed when a large excess of bromomethane reacts with amine L.

f. Draw the structure of the organic compound formed when ethanoyl chloride reacts with amine L in an addition–elimination reaction.

UNIT 6

POLYMERS AND POLYMERIZATION

UNIT 6: POLYMERS AND POLYMERIZATION

Key Unit Competence

To be able to relate the types of polymers to their structural properties and uses

Learning objectives

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

- Define the terms monomer, polymer and polymerization;
- Describe the formation of polymers;
- Describe addition and condensation polymerization;
- Explain the terms thermosetting and thermosoftening of the plastics;
- Discuss the advantages and disadventages of both natural and synthetic polymers;
- Explain the biodegradability property of polymers based on their chemical structure;
- Use equations to distinguish between condensation and addition polymerization;
- Prepare phenol-methanol polymer (Bakelite);
- Relate the structure and properties of polymers to their uses in the plastic and textile industries;
- Reduce polymer wastes by reusing, recycling and appropriate disposal;

Introductory activity

The images below show materials commonly used in our daily life.

Observe carefully the following images in pairs, and answer the questions below:

a. Give the name for each material and one of its uses

b. Search in library (textbooks) and on internet, the chemical nature of each of the material mentioned above

c. Discuss the characteristics of the above materials and identify what do they have in common

Nowadays the materials made of plastics such as fibers, plastic and rubber materials, are all around us and are commonly called polymers by chemists. Polymers are commonly used in household utensils, automobiles, clothes, furniture, space-aircraft, biomedical and surgical components. Polymeric materials are light weight but can possess excellent mechanical properties and can be easily processed by different methods. In this unit you will learn more about polymers, their types and some important-synthetic and natural polymers.

6.1. Definition of monomer, polymer and polymerization

Activity 6.1

1. Explain the following terms:
   a. Polymer
   b. Polymerization
2. Identify the products made of polymers that are used at your home and mention at least 3 materials.

6.1.1. Monomer

The term monomer comes from mono "one" and meros "part",which expresses a single unit or a small molecular subunit that can be chemically bind to another identical or different molecule to form larger molecule (polymer).The monomer is repeated in the polymer chain and it is the basic unit which makes up the polymer. For instance in the large compound formed by $nA \rightarrow -A_n-$ where A is a monomer and the polymer is given by the repeated monomers in the chain; i.e. –A-A-A-A-A-A-. The larger molecules such as carbohydrates, lipids, nucleic acids and proteins are found in living systems, like our own bodies.

$nCH_2 = CH_2 \rightarrow [- CH_2 — CH_2 —]_n$, ethylene ($CH_2 = CH_2$) is a monomer

6.1.2. Polymer

A polymer is a large molecule (macromolecule or giant molecule) composed of smaller molecules (monomers) linked together by intermolecular covalent bonds. Polymers have a high molecular weight in the range of 10^3 to 10^7. A polymer can be represented as $(–A_n–)$ or (– A – A – A – A – A-……) which is a polymer of the monomer A.

Example: $nCH_2 = CH_2 \rightarrow [- CH_2 — CH_2 —]_n$,

Polyethylene, $[- CH_2 — CH_2 —]_n$ is a polymer while ethene,$CH_2 = CH_2$ is a monomer

More examples of polymers are given in the Table 6.1.

Table 6.1: Some examples of polymers and monomers

Monomer	Repeating unit/ Monomeric unit	Polymer
$H_2C{=}CH_2$ *Ethylene*	$-CH_2-CH_2-$	Polyethylene
$H_2C{=}CH$ (Cl) *Vinyl chloride*	$-CH_2-CH(Cl)-$	Polyvinyl chloride (PVC)
$H_2C{=}CH$ (C$_6$H$_5$) *Styrene*	$-CH_2-CH(C_6H_5)-$	Polystyrene

6.1.3. Polymerization

Polymerization is the process in which monomer units are linked by chemical reaction to form long chains (polymers).

For example, a gaseous compound, Butadiene, with a molecular weight of 54 g/mole combines nearly 4000 times by polymerization and gives a polymer, known as polybutadiene.

Butadiene + butadiene + butadiene + … + butadiene → Polybutadiene

Note: 1.The degree of polymerization (n) is defined as the number of monomeric units in a macromolecule or polymer or oligomer (a polymer consisting of few number of monomers units) molecule.

2. A polymer formed by identical monomers is called **homopolymrer** whilea polymer formed by different monomers is a **copolymer**.

Preparation protocol of plastic from milk

Experimental activity for the preparation of plastic from Milk

Materials

- 500ml fresh milk
- 60ml vinegar
- One beaker of 100 mL
- 2 beakers of 1 L each
- 1 spoon
- 1 strainer
- Aluminum foil
- Thermometer
- Hot plate or Bunsen burner and stand
- Matches if using a Bunsen burner

Procedure

1. Assemble all materials and chemicals
2. Turn on the Bunsen burner or hotplate.
3. Place beaker of milk over heat. Stir constantly.
4. Place thermometer into the milk. Heat milk until it reaches 37°C.
5. Remove from heat and immediately add vinegar, stirring constantly. Here, the teacher should ask the students what they think will happen when the vinegar is added.
6. The solution will rapidly separate into curds suspended in a clear yellow liquid.
7. Strain the solution through the strainer into the empty 1L beaker. Hold up the beaker to see the clear liquid.
8. Scoop the curd onto a large piece of aluminum foil and press out into a thin layer. Pass the aluminum foil around the class. Then dry especially overnight

Milk is a colloid, which is defined as a suspension of large molecules of proteins in water. Essentially, milk is a suspension of protein globules in water.

These proteins can undergo polymerization to create a natural plastic, as the casein molecules are associated together in long chains. Proteins are generally unstable and are prone to unfolding, which changes the natural state of the protein. This process is called denaturing. The addition of acid, in this case vinegar, causes the casein protein to unfold and rearrange into the long chains of a polymer. The process then causes the casein to precipitate out of the milk, leaving a clear watery substance behind. The casein can then be formed into various shapes before drying. In our experiment, thermal energy in the form of heat was applied to speed the process and cause a more complete separation.

Checking up 6.1

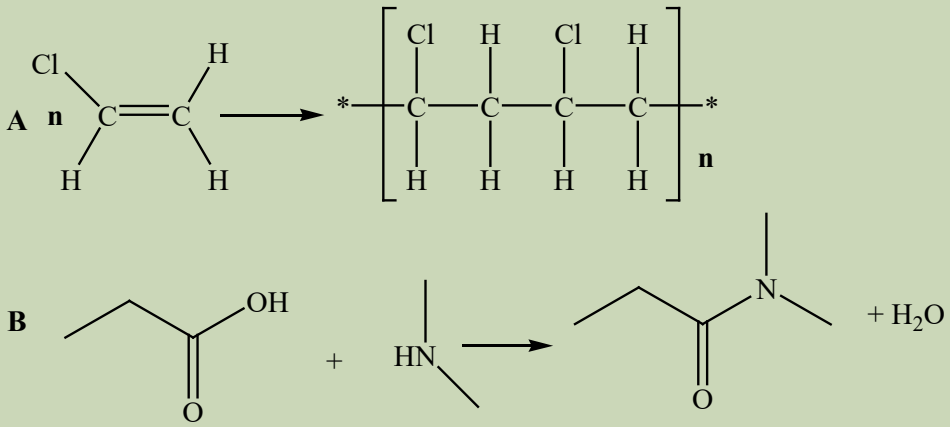
1. Draw two repeat units of the polymer formed from each of the following monomers or pair of monomers.
   a. CH_2=CH-$OCOCH_3$
   b. CH_2=CCl-CH=CH_2
   c. CH_2=CHCl and CH_2=CH-CH_3

2. Draw the monomers from which the following polymers are made:
   a. ---CH_2-CH(CN)-CH_2-CH(CN)-CH_2—
   b. ---CH_2-C(CN)=CH-CH(CN)-CH_2-C(CN)=CH-CH(CN)-CH_2---

6.2. Types of polymerisation

Activity 6.2

1. Observe carefully the following chemical reactions, and then answer the questions;



Compare and contrast the two chemical reactions

2. Distinguish between addition polymerization from condensation polymerization and give an example for each.

There two types of polymerization reaction: Addition polymerization and condensation polymerization.

6.2.1. Addition polymerization

Addition polymerization is a process where monomers are linked together to form a polymer, without the loss of atoms from the molecules. When the monomer molecules add up to form the polymer, the process is called "***Addition polymerization***".

This involves the combination together of monomer units to give new product (polymer) having the same empirical formula to the monomer but having relative molecular weight.The monomer units are usually unsaturated compounds.

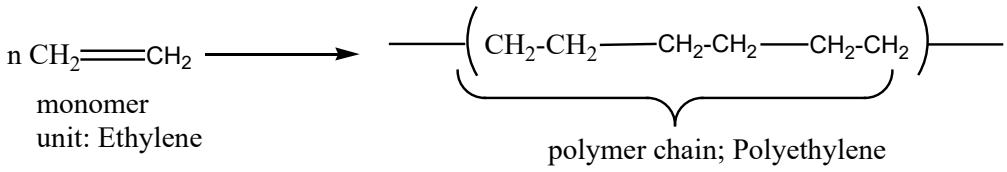
Some examples of addition polymers are polyethylene, polypropylene, polystyrene, polyvinyl acetate, polyvinyl chloride (PVC), rubber, polytetrafluoroethylene (Teflon), etc.

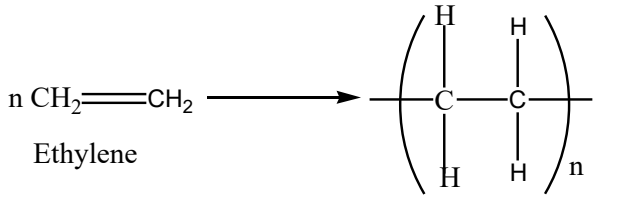
Example 1: Formation of polyethene or polyethylene

Polyethene is formed by addition of $CH_2=CH_2$ monomer molecules linked together as follows

$$n\ CH_2 = CH_2 \rightarrow [-\ CH_2 — CH_2 —]_n$$

Ethene Polyethene





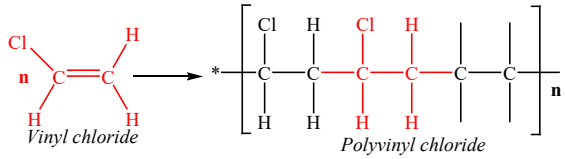
Polyethylene(PE)

Example 2: Formation of PVC (polyvinylchloride)

PVC (polyvinyl chloride) is found in plastic wrap, simulated leather, water pipes, and garden hoses, it is formed from vinyl chloride ($H_2C=CHCl$).

Vinyl is a common name for ethylene, PVC is formed from the following reaction:

$nCH_2=CHCl \rightarrow [-CH_2-CHCl-]_n$, where **n** can be between 700-1500



Example 3: Formation of rubber: Rubber can be natural or synthetic

Rubber is a natural polymer of isoprene (2-methyl-1,3-butadiene). It is formed by a linear 1,4- addition polymer of isoprene.

Natural rubber has elastic properties because it has the ability to return to its original shape after being stretched or deformed. Therefore it is known as Elastomer. Natural rubber is prepared from latex which is a colloidal solution of rubber in water.

Addition polymerization takes place in three steps like initiation, propagation and termination reading to the formation of polymer.

i. Chain initiation

A peroxide molecule breaks up into two reactive free radicals. Light or heat can provide the energy needed for this process. The chain is initiated by free radicals produced by reaction between some of the ethene and the oxygen initiator from peroxide.

The process of initiation involves two parts: generation of initiator free radical and initiation of polymerization reaction.

The generation of free radicals is shown by the following equation:

$$\underset{\textit{Peroxide}}{ROOR} + \text{energy} \longrightarrow \underset{\textit{Free radical initiator}}{2\,RO\bullet}$$

The second part of initiation occurs when the free radical initiator attacks and attaches to a monomer molecule. This forms a new free radical, which is called the activated monomer as indicated in the chemical equation below:

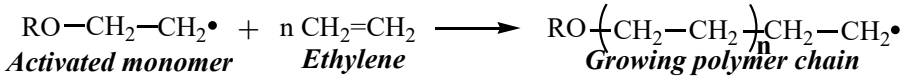
$$\underset{\textit{Free radical initiator}}{RO\bullet} + \underset{\textit{Ethylene}}{CH_2=CH_2} \longrightarrow \underset{\textit{Activated monomer}}{RO-CH_2-CH_2\bullet}$$

ii. Chain propagation

During this step, there is successive addition of large number of monomer molecules to form polymer free radical chain.In the propagation phase, the newly-formed activated monomer attacks and attaches to the double bond of another monomer molecule. This addition occurs again and again to make the long polymer chain.

Example of long chain that can be formed:RO-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2.

The equation of the above polymer can be written as follows:



The "n" stands for any number of monomer molecules or degree of polymerization typically in the thousands.

iii. Chain termination

Termination step involves the coupling of two free radicals in order to produce a final molecule. The process is a termination step because no new free radicals are formed.

The equation representing this step of the chain reaction can be written simply as:

$R^{\cdot} + R^{\cdot} \rightarrow R\text{-}R$

Example:

$R\text{-}(CH_2{=}CH_2)n\text{-}CH_2\text{-}CH_2^{\cdot} + {}^{\cdot}CH_2\text{-}CH_2\text{-}(CH_2\text{-}CH_2)m\text{-}R \rightarrow$

$R\text{-}(CH_2\text{-}CH_2)\ n\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2(CH_2\text{-}CH_2)m\ \text{–}R$

Remember: The R and R' groups can be the original free radicals, the growing polymer chains, or even one of each.

6.2.2. Condensation polymerization

Condensation polymerization is a process where two or more monomers chemically combine to form a polymer with elimination of simple molecules like water, ammonia, hydrogen chloride, alcohol, etc.

In this type of reaction, each monomer generally contains two functional groups for the condensation reaction to take place.

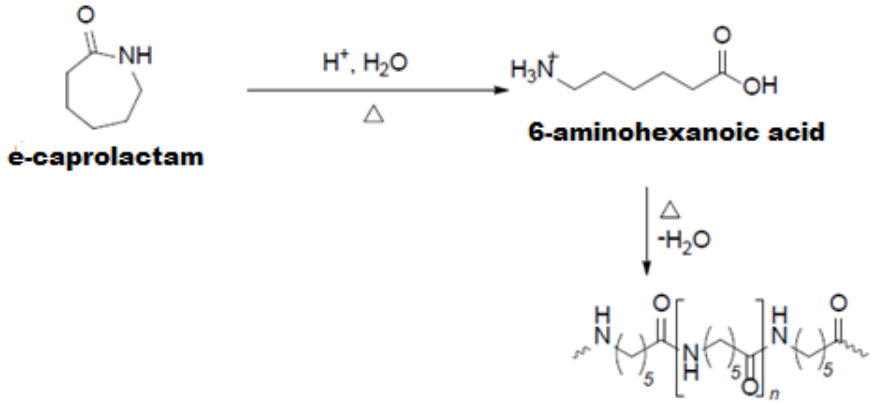
There are two main types: **polyamides** which are formed between a diol with a dicarboxylic acid and **polyesters** which are formed when a dicarboxylic acid and a diamine react to form nylons.The condensation polymers include Nylons, Terylene, Kevlar polymer, proteins, cellulose, Bakelite, Dacron, etc.

Example 1: FORMATION OF POLYAMIDES

This type of polymers is formed by the result of generation of amide bonds in the polymerization reaction.

i. Formation of Nylon

Nylon 6 and nylon- 6, 6 are important examples for this type of polymers nylon 6 is synthesized from e-caprolactam, which on heating decomposes into 6-aminohexanoic acid that polymerizes into nylon 6. Here the number 6 represents the number of carbon atoms present in the monomer unit.



Nylon -6,6 is produced by the condensation reaction between two monomer units adipic acid and 1,6-hexanediamine in the presence of heat. This is formed from a six-carbon diacid and a six-carbon diamine as shown below.

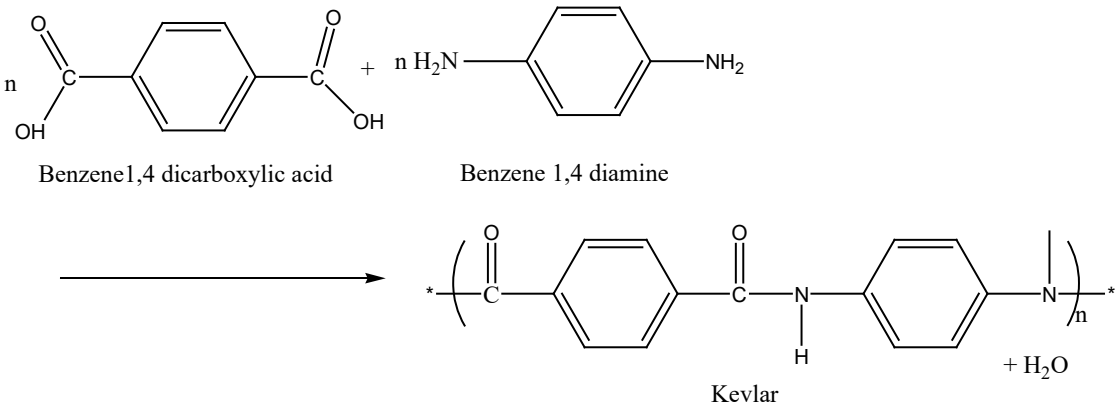
$$nH_2N{-}(CH_2)_6{-}NH_2 + nHOOC{-}(CH_2)_4{-}COOH \xrightarrow{-2nH_20} -(NH{-}(CH_2)_6{-}NH{-}CO{-}(CH_2)_4{-}CO)_n-$$

1, 6-Hexanediamine Adipic acid Nylon -6,6

ii. Formation of Kevlar

Kevlar is formed from the polymerization of benzene -1,4-diamine and benzene-1,4-dioic acid as follows:

Benzene-1,4-dioic acid + Benzene-1,4-diamine → Kevlar + water



Benzene1,4 dicarboxylic acid Benzene 1,4 diamine

Kevlar

In that polymerization $-NH_2$ group of hexamethylenediamine reacts with –COOH group of adipic acid to form –NH-CO- amide linkage with elimination of H_2O.

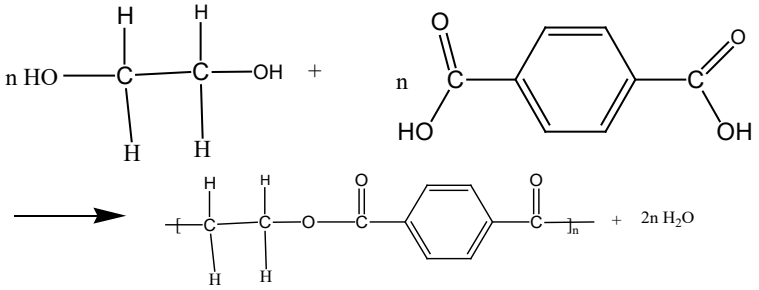
Polyamides such as nylon-6,6 and Kevlar are widely used in clothing. Kevlar has some remarkable properties,including fire resistance and higher strength than steel. It is used to make protective clothing-for example for fighters,bulletproof vests and helmets.

Example 2: FORMATION OF POLYESTERS

i. Formation of Terylene

Terylene is formed by reacting 1,2- ethanediol and benzene -1,4-dicarboxylic acid with loss of water molecules. Terylene comes from terephtalic acid and ethylene glycol.

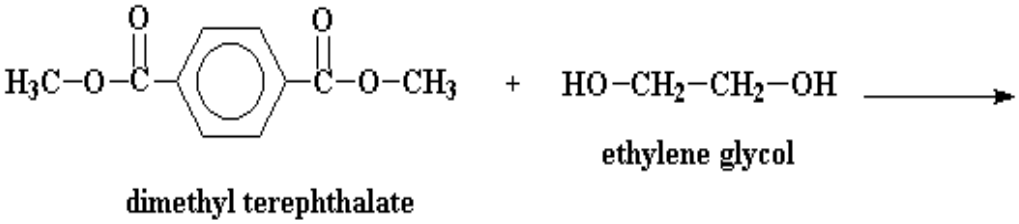
Benzene -1,4-dicaboxylic acid + ethane-1,2-diol (ethylene glycol) → Terylene + water



ii. Formation of Dacron

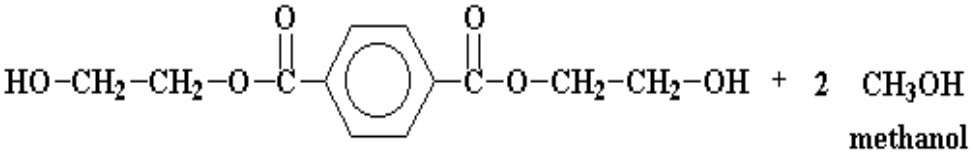
It is made from dimethyl -1,4-benzene dicarboxylate and 1,2-ethane diol:

Dimethyl -1,4-benzene dicarboxylate + 1,2-ethane diol → Dacron + methanol



dimethyl terephthalate

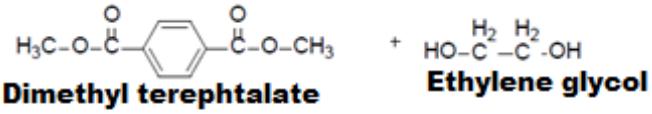
ethylene glycol



bis-(2-hydroxyethyl)terephthalate

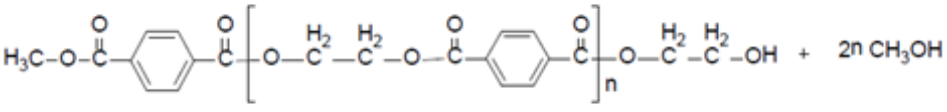
methanol

Or



Dimethyl terephtalate

Ethylene glycol

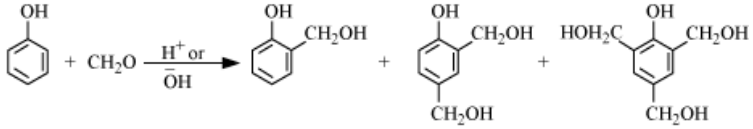


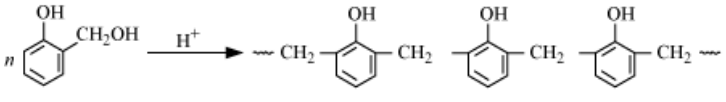
Dacron, a polyester

Other polymer formation:

Formation of bakelite:

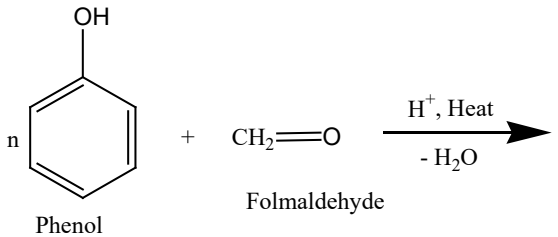
Bakelite (polyoxybenzylmethyleneglycolanhydride) is the oldest synthetic polymer. It is formed from phenol and formaldehyde in the presence of either an acid or a base catalyst. The initial product could be Novalac, then novalac on heating with formaldehyde undergoes cross linking to form bakelite.

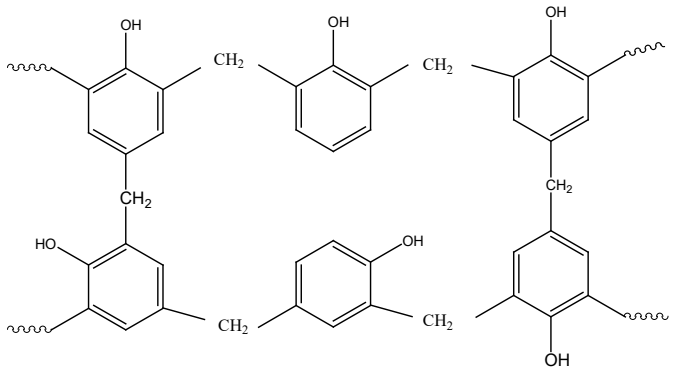




Novolac

The general equation is:





Bakelite

Experiment on the preparation of phenol formaldehyde resin (bakelite)

Chemicals:

- Glacial acetic acid,
- 40% formaldehyde solution,
- Phenol, conc. H_2SO_4

Apparatus Required:

- Glass rod,
- beakers,
- funnel,
- measuring cylinder,
- dropper
- Filter paper

Procedure:

1. Place 5ml of glacial acetic acid and 2.5ml of 40% formaldehyde solution in a 500ml beaker and add 2 grams of phenol.
2. Add few ml of conc. Sulphuric acid into the mixture carefully. Within 5 min, a large mass of plastic is formed
3. The residue obtained is washed several times with distilled water, and filtered product is dried and yield is calculated.

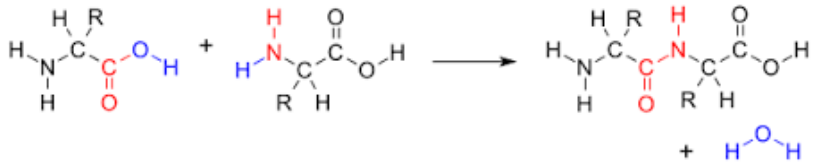
Conclusion:

A mixture of phenol and formaldehyde are allowed to react in the presence of a catalyst. The process involves formation of methylene bridges in *ortho*, *para* or *both ortho* and *para* positions. This results first in the formation of linear polymer (Called *NOVALAC*) and then in to cross-linked polymer called phenol-formaldehyde resin or *bakelite*.

Protein formation:

Polymerization of amino acids:

- Two amino acids can be linked by a condensation reaction (by removing of water molecule)
- Peptide bond is formed between the carbon atom in the acid group and the nitrogen atom in the amine group.
- The result molecule is called a dipeptide
- A chain of amino acids can be built up in this way and is called **polypeptide**
- A protein may just contain one polypeptide or may have two or more chains that interact



The polyester Dacron and the polyamide Nylon-6,6, are two examples of synthetic condensation polymers. Some differences between addition polymerization and condensation polymerization are summarized in Table 6.2.

Table 6.2. Comparison between addition and condensation polymerization

Addition polymerization	Condensation polymerization
1. Involves unsaturated monomer like ethylene, vinyl chloride, styrene etc.	1. Involves substances with at least 2 different reacting functional groups like ethylene glycol (2-COOH groups).
2. Fast addition of monomers.	2. Step-wise slow addition
3. Initiator is necessary to catalyze the polymerization	3. Catalyst is not necessary
4. No elimination products	4. Small molecule like H_2O, HCl, or CH_3OH is often eliminated.
5. Polymers made are, for example, polyethene, polypropylene, polybutadiene, polyvinylchloride.	5. Polymers made are, for example, terylene, nylon, formaldehyde-resins, silicones

Checking up 6.2.

1. Write down a balanced chemical equation for reaction between hexane -1,6-diamine and hexane-1,6-dioyl chloride.
2. Differentiate addition polymers and condensation polymers by using examples.
3. Nylon is a condensation polymer formed from two monomers represented by NH_2-X-NH_2 and HOOC-Y-COOH.
   a. Draw a structure to represent the repeat unit of the nylon polymer from two monomers and indicate the linkage group by a ring.
   b. What is name given to the linkage group in nylon polymer?
4. Nylon 6,6 has a structure containing the following repeat unit:

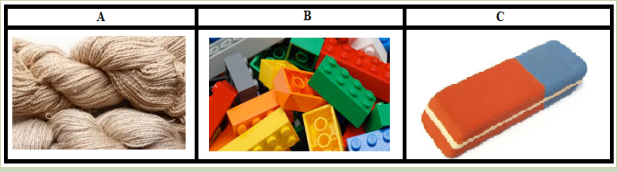
   $$-CO-(CH_2)_4-CO-NH-(CH_2)_6-NH-$$

   a. What type of polymer is this?
   b. Give the structural formulae of the monomers of this polymer.
   c. What natural polymer has the same linkage as Nylon 6,6.

6.3. Classes and types of polymers

Activity 6.3

1. a. Briefly, discuss and emphasize the differences between natural and synthetic polymers
   b. What are the materials used in our daily life that are made of:
      i. Natural polymers
      ii. Synthetic polymers
2. Discuss the use of plastics versus metals
3. Observe carefully the following image and then answer to the questions;



   a. Explain the materials used to make each image
   b. Compare the materials represented by the above images

6.3.1 Classes of polymers

In general, polymers are classified into two classes such as natural polymers and synthetic polymers.

6.3.1.1 Natural polymers

Natural polymers are those that are obtained from natural sources. They are made naturally and are found in plants and animals or other living organisms.

For examples: cotton, silk, wool, natural rubber, cellulose and proteins.

a. Silk

Silk is a fine continuous protein fiber produced by various insects' larvae usually for cocoons.It is mainly a lustrous elastic fiber produced by silkworms and used for textiles.

For example, orb-weaving spiders produce a variety of different silks with diverse properties, each tailored to achieve a certain task. Most arthropod species produce silks used for building structures to capture prey and protect their offspring against environmental hazards.

b. Cotton

Cotton is soft, fluffy staple fiber that grows in a boll, or protective case, around the seeds of the cotton plants. Cotton is natural cellulosic fiber.

c. Proteins

Proteins are highly complex substance made up of hundreds of thousands of smaller units called amino acids which are attached to one another to make along chain. There are around 20 different amino acids that occur naturally in proteins. Many proteins act as enzymes that catalyze biochemical reactions and are essential to metabolic functions.

d. Natural rubber

Natural rubber is an elastic material obtained from the latex sap of trees that can be vulcanized and finished into a variety of products. It is a hydrocarbon polymer of isoprene (2-methylbuta-1,3-diene) obtained from latex. Latex is an emulsion of rubber particles in water that coagulate by addition of ethanoic acid.

The molecular formula of natural rubber is: $-CH_2-C(CH_3)=CH-CH_2-C(CH_3)=CH-CH_2-$ which is polyisoprene, having the monomer of isoprene $(CH_2=C(CH_3)CH=CH_2$.

e. Cellulose

Cellulose is an insoluble substance which is the main constituent of plant cell walls and the vegetable fibres such as cotton. It is a polysaccharide consisting of chains of glucose monomers.

6.3.1.2 Synthetic polymers

A part from the natural polymers, there are also synthetic polymers which are synthesized in the laboratory. They are manufactured from lower mass molecular compounds. Synthetic polymers (polymer made by two different monomers) are copolymers formed when many molecules of buta-1,3-diene or its derivatives chemical are joined with unsaturated compound. They can also be either thermosetting or thermoplastic polymers.

Examples: Polyethene is a polymer formed by linking together a large number of ethene molecules. PVC, Nylons, Terylene and Polystyrene.etc

6.3.2 Types of polymers

The polymers can be classified into three main different types such as (i) plastics, (ii) rubber, and (iii) fibers.

a. Plastics

The plastics are types of polymers that are the most commonly used. Plastics are polymerized organic substances, solid of high molar mass, which at some time in its manufacture can be shaped by flow. They are electrical and thermal insulators. Their advantage is recycling and this allows them to be used many times. Plastics are materials that can be softened (melted) by heat and re-formed (molded) into another shape. The disadvantage of plastics is in their temperature resistance as they get quite fast soft and loose mechanical properties.

Examples: fibers, Polyethylene, Teflon, Plexiglas, PVC, etc.

b. Rubbers

Rubber is a tough elastic polymeric substance made from the latex of a tropical plant or synthetically made. There are two types of rubbers; natural rubber and synthetic rubber.Rubbers are soft and springy and return to their original shape after being deformed.

- **Natural rubber**

Natural rubber is an elastic material obtained from the latex sap of trees that can be vulcanized and finished into a variety of products. Natural rubber is extracted from

rubber producing plants, most notably the tree "Hevea brasiliensis", which originates from South America.

Natural rubber is a polymer of the monomer 2-methylbuta-1,3-diene (isoprene). Poly(2-methylbuta-1,3-diene) can exist in cis- and trans- isomeric forms. Natural rubber is the cis-form.

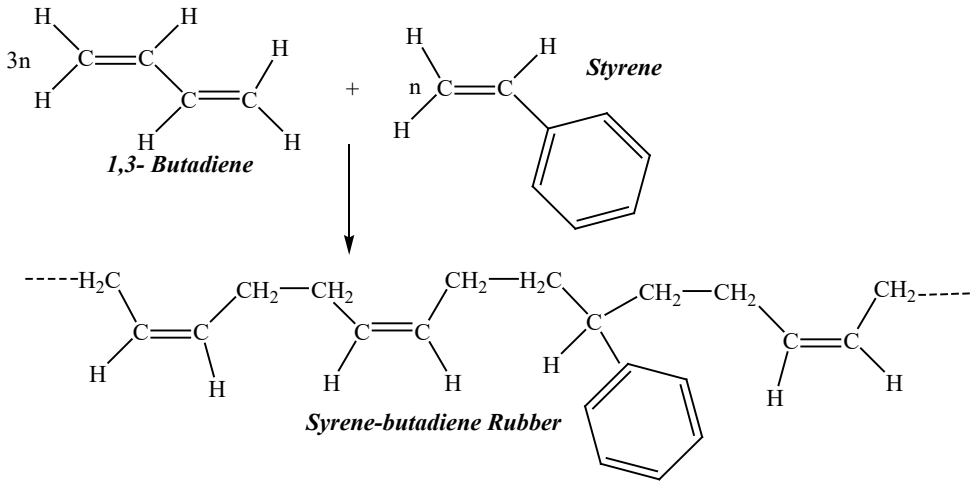
- **Synthetic rubbe**r

A synthetic rubber is any artificial elastomer (man-made polymer having elastic properties)

There are several synthetic rubbers in production. These are produced in a similar way to plastics, by a chemical process known as polymerization. They include neoprene, Buna rubbers, and butyl rubber. Synthetic rubbers have usually been developed with specific properties for specialist applications. Synthetic rubber can be made from polymerizing buta -1,3-diene, CH_2=CH-CH=CH=CH_2.

The synthetic Rubber is an important addition of polymers that are obtained by polymerizing a mixture of two or more monomers. An example is styrene-butadiene rubber (SBR), a synthetic rubber formed by a mixture of 1,3-butadiene and styrene in a 3 to 1 ratio, respectively.

The structure of SBR is the following:



The combination of monomer units gives a new polymer product having the same empirical formula to the monomer but having a higher molecular weight. The monomer units are usually unsaturated compounds (i.e. alkenes and their derivatives).

Alkenes can be made to join together in the presence of high pressure and by adding a suitable catalyst. The π-bond breaks and the molecules are held together.

c. Fibers

Fiber (from Latin Fibra) is a natural or synthetic substance that is significantly longer. Fibers are often used in the manufacture of other materials. In manufacture of strongest engineering materials often fibers are incorporated, for example carbon fiber and ultra-high molecular-weight polyethylene.

Fibers are strong polymers that do not change shape easily. They are made into thin, strong threads which can be woven together, Nylon is an example.

- **Natural fiber**

Natural fibers are substances produced by plants and animals that can be turned into filament, thread or rope and further be woven, woolen, matted or bound.

- **Synthetic fiber**

A man made textile fibers including usually those made from natural materials such as rayon and acetate as well as fully synthetic fibers (such as nylon or acrylic fibers).

Checking up 6.3

1. Polymers found in natural materials can be formed by the reaction between amino acids

   a. Deduce the formula of the product formed when two molecules of alanine, $CH_3CH(NH_2)COOH$ react together and deduce the name of linkage present in the product.

   b. Give the name of the type of naturally occurring polymer containing this linkage.

2. Write the structural formula of;

   a. Polypropylene (PP)

   b. Polyvinyl chloride (PVC)

   c. Polystyrene (PS)

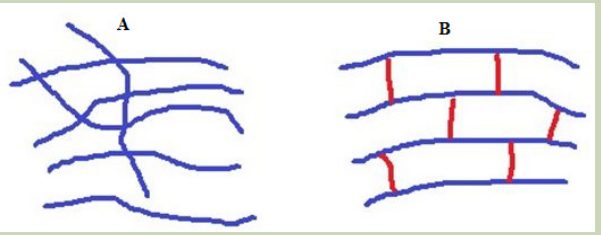
   d. Nylon 6, nylon-6,6

   e. Teflon (polytetrafluoroethylene)

6.4. Properties of polymers

Activity 6.4

1. Differentiate the biodegradable from non-biodegradable polymers.
2. Explain what your understanding by the following terms;
   a. Themosetting plastics
   b. Thermoplastics
3. Observe carefully the following structures and answer the questions that follow:



   a. Compare and contrast the two structures A and B
   b. What do you think are these above structures?

Polymers or in general plastics have different properties depending on their nature. Among the properties, they can be thermosetting or thermosoftening whereas on the other side they can be biodegradable or non-biodegradable.

6.4.1. Thermosoftening and thermosetting properties

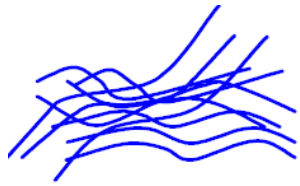
Thermosoftening (thermoplastics) and thermosetting (thermosets) are properties of polymers on how they soften on heating and harden on cooling.

a. Properties of Thermosoftening polymers

Thermosoftening polymers have weak intermolecular forces and they can be remolded into new shapes. They can be softened between 65 °C and 200°C and can be returned to their original state by heating.

At higher temperatures **thermoplastic** becomes liquid and suitable for **injection molding**. After cooling, melt harden and keep a given shape. Disadvantage of thermoplastic is in their temperature resistance, meaning that they get quite fast soft and loose mechanical properties. **Thermoplastic** have linear and complex molecules.

Thermosoftening is a property by which some polymers can be softened on heating. This allow them to cool and harden, and then can be resoftened many times.The following is the structure of thermosoftening polymers.



For the thermosoftening polymers, the Van der Waal's forces between the chains are often very strong and the polymers have relatively high melting and boiling points. Due to their variable chain length, most polymers have different Van der Waal's forces and these polymers tend to melt gradually over a range of temperatures rather than sharply at a fixed temperature. As the chains are not rigidly held in place by each other, polymers tend to be reasonably soft.

The density and strength of addition polymers varies widely and they depend to a certain extent on the length of the hydrocarbon chain, but depend much more strongly on the nature and extent of the branching on the chain.

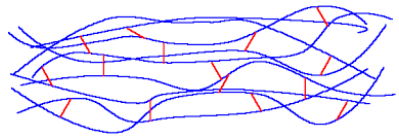
Polymers which have very few branches are very compact and the chains can thus pack together very efficiently.examples P.V.C, Dacron, Polypropene. Etc

b. Properties of Thermosetting polymers

Thermosetting Polymers are some polymers which cannot be reshaped once heated as they are completely decomposed. Thermosetting polymers include phenol-formaldehyde, urea-aldehyde, silicones and allyls. Thermosetting Polymers have cross-links (covalent bonds between chains) that do not break on heating and they comprise three dimensional network structure. The greater the degree of cross-linking makes the polymer more rigid. These polymers are generally insoluble in solvents and have good heat resistance quality.

Thermosetting polymers are generally stronger than thermoplastic polymers due to strong covalent linkage between polymer chains.

When thermosetting plastics or thermosets are molded, covalent bonds are formed between the chains. They are more brittle in nature and their shape is permanent. Once they are softened, they cannot be returned to their original state by heating. Thermosetting polymers include phenol-formaldehyde, urea-aldehyde, silicones and allyls.The following is the structure of thermosetting polymers;



Examples :Bakelite ,epoxy-resins,silicones,formica .etc

Advantages and disadvantages of the above mentioned properties:

- **Advantages**
  - Thermoplastics are convenient for manufacturers to use and they are not expensive. They are even recyclable.
  - Thermosets retain their strength and shape even when heated, they have high heat resistance and structural integrity.
- **Disadvantages**
  - Thermoplasts melt and some degrade in direct sunlight or under high U.V light levels. Many suffer from creep, a relaxation of the material under long term loading. They tend to fracture rather than deform under high stress.
  - Thermosets absorb moisture and toxicity easily.
  - They are not recyclable.

6.4.2. Biodegradable and non-biodegradable properties

These are the properties of polymers depending on how they react overtime as a result of biological activity especially to be broken by microorganisms.

If they do not respond on the degradation or decomposition, they are said to be non-biodegradable polymers.

a. Biodegradable polymers

Biodegradable polymers are the polymers that are fully decomposed into carbon dioxide, methane, water, biomass and inorganic compounds under aerobic or anaerobic conditions and the action of living organisms. Therefore the biodegradable properties are all characteristics of some polymers to be decomposed under aerobic or anaerobic conditions and action of living organisms.

Biodegradation or biotic degradation is a specific property of certain plastic materials. Microorganisms (bacteria, fungi, algae) recognize polymers as a source of organic compounds (e.g. simple monosaccharides, amino acids, etc.) and energy that sustain them.

Biodegradable plastics are plastics that will fully decompose to carbon dioxide, methane, water, biomass and inorganic compounds under aerobic or anaerobic conditions and the action of living organisms. Plastics are typically composed of artificial synthetic polymers.

For biodegradation to happen there are two reactions that can allow it to proceed: biodegradation based on oxidation and the other based on hydrolysis.

Those reactions can occur either simultaneously or successively. The decomposition of condensation polymers (example: polyesters and polyamides) take place through hydrolysis, while polymers with carbon atoms only in main chain (example: polyvinyl alcohol, lignin) decompose by oxidation which may be followed by hydrolysis of products of oxidation.

The advantage of biodegradable plastics is that they decompose into natural substances and do not require separate collection, sorting, recycling or any other final waste solution (disposal at landfills or burning) as is the case with non-biodegradable plastics.

Characteristics of biodegradable polymers:

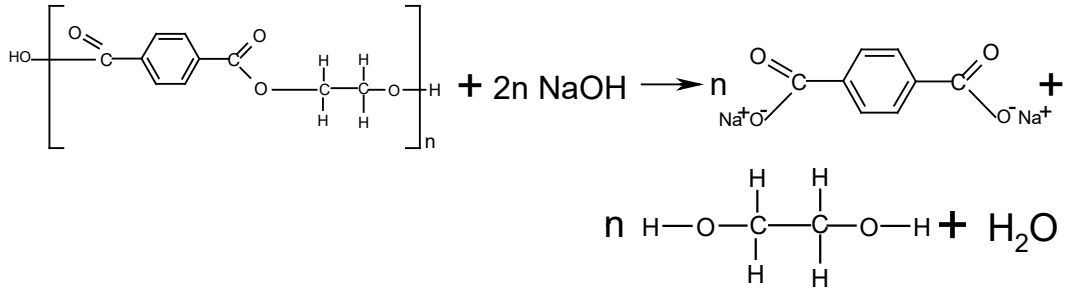
- They are slightly soluble in water;

Example: poly (ethanol)" –$(CH_2\text{-}CHOH)_n$-'' also called poly(vinyl alcohol or PVA)

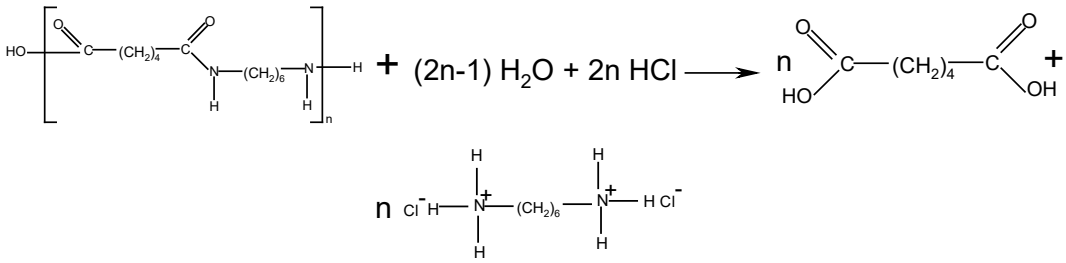
- They decompose slowly at the sunlight (they are photodegradable). They are incorporated while making polystyrene materials like cups. When they are exposed to sunlight for 60 days, they cups break down into dust particles.

The break-up of these polymers is carried out in aqueous solution and can be classed as hydrolysis reactions:

Polyesters are best hydrolyzed in strongly alkaline conditions, in which they undergo saponification:



Polyamides are best hydrolysed in strongly acidic conditions:



The biodegradability of condensation polymers may compromise their effectiveness, since physical and chemical durability is one of the reasons for their widespread use. A balance must be struck between practical durability and long-term biodegradability. The degradable polymers are applied in many areas (Table 6.3).

Table 6.3: Application of biodegradable polymers

Category	Applications
Packaging	Food packaging, garbage bags, wrappers
Housewares	Disposable dinnerware, cups, bottles, containers
Biomaterials	Medical devices, surgical implants, absorbable sutures, tissue engineering, regenerative medicine.
Pharmaceuticals	Controlled release of drugs, homeostatic agents, drugs delivery, tablet coatings, hydrogels
Agriculture	Mulch, Mulch films, plant covering, pots, bags, trays and containers, controlled release of fertilizers, chemicals, etc.
Personal care	Combs, diaper backing, shampoos

b. Properties of non-biodegradable polymers

Most of the major synthesized polymers are non-biodegradable. All kind of plastics and synthetic fibres are non-biodegradable.They are polymers which are resistant to environmental degradation thus accumulate in form of waste. These polymers cannot be changed to a harmless natural state by the action of bacteria, and may therefore damage the environment.

Since the chains of non-biodegradable polymers are non-polar, addition polymers are insoluble in water. Their intermolecular forces are strong and the chains are often tangled, they are generally insoluble in non-polar solvents as well.

In fact the long saturated hydrocarbon chains result in polyalkenes being very unreactive generally, as they cannot react with electrophiles, nucleophiles or undergo addition reactions.

This results in their widespread use as inert materials; they are commonly used as insulators, packaging and in making containers.

However their low reactivity means that they are not easily decomposed in nature and as a result have a very long lifetime. Such substances are said to be non-biodegradable, and constitute an environmental hazard as they are very persistent in nature and thus difficult to dispose of.

Checking up 6.4

1. Polyethene is a non-biodegradable plastic.
   a. Explain the term bio-degradable
   b. Give one environmental benefit of using biodegradable plastics.
   c. Developing biodegradable plastics involves compromise. Suggest one factor that requires careful consideration and explain your choice.
2. Multiple choice questions (choose the letter corresponding to the right answer);

A. The word 'polymer' meant for material made from _____.

   a. Single entity
   b. Two entities
   c. Multiple entities
   d. Any entity

B. One of characteristic properties of polymer material _____ .

   a. High temperature stability
   b. High mechanical strength
   c. High elongation
   d. Low hardness

C. Polymers are _____ in nature.

   a. Organic
   b. Inorganic
   c. Both (a) and (b)
   d. None

D. These polymers cannot be recycled:

   a. Thermoplasts
   b. Thermosets
   c. Elastomers
   d. All polymers

E. In general, strongest polymer group is _____ .

   a. Thermoplasts
   b. Thermosets
   c. Elastomers
   d. All polymers

F. These polymers consist of coil-like polymer chains:

a. Thermoplasts
b. Thermosets
c. Elastomers
d. All polymers.

G. Strong covalent bonds exists between polymer chains in _____ .

a. Thermoplasts
b. Thermosets
c. Elastomers
d. All polymers

H. Following is the unique to polymeric materials:

a. Elasticity
b. Viscoelasticity
c. Plasticity
d. None.

I. Elastic deformation in polymers is due to _____ .

a. Slight adjust of molecular chains
b. Slippage of molecular chains
c. Straightening of molecular chains
d. Severe of Covalent bonds

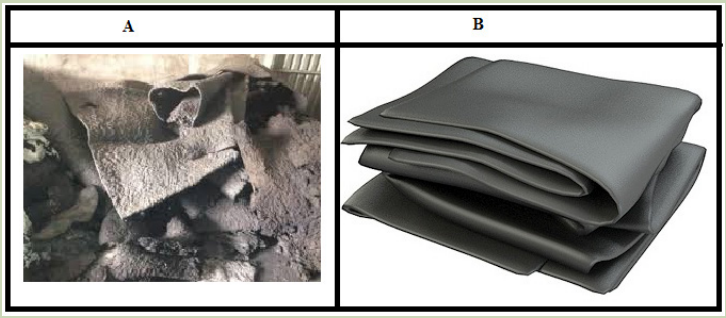
J. Kevlar is commercial name for _____ .

a. Glass fibers
b. Carbon fibers
c. Aramid fibers
d. Cermets

6.5. Importance of vulcanisation in rubber processing

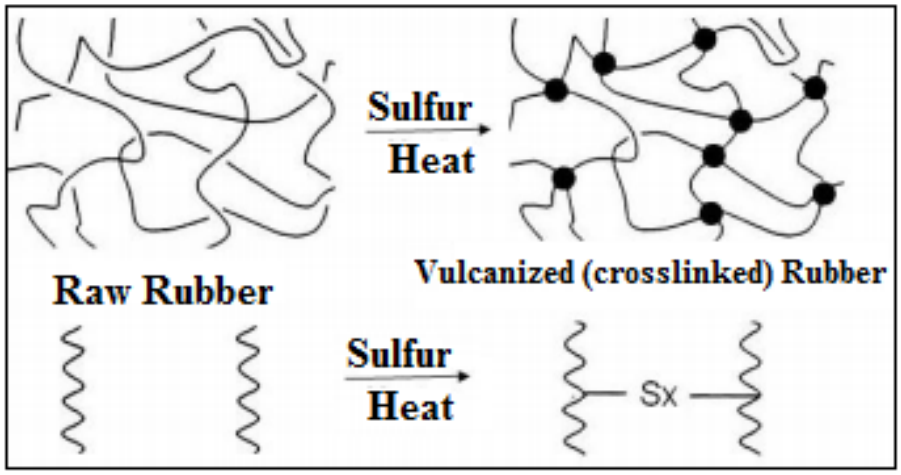
Activity 6.5

1. Explain what do you understand by the term vulcanization
2. Observe carefully the images below and answer the questions that follows:



i. Do A and B have any relationship? If yes what is it?
ii. Compare and contrast A and B.

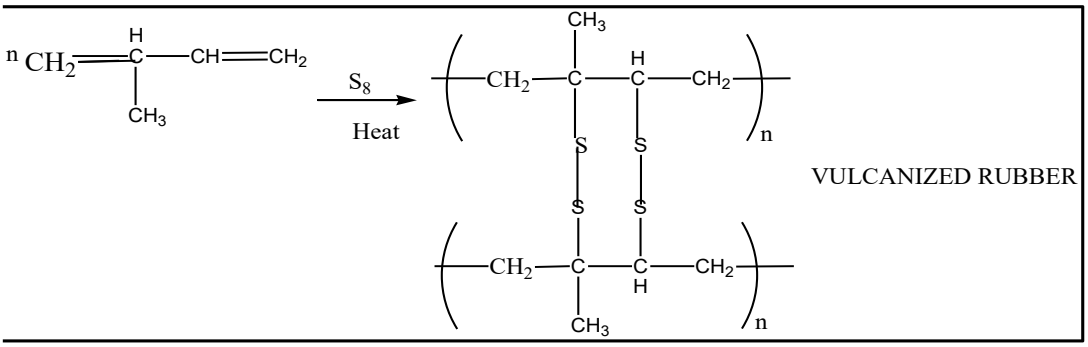
Vulcanization is process used to convert natural rubber or related polymers to improve its resilience, elasticity and durability by heating them with Sulphur or other equivalent curatives or accelerators. During this process, the rubber undergoes a multiple series of chemical change.



The vulcanization process was discovered in 1839 by Charles Goodyear in USA and Thomas Hancock in England. Both discovered the use of Sulfur and White Lead as a vulcanization system for Natural Rubber.

Vulcanization of rubbers by sulfur alone is an extremely slow and inefficient process. The chemical reaction between sulfur and the Rubber Hydrocarbon occurs mainly at the C = C (double bonds) and each cross-link requires 40 to 55 sulphur atoms (in the absence of accelerator.

The following is a chemical equation that shows vulcanization:



Importance of vulcanization is that, it converts the raw rubber into more durable rubber with high tensile strength. It can withstand high temperature between 40 and 100^0 centigrade.

By heating rubber with sulphur, sulphur atoms are introduced between the chains and improve its elasticity .The properties of rubber improved by vulcanization include tensile strength; elasticity; hardness; tear strength; abrasion resistance; and resistance to solvents.

Another important of vulcanization of rubber is the cross links that may be derived from carbon to carbon or through an oxygen atom or through sulphur atom, or through all the three, therefore, percentage elongation at break decreases. The vulcanization decreases the tendency of water absorption of rubber.

Checking up 6.5

1. a. The vulcanization is a process used to convert the natural rubber into more durable materials. Explain five important uses of vulcanization.

   b. Name two substances added to natural rubber during vulcanization process as:

   i. Accelerators
   ii. Fillers
   iii. Anti-oxidants

2. a. What is vulcanized rubber?

   B. Give two useful items of vulcanized rubber

3. Describe briefly the process of vulcanization of rubber.

6.6. Uses of polymers and their effect on the environment

Activity 6.6

1. List at least 3 commonly used polymers in daily life.
2. Explain why burning plastics such as PVC is particularly dangerous.
3. Look at the image below and answer the questions:

Analyze the above image and discuss the impacts of the materials contained in the said image on the environment.

Polymers are widely used materials in our daily life. To date, the importance of polymers is highlighted in their applications in different areas of sciences, technologies and industry from basic uses to biopolymers and therapeutic polymers.

6.6.1. Uses of polymers

Polymers found many uses in our daily life:

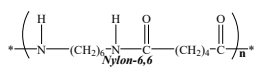
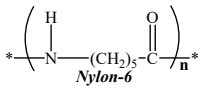
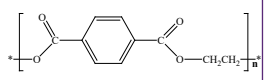
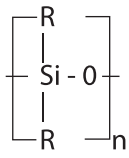
Plastics are inexpensive, lightweight, strong, durable, corrosion-resistant materials, with high thermal and electrical insulation properties.

In general due to the properties of polymers, they are used to make a vast array of products that bring medical and technological advances, energy savings and numerous other societal benefits.

The following Table 6.4 shows the uses of the following commonly known polymers:

Table 6.4: Uses of commonly used polymers

Name	Chemical Formula	Properties	Uses
Polyethylene (PE)	- [CH_2 - CH_2]n–	Thermoplastic;translucent; Permeable by hydrocarbons,alcohol, and gas;resistant to X rays and chemical agents	Film, bags, pipe, insulating sleeves, bottle stoppers, lids, plastic wrap, toys
Polypropylene (PP)	CH_3 | - [CH_2 - CH]n- Monomer is propene	Thermoplastic; low density; durable; resistant to X rays; permeable by water; impact resistant and temperature resistant 135°C	Household items, plastic wrap, automobile parts,batteries, bumpers,garden furniture,syringes, bottles, appliances
Polystyrene (PS)	C_6H_5 - [CH_2 – CH]n– Monomer is styrene	Thermoplastic; transparent; nontoxic; optical and electricalproperties; easy to color;resistant to X rays, oils,and grease.	Plastic wrap, kitchen utensils, furniture covers, thermal insulation, toys, office supplies, disposable razors
Polyvinyl Chloride (PVC) - [Cl-CH – CH_2] n– Industries	- [Cl-CH – CH_2]n– Monomer is Cl-CH=CH_2 Vinyl Chloride	Thermoplastic; soft or rigid; opaque or transparent; fire resistant; resistant to X rays, acids, bases, oils, grease, and alcohol.	Household items, electric wire insulation, water pipes, floor coverings, window and door coverings, baggage, vinyl, sport and camping gear, items for chemical and automobile

Polytetrafluoroethylene (PTFE) or Teflon	-[CF_2 - CF_2]n- The monomer is $F_2C=CF_2$ Tetrafluoroethylene	Chemically inert, antiadhesive, impermeable to water and grease, heat and corrosion resistant	Orthopedic and prosthetic appliances, hearing aids, joints, upholstery, corrosion resistant mechanical parts, electrical insulation, frying pan coatings
Polymethyl Methacrylate (PMMA) or Plexiglas	CH_3 | -[CH_2 – C-]n | $COOCH_3$	Thermoplastic, optical properties, ages well, weather resistant	Glass substitute, neon signs, windows, portholes, optical fibers, dentistry, appliances, contact lenses
Polyamides (PA) (examples: Nylon6,6; Nylon6)	 	Thermoplastic, mechanical properties, durable to temperatures of 100°C, resistant to X rays and fuel, impermeable to odors and gas,	Food wrap, counters, electricity, fuel pipes, shoes, ski bindings, bicycle seats
Polyesters		Thermosetting, transparent, mechanical properties at high temperatures, electrical properties, resistant to impact, easy to work with	Textiles, plastic wrap, bottles, switches, electric sockets and fuses, appliances.
Silicone	 Examples: R = CH_3- or C_6H_5-	Fluid, lubricant, antiadhesive, slightly toxic	Fluid for electrical transformers, putty,molding, antiadhesive,coverings, varnish, wax,burn treatments,cosmetic surgery

Phenol formaldehyde polymers		Thermosetting, long lasting	Used in layers, Bakelite, Durable varnish

6.6.2. Effects of polymers on environment

Polymers or polymeric materials have eased the life of people but there are dangerous to the environment.

However, concerns about usage and disposal are diverse and include accumulation of waste in landfills and in natural habitats, physical problems for wildlife resulting from ingestion or entanglement in plastic, the leaching of chemicals from plastic products and the potential for plastics to transfer chemicals to wildlife and humans. In the polymerization of compounds, some additive chemicals can be potentially toxic (for example lead and tributyl tin in polyvinyl chloride, PVC). Further substantial quantities of plastic have accumulated in the natural environment and in landfills.

The rural areas are more prone to this type of contamination and the related effects, as a majority of the people from these areas as there is over use of plastics on a large scale. Discarded plastic contaminates a wide range of natural terrestrial, freshwater and marine habitats.

When dumped in landfills, plastic materials interact with water and form hazardous chemicals which may be toxic to humans and other aquatic organisms. If these compounds seep down towards groundwater aquifers, they degrade the water quality, leading to groundwater pollution.

Many of plastics waste lead to the formation of persistent organic pollutants (POPs), compounds which are very dangerous to the whole environment. These compounds persist in the environment and due to their property of bio-accumulation; they have high levels of toxicity in the food chain. Blockage due to plastic accumulation may form breeding grounds for mosquitoes and other harmful vector insects, which might cause numerous diseases in humans.

Burning plastic leads to the contamination of the atmosphere, due to the release of other poisonous chemicals, leading to air pollution. Recycling them requires carefull attention as they lead to the development of skin and respiratory problems due to inhalation of toxic chemicals.

When plastic is burned they release toxic chemicals that are deposited in soil and surface water and on plants.

Non-biodegradable polymers or long term biodegradable materials, especially plastic bags when they in the soil, they do not allow rain water for penetration which causes soil erosion.

NB: Rwanda has taken a tremendous decision of stopping the use of plastic bags in the country, which has got promising result for the environment and the users in general.

Checking up 6.6

1. Give one large scale use for polyester polymers and state the property of polyesters on which the use depends.
2. Enumerate three environmental problems caused by the widespread use of plastics as polymers.

6.7. Management of old polymer materials

Activity 6.7

1. Observe carefully the below image and then provide the information it teaches you.

2. In your own words, explain your understanding of:
   a. Polymers reuse
   b. Polymer recycling
   c. Polymer disposal

Plastics have transformed everyday life; its usage is increasing gradually all over the world. It is evident that plastics bring many societal benefits and offer future technological and medical advances. However, concerns about usage and disposal are diverse and include accumulation of waste in landfills and in natural habitats, physical problems for wildlife resulting from ingestion or entanglement in plastic, the leaching of chemicals from plastic products and the potential for plastics to transfer chemicals to wildlife and humans.

The management of waste materials including polymers involves improvement of effects caused by these materials. A major part of plastic produced is used to make some disposable items of packaging or other short-lived products that are discarded within a period of manufacture. Due to the durability of the polymers, we have seen that substantial quantities of discarded end-of-life plastics are accumulating as debris in landfills and in natural habitats worldwide. A number of waste prevention techniques such as reuse, recycling and disposal of plastics are discussed below.

a. Reuse

This is a process of using the polymers more than once. This encompasses the entire spectrum of used goods. Spanning from collectables, antiques and memorabilia to general used goods retail and wholesale. Dealing in secondhand items typically involves the salvage of used items and may dismantle into components. Beyond salvage and to enhance reuse the industry includes repair and refurbish, remanufacturing.

There is considerable scope for re-use of polymer materials for the transport of goods, and for potential re-use or re-manufacture from some plastic components in high-value consumer goods such as vehicles and electronic equipment.

b. Recycle

Recycling is one of the most important activities that can be applied to reduce the impacts of the plastics used in industry. Recycling is a waste-management strategy; it is a technique that can be used to reduce the environmental impact and resource depletion.

Recycling provides opportunities to reduce oil usage, carbon dioxide emissions and the quantities of waste requiring disposal. Today's recycling industry has evolved largely into a service industry involved in the collection, sorting, processing and transportation of waste streams and by-products.

Different polymer materials need to be collected, separated and cleaned. Further, they are melted down before being changed into a new material. Some plastics cannot be melted – they burn or harden instead of melting. It is even more difficult to recycle these plastics as they can only be used in the same shape as they were originally cast.

The biodegradable materials can be recycled, broken down into their original components and reused, but they still need to be collected, separated and cleaned.

Plastic materials can be recycled in a variety of ways and the ease of recycling varies among polymer type, package design and product type.

c. Disposal

Old polymers disposal is the action of getting rid of old polymers. The disposal of non-biodegradable polymers is a significant problem.

There are three options:

i. Burying in landfill sites

This is widespread in all developed countries but is a completely unsustainable

practice, as each landfill site will eventually fill up. Landfill sites are also unsightly and unhygienic.

iv. Burning

This is a technique to dispose some materials. However, burning polymers releases greenhouses gases such as carbon dioxide and can also release toxic gases, depending on exactly type of polymer being burned.

Checking up 6.7

List the advantages and disadvantages for each of the method to deal with the old polymers

END UNIT ASSESSMENT

1. Explain the terms crosslinking and thermosetting with reference to condensation polymers.
   For what purposes are thermosetting polymers suitable?

2. a. How the chemical inertness of poly(ethene) arise?
   b. How does it increase the usefulness of the material?
   c. How does it affect the disposal of waste polyethene?

3. a. What type of functional group joins the repeating units in nylon?
   b. In what way does the structure of nylon resemble that of a polypeptide?
   c. What type of interaction takes place between polymer molecules which contain the functional group present in polypeptide?

4. Identify 3 examples of synthetic polymers

5. What is the benefit of cross-linking polymer chains?

6. a) Give one example for each of the following type of polymer. Write the structural formula of the polymer and monomer unit. Give at least one use of the polymer named
   i. Natural addition polymer
   ii. Synthetic addition polymer
   iii. Natural condensation polymer
   iv. Synthetic condensation polymer

   b. State the role of each of the following in the manufacture of plastics
   i. Fillers
   ii. Plasticizers

c. i. what is meant by vulcanization?

ii. Discuss the effect of vulcanization on rubber molecules and state how it affects the physical properties of rubber.

iii. Name the monomer units in natural rubber

iv. Name one commercial synthetic rubber. Write equation to show how it is formed and give one use of it

UNIT 7

SOLVENT EXTRACTION AND COLLIGATIVE PROPERTIES

UNIT 7: SOLVENT EXTRACTION AND COLLIGATIVE PROPERTIES

Key Unit Competency

The learner should be able to apply partition and Raoult's law to separate mixtures, determine the molecular and formula masses of compounds using colligative properties.

Learning objectives

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

- Define partition coefficient and solvent extraction;
- State the Raoult's law;
- State and explain the advantages of carrying out distillation processes under reduced pressures;
- Discuss the chemical principles upon which simple distillation and steam distillation are based;
- State examples of the applications of the distillation methods used in various industries;
- Describe the effect of the solute on vapor pressure, boiling and freezing points of the solvent;
- Explain colligative processes;
- Carry out separation experiments based on the solute partitioning between two immiscible solvents;
- Calculate the amount of the solute extracted from the solvent;
- Interpret boiling point and vapor pressure composition curves of both ideal and non-ideal mixture;
- Calculate the molecular mass of substances using steam distillation;
- Calculate molecular mass of polymers using colligative properties and steam distillation;
- Interpret the boiling point composition curves of azeotropic mixtures;
- Apply Raoult's Lawto calculate vapor pressure of given solutions and mole fractions;
- Carry out experiments to explain colligative properties;
- Apply colligative properties to determine the molecular mass of the solute in a solution.

Introductory activity

1. Describe the phase diagram for water.
2. Have you ever heard the term "solvent extraction"? If yes can you tell what it is about and give an example of a solvent extraction?
3. Describe the process of producing banana juice? Is there any application of solvent extraction?
4. Take a tea bag and put it in water (cold or hot); what do you observe? Explain your observation
5. You are provided with the following materials: separating funnel, 1,1,1-trichloroethane, iodine, water, retort stand and its accessories:

Procedure:

Put water into the separating funnel and add 1,1,1-trichloroethane in the water and shake well.

Add iodine in the mixture and shake well, after standing, observe well.

What happens to the iodine? How do you compare the coloration of the two phases? What explanation can you give?

When traditional healers crush leaves of a healing plant, mix with water, filter and give you the filtrated mixture as medicine, they have applied solvent extraction technique, using water as solvent, to extract the medicinal ingredients.

When you prepare your cup of tea, putting a tea bag in the hot water, the color of water change to brown black; you have solvent extracted a certain number of substances present in the tea leaves by hot water, and left other in the tea residue.

Solvent extraction is the separation of a particular substance from a mixture by dissolving that substance in a solvent that will dissolve it, but which will not dissolve any other substance in the mixture.

Let us start with two solvent systems of water and an organic liquid, two immiscible solvents.

When water and an organic liquid are shaken together, and then allowed to stand, the liquids separate into a two phase system with the more dense liquid on the bottom.

If a solute is added to a system of two liquid layers, made up of two immiscible components, then the solute will **distribute** itself between the two layers so that the ratio of the concentration in one solvent to the concentration in the second solvent remains constant at constant temperature. A quantitative measure of how a component will distribute between the two phases is called the distribution or partition coefficient.

7.1. Definition of partition coefficient and solvent extraction

The ability of a solute (inorganic or organic) to distribute itself between an aqueous solution and an immiscible organic solvent has long been applied to separation and purification of solutes either by extraction into the organic phase, leaving undesirable substances in the aqueous phase; or by extraction of the undesirable substances into the organic phase, leaving the desirable solute in the aqueous phase. Species that prefer the organic phase (e.g., most organic compounds) are said to be lipophilic ("liking fat") or hydrophobic ("disliking water"), while the species that prefer water are said to be hydrophilic (" liking water") or lipophobic ("disliking fat").

7.1.1. Partition coefficient

Partition means"divided into two parts with a boundary or an interface".

When a solute is added to two immiscible solvents in contact with each other at constant temperature, the solute gets distributed or partitioned between the two solvents with different equilibrium concentrations.

For example, when iodine is added to water and carbon tetrachloride, it distributes in such a way that the equilibrium ratio of the concentrations of iodine in the two solvents is constant at any given temperature. If C_A and C_B are the concentrations of iodine in water and carbon tetrachloride respectively, then $\frac{C_A}{C} = K_D$

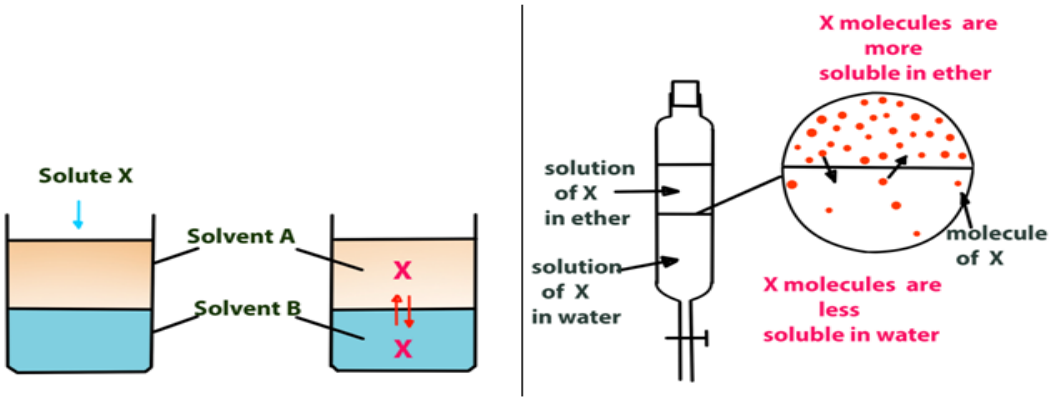


Figure 7.1: Distribution of solute X between solvent A and B

The constant K_D is called the distribution or partition coefficient of the solute between the two solvents at a given temperature. The value of K_D depends on the nature of the solute and the solvent pair. The equation above is the mathematical form of the Nernst Distribution Law (or Nernst's Partition law) or simply Distribution law or Partition law.

This law states that at constant temperature, when different quantities of a solute are allowed to distribute between two immiscible solvents in contact with each

other then at equilibrium the ratio of the concentration of the solute in two layers is constant. The solutions where this law applies are called "ideal solutions". However, if the amount of the solute added is sufficiently small, then the distribution coefficient is relatively independent of the concentration.

7.1.2. Solvent extraction

The term solvent extraction refers to the distribution of a solute between two immiscible liquid phases in contact with each other, i.e., a two-phase distribution of solute.

Solvent extraction has become a very powerful method of separation for various reasons. One amongst them is, it is very simple, rapid, selective and sensitive. This method does no need any kind of sophisticated instrument apart from a separating funnel.

It is the partial removal of a solute from one liquid (usually water) into another immiscible liquid (e.g. ether). This is a method of separating one component from a mixture. It is based on finding a solvent which dissolves the desired component much better than it does for any of the others. Solvent extraction is also called liquid-liquid extraction and partitioning.

For the solvent extraction to succeed, the following considerations are recommended:

- the solvent to be used must be a good solvent for the solute and chemically unreactive with the solute
- the solvent must be immiscible with water or any other solvent involved
- the solvent must be volatile, to facilitate the separation with the solute at the end of the operation; example, the most used solvent is ether that fulfills those requirements,

Activity 7.1:

In an experiment, 100 cm^3 of 0.10$moldm^{-3}$ aqueous propanoic acid was shaken with 50 cm^3 of organic solvent which is immiscible with water, until equilibrium was reached. 10.0 cm^3 of aqueous layer required 12.0 cm^3 of 0.02$moldm^{-3}$ $NaOH$ for reaction in a titration.

Questions:

a. Calculate the concentration of propanoic acid in aqueous layer and in organic layer.

b. Calculate the equilibrium ratio between the concentration of propanoic acid in organic layer and in aqueous layer;

c. What is the name of that ratio?

Multiple extractions

The process of extraction when carried out with the total amount of the given solvent in a single operation is referred to as **simple extraction**. But to recover the maximum amount of the substance from a solution, the extraction is made in two or more successive operations using small portions of the solvent provided. This is called **multiple extractions**. In such a process the aqueous solution is first extracted with a portion of the solvent in a separatory funnel. The aqueous layer from which some substance has been removed is then transferred to another funnel. This is shaken with a second portion of the solvent. Similarly, the aqueous layer from the second extraction is treated with a third portion of solvent, and so on.

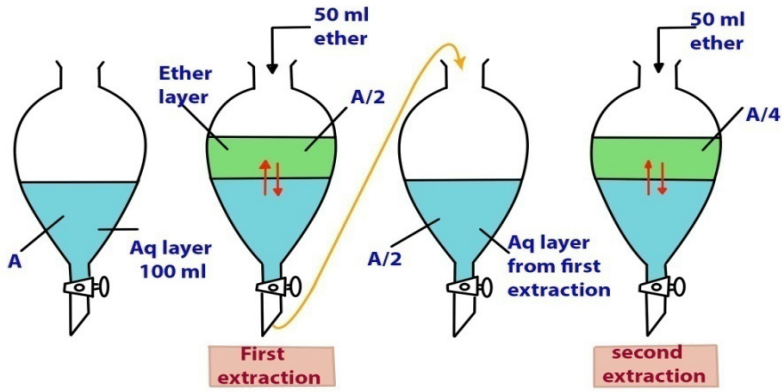


Figure 7.2: Multiple extractions, ether is used in two successive portions of 50 mL each

Example:

The partition coefficient of a substance **X** between methylbenzene and water is 8.0, **X** being more soluble in methylbenzene than water.

The mass of **X** extracted from an aqueous solution containing 6.0 g of X may be calculated as follows:

If shaken with **one portion** of 100cm^3 of methylbenzene:

Let **x** be the mass of **X** extracted.

Mass of X remaining in aqueous solution= (6.0-**x**)g

Using $\frac{[X]_{org}}{[X]_{q}} = 8.0$

$$\frac{x/50}{(6.0-x)/100} = 8.0 \Rightarrow x = 5.33g$$

If shaken with **two successive portions** of 50 cm^3 of methylbenzene:

1st extraction:

Let $\mathbf{x_1}$ be the mass of **X** extracted.

Mass of **X** remaining in aqueous solution=(6.0-$\mathbf{X_1}$)g

Using $\frac{[X]_{org}}{[X]_{q}} = 8.0$

$$\frac{x_1/50}{(6.0-x_1)/100} = 8.0 \Rightarrow x_1 = 4.80g$$

Mass of X remaining in aqueous solution= (6.0-4.8) g=1.2g

2nd extraction:

Let $\mathbf{X_2}$ be the mass of **X** extracted.

Mass of **X** remaining in aqueous solution= (1.2-X_2)g

Using $\frac{[X]_{org}}{[X]_{aq}} = 8.0$

$$\frac{x_2/50}{(1.2-x_2)/100} = 8.0 \Rightarrow x_2 = 0.96g$$

Total mass extracted= (4.8+0.96) g=5.76g

Mass of **X** extracted in (i) is less than that in (ii). This shows that it is **more efficient** to use a solvent in **several smaller portions** than all at once when extracting a solute from another solvent.

Limitation of Nernst Distribution Law

The law is valid only when the molecular state of the solute is the same in both the solvents. If the solute undergoes dissociation or association in any one of the solvents, then in such cases the distribution law no longer holds.

Checking up 7.1:

1. The distribution constant of a certain solid X between two immiscible solvents A and B is 8 at 298K. If the solubility of the solid in solvent A is 4.2 mol dm^{-3}, what is the solubility in B?
2. In the distribution of iodine between carbon disulphide and water, the following results were obtained:

Number of experience	1	2	3	4
Concentration of iodine in water gdm^{-3}	0.1	0.161	0.314	0.423
Concentration of iodine in carbon disulphide gdm^{-3}	41	66	129	174

Calculate the distribution constant of iodine between carbon disulphide and water. What could be predicted regarding the molecular state of iodine in these solvents?

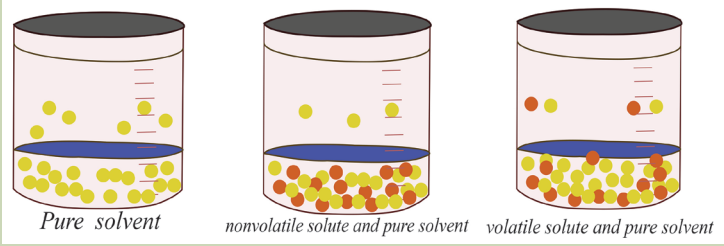
7.2. Raoult's law and colligative properties

7.2.1 Raoult's law and ideal solutions

Activity 7.2 (a)

Observe well the figure below and answer the following questions:

1. What is vapour pressure?
2. What effect the solutes have on the vapor pressure?



Let's consider the figures above; the figure at the left side shows that some molecules exist as gaseous molecules above the liquid phase. Those molecules exert a pressure on the surface of the liquid. That pressure is called "**vapour pressure"** of the solvent or liquid. Equilibrium will be reached when there is balance between the number of molecules leaving the liquid phase to enter the vapour phase and the number of molecules leaving the vapour phase to enter the liquid phase. Vapour pressure increases with increasing temperature. When the vapour pressure is equal to atmospheric pressure, the liquid starts to boil.

On the right side of the figure, we see lesser gaseous molecules in the container with nonvolatile solute, and still lesser in the container with a volatile solute. In both cases we see that introduction of a solute into a solvent causes a decrease in its vapour pressure.

Another observation is that in the container with two volatile liquids, the total vapour pressure is the sum of the vapour pressures of the two solvents; in this case the vapour pressure of each solvent is called "partial vapour pressure".

Ideal solution

Let's consider a binary solution of two volatile liquids and indicate the two components as A and B. When taken in closed vessel, they would evaporate and equilibrium would be established between liquid and vapour phases. Let's consider, P_{total} , the total vapour pressure, P_A and P_B the partial vapour pressures of the two components A and B respectively. These partial pressures are related with their mole fractions in the solution; x_A and $x_{\mathbf{B}}$.

The French chemist, François -Marie Raoult, in 1886 gave the quantitative relationship between vapour pressures and mole fractions of components. The relationship is known as the Raoult's law which states that" the partial vapour pressure of a volatile component of ideal solution is product of its mole fraction and vapour pressure of the pure component at constant temperature.

For component A: $P \propto x_A$ (Vapour pressure is proportional to mole fraction)

$$P_A = x_A P_A^0$$

where P_A^0 represents the vapour pressure of pure component A at the same temperature.

$$P_B = x_B P_B^0$$

where P_B^0 represents the vapour pressure of pure component B at the same temperature.

According to Dalton's law of partial pressures, the total pressure over the solution phase in the container will be the sum of partial pressures of the components of the solution.

$$P_{Total} = P_A + P_B$$

$$P_{Total} = x_A P_A^0 + x_B P_B^0$$

The sum of mole fraction is 1:

$$x_A + x_B = 1$$

$$x_A = 1 - x_B$$

$$P_{Total} = (1 - x_B)P_A^0 + x_B P_B$$

$$P_{Total} = P_A^0 - x_B P_A^0 + x_B P_B$$

$$P_{Total} = P_A^0 - x_B (P_B - P_A)$$

Raoult's law is applicable only if the liquids are miscible.

If the values of P_A and P_B are plotted against the values of x_A and x_B for a solution, two straight lines are obtained (figure 7.3) and the total vapour pressure P_{total} of the solution is the sum of partial vapour pressures P_A and P_B.

A solution which obeys Raoult's law over the entire range of concentration at all temperature is known as an ideal solution.

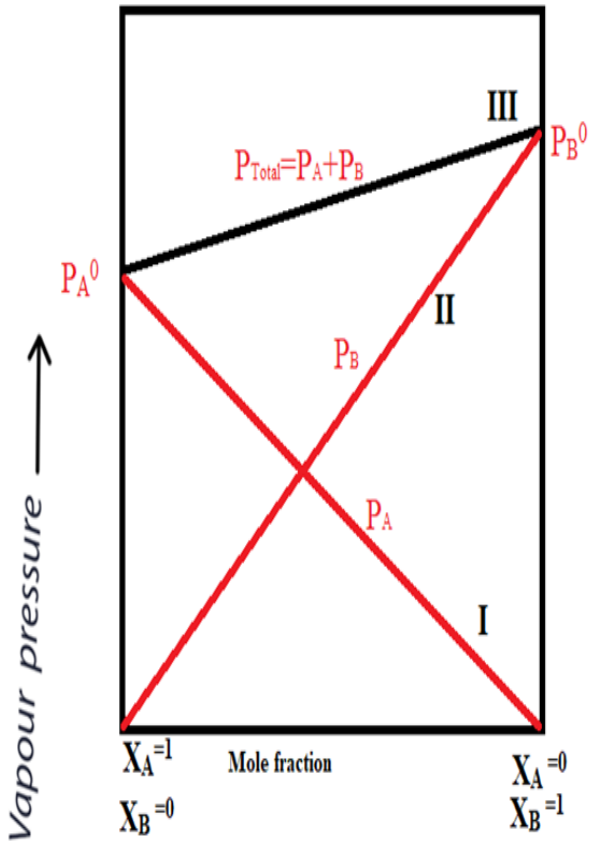


Figure 7.3: A plot of vapour pressure and mole fraction of an ideal solution at constant temperature

Raoult's law describes the behavior of ideal solutions of completely miscible and volatile liquids. Ideal solution is defined as the one in which each component obeys Raoult's law over the entire concentration range. Besides obeying Raoult's law, an ideal solution shows two more properties:

a. When such solution is prepared, no heat is evolved or absorbed, i.e.

$$\Delta H_{mix} = 0$$

b. The volume of such a solution is the sum of the volumes of its components, i.e. $\Delta V_{mix} = 0$

In fact, liquid-pairs rarely form ideal solutions. Benzene-toluene, ethene chloride-ethene bromide and carbon tetrachloride-silicon tetrachloride are few examples of liquid pairs which form very nearly ideal solutions.

A binary solution of components A and B will behave ideally when intermolecular force between a molecule of A and a molecule of B (A-B interactions) is same as intermolecular force between two molecules of A (A-A interactions) or the force acting between two molecules of B (B-B interactions). This means that one component likes itself as much as it likes the other component. This is due to similarity in their structure that their solutions behave ideally.

At any fixed temperature, the vapour phase is always richer in the more volatile component compared to the solution phase. In other words, mole fraction of the more volatile component is always greater in the vapour phase than in the solution phase. The composition of vapour phase in equilibrium with the solution is determined by the partial pressure of components.

If y_1 and y_2 are the component 1 and 2 respectively in the vapour phase, then using Dalton's law of partial pressure,

$$P_1 = y_1 \times P_{total} \text{ or } y_1 = \frac{P_1}{P_{Total}}$$

Consider y_A and y_B the mole fractions of components A and B respectively in the vapour phase.

$$P_A = y_A P_{total} \Rightarrow y_A = \frac{P_A}{P_{total}}$$

$$P_B = y_B P_{total} \Rightarrow y_B = \frac{P_B}{P_{total}}$$

Example:

Vapour pressure of chloroform and dichloromethane at 25°C are 200 mm Hg and 415 mm Hg respectively.

i. Calculate the vapour pressure of the solution prepared by mixing 25.5 g of chloroform and 40g of dichloromethane at 25°C.
ii. Calculate the mole fraction of each component in vapour phase.

Answer:

i. The number of moles in the solution:

$$n_{CH_2Cl_2} = \frac{40g}{85g/mol} = 0.470mol$$
$$n_{CHCl_3} = \frac{25.5g}{119.5g/mol} = 0.213mol$$

Total number of moles in the solution

$$n_{total} = 0.470\ mol + 0.213\ mol = 0.683\ mol$$

Mole fractions in the solution:

$$x_{CH_2Cl_2} = \frac{0.470\ mol}{0.683\ mol} = 0.688$$
$$x_{CHCl_3} = \frac{0.213\ mol}{0.683\ mol} = 0.312$$

$$P_{total} = P^0_{CHCl_3} + \left(P^0_{CH_2Cl_2} - P^0_{CHCl_3}\right)x_{CH_2Cl_2}$$
$$P_{total} = 200 + (415 - 200) \times 0.688$$
$$P_{total} = 347.9\ mm\ Hg$$

The vapour pressure of the solution is 347.9 mm Hg.

ii. The vapour pressure of each component in vapour phase:

$$P_{CH_2Cl_2} = x_{CH_2Cl_2} P^0_{CH_2Cl_2}$$
$$P_{CH_2Cl_2} = 0.688 \times 415\ mm\ Hg = 285.5\ mm\ Hg$$
$$P_{CHCl_3} = x_{CHCl_3} P^0_{CHCl_3}$$
$$P_{CHCl_3} = 0.312 \times 200\ mm\ Hg = 62.4\ mm\ Hg$$

Consider y_A and y_B the mole fractions of components A and B respectively in the vapour phase.

$$P_A = y_A P_{total}$$
$$P_B = y_B P_{total}$$

The mole fraction in vapour phase is given by the following equation:

$$y_A = \frac{P_A}{P_{total}}$$
$$y_B = \frac{P_B}{P_{total}}$$

$$y_{CH_2Cl_2} = \frac{285.5}{347.9} = 0.82$$
$$y_{CHCl_3} = \frac{62.4}{347.9} = 0.18$$

Since dichloromethane is more volatile than chloroform and the vapour phase is also richer in dichloromethane, it may be concluded that at equilibrium, vapour pressure will be always rich in the component which is more volatile.

Another type of solutions is solids in liquid solution, in which we take the solid as the solute and the liquid as the solvent. Generally, the solute is nonvolatile in nature and the vapour pressure is less than the pure vapour pressure of the solution.

Examples:

- Solution of sugar, salt or glucose and water
- Solution of iodine and sulfur in carbon disulphide

Vapour pressure produced by the solution of nonvolatile solute and solvent results in the vapour pressure of the solution solely from the solvent. This vapour pressure is lower than the vapour pressure of the pure solvent at the same temperature.

The decrease in vapour pressure is due to:

The surface area of the solution is occupied by both nonvolatile solute and the pure solvent particles which results in the reduction of the surface for the solvent particles. As evaporation is a surface phenomenon, the more the surface area is, the greater the evaporation and hence more the vapour pressure. In a pure solvent, there is more surface area available for the particles to vaporize, therefore have more vapour pressure. On the other hand, when we add a nonvolatile solute, the solvent particles get less surface area to escape and hence exert low vapour pressure.

The number of particles escaping the surface is much greater in pure solvent than that of solution containing nonvolatile solute.

Calculation of the vapour pressure of Solutions of Solids in Liquids

Let's A be the solvent and B a solute; according to Raoult's law, the partial pressure of individual component is directly proportional to its mole fraction.

If P_A is the vapour pressure of the solvent, χ_A its mole fraction and P_A^0 is the vapour pressure of the pure solvent, then, by Raoult's law we have:

$$P_A \propto \chi_A$$

$$P_A = \chi_A P_A^0$$

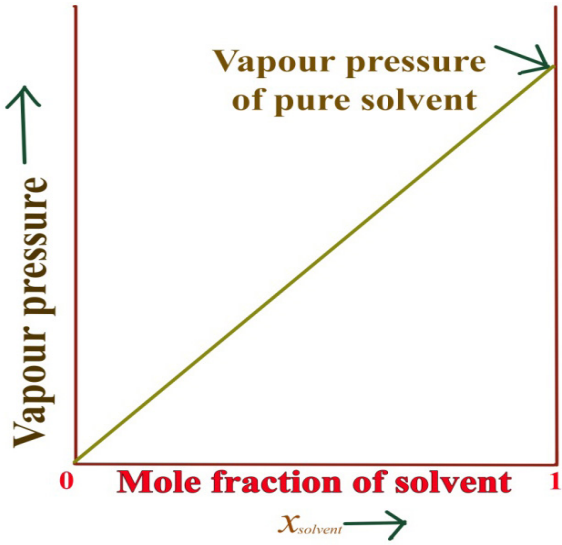


Figure 7.4: Vapour Pressure and mole fraction solid in liquid solution.

Example:

An aqueous solution of glucose is made by dissolving 10 g of glucose, ($C_6H_{12}O_6$), in

90 g of water at 30°C. If the vapour pressure of pure water at 30°C is 32.8 mmHg, what would be the vapour pressure of the solution?

Data:

Mass of glucose: 10g

Molar mass of glucose= 180g/mol

Mass of water: 90g

Molar mass of water: 18g/mol

Vapour pressure of pure water: 32.8 mmHg

Calculation of moles of water and glucose

$$\text{moles of water} = \frac{90\ \text{g}}{18\ \text{g/mol}} = 5\ mol$$

$$\text{moles of glucose} = \frac{10\ \text{g}}{180\ \text{g/mol}} = 0.0555\ mol \approx 0.056\ mol$$

$$\text{mole fraction of water} = \frac{5\ \text{mol}}{5\text{mol} + 0.056\text{mol}} = 0.989$$

Application of Raoult's law to calculate the vapour pressure of solution:

$$\text{P}_{\text{water}} = \chi_{water} P^{0}_{water} \Rightarrow \text{P}_{\text{water}} = 0.989 \times 32.8\ mm\ Hg = 32.4392\ mm\ Hg \approx 32.44\ mm\ Hg$$

Note: The vapour pressure of nonvolatile component is negligeable.

Checking up 7.2(a)

1. What is the vapor pressure of an aqueous solution that has a solute mole fraction of 0.1000? The vapor pressure of water is 25.756 mmHg at 25 °C.
2. The vapor pressure of an aqueous solution is found to be 24.90 mmHg at 25°C.What is the mole fraction of solute in this solution? The vapor pressure of water is 25.756 mm Hg at 25 °C.
3. How many grams of nonvolatile compound B (molar mass= 97.80 g/mol) would need to be added to 250.0 g of water to produce a solution with a vapor pressure of 23.756 torr? The vapor pressure of water at this temperature is 42.362 torr.
4. At 29.6 °C, pure water has a vapor pressure of 31.1 torr. A solution is prepared by adding 86.8 g of "Y", a nonvolatile non-electrolyte to 350. g of water. The vapor pressure of the resulting solution is 28.6 torr. Calculate the molar mass of Y.
5. The vapor pressure of pure water is 23.8 mmHg at 25.0 °C. What is the vapor pressure of 2.50 molal $C_6H_{12}O_6$.

Non-ideal Solutions

Activity 7.2 (b):

You are given the following solutions:

Chloroform-acetone, water-propanol, n-hexane-n-heptane, ethanol-chloroform, ethanol-cyclohexane, ethanol-acetone, phenol-aniline, benzene-toluene.

Choose the solutions which obey Raoult's law and explain why others do not obey it.

Most of liquid-liquid solutions do not obey Raoult's law over the entire range of concentrations. Such solutions are called non-ideal solutions. Besides Raoult's law, non- ideal solutions do not obey the other two conditions: their formation is accompanied by changes of heat and volume. When non-ideal solutions are prepared, some energy is either released or absorbed and the volume of the solution is different from the sum of volumes of the components. The non-ideal behavior of most of liquid-liquid solutions is due to the intermolecular forces between molecules. Vapour pressure of non-ideal solutions is either higher or lower than what predicted by Raoult's law. Based upon this, there are two types of non-ideal solutions namely, the non-ideal solutions with positive deviations and those with negative deviations. Most of the real mixtures are non- ideal.

Non-ideal solutions with negative deviations

In some liquid solutions, the observed vapour pressure of the solution is lower than the ideal value as expected from Raoult's law. Such deviation is called **negative deviation.**

From the figure **7.5**, it can be seen that the experimental curve in solid line always lies below the ideal behavior curve shown in dotted line. Negative deviations are exhibited by the solutions of liquids when a molecule of A attracts a molecule of B more strongly than another molecule of A. Similarly; a molecule of B attracts a molecule of A more strongly than another molecules of B. The result is that molecules of both liquids A and B are more strongly attracted in the liquid phase in their solution rather than in pure liquids. This decreases their tendencies to escape into the vapour phase and the observed vapour pressure is less than the ideal value. In the solution that shows negative deviations the intermolecular forces between the molecules of the two liquids (A-B interactions) are stronger than those in pure liquids. As a result of stronger forces, the average intermolecular distance decreases. This results in decrease in the volume, i.e., $\Delta V_{mixing} < 0$; since the molecules are drawn closer to each other due to the attractive force between them, work is done by them and some energy is released. Thus, the process of mixing of the two liquidsis exothermic, i.e., $\Delta H_{mixing} < 0$.

Examples:

i. Acetic acid-pyridine
ii. Phenol-aniline
iii. chloroform-acetone
iv. water-nitric acid
v. water- sulphuric acid
vi. water-hydrochloric acid

In a mixture of phenol and aniline, the intermolecular hydrogen bond between phenolic proton and lone pair on nitrogen atom of aniline is stronger than the respective intermolecular hydrogen bond between similar molecules; the molecules in the mixture are more strongly bonded than those in the pure liquids. Similarly, propanone-trichloromethane mixture forms a solution with negative deviation from Raoult's law. When the liquids are mixed, hydrogen bonds are formed between the propanone and trichloromethane molecules (figure 7.7). There is no hydrogen bonding in pure liquid propanone or in pure liquid trichloromethane.

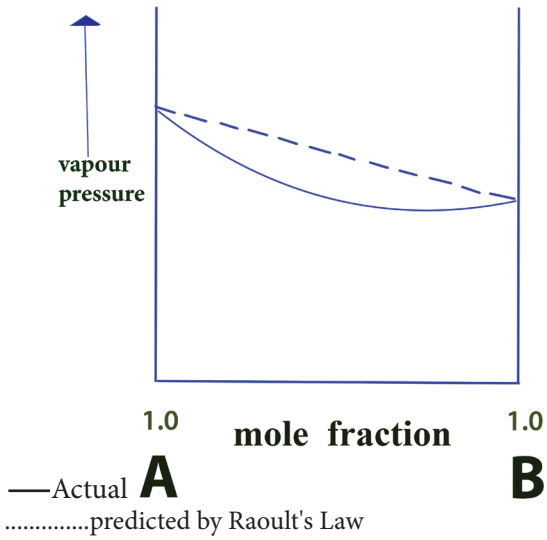


Figure 7.5: Negative deviation

Non-ideal solutions with positive deviations

The solutions whose vapour pressure is higher than that expected from Raoult's law are said to show positive deviations.

It should be noted from the figure 7.6 that solid lines represent the experimentally observed vapour pressure curves of the solution. These curves always lie above the ideal behaviour lines which are represented by dotted lines. In liquid-liquid solutions which show positive deviations, each molecule is more strongly bound to another of same kind than that of different kind. The intermolecular forces between $A-B$ molecules are weaker than those between $A-A$ or between $B-B$ in the separate liquids. Thus, in such solutions molecules of both components A and B are less strongly attracted to the liquid phase than in pure liquids A and B. They have greater tendency to escape into vapour phase. In solution showing positive deviation as a result of weakening of intermolecular forces, the average intermolecular distance increases. Since molecules move away against intermolecular forces of attraction, some work has to be done for which some energy is used up. The process of mixing of the liquids is endothermic, means, $\Delta H_{mix} > 0$.

Also, due to increase in average intermolecular distance, there is an increase in the volume, i.e., $\Delta V_{mix} > 0$.

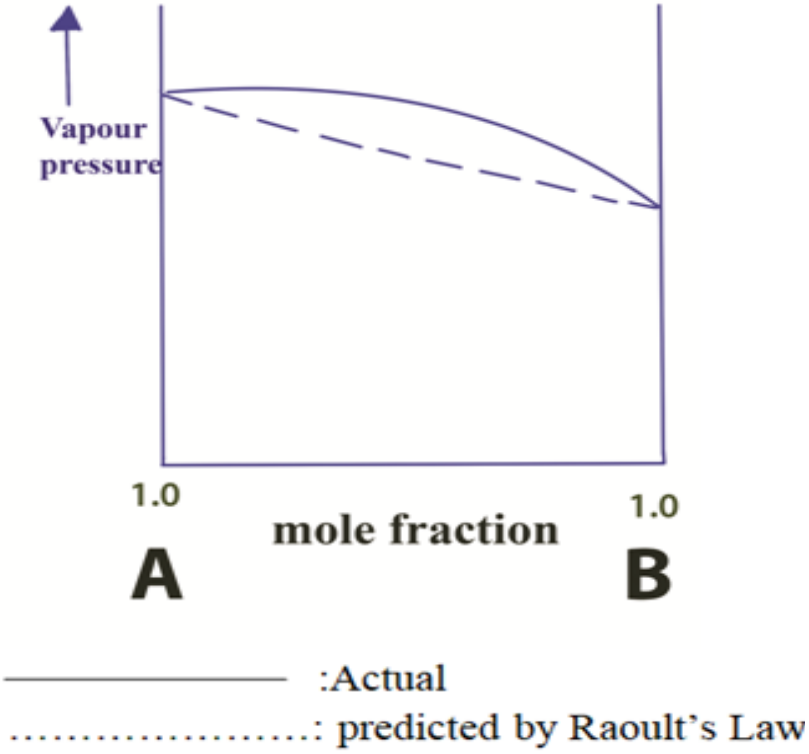
Examples of non-ideal solutions showing positive deviation from Raoult's law:

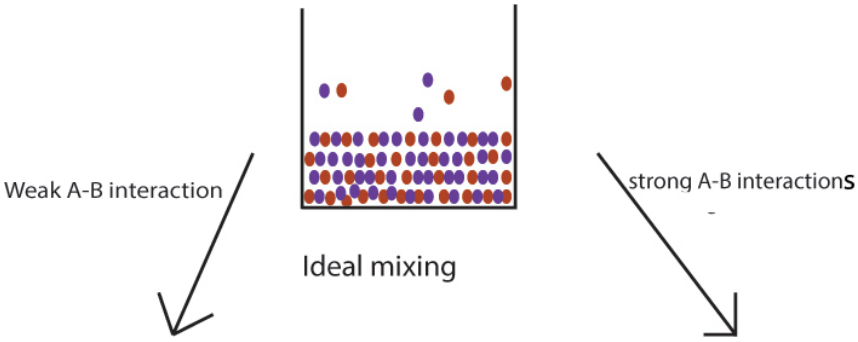
i. Benzene-cyclohexane
ii. n-butane-n-heptane
iii. carbon disulphide-acetone
iv. carbon tetrachloride-benzene

v. ethanol-acetone
vi. ethanol-hexane
vii. ethanol-chloroform
viii. water-ethanol
ix. water-propanol
x. ethanol-cyclohexane

Example:

When hexane and ethanol are mixed, the ethanol molecules are separated. The hydrogen bonds are broken and much weaker Van der Waals forces hold the ethanol and hexane molecules together in the mixture. The ease of escape into the vapour is caused by the hexane molecules, which cannot form hydrogen bonds, coming between the ethanol molecules and disrupting the hydrogen bonding, making it easier for ethanol molecules to escape into the vapour.





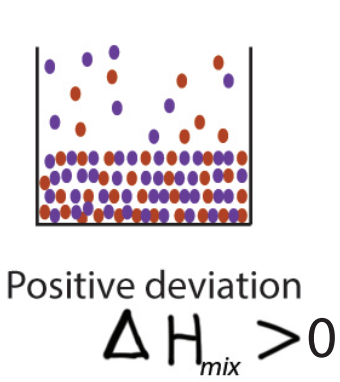


Figure 7.6: Positive deviation

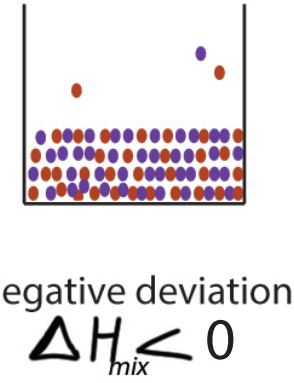


Figure 7.7: intermolecular forces in non ideal solution

Azeotropic mixtures

All non-ideal solutions with large deviations show either maxima or minima in vapour pressure compositions curves. The solutions with positive deviations show maxima and those with negative deviations show minima.

The solution corresponding to maximum or minimum has a unique property that the vapour formed on their evaporation has the same composition as the the liquid phase of the solution. Such solution boils at constant temperature and can not be separated by fractional distillation. Such a solution is called Azeotropic mixtures or azeotropes. The azeotrope is defined as the mixture of liquids which boils at constant temperature like a pure liquid and possesses the same composition of components in the solution as well as in vapour phase.

The term azeotrope stems from a Greek word meaning boiling without changing. Each azeotrope has a characteristic boiling point.

Azeotropes formed by the solutions showing positive deviations from Raoult's law are called minimum boiling azeotropes or positive azeotropes; such an azeotrope

has the maximum vapour pressure and, therefore the minimum boiling point among all the mixtures formed by these two liquids. These azeotropes always have boiling point lower than either of the components.

Examples: Ethanol-water mixture

The fractional distillation is able to concentrate the alcohol to the best up to 95% by mass of alcohol. Once this composition is reached, the solution and vapour have the same composition, and no additional fractionation occurs. Other methods of separation have to be used for preparation of 100% ethanol.

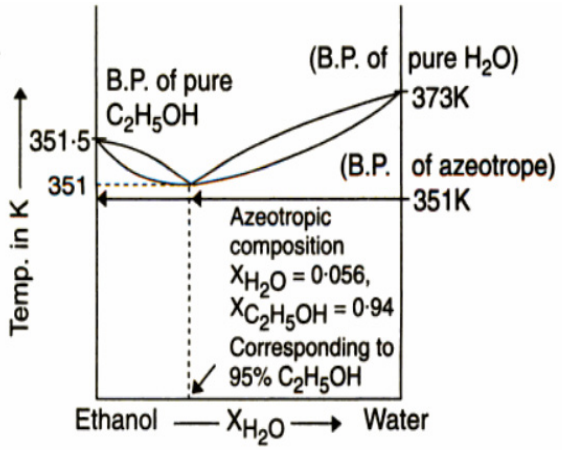


Figure 7.8: Boiling point diagram for ethanol-water mixture

Azeotropes formed by the solutions showing negative deviations from Raoult's law are called the maximum boiling azeotropes or negative azeotropes. These azeotropes have boiling points higher than either of the components.

Azeotropes consisting of two constituents are called binary azeotropes. Those consisting of three constituents are called ternary azeotropes. Azeotropes of more than three constituents are also known.

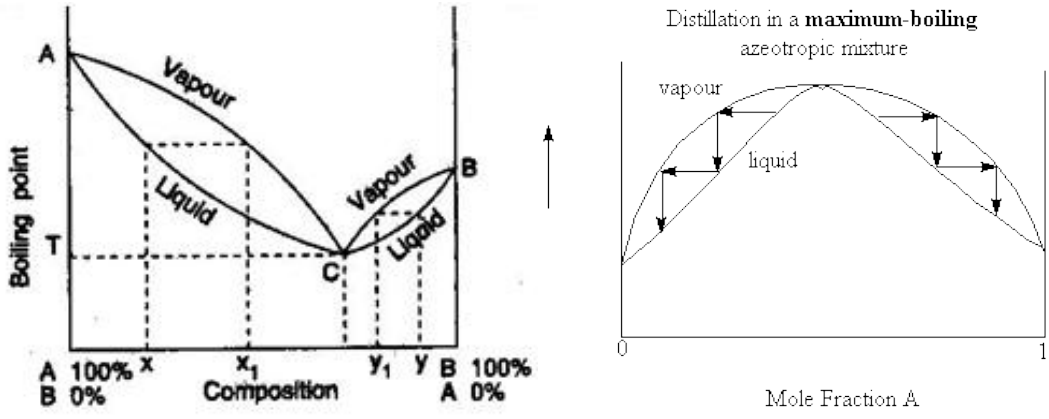


Figure 7.9: Diagrams of minimum and maximum azeotropes

Examples of azeotropes with minimum boiling points and maximum boiling points:

Components		Mass % of B	Boiling points (°C)		
A	B		A	B	Azeotrope
Minimum boiling azeotropes					
water	ethanol	95.57	100	78.5	78
water	propanol	71.70	100	97.2	87.7
chloroform	ethanol	6.8	61.2	78.3	59.3
acetone	Carbon disulphide	67	56.2	46.2	39.2
Maximum boiling azeotropes					
H_2O	HCl	20.3	100	-85	110
H_2O	HNO_3	58.0	100	86	120.5
H_2O	HI	57	100	-34	127
H_2O	$HClO_4$	71.6	100	110	203

Checking up 7.2 (b)

On the basis of information given below answer the following questions:

Information:

- In bromoethane and chloroethane mixture intermolecular interactions of A-A and B-B type are nearly the same as A-B type interactions.
- In ethanol and acetone mixture A-A or B-B type intermolecular interactions are stronger than A-B type interactions.
- In chloroform and acetone mixture A-A or B-B type intermolecular interactions are weaker than A-B type interactions.

Questions:

1. a. Which solution will obey the Raoult's law?
   b. Which solution will deviate from Raoult's Law and which kind of deviation?

11. On the basis of information given below, mark the correct option.
    Information: on adding acetone to methanol some of the hydrogen bonds between methanol molecules break.
    a. At specific composition methanol-acetone mixture forms minimum boiling azeotrope and will show positive deviation from Raoult's law.
    b. At specific composition methanol-acetone mixture will form minimum boiling azeotrope and will show negative deviation from Raoult's law.

c. At specific composition methanol-acetone mixture will form maximum boiling azeotrope and will show negative deviation from Raoult's law.

Application of Raoult's Law

Activity 7.2(c):

Use search internet or other resources and then discuss about Raoult's law and its applications then write a report about your findings.

Questions:

1. Have you carried out a distillation? If yes, what the principle that underlies that separation technique?
2. Have you heard about the production of a local and illegal alcohol called Kanyanga? If yes, do you have an idea of how it is made?
3. Distinguish simple distillation from fractional distillation.

Fractional distillation

Distillation is a separation technique that separates liquid components of a solution according their boiling points. A simple distillation uses a simple condenser; it works well for most routine separation and purification procedures for organic liquids with large differences in their boiling points. When the boiling point differences of the components to be separated are not large, fractional distillation must be used. When an ideal solution of two liquids, such as benzene (boiling point 80°C) and toluene (boiling point 110°C), is distilled by simple distillation, the first vapor produced will be enriched in the lower-boiling component (benzene).

However, when that initial vapour is condensed and analyzed, the distillate will not be pure benzene. The boiling point difference of benzene and toluene (30°C) is too small to achieve a complete separation by simple distillation. So, fractional distillation is an application of Raoult's law illustrated in figure 7.10.

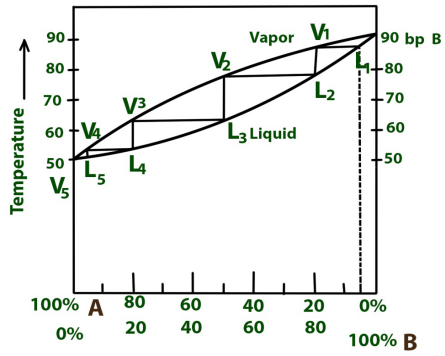


Figure 7.10: The phase diagram for a fractional distillation of an ideal *two-component system*

The horizontal and vertical lines shown in figure above represent the processes that occur during a fractional distillation. Each of the **horizontal lines** (L_1V_1, L_2V_2, and so on) represents both the **vaporization** step of a given vaporization-condensation cycle and the composition of the vapour in equilibrium with liquid at a given temperature. For example, at 63°C a liquid with a composition of 50% A (L_3 on the diagram) would yield vapor of composition 80% A (V_3 on diagram) at equilibrium. The vapor is richer in the lower-boiling component A than the original liquid was.

Each of the **vertical lines** (V_1L_2, V_2L_3, etc.) represents the **condensation** step of a given vaporization-condensation cycle. The composition does not change as the temperature drops on condensation. The vapor at V_3, for example, condenses to give a liquid (L_4 on the diagram) of composition 80% A with a drop in temperature from 63 to 53°C. In the example shown above, pure A boils at 50°C, and pure B boils at 90°C.

These two boiling points are represented at the left-and right-hand edges of the diagram, respectively. Now consider a solution that contains only 5% of A but 95% of B. (Remember that these are mole percentages). This solution is heated (following the dashed line) until it starts boiling at L_1 (87°C). The resulting vapour has composition V_1 (20% A, 80% B).

The vapour is richer in A than the original solution was, but it is by no means pure A. In a simple distillation apparatus, this vapor would be condensed and passed into the receiver in a very impure state.

However, with a fractionating column in place, the vapor is condensed in the column to give liquid L_2 (20% A, 50% B), which is condensed to give liquid L_3. Liquid L_3 is revaporized (boiling point 63°C) to give vapor of composition V_3 (80% A, 20% B), which condense to give liquid L_4. Liquid L_4 is revaporized (boiling point 53°C) to give a vapour of composition V_4 (95% A, 5% B).

This process continues to V_5, which condenses to give nearly pure liquid A. The fractionating process follows the stepped lines in the figure 7.10 downward and to the left. Fractional distillation can be compared to successive solvent extraction or continuous simple distillation to get much amount of solute and concentrate it.

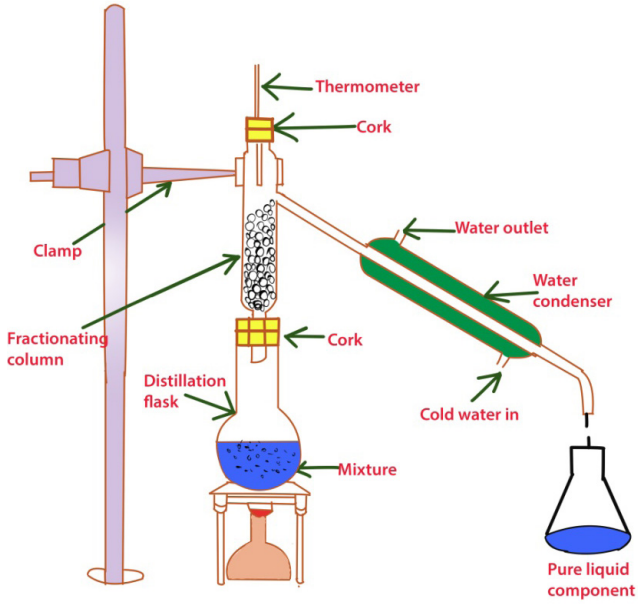


Figure 7.11: Laboratory setting of fractional distillation

Industrial application of fractional distillation: crude oil refinery.

Crude oil is a complex mixture of hydrocarbons of different chain lengths, from the short one such as CH_4, methane, to the very long ones with more than 20 carbon atoms (C-20). Due to their boiling points which are not very different, there are separated, through fractional distillation, into different fractions of hydrocarbons called: kerosene, naphtha, etc... (Fig.7.12)

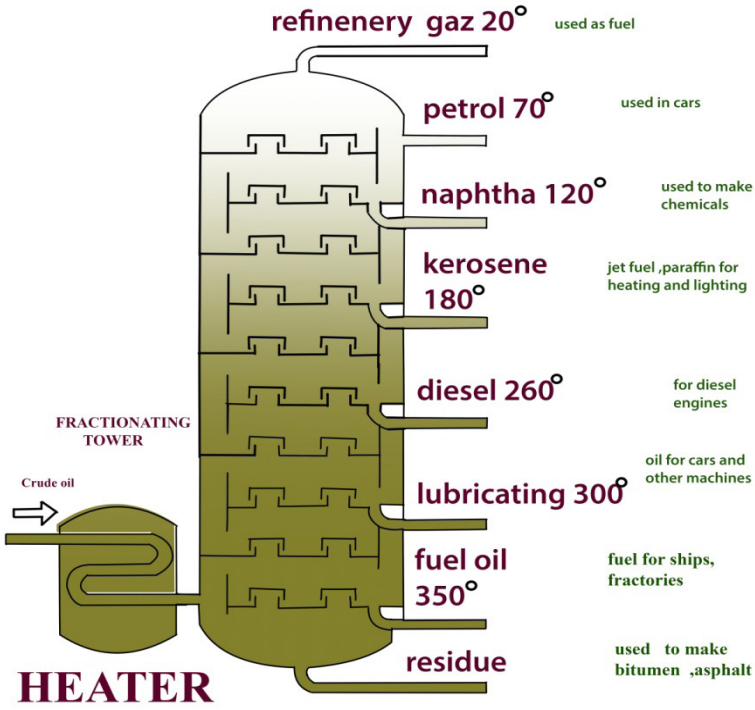


Figure 7.12: Illustration of crude oil refinery

In short: Condensation takes place in discs which increases surface area found in fractionating column. Further heating of the mixture produces more vapour, which in turns will reheat the condensed liquid in discs. During the distillation, the temperatures decrease progressively from the bottom to top of column.

Steam distillation

Activity 7.2 (d)

When people suffer from flue, cold or any other respiratory infections, they collect Cyprus, eucalyptus, and other leaves. They boil them in water and expose themselves to the vapour released. Explain how they are cured.

Distillation using water vapor is called steam distillation. Steam distillation can be used when the material to be distilled has a high boiling point and presents the risk that decomposition might occur if direct distillation is employed. The liquid is added to the still, and steam is passed through it. The solubility of the steam in the liquid must be very low. Most essential oils have been obtained by steam distillation, or, in the more general sense, by hydrodistillation. Essential, volatile, or ethereal oils are mixtures composed of a variety of volatile, liquid, or solid compounds that vary

widely in concentration and boiling points. They are present in the interstices of vegetable tissues and can be extracted by hydrodistillation.

Considering the manner in which the contact between water and the original matrix is promoted, a terminology that distinguishes three types of hydrodistillation has been developed:

- Water distillation,
- Steam distillation, and
- Direct steam distillation.

When the first method is employed, the material to be distilled comes in direct contact with boiling water.

In the second method, the material is supported on a perforated grid or screen held some distance above the bottom of the still. In this case, low-pressure, saturated, wet steam rises through the material. The typical features of this method are that the steam is always fully saturated, wet, and never superheated, and the material is only in contact with steam, and not with boiling water. The last type of hydrodistillation, direct steam distillation, resembles the preceding type, except that no water is kept in the bottom of the still, but live steam, saturated or superheated, is passed through the sample, and the process is frequently maintained at higher than atmospheric pressures.

Steam distillation is the most commonly used method for collecting essential oils. Use of this method is prevalent not only because it yields exceptionally pure and clean products, but because it allows for collection of temperature-sensitive aromatic compounds. Unlike simple distillation, steam distillation involves a pressurized system. When the system is pressurized, essential oils can be distilled at temperatures well below their normal boiling point; thus protecting the integrity of their delicate and complex chemical nature.

When using steam distillation, it is vital to pay careful attention to the heat source. The temperature of the system must remain within a strict range; too low and the essential oils will not be distilled, too high and there is risk of damaging the essential oils or collecting unwanted, non-aromatic compounds. Temperatures required for optimal steam distillation typically fall between 60° C and 100° C. One benefit of steam distillation is that the temperature can be continuously adjusted and precisely controlled to ensure that the system always remains within the optimal temperature range. Similarly, pressure must also be rigidly controlled. To do so, steam distillation requires the use of a "closed system." This means that the system is pressurized to a level above that of atmospheric pressure.

Steam distillation is conducted in a distillation still that uses steam water to remove the essential oil from the plant material. Heat is applied to the water, which produces

steam.

The steam rises and moves through a chamber holding the plant material. As the steam forces its way through the plant material, it ruptures small glands that hold the essential oil. Since essential oils contain only aromatic compounds that are readily volatile, the essential oil is easily carried by the steam into the condensing tube. Once there, the liquid is condensed and accumulates in the collecting still. After removal from the still, a mixture of essential oil and water will be formed. Because essential oils are not water soluble, the mixture will naturally separate into two layers (figure 7.14). The watery layer is called hydrosol and is often sold as floral water.

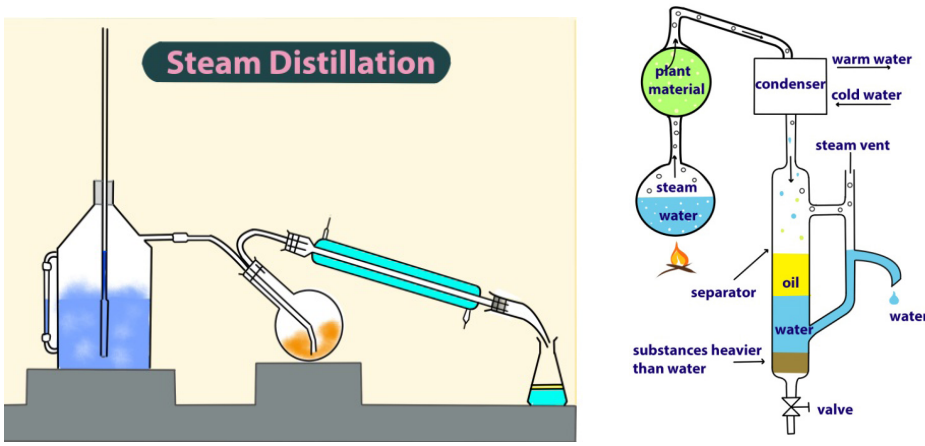


Figure 7.13: The laboratory set up for steam distillation

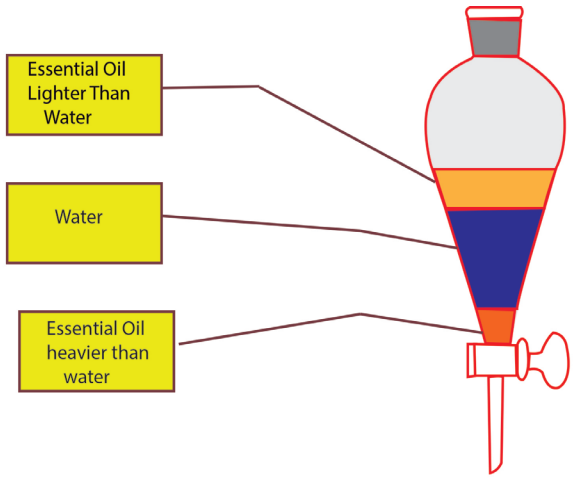


Figure 7.14: Illustration of essential oil and water mixture after steam distillation

Applications

Steam distillation is widely used in the manufacturing of essential oils, for instance perfumes. This method uses a plant material that contains of essential oils. Mainly

orange oil is extracted on a large scale in industries using this method. Application of steam distillation can be found in the production of consumer food products and petroleum industries. They are used in separation of fatty acids from mixtures.

Checking up 7.2 (d)

Explain how the essential oils can be obtained from plants?

7.2.2. Colligative properties

Activity 7.3:

1. The photos you see here have been taken in Europe or North America during winter.

On the left, someone is pouring a liquid, an antifreeze in the radiator of his/her car.

On the right, workers are spreading salt from a truck on a road covered by ice.

Question: Do you have an idea why those persons are doing that?

2. Take a container and divide it into two compartments with a thin membrane containing microscopic pores large enough to allow water molecules but not solute particles to pass through.

Then add a concentrated salt solution to one compartment and a more dilute salt solution to the other. Initially, the two solutions levels start out the same.

   a. What is the name of the membrane?
   b. Observe well and after a while, write your observations.
   c. Name the process observed and explain it and explain how it can be stopped.
   d. Draw with labels the phenomenon.

3. Have you ever heard these words "colligative properties"? If yes explain what they mean and give example to illustrate.

The state of water depends on both pressure and temperature. At sea level, pure liquid water freezes to form solid ice at 0°C and boils to form vapor at 100°C.

However, the addition of particles to water can affect its boiling and freezing points. Particles interfere with the ability of the water molecules to vaporize or freeze. The boiling temperature of water varies depending on the solutes it contains.

Liquid solutions have physical properties significantly different from those of the pure solvent, a fact that has great practical importance. The properties of dilute solutions containing nonvolatile solute, which depend upon relative number of solute and solvent particles but no depending upon their nature, are called **colligative properties**.

Definition of colligative properties of solutions

Colligative properties are properties that depend only on the number of particles present in solution and not in any way on the nature of the solute particles. These properties are bound together by a common origin; they all depend on the number of solute particles present, regardless of whether they are atoms, ions, or molecules.

The colligative properties are Vapour pressure lowering, Freezing point depression, Boiling point elevation and Osmotic pressure.

Lowering of vapour pressure

Molecules can escape from the surface of a liquid into the gas phase by evaporation. In closed container, the pressure exerted by the vapour in the space above the liquid, if the dynamic equilibrium between liquid and vapour is reached, is called the vapour pressure of the substance. The vapour pressure of a liquid is the pressure exerted by its vapour when the liquid and vapour phase are in dynamic equilibrium. A substance with no quantifiable vapour pressure is called nonvolatile and the one that exerts vapour pressure is called volatile.

According to Raoult's law, the vapour pressure exerted by a component of a solution at a given temperature is equal to the mole fraction of that component in the solution multiplied by the vapour pressure of that component in pure state.

In a solution of nonvolatile solute in a volatile solvent the vapour pressure will be exerted by the solvent molecules only because the solute is non volatile i.e., does not go into vapour state. Therefore, the vapour pressure of its solution is always less than that of the pure solvent.

In the pure solvent, the molecules occupy large surface and they escape easily; in the solution of nonvolatile solute and solvent, the solute molecules reduce the surface of the solvent molecules which lead to the reduction of molecules of solvent

escaping. According to Raoult's law:

$$P_1 = \chi_1 P_1^0 \qquad (1)$$

A solution containing only one solute, $\chi_1 \quad 1 \quad \chi_2$, where χ_2 is the mole fraction of the solute.

Equation (1) can therefore be rewritten as:

$$P_1 = (1 - \chi_2)P_1^0 \Rightarrow P_1 = P_1^0 - \chi_2 P_1^0$$
$$P_1 - P_1^0 = \Delta P = \chi_2 P_1^0$$

The decrease in vapour pressure, ΔP, is directly proportional to the solute concentration (measured in mole fraction).

In the case of solution of two or more volatile components, the total vapour pressure over the solution is the sum of the partial vapour pressures of each volatile component. Consider the ideal solution containing two volatile liquid, 1 and 2.

By Raoult's law, the partial pressures of component 1 and 2 vapours above the solution are:

$$P_1 = \chi_1 P_1^0 \quad \text{and } P_2 = \chi_2 P_2^0$$

The total vapour pressures over the solution, P_{total}:

$$P_{total} = P_1 + P_2 = \chi_1 P_1^0 + \chi_2 P_2^0$$

Example:

Calculate the vapour pressure of a solution made by dissolving 218 g of glucose (molar mass=180.2g/mol) in 460 mL of water at 30°C. What is the vapour pressure lowering? The vapour pressure of pure water at 30°C is 31.82 mm Hg. Assume the density of the solution is 1.00 g/mL.

Answer:

The vapour pressure of the solution:

$$n_{water} = 460\ mL \times \frac{1.00\,g}{mL} \times \frac{1\,mol}{18.02} = 25.5\ mol$$
$$n_{glucose} = 218\ g \times \frac{1\,mol}{180.2} = 1.21\ mol$$

The mole fraction of water, χ_1, is given by:

$$\chi_1 = \frac{n_{water}}{n_{water} + n_{glucose}} = \frac{25.5\ \text{mol}}{25.5\ \text{mol} + 1.12\ \text{mol}} = 0.955$$

Therefore, the vapour pressure of the glucose solution is:

$$P_1 = \chi_1 P_{water} \Rightarrow P_1 = 0.955 \times 31.82\ \text{mm Hg}$$
$$P_1 = 30.4\ \text{mm Hg}$$

Finally, the vapour pressure lowering is $\Delta P = (31.82 - 30.4)\ \text{mm Hg} = 1.4\ \text{mm Hg}$

Boiling point elevation

Boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure. As the vapour pressure of a solution containing a nonvolatile solute is lower than that of the pure solvent, its boiling point is higher than that of the pure solvent, because to reach atmospheric pressure at which the solution should boil we need to raise the temperature. The solution has lower vapour pressure than the solvent at the same temperature, figure 7.15. The increase in boiling point is known as elevation in boiling point, ΔT_b.

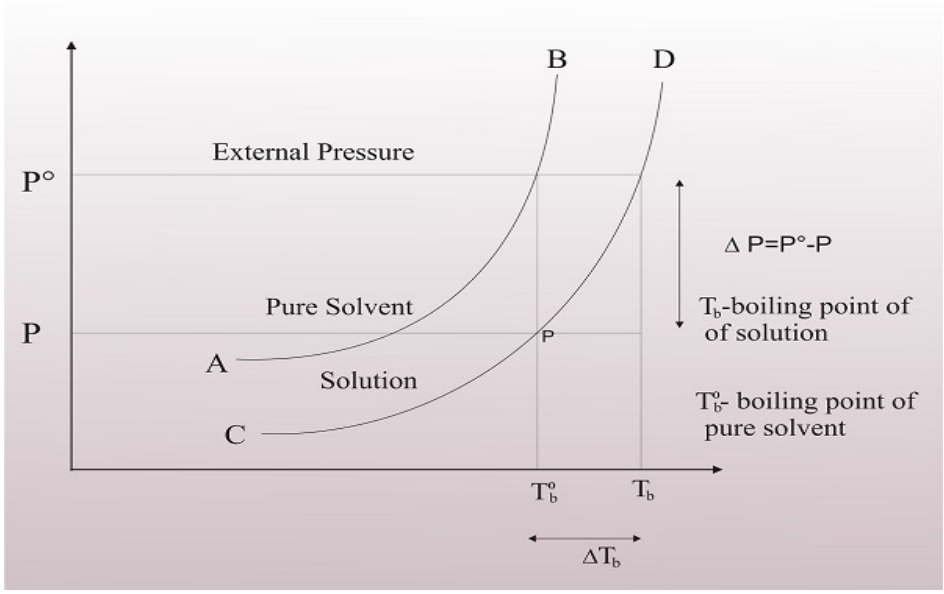


Figure 7.15: Vapour pressure curves explaining the elevation of boiling point

The boiling point elevation (ΔT_b) is defined as the boiling point of the solution (T_b) minus the boiling point of the pure solvent (T_b^0); $\Delta T_b = T_b - T_b^0$. Because $T_b > T_b^0$, ΔT_b is a positive quantity.

The value of ΔT_b is proportional to the vapour pressure lowering which depends also

to number of particles in solution, and so it is also proportional to the concentration (molality) of the solution. That is, $\Delta T_b \propto m \Rightarrow \Delta T_b = K_b m$; where m is the molality of the solution and K_b is the molal boiling point elevation constant(ebullioscopic constant). The unit of K_b is °C/m.

Freezing point depression

Freezing point is the temperature at which the solid and the liquid forms have the same vapour pressure. The freezing point of the solution of nonvolatile solute is always less than that of the pure solvent. Thus, there is a depression in the freezing point of the solution. This is because the vapour pressure of the solution is always less than that of the pure solvent.

The freezing point depression $(\Delta T_f)$is defined as the freezing point of the pure solvent (T_f^0)minus the freezing point of the solution (T_f): $\Delta T_f = T_f^0 - T_f$.

Because $T_f^0 > T_f$, ΔT_f is a positive quantity. ΔT_f is proportional to the concentration (molality) of the solution. $\Delta T_f \propto m \Rightarrow \Delta T_f = K_f m$ Where m is the concentration of the solute in molality units, and K_f is the molal freezing point depression constant (cryoscopic constant. Like K_b, the unit of K_f is °C/m.

So, if $m = 1$, i.e., one mole of solute is dissolved in one kg of the solvent, then, $\Delta T_f = K_f$.

Thus, the molal freezing point depression constant is equal to the depression in the freezing point produced when one mole of solute is dissolved in 1 kg of the solvent.

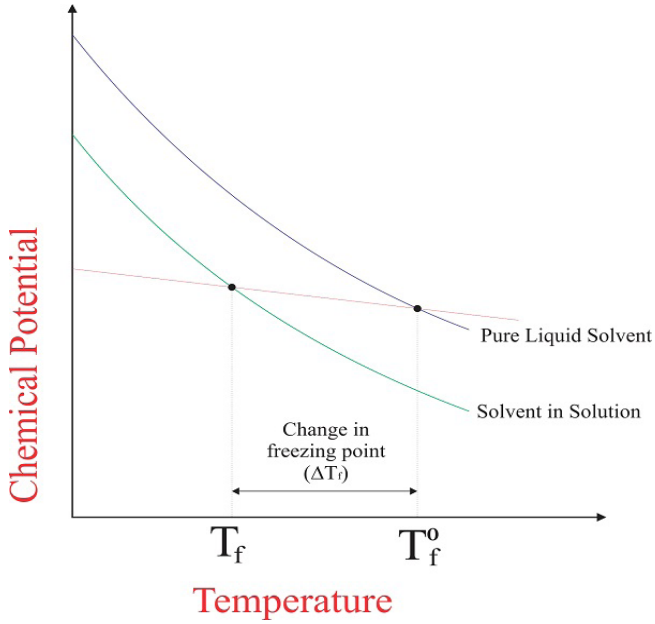


Figure 7.16: Freezing point depression

Example:

Ethylene glycol is common automobile antifreeze. It is water soluble and fairly nonvolatile (b.p 197°C). Calculate the freezing point and boiling point elevation of a solution containing 651 g of this substance in 2505 g of water. The molal mass of ethylene glycol (EG) is 62.01 g. K_f=1.86°C/m and K_b=0.52°C/m.

Answer:

Calculate the molality of ethylene glycol (m):

$$n = \frac{mass_{EG}}{Mm}$$

$$m = \frac{n}{mass_{water(Kg)}} \Rightarrow m = \frac{mass_{EG}}{Mm \times mass_{water}}$$

$$m = \frac{651}{62.01 \times 2.505} = 4.12$$

The molality of EG is 4.12 mol/Kg (m=mol/Kg)

Calculation of freezing point depression and boiling point elevation:

$$\Delta T_f = K_f m \Rightarrow \Delta T_f = \left(1.86^\circ C/m\right)\left(4.12m\right) = 7.66^\circ C$$

$$\Delta T_b = K_b m \Rightarrow \Delta T_b = \left(0.52^\circ C/m\right)\left(4.12m\right) = 2.14^\circ C$$

Osmotic pressure

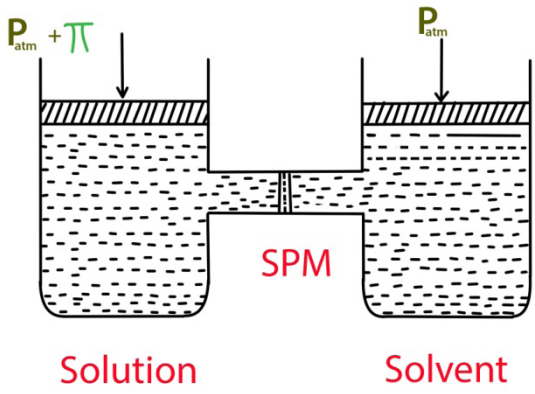
Osmosis is the phenomenon of spontaneous flow of the solvent molecules through a semipermeable membrane from pure solvent to solution or from a dilute solution to concentrated solution. It was first observed by Abbe Nollet. Some natural semipermeable membranes are animal bladder, cell membrane.

You must have observed that if resins are soaked in water for some time, they swell. This is due to the flow of water into the resins through its skin which acts as a semipermeable membrane (permeable only to the solvent molecules). This phenomenon is also observed when two solutions of different concentrations in the same solvent are separated by a semipermeable membrane. In this case the solvent flows from a solution of lower concentration to a solution of higher concentration. The process continues till the concentrations of the solutions on both sides of the membrane become equal. The spontaneous flow of the solvent from a solution of lower concentration (or pure solvent) to a solution of higher concentration when the two are separated by a semipermeable membrane is known as osmosis. The

pressure required to prevent osmosis by pure solvent is called osmotic pressure of solution, π.

Thus, osmotic pressure may be defined as the excess pressure that must be applied to the solution side to just prevent the passage of pure solvent into it when the two are separated by a perfect semipermeable membrane.

This is illustrated in figure 7.16. For dilute solutions, it has been found that osmotic pressure is proportional to the molarity, C of the solution at a given temperature, T.



SPM: Semipermeable Membrane

Figure 7.16: The excess pressure equal to the osmotic pressure must be applied on the solution side to prevent osmosis

It two solutions of the same osmotic pressure are separated by a semipermeable membrane, there is no osmosis. The two solutions are called isotonic solution. Hypotonic solution is the less concentrated solution and hypertonic solution the more concentrated one.

The osmotic pressure is a colligative property. It depends on the number of particles of solute present in the solution and not on their nature.

$$\pi = \frac{n_{solute}}{V_{solution}} RT; \left(n_{solute} = \frac{m_{solute}}{Mm} \right)$$

$$\pi = \frac{m_{solute}}{Mm V_{solution}} R \times T \Rightarrow \pi = MRT \text{ where M is the molarity of the solution}$$

If the density of solution is known, we can use the following formula:

$$Mm = \frac{m_{solute} \times R \times T}{\pi \times V_{solution}}; (d = \frac{m_{solute}}{V_{solution}})$$

$$Mm = \frac{d \times R \times T}{\pi}$$

$$\pi = \frac{d \times R \times T}{M_{solute}}$$

Applications of colligative properties

As seen in the introductory activity (7.4), one of the colligative properties, the freezing point depression is applied to de-ice roads in countries which experience very cold winters.

Colligative properties of non electrolyte solutions provide a means of determination of molar masses and molecular formulae of dissolved solutes which are nonvolatile. Osmotic pressure and changes in freezing point, boiling point, and vapor pressure are directly proportional to the concentration of solute present. Consequently, we can use a measurement of one of these properties to determine the molar mass of the solute from the measurements. In practice, only freezing point depression and osmotic pressure are used because they show the most pronounced changes.

- **Determination of molar mass from relative lowering of vapour pressure**

Relative lowering of vapour pressure is the ratio of lowering in vapour pressure to vapour pressure of pure solvent. The relative lowering in vapour pressure of solution containing a nonvolatile solute is equal to the mole fraction of solute in the solution.

$$\frac{P_A^0 - P_A}{P_A^0} = \chi_B$$

Where, $\frac{P_A^0 - P_A}{P_A^0} = \text{relative lowering of vapour pressure}$

$$\frac{P_A^0 - P_A}{P_A^0} = \frac{n_B}{n_A + n_B}$$

For dilute solutions, $n_B < n_A$. Therefore the term n_B can be neglected in the denominator.

$$\frac{P_A^0 - P_A}{P_A^0} = \frac{n_B}{n_A} = \chi_B$$

$$\frac{n_B}{n_A} = \frac{W_B / M_B}{W_A / M_A} = \frac{W_B . M_A}{W_A . M_B} = \chi_B$$

or

$$\frac{P_A^0 - P_A}{P_A^0} = \frac{W_B . M_A}{W_A . M_B}$$

$$M_B = \frac{W_B}{W_A} \times M_A \times \frac{P_A}{(P_A^0 - P_A)}$$

The above expression is used to determine the molecular mass of the solute B, provided the relative lowering of vapour pressure of a solution of known

concentration and molecular mass of solvent are known. Where, W_B and W_A = mass of Solute and solvent respectively. M_B and M_A = molecular weight of solute and solvent respectively. However, the determination of molecular mass by this method is often difficult because the accurate determination of lowering of vapour pressure is difficult. Ostwald and Walker method is used to determine the relative lowering of vapour pressure.

Examples

1. The relative lowering of vapour pressure produced by dissolving 7.2 g of a substance in 100g of water is 0.00715. What is the molecular mass of the substance?

Solution:

We know that $\frac{P_A^0 - P_A}{P_A^0} = \frac{W_B.M_A}{W_A.M_B}$

Substituting the values we get

$$0.00715 = \frac{7.2 \times 18}{M_B \times 100}$$

$$M_B = \frac{7.2 \times 18}{0.00715 \times 100} = 181.26$$

Molecular mass of the substance is 181.26 amu

2. The vapour pressure of 5% aqueous solution of a nonvolatile organic substance at 373 K is 745 mm Hg. Calculate the molar mass of the substance.

Solution

From the given data, for 100 g of solution,

Mass of solute, W_2= 5g

Mass of solvent (water), W_1= (100-5) g= 95 g= 0.095 Kg

Vapour pressure of the solution, P_s=745 mm Hg

The vapour pressure of the pure solvent (water), $P_s^\circ = 760 \text{ mm Hg}$

Molar mass of the solute, M_2=?

Molar mass of the solvent (water), M_1=18 g/mol

From Raoult's law: $\frac{P_s^\circ - P_1}{P_s^\circ} = \frac{n_2}{n_1 + n_2} = \frac{W_2/M_2}{(W_1/M_1) + W_2/M_2}$

$$\frac{760 - 745}{760} = \frac{5/M_2}{(95/18) + 5/M_2} = \frac{5/M_2}{5.278 + 5/M_2}$$

The above equation may be rewritten

$$\frac{760}{15} = \frac{5.278 + 5/M_2}{5/M_2} = \frac{5.278M_2 + 5}{5} = 1.0556M_2 + 1$$

$$50.67 = 1.0556M_2 + 1 \Rightarrow M_2 = 47 \text{ g mol}^{-1}$$

- **Determination of molar mass from elevation of boiling point (ΔT_b)**

The molar mass of a non electrolyte can be calculated from the elevation of boiling point:

where, W_2 is the mass of solute (in grams), and M_2 is the molar mass of the solute (in g/mol) and, W_1 is the mass of the solvent in Kg units.

This gives

$M_2 = \frac{K_b \times W_2}{W_1 \times \Delta T_b} = \frac{K_b \times W_2}{W_1/1000 \times \Delta T_b} = \frac{1000 \times K_b \times W_2}{W_1 \times \Delta T_b}$ (the mass of solvent is expressed in grams)

The constant K_B is called the molal elevation constant or ebullioscopic constant for the solvent. K_B may be defined as the elevation in boiling point when one mole of a solute is dissolved in one kilogram of the solvent. K_B is expressed in degree per molality.

Examples

1. A solution containing 4.2 grams of an organic compound in 50 grams of acetone shows an elevation of boiling point by 1.8 K. Determine the molar mass of the organic compound. K_b of acetone=1.71 K kg /mol.

Solution

Mass of organic compound, W_2=4.2 g

Mass of acetone (solvent), W_1=50 g

ΔT_b=1.8 K

K_b= 1.71 K Kg/mol

If the molar mass of the solute is M, then

$$M = \frac{1000 \times K_b \times W_2}{W_1 \times \Delta T_b} = \frac{1000 \times 1.71 \times 4.2}{50 \times 1.8} g\ mol^{-1} = 79.8\ g\ mol^{-1}$$

2. The boiling point of benzene is 353.23 K. when 1.80 g of a non-volatile solute was dissolved in 90g of benzene; the boiling point is raised to 354.11 K. calculate the molar mass of the solute. K_b for benzene is 2.53 K kg/mol.

Answer:

$$\Delta T_b = 354.11K - 353.23K = 0.88K$$

$$M_B = 2.53 \times \frac{1.8}{0.88} \times \frac{1000}{90} = 58$$

Therefore, molar mass of the solute is 58g/mol.

- **Determination of molar mass from depression in freezing point**

The molar mass of a non-electrolyte solute can be obtained from the freezing point depression.

$$\Delta T_f = K_f m = \frac{K_f n_2}{W_1} = \frac{K_f W_2}{W_1 M_2}$$

where, W_2 is the mass of solute (in grams), and M_2 is the molar mass of the solute (in g/mol) and, W_1 is the mass of the solvent in Kg units.

This gives

$$M_2 = \frac{K_f \times W_2}{W_1 \times \Delta T_f} = \frac{K_f \times W_2}{W_1/1000 \times \Delta T_f} = \frac{1000 \times K_f \times W_2}{W_1 \times \Delta T_f}$$ (the mass of solvent is expressed in grams)

The method of obtaining the molar mass of a solute from the freezing point depression is used for the substances which are affected by heat such as, proteins.

The constant (K_f), for a solution, is called molal depression constant or molal cryoscopic constant for the solvent. K_f may be defined as the depression in freezing point of a solution when one mole of a solute is dissolved in 1 kilogram of the solvent.

Examples:

1.00g of non-electrolyte solute dissolved in 50g of benzene lowered the freezing point of benzene by 0.40K. The freezing point depression constant of benzene is 5.12 K Kg/mol. Find the molar mass of the solute.

Solution:

$$M_B = K_f \times \frac{W_B}{\Delta T_f} \times \frac{1000}{W_A} \ , \quad M_B = 5.12 \times \frac{1.00}{0.40} \times \frac{1000}{50} = 256$$

Thus, molar mass of the solute is 256g/mol.

This property is used in the countries that experience cold winter where salt is spread on the roads to de-ice the roads; salt mixed with ice decreases the freezing temperature of water and the ice liquefies or melts at temperatures below zero.

- **Determination of molar mass from osmotic pressure**

Because small pressures can be measured easily and accurately, osmotic pressure measurements provide a useful way of molar masses determination of large molecules, like protein, polymers and other macromolecules. The osmotic pressure method has the advantage over other methods as pressure measurement is around the room temperature and the molarity of the solution is used instead of molality. As compared to other colligative properties, its magnitude is large even for very dilute solutions. The technique of osmotic pressure for determination of molar mass of solutes is particularly useful for biomolecules as they are generally not stable at higher temperature and polymers have poor solubility.

$$\pi v = nRT; \left(M = \frac{n}{V} = \frac{m}{MmV} \right)$$

$$\pi = \frac{m}{MmV} RT$$

$$Mm = \frac{mRT}{\pi \times V}; (d = \frac{m}{V})$$

$$Mm = \frac{d \times R \times T}{\pi}$$

$$\pi = \frac{d \times R \times T}{Mm}$$

Where, d = density, R = gas constant

T = temperature, Mm = molar mass of solute

Note: Osmotic pressure method is preferred for determination of very high molecular mass because osmotic pressure effects for small mole fractions are much higher than the effects on freezing and boiling points i.e.osmotic pressure changes for very

small mole fraction can be more easily determined than freezing point changes.

Examples

1. The osmotic pressure of aqueous solution of a certain protein was measured in order to determine the molar mass of the protein. The solution contained 3.50 mg of protein dissolved in sufficient water to form 5.00 ml of solution. The osmotic pressure of the solution at 25°C was found to be 1.54 torr. Calculate the molar mass of the protein.

Solution

Calculate the molarity:

$$M = \frac{\pi}{RT} = \frac{(1.54\ \text{torr})\left(\frac{1\ \text{atm}}{760\ \text{torr}}\right)}{\left(0.0821\frac{\text{L atm}}{\text{mol K}}\right)(298\ \text{K})} = 8.28\times10^{-5}\,mol/L$$

Find the number of moles:

$$M = \frac{n}{V} \Rightarrow n = MV$$
$$n = \left(8.28\times10^{-5}\ \text{mol/L}\right)\left(5.00\times10^{-3}\,L\right) = 4.14\times10^{-7}\,mol$$

Find the molar mass

$$\text{Molar mass} = \frac{\text{mass}}{\text{number of moles}} = \frac{3.50\times10^{-3}\ \text{g}}{4.14\times10^{-7}\ mol} = 8.45\times10^{3}\ \text{g/mol}$$

The molar mass of protein is $8.45\times10^{3}\ \text{g/mol}$.

2. A 50.00 mL sample of an aqueous solution contains 1.08 g of human serum albumin, a blood plasma protein. The solution has an osmotic pressure of 5.85 torr at 298 K. what is the molar mass of the albumin?

Answer:

1atm=760mmHg=760torr= 101325Pa

$\pi = MRT$ where M is molarity, R is gas constant and T is the temperature

$$\pi = \frac{\text{m}}{\text{MmV}} RT \Rightarrow Mm = \frac{mRT}{\pi V}$$

$$Mm = \frac{mRT}{\pi V} \Rightarrow Mm = \frac{1.08 \times 0.0821 \frac{L\ \text{atm}}{\text{mol K}} \times 289\ \text{K}}{\frac{5.85}{760}\ \text{atm} \times 50 \times 10^{-3}\ L} = 68{,}631\ \text{g/mol}$$

Reverse Osmosis and Water Purification

If a pressure higher than the osmotic pressure is applied to the more concentrated solution side, the direction of flow of the solvent can be reversed. As a result, the pure solvent flows out of the solution through the semipermeable membrane. This process is called reverse osmosis. It is of great practical application as it is used for desalination of sea water to obtain pure water. When pressure more than osmotic pressure is applied, pure water is squeezed out of the sea water through the membrane.

These days many countries, such as desert Arab countries, use desalination plants based on this technology to meet their potable water requirements.

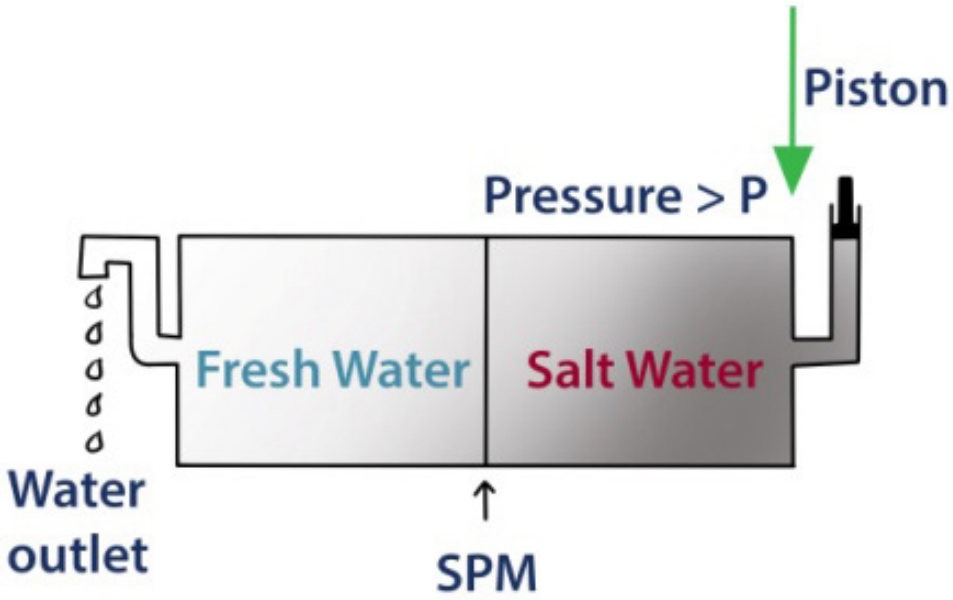


Figure 7.17: Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution

Checking up 7.3

1. Why is the osmotic pressure measurement preferred for determining the molecular mass of proteins?
2. The vapour pressure of pure benzene at certain temperature is 0.850 bar. A nonvolatile, non electrolyte solid weighing 0.5 g is added to 39.0 g of benzene (molar mass = 78 g/mol). The vapour pressure of the solution is 0.845 bar. What is the molecular of the solid substance?
3. Vapour pressure of water at 293 K is 17.535 mm Hg. Calculate the vapour pressure of water at 293 K when 25 g of glucose is dissolved in 450 g of water.
4. An organic liquid C has a freezing point of 198.5 °C and molal depression constant of 45.5°C/m. When 0.049 g of a substance A was dissolved in 0.521 g of C, the resultant mixture was found to freeze at 186°C. Calculate the molar mass of A.
5. Water boils at 100°C at a pressure of 760 mm Hg. When the pressure is reduced to 660 mm Hg, water boils at 96°C. explain this observation.

END UNIT ASSESSMENT

1. Colligative properties are observed when:
   a. a non-volatile solid is dissolved in a volatile liquid
   b. a non-volatile liquid is dissolved in an another volatile liquid
   c. a gas is dissolved in a non-volatile liquid
   d. a volatile liquid is dissolved in an another volatile liquid

   Mark the correct option(s).

2. Which of the following binary mixtures will have same composition in liquid and vapour phase?
   a. Benzene-Toluene
   b. Water-Nitric acid
   c. Water-Ethanol
   d. n-Hexane-n-Heptane

3. Considering the following couples of solvents, predict which mixture will show a positive deviation from Raoult's law.
   a. Methanol and acetone
   b. Chloroform and acetone
   c. Nitric acid and water
   d. Phenol and aniline

4. Relative lowering of vapour pressure is a colligative property because
   a. It depends on the concentration of a non-electrolyte solute in solution and does not depend on the nature of the solute molecules.
   b. It depends on number of particles of electrolyte solute in solution and does no t depend on the nature of the solute molecules.
   c. It depends on the concentration of anon-electrolyte solute in solution as well as on the nature of the solute molecules.
   d. It depends on the concentration of an electrolyte or a non-electrolyte solute in solution as well as on the nature of solute molecules.

   Mark the correct option(s).

5. If two liquids A and B form minimum boiling azeotrope at some specific composition:

   a. A-B interactions are stronger than those between A-A or B-B

   b. Vapour pressure of solution increases because more number of molecules of liquids A and B can escape from the solution

   c. Vapour pressure of solution decreases because less number of molecules of only one of the escape from the solution

   d. A-B interactions are weaker than those between A-A or B-B.

   Mark the correct option(s).

6. Colligative properties depend on

   a. The nature of the solute particles dissolved in solution

   b. The number of solute particles in solution

   c. The physical properties of the solute particles dissolved in solution

   d. The nature of the solvent particles.

   Mark the correct option(s).

7. If 0.500 grams of caffeine is dissolved in 100 mL of water, what percentage of caffeine can be separated from the water using a single 40 mL sample of methylene chloride? The distribution coefficient = 4.6

8. Benzoic acid can be separated from water using octanol as the organic solvent. The distribution coefficient for this water/octanol system is P = 1.87. Assuming that 1 gram of benzoic acid has been dissolved in 100 mL of water, how many 20 mL extractions must be done to extract 60+ percent of the benzoic acid from the water?

9. A 0.100 gram sample of phthalic acid was dissolved in 100 mL of water. When 25 mL of diethyl ether was used to extract the phthalic acid, 0.042 grams of phthalic acid were recovered. What is the distribution coefficient for this extraction?

10. What mass of ethylene glycol ($C_2H_6O_2$, molar mass=62.1 g/mol), the main component of antifreeze, must be added to 10.0 L of water to produce a solution for use in a car's radiator that freezes at -23.3°C? Assume the density of water is exactly 1g/ml. K_f=1.86°C.kg/mol

11. A chemist is trying to identify a human hormone that controls metabolism by determining its molar mass. A sample weighing 0.546g was dissolved in 15.0 g benzene, and the freezing point depression was determined to be 0.240°C. Calculate the molar mass of the hormone. K_f for benzene is 5.12°C. Kg/mol.
12. To determine the molar mass of a certain protein, 1.00×10^{-3} g of it dissolved in enough water to make 1.oo mL of solution. The osmotic pressure of this solution was found to be 1.12 torr at 25.0°C. Calculate the molar mass of protein.
13. The molecular masses of polymers are determined by osmotic pressure method and not by measured other colligative properties. Give two reasons.
14. Non-ideal solutions exhibit either positive or negative deviations from Raoult's law. What are these deviations and why are they caused? Explain with one example for each type.

UNIT 8

QUANTITATIVE CHEMICAL EQUILIBRIUM

UNIT 8: QUANTITATIVE CHEMICAL EQUILIBRIUM

Key Unit Competence

To write expressions and calculate the values of equilibrium constant, interpret the values of Kc in relation to the yield of the products in reversible reactions.

Learning objectives

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

- Explain how the temperature affects the magnitude of equilibrium constant Kc;
- Derive the relationship between Kc and Kp;
- Write expression for Kc and Kp;
- Interpret the Kc values in relation to the yield of the reversible reactions;
- Compare the Kc value with Qc value and predict if a reaction is at equilibrium or not.
- Compare and interpret the values of Kc and Kp of different reactions;
- Perform calculations involving equilibrium constants in terms of concentration(Kc), and partial prsessure (Kp).

Introductory activity

1. Observe carefully the following chemical equations and answer the question.

   A: $I_2(g) + H_2(g) \rightleftarrows 2HI(g)$

   B: $2Na(s) + 2H_2O(l) \rightarrow 2NaOH_{(aq)} + H_{2(g)}$

   Differentiate between the two chemical equations.

2. Consider the reversible reaction: $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ which is used in the Contact process for the manufacture of sulphuric acid in the presence of catalyst V_2O_5. The reaction produces the energy $\Delta H = -196$ KJ/mol.

   a. State and explain the effect of raising the temperature on the position of equilibrium of this reaction.

   b. What is the effect of the catalyst on the position of equilibrium in this reaction?

   c. What is the effect of increasing the concentration of oxygen (at the same temperature)

   d. What is the effect of increasing the concentration of SO_3

3. Ethane can be cracked at high temperatures according to the equation $C_2H_6(g) \rightarrow C_2H_4(g) + H_2(g)$. If the standard enthalpy of formation of ethene is positive,

   Explain the effect of increasing temperature on the position of equilibrium.

4. Ammonia is manufactured by the Haber - Bosch process according to the equation

   $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ $\Delta H = -92$Kjmol-1

   State and explain the effect of high temperatures on

   a. The rate of the above reaction
   b. The yield of ammonia.

5. State, giving reasons, how an increase in pressure affects the position of equilibrium in the reaction above.

In most of the chemical reactions, the reactants are not completely converted into products. The reaction proceeds to a certain extent and reaches a state at which the concentrations of both reactants and products remain constant with time.

Chemical equilibrium is the state in which both reactants and products of a chemical reaction are present in concentrations that do not change with time. Chemical equilibrium deals with the reversible reactions, which reach equilibrium state; where the forward reaction proceeds at the same rate as the reverse reaction. The scope of chemical equilibrium includes the study of characteristics and factors affecting the chemical equilibrium.

8.1. Definition and characteristics of equilibrium constant Kc

Activity 8.1

1. a. Discuss the effect of a decrease in pressure on each of the following equilibrium?

   b. $N_2O_4(g) \rightleftarrows 2NO_2(g)$

   c. $H_2(g) + I_2(g) \rightleftarrows 2HI(g)$

   d. $CO(g) + 2H_2(g) \rightleftarrows CH_3OH(g)$

2. Explain the effect of an increase in temperature on each of the following reaction at the equilibrium.
   $PCl_5(g) \rightleftarrows PCl_3(g) + Cl_2(g)$; $\Delta H = +87.9kJ/mol$

8.1.1. Definition

The equilibrium constant expresses ratio between the concentrations of the products and the concentrations of the reactants under the given conditions. The equilibrium constant is symbolized by K_c, and the ratio Q expresses the value of the reaction quotient when the forward and reverse reactions occur at the same rate. When the reaction reaches the equilibrium, no change is observed between the chemical composition of the mixture with time and the enthalpy of the products is equal to that of the reagents while the Gibbs free energy change for the reaction is equal to zero.

By definition: The equilibrium constant, Kc, is the ratio of the equilibrium concentrations of products over the equilibrium concentrations of reactants each raised to the power of their stoichiometric coefficients at given temperature.

8.1.2. Characteristics of equilibrium

Consider the following reversible reaction involving homogeneous system;

$aA + bB \rightleftarrows cC + dD$

The equilibrium constant Kc is equal to:

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Note: All the concentrations used to calculate Kc are measured at homogeneous equilibrium.

Where, A, B, C, and D are chemical species, and a, b, c, and d are their respective stoichiometric coefficients.

- If Kc value >> 1, the direct reaction is favored and the reaction mixture contains mostly products.
- If Kc value <<1, the reverse reaction is favored and the reaction mixture contains mostly reactants.
- If the Kc value is close to 1 ($0.10 < Kc < 10$), the mixture contains appreciable amounts of both reactants and products

Examples: Write the equilibrium constant expression, Kc, for the following reactions:

(1) $H_2(g) + I_2(g) \rightleftarrows 2HI(g)$; $\quad K_c = \frac{[HI]^2}{[H_2][I_2]}$

(2) $N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$; $\quad K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$

Note:

i. The equilibrium can be approached from either direction (forward or backward direction).
ii. The equilibrium constant Kc does not depend on the initial concentrations of reactants and products but it depends on temperature.

The equilibrium is described as homogeneous if all species are in the same phase and heterogeneous if they are in different phases.

Worked examples:

Write the equilibrium constant expression, Kc, for the reactions

1. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
2. $2\,HI(g) \rightleftharpoons H_2(g) + I_2(g)$

Evaluating K_c for a reaction:

In order to determine the value of an equilibrium constant, when amounts of reactants are known at equilibrium. The amount of one of the substances in the equilibrium mixture is found by experiment. The amounts of the others can then be worked out from the stoichiometric equation as shown in the following worked example.

Examples

1. 2.0 mol of ethanoic acid and 2.0 mol of ethanol are mixed and allowed to come to equilibrium with the ethyl ethanoate and water they have produced. At equilibrium, the amount of ethanoic acid present is 0.67 mol. Calculate K_c.

Solution

$$CH_3CO_2H + C_2H_5OH \rightleftarrows CH_3CO_2C_2H_5 + H_2O$$

Number of moles at the start of the reaction:	2.0	2.0	0	0
Number of moles at equilibrium:	2 – 0.067	2 – 0.067	0.67	0.67
	1.33mol	1.33 mol		
Concentrations at equilibrium	$\frac{1.33}{V}$	$\frac{1.33}{V}$	$\frac{0.67}{V}$	

Where V is the total volume of the mixture.

The equilibrium constant is written as:

$$K_C = \frac{[CH_3CO_2C_2H_5][H_2O]}{[CH_3CO_2H][C_2H_5OH]} = \frac{\frac{1.33}{V} \times \frac{1.33}{V}}{\frac{0.67}{V} \times \frac{0.67}{V}} = 4.0\,(No\ units)$$

2. A 10.0 cm^3 mixture contains the initial amounts /mol ethanol 0.0515; ethanoic acid 0.0525; water 0.0167; ester 0.0314 in acidic medium. The equilibrium amount of ethanoic acid = 0.0255 mol.

Since the amount of ethanoic acid has decreased by 0.0270 mol, ethanol has decreased by the same amount, and ester and water both increased by this amount.

Solution

Species	$CH_3CO_2H + C_2H_5OH \rightleftarrows CH_3CO_2C_2H_5 + H_2O$			
Initial amount/mol	0.0525	0.515	0.0314	0.0167
Equilibrium amount/mol	0.0255	0.0245	0.0584	0.0437

$$K_C = \frac{[CH_3CO_2C_2H_5][H_2O]}{[CH_3CO_2H][C_2H_5OH]}$$

All the substances are present in the same volume of solution, therefore,

$$K_C = \frac{0.0584 \times 0.0437}{0.0255 \times 0.0245} = 4.1$$

From the calculations of all the mixtures, an average value of K_c at the chosen temperature can be found. For this equilibrium K_c is dimensionless because:

$$KC = \frac{[\text{ester/moldm}^{-3}]\ [\text{water/moldm}^{-3}]}{[\text{acid/moldm}^{-3}]\ [\text{alcohol/moldm}^{-3}]}$$

therefore the concentration units cancel out, and K is a unitless number.

Characteristics of the equilibrium constant Kc

The equilibrium constant, K_c is governed by temperature, which is the only factor that can change the internal potential energy of the reactants or products.

i. If the forward reaction is exothermic, K_c decreases with the increase in temperature.
ii. If the forward reaction is endothermic, K_c increases with the increase in temperature.
iii. The application of a catalyst to a reaction has no effect on a Kc value.

Checking up 8.1

1. An important step in the manufacture of sulphuric acid is the catalytic oxidation of sulphur dioxide, SO_2 to sulphur trioxide, SO_3.
   $2SO_2(g) + O_2(g) \rightleftarrows 2SO_3(g)\ \Delta H = -196kJmol\text{-}1$

   For each of the following changes, state how the equilibrium will react to the change and give your reasoning.

   a. Decrease in pressure

   b. Reduction of catalyst efficiency by 50%.

2. Ammonia is manufactured by the Haber - Bosch process by mixing hydrogen and nitrogen at 700K and 200 atmospheres pressure and using an iron catalyst with a potassium hydroxide promoter. $N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)\ \Delta H = -92kJ$
   Explain why the use of high pressure favors ammonia formation.

8.2. Deriving equilibrium constant Kc

Activity 8.2

1. Write an expression for the chemical equilibrium, K_c, for each of the following reactions;

   a. $Sn^{2+}(aq) + 2F^{2+}(aq) \rightleftarrows Sn^{4+}(aq) + 2Fe^{2+}(aq)$

   b. $Ag^{+}(aq) + Fe^{2+}(aq) \rightleftarrows Fe^{3+}(aq) + Ag(s)$

   c. $2Cr^{3+}(aq) + Fe(s) \rightleftarrows 2Cr^{2+}(aq) + Fe^{2+}(aq)$

2. Equilibrium is established in the reaction
   $A(aq) + B(aq) \rightleftarrows 2C(aq)$
   If equilibrium concentrations are [A] = 0.25, [B] = 0.40, [C] = 0.50 mol dm^{-3}, what is the value of K_c ?

3. The following reaction was allowed to reach equilibrium:
   $2D(aq) + E(aq) \rightleftarrows F(aq)$
   The initial amounts of the reactants present in 1.00 dm^3 of solution were 1.00 mol D and 0.75 mol E. At equilibrium, the amounts were 0.70 mol D and 0.60 mol E. Calculate the equilibrium constant K_c

8.2.1. Deriving equilibrium constant Kc from thermodynamic approach

The equilibrium constant gives the rate of transformation and expresses the ratio of the concentrations between the products and the reagents under the given conditions.

A relation can be derived between the change of standard free enthalpy and the equilibrium constant. Enthalpies and entropies are important thermodynamic functions used for a wide variety of applications. Enthalpy and entropy express the energy and the randomness of a reaction respectively. In chemistry, the temperature is an important factor that often can influence the rate of the reaction.

The application of thermodynamic data is expanded due to the introduction of the Gibb's energy, because of its link to the equilibrium constant, *Kc*.

A relationship between the equilibrium constant, Kc, and Gibb's energy, *G*, entropy *S* at temperature *T* have been introduced.

According to the mass action law, for a general reaction of ***a* moles** of **A** and ***b* moles** of **B** that produce ***c* moles** of **C** and ***d* moles** of **D** is represented by:

$$a\,\mathbf{A} + b\,\mathbf{B} \rightleftarrows c\,\mathbf{C} + d\,\mathbf{D}$$

The concentrations or activities of **A, B, C,** and **D** are represented by **[A], [B], [C]** and **[D]** respectively. For any system, **a reaction quotient, *Q* can be expressed as:**

$$Q = \frac{[C]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b} \quad \textbf{(1)}$$

The data derived from experiments, show that, over time, the **quotient *Q*** tends to approach a constant ***K*** for a given reaction in a closed system. Such a state is called ***equilibrium.***

The constant *K* depends on temperature and the nature of the reactants and products. Thus, *K* is called the equilibrium constant.

$$K = \frac{[C]^c[\mathrm{D}]}{[\mathrm{A}]^a[\mathrm{B}]} \quad \textbf{(2)}$$

The use of thermodynamic functions covers a wide range of concentrations rather than using concentrations to define the **reaction quotient** or **equilibrium constant *K*.** Furthermore, the energy is the driving force for reactions. The tendency for a reaction to reach equilibrium is driven by the Gibbs free energy change, symbolized by Δ***G*** and the relationship between K and Δ***G*°** is given by the expression.

$$\Delta G^\circ = -RT\ln K \quad \textbf{(3)}$$

At the *standard conditions*, activities of all the reactants and products are unity (equal to 1). In this system, ***Q* = 1**.

Based on the equation (2), if ***Kc* > 1**, the ***forward reaction is spontaneous***.

To generalize the free Gibb's energy change, **Δ*G* in a system, at non-standard conditions,** we obtain:

$\Delta G = \Delta G^o + RT \ln Q$ *(4)*

At the equilibrium, *"$Q \rightarrow K$" and* **$\Delta G = 0$,** *the* equation (4) can be written as:

$\Delta G = \Delta G^o + RT \ln Q = 0$ (5)

From the equation (5), we get:

$\Delta G^o = - RT \ln Q$ (6)

If ***$\Delta G = 0$),*** the system has reached an equilibrium state. From the relations (3) and (4), we can summarize that: $G = \Delta G^o + R T \ln Q$ and $\Delta Go = - R T \ln K$

The relation above can be written as $\Delta G = - R T \ln K + R T \ln Q$ Or

$\Delta G = R T \ln Q - R T \ln K$ (7)

Applying the law of logarithm, we have log a/b = log a –log b, then the relation (7) becomes:

$\Delta G = R T \ln Q/K$ (8)

The value of **ΔG can inform us on the spontaneity of a reaction:**
If *ΔG is positive ($\Delta G > 0$),* the reverse reaction is spontaneous
If ***ΔG is positive ($\Delta G < 0$),*** the forward reaction is spontaneous

The relation (8) allows to determine in which direction a reaction will proceed under non-standard conditions and the ratio Q/K determines the sign of ΔG:

1. If $Q/K < 1$, ΔG is negative and the reaction is spontaneous
2. If $Q/K = 1$, $\Delta G = 0$ and the system is at equilibrium
3. If $Q/K > 1$, ΔG is positive and the reaction is spontaneous in the opposite direction

8.2.2. Deriving equilibrium constant Kc from kinetic approach

In kinetics, there is a relationship between the equilibrium constant and the rate constant which is used to express the rate law as constant of proportionality. Consider the reaction: $N_2O_4\ (g) \rightleftarrows 2NO_2(g)$

- In chemical kinetics, the rate of forward reaction is written as: $R = kf[N_2O_4]$ where R = rate of the forward reaction and kf is the rate constant for the said reaction.
- Similarly, the rate of backward reaction at equilibrium is: $R = kb[NO_2]^2$, kb is the rate constant for backward reaction.

At the equilibrium, both the two rates are equal, therefore: $kf[N_2O_4] = kb[NO_2]^2$

The relation can be rearranged and we get: $\frac{[NO_2]^2}{[N_2O_4]} = \frac{k_f}{k_b} = K_c$

Thus, the equilibrium constant is the ratio of the forward and reverse rate constants which are both constant values at a given temperature.

Checking up 8.2

1. Express the equlilibrium constant, K_c , and state its units in each of the following reactions.
   a. $I_2(aq) + I^-(aq) \rightleftarrows I_3^-(aq)$
   b. $N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$
2. Consider the reaction between sulphur dioxide and oxygen to produce sulphur trioxide at 700°C:
   $2SO_2(g) + O_2(g) \rightleftarrows 2SO_3(g)$ ΔH = -ve
   a. Write the expression for the equilibrium constant, K_c, for the above reaction and give its units.
   b. The equilibrium mixture of the above reaction at 700o C contains 0.4 moles of sulphur dioxide, 0.03 moles of oxygen and 1.00 mole of sulphur trioxide in a 2.0 dm3 container. Calculate the value of Kc

8.3. Mass action law and equilibrium constant expression

Activity 8.3

1. Explain briefly the mass action law.
2. By giving an example, deduce the unit of concentration.

8.3.1. Mass action law

In chemistry, all the species involved in the chemical reaction must be equal in both sides of reaction (reactants and products). This is the basic explanation of the mass action law which can be defined as follows: Law of Mass Action or Equilibrium law states that"The ratio of an equilibrium concentrations of products and reactants each raised to the power of their coefficients in the balanced stoichemetric equations is a constant, Kc, at a constant temperature".

The molar concentration i.e. number of moles per litre is also called Active Mass. It is expressed by enclosing the symbols of formulae of the substance in brackets.

For example, **molar concentration of A** is expressed as **[A]**.

Consider a simple reversible reaction: **aA + bB ⇌ cC + dD** (At a certain temperature)

According to law of mass action: the total mass of A and B involved in the collision must be equal to the total mass of new formed compounds

Rate of **forward reaction**: **$[A]^a[B]^b$,** $R_f = K_f [A]^a[B]^b$

Rate of **backward reaction**: **$[C]^c[D]^d$,** $R_f = K_b [C]^c[D]^d$

8.3.2. Equilibrium constant expression

Consider a general reaction: aA + bB ⇌ cC + dD, the equilibrium constant is expressed as:

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Where C and D are products formed and A and B are reactants; a, b, c and d are powers or stoichiometric coefficients.

Based on the types of reaction, some of reactants or products formed can be in different state such as gas, liquid or solid.

As a general rule, the concentration of pure solids and pure liquids *are not included in equilibrium constant expressions and calculations.*

Examples of equilibrium constant expressions

1. $CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$

   $K_c = [CO_2]$

2. $C(s) + H_2O(g) \rightleftarrows CO(g) + H_2(g)$

   $$K_C = \frac{[CO][H_2]}{[H_2O]}$$

3. $(NH_4)_2CO_3(s) \rightleftarrows 2NH_3(g) + H_2O(g) + CO_2(g)$

   $K_c = [NH_3]^2[H_2O][CO_2]$

4. $HNO_2(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + NO_2^-(aq)$: $K_C = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$

5. $NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$: $K_C = \frac{[NH_4^+][OH^-]}{[NH_3]}$

6. $PbCl_2(s) \rightleftarrows Pb^{2+}(aq) + 2Cl^-(aq)$ $\quad K_C = [Pb^{2+}][Cl^-]^2$

K_c expression and deriving units of K_c:

If you look into the expression of Kc and derive the units, you find the units of Kc to be in mol/l if the concentrations in Kc expression are molar concentrations. But generally those concentrations are taken as equal to activities. Since the activity has no units, then generally Kc is written without units.

Example:

For the reaction, $N_2O_4(g) \rightleftarrows 2NO_2(g)$, calculate Kc from the following equilibrium concentrations: $[N_2O_4] = 0.0613$ M; $[NO_2] = 0.1839$ M and deduce its units.

Solution: $Kc = [NO_2]^2/[N_2O_4]$

$= 0.1839\ M)^2/ 0.0613\ M$

$=0.5517M$

Units of $Kc = M^2/M=M$

Checking up 8.3

Express the equilibrium constant (K_c) for each reaction and state its units

$2P(g) + Q(g) \rightleftarrows 2R(g)$

$Ag(s)+(aq) + Fe^{2+}(aq) \rightleftarrows Fe^{3+}(aq) + Ag(s)$

$H_2O(g) + CO(g) \rightleftarrows H_2(g) + CO_2(g)$

$SO_2(g) + O_2(g) \rightleftarrows 2SO_3(g)$

$PCl_5(g) \rightleftarrows PCl_3(g) + Cl_2(g)$

$2Cr^{3+}(aq) + Fe(s) \rightleftarrows 2Cr^{2+}(aq) + Fe^{2+}(aq)$

8.4. Definition of equilibrium constant in terms of partial pressures "Kp"

Activity 8.4

1. Write down the ideal gas equation and explain all terms involved in.
2. Explain the term "partial pressure''

For gaseous equilibria, the concentration of reactants and products can be expressed

in terms of pressures of the different components. If the reaction mixture behaves as an ideal gas, the ideal gas equation is PV = nRT. The molar concentration [X], which is n/V, is then equal to P/RT. This shows that, at a given temperature when T is constant, the pressure of a component is proportional to its molar concentration.

The equilibrium constant with the concentrations of reactants and products expressed in terms of molarity is expressed by Kc.

Consider the generalized reaction **aA + bB ⇌ cC + dD, the equilibrium constant is:**

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

However, since the pressure is proportional to the concentration for gases in a closed system, the equilibrium constant can be written in terms of the pressures of the different components rather than their molecular concentrations and Kp expression is used.

For the above generalized reaction: $K_p = \frac{(pC)^c(pD)^d}{(pA)^a(pB)^b}$

Where P is the partial pressure

Example: Consider the reaction, $H_2(g) + I_2(g) \rightleftarrows 2HI(g)$, where gaseous compounds are involved in the reaction, the equilibrium constant can be written as;

$$K_p = \frac{(pHI)^2}{(pH_2)\times(pI_2)}$$

Where pHI, pH_2 and pI_2 are the partial pressures of the different compounds. If no other gases are present. The sum of the partial pressures is equal the total pressure P.

If $p_{HI} = 0.50, p_{H_2}\ p_{I_2}$

$$K_p = \frac{[C]^c(RT)^c[D]^d(RT)^d}{[A]^a(RT)^a[B]^b(RT)^b}$$

$$K_p = \frac{[C]^c[D]^d(RT)^{c+d}}{[A]^a[B]^b(RT)^{a+b}}$$

$$K_p = K_C[RT]^{(c+d)-(a+b)}$$

$$K_p = K_C[RT]^{\Delta n}$$

$$K_p = \frac{(pHI)^2}{(pH_2)\times(pI_2)} = \frac{(0.50)^2}{(0.30)\times(0.30)} = 2.78$$

Determination of the partial pressure

The total pressure P of a mixture of gases is equal to the sum of partial pressures of the component present in the mixture of that gas. This commonly referred to as Dalton's law of partial pressure.

It is expressed as: $P_{total} = p_w + p_x + p_y + \ldots$ (1)

Where P is the partial pressure of the components w, x, y, etc.

For example, the partial pressures of the above components are given by ideal gas equation:

$$P_W = \frac{n_W RT}{V}, P_X = \frac{n_X RT}{V}, P_Y = \frac{n_Y RT}{V} (2)$$

$$\text{Thus } P_{Total} = \frac{n_W RT}{V} + \frac{n_X RT}{V} + \frac{n_Y RT}{V} (3)$$

In accordance with Dalton's law of gaseous mixture, the molar fraction of each gas is expressed as:

$$X_W = \frac{n_W}{n_T}, X_X = \frac{n_X}{n_T}, X_Y = \frac{n_Y}{n_T} (4)$$

Where X_w, X_x and X_y are molar fractions of gases w, x and y respectively.

From the relation (4), the number of total number of moles for each component forming the gas mixture can be calculated as follows:

$n_w = X_w n_T$, $n_x = X_x n_T$, $n_y = X_y n_T$ (5)

By replacing the relation (5) in the equation (2), we get:

$$P_W = \frac{X_W n_T RT}{V}$$

$$P_X = \frac{X_X n_T RT}{V}$$

$$P_Y = \frac{X_Y n_T RT}{V}$$

$$\text{Because } P_{Total} = \frac{n_T RT}{V}, \text{then}$$

$$P_W = X_W P_{Total}$$

$$P_X = X_X P_{Total}$$

$$P_Y = X_Y P_{Total}$$

Where P_w, P_x and P_y are partial pressures for the gases w, x and y in the mixture. For

any mixture of gases, the sum of all the molar fractions of all the components is given by $X_w+X_x+X_y+\ldots = 1$

Checking up 8.4

1. The gases SO_2, O_2 and SO_3 are allowed to reach the equilibrium. The partial pressures of the gases are $P_{SO_2} = 0.050$ atm, $P_{O_2} = 0.025$ atm, $P_{SO_3} = 1.00$ atm. Find the values of K_p for the equilibria.
   a. $SO_2(g) + ½\ O_2(g) \rightleftarrows SO_3(g)$
   b. $2SO_2(g) + O_2(g) \rightleftarrows 2SO_3(g)$
2. Study the following equilibrium:
   $H_2O(g) + CO(g) \rightleftarrows H_2(g) + CO_2(g)$
   a. Write an expression for K_p
   b. Would you expect an increase in total pressure to affect the yield of hydrogen? Explain your answer.
3. A certain temperature, the partial pressures of sulphur dioxide and oxygen are 0.25 and 0.64 atmospheres respectively. The total pressure of the system being 1.04 atmospheres.
   Calculate the K_p of the reaction
   $2SO_2(g) + O_2(g) \rightleftarrows 2SO_3(g)$

8.5. Relationship between Kc and Kp

Activity 8.5

Explain the terms Kc and Kp

The pressure and molarity are related by the Ideal Gas Law, PV = nRT where

P = nRT/V

Consider the general reaction:

$aA(g) + bB(g) \rightarrow cC(g) + dD(g)$

$$K_p = \frac{(pC)^c(pD)^d}{(pA)^a(pB)^b} \qquad (6)$$

It is known that:

$P_A = \frac{n_A RT}{V}$, where $[A] = \frac{n_A}{V}$ and $P_A = [A]\ RT$ (7)

$P_B = \frac{n_B RT}{V}$, where $[B] = \frac{n_B}{V}$ and $P_B = [B]\ RT$ (8)

$P_C = \frac{n_C RT}{V}$, *where* $[C] = \frac{n_C}{V}$ *and* $P_C = [C]\,RT$ (9)

$P_D = n_D RT/V$ Where $[D] = n_D/V$ and $P_D = [D]RT$ (10)

Replacing (7), (8), (9) and (10) in the relation (6), we get;

$$K_p = \frac{[C]^c (RT)^c [D]^d (RT)^d}{[A]^a (RT)^a [B]^b (RT)^b}$$

$$K_p = \frac{[C]^c [D]^d (RT)^{c+d}}{[A]^a [B]^b (RT)^{a+b}}$$

$$K_p = K_C [RT]^{(c+d)-(a+b)}$$

$$K_p = K_C [RT]^{\Delta n}$$

Where R (ideal gas constant) = 0.0821 L.atm/K. mol^{-1}; T = temperature in Kelvin

Δn = moles of gaseous products - moles of gaseous reactants

K_p = equilibrium constant in gaseous phase expressed in partial pressures

K_c = equilibrium constant in molar concentrations

Note: Kc = Kp when the number of gas molecules are the same in both sides

(Δn = 0).

Characteristics of equilibrium constant

- The value of the equilibrium constant is independent of the original concentration of reactants.
- The equilibrium constant has a definite value for every reaction at a particular temperature. However, it varies with change in temperature.
- For a reversible reaction, the equilibrium constant for the forward reaction is inverse of the equilibrium constant for the backward reaction.
- In general, **$K_{forward}$ reaction = 1/$K'_{backward}$ reaction and vice-versa**
- The value of an equilibrium constant tells the extent to which a reaction proceeds in the forward or reverse direction.
- The equilibrium constant is independent of the presence of catalyst.

Checking up 8.5

1. a. Derive the relationship between K_p and K_c for the reaction;

$$2SO_2(g) + O_2(g) \rightleftarrows 2SO_3(g)$$

b. Calculate the K_p for the reaction at 4500^0C if K_c is 0.2 atm^{-1} ($R = 0.082$ atm $mol^{-1}K^{-1}$)

c. 2000 cm^3 of sulphur dioxide was mixed with 1000 cm^3 of oxygen at 300^oC and 10 atmospheres pressure in the presence of a catalyst. When equilibrium had been attained, it was found that 1333 cm^3 of sulphur dioxide remained.

i. Write a balanced equation for the reaction between sulphur dioxide and oxygen.
ii. State the name of catalyst.
iii. Write an expression for the pressure equilibrium constant K_p.
iv. calculate the partial pressure of each of the gases at equilibrium.
v. Calculate the equilibrium constant,Kp, for the reaction.

8.6. Calculations on Kc and Kp

Activity 8.6

1. Write down the formula of K_c and the one of K_p for the following reaction:

$$2A(g) + B(g) \rightleftarrows 3C(g)$$

2. In Haber's process for manufacturing ammonia, $N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$, 46KJ of energy is given out per mole of Ammonia formed.

a. If 1.02×10^6 kg of Ammonia are produced per day, calculate how much heat energy is given out each day.

b. An equilibrium mixture in a sealed 2dm^3 container at 700K and a pressure of 200 Kpa contains 0.6 mol of nitrogen and 2.0 mol of hydrogen.

i. Calculate the equilibrium concentration of each component.
ii. Calculate the equilibrium constant ,Kc including the units.

Calculations involving K_c and K_p require knowing the number of moles at the equilibrium state. K_c is derived from molar concentration of all the reactants and products at equilibrium while K_p requires the partial pressure of all the reactants and products at equilibrium.

8.6.1. Calculations Involving K_c

The value of Kc is calculated using the concentrations of the reactants and products

at equilibrium. If these values are quoted they can be calculated from the initial concentrations of the reactants.

Worked examples:

1. The following table shows the equilibrium concentrations, for the reaction below, at 700K:

   $H_2(g) + I_2(g) \rightleftarrows 2HI(g)$

$[H_2]$/mol dm^{-3}	[I2]/mol dm^{-3}	[HI]/mol dm^{-3} by $1.65x10^{-2}$
$1.71x10^{-3}$	$2.91x10^{-3}$	10^{-2}

   a. Write an expression of the equilibrium constant K_c.

   b. Calculate the values of K_c at 700K.

Solution:

a. $$K_C = \frac{[HI]^2}{[H_2][I_2]}$$

b. Substitute the values quoted into this expression:

$$K_C = \frac{(1.65\times10^{-2})^2}{(1.71\times10^{-3})(2.91\times10^{-3})} = 54.7$$

2. The data given below show the number of moles of each component of the esterification reaction at the equilibrium.

   $CH_3COOH(aq) + CH_3CH_2OH(aq) \rightleftarrows CH_3COOCH_2CH_3(aq) + H_2O(l)$

   0.829 mol 0.009 mol 0.171 mol 0.171 mol

Calculate the value of the equilibrium constant, Kc.

Solution

First you need to write an expression for expression Kc;

$$K_C = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$$

In this case we can use moles to find the value of K_c rather than molarity, because there are the same number of moles on both sides of the equation and so the volume terms cancel out. Substituting the values quotes into the expression gives:

$$K_C = \frac{(0.171\times0.171)}{(0.829\times0.009)} = 3.92$$

If the moles or molarity of the components of the reaction are not quoted at equilibrium then these need to be calculated:

Worked examples:

1. Consider the formation of hydrogen iodide: $H_2(g) + I_2(g) \rightleftarrows 2HI(g)$
   Suppose a mole of hydrogen is mixed with b mole of iodide and allowed to reach the equilibrium so that x mol of HI are formed then;

$$H_2(g) + I_2(g) \rightleftarrows 2HI(g)$$

Mol at start	a	b	0
Mole at equilibrium	a-x/2	b-x/2	x

From the balanced equation, 1 mole of hydrogen reacts with 1 mole of iodine to form 2 moles of hydrogen $K_C = \dfrac{x^2}{\left(a-\frac{x}{2}\right)\left(b-\frac{x}{2}\right)}$

2. Consider the esterification reaction:

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftarrows CH_3COOCH_2CH_3(l) + H_2O\ (l)$$

Mol at start	a	b	0	0
Mol at equilibrium	a-x	b-x	x	x

From the balanced equation, 1 mol of acid reacts with 1 mol of alcohol to form 1 mol of ester and 1 mol of water.

This means that:

- The amount of the two products formed is the same (x)
- The amount by which the two reactants are reduced equals the amount of each product formed (x)

$$K_C = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]} = \frac{\left(\frac{x}{V}\right)\times\left(\frac{x}{V}\right)}{\frac{(a-x)}{V}\times\frac{(a-x)}{V}}$$ where V = volume in dm^3

Cancelling V gives:

$$K_C = \frac{x^2}{(a-x)(b-x)}$$

3. For the equilibrium below:

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftarrows CH_3COOCH_2(l) + H_2O(l)$$

Mole at start	1	0.33	0	0
Mole at equilibrium	(1.0.293)	(0.33-0.293)	0.293	0.293
	0.707	0.037		

$$K_C = \frac{(0.293 \times 0.293)}{(0.707 \times 0.037)} = 3.31$$

4. 0.206 mol of hydrogen and 0.144 mol of iodine were heated at 683 K at equilibrium 0.258 mol of HI were present.
   a. Calculate the value of K_c at this temperature.
   b. If the value for K_c is 54 at 700K deduce whether this reaction is exothermic or endorthermic.

Solution

a.

	$H_2(g)$	+	$I_2(g)$	⇄	2HI(g)
Mole at start	0.206		0.144		0
Mole at equilibrium	$0.206-\frac{0.258}{2}$		$0.144-\frac{0.258}{2}$		0.258
	0.077		0.015		0.258

$$K_C = \frac{(0.258)^2}{(0.077 \times 0.015)} = 57.63$$

   b. As the temperature increases the value of K_c decreases so the forward reaction is exothermic.

5. Consider the gaseous equilibrium: $N_2O_4(g) \rightleftarrows 2NO_2(g)$. At 300 K 1.0 mol of $N_2O_4(g)$ is 20% dissociated in a 2.0 dm^3 flask. Calculate the value of K_c for this reaction.

Solution

If N_2O_4 is 20% dissociated then 80% remains at equilibrium i.e 1.0x80/100 = 0.8mol. 20% has been converted into nitrogen dioxide.

$$N_2O_4(g) \rightleftarrows 2NO_2(g)$$

Mole at start	1.0	0
Mole at equilibrium	0.8	2x0.2 = 0.4

$$K_C = \frac{[NO_2]}{[N_2O_4]} moldm^{-3}$$

It is possible to use moles in the K_c expression since the units for K_c are $moldm^{-3}$.

$$K_C = \frac{\left(\frac{0.4}{V}\right)}{\frac{0.8}{V}} = \frac{0.16}{0.8 \times V} \text{ where } V = 2dm^3$$

$$K_C = \frac{0.16}{0.8 \times 2} = 0.1 mo\,ldm^{-3}$$

6. 3.00 mol of PCl_5 kept in 1L closed reaction vessel was allowed to attain equilibrium at 380K. Calculate composition of themixture at equilibrium. *Kc*= 1.80

Solution

Let x mol per liter of PCl_5 be dissociated,

Concentration(M)	$PCl_5 \rightleftarrows PCl_3 + Cl_2$		
Initial	3	0	0
Change	-x	+x	+x
Equilibrium	3-x	x	X

$Kc = [PCl_3][Cl_2]/[PCl_5]$

$1.8 = x^2/ (3 – x)$

$x^2 + 1.8x – 5.4 = 0$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$x = [–1.8 \pm \sqrt{(1.8)^2 – 4(–5.4)}]/2$

$x = [–1.8 \pm \sqrt{3.24 + 21.6}]/2$

$x = [–1.8 \pm 4.98]/2$

$x = [–1.8 + 4.98]/2 = 1.59$

as value of x cannot be negative hence we neglect that value (x= -3.39)

$[PCl_5] = 3.0 – x = 3 –1.59 = 1.41$ M

$[PCl_3] = [Cl_2] = x = 1.59$ M

8.6.2. Calculations involving K_p knowing the values of the partial pressures

Worked example

1. The partial pressures of the gases at equilibrium in the Haber process at 640 K are hydrogen 40kPa; nitrogen 10 kPa; ammonia 15kPa. Use these data to calculate a value for K_p at 640 K.

Solution

First write the equation and then an expression for K_p,

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

$$K_p = \frac{p_{NH_3}{}^2}{\left(p_{N_2}\right)\left(p_{H_2}\right)^3}$$

Now substitute the values quoted into the expressions:

$$K_p = \frac{(15)^2}{(10)(40)^3} = 3.5 \times 10^{-4}$$

It is important to note that K_p is a constant at constant temperature. Altering the partial pressures of the reactants will shift the equilibrium position but the value of K_p remains constant.

Using total pressure:

The sum of the partial pressures of the individual gases in a mixture is equal to the total pressure exerted by the mixture of gases.

Example:

In the Haber process: total pressure = $P_{NH_3} + P_{N_2} + P_{H_2}$, this is useful expression that is needed in the calculations.

Worked examples:

1. In the contact process, at equilibrium and with a total pressure of 120 kPa, the partial pressures of sulphur dioxide and sulphur trioxide are 33 kPa and 39 kPa respectively. Calculate a value of K_p stating the units.

Solution:

First write the equation for the process and then an expression for Kp,

$2SO_2(g) + O_2(g) \rightleftarrows 2SO_3(g)$

$$K_p = \frac{p_{SO_3}{}^2}{\left(p_{O_2}\right)\left(p_{SO_2}\right)^2} \text{ Unit is 1/kPa or } (\text{kPa})^{-1}$$

Before the partial pressures can be substituted into the expression we need to find the partial pressure of oxygen, which is not quoted in the question

Using: Total pressure = the sum of the partial pressures ⇄ 120 = 33+39 + P_{SO_2}

$P_{SO_2} = 120 - (33 + 39) = 48$

$$K_p = \frac{(39)^2}{(48)(33)^2} = 0.029$$

The partial pressure of each gas = mole fraction x total pressure.

A gaseous mixture contains 7 moles of X, 2 moles of Y and 1 mole of Z at equilibrium at a total pressure of 100 kPa. Calculate the value of K_p for the reaction:

X(g) + Y(g) ⇄ 2Z(g)

Solution

First calculate the mole fractions of each gas:

The total number of moles = 10

The mole fractions of the gases are: X = 7/10 = 0.7; Y = 2/10 = 0.2; Z = 1/10 = 0.1.

Using: the partial pressure of each gas = mole fraction x total pressure

The total pressure are:

P_x =0.7x100 = 70kPa; P_y = 0.2x100 = 20kPa; P_z = 0.1x100 = 10kP_a

Knowing the values of the partial pressures of the gases at equilibrium, we can now calculate the value of the equilibrium constant, K_p.

$$K_p = \frac{(p_z)^2}{(p_x)(p_y)}$$

$$K_p = \frac{(10)^2}{20 \times 70} = 0.071$$

8.6.3. Relating K_c to K_p

Worked examples:

1. For contact process: $2SO_2(g)+O_2(g) \rightleftarrows 2SO_3(g)$

$$K_p = \frac{(p_{SO_3})^2}{(p_{O_2})(p_{SO_2})}$$

$$K_p = K_C(RT)^{2-(2+1)} = \frac{K_C}{RT}$$

$$K_p = \frac{(p_{NH_3})^2}{(p_{H_2})(p_{N_2})^2} = K_C(RT)^{2-(1+3)} = \frac{K_C}{(RT)^2}$$

2. Iodine and hydrogen were allowed to react at 450^{0}C to give HI(g) according to the following equilibrium.
$H_2(g) + I_2(g) \rightleftarrows 2HI(g)$

   a. Write down the mathematical expression of K_p.

   b. 0.50 moles of hydrogen $H_2(g)$ and 0.50 moles of I_2 (g) were allowed to react in a closed vacuum at 450°C under the pressure of 2.0 atm and the equilibrium is established if the number of moles of I_2 is 0.11 moles.

      i. Calculate partial pressure for each gas
      ii. Calculate then the value of K_p
      iii. Hence, deduce from the above the value of K_c.

Solution

a. The mathematical expression is $K_p = \frac{(pHI)^2}{(pH_2)\times(pI_2)}$

b. Let us consider the following table:

Number of moles (mol)	$H_2(g) + I_2(g) \rightleftarrows 2HI(g)$		
Initial	0.50	0.50	0
Changes	-0.39	-0.39	+0.78
Equilibrium	0.11	0.11	0.78

i. Mole function of each gas

$$X_{I_2} = X_{H_2} = \frac{n_{H_2}}{n_{H_2} + n_{I_2} + n_{HI}} = \frac{0.11}{0.1 + 0.11 + 0.78} = 0.11$$

$$X_{HI} = \frac{n_{HI}}{n_{H_2} + n_{I_2} + n_{HI}} = \frac{0.78}{0.1 + 0.11 + 0.78} = 0.78$$

The partial pressure of each gas is given by:

$P_i = X_i P_{total}$

$\Rightarrow P_{H_2} = P_{I_2} = 0.11 \times 2 = 0.22atm$

$P_{HI} = X_{HI} P_{total} = 0.78 \text{x} 2 = 1.56$ atm

ii. The partial pressure equilibrium constant is

$$K_p = \frac{(1.56atm)^2}{(0.22atm) \times (0.22atm)} = 50.28$$

iii. K_c is equal to $K_p = 50.28$, since $\Delta n = 2-(1+1) = 0$

$K_c = 50.28$

4. Antimony pentachloride dissociates in antimony dichloride and chlorine. At 180^{0}C it was found that it is dissociated to 29.2%. Calculate K_p and K_c for the dissociation at this temperature, if we started with 2 moles of $SbCl_5$ in a container of 1 liter.

Solution

Expression of K_c and K_p:

$Sbcl_5 \rightleftarrows Sbcl_3 + cl_2$

$$K_C = \frac{[SbCl_3][Cl_2]}{[SbCl_5]} = K_p(RT)^{-1}$$

V = 1L

	$SbCl_5 \rightleftarrows SbCl_3 + Cl_2$
Initial state	2 0 0
Equilibrium	2(1-0.292) 0.292x2 0.292x2

$$K_C = \frac{0.292 \times 0.292 \times 2}{2(1-0.292)} = \frac{0.341056}{1.416} = 0.24$$

$$K_p = \frac{0.24}{(0.082 \times 455)^2} = 0.24 \times 0.082 \times 455 = 8.95$$

Checking up 8.6 chemical equilibrium

1. An aqueous solution is made by dissolving 1.00mol of $AgNO_3$ and 1.0mol of $FeSO_4$ in water and making up to 1.00dm^3. When the equilibrium, $Ag^+(aq) + Fe^{2+}(aq) \rightleftarrows Fe^{3+}(aq) + Ag(s)$ is established, $[Ag^+] = [Fe^{2+}] = 0.44$ moldm^{-3}, and $[Fe^{3+}] = 0.56$moldm^{-3}. Find K_c for the equilibrium.

2. Iron is added to a solution containing the ions Cr^{3+}, Cr^{2+} and Fe^{2+}. The equilibrium concentrations of the ions present in solution are $[Cr^{3+}] = 0.03$ moldm^{-3}, $[Cr^{2+}] = 0.27$ moldm^{-3}, $[Fe^{2+}] = 0.11$moldm^{-3}. Find K_c for the equilibrium $2Cr^{3+}(aq) + Fe(s) \rightleftarrows 2Cr^{2+}(aq) + Fe^{2+}(aq)$.

3. For the following equilibrium:
   $CH_3COOH(aq) + CH_3CH_2OH(aq) \rightleftarrows CH_3COOCH_2CH_3(aq) + H_2O(l)$

   When 1 mol each of ethanoic acid and ethanol are mixed together at a fixed temperature 0.333 mol of acid remain at equilibrium. Calculate the value of K_c at this temperature.

8.7. Comparison between reaction quotient Qc and equilibrium constant Kc

Activity 8.7

1. What do you understand by the term reaction quotient
2. By giving an example differentiate the reaction quotient and reaction constant Kc.

The **reaction quotient, Q,** is the resulting value when we substitute reactant and the product concentrations into the equilibrium expression. A reaction quotient (Q_r or Q) is a function of the activities or concentrations of the chemical species involved in a chemical reaction.

The difference is that Q can be calculated at any conditions (not only on equilibrium conditions) while the equilibrium constant is determined when there is a reversible reaction.

Example:

Consider for the following general equation:

aA + bB ⇄ cC + dD

The reaction quotient $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

The reaction quotient Q is obtained at any time of the reaction but Kc is only applicable for the 'equilibrium' concentrations of reactants and products.

Q is dependent on both concentration and temperature. It tells us whether the reaction will move forward or backward and it is not a constant value. If any reactant is added and reaction move forwad, it means that Q is affected but not the equilibrium constant Kc.

8.7.1. Using equilibrium constant to predict the direction of net reaction

For a reaction of known Kc value, the direction of the net reaction can be predicted by calculating the reaction quotient, Q. Consider the reaction:

pA + qB ⇌ rC + sD;

$$Q = \frac{[C]^r[D]^s}{[A]^p[B]^q}$$

- **If Q = Kc,** the reaction is at equilibrium and the concentrations will not change since the rates of forward and backward reactions are equal.
- **If Q < Kc,** the ratio of products over the reactants is too small and the reaction is not at equilibrium; the reaction will move toward the equilibrium by forming more products.
- **If Q > Kc,** the ratio of products over the reactants is too large and the reaction is not at equilibrium; the reaction will move toward the equilibrium by forming more reactants.

8.7.2. Worked example to predict the direction the reaction

For the reactions:

1. $N_2(g) + O_2(g) \rightleftarrows 2NO(g)$, the equilibrium constant, K_c is 1.0×10^{-5} at 1500 K. Predict the direction of the reaction if the reactants and products have the following concentrations:

   $[N_2] = 0.05M \quad [O_2] = 0.02M \quad [NO] = 0.30M$

Solution

The reaction quotient Q is equal to:

$$Q = \frac{[NO]^2}{[N_2][O_2]} = \frac{(0.30)^2}{(0.05)\times(0.02)} = 90$$

Compare Q to K: Q (90) > K (1.0×10^{-5})

Prediction of the direction of reaction: Q > K

- The reverse reaction is favored.
- The reaction moves from right to left until the equilibrium is established.

2. $H_2(g) + I_2(g) \leftrightarrow 2HI(g)$

   K_c = 57.0 at 700K. At time t, the molar concentration of H_2 = 0.10M, I_2 = 0.20M and HI = 0.40M.

   The reaction quotient is: $Q = (0.40)_2 / (0.10)(0.20)$

   $Q = 8.0$

At the time t, Q is less than Kc and Q has to upgrade itself to reach Kc. In order to increase the value of Q for the reaction to produce more products, the reaction will be shifted in forward direction.

If at a certain time t_2 you find Q greater than K_c, then Q has to lower itself by increasing the concentration of reactants, the reaction is shifted in backward direction.

For the reversible reactions, they have a tendency to reach the equilibrium state by favouring either the backward or forward direction.

Checking up 8.7

1. At 1000 K, the value of K_p for the reaction $2SO_3(g) = 2SO_2(g) + O_2(g)$ is 0.338. Calculate the value for Q, and predict the direction in which the reaction will proceed toward equilibrium if the initial pressures of reactants are $P_{SO_3} = 2 \times 10^{-3}$atm; $P_{SO_2} = 5 \times 10^{-3}$atm; $P_{O_2} = 3 \times 10^{-2}$ atm.

2. Write the equilibrium constant expression for each of the following reactions.

   a. $2\ H_2O_2(g) \rightleftarrows 2\ H_2O(g) + O_2(g)$

   b. $6\ H_2O_2(g) \rightleftarrows 6\ H_2O(g) + 3\ O_2(g)$

   c. The reverse of the reaction in part a

   d. $2\ PbS(s) + 3\ O_2(g) \rightleftarrows 2\ PbO(s) + 2\ SO_2(g)$

   e. $MgCl_2(s) \rightleftarrows Mg^{2+}(aq) + 2\ Cl^-(aq)$

END UNIT ASSESSMENT

1. Nitrogen monoxide gas (NO) was allowed to react with hydrogen gas (H_2) in a litre container according to the equation:
$2NO(g) + 2H_2(g) \rightleftarrows N_2(g) + 2H_2O(g)$

   Initially before the reaction started; the concentration of each gas was: $NO(g) = 0.10$ mol/litre, $H_2(g) = 0.050$ mol/litre, $H_2O(g) = 0.10$ mol/litre, $N_2(g) = 0.00$ mole/litre. When the reaction reached equilibrium, the concentration of each gas was equal to 0.062 mol/litre. When the reaction reached equilibrium, the concentration of each gas was equal to 0.062 mole/litre.

   a. Write the mathematical expression of equilibrium constant, K_c.

   b. Calculate the equilibrium constant, K_c.

   c. Determine the mathematical expression of equilibrium constant, K_p in relation to the equilibrium constant K_c

   d. Calculate K_p, by using the value of K_c (in 1.b) above.

   (R =0.082 L.Atm. K^{-1} mol^{-1}, temperature K = 298 Kelvin)

2. This question refers to the Haber process for the synthesis of ammonia. The equation which presents the reaction is given below.

   $N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$ $\Delta H^o = -92kJ\ mol^{-1}$

   a. Explain what is meant by the term '' dynamic equilibrium".

   b. i. Write the expression for the equilibrium constant K_p, for the above process

      ii. If the pressure is measured in atmospheres, what will be the units of K_p?

   c. State and explain the effect on the above equilibrium:

   i. Increasing the pressure

   ii. Increasing the temperature

   d. Name the catalyst used in the Haber process.

   e. i. Describe the function of a catalyst in terms of energy of activation and use a diagram to illustrate its effect.

      ii. Describe the effect of catalysts on the position of equilibrium and its effects on the concentrations of reacting substances at equilibrium.

3. Nitrogen tetroxide, $N_2O_4(g)$, decomposes according to the equation

$$N_2O_4(g) \rightleftarrows 2NO_2(g)$$

a. Write an expression for the equilibrium constant, K_c, for the above reaction

b. Explain the effect on the composition of the equilibrium mixture when the pressure is doubled.

4. Consider the following equilibrium reactions:

Reaction I: $3Fe(s) + 4H_2O(g) \rightleftarrows Fe_3O_4(s) + 4H_2(g)$

Reaction II: $CO(g) + Cl_2(g) \rightleftarrows COCl_2(g)$

a. Write expressions for the equilibrium constant, K_p.

i. for reaction I
ii. for reaction II

b. State, giving reasons, how an increase in pressure affects the position of equilibrium in each reaction above.

5. The production of ammonia in the Haber process involves the reaction:

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

a. Write an expression for the equilibrium constant, K_c, for the above reaction.

b. 0.20 mol of $N_2(g)$ and 0.20 mol of $H_2(g)$ were reacted in a 1 dm^3 closed container. (Until equilibrium) was reacted. At equilibrium, the concentration of $NH_3(g)$ was 0.060 $moldm^{-3}$.

i. Calculate concentrations of $N_2(g)$ and $H_2(g)$ at equilibrium.
ii. Calculate the value of K_c and state its units.

c. How does an increase in pressure affect the yield of ammonia? Explain your answer.

d. The actual conditions used in the Haber process are a temperature of 500°C and a pressure of 200 atmospheres. Why are these conditions used instead of the conditions that would give the highest yield?

e. Give one large scale use of ammonia.

6. Methane gas reacts with steam according to the equation given below:
$CH_4(g) + H_2O(g) \rightleftarrows 3H_2(g) + CO_2(g)$ **Δ H°**$+210\ kJmol^{-1}$

   a. How does an increase in pressure affect the equilibrium position? Explain your answer.

   b. Write an expression for the equilibrium constant, K_c, and state its units.

UNIT 9

pH OF ACIDIC AND ALKALINE SOLUTIONS

UNIT 9: pH OF ACIDIC AND ALKALINE SOLUTIONS

Key Unit Competency

To be able to:

- Prepare solutions, measure their pH, and calculate the pH of acidic and alkaline solutions.
- Explain the concept of buffer solution, hydrolysis of salts and discuss its applications in manufacturing industry and biological processes.

Learning objectives

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

- Define the degree of ionization (α);
- Define the terms Ka, pH, pKa, Kb, Pkb and Kw;
- Write equations for salt hydrolysis reactions and the expression for the hydrolysis constant;
- Explain how buffer solution control pH;
- Explain the buffer capacity in relation to buffer range;
- Describe the applications of buffer solution in domains such as biological processes, agriculture, natural system (e.g. lakes) and industrial manufacture of cosmetic and drugs.
- Perform calculations involving pH, Ka, pKa, Kb, pKb and Kw;
- Interpert th values of Ka and Kb in relation to the strength of acids and bases;
- Prepare different solutions and appropriately use pH-meter to measure their pH;
- Compare the strength of acids and bases on the same concentration using the values of Ka and Kb;
- Relate the values of pH and pOH;
- Calculate the pH and the hydrolysis constant of aqueous solutions of salts;
- Perform experiments to show that hydrolysis of some salts results in neutral, acidic and alkaline solutions;
- Prepare buffer solutions of different pH values;
- Derive Henderson-Hasselbalch relation and use it to calculate the pH of buffer solution.

Introductory activity

a)

b)

c)

d)

e)

f)

Observe the above representations a, b, c, d, e and f which represent some useful products made of acids, bases and salts and answer to the following questions.

1. Identify one chemical substance found in each product above.
2. State whether the chemical substance identified above is an acid, a base or a salt.
3. What do you comment about the pH of the chemical substance in (1)

Many fruit juices and other soft drinks contain acids and this can be identified by their sour or sharp taste. They contain many dissolved compounds of which acids are among. Some acids are chemicals that can be harmful or dangerous to human and should never be tested by drinking them (i.e. sulphuric acid used in car batteries).

Bases are products commonly used in our daily life such as soap, toothpaste, magnesium syrup, baking soda. Solutions of bases are slippery on touch because they attack oils on the skin and convert them into soaps. This makes them to be good cleaning agents. Bases dissolve in water to form solutions called alkaline solutions.

Acids can react with bases to form compounds known as salts which are of great importance in nature. For example ammonium chloride is used as an electrolyte in dry cells, calcium carbonate is used to manufacture cement, potassium nitrate is used as a fertilizer, magnesium sulphate and iron (II) sulphate used to manufacture of drugs.

9.1. Degree of ionization in relation to strength of acids and bases

Activity 9.1

(a) Explain the following terms;
  (i) an acid
  (ii) a base

(b) Give an example of an acid and a base which you encounter in your daily life.

(c) Explain the difference between a strong acid and a strong base.

(d) How is a weak acid different from a weak base?

(e) Give an example of weak acids and weak bases.

(f) Write down chemical equations to show ionization of a weak acid and weak base in water.

9.1.1. Acids and bases

In the previous years of your study, an acid has been defined as a substance that donates hydrogen ions while a base was defined as a substance that accepts hydrogen ions. Acidity and alkalinity are measured with a logarithmic scale called pH.

- **Strong and weak acids**

When an acid is dissolved in water, there are more hydrogen ions than hydroxide ions in the solution meaning that the solution is acidic. We can distinguish strong and weak acids.

A strong acid is ionized completely when dissolved in water. For example hydrochloric acid ionizes completely in water to form hydrogen or hydroxonium ions and chloride ions as illustrated below. The direct arrow indicates that the compound is completely ionized.

$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$

$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$

Other strong acids include sulphuric acid (H_2SO_4), nitric acid (HNO_3), perchloric acid ($HClO_4$) and many others.

When a weak acid is dissolved in water, only a small proportion of it ionizes to form ions. For example ethanoic acid ionizes partially in water to form ethanoate ions and hydrogen or hydroxonium ions. The following illustration shows that the ethanoic acid as a weak acid dissolves partially in water, the direct and indirect arrows symbolize the partial ionization or an equilbrium dissocition reaction

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

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

Other weak acids include sulphurous acid (H_2SO_3), carbonic acid (H_2CO_3), phosphoric acid (H_3PO_4), methanoic acid (HCOOH) etc. In general the organic acids are known to be weak acids.

The strength of an acid can be influenced by four factors namely:

(a)Bond strength: When the bond holding a hydrogen atom is strong, the compound formed is a weak acid since the bond cannot be easily broken to release hydrogen ions in solution. As an example, consider the halogen acids HF, HCl, HBr and HI. Their bond strength decreases with a decrease in electronegativity of the halogen atoms down the group 17. HI is a stronger acid than HCl or HBr because of a weak H – I bond due to its lower electronegativity of iodine atom than Cl or Br. This bond is easily broken down to release hydrogen ions in solution.

HF is a weak acid due to its strong H – F bond caused by a highly electronegativity of fluorine atom. This bond is not easily broken down to release hydrogen ions in solution.

(b)Nature of the solvent: The more basic the solvent in which the acid is dissolved, the stronger the acid. This is because the proton released by the acid is easily accepted by the basic solvent. This enables the acid to continue ionizing in the solvent to produce hydrogen ions e.g. Benzoic acid is a stronger acid in aqueous ammonia than in water.

(c) Presence of a halogen atom in organic acids: The halogen atom increases acidity because, being more electronegative than carbon it tends to withdraw electrons towards itself (negative inductive effect). This reduces the electron density in the O – H bond thus weakening it. In solution, the O – H bond is easily broken down to release hydrogen ions.This explains why chloroethanoic acid is a stronger acid than ethanoic acid.

(d) Number of carbon atoms in organic acids: As the number of carbon atoms increases, the acidity of the organic acid decreases.
This is because a long chain alkyl group pushes electrons towards the carboxyl group (positive inductive effect) increasing the electron density on the O – H bond. This makes the O – H bond stronger and not be easily broken down to release hydrogen ions in solution.This explains why methanoic acid is a stronger acid than ethanoic acid.

- **Strong and weak bases**

When a base is dissolved in water, there are more hydroxide ions in the solution than hydrogen ions. This kind of solution is called **alkaline**. Strong and weak bases can be distinguished based on their ionization character.

When a strong base is dissolved in water, it ionizes completely. For example sodium hydroxide (NaOH) ionizes in water to form sodium ions and hydroxyl ions. Similarly, potassium hydroxide (KOH) is a strong base because it dissociates completely when dissolved in water as illustrated below:

$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$

$KOH(aq) \longrightarrow K^+(aq) + OH^-(aq)$

For weak base, they dissolve partially in water. For example ammonia solution ionizes partially in water to form ammonium ions and hydroxyl ions..

$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Phenylamine ($C_6H_5NH_2$) and Hydroxylamine (NH_2OH) are other examples of weak bases

9.1.2. Degree of ionization (α)

An acid or a base when dissolved in water, it ionizes completely or partially depending on its characteristic as strong or weak.

The degree of ionization can be defined as the ratio of the number of ionized molecules to the total number of molecules dissolved in water.It is symbolized by α_a in the case of acid and α_b in the case of base.

$$\alpha = \frac{\text{Number of ionized molecules}}{\text{Total number of molecules dissolved in water}}$$

When a weak acid or weak base is dissolved in water, partial ionization occurs such that equilibrium is set up between the undissolved molecules and the ions formed in water. This equilibrium is known as ionic equilibrium of an acid or base.

The degree of ionization is a fraction ranging from 0 to 1. α is equal to zero for the insoluble substances or non-electrolytes (i.e. substances which do not ionize in water). α is equal to 1 for strong electrolytes such as strong acids or bases because they ionize completely in water. a is less than 1 in the case of weak electrolytes such as weak acids or bases because they ionize partially in water.
The degree of ionization can also be expressed as percentage as shown by the relation below.

$$\alpha = \frac{Concentration\ of\ the\ individual\ constituent\ ions}{Original\ concentration\ of\ the\ electrolyte}$$

The greater the degree of ionization, the stronger the acid or base. For example, the concentration of an acid that undergoes ionization is equal to the concentration of hydrogen ions formed as shown below.

$$HA\ (aq) \longrightarrow A^-\ (aq) + H^+\ (aq)$$

$$\text{Percentage ionization} = \frac{[H^+]}{[HA]} \times 100\ \%$$

Example

What is the degree of dissociation of a weak acid in a 0.25M solution, given the concentration of H^+ as 0.001 mol dm^{-3}?

Solution

Degree of dissociation: $\alpha_a = \frac{[H^+]}{[Acid]}$

$$\alpha = \frac{0.001}{0.25} = 0.004 = 0.4\%$$

Checking up 9.1

1. A 0.1moldm^{-3} methanoic acid solution contains 0.0042 moldm^{-3} of hydrogen ions. Calculate the percentage of the acid that is ionized.
2. A solution of 0.035M nitrous acid contains 0.0037M of hydrogen ions. Calculate the percentage ionization of the acid.

9.2. Explanation of acid and base dissociation constants (K_a and K_b)

Activity 9.2

1. Explain your understanding of the following expressions
   (a) Acid dissociation constant.
   (b) Base dissociation constant.
2. (a) Draw an equation to show ionization of ethanoic acid in water.
   (b) Derive an expression for acid dissociation constant, K_a of ethanoic acid in water.
3. (a) Express an equation for the ionization of methylamine in water.
   (b) Write the expression for the base dissociation constant, K_b of methylamine.

Weak electrolytes such as weak acids or weak bases are partially ionized in water thus their dissociation is reversible and can reach equilibrium. Therefore the equilibrium constants can be used to explain the strength of acids and bases based on their ionization reactions.

9.2.1. Acid dissociation constant, K_a

The acid dissociation constant also known as acidity constant or acid ionization constant is the equilibrium constant for the ionization reaction of an acid. It is denoted by K_a.

This constant is a quantitative measure of the strength of the acid in solution in units of moldm^{-3}. Acid dissociation constants are mostly associated with weak acids because strong acids are completely ionized in the aqueous solution and their K_a values are extremely large or infinity.

Consider a weak acid HA, its ionization is represented as follows:

$$HA\ (aq) \rightleftharpoons A^-\ (aq) + H^+\ (aq)$$

The equilibrium constant for the dissociation of HA is as follows:

$$K_a = \frac{[A^-][H^+]}{[HA]}$$

9.2.2. Base dissociation constant, K_b

The base dissociation constant also known as base ionization constant is the equilibrium constant for the ionization reaction of a weak base denoted by K_b. The equilibrium constant K_b measures the strength of the base in solution in units of moldm^{-3}. Base dissociation constants are mostly associated with weak bases because strong bases

are completely ionized in the aqueous solution and their K_b values are extremely large.

Consider a weak base, BOH undergoing ionization which is represented as follows:

$$BOH\ (aq) \rightleftharpoons OH^-\ (aq) + B^+\ (aq)$$

The base dissociation constant K_b can be expressed by applying the equilibrium law:

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

Note: K_b provides a measure of the strength of the base. When Kb is large, the base is highly dissociated, and the base is strong. And when K_b is small, very little of the base is dissociated and the base is weak.

9.2.3 Relationship between equilibrium (dissociation) constant and the degree of ionization α; Ostwald's dilution law

The relationship between the equilibrium constant and the degree of dissociation of weak electrolytes has been introduced by Ostwald in 1888.

The Ostwald's dilution law states that "*the degree of ionization of a weak electrolyte is inversely proportional to the square root of the molar concentration of the electrolyte".*

$$a = \sqrt{\frac{Ka}{C}}$$

Where C is the molar concentration and K_a is the equilibrium constant.

Consider the dissociation equilibrium of formic acid HCOOH which is a weak electrolyte in water.

$$HCOOH\ (aq) \rightleftharpoons H^+(aq) + HCOO^-(aq)$$

$$Ka = \frac{[H^+][HCOO^-]}{[HCOOH]}$$

Where α is the degree of ionization and represents the fraction of the total concentration of HCOOH that exists in the completely ionized state. Further (1 – a) is the fraction of the total concentration of HCOOH in the unionized state.

Relationship between Ka and a.

If the total concentration of the acid is **C** at the initial step and its degree of ionization is a**C;** at the equilibrium Ca, Ca and C (1 – a) represent the concentration of H^+, $HCOO^-$ and HCOOH respectively as shown below.

If a is too small, $K_a = \alpha^2 C$

Equation	HCOOH	⇌	H^+	$HCOO^-$
Initial concentration	C		0	0
Concentration on ionization	Ca		Ca	Ca
Concentration at equilibrium	C –Ca		Ca	Ca

Applying the equilibrium law, we got: $K_a = \frac{(C\alpha C\alpha)}{[C - C\alpha]} = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$

For a weak acid, a is too small such that 1-a ≈ 1

Therefore,

$$K_a = C\alpha^2$$

$$\alpha^2 = \frac{K_a}{C}$$

$$\alpha = \sqrt{\frac{K_a}{C}}$$

The higher the Ka value, the greater the degree of ionization and the stronger the acid.

The relation $K_a = \frac{C\alpha^2}{1-\alpha}$ is known as Ostwald's dilution law

Similarly for weak bases, $K_b = \frac{C\alpha^2}{1-\alpha}$

Where any a = = $\sqrt{\frac{K_a}{C}}$ at a = small value

Kb = dissociation constant for weak bases.

The higher the Kb value, the greater the degree of ionization and the stronger the base.

Worked examples

1. (a) A solution of a weak acid, HA contains 0.25M, given the concentration of H^+ as 0.001 $moldm^{-3}$.Calculate the dissociation constant of HA.

(b) Determine the degree of ionization of this acid in 1M solution?

Solution:

(a) Dissociation Constant: $K_a = \frac{[H^+][A^-]}{[HA]}$

$$K_a = \frac{0.001 \text{ x } 0.001}{0.25}$$

$$K_a = 4.0 \text{ x } 10^{-6} \text{ moldm}^{-3}$$

(b) Degree of dissociation in a 1 M solution:

$$\alpha = \sqrt{\frac{K_a}{[HA]}}$$

$$\alpha = \sqrt{\frac{4.0\ x\ 10-6}{1}}$$

$$\alpha = 0.002$$

$$\alpha = 0.2\%$$

2. Calculate the degree of ionization of 0.1M acetic acid, CH_3COOH if its ionization constant $K_a = 1.8 \text{ x} 10^{-5}$ moldm^{-3}.

Solution:

$$\alpha = \sqrt{\frac{K_a}{C}}$$

$$\alpha = \sqrt{\frac{1.8 \times 10^{-5}}{0.1}}$$

$$\alpha = 0.013 = 1.3\%$$

Checking up 9.2

1. Calculate the degree of ionization of a 0.04M ethanoic acid solution at 25 ^{0}C given that its
   K_a is 1.3 x 10^{-5} mol dm^{-3}.
2. The acid dissociation constant of a monobasic acid is 4.39 x 10^{-5} mol dm^{-3} at 25 ^{0}C. Calculate the degree of ionization of a 0.01M solution of the acid.
3. (a) Write an equation for the ionization of methylamine in water.
   (b) Express the dissociation constant Kb for methylamine.
   (c) The hydroxyl ion concentration of a 1M methylamine solution is 0.04 moldm^{-3}. Calculate the K_b for methylamine.

9.3. Relationship between K_a and K_b

Activity 9.3

1. Ammonium ion is a conjugate acid.
   (a) Represent the ionization of ammonium ions in water by its appropriate reaction equation.
   (b) Write down an expression for the acid dissociation constant, K_a of ammonium ions in water.
2. Ammonia is a conjugate base.
   (a) Write the chemical equation for ionization of ammonia in water.
   (b) Write an expression for the base dissociation constant, K_b of ammonia in water.

The relationship between Ka and Kb is derived from the dissociation of conjugate acid and conjugate base. For example considering NH_4^+ and NH_3; NH_4^+ is a conjugate acid and NH_3 is a conjugate base.

The ionization of a conjugate acid in water is shown below:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$$

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

The ionization of a conjugate base in water is indicated below:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Multiplying Ka by Kb = $\frac{[NH_3][H_3O^+]}{[NH_4^+]} \cdot \frac{[NH_4^+][OH^-]}{[NH_3]}$

$$Ka \times Kb = [H_3O^+][OH^-]$$

$$Ka \times Kb = Kw$$

$$K_a \times K_b = 10^{-14}$$

Ka and Kb are related each other through the ionization constant.

When we multiply by–log10 to both sides, we get:

$-\log_{10} Ka = pKa$, $-\log_{10} Kb = pKb$ and $-\log_{10} Kw = pKw$ therefore $pKa + pKb = pKw$

Hence $pK_a + pK_b = 14$

Checking up 9.3

1. (a) Ethyl ammonium ion, $CH_3CH_2\text{-}NH_3^+$ is a conjugate acid. Write an equation for the ionization of this ion in water.
   (b) Write the expression of acid dissociation constant, K_a, of ethyl ammonium ions in water.
2. (a) Ethylamine, $CH_3CH_2\text{-}NH_2$ is a conjugate base. Write the chemical equation for ionization of ethylamine in water.
   (b) Write an expression for the base dissociation constant, K_b of ethylamine in water.
3. From the reactions above, derive an expression to show the relationship between K_a and K_b.

9.4. Use of K_a or pK_a and K_b or pK_b to explain the strength of acids and bases

Activity 9.4

1. (a) Ethanoic acid has pK_a of 4.77 at 25 ^{0}C. What is meant by pK_a of the acid?
   (b) Given the following acids and their corresponding K_a values in the table below,

Acid	Formula	K_a / moldm^{-3}
Phenol	C_6H_5OH	1.0×10^{-10}
Ethanoic acid	CH_3COOH	1.8×10^{-5}
Methanoic acid	HCOOH	1.8×10^{-4}

State the strongest and the weakest acid and justify your answer.

2. The ionization of ethanoic acid in water is shown by the following equation :

$$CH_3COOH_{(aq)} \rightleftarrows CH_3COO^-_{(aq)} + H^+_{(aq)}$$

Use the above equation to write to relate the acid dissociation constant, K_a and the degree of ionization, a

The acidic and basic dissociation constants are respectively represented by K_a and K_b. Based on the negative logarithm, pK_a and pK_b are derived from $-log_{10}K_a$ and $-log_{10}K_b$ respectively. Therefore, K_a, pK_a, K_b and pK_b are more helpful in predicting whether a species donates or accepts a proton.

9.4.1. Use of K_a or pK_a

K_a or K_b is a measure of how completely an acid or a base dissociates into ions in water.

Another way to express acid strength is the use of pK_a or pK_b to express the basic strength of a solution.

$pK_a = -\log K_a$ or $pK_b = -\log K_b$.

In the case of weak acid, the degree of ionization a is directly proportional to the square root of acid dissociation constant K_a, $a = \sqrt{\frac{Ka}{Ca}}$. This relation shows that the higher the value of K_a, the stronger the acid due to the increase of the degree of ionization with the dilution.

A smaller K_a value means that a little quantity of the acid dissociates into its ions in water thus weak acid. The pK_a gives the same information but in a different way. The smaller the pK_a value, the larger the K_a value and the stronger is the acid as shown in the table 9.1.

Table 9.1: K_a and pK_a of some acids at 25 °C

	Acid	Conjugated base	Ka	pKa
STRONG ACID	HI	I^-	$1.0x10^{10}$	-10.0
	$HClO_4$	ClO_4^-	$4.0x10^8$	-8.6
	HBr	Br^-	$1.0x10^8$	-8.0
	HCl	Cl^-	$1.0x10^6$	-6.0
	H_2SO_4	SO_4^{2-}	$1.0x10^4$	-4.0
	HNO_3	NO_3^-	$1.0x10^2$	-2.0
	H_3O^+	OH^-	55.5	-1.75

WEAK ACIDS	HIO_3	IO_3^-	$1.69x\ 10^{-1}$	0.77
	H_3PO_4	$H_2PO_4^-$	$7.5x10^{-3}$	2.15
	HF	F^-	$3.53x\ 10^{-4}$	3.45
	C_6H_5COOH	$C_6H_5COO^-$	$6.46x\ 10^{-5}$	3.75
	CH_3COOH	CH_3COO^-	$1.75x10^{-5}$	4.76
	H_2CO_3	HCO_3^-	$4.30x10^{-7}$	6.37
	H_2S	HS^-	$1.0x10^{-7}$	7.00
VERY WEAK ACIDS	HSO_3^-	SO_3^{2-}	$6.43x10^{-8}$	7.19
	$H_2PO_4^-$	HPO_4^{2-}	$6.34\ x10^{-8}$	7.20
	HCN	CN^-	$4.93\ x10^{-10}$	9.31
	HCO_3^-	CO_3^{2-}	$5.618x10^{-11}$	10.25
	HPO_4^{2-}	PO_4^{3-}	$4.20x10^{-13}$	12.28
	HS^-	S^{2-}	$1.20x10^{-13}$	12.92
	H_2O	OH^-	$1.0x10^{-14}$	15.75

Generally pK_a is greater than three ***($pK_a > 3$)*** when the acid is weak and when K_a increases, pK_a decreases and the acid is strong due to large amount of ions in water.

For strong acids, pK_a is less than zero ***($pK_a < 0$).***

9.4.2. Use of K_b or pK_b

K_b is the base dissociation constant and pK_b simply expresses its negative logarithm. K_b is a measure of how completely a base dissociates into its ions in water.

The larger the value of K_b the higher the level of dissociation and the stronger the base.Similarly, the lower the pK_b value the stronger the base (Table 9.2).

For a weak base, $a = \sqrt{\frac{Kb}{Cb}}$.The degree of ionization is proportional to the square root of base dissociation constant, K_b. This means that the higher the K_b value, the stronger the base because the degree of ionization increases with dilution.

Table 9.2: K_b and pK_b of some bases in water at 25 ˚C

Base	K_b (mol / dm³)	pK_b
$C_6H_5NH_2$	4.2×10^{-10}	9.38
C_5H_5N	1.7×10^{-9}	8.77
NH_3	1.8×10^{-5}	4.75
$HO\text{-}CH_2CH_2\text{-}NH_2$	3.2×10^{-5}	4.49
$(CH_3CH_2)_3N$	5.2×10^{-5}	4.28
CH_3NH_2	4.4×10^{-4}	3.36
$CH_3CH_2NH_2$	5.4×10^{-4}	3.27
$(CH_3)_2NH$	5.9×10^{-4}	3.23
$(CH_3CH_2)_2NH$	8.6×10^{-4}	3.07

Checking up 9.4

1. You are provided with the following acidic solutions and their respective K_a values
   1M HF, $K_a = 6.3 \times 10^{-4}$ mol dm^{-3}
   1M HCN, $K_a = 6.2 \times 10^{-10}$ mol dm^{-3}
   1M $H_2C_2O_4$, $K_a = 5.0 \times 10^{-2}$ mol dm^{-3}
   1M CH_3COOH, $K_a = 1.25 \times 10^{-3}$ mol dm^{-3}
   a. (Calculate the pKa values of each of the acids listed above.
   b. State and explain which one is a strongest acid and weakest acid?
   c. Rewrite the acids in a decreasing order of their acid strength.
2. What is the pK_b of a base whose conjugate acid has a pK_a of 7.29?
3. a. A solution contains 0.45 mol dm^{-3} of NaN_3. Write an equation for the ionization of NaN_3 in water.
   b. Calculate the K_b value of NaN_3 given K_a and K_w as 1.9×10^{-5} mol dm^{-3} and 10^{-4} mol^2 dm^{-6} respectively.

9.5. Explanation of ionic product of water

Activity 9.5

Water is a neutral liquid at pH = 7

a. Explain why at 25 ˚C water has a pH equals to 7.

b. (Demonstrate how the ionization of water molecules is made.

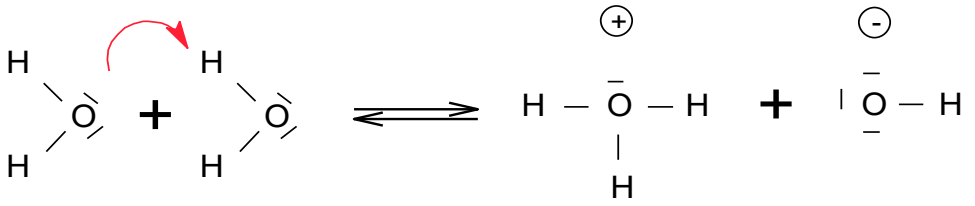
c. What do you understand by "Ionic product of water ?

Water is a weak electrolyte and neutral in nature. Pure water is commonly known as universal solvent and water takes part in many equilibrium reactions. Water ionizes as shown by the reaction equation as follows:

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

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

The mechanism of this reaction is represented as follows:



From the reaction equation (1) and by applying the equilibrium law; we obtain:

$$K_c = \frac{[H^+]\,OH^-]}{[H_2O]} \text{ or } \frac{[H_3O^+]\,[OH^-]}{[H_2O]},\ Kc[H_2O]=Kw$$

Then $K_w = [H^+]\,[OH^-]$ or $Kw = [H_3O^+]\,[OH^-]$

K_w is equilibrium constant and is called the ***ionic product of water***.

If water is pure, the equilibrium shows equal number of hydrogen ions and hydroxyl ions and the concentrations of the two types of ions are equal (1.0×10^{-7} moldm^{-3})

At room temperature (25 °C or 298 K), K_w is equal to 1.0×10^{-14} mol^{2}dm^{-6}. The values of K_w vary with temperature as for other equilibrium constant.

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

$K_w = [H^+]^2$; since $[H^+] = [OH^-]$

$1.0x10^{-14} = [H^+]^2$

$[H^+] = 1.0x10^{-7}$ and $[OH^-] = 1.0x10^{-7}$

The ionic product of water increases with temperature (**Table 9.3).** However at all temperatures, the concentration of H^+ ions remains equal to the concentration of OH^- ions in pure water.

Table 9.3 Variation of the ionic product of water with temperature

Temperature (K)	K_w ($mol^2\ dm^{-6}$)
293	0.687×10^{-14}
298	1.008×10^{-14}
313	2.917×10^{-14}
323	5.474×10^{-14}
373	5.6×10^{-14}

The relationship between K_w and pK_w is the same as that between K_a and pK_a, or $[H^+]$ and pH.

$pK_w = -\log_{10}K_w$. Because the value of K_w is $10^{-14} mol^2\ dm^{-6}$, this implies that the value of pK_w is equal to 14.

Checking up 9.5

1. a. Write an expression for the ionic product, K_w of water.
   b. State the units of K_w.
2. a. At 30 °C, K_w value is $1.471 \times 10^{-14}\ mol^2\ dm^{-6}$. Calculate the pH of pure water at this temperature.
   b. Is the water now acidic, alkaline or still neutral? Explain your answer.
3. Define pK_w and state the value of pK_w at 30 °C.

9.6. Definition and calculations of pH and pOH of acidic and alkaline solutions

Activity 9.6

1. A fruit juice has pH of 3.5.
   (a) After analyzing that juice and get pH = 3.5, what is your conclusion?
   (b) Apply the expression of pH and Calculate the concentration of hydrogen ions in the juice
2. Calculate the concentration of H^+ ions and hence the pH of 0.025M nitric acid solution.
3. Calculate the pH of a 0.02 $moldm^{-3}$ sulphuric acid solution.
4. Calculate the pH of a 0.01M ammonia solution with a degree of dissociation of 0.04.
5. A solution with pH of 9.50 has a pOH of _____?
   A. 9.50 B. 0.50 C. 4.50 D. 19.0
6. The pH of a popular soft drink is 3.4. What is its hydroxonium ion concentration?
   A. 5.0×10^{-4} M B. 4.0×10^{-4} M
   C. 2.5×10^{3} M D. 5.0×10^{-5} M
7. A solution with a $[OH^-]$ of 1.20×10^{-7} M has a pOH and a pH of _____.
   A. 6.92 and 7.08 B. 7.08 and 6.92
   C. 5.94 and 8.06 D. 5.35 and 8.75

The pH is a scale commonly used to measure the degree of acidity or alkalinity of a solution.It is measured on a scale of 0 to 14. The term pH is derived from "p," which is a mathematical symbol expressing the negative logarithm, and "H," the chemical symbol for Hydrogen. In general pH can be defined as the negative logarithm of Hydrogen ion activity or pH = -log $[H^+]$

Both pH and pOH are two methods that are used to describe the strength of acids, alkali, or ionizable salts (i.e. salt of a weak acid and strong base, salt of weak base and a strong acid or salt of weak acid and weak base).The pH is a measure of the hydrogen ion concentration of a solution.

Within this section, the following terms will be commonly used such as $[H^+]$ = hydrogen ions concentration; $[OH^-]$ = hydroxide ions concentration.

The pH can be expressed as the negative logarithm of the concentration of $[H^+]$ in a solution. The Solutions having a high concentration of hydrogen ions have a low **pH** and solutions with a low concentrations of H^+ ions have a high **pH**. On the other hand, **"pOH"** is the negative of the logarithm of the concentration of hydroxide ions in a solution.It describes how alkaline a solution is; the more alkaline a solution is, the higher the concentration of hydroxide ions in the solution.

Importance of pH and pOH

Knowing the pH and pOH is important because it helps us to find the concentration of hydrogen or hydroxide ions in the solution; it allows determining the acidity and alkalinity of the solution. While knowing the pH of a solution, the strength of the acid and base in the solution can be determined and the separation of strong and weak acids or strong and weak bases can be done based on the value of pH or pOH.

Mathematically pH or pOH can be expressed as follows:

$$\mathbf{pH = -log = -log_{10}[H^+]}$$

Or $pH = -\log_{10}[H_30^+]$

For pure water, $[H^+] = 1.0x10^{-7}M$

$pH = -\log_{10}(1.0x10^{-7}) = -(-7)$

pH = 7

The value 7 is the pH of pure water at 25°C. It also defines the standard pH for all neutral solutions.

Similarly, pOH is defined as the negative logarithm in base 10 of hydroxyl ion concentration.

$$\mathbf{pOH = -log_{10}[OH^-]}$$

For pure water, $[OH^-] = 1.0x10^{-7}$

$pOH = -\log_{10}(1.0x10^{-7}) = -(-7)$

pOH = 7

The Figure 9.1 shows the location of acidic, neutral and alkaline compounds based on pH scale while the Figure 9.2 shows the pH or pOH scale (from 0 to 14). Figure 9.3 shows examples of compounds corresponding to different values of the pH scale.

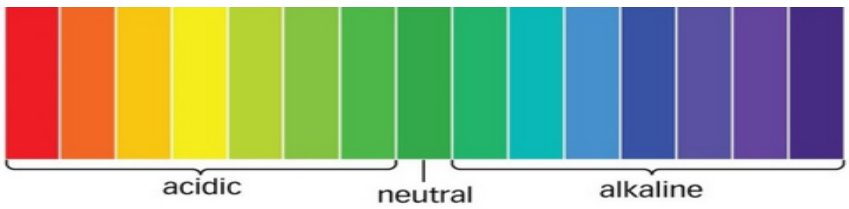


Figure 9.1. Values of pH for acidic, neutral and alkaline solutions.

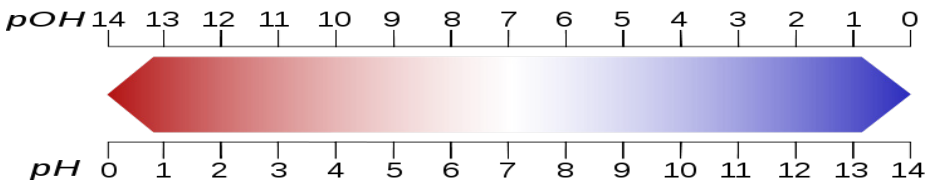


Figure 9.2. The pH scale

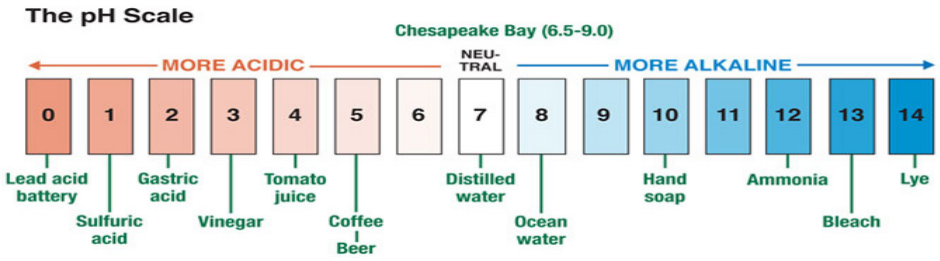


Figure 9.3. The pH of some solutions

The pH of strong acids is ranged from 1-3 and weak acids from 4-6. Strong bases have values of pH ranging from 11 to 14 and weak bases have values of pH ranging from8 to 10.

Relationship between pH, pOH and pK_w

In any solution at 298 K, $K_w = [H^+]\,[OH^-] = 1.0\times10^{-14}\ mol^2dm^{-6}$

If $pH = -\log_{10}[H^+]$ and $pOH = -\log_{10}[OH^-]$,

Then, $pK_w = -\log_{10}[K_w]$

$pK_w = -\log_{10}(1.0\times10^{-14})$

$pK_w = 14$

From $[H^+]\,[OH^-] = K_w$

$-\log_{10}[H^+] - \log_{10}[OH^-] = -\log_{10}[K_w]$

$$pH + pOH = pKw$$

It means that pH of alkaline solutions can be calculated from the following expression;

$pH = pK_w - pOH$ thus $pH = 14 - pOH$.

Note:

When a drop of hydrochloric acid is added to water, the concentration of hydrogen ions increases and pH decreases. The pH of an acidic solution is less than 7. On the

other hand when sodium hydroxide is added to water, the added hydroxyl ions reduce the concentration of hydrogen ions and pH increases. pH of an alkaline solution is greater than 7. The Table 9.4 shows the variation of pH in function of the hydrogen ion concentrations.

Table 9.4.Variation of pH with hydrogen ions concentration

$[H^+]$/ moldm^{-3}	pH	Conditions
1.0	0	Highly acidic
1.0×10^{-1}	1	
1.0×10^{-2}	2	
1.0×10^{-3}	3	
1.0×10^{-4}	4	Slightly acidic
1.0×10^{-5}	5	
1.0×10^{-6}	6	
1.0×10^{-7}	7	Neutral
1.0×10^{-8}	8	
1.0×10^{-9}	9	
1.0×10^{-10}	10	Slightly alkaline
1.0×10^{-11}	11	
1.0×10^{-12}	12	
1.0×10^{-13}	13	Highly alkaline
1.0×10^{-14}	14	

9.6.1. pH of strong acids

Strong acids like hydrochloric acid has a pH around 0 to 1.The lower the pH, the higher the concentration of hydrogen ions in the solution. A strong acid is one which completely dissociates into its ions in water.

This makes calculating the hydrogen ion concentration, which is the basis of pH, easier than for weak acids. The following are examples on how to determine pH of a strong acid.

1. Determine the pH of a 0.025 M solution of hydrobromic acid (HBr) solution

Hydrobromic acid or HBr, is a strong acidand will ionize completely in water by giving H^+ and Br^- ions. For every mole of HBr, there will be 1 mole of H^+ and the concentration of H^+ will be the same as the concentration of HBr. Therefore, $[H^+]$ = 0.025 M.

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

$pH = - \log (0.025)$
$pH = -(-1.602)$
$pH = 1.602$

2. Calculate the pH of a 0.01M hydrochloric acid solution.
Solution:
Hydrochloric acid dissociates as follows: $HCl\ (aq) \longrightarrow H^+\ (aq) + Cl^-\ (aq)$
Since 1 mole of HCl ionizes to produce 1 mole of H^+ ions in solution, it means that [HCl] is equal to $[H^+] = 0.01M$

Therefore; $pH = -\log_{10}[H^+]$

$pH = -\log_{10} (0.01)$
$pH = -\log_{10} (1.0 \times 10^{-2})$
$pH = 2$

3. Calculate the pH of a solution containing 0.32 $moldm^{-3}$ of sulphuric acid.
Solution:

$H_2SO_4\ (aq) \longrightarrow 2H^+\ (aq) + SO_4^{2-}\ (aq)$
1 mole of H_2SO_4 ionizes to produce 2 moles of H^+ ions.
Thus, $[H^+] = 2[H_2SO_4]$
$= 2 \times 0.32 = 0.64M$
$pH = -\log_{10}[H^+]$
$pH = -\log_{10} (0.64)$
$pH = -\log_{10} (6.4 \times 10^{-1})$
$pH = 0.194$

4. Calculate the concentration in $moldm^{-3}$ of sulphuric acid solution of pH 3.5
Solution:

$pH = -\log_{10}[H^+]$
$3.5 = -\log_{10}[H^+]$
$[H^+] = 10^{-3.5}$
$[H^+] = 3.16 \times 10^{-4}\ moldm^{-3}$

From the equation of ionization: H_2SO_4 (aq) ⟶ $2H^+$ (aq) + SO_4^{2-} (aq)

2 moles of H^+ were produced by 1 mole of H_2SO_4

3.16×10^{-4} moles of H^+ are produced by $\left(\frac{1}{2} \times 3.16 \times 10^{-4}\right)$ moles of H_2SO_4

Concentration of H_2SO_4 = **1.58×10^{-4} moldm^{-3}**

9.6.2. pOH and pH of strong bases

Examples

1. Calculate the pOH of a solution 0.024M sodium hydroxide.

Solution:

NaOH (aq) ⟶ Na^+ (aq) + OH^- (aq)

1 mole of NaOH produces 1 mole of OH^-

Therefore $[OH^-] = [NaOH] = 0.024M$

$pOH = -\log_{10}[OH^-]$

$pOH = -\log_{10}(0.024)$

$pOH = -\log_{10}(2.4 \times 10^{-2})$

pOH = 1.62

2. Calculate the pH of 0.02M sodium hydroxide solution.

Solution:

NaOH (aq) ⟶ Na^+ (aq) + OH^- (aq)

$[OH^-] = [NaOH] = 0.02M$

$pOH = -\log_{10}[OH^-]$

$pOH = -\log_{10}(0.02)$

$pOH = -\log_{10}(2.0 \times 10^{-2})$

pOH = 1.699

but pH = 14 – pOH

pH = 14 – 1.699

pH = 12.30

3. What is the molarity of a solution of potassium hydroxide of pH 13.32 at 25 ^{0}C?

Answer

pOH = 14 – pH

pOH = 14 – 13.32

pOH = 0.68

From $pOH = -\log_{10}[OH^-]$

$0.68 = -\log_{10}[OH^-]$

$[OH^-] = 10^{-0.68}$

$[OH^-] = 0.2$

KOH (aq) ⟶ K^+ (aq) + OH^- (aq)

From the equation of ionization, 1 mole of OH^- was produced by 1 mole of KOH

Hence, the **molarity of KOH = $[OH^-]$ = 0.2M**

9.6.3. pH of weak acids

A weak acid is partially ionized in aqueous solution.
Consider a weak acid HA, whose concentration is C_a and is undergoing ionization.

$HA(aq) \longrightarrow H^+(aq) + A^-(aq)$ (1)

Applying the equilibrium law,

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad (2)$$

The equilibrium constant K for a weak acid is expressed as acid dissociation constant K_a.

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

Since the mole ratio is 1:1 from the equation (1), it means that at equilibrium $[H^+] = [A^-]$ and $[HA] = Ca$ = *the concentration of undissociated acid.*

$$K_a = \frac{[H^+]^2}{C_a} (3)$$

$$[H^+]^2 = K_a C_a$$

$$[H^+] = \sqrt{K_a C_a}$$

$$[H^+] = (K_a C_a)^{\frac{1}{2}}$$

(4)

It is well known that $pH = -\log_{10}[H^+]$ and the

pH relation of a weak acid is therefore determined from the formula below;

$$pH = -\log_{10}\left(\sqrt{Ka.Ca}\right)$$

$$pH = -\log_{10}(K_a . C_a)^{\frac{1}{2}} \qquad (5)$$

The above expression can be simplified as follows;

$$pH = -\log Ka^{½} + -\log Ca^{½} \qquad (6)$$

The relation (7) is the expression used to determine the pH of weak acid

$$pH = \frac{1}{2} pK_a - \frac{1}{2} \log C_a \qquad \textbf{(7)}$$

Examples

1. Calculate the pH of a 0.1moldm^{-3} ethanoic acid solution of K_a 1.0x10^{-5} moldm^{-3}.

Solution:

$C_a = 0.1 moldm^{-3}$, $K_a = 1.0x10^{-5}\ moldm^{-3}$

$[H^+] = \sqrt{Ka.\ Ca}$

$[H^+] = \sqrt{(1.0 \times 10^{-5})x\ 0.1}$

$[H^+] = 1.0x10^{-3}\ moldm^{-3}$

From $pH = -\log_{10}[H^+]$

$pH = -\log_{10}(1.0x10^{-3})$

pH = 3

pH = ½ pKa – ½ log Ca

= ½ x 5 + 0.5 = 3

2. The pH of a 0.01M methanoic acid is 3.63. Determine the value of:

(a) the acid dissociation constant, K_a

(b) pK_a of methanoic acid.

Solution:

(a) From the equation of ionization: $HCOOH\ (aq) \rightleftharpoons HCOO^-\ (aq) + H^+\ (aq)$

$pH = -\log_{10}[H^+]$

$3.63 = -\log_{10}[H^+]$

$[H^+] = 10^{-3.63}$

$[H^+] = 2.399x10^{-4}\ moldm^{-3}$

$Ka = \frac{[H^+]2}{Ca}$

$Ka = \frac{(2.399 \times 10-4)}{0.01}$

$Ka = 5.49 \times 10^{-6} moldm^{-3}$

(b) $pK_a = -\log_{10} K_a$

$pK_a = -\log_{10}(5.49 \times 10^{-6})$

$pKa = 5.26$

3. A solution of 0.01 $moldm^{-3}$ of chloroethanoic acid is 18% ionized, calculate:

a. The acid dissociation constant, K_a.

b. pH of the solution

Solution:

a. From the equation of ionization:

$ClCH_2COOH\ (aq) \rightleftharpoons ClCH_2COO^-\ (aq) + H^+\ (aq)$

$$K_a = \alpha^2.C_a$$

$$K_a = \left(\frac{18}{100}\right)^2 \text{ x } 0.01$$

$$\underline{\mathbf{K_a = 3.24 \times 10^{-4}\ moldm^{-3}}}$$

b. From

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO-]}$$

$$K_h = \frac{C\alpha\ .C\alpha}{C - C\alpha} = \frac{C^2\ \alpha^2}{C\ (1-\alpha)}$$

$[H^+] = 1.8 \times 10^{-3}\ moldm^{-3}$

$pH = -\log_{10}[H^+]$

$= -\log_{10}(1.8 \times 10^{-3})$

$$\underline{\mathbf{pH = 2.745}}$$

9.6.4. pOH and pH of weak bases

Weak bases are those that undergo partial ionization in water. For example consider the ionization of a weak base; BOH

$BOH\ (aq) \rightleftharpoons B^+\ (aq) + OH^-\ (aq)$ (8)

Applying the equilibrium law,

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

Since K is the equilibrium constant for the base ionizing, it is then called base dissociation constant, *Kb*. Let *Cb* be the concentration of the solution.

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \quad (9)$$

Since mole ratio is 1:1, then $[B^+] = [OH^-]$

Hence $K_b = \frac{[OH^-]^2}{Cb}$ (10)

$$[OH^-]^2 = K_b.C_b$$

$$[OH^-] = \sqrt{Kb.Cb}$$

$$[OH^-] = (K_b \,.\, C_b)^{\frac{1}{2}} \quad (11)$$

From $pOH = -\log_{10}[OH^-]$

$$pOH = -\log_{10}(\sqrt{Kb.Cb}) \quad (12)$$

$$\boxed{pOH = -\log_{10}(K_b \,.\, C_b)^{\frac{1}{2}} \quad (13)}$$

From the relation (13), the pH of weak base can be determined as follows:
We have seen that pH + pOH = 14, then pH = 14 – pOH (14)

Note:
When water ionizes, two different ions are formed i.e. hydrogen and hydroxyl ions.

$$[H^+]\,[OH^-] = K_w \quad (15)$$

$$[H^+] = \frac{Kw}{[OH-]}$$

$$[H^+] = \frac{Kw}{(\sqrt{Kb.Cb})}$$

Remember that $pH = -\log_{10}[H^+]$

$$pH = -\log_{10}\left(\frac{Kw}{(\sqrt{Kb.Cb})}\right) \quad (16)$$

$$pH = -\log_{10}K_w - (-\log_{10} Kb^{\frac{1}{2}} + -\log_{10} Cb^{\frac{1}{2}})$$

Therefore pH of a weak base = $pKw - \frac{1}{2}pK_b + \frac{1}{2}\log_{10}C_b$ (17)

$$\boxed{pH = pK_w - \tfrac{1}{2}\,pK_b + \tfrac{1}{2}\log_{10}C_b \quad \text{or } pH = 14 - \tfrac{1}{2}\,pK_b + \tfrac{1}{2}\log_{10}C_b} \quad (18)$$

Examples
1. Calculate the pH of a 0.01M ammonia solution whose K_b is 1.584×10^{-5} moldm^{-3}.
Solution

$$NH_4OH\,(aq) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

$$K_b = \frac{[OH^-]^2}{C_b}$$

$$[OH^-] = \sqrt{K_b C_b}$$

$$[OH^-] = \sqrt{(1.584 \times 10^{-5}) \times 0.01}$$

$$[OH^-] = 3.98 \times 10^{-4}\, moldm^{-3}$$

From $pOH = -\log_{10}[OH^-]$

$= -\log_{10}(3.98 \times 10^{-4})$

$= -(-4) \log^{10} - \log_{10} 3.98$

pOH = 3.4

Also from pH = 14 – pOH

pH = 14 – 3.4

pH = 10.6

2. What is the base dissociation constant, K_b for a 0.01M phenylamine solution of pH 10.9?

Solution:

$C_6H_5\text{-}NH_2\,(aq) + H_2O\,(l) \rightleftharpoons C_6H_5\text{-}NH_3^+\,(aq) + OH^-\,(aq)$

pOH = 14 – pH

pOH = 14 – 10.9

pOH = 3.1

$pOH = -\log_{10}[OH^-]$

$3.1 = -\log_{10}[OH^-]$

$[OH^-] = 10^{-3.1}$

$[OH^-] = 7.9 \times 10^{-4}\ moldm^{-3}$

From $K_b = \frac{[OH^-]^2}{C_b}$

$$K_b = \frac{(7.9 \times 10^{-4})^2}{0.01}$$

Kb = 6.3 x 10^{-5} moldm^{-3}

3. Calculate the base dissociation constant, K_b of a 0.01M phenylamine which is 8% ionized.

Solution:

$A = 8\% = \frac{8}{100} = 0.08$

$$ph\text{-}NH_3OH\ (aq) \rightleftharpoons ph\text{-}NH_3^+\ (aq) + OH^-\ (aq)$$

Equation	$ph\text{-}NH_3OH$	$\rightleftharpoons$	$ph\text{-}NH_3^+$	OH^-
Original concentration	C		0	0
Concentration on ionization	Ca		Ca	Ca
Concentration at equilibrium	C –Ca		Ca	Ca

From the dissociation equation,

$[OH^-] = C\alpha$

$[OH^-] = 0.01 \times 0.08$

$[OH^-] = 0.0008\ moldm^{-3}$

Applying the equilibrium law,

$$K_b = \frac{[OH^-]^2}{C_b}$$

$$K_b = \frac{(0.0008)^2}{0.01}$$

Kb = 6.4 x 10^{-5} moldm^{-3}

Checking up 9.6

1. A solution of propanoic acid contains 0.05moles in 1dm^3. It has a pH of 4. What is the acid dissociation constant, K_a of propanoic acid?
2. Methanoic acid solution contains 0.001$moldm^{-3}$ and is 1% ionized. Calculate its pH given that its K_a is 1.0x10^{-7} $moldm^{-3}$
3. Determine the molarity of sodium hydroxide solution whose pH is 6.9
4. Calculate the pOH of a solution containing 2.2 x 10^{-5} $moldm^{-3}$ of potassium hydroxide
5. What is the pH of 0.4M sodium hydroxide solution?
6. Calculate the pOH and pH of a 0.005 $moldm^{-3}$ ammonia solution of K_b = 1.85x$10^{-5}$$moldm^{-3}$
7. A solution of phenylamine contains 0.01$moldm^{-3}$ and is 8% ionized. Calculate the base dissociation constant, K_b and hence pH of the solution.
8. A solution of 0.01M ammonia has a pH of 10.6.Calculate its base dissociation constant, K_b and its degree of ionization.
9. Calculate the molarity of a solution of sulphuric acid whose pH is 4.36
10. Calculate the pH of a solution containing 0.05M hydrochloric acid.

9.7. Salt hydrolysis

Activity 9.7.

1. What do you understand by the term "a salt"?
2. Explain two types of salts. Give examples in each case.
3. Discuss how salts are formed. Explain any four methods of preparing salts.
4. What do you understand by "salt hydrolysis"?
5. Give four examples of salts which undergo hydrolysis.
6. a. (i) Write an equation for the hydrolysis of sodium benzoate in water.
   (ii) Write an expression for the hydrolysis constant, K_h of sodium benzoate.
   b. A solution contains 0.2 moles of sodium benzoate per litre at 25 ^{0}C. Calculate the pH of the solution given that the hydrolysis constant, K_h of sodium benzoate is 1.6 x 10^{-10} mol dm^{-3} at 25 ^{0}C.

In the previous sections, we have seen that the pH value can be used to determine the strength of acid or a base. When the concentrations of $[H^+] > [OH^-]$, the water becomes acidic and when $[H^+] < [OH^-]$, the water acquires basic nature. A salt hydrolysis is a phenomenon that is observed when there is change of the concentrations of hydrogen or hydroxyl ions in a solution.

A salt is a chemical substance formed when either part or all the ionizable hydrogen of an acid have been replaced by a metallic ion or ammonium radical.Salts are strong electrolytes because when dissolved in water they dissociate almost completely into two different ions such as cations and anions.

Salt hydrolysis *is defined as a reaction in which the cation or anion or both of a salt react with water to form an acidic or alkaline solution*.

When the cations from the salt are more reactive than anions, they interact with water molecules detaching hydroxyl ions. This leaves hydrogen ions in solution making it acidic.

$X^+ (aq) + H_2O (l) \rightleftharpoons XOH (aq) + H^+ (aq)$ (19)

When the anions from the salt are more reactive than cations, they interact with water removing hydrogen ions and releasing the hydroxyl ions in solution. This results in the alkaline solution.

$X^-(aq) + H_2O(l) \rightleftharpoons XH (aq) + OH^-(aq)$ (20)

In general, the process of salt hydrolysis is the reverse of neutralization: Salt + Water $\leftrightarrow$ Acid + Base

If acid is stronger than base, the solution is acidic and in case base is stronger than acid, the solution is alkaline. When both the acid and the base are either strong or weak respectively, the solution is generally neutral in nature. As the nature of the cation or the anion of the salt determines whether its solution will be acidic or basic, it is proper to divide the salts into four categories.

(i) Salt of a strong base and a weak acid.

(ii) Salt of weak base and strong acid.

(iii) Salt of weak base and weak acid.

(iv) Salt of a strong acid and a strong base.

9.7.1. Salt of weak acid and strong base

The solution produced by a strong base and a weak acid is basic. The anion reacts with water to form a weak acid and OH- ions.

Examples

Na_2CO_3 from NaOH and H_2CO_3

CH_3COONa from CH_3COOH and NaOH

C_6H_5COONa from C_6H_5COOH and NaOH

K_3PO_4 from KOH and H_3PO_4

Consider sodium ethanoate, CH_3COONa compound which t ionizes completely in water as follows:

$CH_3COONa (aq) \longrightarrow CH_3COO^- (aq) + Na^+ (aq)$

Ethanoate ions disturb the ionic equilibrium of water where they accept hydrogen ions from water. This makes the resultant solution alkaline due to excess hydroxyl ions present. Such a solution has pH value greater than 7. The ions produced CH_3COO^- in

turn react with water to form a weak acid, CH_3COOH and OH^- ions as follows:

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

Equation	**CH_3COO^-**	⇌	**CH_3COOH**	**OH^-**
Initial concentration	C		0	0
Concentration on ionization	Ca		Ca	Ca
Concentration at equilibrium	C –Ca		Ca	Ca

Applying the equilibrium law;

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

K_h is the hydrolysis constant of the salt. Since the salt is fully ionized, the original concentration of the salt, C_s is equal to $[CH_3COO^-]$. On hydrolysis, $[CH_3COOH]$ is equal to $[OH^-]$ because the mole ratio is 1:1. The concentration of water is taken to be constant and does not appear in the $K_h$expression.

$$K_h = \frac{[OH^-]^2}{C_s}$$

$$[OH^-]^2 = K_h C_s$$

$$[OH^-] = \sqrt{K_h C_s}$$

$$[OH^-] = (K_h C_s)^{1/2}$$

$$pOH = -\log_{10}[OH^-]$$

$$pOH = -\log_{10}(K_h C_s)^{1/2}$$

pH of the resultant solution on this hydrolysis is then calculated from, **pH = 14 – pOH**

9.7.2. Salt of weak base and strong acid

These are salts which undergo cation hydrolysis to form acidic solutions.

Examples of such salts include;

NH_4Cl from NH_3 (aq) and HCl
NH_4NO_3 from NH_3 (aq) and HNO_3
$(NH_4)_2SO_4$ from NH_3 (aq) and H_2SO_4
$C_6H_5NH_3Cl$ from C_6H_5-NH_2 and HCl

Ammonium chloride as an example ionizes fully in water as follows:

$$NH_4Cl\ (aq) \longrightarrow NH_4^+\ (aq) + Cl^-\ (aq)$$

Ammonium ions disturb the ionic equilibrium of water by accepting hydroxyl ions from water. This makes the resultant solution acidic due to excess hydrogen ions from water thus a pH value less than 7.

$$NH_4^+\ (aq) + H_2O\ (l) \rightleftharpoons NH_4OH\ (aq) + H^+\ (aq)$$

Applying the equilibrium law;

$$K_h = \frac{[H^+]^2}{C_s}$$

$$[H^+] = \sqrt{K_h C_s}$$

$$[H^+] = (K_h C_s)^{1/2}$$

$$pH = -\log_{10}[OH^-]$$

$$pH = -\log_{10}(K_h C_s)^{1/2}$$

9.7.3. Salt of weak base and weak acid

These are salts which undergo both cation and anion hydrolysis when dissolved in water.

The nature of the resultant solution depends on the relative strength of the weak base and the weak acid. It may finally be acidic, alkaline or neutral.

E.g. if K_b of the anion is greater than K_a for the cation, the solution formed is alkaline because the anion is greatly hydrolyzed to produce more hydroxyl ions in solution.

When the K_b of the anion is less than K_a the cation, the resultant solution is acidic because the cation will be hydrolyzed to a greater extent producing excess hydrogen ions in solution.

And if K_b is approximately equal to K_a, the resultant solution is neutral.

Examples of such salts include:

$CH_3COO^-NH_4^+$ from CH_3COOH and NH_3 (aq)

$(NH_4)_2CO_3$ from NH_3 (aq) and H_2CO_3

$C_6H_5COO^-NH_4^+$ from C_6H_5COOH and NH_3 (aq)

Ammonium acetate as an example ionizes in water as follows;

$$CH_3COO^-NH_4^+ (aq) \rightleftharpoons CH_3COO^- (aq) + NH_4^+ (aq)$$

Since the acid and the base are both weak, their conjugate base, CH_3COO^- and conjugate acid, NH_4^+ ions are relatively strong. They accept H^+ and OH^- ions respectively from water and undergo considerable hydrolysis

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

$$NH_4^+ (aq) + H_2O (l) \rightleftharpoons NH_4OH (aq) + H^+ (aq)$$

The equation for the overall hydrolysis may be represented as follows:

$$CH_3COO^- (aq)\ NH_4^+ (aq) + H_2O (l) \rightleftharpoons CH_3COOH (aq) + NH_4OH (aq)$$

Therefore, the resultant solution of the above salt hydrolysis is neutral.

9.7.4. Salt of strong acid and strong base

Salts of strong acids and strong bases dissolve in water to give neutral solutions.
For example;

NaCl from NaOH and HCl
KCl from KOH and HCl
Na_2SO_4 from NaOH and H_2SO_4
KNO_3 from KOH and HNO_3

Aqueous solutions of the salts consist of ions with very little affinity for hydrogen ions or hydroxyl ions in water. The ions of such salts are only hydrated (i.e. surrounded by water molecules).

For example; Sodium chloride dissociates in water to give the anion Cl^-.

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

H^+ and Cl^- constitute an acid-base conjugate pair.

$$HCl (aq) + H_2O (l) \longrightarrow H_3O^+ (aq) + Cl^- (aq)$$

(Conjugate base)

Since hydrochloric acid is a strong acid, Cl^- is very weak base. Cl^- is unable to accept a proton (H^+) from an acid, particularly water. That is why Cl^- does not hydrolyze. The pH of sodium chloride solution remains unaffected.

Hydrolysis constant, K_h and the degree of hydrolysis

Consider a salt, CH_3COONa whose concentration is C_s. The salt undergoes anion hydrolysis as follows:

Equation	**CH_3COO^-**	⇌	**CH_3COOH**	**OH^-**
Initial concentration	C		0	0
Concentration during ionization	Cα		Cα	Cα
Concentration at equilibrium	C –Cα		Cα	Cα

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$K_h = \frac{(C\alpha C\alpha)}{[C - C\alpha]} = \frac{C^2\alpha^2}{C(1-\alpha)}$$

$$K_h = \frac{C\alpha^2}{1-\alpha}$$

But α is very small compared to 1 such that 1–α is approximately equal to 1

$$K_h = C\alpha^2$$

$$\alpha^2 = \frac{K_h}{C}$$

$$\alpha = \sqrt{\frac{K_h}{C}}$$

Relationship between K_a or K_b with K_w and K_h

Considering K_h of CH_3COONa and K_a of CH_3COOH:
Anion hydrolysis from the salt:

CH_3COO^- (aq) + H_2O (l) ⇌ CH_3COOH (aq) + OH^- (aq)

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

Dissociation of the acid:

CH_3COOH (aq) ⇌ CH_3COO^- (aq) + H^+ (aq)

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$\text{Multiplying } K_a \text{ by } K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \times \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$K_a \times K_h = [H^+][OH^-]$$

$$K_a \times K_h = K_w$$

$$K_h = \frac{K_w}{K_a}$$

Considering K_h of NH_4Cl and K_b of NH_4OH

Cation hydrolysis: NH_4^+ (aq) + H_2O (l) $\rightleftharpoons$ NH_4OH (aq) + H^+ (aq)

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]}$$

Dissociation of the base: NH_4OH (aq) $\rightleftharpoons$ NH_4^+ (aq) + OH^- (aq)

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

$$\text{Multiplying } K_h \text{ by } K_b = \frac{[NH_4OH][H^+]}{[NH_4^+]} \times \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

$$K_h \times K_b = [H^+][OH^-]$$

$$K_h \times K_b = K_w$$

$$K_h = \frac{K_w}{K_b}$$

Examples

1. Calculate the pH of a solution made by dissolving 8.4g of sodium ethanoate, CH_3COONa in 1 dm^3 of water. (K_h= 5.5 x 10^{-10} $moldm^{-3}$)

   Answer

   Molar mass of CH_3COONa = 84g/mole

   Salt concentration = $\frac{8.4}{84}$ = 0.1$moldm^{-3}$

   The salt undergoes anion hydrolysis:

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

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$Kh = \frac{[OH-]^2}{Cs}$$

$$[OH^-] = \sqrt{Kh.Cs}$$

$$[OH^-] = \sqrt{(5.5\ x\ 10^{-10})\ x\ 0.1}$$

$[OH^-] = 7.416 \times 10^{-6}$ moldm^{-3}

Then from, $pOH = -\log_{10}[OH^-]$

$pOH = -\log_{10}(7.416 \times 10^{-6})$

$pOH = -(-6)\ log_{10}{}^{10} - log_{10}{}^{7.416}$

$pOH = 5.13$

$pH = 14 - pOH$

$pH = 14 - 5.13$

pH = 8.87

2. The acid dissociation constant, K_a of a 0.1M sodium ethanoate, CH_3COONa solution is 1.8×10^{-5} moldm^{-3} at 25 ^{0}C. Calculate:

Given K_w as 1.0×10^{-14} mol^{2}dm^{-6}

a. the hydrolysis constant K_h .
b. the degree of hydrolysis of sodium ethanoate.
c. the pH of the solution

Solution:

(a) Sodium ethanoate undergoes anion hydrolysis.

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

$K_a . K_h = K_w$

$$K_h = \frac{Kw}{Ka}$$

$$K_h = \left(\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}\right)$$

$K_h = 5.6 \times 10^{-10}$ moldm^{-3}

(b) From $K_h = C\alpha^2$

$$\alpha = \sqrt{\frac{Kh}{C}}$$

$$\alpha = \sqrt{\left(\frac{5.6\ x\ 10^{-10}}{0.1}\right)}$$

$\alpha =$ **7.45×10^{-8}**

(c) From the equation of salt hydrolysis, $[OH^-] = Ca$

$[OH^-] = (7.45 \times 10^{-8}) \times 0.1$
$= 7.45 \times 10^{-6}$ mol dm^{-3}
$pOH = -\log_{10} [OH^-]$
$pOH = -\log_{10} (7.45 \times 10^{-6})$
$pOH = -(-6)\ log_{10}{}^{10} - log_{10}{}^{7.45}$
$pOH = 5.13$
$pH = 14 - pOH$
$pH = 14 - 5.13$
$\underline{pH = 8.87}$

Checking up 9.7

1. Calculate the pH of a 0.1moldm^{-3} ammonium chloride solution whose K_h is 6.34x10^{-8} moldm^{-3}
2. What is the hydrolysis constant, K_h of 0.1 moldm^{-3} aqueous solution of sodium propanoate of pH 8.9 given that K_w is 1.0 x 10^{-14} mol^{2}dm^{-6}?
3. Calculate the hydrolysis constant, K_h and pH of a 0.01M ammonium chloride solution at 25 $^{\circ}$C. (K_w = 1.0 x 10^{-14} mol^{2}dm^{-6} and K_b = 1.8 x 10^{-5} moldm^{-3})
4. Ammonium chloride undergoes hydrolysis according to the following equation:

$$NH^+_{4\,(aq)} + H_2O_{(aq)} \rightleftarrows NH_{3(aq)} + H^+_{(aq)}$$

If the hydrolysis constant for ammonium chloride, K_h at 25 ^{0}C is 5.6 x 10^{-10} mol dm^{-3}. Calculate;

(a) pH of a 0.1M ammonium chloride solution

(b) the percentage hydrolysis of this solution

9.8. Buffer solution

Activity 9.8

1. Explain the term buffer solution.
2. Analyze and differentiate the types of buffer solutions.
3. Discuss how pH and pOH of a buffer solution can be calculated.

9.8.1. Definition of buffer solution

Buffer solution is a solution that resists a pH change when a small amount of a base or acid is added to it.

A buffer solution consists of a solution of a weak acid and its salt with a strong base. This is called an *acidic buffer*. Examples of acidic buffers include: Ethanoic acid and sodium ethanoate solution, carbonic acid and sodium hydrogen carbonate.

A buffer solution may also consist of a solution of a weak base and its salt of strong acid. This is called a *basic or alkaline buffer*. Examples of basic buffers include: Aqueous ammonia and ammonium chloride solution, aqueous ammonia and ammonium sulphate or ammonium nitrate.

In general a buffer solution is an aqueous solution which involves the mixture of a weak acid and its conjugate base, or vice versa.

9.8.2. pH of buffer solution

The pH of a buffer solution or the concentration of the acid and base can be calculated using the **Henderson-Hasselbalch equation.** Henderson-Hasselbalch equation was given by *Lawrence Joseph Henderson* **(1878-1942)** and *Karl Albert Hasselbalch* **(1874-1962).**

Henderson-Hasselbalch Equation is *a rearrangement of the K_a expression* followed by the use of negative logarithms.

pH of an acidic buffer

An acidic buffer consists of a weak acid and its salt of strong base e.g. CH_3COOH/ CH_3COONa.

Ionization of the weak acid and the salt is as follows:

Weak acid: $CH_3COOH\,(aq) \rightleftharpoons CH_3COO^-\,(aq) + H^+\,(aq)$ *Equation (i)*

Its salt of strong base: $CH_3COONa\,(aq) \longrightarrow CH_3COO^-\,(aq) + Na^+\,(aq)$ *Equation (ii)*

The weak acid ionizes partially whereas its salt of strong base ionizes completely in solution.

Applying the law of mass action to equation (i);

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$[H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]}$$

Since sodium ethanoate is completely ionized, the concentration of the salt is taken as [CH_3COO-]. The concentration of ethanoate ions from the weak acid is taken as negligible since it is weakly ionized.

$$[H^+] = \frac{K_a[Acid]}{[Salt]}$$

Taking negative logarithms to base 10 on both sides;

$$-\log[H^+] = -\log K_a - \log\frac{[Acid]}{[Salt]}$$

$$-\log[H^+] = -\log K_a + \log\frac{[Salt]}{[Acid]}$$

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

This equation is known as the **Henderson-Hasselbalch** equation.

Therefore, the pH of an acidic buffer depends on the relative concentration of the salt and the acid in the mixture.

Examples

1) 0.61g of benzoic acid, C_6H_5COOH were dissolved in $1dm^{-3}$ of 0.02M sodium benzoate to form a buffer solution. Calculate the pH of the buffer solution formed. (C=12, H=1, O=16, $K_a=6.3\times10^{-5}$ $moldm^{-3}$)

Solution:

Molar mass of C_6H_5COOH = (12x7)+(1x6)+(16x2) = 122g/mole

$$[Acid] = \frac{0.61}{122} = 0.05 moldm^{-3}$$

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

$$pH = \log(6.3\times10^{-5}) + \log\frac{0.02}{0.05}$$

pH = 3.803

2) a) Calculate the pH of a buffer solution containing 4.1g of sodium ethanoate, CH_3COONa per litre and 0.01M ethanoic acid of $K_a = 1.7\times10^{-5}$ $moldm^{-3}$ (C=12, H=1, O=16, Na=23)

(b) Calculate the pH change of the buffer solution when $1cm^3$ of 1M sodium hydroxide is added.

Solution:

Molar mass of CH_3COONa = (12x2)+(1x3)+(16x2)+(23x1) = 82g/mole

$$[Salt] = \frac{4.1}{82} = 0.05 moldm^{-3}$$

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

$$pH = \log(1.7\times10^{-5}) + \log\frac{0.05}{0.01}$$

pH = 5.469

b. Added OH- ions react with ethanoic acid. This decreases the concentration of ethanoic acid but increases the concentration of sodium ethanoate.

Moles of 1M NaOH added = $\frac{1x1}{1000}$ = 0.001moles

New [Acid] = 0.01 – 0.001 = 0.009 moldm^{-3}

New [Salt] = 0.05 + 0.001 = 0.051 moldm^{-3}

$$New\ pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

$$pH = \log(1.7\times10^{-5}) + \log\frac{0.051}{0.009}$$

pH = 5.523

Therefore, pH change = 5.523 – 5.469 = **0.054 units**

pH and pOH of a basic buffer

A basic buffer consists of a solution of a weak base and its salt of strong acid e.g. NH_4OH/NH_4Cl.

Ionization of the weak base and its salt is as follows:

Weak base: $NH_4OH\ (aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ *Equation (i)*

Its salt of strong acid: $NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$ *Equation (ii)*

Applying the law of mass action to equation (i):

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

$$[OH^-] = \frac{K_b[NH_4\,OH]}{[NH_4^+]}$$

Since the base is very weak, it can be assumed that all the ammonium ions come from the fully ionized ammonium chloride. The concentration of ammonium ions from the weak base is considered negligible.

Thus, $[OH^-] = \frac{K_b[Base]}{[Salt]}$

From the ionic product of water, Kw = $[H^+]$ $[OH^-]$

$[H^+] = \frac{Kw}{[OH-]}$; substituting in the expression of $[OH^-]$ from abo\

$[H^+] = \frac{Kw}{[\frac{Kb\ [Base]}{[Salt]}]}$

$[H^+] = \frac{Kw\ [Salt]}{Kb\ [base]}$; Remember that: pH = -log$[H^+]$

$pH = -log\left(\frac{Kw\ [Salt]}{Kb\ [base]}\right)$

$pH = -log\left(\frac{Kw}{Kb}\right).\left(\frac{[Salt]}{[Base]}\right)$

$pH = (-log\ K_w) - (-log\ K_b) + -log\frac{[Salt]}{[Base]}$

$$pH = pK_w - pK_b + \log\frac{[Base]}{[Salt]}$$

The weak base and its salt of strong acid ionizes as follows:

Weak base: $NH_4OH\ (aq) \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$ *Equation (i)*

Its salt of strong acid: $NH_4Cl(aq) \longrightarrow NH_4^+\ (aq) + Cl^-\ (aq)$ *Equation (ii)*

Applying the equilibrium law to equation (i):

$$K_b = \frac{[NH_4^+]\ x\ [OH^-]}{[NH_4OH]}$$

$$[OH^-] = \frac{K_b[NH_4OH]}{[NH_4^+]}$$

Since the base is partially ionized, it can be assumed that all the ammonium ions are from the fully ionized ammonium chloride. The concentration of ammonium ions from the weak base is negligible.

Thus, $[OH^-] = \frac{K_b[\text{Base}]}{[\text{Salt}]}$

$-\log [OH^-] = -\log K_b - \left(\log \frac{[\text{Base}]}{[\text{Salt}]}\right)$

$-\log [OH^-] = -\log K_b + \left(\log \frac{[Salt]}{[Base]}\right)$

Examples

1. A solution consists of 0.01M ammonia solution and 2.13g of ammonium chloride, K_b for ammonia solution is 1.8×10^{-5} moldm^{-3}. (N=14, H=1, Cl=35.5)

(a) Calculate the pH of the buffer solution

(b) Calculate the pH change on addition of 1cm^3 of 1M hydrochloric acid.

Solution:

a. Molar mass of NH_4Cl = (14x1)+(1x4)+(35.5x1) = 53.5g/mole

$$[Salt] = \frac{2.13}{53.5} = 0.04 moldm^{-3}$$

$$pH = pK_W - pOH, \ where \ pK_W = 14$$

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

$$= -\log(1.8 \times 10^{-5}) + \log \frac{[0.04]}{[0.01]}$$

pOH = 5.347

pH = 14 – 5.347

pH = 8.653

b. Addition of hydrochloric acid decreases the concentration of ammonia solution since it reacts with it to form ammonium chloride thus the concentration of ammonium chloride is increased.

$$Moles \text{ of HCl added} = \left(\frac{1 \times 1}{1000}\right) = 0.001 \text{moles}$$

New $[NH_4OH]$ = 0.01 – 0.001 = 0.009 moldm^{-3}

New $[NH_4Cl]$ = 0.04 + 0.001 = 0.041 moldm^{-3}

$$pOH = -\log(1.8\times10^{-5}) + \log\left(\frac{0.041}{0.009}\right)$$

$$= 5.503$$

New pH = 14-5.503

pH = 8.497

Therefore, pH change = 8.653-8.497 = **0.156 units.**

2. Calculate the pH of the solution made by adding 30cm^3 of 0.1M hydrochloric to 80cm^3 of 0.1M ammonia solution. (K_b of ammonia solution = 1.8x10^{-5} moldm^{-3})

Solution:

$$Moles \text{ of HCl reacted} = \left(\frac{0.1\times30}{1000}\right) = 0.003 \text{moles}$$

$$Moles \text{ of } NH_4OH \text{ reacted} = \left(\frac{0.1\times80}{1000}\right) = 0.008 \text{moles}$$

From the equation of the reaction;

$NH_4OH\ (aq) + HCl\ (aq) \longrightarrow NH_4Cl\ (aq) + H_2O\ (l)$

Mole reaction is 1:1. This means that 0.003 moles of HCl reacted with 0.003 moles of NH_4OH to form 0.003 moles of NH_4Cl.

Therefore; moles of unreacted (excess) ammonia solution = 0.008 – 0.003 = 0.005 moles.

The resultant solution is a buffer solution consisting of 0.003 moldm^{-3} of NH_4Cl and 0.005 moldm^{-3} of NH_4OH

$$pOH = pK_b + \log\frac{[Salt]}{[Base]}$$

$$= -\log(1.8\times10^{-5}) + \log\frac{[0.03]}{[0.005]}$$

$$pOH = 4.523$$

But $pH = pK_w - pOH$

pH = 14 – 4.523

pH = 9.477

Checking up 9.8

1. A buffer solution of pH 4.0 is made using benzene carboxylic acid and sodium benzene carboxylate. Calculate the mass of sodium benzene carboxylate (molecular mass=144) that should be dissolved in 1.0 dm^3 of a 0.012 $moldm^{-3}$ solution of benzene carboxylic acid (Ka for $C_6H_5COOH = 6.31 \times 10^{-5}$ $moldm^{-3}$)
2. a. Calculate the pH of a buffer solution containing 7.2g of sodium benzoate in 1 dm^{-3} of 0.02M benzoic acid. (C=12, H=1, O=16, Na=23, Ka=6.25×10^{-5} $moldm^{-3}$)
   b. Evaluate how will the pH change if 1cm^3 of 0.01M of sodium hydroxide is added to the solution.
3. Calculate the pH of a buffer solution formed when 10cm^3 of 0.1M hydrochloric acid is added to 100cm^3 of 0.05M ammonia solution. K_b of ammonia solution is 1.8×10^{-5} $moldm^{-3}$
4. a. Calculate the pH of a buffer solution formed when 80cm^3 of 0.4M ammonia solution is mixed with 100cm^3 of 0.1M hydrochloric acid.
   b. Calculate the pH change when 0.7cm^3 of 1M hydrochloric acid solution was added.

9.9. Preparation of buffer solutions of different pH

Activity 9.9

1. Write an expression to show Henderson-Hasselbalch equation.
2. Explain how Henderson-Hasselbalch equation is used for the determination of the mass of salt to be dissolved when preparing an acidic buffer solution.
3. State two methods of preparing buffer solutions of different pH.

A buffer solution is a solution that resists a change in pH, because it contains species in solution able to react with any added acid or base.

In general, preparing a buffer solution requires either a weak acid and a salt of the acid's conjugate base or a weak base and a salt of the base's conjugate acid.

9.9.1. By mixing weak acid and its corresponding salt or weak base and its corresponding salt

It is very important to prepare buffer solutions of known pH in the laboratory. Using the **Henderson-Hasselbalch equation,** there are two terms which determine the final pH of the solution that is pK_a, whose value is responsible for the 'coarse selection' of pH and the ratio [conjugate base]/ [acid] that provides 'fine tuning' to the final pH.

So, to prepare an acidic buffer solution of known pH, select an acid whose pK_a is within the range of one unit of the desired pH. The ratio of salt to acid concentrations is then adjusted to achieve the desired pH.

Example

Suppose you want to prepare an acidic buffer with a pH of 4.0. A suitable weak acid would be ethanoic acid CH_3COOH because its pK_a is 4.8. The conjugate base is ethanoate ion CH_3COO^-, which is provided by the sodium ethanoate salt, CH_3COONa. Ethanoic acid is available as a laboratory bench reagent with concentration of 1.0 mol dm^{-3}.

The question is, what mass of sodium ethanoate should I add to the ethanoic acid to make this buffer solution?

Using the Henderson-Hasselbalch equation;

$$pH = pK_a + \log_{10}\left(\frac{[Conjugate\ base]}{[Acid]}\right)$$

Substitute the known quantities:

$$4.0 = 4.8 + \log_{10}\left(\frac{[Conjugate\ base]}{1.0}\right)$$

$$4.0 = 4.8 + \log_{10}[Conjugate\ base]$$

$$\log_{10}[\text{conjugate base}] = -0.8$$

$$[\text{Conjugate base}] = 0.16 \text{ mol dm}^{-3}$$

Therefore, the concentration of the conjugate base is 0.16 mol dm^{-3}.

The molar mass of sodium ethanoate is 82.0 g mol^{-1}. So 0.16 moles of sodium ethanoate has a mass given by:

Mass =Moles × molar mass

= (0.16 moles) × (82.0 g mol^{-1})

= 13g

Therefore, an acidic buffer solution of pH 4.0 will be prepared by dissolving 13 g of sodium ethanoate in 1.0 dm^3 of 1.0 mol dm^{-3} ethanoic acid in a volumetric flask. Insert a calibrated pH meter to monitor the pH of the prepared acidic buffer solution.

Note that it is the ratio of acid to conjugate base that is important in determining the pH of the buffer solution not the concentrations. However, when more concentrated solutions are used, the buffer solution can efficiently react with added acid and base before becoming saturated.

9.9.2. By partial neutralization

Buffers can also be prepared by the partial neutralization of a weak acid by a strong base through titration process.

This is done by running excess weak acidic solution from the burette into a strong basic solution in the conical flask until half neutralization takes place. A weak acid is partially neutralized by the strong base to form salt of weak acid. This salt is formed together with excess of the weak acidic solution which makes the resultant solution a buffer solution. Do this while measuring the pH of the resultant buffer solution with a pH meter.

For example reacting 40 ml of 1.0M propanoic acid (C_2H_5COOH) solution (pK_a is 4.87) with 60.0 ml of 0.10 M sodium hydroxide solution (NaOH). This will produce a buffer solution consisting of propanoic acid and sodium propanoate of pH 4.13.

Checking up 9.9

The following materials and chemicals are provided by the technician laboratory.

- 100ml Beaker,
- 10ml measuring cylinder,
- 50ml measuring cylinder,
- Electronic weighing scale,
- Calibrated pH meter,
- Glass rod,
- 100ml volumetric flask
- Ethanoic acid,
- sodium ethanoate and distilled water

Procedure

1. Measure exactly 50 ml of distilled water to a 100 ml beaker.
2. Using a measuring cylinder, add 5 ml of 0.3M ethanoic acid to the beaker.
3. Then weigh exactly 0.3g sodium ethanoate (CH_3COONa)
4. Add a little of the sodium ethanoate at a time, stirring the mixture with a glass rod to dissolve.
5. Insert the calibrated pH meter into the resultant solution in the beaker and measure its pH.
6. Quantitatively transfer the buffer solution to a 100 ml volumetric flask.Add distilled water up to the mark. Cap and invert the flask twice to mix.

Questions

a. What is the pH of the prepared buffer solution from the pH meter?

b. Given K_a of ethanoic acid as 1.8×10^{-5} mol dm^{-3} and using the Henderson-Hasselbalch equation, Calculate the pH of the buffer solution.

c. Comment about the difference in the experimental pH and the calculated pH, if any.

9.10. Explanation of the working of buffer solutions

Activity 9.10

1. a. Explain what is meant by a buffer solution?
   b. How does buffer acts?
2. Explain each of the following terms as used in the study of buffer solutions.
   a. Buffer capacity
   b. Buffer range
3. Explain two applications of buffer solutions that are used in:
   a. Biological processes
   b. Manufacturing industry

In a buffer solution, the weak acid and the conjugate base or weak base and its conjugate acid are responsible for controlling pH.

9.10.1 Working process of an acidic buffer

Consider a buffer solution made of ethanoic acid and sodium ethanoate solutions. Ethanoic acid is partially ionized because it is a weak acid whereas sodium ethanoate is fully ionized because it's a strong electrolyte.

$$CH_3COOH\,(aq) \rightleftharpoons CH_3COO^-\,(aq) + H^+\,(aq)$$

$$CH_3COONa\,(aq) \longrightarrow CH_3COO^-\,(aq) + Na^+\,(aq)$$

Such a solution contains few hydrogen ions from the acid and a large proportion of ethanoate ions from the salt.

When a small amount of an acid is added, the added hydrogen ions react with ethanoate ions to form ethanoic acid. This prevents an increase in the concentration of hydrogen ions in the solution hence pH remains constant.

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

When a small amount of a base is added, the added hydroxyl ions react with ethanoic acid to form water. This prevents an increase in the concentration of hydroxyl ions hence pH is kept constant.

$$CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l)$$

9.10.2. Working process of a basic buffer

Consider a buffer solution of aqueous ammonia and ammonium chloride. Aqueous ammonia is partially ionized while ammonium chloride is completely ionized because it is a strong electrolyte.

$$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

Such a solution contains a few hydroxyl ions and a large proportion of ammonium ions from the salt.

When a small amount of a base is added, the added hydroxyl ions react with ammonium ions to form un ionized aqueous ammonia. This prevents any increase in the concentration of hydroxyl ions in the solution hence no change on pH.

$$NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_4OH(aq)$$

Similarly when a small amount of an acid is added, the added hydrogen ions react with un ionized aqueous ammonia to form water. This prevents an increase in the concentration of hydrogen ions thus keeping pH constant.

$$NH_4OH(aq) + H^+(aq) \longrightarrow NH_4^+(aq) + H_2O(l)$$

9.10.3. Definition of buffer capacity and buffer range

Buffer capacity

This is a measure of the ability of a buffer solution to resist changes in pH when a base or acid is added. On addition of a base or acid to a buffer system, the effect on pH change can be large or small depending on the initial pH of the solution and it's ability to resist that pH change.

Buffer capacity is therefore defined as the number of moles of acid or base which

when added to one litre of a buffer solution changes its pH by 1.

Buffer capacity (β) ***has no units since it is a ratio of number of moles of acid or base added, to change in pH of buffer solution.***

Mathematically;

$$\beta = \frac{\Delta n}{\Delta pH}$$

where; β = Buffer capacity

Δn = number of moles of acid or base added

ΔpH = Difference between final and initial pH

Example:

To a buffer solution, 0.02 moles of acid was added. If the initial and final pH of the buffer was 4.75 and 5.20 respectively, calculate the buffer capacity of the solution.

Solution:

$$\beta = \frac{\Delta n}{\Delta pH}$$

$$= \frac{0.02}{(5.20 - 4.75)}$$

$$= 0.044$$

Buffer capacity is the efficiency of the buffer solution to control pH. The acid added to one litre of buffer solution changes its pH by only 1 unit.The buffer capacity is maximum at pH=pKa where [acid]=[conjugate base].

Buffer range

Buffer range is the pH range within which the buffer solution is effective.

Buffer range corresponds to the change in pH of about ±1. For example, acetic acid/ sodium acetate buffer works at optimum pH of 4.8. This means that it would work from pH 3.8 on addition of an acid to pH 5.8 when a base is added. Beyond this pH range, the buffer has no capacity to buffer the solution.

The effective buffer range of buffer solutions is different and depends on the acid or base dissociation constant.

Table 9.5. pKa and pH ranges of different buffer solutions.

Buffer	pKa	pH range
Carbonate	10.3	9.3 – 11.3
Citrate	6.4	5.4 – 7.4
Phosphate	2.1	1.1 – 3.1
Borate	9.2	8.2 – 10.2
Ammonia	9.3	8.3 – 10.3
Acetate	4.8	3.8 – 5.8

9.10.4. Applications of buffer solutions

pH of various solutions has to be controlled either in industries or in cells of living organisms because any slight change may greatly affect the functioning of the whole system.

In biological processes

- Buffer solutions are used to maintain the pH of human blood constant at 7.4. Intravenous injections must be correctly buffered so that they do not change the pH of blood in humans.
- Proteins in living organisms act as buffers by controlling pH in body cells. They are composed of amino acids linked together in long chains. Each amino acid has two functional groups; the amino group and acidic carboxyl group. The carboxyl group donates hydrogen ion when pH in body cells is high (alkaline). Amino group accepts hydrogen ion from body cells when pH is low (Acidic).
- Buffers keep the correct pH for enzymes to work in many organisms. Enzymes work best in a specific range of pH. If this pH is not controlled, the rate of enzyme activity slows down or enzymes stop working due to denaturation.
- In bacteriological research, culture media are generally buffered to maintain the pH as bacteria required a constant pH all the time to grow.

In agricultural processes

- Plants grow well in soils with a narrow pH range. Some soils become acidic due to acidic rains which is a serious problem to plant or crop growth. Organic matter and mineral salts in a fertile soil act as buffers. It is important to maintain
- pH of the soils for proper growth of vegetation and soil microorganisms.

In natural systems

- Water bodies such as lakes, rivers and streams are important habitats for aquatic organisms e.g. fish and young amphibians. They should have a stable pH to ensure survival of these organisms. Otherwise extreme pH may cause physical damage to the gills and fins of fish.

In industries

- Buffer solutions are used in fermentation to control pH changes such that anaerobic fermentation bacteria are not killed. This prevents the solutions from becoming too acidic and spoiling the product.
- Buffer solutions are used in manufacture of cosmetics whose pH must be controlled to prevent adverse effects on body cells.
- They are used in the production of pharmaceutical drugs to prevent deterioration when the drug is administered or stored. Buffers ensure stability and clinical effectiveness of the drugs.
- Dyes used in textile industries are buffered in order to maintain colour strength in different fabrics after production.
- Buffers are used in leather industries to control pH during tanning and dyeing. This gives a product of fine texture and colour.

Checking up 9.10

1. a. (i) What is meant by a Bronsted-Lowry acid?
   (ii) Write an equation to show that ethanoic acid is a Bronsted-Lowry acid.

   b. A buffer solution contains ethanoic acid and sodium ethanoate. With the aid of equations, explain how this buffer solution resists change in pH when a small amount of acid or base is added.

   c. Calculate the pH of a buffer solution which consists of 0.20 mol dm^{-3} of ethanoic acid and 0.25 mol dm^{-3} of sodium ethanoate. (K_a of ethanoic acid is 1.75×10^{-3} mol dm^{-3})
2. Explain why most often buffer solutions are prepared such that the concentration of the conjugate acid or base are similar?
3. Explain why the pH does not change very much on addition of small amount of strong acid or base to a buffer solution?
4. What is meant by "buffer capacity"? What determines buffer capacity of a solution?

END UNIT ASSESSMENT

SECTION A: Multiple choice questions

1. In Bronsted-Lowry definition of acids and bases, an acid

A. Is a proton donor

B. Is a proton acceptor

C. Forms stable hydrogen bonds

D. Breaks stable hydrogen bonds

2. In the following reaction in aqueous solution, the acid reactant is _____ ad its conjugate base product is ___. $CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$

A. CH_3COOH, CH_3COO^-

B. NH_3, NH_4^+

C. CH_3COOH, NH_4^+

D. NH_3, CH_3COO^-

3. Which one of the following is a conjugate acid of the hydrogen phosphate ion, HPO_4^{2-}?

A. H_3PO_4

B. PO_4^{3-}

C. $H_2PO_4^-$

D. HPO_4^{3-}

4. Which one of the following is a strong acid?

A. HNO_2

B. H_2SO_3

C. H_2CO_3

D. $HClO_4$

5. Which one of the following ions form an alkaline solution?

A. Cl^-

B. SO_4^{2-}

C. NO_3^-

D. CO_3^{2-}

6. What is the hydroxonium ion concentration of a 0.20M solution of ammonia? The Kb value of ammonia is 1.8×10^{-5} mol dm^{-3}.

A. 2.8×10^{-10}

B. 5.2×10^{-12}

C. 1.8×10^{-5}

D. 1.9×10^{-3}

7. A cup of coffee has a hydroxide ion concentration of 1.0×10^{-10} M. what is the pH of this coffee?

A. 10 B. 4

C. 7 D. 1

8. How would you calculate Kb for the formate ion, given that the Ka for formic acid is 1.8×10^{-4}? ($Kw = 1.0 \times 10^{-14}$)

A. $K_b = Ka \times K_w$ B. $K_b = K_w + K_a$

B. $K_b = K_w/K_a$ D. $K_b = K_a/K_w$

9. In anionic hydrolysis, the pH of the resultant solution is

A. Greater than 7 B. Less than 7

C. Equal to 7 D. Less than zero

10. When a salt of strong acid and weak base is dissolved in water, _____ occurs to give _____ solution.

A. Ionization, basic B. Ionization, acidic

C. Hydrolysis, acidic D. Hydrolysis, basic

SECTION B:

11. Benzoic acid is a weak acid.

a. What is meant by a weak acid?

b. The acid dissociation constant of benzoic acid (Ka) is 6.4×10^{-5} mol dm^{-3}. Calculate the pH of 0.1 mol dm^{-3} benzoic acid (C_6H_5COOH) solution.

12. Calculate the pH of 0.1mol dm^{-3} ethanoic acid (CH_3COOH) solution at 25 ^0C.

Ka of CH_3COOH is 1.8×10^{-5}

13. a. Write an equation of the reaction for the dissociation of propanoic acid in aqueous solution

b. Write an expression for the acid dissociation constant, K_a of propanoic acid

14. Some foodstuffs contain "acidity regulators" which have a buffering action on the pH. Mixtures of citric acid and its sodium salt are often used for this purpose.

$C_5H_7O_4COOH \rightleftharpoons C_5H_7O_4COO^-(aq) + H^+(aq)$

Citric acid $K_a = 7.4x10^{-4}$ mol dm^{-3}

a. The concentration of citric acid in lemon juice is 0.23 mol dm^{-3}. Assuming that no other acid is present. Calculate the pH of lemon juice.

b. Write equations to show how citric acid and sodium citrate buffer system regulates the acidity on addition of:

i. H^+ ions

ii. OH^- ions

c. Calculate the pH of the solution containing 0.20 mol dm^{-3} citric acid and 0.3 mol dm^{-3} sodium citrate.

15. A 0.01M solution of ammonia is 4.0% ionized.

a. Calculate the pH of the solution

b. Determine the base dissociation constant, K_b for the ammonia solution

16. a. A 0.1M ethanoic acid solution was titrated with 0.1M sodium hydroxide solution until the acid was exactly half-way neutralized. Calculate the pH of the resultant solution. ($K_a = 1.8 \times 10^{-5}$ mol dm^{-3})

b. Two drops of aqueous sodium hydroxide were added to the resultant solution in

c. State what happened to the pH of the solution and explain your answer.

17. A buffer solution of pH 4.5 was prepared from ethanoic acid ($Ka = 1.8 \times 10^{-5}$) and sodium ethanoate. The concentration of sodium ethanoate was 0.2 mol litre-1.

a. Write equation for the reaction that took place o addition of small amount of:

i. dilute hydrochloric acid

ii. dilute sodium hydroxide

b. Calculate the concentration of ethanoic acid in the buffer solution

18. At 27 ^{0}C, ammonia has a base dissociation constant, K_b of 1.8×10^{-5} mol dm^{-3}

a. Write an expression for K_b of ammonia

b. Calculate the concentration of OH^- ions in 0.1M ammonia solution at 25 ^{0}C. State any assumptions made

c. Calculate the change in OH^- concentration which occurs when 0.01 moles of ammonium chloride are added to 1.0 dm^3 of the solution in (b) above.

19. a. Write an equation for the hydrolysis of sodium ethanoate in water.

b. Write an expression for the hydrolysis constant, K_h of sodium ethanoate.

c. Calculate

i. The value of Kh of sodium ethanoate and indicate its units (K_a for CH_3COOH is 1.8×10^{-5}, $K_w = 1 \times 10^{-14}$)

ii. The pH of a 0.1M sodium ethanoate solution.

20. A solution containing 2.3×10^{-3} mol dm^{-3} of aluminium hydroxide ionizes in water ($Kw = 1.0 \times 10^{-14} mol^2 dm^{-6}$)

a. Write the equation for the ionization of aluminium hydroxide in water.

b. Calculate the pH of the resultant solution.

c. Explain what is meant by the term buffer solution?

d. Discuss the applications of buffer solutions in nature.

UNIT 10

INDICATORS AND TITRATION CURVES

UNIT 10: INDICATORS AND TITRATION CURVES

Key Unit Competence

To be able to relate curves to the type of acid orbase titrated, properly choose and use indicators in acid and base titration

Learning objectives

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

- Explain how the indicator works;
- Explain what is meant by the pH range of indicator;
- State the criteria for the selection of acid-base indicator for the use in titrations;
- Describe the changes in pH durind acid/base titrations;
- Perform experiments to show that the effectivenees of different indicators is related to the pH changes which occur during titration;
- Draw and interpret titration curves for various acid/base titrations;
- Match the titration curve to the type of acid and base titrated;
- Interpret pH curves of different titration reactions.

Introductory Activity

1. Explain the difference between acid and base.
2. Discuss the relationship between end point and equivalence point during titration

10.1. Definition of acid-base indicator

Activity 10.1

You are provided with different indicators, one acid and one base.

- **Indicators:**
  - Phenolphthalein indicator.
  - Methyl orange.
  - Litmus papers.
  - Methyl red.
- **Acid:** HCl(aq)
- **Base:** NaOH(aq)

Carry out different tests on acid and base above using different indicators and write down your observations.

An indicator is a substance which changes colour according to the nature of solution. An acid have indicator changes the colour according to wheather the medium is acidic or basic. Therefore it can be used to know if a solution is acidic or basic. It can also be used to determine the end point in a titration.

The substances that change colour when the acidity of the solution changes are known as *acid-base indicators*. A very common indicator used is litmus, which is obtained from lichen. Litmus paper is prepared by soaking absorbent paper with litmus solution and then drying it.

Acid-base indicators are used to find out the equivalence point of a titration.They change their colour within a certain pH range.

The titration is a process commonly used to determine the concentration of an acid or a base. During the titration, there are two main key points:

a. The amount of acid or a base mixed together must be controlled and measured

b. There must be some way of determining when enough acid or a base has been added to neutralize the solution.

The equivalence point informs us when enough acid or base has been added to neutralize the solution. The pH changes considerably near the equivalence point. A titration curve can be plotted to show the changes in pH.

In the previous units, it has been seen that acids are substances which donate a proton and become electron acceptors. Bases are proton acceptors and electron donors. During the titration process the concentration of unknown (acid or a base) is determined. Indicators are weak acids whose conjugate base is of different color. Indicators are weak organic acids or bases which changes color whenever there is a change in pH.

Indicators are used in titration solutions to indicate the completion of the acid-base reaction. Universal indicator is a mixture of indicators which give a gradual change in color over a wide pH range. The pH of a solution can be approximately identified when a few drops of universal indicator are mixed with the solution.

Checking up 10.1

Explain why each of the following procedures is used during acid –base titration in the laboratory.

1. After cleaning the burette some of the solution to be put inside it is added to the burette and rolled around inside them and then discarded.
2. You constantly swirl the reaction vessel as you perform the titration.
3. You should always keep your eye in line with the meniscus of the burette when reading the burette volume.

10.2. The pH range of indicators

Activity 10.2

1. Discuss your understanding of ionization of both weak acids and weak bases.
2. Discuss ionization of both strong acids and strong bases.
3. Explain the term conjugate base.

Weak acids or weak bases are classifies as weak electrolytes which ionize partially in solution while strong acids or strong bases as strong electrolytes ionize completely in solution.

Examples:

i. $CH_3COOH\ (aq) \rightleftharpoons CH_3COO^-_{(}aq_{)} + H^+(aq)$ (weak acid.)

ii. $NH_4OH\ (aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ (weak base)

iii. $HCl\ (aq) \longrightarrow Cl^-(aq) + H^+(aq)$ (strong acid)

iv. $NaOH\ (aq) \longrightarrow Na^+(aq) + OH^-(aq)$ (strong base)

For an acid to donate a proton there must be a base to receive it as indicated in the following examples

$Acid \longrightarrow Base + H^+$

$Base + H^+ \longrightarrow Acid.$

The relationship between bases and acids to donate or receive electrons is called ***conjugate acid-base pair***.

10.2.1. Explanation on how indicators work

Indicators are weak organic acids (HIn) that change color when deprotonated (In). A few drops of indicator added to the analyte solution before the beginning an acid-base titration. The acid and base formed by indicators have different and intense colors; they operate at different pH ranges.

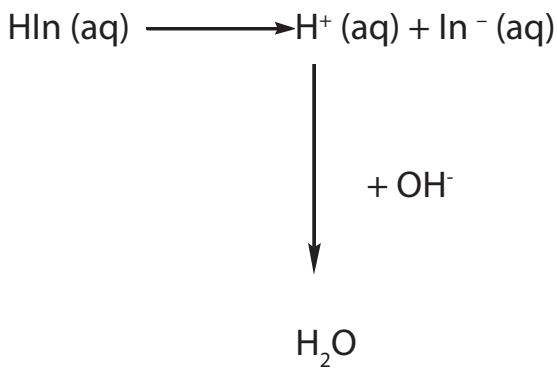
The partial dissociation of indicators as weak acid is shown in the example below:

$HIn\ (aq) \rightleftharpoons H^+(aq) + In^-(aq)$

acid form base form

At the end-point of an acid-base titration the pH changes very rapidly, and the indicator equilibrium moves from all HIn to all In^- (or vice versa).

Under high pH (alkaline) the concentration of OH^- ions is high H^+ ions will be removed as water (H_2O) as follows:



At this point the equilibrium shifts to the right.

Under low pH (acidic) the concentration of H^+ ions is high and the equilibrium shifts to the left as predicted by Lechatelier's principle.

Comparison between indicators and buffers.

Buffers are solutions which have the ability to resist changes of acidic or alkalinity and their pH remain almost constant. A good example is Blood which contains ions such as PO_4^{3-} and HCO_3^-. These are responsible for maintaining the pH of Blood at 7.4; a small change in pH of blood can be fatal. Buffers can be made from a mixture of a weak acid and the soluble salt of that acid.

The colour change and the pH range of some common indicators are shown in the Table 10.1.

10.2.2. The pH range of indicators

At a low value of pH, a weak acid indicator is almost completely in the HIn form, the color of which predominates. As the pH increases, the intensity of the color of HIn decreases and the equilibrium is pushed to the right. Therefore, the intensity of the color of In^- increases. An indicator is most effective if the color change is distinct and over a small pH range.

For most indicators the range is within ±1 of the pKIn value.

When only the color of the non-ionized form of indicator is seen,

[In–]/[HIn] = 1/10. Therefore,

pH = p*Ka*+ log 1/10

= p*Ka*–1

When only the color of the ionized form is observed, [In–] / [HIn] = 10/1, and

pH = p*Ka*+ log 10/1

= p*Ka*+ 1

So the pH in going from one color to the other has changed from p*Ka* –1 to p*Ka* + 1.

This is a pH change of 2, and most indicators require a transition range of about two pH units.

Therefore, the change of color does not occur with a well determined pH, but in an interval of pH of two units around the pK_{In}. This interval is called pH range of

indicator: $pH = pK_I + 1$

The colour change and the pH range of some common indicators are shown in the Table 10.1.

Table 10.1. Example of some common indicators and their pH range

Indicator	pKIn	Color		pH range
		Acid	Base	
Methyl orange	3.7	Red	Yellow	3.2 - 4.4
Bromophenol blue	4.0	Yellow	Blue	3.0 – 4.6
Bromocresol Green	4.7	Yellow	Blue	3.8 - 5.4
Methyl red	5.1	Red	Yellow	4.8 - 6.0
Bromothymol blue	7.0	Yellow	Blue	6.0 - 7.6
Phenol red	7.9	Yellow	Red	6.8 - 8.4
Phenolphthalein	9.3	Colorless	Red	8.2 - 10.0

A good indicator for a specific acid-base titration has an endpoint with a pH at or near the pH of the equivalence point.

10.2.3. Choice of indicators

It is important to choose the correct indicator to be used. An indicator is appropriate for a given titration if the rapid change of pH at equivalence overlaps the pH range of the indicator. The table 10.2 summarizes some types of titrations and the choice of appropriate indicators for them.

Table 10.2: Types of titrations and choice of indicator

Acid	Base	pH change	Choice of indicator
HCl	NaOH	3 to 11	methyl orange or phenolphthalein – the pH change here is over a very wide range
HCl	NH_3	3 to 7	Methyl orange
CH_3COOH	NaOH	7 to 11	phenolphthalein
CH_3COOH	NH_3	no sharp change	no suitable indicator – a pH meter is not suitable either as there are no sudden pH changes
HCl	Na_2CO_3	6.5 to 9.5 (pKa_1) 2.5 to 5.5 (pKa_2)	phenolphthalein for pKa_1 methyl orange for pKa_2
$H_2C_2O_4$	NaOH	to 3.5 (pKa_1) 5 to 11 (pKa_2)	methyl orange for pKa_1 phenolphthalein for pKa_2 (the first pH change only just falls within the range of methyl orange, so a pH meter more suitable here)

The pH at the equivalence-point must be known for the proper selection of an indicator

Note: Choose an indicator whose range lies on vertical section of the pH curve.

Checking up 10.2

1. Write the equation to show ionization of the weak acid $HClO_2$ and the expression for its equilibrium constant.
2. How can you use Ka values to compare the strength of two acids?

10.3. Acid-base titration curves

Activity 10.3

Explain how Acid—Base indicators are used to determine the equivalence point of a titration.

A titration curve is normally a plot of pH versus volume of titrant. It shows how the pH of an acid or base change as it is neutralized. For example as a base is added to acid, a gradual increase in pH will occur until the solution gets close to the equivalence point. Near the equivalence point, a rapid change in pH occurs. At the equivalence point, equivalent amounts of acid and base have been added and the pH will reflect which species are present. Beyond the equivalence point, when excess base is added an abrupt increase of PH is observed as a steep increase of the titration curve.

Titrations can result in acidic, basic, or neutral solutions at the equivalence point.

We can distinguish the following titration curves:

a. Strong acids – strong base titration curve where strong acids and bases are completely converted to H_3O^+ and OH^- in water solution. This titration results in a neutral solution at the equivalence point.

b. Strong acids titrated with weak bases result in acidic solutions at the equivalence point.

c. Weak acids titrated with strong bases result in a basic solution at the equivalence point.

d. Weak base and weak acid

Note: The following points are considered to plot pH titration curves:

- use graph paper
- orientation of axis
- naming of axis
- graduation of axis
- joining/matching points

a. Titration curve for a strong acid neutralised by a strong base

This titration is made by using 1mol/dm^3 of sodium hydroxide (NaOH) which is added to 50 cm^3 of 1mol/dm^3 hydrochloric acid (HCl).

Start with 50$cm^3$of one mol/dm^3 HCl in the flask; HCl is a strong acid and it fully ionizes.

We obtain: $[H_3O^+] = [HCl] = 1 mol/dm^3$ with pH → 0. The curve starts at zero. As the alkali is added to the acid, it neutralizes an equal volume of acid forming a salt and water. The remaining acid is diluted by the increased volume of water, then the concentration of hydrogen ions decreases and the pH increases. When $50cm^3$ of alkali have been added, the acid is completely reacted leaving salt and water. The pH is 7 and it is indicated by inflexion point. Further addition of alkali has no acid to react with, and therefore, pH rises to its final value of 14 due to excess strong alkali added.

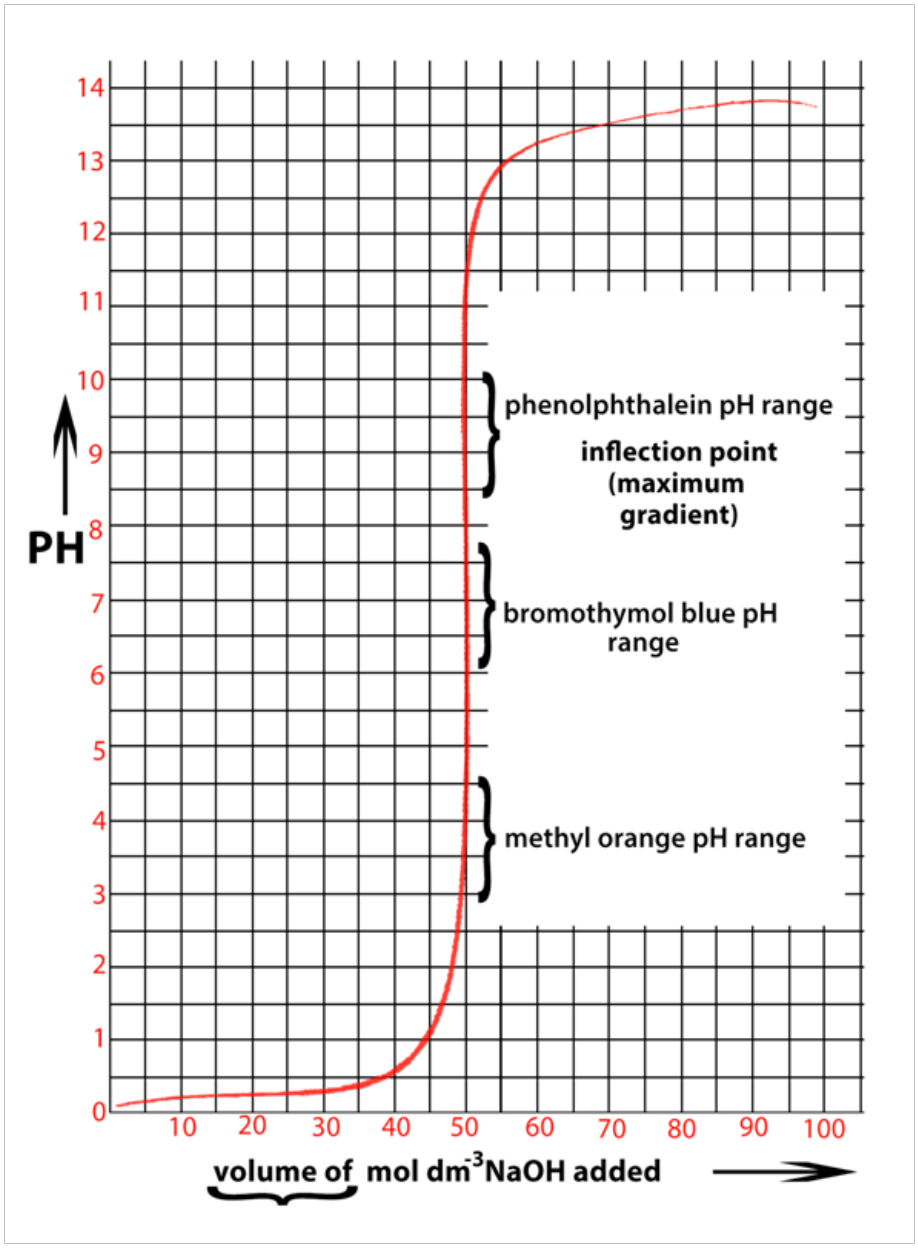


Figure 10.1: Titration curve for a strong acid with a strong base

b. Titration curve for a weak acid neutralised by a strong base

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

$$Ka = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

$$[H_3O^+] = \sqrt{Kax[CH_3COOH]}$$

This curve shows what happens when 1mol/dm^3 sodium hydroxide is added to 50cm^{3}of one mol/dm^3 ethanoic acid.
Start with 50cm^{3}of 1mol/dm^3 ethanoic acid in the flask. Ethanoic acid is a weak acid and so ionizes partly in solution. ($K_a = 1.8x10^{-5}$ mol/dm^3)

This makes the usual assumption.

pH = 2.37 The curve starts at this point.

After a rapid initial rise in pH the buffered region is reached and the pH changes more slowly as alkali is added because as OH^- remove H_3O^+ more acid splits up producing new H_3O^+ ions.

When 25cm^3 of alkali have been added half of the acid has been turned into its salt.

Ka = $[H_3O^+]$ or pKa =pH.

When 50 cm^3 of acid have been added all of the acid has been turned into its salt CH_3COONa. The inflexion point is at 9.24 not at 7.

From 50 cm^3 onwards the curve is the same as that of strong acid-strong base.

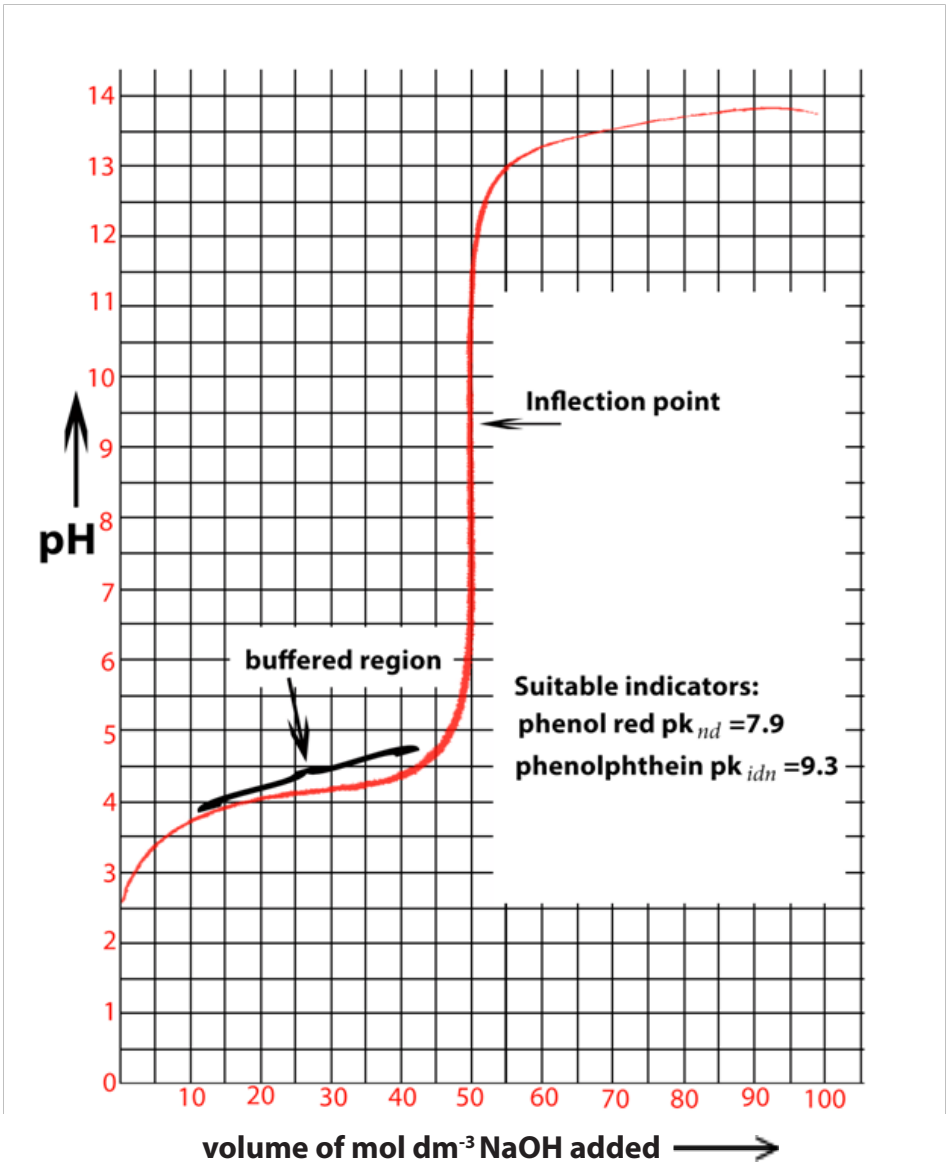


Figure 10.2: Titration curve for a weak acid with a strong base

c. Titration of a strong acid neutralised by a weak base

This curve can be drawn when 1mol/dm^3 ammonia is added to 50cm^{3}of 1mol/dm^{3}of hydrochloric acid.

First part of the curve is the same as that of strong acid and strong base. When 50cm^3 of alkali have been added; all the acid has reacted producing a salt NH_4Cl.This is an acidic salt due to the hydrolysis of ammonia ion and the pH is 4.8

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$$

From 50 cm^3 onwards, all the acid is completely reacted by aqueous ammonia. The excess ammonia solution added rises the pH towards 10 to 14.

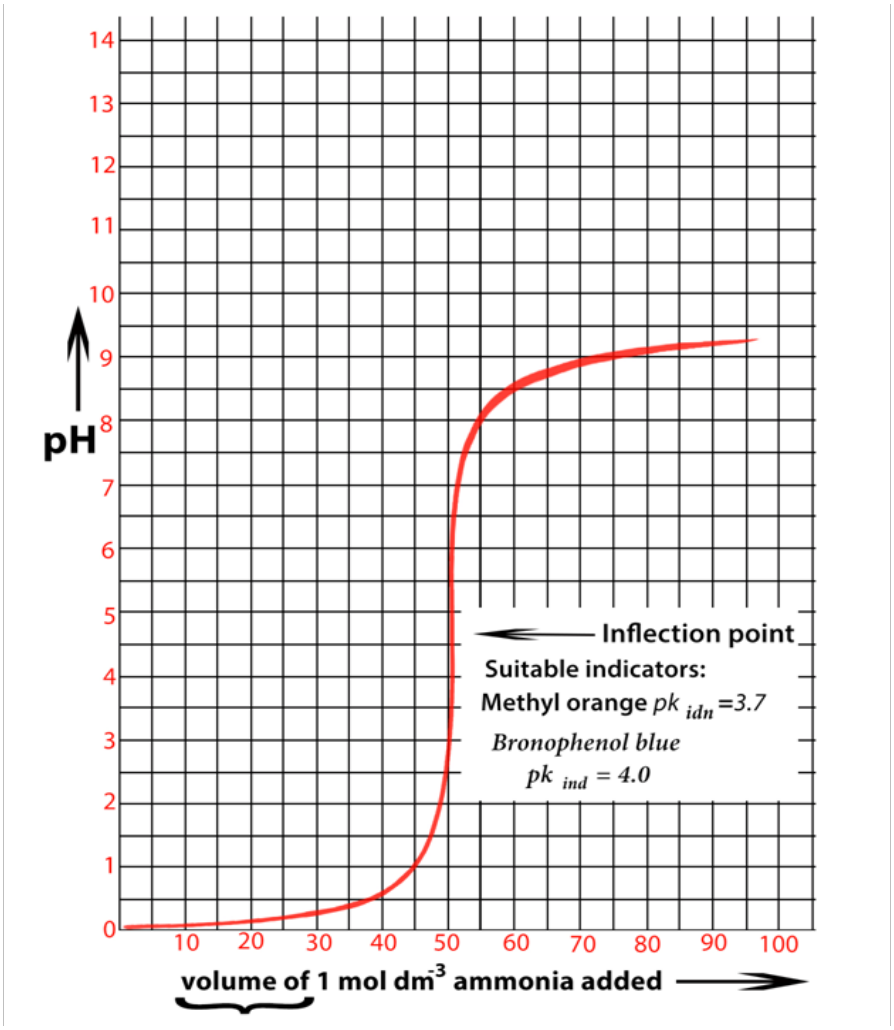


Figure 10.3: Titration of a strong acid with a weak base

d. Titration curve for weak acid neutralised by a weak base:

This curve is obtained by using 1mol/dm^3 ammonia solution added to 50 cm^3 of 1mol/dm^3 ethanoic acid.

Add 50 cm^3 of 1mol/dm^3 ethanoic acid in a conical flask and titrate it with ammonia solution from the burette.

The last part of the curve obtained by this titration is similar to that of weak base against strong acid. The central part (middle point) with the inflexion point is different from all other titration curves because it does not have the vertical section. This means that pH never changes rapidly enough to make the indicator give a sharp colour change.

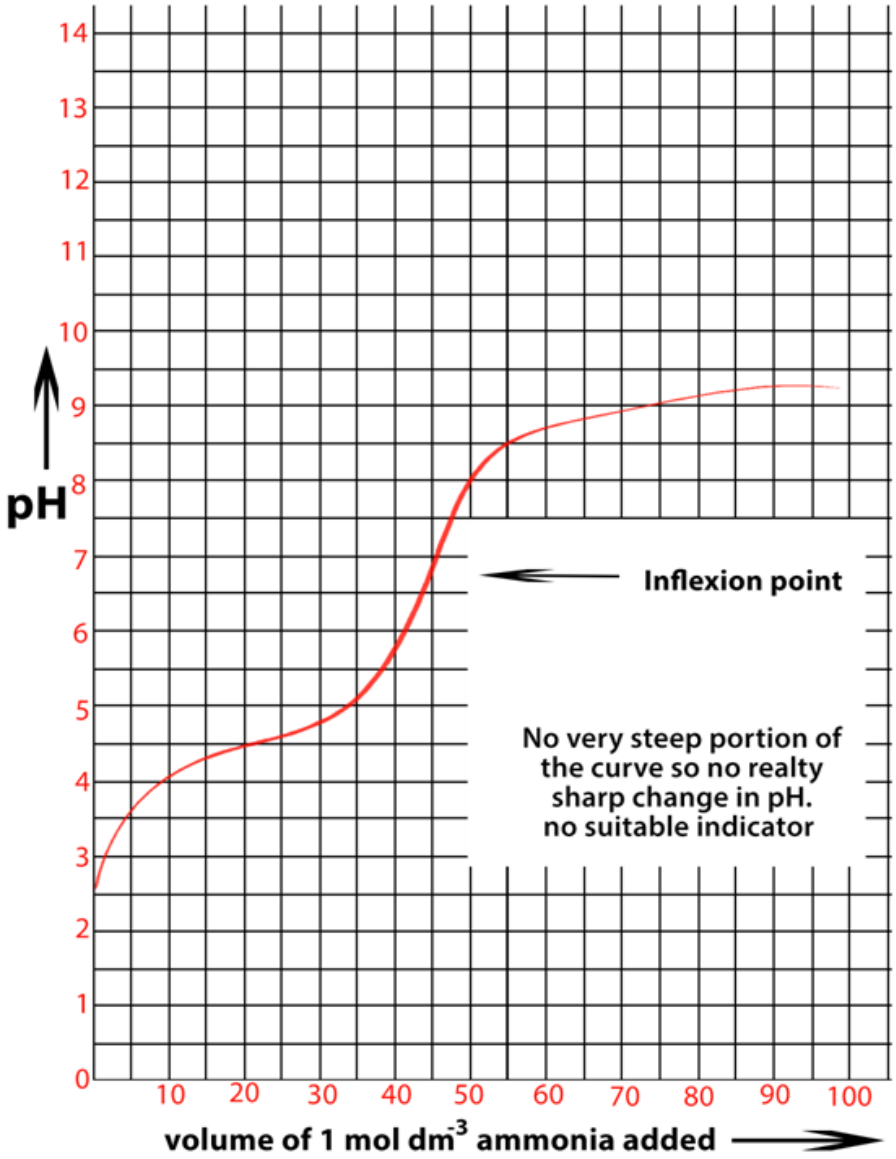


Figure 10.4: Titration curve for weak acid with a weak base

Checking up 10.3

A titration is performed by adding a standardized solution of NaOH of unknown concentration of HCl and the following data were obtained:

Initial reading of acid 1.55 cm^3.

Initial reading of base 0.75cm^3.

Final reading of acid 44.25cm^3.

Final reading of base 32.50cm^3.

Concentration of standard base solution 0.383M.

a. Is the concentration of unknown acid greater than or less than 0.383M?

b. Calculate the concentration of the unknown acid

END UNIT ASSESSMENT

1. A Laboratory assistant was given an assignment of standardizing a solution of sodium hydroxide NaOH which was to be used in the laboratory to do this he carefully weighed 2.878g solid Potassium hydrogen phthalate ($KHC_8H_4O_4$) often abbreviated as KHP in laboratory manuals this was dissolved in some distilled water and titrated with the solution of sodium hydroxide which was to be standardized. It required 23.65 cm^3 of the base to just neutralize the sample of KHP (to reach the end point.)

   Given the equation for the reaction as: $HC_8H_4O_4^- + OH^- \rightleftarrows H_2O + C_8H_4O_4^{2-}$
   Calculate the concentration of sodium hydroxide NaOH Solution

   in mol/dm^3

2. Consider the titration curve for titrating a strong acid like HCl and a strong base like sodium hydroxide NaOH Select all the true statements from among the following.

   a. At the beginning of the titration the pH of the solution was 7.
   b. At the beginning of the titration the pH of the solution was will be below 7.
   c. At first the pH of the solution rises rapidly as the base is added.
   d. The PH of the solution rises at a constant rate as the base is added.
   e. At the equivalence point of the titration the pH is 7.
   f. The PH of the solution changes very rapidly around the equivalent point of the titration
   g. When you move past the equivalence point the pH of the solution rises rapidly.
   h. After passing over the equivalence point the pH of the solution will be greater than 7.

      i. Any indicator that changes color from perhaps a pH of 4 to 10 would be a good choice of indicator. For this titration.

3. Which of the following would be the correct type of indicator for the titration between a strong acid and weak base.

   a. Methyl Yellow pKin=3.5.
   b. Congo Red pKin =4.0
   c. Bromothymol blue pKin =7

UNIT 11

SOLUBILITY AND SOLUBILITY PRODUCT OF SPARINGLY SOLUBLE SALTS

UNIT 11: SOLUBILITY AND SOLUBILITY PRODUCT OF SPARINGLY SOLUBLE SALTS

Key Unit Competence

To be able to calculate the solubility product constant of sparingly soluble salts and deduce the applications of common ion effect in the industry.

Learning objectives

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

- Define the term solubility product Ksp;
  State and explain the factors that affect the solubility of sparingly soluble salts;
- State and explain the applications of solubility product;
- Explain common ion effect on the solubility of sparingly soluble salt;
- Explain the relationship between kidney stone formation and solubility and the solubility product;
- Explain the applications of the solubility product and the common ion effect;
- Perform a simple experiment to determine the solubility product of sparingly soluble salt;
- Write the equations of dissociation and Ksp expression for sparingly soluble salts;
- Calculate the molar concentration of ions and Ksp values for sparingly soluble salts;
- Relate the solubility product principle to the selective precipitation of substances;
- Use the values of Ksp and Qc to predict if a mixture of solutions will form a precipitate or not;
- Relate the common ion effect to the solubility to the sparingly soluble salt.

Introductory activity 11:1.

1. Identify substances which are soluble in water from the following list
   $CuSO_4$, $Pb(NO_3)_2$, $CaCl_2$ AgI.
2. Explain what happens when ionic salts dissolve in water.

This unit introduces us to solubility equilibria which are found in saturated solutions of slightly soluble ionic salts. We will discuss the difference between solubility equilibria and dissociation equilibria and we will clarify some possible points of confusion in solving problem related to equilibria products.

11.1. Definition of solubility and molar solubility

Activity 11.1

1. Differentiate between solubility and Molar solubility and state the units.
2. What is the difference between solubility equilibria and other equilibrium systems.

Solubility

In the previous units, it has been mentioned that a solution is made by a solute which is dissolved in a solvent. Similarly, the *solubility* is a *chemical* property referring to the ability for a given substance, the solute, to dissolve in a solvent. In this section, we will deal with solubility which is a term that refers to the maximum amount of solid (either in moles or grams) that actually does dissolve in a solvent at equilibrium, producing ions; this amount can be calculated for a particular solid.Solubility may be considered to be an equilibrium between solid and ions in solution.

In general, the solubility of a solid in water is given by the maximum number of grams or number of moles of the solid that will dissolve in 100g of water at a given temperature. Generally the solubility of salts increases with increased temperature.

Solubility is most fundamentally expressed in molar (mol l^{-1} of solution) or molal (mol kg^{-1} of water) units. A solution that contains the maximum possible amount of the solute in said to be "saturated".

Molar solubility

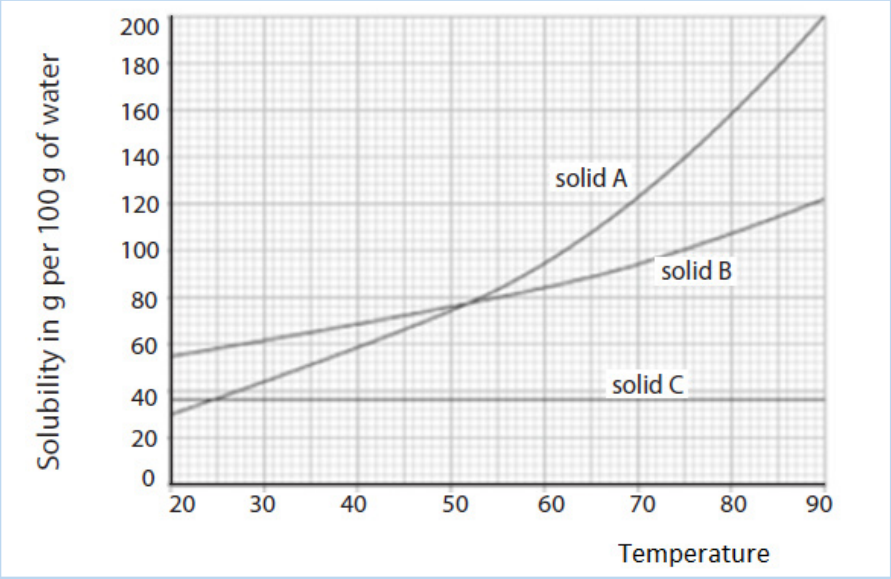
Molar solubility can be expressed as the number of moles of a solute that can be dissolved per liter of solution at saturation.

Most ionic salts are soluble in water while some are sparingly soluble (often called insoluble)

- All Nitrates,
- Generally Group I carbonates, except lithium carbonate are soluble but group II carbononates are sparingly soluble.
- All Chlorides except lead chloride, silver chloride and mercury chlorid
- Sodium, Potassium, and Ammonium Sulphate are also soluble, the rest of the sulphate are insoluble.

Checking up 11.1

Insoluble substances such as AgCl, $Ca_3(PO_4)_2$ partly dissolve and they form a heterogenous mixture. Solubility of solutes often increases with increased temperature. Observe the graph below and answer the following questions.



1. Explain the nature of the graph.
2. Identify the letter corresponding to:
   a. Salt whose solubility is not affected by an increase in temperature.
   b. Salt which dissolves highly with increased temperature.
   c. Salt which moderately dissolve with increased temperature.

11.2. Unsaturated, saturated and super saturated solutions

Activity 11.2

1. Dissolve two spatula full end of Copper II sulphate in 100cm^3 of distilled water. State what is observed
2. Without changing the volume of water add extra spatula full of copper II sulphate crystals stepwise, state what is observed. Keep on stirring until there is no further change.

All the beginning of the activity, you noticed that all the amount of the salt added to water dissolved completly. If more solid as added to an unsaturated solution, it dissolves until the solution is saturated (at which point there is solid in equilibrium with the solvated ions).

A saturated solution is one which contains the maximum amount of dissolved solid at a particular temperature in the presence of undissolved solute. A solution will be saturated when the solid is in equilbrium with its ions dissolved.

Checking up 11.2

The term "solubility equilibria" refers to the kind of equilibria that exists in saturated solution of slightly soluble ionic solids.

Explain what will be the concentration of the ions in a saturated solution.

A super saturated solution contains more solute than a saturated solution. This kind of solution is instable and any disturbance, such as shaking, will cause the excess solute to precipitate, Adding a crystal of solute to a super saturated solution, the precipitation will be observed and will cause the crystal to grow bigger in size until the solubility equilibrium is achieved.

11.3. Equations of the dissociation of sparingly soluble salts in water

Activity 11.3

Write equations to show the dissociation of the following substances in water.

1. Barium sulphate.
2. Silver Iodide.
3. Silver carbonate.
4. Calcium phosphate.

A sparingly soluble solute is one which slightly dissolves in a given solvent. It partly dissociates into component ions.

The main examples of sparingly soluble salts include; Barium sulphate, $BaSO_4$; and Silver chloride ,AgCl and lead(II) chrolide, $Pbcl_2$

As stated previously, when salts dissolve in water, they dissociate into ions.

$$AgCl_{(s)} \overset{H_2O}{\rightleftharpoons} Ag^{+}_{(aq)} + Cl^{-}$$

$$BaSO_{4(s)} \overset{H_2O}{\rightleftharpoons} Ba^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

$$PbCl_{2(s)} \overset{H_2O}{\rightleftharpoons} Pb^{2+}{}_{(aq)} + 2Cl^{-}{}_{(aq)}$$

$$Ca_3(PO_4)_{2(S)} \overset{H_2O}{\rightleftharpoons} 3Ca^{2+}{}_{(aq)} + 2PO_4^{3-}{}_{(aq)}$$

Checking up 11.3

1. Write balanced equations for the dissociation of some sparingly soluble ionic solts.
2. Write down the ionic equations for each of the reactions in 1 above

11.4. Definition of solubility product ksp

Activity 11.4.

3. Differentiate solubility and solubility product:
4. State the units of Ksp.

In the previous sections, we have seen that solubility of a solid is expressed as the concentration of the "dissolved solid" in a saturated solution. A solution is made of solute and solvent.

The solubility product is the equilibrium constant expressed in terms of concentrations of the ions produced from a sparingly soluble solid in contact with a saturated solution.

The equilibrium constant for the system is given the symbol (Ksp) where the sp added to k tell us that this equilibrium constant is a solubility product. Equilibrium is set up between the undissolved solid and the hydrated ions in solution. A precipitate will appear if the solubility product is exceeded for the system containing silver chloride.

Examples of expression of Ksp for some compounds

$$\mathbf{AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)}$$

$$\text{Ksp of AgCl} = [Ag^{+}]\,[Cl^{-}]$$

There is no denominator in the expression for the solubility product because the denominator is a pure solid and pure solids and liquids are never included in equilibrium constant expression.

A solubility product is generally a special example of a heterogeneous equilibrium constant. It involves more than one phase; that is solids in contact with liquids.

v. Solubility product for lead II sulphate ($PbSO_4$)

Suppose you made a saturated solution of lead (II) sulphate $PbSO_4$ by shaking the solid with water until no more would dissolve. Lead (II) Sulphate is almost insoluble in water and a white solid would be observed suspended in the water; after sometime the solid will settle to the bottom.

Lead (II) Sulphate is an ionic compound and some Lead (II)ions (Pb^{2+}) and Sulphate ions(SO_4^{2-}) will break away from the lattice and go into solution; others which had

broken off previously will return to attach themselves to the solid; this results into an equilibrium as follows.

$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$

$Ksp = [Pb^{2+}][SO_4^{2-}]$

vi. Solubility product for lead II iodide (PbI_2)

$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$

$Ksp = [Pb^{2+}][2I^-]^2$

Note: In brief, the formula for the solubility products is the product of molar concentration of the respective ions, each concentration raised to the power of the stochiometric coefficient in the dissociation equation.

Solubility products are only constant at a particular temperature which is usually 298K.

Checking up 11.4

Express the solubility product Ksp for the following sparingly soluble salts.

a. AgI(s)
b. $CaSO_4(s)$
c. Ag_2CO_3 (s)
d. $Li_3PO_4(s)$.

11.5. Relationship between solubility(s) and solubility product (Ksp)

Activity 11.5

1. Explain the meaning of the term solubility equilibrium.
2. What is meant by the term solubility product?

Solubility equilibrium refers to kind of equilibrium that exists in saturated solutions of sparingly soluble ionic salts.Solubility is normally expressed in $moldm^{-3}$ or (gdm^{-3}).

The term solubility product refers to the numerical value of the equilibrium constant for the equation that represents the substance dissolved in water.

Determination of the solubility product from solubility

The solubility can be denoted by using '**s**' and solubility product is expressed by Ksp

The the term solubility product constant suggests that Ksp is related to the solubility

of ionic solute . However ,this does not mean that Ksp and molar solubility ,molarity of solute in a saturated solution are equivalent .It means that one can determine Ksp,from molar solubility from Ksp.

Consider the following reaction:

$A_mB_n\,(s) \rightleftharpoons mA^{n+}\,(aq) + nB^{m-}(aq)$

The expression of solubility of product constant is given by

$Ksp = [A^{n+}]^m[B^{m-}]^n = (ms)^m + (ns)^n$

$= m^m x n^n x S^{m+n}$

$$s = \sqrt[m+n]{\frac{Ksp}{m^m . n^n}}$$

Checking up 11.5

A saturated solution of a sparingly soluble salt has the following equilibrium:

$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$

a. Write the solubility product expression Ksp for this system.

b. Using 's' as solubility of the salt in moles per liter calculate Ksp for this system.

11.6. Calculations involving solubility product

In solubility equilibria calculations, it is usually expressed as grams of solute per liter of solution.

Since Ksp is expressed in molar concentrations, solubility expressed in grams per litre must be converted into molar solubility.

Activity 11.6

Write solubility product expressions,Ksp for each of the following solubility equilibria:

a. $PbSO_4\,(s) \rightleftharpoons Pb^{2+}\,(aq) + SO_4^{2-}\,(aq)$

b. $PbI_2\,(s) \rightleftharpoons Pb^{2+}\,(aq) + 2I^-\,(aq)$

Molar solubility, solubility and solubility product all refer to a saturated solution.

Worked examples:

1. The solubility of calcium carbonate $CaCO_3$, at 298K is 6.9×10^{-3} $moldm^{-3}$. Calculate the solubility product at this temperature.

Solution

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

Key point

Every mole of calcium carbonate which dissolves gives 1 mole of calcium ions and 1 mole of carbonate ions; in solution; so 6.9×10^{-3} moles of calcium carbonate dissolves in $1dm^3$of solution, then there will be 6.9×10^{-3} moles of calcium carbonate ions and 6.9×10^{-3} moles of CO_3^{2-} ions in dm^3 of the solution.

$[Ca^{2+}]=6.9\times10^{-3}\,moldm^{-3}$

$[CO_3^{2-}]=6.9\times10^{-3}\,moldm^{-3}$

$Ksp=[Ca^{2+}][CO_3^{2-}]$

$=(6.9\times10^{-3}\,moldm^{-}3)^2$

$=4.8\times10^{-9}mol^2dm^{-6}$

2. The solubility of calcium sulphate $CaSO_4$ at 298K is $0.67g/dm^3$. Calculate the solubility product at this temperature. (O=16, S=32, Ca=40)

solution

$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq)+ SO_4^{2-}(aq)$

Key point: number of moles=mass(g)/molar mass($gmol^{-1}$)

The concentration is given in g/dm^3; Convert it to mol/dm^3

1 mole of $CaSO_4$ weighs:40+32+(16×4)=136g

0.67 corresponds to $0.67/136=4.93\times10^{-3}$ mol/dm^3

The solubility of calcium sulphate is 4.93×10^{-3} mol/dm^3

Each mole of calcium sulphate that dissolves produce 1 mole of Ca^{2+} ions and 1 mole of SO_4^{2-} ions in solution.

$[Ca^{2+}]=4.93\times10^{-3}$ mol/dm^3

$[SO_4^{2-}]=4.93\times10^{-3}$ mol/dm^3

$$K_{sp}=[Ca^{2=}][SO_4^{2-}]$$
$$K_{sp}=(4.93\times10^{-3})^2$$
$$=2.4\times10^{-5}mol^2dm^{-6}$$

3. The solubility of lead II chloride, $PbCl_2$ is 0.016moldm^3 at 298k. Calculate the solubility product at this temperature.

Solution

$PbCl_2(S) \rightleftharpoons Pb^{2+}(aq)+ 2Cl^-(aq)$

Key point

The ratio of the ions in the compound is 1:2; each mole of lead(II) chloride produces 1 mole of lead II, and $[Pb^{2+}]=0.016$ moldm^{-3}. However, each mole of lead (II) chloride produces 2 moles of chloride ions in solution. If 0.016 mol of lead (II)chloride dissolves, there will be twice this amount of chloride ions present.

Then, $[Cl^-]=0.016\times2=0.032$ mol/dm^3

$Ksp=[Pb^{2+}][Cl^-]^2=0.016\times(0.032)^2$

$=1.6\times10^{-5}mol^3dm^{-9}$

4. The solubility of calcium phosphate, $Ca_3(PO_4)_2$ is 7.7×10^{-4}g/dm^3 at 250c. Calculate the solubility product at this temperature. (O =16, P =31,Ca=40)

Solution

$Ca_3(PO_4)_2(s) \rightleftharpoons 3\ Ca^{2+}(aq)+ 2PO_4^{3-}(aq)$

Key point

Convert the concentration in g/dm^3 to mol/dm^3

Number of moles= mass(g)/ molar mass(g)

1 mole of $Ca_3(PO_4)_2$ weighs 310g.

Concentration in moldm^{-3}=$7.7\times10^{-4}/310=2.48\times10^{-6}$mol/dm^3

Each mole of calcium phosphate that dissolves produces 3 moles of calcium ions in solution and 2 moles of phosphate ions.

$[Ca^{2+}]= 3\times2.48\times10^{-6}= 7.44\times10^{-6}mol/dm^3$

$[PO_4^{3-}]=2\times2.48\times10^{-6}= 4.96\times10^{-6}\ mol/dm^3$

$Ksp=[Ca^{2+}]^3\ [PO_4^{3-}]^2$

$=(7.44\times10^{-6})^3\times(4.96\times10^{-6})^2= 1.0\times10^{-26}mol\ dm^{-15}$

Calculating solubility from solubility product

Examples

1. Calculate the solubility in mol/dm^3 of silver chloride, AgCl, at 298K if its solubility product is $1.8\times10^{-10}\ mol^2\ dm^{-6}$

   Solution

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

Key points

For every mole of silver chloride that dissolves, the solution will contain 1 mole of $Ag^+(aq)$ and 1 mole of $Cl^-(aq)$ so if "s" moles dissolved, the solution will contain "s" moles of each ion.

$[Ag+]=$ **S** $mol\ dm^{-3}$

$[Cl^-]=$ **S** $mol\ dm^3$

$Ksp= [Ag^+][Cl^-]$

$1.8\times10^{-10}=s\ x\ s$

$S=\sqrt{1.8\ x\ 10^{-10}}$

$S =1.3\times10^{-3} mol/dm^3$

2. Calculate the molar solubility of $PbSO_4$ (lead II sulphate), given its solubility product equal to 1.6×10^{-8}.

Solution

$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq)+ SO_4^{2-}(aq)$

Key point

One mole of lead II sulphate dissolves to produce 1 mole of a Pb^{2+} and 1 mole of SO_4^{2-} ions in solution.

$[Pb^{2+}]=s moldm^{-3}$

$[SO_4^{2-}]=s moldm^{-3}$

Where "s"= $moldm^{-3}$ $PbSO_4$ that dissolved (the molar solubility)

$Ksp=[Pb^{2+}][SO_4^{2-}]=1.6\times10^{-8}$

$(s)(s)= 1.6\times10^{-8}$

$s = \sqrt{1.6\ x\ 10^{-8}} = 1.26\ x\ 10^{-4}$

Molar solubility= $1.26\times10^{-4}M$

3. Calculate the solubility in mol/dm^3 of silverI sulphide, Ag_2S at 298K if its solubility product is 6.3×10^{-51} mol^3dm^{-9}

Solution

$Ag_2S(s) \rightleftharpoons 2Ag^+(aq)+S^{2-}(aq)$

Key point

For every one mole of silver I sulphide that dissolves, the solution will contain 2 moles of Ag^+ and 1 mole of S^{2-}ions. We will call the solubility of silver I sulphide "s" $moldm^{-3}$.

$[Ag^+]=2s moldm^{-3}$

$[S^{2-}]=s moldm^{-3}$

$Ksp=[Ag^+]^2[S^{2-}]$

6.3×10^{-51} $mol^3dm^{-9}=(2s)^2\times s$

$4s^3=6.3\times10^{-51}$ mol^3dm^{-9}

$$S = \sqrt[3]{\frac{6.3\ x\ 10^{-51}}{4}}$$

$S=1.2\times10^{-17}mol\ dm^{-3}$

4. Calculate the solubility in g dm^{-3} of chromium III hydroxide, $Cr(OH)_3$ at 25^0C if its solubility product is $1.0\times10^{-33}mol^4\ dm^{-12}$(H=1, O=16,Cr=52)

Solution

$Cr(OH)_3(s) \leftrightarrow Cr^{3+}(aq) + 3OH^-(aq)$

Key points

Work out the solubility in $moldm^{-3}$

Number of moles=mass(g)/ molar mass(g)

1mole of $Cr(OH)_2$ produces 1 mole of $Cr^{3+}_{(aq)}$ and 3 moles of OH^- ions

$[Cr^{3+}]$= S $moldm^{-3}$

$[OH^-]$=3S $moldm^{-3}$

$Ksp=[Cr^{3+}][OH^-]^3$

$1.0\times10^{-33}=S\times(3S)^3$

$$S = \sqrt[4]{\frac{1.0\ x\ 10^{-3}}{27}}$$

$27S^4= 1.0\times10^{-33}$

$S=2.47\times10^{-9} moldm^{-3}$

Convert this solubility into gdm^{-3}. 1 mole of $Cr(OH)_3$ weighs 103 g. 2.47×10^{-9}moles will weigh $2.47\times10^{-9}\times103$ $g/dm^3=2.5\times10^{-7} g/dm^3$

Checking Up 11.6

1. Calculate the molar solubility of $Sr_3(AsO_4)_2$ given its solubility product equal 4.29×10^{-19}
2. Given that the molar solubility of Ag_2CO_3 is equal to 1.27×10^{-4}M. Calculate its solubility product.
3. The Ksp of $Mg(OH)_2$ is 1.8×10^{-11}
   a. Calculate the solubility of $Mg(OH)_2$ in pure water.
   b. Calculate the molar solubility of $Mg(OH)_2$ in a solution of $_pH$ of 11.22.

11.7. Definition and calculation of ionic product (QC)

Activity 11.7

a. Explain the meaning of the term ionic product.

b. State the difference between ion product and solubility product.

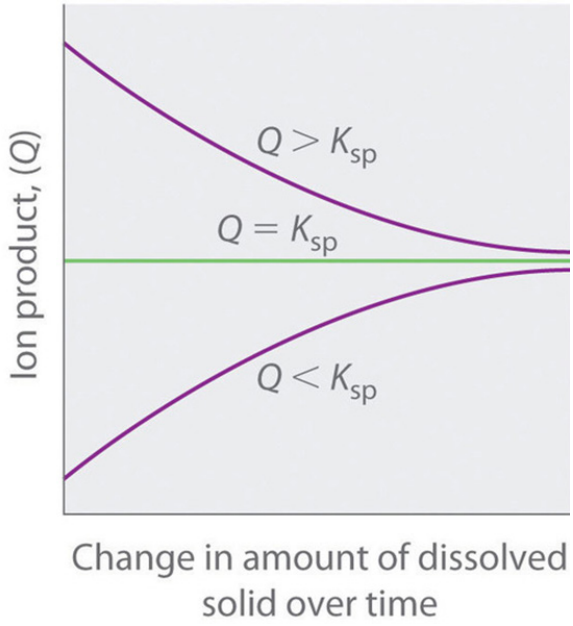
The ionic product (Q) of salt is the product of the concentrations of the ions in solution raised to the same power as in solubility product expression. Whereas the solubility product Ksp describes the equilibrium concentrations, the ion product describes concentrations that are not necessarily equilibrium concentrations. Ksp is applicable to saturated solutions only, whereas ion product is applicable to all types of solutions of any concentration.

The ion product tells chemist whether a precipitate will form when solutions of two soluble salts are mixed.

i. Q>Ksp, the solution is supersaturated and the ionic solid will precipitate

ii. Q<Ksp, the solution is unsaturated and more of the ionic solid, if available will dissolve. No precipitate occurs

iii. Q=Ksp, the solution is saturated, at equilibrium. Precipitate will not form, the rate of dissolution is equal to the rate of precipitation, no net change in the amount of dissolved solid will occur.



The process of calculating the value of the ion product and comparing it with the magnitude of solubility determining whether a solution is unsaturated saturated or supersaturated.

Strategy

i. Write the balanced equilibrium equation for precipitation reaction and the expression for Ksp.

ii. Determine the concentrations of all ions in solution when the solutions are mixed and use them to calculate the ion product(Q)

iii. Compare the values of Q and Ksp to decide whether a precipitate will form.

Worked examples

1. Will a precipitate of lead II chloride be formed if 10 cm^3 of 0.10 mol dm^{-3} lead II nitrate solution, $Pb(NO_3)_2$ is mixed with 10 cm^3 of 0.20 mol dm^{-3} hydrochloric acid, HCl? Ksp ($PbCl_2$) =1.6×10^{-5} mol^3dm^{-9} at 298K.

Solution

$Ksp = [Pb^{2+}] [Cl^-]^2 = 1.6\times10^{-5}\ mol^3/dm^{-9}$

When the solutions are mixed, all the ion concentrations will decrease. In this case each solution is being diluted from10cm^3 to a total volume of 20cm^3; so, each is diluted by a factor of 2.

Before the reaction takes place; the ion concentrations are;

$[Pb^{2+}] = 0.050\ mol/dm^3$

$[Cl^-] = 0.10\ mol/dm^3$

Multiplying the ion concentration together we get; $[Pb^{2+}] [Cl^-]^2 = 0.050 \times (0.10)^2$

$Q = 5.0\times10^{-4}\ mol^3/dm^{-9}$

This answer is bigger than that solubility product. Because Q>Ksp we predict that $PbCl_2$ will precipitate when the two solutions are mixed $PbCl_2$ will continue to precipitate until the system reaches equilibrium; which occurs when;

$[Pb^{2+}] [Cl^-]^2 = Ksp = 1.6\times10^{-5}$

2. Will a precipitate of calcium hydroxide; $Ca(OH)_2$ form if 5.0cm^3 of 0.05moldm^{-3} sodium hydroxide solution; NaOH, is added to 5.0cm^3 of 0.05moldm^{-3} calcium chloride solution. $CaCl_2$? Ksp($Ca(OH)_2$) = $5.5 \times 10^{-6}\ mol^3\ dm^{-9}$ at 298K

Solution

$Ksp = [Ca^{2+}] [OH^-]^2 = 5.5\times10^{-6}\ mol^3\ dm^{-9}$

Mixing; dilutes the solutions by a factor of 2 ion concentration before reaction takes place is

$[Ca^{2+}] = 0.025\ mol\ dm^{-3}$

$[OH^-] = 0.025\ mol\ dm^{-3}$

Multiplying ion concentrations together we get

$[Ca^{2+}] [OH^-]^2 = 0.025 \times (0.025)^2$

$Q=1.6\times10^{-5}\ mol^3\ dm^{-9}$

Q>Ksp calcium hydroxide will precipitate when the two solutions are mixed until the ion concentrations are sufficiently reduced ;(i.e. until the system reaches equilibrium)

3. Will a precipitate of calcium hydroxide form if 5.0 cm^3 of ammonia solution containing OH^- ions with concentration of $2.0 \times 10^{-3}\ mol/dm^3$ is added to 5.0 cm^3 0f 0.05 mol dm^3 is added to 5.0 cm^3 of 0.05 mol dm^{-3} calcium chloride solution. $CaCl_2$? Ksp $(Ca(OH)_2) = 5.5\times10^{-6}$ mol3dm^{-9} at 298K.

Solution

$Ksp= [Ca^{2+}] [OH^-]^2=5.5\times10^{-6}$
Ion concentration before reaction is
$[Ca^{2+}] = 0.025 moldm^{-3}$
$[OH^-] = 1.0\times10^{-3} moldm^{-3}$
Multiplying ion concentration together gives $0.025 \times (1.0\times10^{-3})^2$
$Q = 2.5\times10^{-5}\ mol^3dm^{-9}$
Q>Ksp this means that $Ca(OH)_2$ wiii precipitate when the two solutions are mixed.

11.8. Predicting precipitation reactions using the ionic product and Ksp

Activity 11.8.

We can predict the precipitation of the salt if we have its solubility at a given temperature.

a) What do you understand with solubility?

b) How do we call the solution which

(i) Cannot dissolve any more amount of a solute?

(ii) Contains more solute than it can dissolve?

c) Which of the above solution the precipitate has already formed?

The ion product ($\mathbf{Q_{sp}}$) can be used to determine in which direction a system must shift in order to reach equilibrium. From these calculations we can ***determine whether a precipitate will form*** in a given solution. We compare ***Qsp*** with ***Ksp.***

There are **three possible situations:**

► ***Case 1*, $\mathbf{Q_{sp} = K_{sp}}$:**

Solid and solution **are in equilibrium**; *neither forward nor reverse process is favored*.

The solution is ***just saturated or at equilibrium.***

► ***Case 2*, $\mathbf{Q_{sp} > K_{sp}}$:**

Reverse process is favored; **precipitation occurs** to form more solid.

This means that ***there are too many ions in the solution.*** In order to return to equilibrium, the excess ions will precipitate to form more solid.

► ***Case 3*, $\mathbf{Q_{sp} < K_{sp}}$:**

Forward process is favored; **no precipitation occurs**; if solid is present, more solid can dissolve.

This means ***there are not enough ions in the solution.*** In order to return to equilibrium, more of the solid salt must dissociate into its ions.

Note: The ion product $\mathbf{Q_{sp}}$ can also be written as $\mathbf{Q_{ip}}$.

Working Example

If 0.100 L of 0.0015 M $MgCl_2$ and 0.200 L of 0.025 M NaF are mixed, should a precipitate of MgF_2 form? If yes, determine the mass of the precipitate.

Answer:

Let us assume that the final volume of the mixture is 0.100L + 0.200L=0.300L.

Step 1: *Initial concentrations of ions:* First we need to determine $[Mg^{2+}]$ and [F-] as they initially exist in this mixed solution.

$$\left[Mg^{2+}\right] = \frac{(n_{Mg^{2+}})_{initial}}{V_{total}} = \frac{0.100L \times 0.0015mol.L^{-1}}{0.300L} = 5.0 \times 10^{-4} M$$

$$\left[F^{-}\right] = \frac{(n_{F^{-}})_{initial}}{V_{total}} = \frac{0.200L \times 0.0025mol.L^{-1}}{0.300L} = 1.7 \times 10^{-2} M$$

Step 2: *Evaluation of Q_{ip}*

$$Q_{ip} = \left[Mg^{2+}\right]\left[F^{-}\right]^2 = \left(5.0 \times 10^{-4}\right)(1.70 \times 10^{-2})^2 = 1.4 \times 10^{-7}$$

Step 3: *Comparison of Q_{ip} and Ksp*

$Q_{ip} = 1.4 \times 10^{-7}$ and Ksp=3.7×10^{-8} .Because $Q_{ip} > Ksp$, we conclude that precipitation should occurs.

Due to the fact that Mg^{2+} ions exist in are in little quantity, so Mg^{2+} will be totally precipitated in form of MgF_2.

$$\text{Number of moles of } Mg^{2+} = M \times V = (0.0015mol.L^{-1}) \times 0.100L = 1.5 \times 10^{-4} mol$$

$$\text{Masse of the precipitate of } MgF_2 = n \times Mw = 1.5 \times 10^{-4} mol \times 62g / mol = 9.30mg \text{ of } MgF_2$$

Checking up 11.8

Ammonia is a weak base which reacts with water to produce hydroxide ions. A 1.0 $moldm^{-3}$ solution of ammonia has $[OH^-] = 4.2 \times 10^{-3}$ mol dm^{-3}. Ammonia solution was added to 10 cm^3 0.10 mol dm^{-3} solution of magnesium nitrate, calcium nitrate, strontium nitrate and barium nitrate. (All the nitrates have the formula $X(NO_3)_2$. The experiments were then repeated with 10 cm^3 samples of a 1.0 mol dm^{-3} solution of sodium hydroxide, where $[OH^-]$ = 1.0 mol dm^{-3}. In which cases will a precipitate be formed?

Solubility products (in mol^3dm^{-9});

$Mg(OH)_2 = 1.1 \times 10^{-11}$

$Ca(OH)_2 = 5.5 \times 10^{-6}$

$Sr(OH)_2 = 3.2\times10^{-4}$

$Ba(OH)_2 = 5.0\times10^{-3}$

11.9. Separation of ions by fractional precipitation

Suppose you are given an aqueous solutions containing two ions: Ag^+ and K^+. How can you proceed to separate the two cations. Ions can be separated from each other basing on the solubility of their salts in water. This is done by using a reagent that forms a precipitate with one or a few of the ions in solution (fractional precipitation).

Examples

1. A solution containing both Ag^+ and Cu^{2+}

   If hydrochloric acid solution is added to this solution, AgCl ($Ksp=1.8\times10^{-10}$) precipitates, while Cu^{2+} remains in solution because $CuCl_2$ is soluble. The reagent HCl forms a precipitate with Ag^+.

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

2. Fractional precipitation of a carbonate (CO_3^{-2}) and a Chloride (Cl^-).

   A solution suspected to contain chloride and a carbonate is mixed with a solution of Silver nitrate

   A solution of Silver nitrate precipitates out both the Carbonate and a Chloride forming Silver carbonate and Silver Chloride respectively.

   We can distinguish both the carbonate and a chloride by using concentrated nitric acid.

Observations:
Carbonate reacts to give carbon dioxide gas. There is no observable change with a Chloride.

A solution contains $1.0\ x10^{-2}$ M Ag^+ and $2.0\ x10^{-2}$ M Pb^{2+}

When Cl^- ion is added to the solution, both AgCl ($Ksp = 1.8x10^{-10}$) and $PbCl_2$ ($Ksp = 1.7x10^{-3}$) precipitate from the solution. What concentration of Cl^- ions is necessary to begin the precipitation of each salt, and which salt precipitates first?

Solution

The salt requiring the lower concentration of Cl^- ions will precipitate out first. For AgCl we have: Ksp $[Ag^+][Cl^-] = 1.8 \times 10^{-10}$ Because $[Ag^+] = 1.0 \times 10^{-10}$ M, the greatest concentration of Cl- ions that can be present without causing precipitation of AgCl can be calculated from the Ksp expression

Ksp $= [1.0 \times 10^{-2}][Cl^-] = 1.8 \times 10^{-10}$.

$[Cl^-] = \frac{1.8 \times 10^{-10}}{1.0 \times 10^{-2}} = 1.8 \times 10^{-8} M$. Any small Cl^- concentration in excess to this will cause AgCl to precipitate from solution.

For $PbCl_2$ Ksp $= [Pb^{2+}][Cl^-]^2 = 1.7 \times 10^{-5}$

$[Cl^-]^2 = [Cl^-]^2 = \frac{1.7 \times 10^{-5}}{2.0 \times 10^{-2}} = 8.5 \times 10^{-4} M$ $[Cl^-] = \sqrt{8.5x10^{-4}} = 2.9 \times 10^{-2}$ M.

Thus, the concentration of Cl^- ions in excess of 2.9×10^{-2} will cause $PbCl_2$ to precipitate.

Checking up 11.9

1. State one importance of fractional precipitation.
2. Write ionic equations to show precipitation of silver shloride and silver carbonate when a solution of silver nitrate is added to their saturated solution.

11.10. Common ion effect and solubility

Activity 11.10

Give example of pairs of ionic salts with common ions.

It is known that the solubility of a sparingly soluble ionic substance is obviously decreased in a solution of another ionic compound when the two substances have an ion in common. This can be explained by Lechatelier's principle. Common ion effect is the decrease of solubility of a sparingly soluble salt caused by the presence of a common ion.

For example, molar solubility of $BaSO_4$ in pure water is 1.1×10^5M; but if $BaSO_4$ is dissolved in an aquous solution arleady containing SO_4^{2-} or Ba^{2+} ion, its solubility will be lower than 1.1×10^{-5}M

Consider the following example: $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

If sulphuric acid (H_2SO_4) is added to the solution of $BaSO_4$, the concentration of SO_4^{2-} ions increased and shifts equilibrium to the left side of the reaction. As a result, barium gets precipitated as $BaSO_4(s)$. H_2SO_4 is a strong acid and it dissociates completely as indicated in the equation:

$$H_2SO_4(aq) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$$

The sulphate ion (SO_4^{2-}) is the common ion among these two reactions thus when its concentration increases due to dissociation of sulphuric acid it shifts equilibrium to the left side of the reaction resulting in the precipitation of barium as $BaSO_4(s)$.

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

This phenomenon of "Common Ion Effect" is widely used for the complete precipitation of soluble or sparingly soluble salts.

The solubility product expression tells us that the equilibrium concentration of the cation and the anion are inversely related. When the concentration of the anion increases; the maximum concentration of cation needed for the precipitation to occur decreases; and vice versa, because why Ksp is constant. Consequently, the solubility of an ionic compound depends on the concentration of the other salt that contain the same ions as the given salt.

Calculations on the common ion effect

1. Calculate the solubility of calcium sulphate in $moldm^{-3}$ in
   a. Water
   b. Dilute sulphuric acid of concentration 0.50 $moldm^{-3}$
   Ksp =2.4×10^{-5} mol^2dm^{-6}

Solution

a. If the solubility of calcium sulphate is "S" $moldm^{-3}$

$[Ca^{2+}]$ = s$moldm^{-3}$and $[SO_4^{2-}]$ = S$moldm^{-3}$
Ksp = $[Ca^{2+}][SO_4^{2-}]$t
2.4×10^{-5}=S x S
$S=\sqrt{2.4X10^{-5}}$

S =$4.9 \times 10^{-3}moldm^{-3}$

b. We can represent the solubility of calcium sulphate "S" $moldm^{-3}$ but a part of SO_4^{2-} ions concentration is coming from sulphuric acid and a part from calcium sulphate.

$[Ca^{2+}]$ =S $moldm^{-3}$
H_2SO_4 has a SO_4^{2-} ion concentration of 0.50$moldm^{-3}$; In addition, the dissolved calcium sulphate is supplying an extra "S" $moldm^{-3}$ so $[SO_4^{-2}]$ = (0.50 + S) $moldm^{-3}$ The value

of S will be very small compared to 0.50moldm^{-3} and so we make an approximation that (0.50 +S)≈0.50.so this gives us:

$[SO_4^{2-}] = 0.50 moldm^{-3}$

$Ksp = [Ca^{2+}][SO_4^{2-}]$

$2.4 \times 10^{-5} = S \times 0.50$

$S = \frac{2.4X10-5}{0.50} = 4.8 \times 10^{-5}$ moldm^{-3}

Solubility of $CaSO_4$ decreases in the presence of sulphuric acid.

Key point

If you have a saturated solution of a sparingly soluble substance A, and you mix it with a solution of a substance B which contain an ion in common with A, you can assume that the concentration of the common ions is the same as its concentration in B.

2. The Ksp of $PbSO_4$ is $1.6x10^{-8}$

a. Calculate the solubility of $PbSO_4$ in a 0.25M solution of $Pb(NO_3)_2$

b. Compare solubility of $PbSO_4$ in pure water and in a 0.25M solution of $Pb(NO_3)_2$

Solution

a.

	$PbSO_4(s) \rightleftharpoons Pb_2+(aq) + SO_4^{2-}(aq)$		
Initial	-	0	0.25M
Change	-	+X	+X
Equilibrium	-	X	0.25M+ X

$[SO_4^{2-}]$ =0.25M+ X≈ 0.25M , Assuming that x is very small so it is negligible.

(0.25M)(x) =$1.6x10^{-8}$

$x = \frac{1.6x10-8}{0.25} = 6.4x10^{-8}M$

Molar solubility =$6.4x10^{-8}$ M

b. The solubility of lead sulphate in pure water is higher compared to the solubility of it in presence of a common ion from lead nitrate; this illustrates the common ion effect.

Checking up 11.10

The Ksp of $Ca(OH)_2$ is $5.5x10^{-6}$

a. Calculate the solubility of $Ca(OH)_2$ in pure water.

b. Calculate the solubility of $Ca(OH)_2$ in 0.77M solution of $Ba(OH)_2$

11.11. The pH and solubility

Activity11.11

1. Explain the meaning of the term pH
2. Explain how pH affects the solubility of a solute.

The term pH refers to the concentration of $[H^+]$ ions in solution.

The pH can be found if the $[H^+]$ ions in a solution is known.

Changes in pH

Some sparingly soluble salts produce ions such as, PO_4^{3-}, $C_2O_4^{2-}$, OH^-, CO_3^{2-} which behave like bases; these can combine with hydrogen ions to form weak and poorly dissociated acid molecules.

Example

$$CO_3^{2-}(aq) + 2H^+(aq) \rightleftharpoons H_2CO_3(aq)$$

$$H_2CO_3(aq) \rightleftharpoons 2H^+(aq) + CO_3^{2-}(aq)$$

This reduces the concentration of H^+ ions in the solution and for such salts their solubility will always increase with a decrease of PH or addition of a dilute acid to the solution, the excess H^+ ions will combine with the base-like ions thereby reducing their concentration and allowing the dissolution of more salt.

Checking up 11.11

1. The solubility product of silver oxalate $Ag_2C_2O_4$ is given by the expression, Ksp $= [Ag^+]^2 [C_2O_4^{2-}]$. Explain how the solubility of silver oxalate would be affected if a few drops of the following solutions are added.
   a. Concentrated ammonia solution
   b. Sodium oxalate
2. Strontium hydroxide is sparingly soluble in water.
   a. Write the equation for the solubility of strontium hydroxide in water.
   b. Write an expression for the solubility product (Ksp) of strontium hydroxide.
   c. Sodium hydroxide was added to a saturated solution of strontium hydroxide.
      i. State what happened to the solubility of strontium hydroxide in water.
      ii. Explain your answer in (i) above.

11.12. Complex ion formation and solubility

1. What do you understand with complex-ion?
2. In Chemistry qualitative tests, precipitation reactions are often used. Some precipitate may disappear when excess of reagent is used or by adding another different reagent. Describe what happens when a precipitate dissolves when different solvent is used (for example changing water solvent to ammonia solvent).

The **solubility is increased due complexation** between Ag^+ and NH_3 in which is a ligand. Therefore *silver bromate dissolves in ammonia*. This is very important in cation identification and in precipitate dissolution.

Note: This effect explains why some transition metals that can lead to complex formation can dissolve in excess NaOH and/or even not in ammonia. A part from that, we can add Pb^{2+}, Al^{3+},Zn^{2+}, Ag^+, Sn^{4+}, Sn^{2+}.

Briefly, the solubility of a slightly soluble ionic compound is increased when a second solute that furnishes a ligand species is added to the solution. So, this process is known as Complex-ion effect to the solubility which increases solubility.

Working Example

Calculate the solubility of $AgBrO_3$ in 0.5 M NH_3 (ammonia). Conclude. Ksp($AgBrO_3$) = 5.8×10^{-5} and K_f ($Ag(NH_3)_2^+$ = 2.07×10^7.

Solution:

Let us write possible chemical reaction:

$$(1)\quad AgBrO_3(s) \rightleftharpoons Ag^+_{(aq)} + BrO_3^-{}_{(aq)} \quad Ksp=5.8*10^{-5}$$

$$(2)\quad Ag^+(aq) + 2\ NH_{3(aq)} \rightleftharpoons Ag(NH_3)_2^+ \quad K_f=2.07*10^7$$

$$(3):Net:\ AgBrO_3(s) + 2\ NH_{3(aq)} \rightleftharpoons Ag(NH_3)_2^+ + BrO_3^-{}_{(aq)} \quad Kc=?$$

First, notice that the dissolution reaction is a net reaction. The equilibrium Kc for this reaction is the product of $\mathbf{K_f}$ (which is specific to the complex formation, Silver diamino ion) and **Ksp** for $AgBrO_{3(S)}$

$$Kc = \frac{[Ag(NH_3)_2^+][BrO_3]}{[NH_3]^2} = \frac{[Ag(NH_3)_2^+]}{[NH_3]^2} \times \frac{[Ag^+][BrO_3]}{[Ag^+]} = \frac{[Ag(NH_3)_2^+]}{[NH_3]^2[Ag^+]} \times [Ag^+][BrO_3] = K_f \times Ksp$$

$Kc = 2.05 \times 10^7 \times 5.85 \times 10^{-5} = 1199.3 >> 1$, so this reaction is fast and complete that is the dissolution of $AgBrO_3$ *wll* favor the forward reaction leading to the significant dissolution of $AgBrO_3$ and all most the silver ion exist in solution as $[Ag(NH_3)_2]^+$ instead of free ion Ag^+.

Let us summarize the information in the following table:

Concentration in **M**	$AgBrO_{3(S)} + 2NH_{3(aq)} \rightleftharpoons$ false	$Ag(NH_3)_2^+{}_{(aq)}$	+	$BrO_3^-{}_{(aq)}$
Initial	-	0.5	0	0
Changes	-	-2S	S	S
Equilibrium	-	0.5-2S	S	S

$$Kc = \frac{[Ag(NH_3)_2^+][BrO_3^-]}{[NH_3]^2} = \frac{S.S}{(0.5-2S)^2} = \left(\frac{S}{0.5-2S}\right)^2$$

$$\left(\frac{S}{0.5-2S}\right)^2 = 1199.3 \leftrightarrow \frac{S}{0.5-2S} = \pm\sqrt{1199.3}$$

Solving with respect to S, we get S=0.246M

$Thus, S = [Ag(NH_3)_2^+] = [BrO_3^-] = 0.246M$

Please, remark that free Ag^+ is too low and is equal to 2.378×10^{-4}M; $[NH_3] = 0.5 - 2 \times 0.246 = 8.0 \times 10^{-3} M$

Please remark that free $[Ag^+]$ is too low and is equal to **2.378×10^{-4} M** (from Ksp/ $[BrO_3^-]$**;** $[NH_3] = 0.5 - 2 \times 0.246 =$ **8.0×10^{-3} M**

If a sparingly soluble solid is placed in contact with a ligand that can bind to the metal ion more strongly than anion of the salt then formation of a complex ion will be favored and the solubility of the solid will be greater.

Checking up 11.12

1. State and explain the complex-ion effect to the solubility.
2. Using the data below, show how silver chloride, AgCl, is more soluble in ammonia solution than it does in water because silver ions form complex ions with NH_3.

$AgCl_{(s)} \rightleftarrows Ag^+_{(aq)} + Cl^-_{(aq)}$; $K_{sp} = 1.6 \times 10^{-10}$;

$Ag^+_{(aq)} + 2NH_{3(aq)} \rightleftarrows Ag(NH_3)2^+_{(aq)}$; $K_f = 1.7 \times 10^7$;

11.13. Applications of solubility product

Activity 11.13

According to your experience or by doing research, give example of application of the solubility product.

Some areas where solubility product is used:

a. Volumetric analysis:

The concentration of Chloride ions in a solution of soluble Chloride salt can be determined by titration with a standard solution of silver nitrate Potassium chromate is used as an indicator. A white precipitate of silver Chloride forms first due to lower solubility of silver Chloride , the end point is indicated by the formation of a red precipitate of silver chromate This can be seen from the solubility product (Ksp) value of silver chloride and silver chromate. Ksp (Ag = 1.2 x10 $^{-10}$ mol^{2}dm^{-6} Ksp (Ag_2CrO_4) = 2.4x10^{-12} mol^{2}dm^{-9} . Low concertation of Ag^+ ions are needed to form a precipitate with chloride ions than chromate ions .

b. Production of soap: saponification.

Brine concentrated solution of sodium chloride (NaCl) is added to the mixture of fats and oils together with NaOH solution to precipitate out soap. Soap and sodium chloride are present in the form of ions.

Soap equilibrium: $C_{17}H_{35}COO^-Na^+(s) \rightleftharpoons C_{17}H_{35}COO^-(aq) + Na^+(aq)$

When brine is introduced to the soap mixture, it introduces a common ion effect which effects the equilibrium system in the backward direction. This is due to high concentration of sodium ions (Na^+) from sodium chloride. As a result, the stearate ion ($C_{17}H_{35}COO^-$) combines with the excess sodium ions to form soap which floats on top. The presence of a high amount of a common ion, Na^+, from the brine (Nacl (aq), causes the precipitation of the soap (salt), $C_{17}H_{35}COO^-Na^+$

Checking up11.13

The solubility product of Bi_2S_3 is listed as an unimaginably small number, 1x10$^{-97.}$

1. Calculate the solubility of Bi_2S_3 in pure water.
2. Suppose you tried to dissolve some Bi_2S_3 in a solution of 0.50M Na_2S how many grams of Bi_2S_3 would theoretically dissolve in one litre of this solution?

END UNIT ASSESSMENT

1. Consider two compounds A and B where A has a solubility product of 3.3×10^{-3} while B has a solubility product of 4.4×10^{-7}.Can we conclude that compound has ahigher Molar solubility than B. Explain your answer?
2. Write the solubility product expressions for the following solubility equilibria.

   a. $Hg_2Cl_2 \rightleftharpoons Hg_2^{2+} + 2\ Cl^-$

   b. $Sr_3(AsO_4)_2 \rightleftharpoons 3Sr^{2+} + 2\ AsO_4^{3-}$
3. Consider a compound with the formula L_3X_4 that dissolve to produce $L^{4+}$and X^{3-}ions in solution if the solubility product of this compound is 8.2×10^{-24}. Calculate the molar solubility of the compound.
4. Explain what is meant by the term common ion effect and how is it accounted for by applying Lechatelier's principle.
5. Calculate the molar solubility of $Ba(IO_3)_2$ given that its Ksp is equal to 1.5×10^{-9}.
6. Barium sulphate is sparingly soluble in water.

   a. Write an equation for the solubility of barium sulphate in water.

   b. Write an equation for the solubility product of barium sulphate.

   c. A saturated solution of barium sulphate contains 0.002563g per litre of solution. Calculate the solubility product of barium sulphate.

   d. Calculate the solubility of $BaSO_4$ in $1dm^3$ of 0.1M $BaCl_2$ solution.
5. Will a precipitate form if 25.0 mL of 1.4×10^{-9} M NaI and 35.0 mL of 7.9×10^{-7} M $AgNO_3$ are mixed? (K_{sp} for AgI at 25°C is 8.5×10^{-17})
6. The concentration of Ca^{2+} in blood is 0.0035 M. If an oxalate solution with oxalate ion concentration 1×10^{-6} M is added to it.

   a. Predict whether precipitation occurs or not.

   b. The said precipitate in **(a)** above is an example of a "***kidney stone***". Use your knowledge in Chemical Equilibrium and Solubility of sparingly soluble compounds to explain the effect of the pH on these kidney stones. (Solubility product of calcium oxalate = 2.300×10^{-9})

UNIT 12
ELECTROCHEMICAL CELL AND APPLICA TIONS

UNIT 12. ELECTROCHEMICAL CELL AND APPLICATIONS

Key Unit Competency:

To be able to explain the working and industrial applications of electrochemical and electrolytic cells

Learning objectives

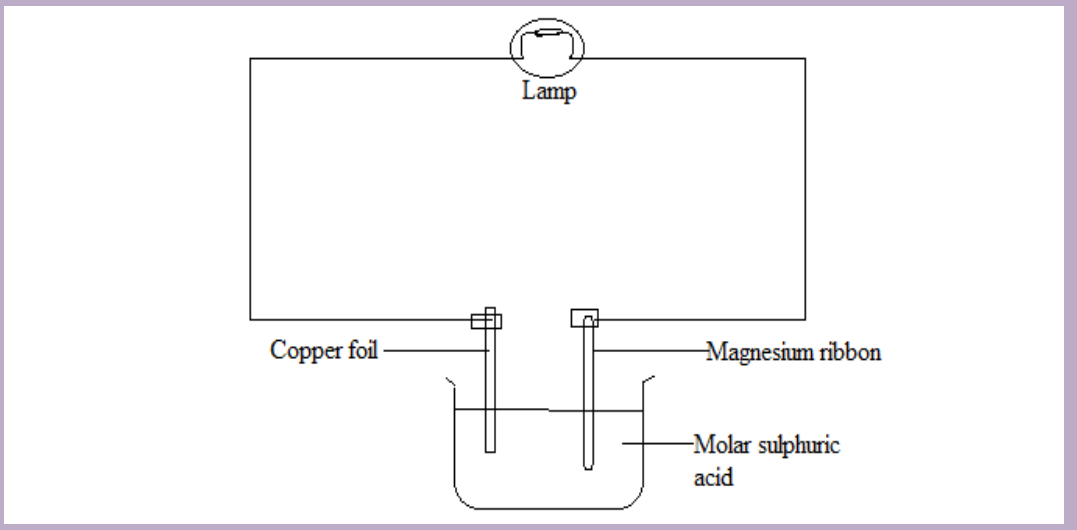
At the end of this unit, students will be able to:

- Define the term electrochemical cell.
- Construct a simple galvanic cell.
- Describe the standard hydrogen electrode.
- Explain the working of galvanic cells using the fully labelled diagram.
- Use the e.m.f. of the galvanic cell to predict if the cell will generate current or not.
- Record the results of a measurement accurately using a voltmeter.
- Calculate standard cell potentials from standard electrode potentials of two half cells.
- Use standard electrode potentials of cells to determine the direction of electron flow and feasibility of a reaction.
- Predict how the value of an electrode potential varies with concentration using Le Chatelier Principle.
- Apply the principles of redox processes to energy storage devices.
- Compare electrochemical cell with electrolytic cell.
- Properly use electrolytic cell to carry out electroplating of graphite by copper.
- Describe industrial applications of electrochemical cells.
- Appreciate contributions of electrochemistry to the social and economic development of the society.
- Develop a culture of team work, sense of responsibility in group activities and experiments.

Introductory Activity

Activity 1

Set up the circuit shown in the following figure using 1.25 V, 0.25 A lamp bulb, and a beaker two-thirds full of a 1 molar solution of sulphuric acid.

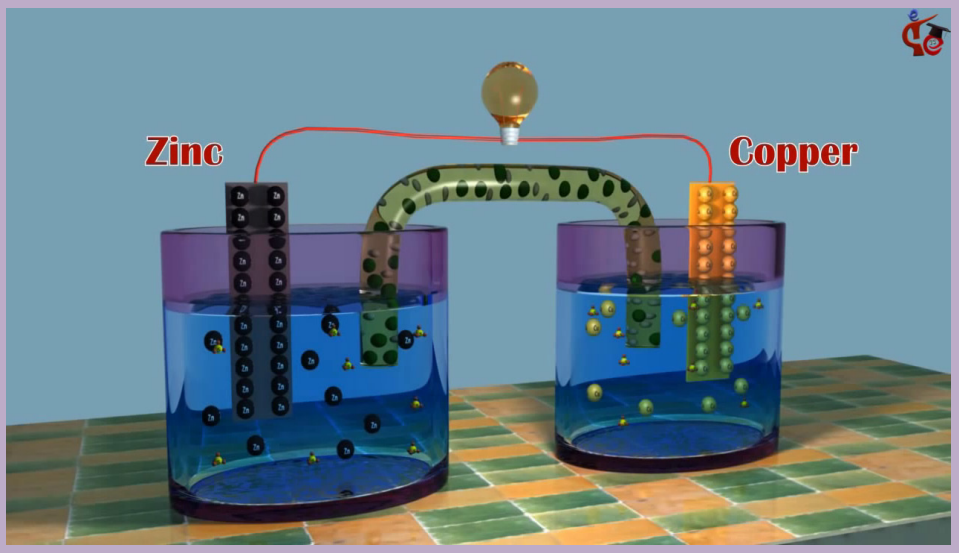


Into the beaker place strips of magnesium ribbon and copper foil, thoroughly cleaned by abrasive paper, and connect them up to the circuit using the crocodile clips on the ends of the connecting wires.

1. What do you observe?
2. From your observations, suggest the importance of this apparatus.
3. Describe what is happening to allow these observations.

Activity 2

Do research in the library, textbooks, and if you have access to Internet try to access the video on the following link: ***http://www.youtube.com/watch?v=C26pH8kC_Wk*** which shows how an electrochemical cell work to help you answer the discussion questions.



Discuss each question with your partner(s) and try to write down your best answers while watching this video.

Discussion questions:

1. The half-cell at anode consist of _____
2. The half-cell at cathode consist of _____
3. What is the salt bridge used in the experiment?
4. What is the function of salt bridge?
5. Which direction does the electron flow?
6. Why Zn is likely to lose electron?
7. Which metal undergoes oxidation?
8. Which metal undergoes reduction?
9. What can you observe during the oxidation process?
10. Which metal undergoes reduction?
11. What can you observe during the reduction process?
12. How are the excessive SO_4^{2-} ions neutralised?
13. How are the excessive Zn^{2+} ions neutralised?
14. Identify the important characteristics of a cell.
15. Suggest any use of this electrochemical cell.

12.1. Definition of electrochemical cell

Activity 12.1

Basing on the observations and the answers provided in the introductory activity above, suggest a definition of an electrochemical cell.

An electrochemical cell is a device which is capable of either producing electrical energy from chemical reactions or causes chemical reactions to take place through the introduction of electrical energy.

There are two types of electrochemical cells: galvanic (voltaic) cells and electrolytic cells.

A galvanic (voltaic) cell is a device used to convert chemical energy of a redox reaction into electrical energy.

Electrolytic cell is a type of chemical cell in which the flow of electric energy from an external source causes a redox reaction to occur.

A galvanic cell is named after Luigi Galvani, an Italian physicist (1780). It is also called Voltaic cell, after an Italian physicist, Alessandro Volta (1800). Both L. Galvani and A. Volta contributed greatly in the existence of this type of electrochemical cells.

Both types of cells contain electrodes where the oxidation and reduction reactions occur. Oxidation occurs at the electrode called the anode and reduction occurs at the electrode called the cathode.

12.2. Description of electrochemical cells

Activity 12.2 (a)

A Daniell cell is an electrochemical cell consisting of a zinc electrode in zinc sulphate solution and a copper electrode in copper sulphate solution, linked by a salt bridge. Use the method below to make one.

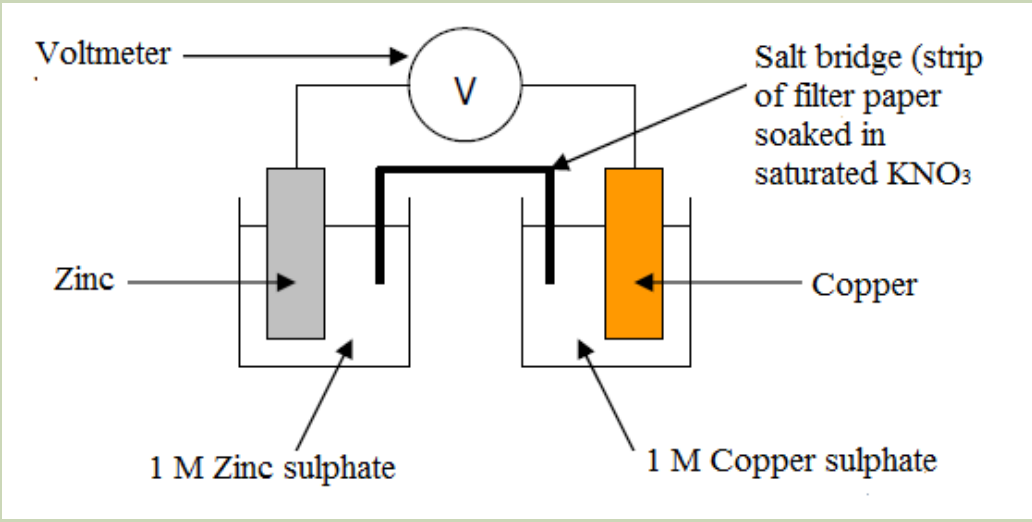
Equipment and materials

- A piece of zinc rod or plate
- Two (2) beakers

- A piece of copper rod or plate
- One (1) voltmeter
- 1 mol dm^{-3} copper sulphate solution
- Connecting wires and crocodile clips (or similar)
- 1 mol dm^{-3} zinc sulphate solution
- A plastic tube (or a U-tube), full of 2 M potassium nitrate (or 2 M sodium chloride) solution stoppered on both sides by a cotton wool soaked in that potassium nitrate (or sodium chloride) solution, acting as a salt bridge.

Procedure

Set up the apparatus as shown below.



Connect the voltmeter leads to the two electrodes. Read the voltmeter.

With the voltmeter connected correctly (with the voltage positive), remove the salt bridge. Note what happens

Discussion questions

16. The cell may be described as being made up of two half cells. Each has a metal (the electrode) in a solution of its ions. In this cell, zinc is the negative electrode and copper is the positive electrode. Describe, using ionic equations, what happens in the cell.
2. Draw the above electrochemical cell. Add the labels 'negative terminal' and 'positive terminal'. Show the direction of:
    a. The flow of electrons
    b. The (conventional) current.

3. Using your observations, explain the purpose of the salt bridge and use any relevant document to explain how it works.

Oxidation-reduction (or redox) reactions take place in electrochemical cells. Spontaneous reactions occur in galvanic (voltaic) cells; non-spontaneous reactions occur in electrolytic cells. Both types of cells contain electrodes where the oxidation and reduction reactions occur. Oxidation occurs at the **anode** and reduction occurs at the **cathode**.

The anode of an electrolytic cell is positive, since it attracts anions from the solution, whereas the cathode is negative and attracts positive ions. In a galvanic cell, the anode is negatively charged, since the spontaneous oxidation at the anode is the *source* of the cell's electrons or negative charge. The cathode of a galvanic cell is its positive terminal.

In both galvanic and electrolytic cells, oxidation takes place at the anode and electrons flow from the anode to the cathode.

In this unit, we will deal with galvanic cells especially because electrolytic cells were dealt with in Senior 5. As said above, the redox reaction in a galvanic cell is a spontaneous reaction. For this reason, galvanic cells are commonly used as batteries or sources of energy. Galvanic cell reactions supply energy which is used to perform work. Galvanic cells are electrochemical cells which use the transfer of electrons in redox reactions to supply an electric current.

The energy is harnessed by putting the oxidation and reduction reactions in separate containers, connected by a salt bridge, or separated by a porous membrane (an apparatus that allows electrons to flow).

A galvanic cell generally consists of two different metal rods called electrodes. Each electrode is immersed in a solution containing its own ions (in the separate containers) and these form a half cell. The solutions in which the electrodes are immersed are called electrolytes i.e. made of ions.

One electrode acts as anode in which oxidation takes place and the other acts as the cathode in which reduction takes place.

12.2.1 Half cells and Redox reactions in half cells

Each chamber of an electrochemical cell constitutes a half-cell containing an electrode and an electrolyte. Half-cells are sometimes known as redox electrodes or redox couples.

Types of half cells

The half cells may be categorized into three types: *Metal*, *non-metal* and *ion half-cells*.

1. Metal half cells

This half cell is made of metal and its aqueous ions. It consists of a metal (electrode) dipped into an aqueous solution containing its own ions. For example: Zn/Zn^{2+} half cell.

2. Non-metal half cells

This half cell is made from a non-metal and its aqueous ions. For example, hydrogen half cell comprises hydrogen gas in contact with hydrogen ions: $H_2/2H^+$

3. Ion half cell

This type of half cell consists of an inert electrode such as platinum electrode dipping into a solution containing ions of the same metal in two different oxidation states. For example, a half cell containing $Fe^{3+}(aq)$ and $Fe^{2+}(aq)$ ions: $Fe^{3+}(aq), Fe^{2+}(aq)/Pt$

Working of a half cell

The simplest half-cell consists of a metal placed in solution of its ions.

If a piece of metal is put into a solution of its own ions, atoms from the metallic structure pass into a solution and form hydrated metal ions. At the same time hydrated, metal ions gain electrons from the metal structure to form metal atoms. Eventually, an *equilibrium is established.*

For example, when a strip of zinc metal is dipped in aqueous solution of zinc sulphate, some zinc atoms are oxidized. Each zinc atom that is oxidized leaves behind 2 electrons and enters the solution as Zn^{2+} ion.

$$\textbf{Oxidation: } Zn(S) \rightarrow Zn^{2+}(aq) + 2e$$

At the same time, some Zn^{2+} ions in the solution gain 2 electrons from the zinc strip and deposit as zinc atoms. They are reduced.

$$\textbf{Reduction: } Zn^{2+}(aq) + 2e \rightarrow Zn(s)$$

The opposing oxidation and reduction processes quickly come to an equilibrium:

$$Zn^{2+}(aq) + 2e^- \underset{\text{Oxidation}}{\overset{\text{Reduction}}{\rightleftharpoons}} Zn(s)$$

A strip of metal used in an electrochemical experiment is called an Electrode. By convention, the equilibrium is written with the electrons on the left-hand side. The electrode potential of the half-cell indicates its tendency to lose or gain electrons in the equilibrium.

12.2.2 Constructing cells from half cells

A simple electrochemical cell can be made by connecting together two half cells with different electrode potentials.

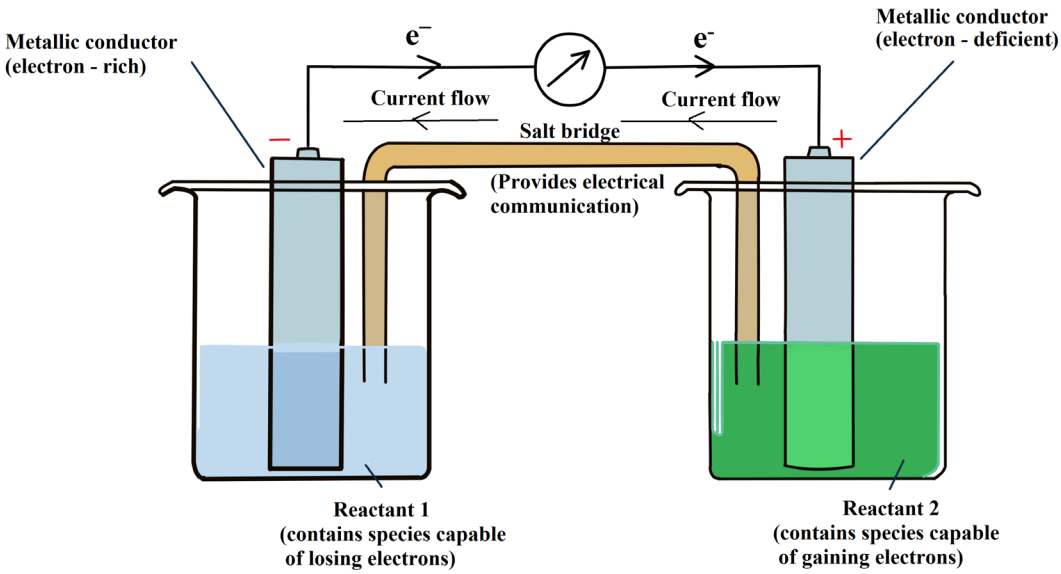


Figure 12.1: A general cell constructed from its half-cells

- One half cell releases electrons (oxidation at the anode).
- The other half cell gains electrons (reduction at the cathode).

Note that, in the electrochemical cell, the electrons flow from the negative terminal (anode) to the positive terminal (cathode) and the current flows in the opposite direction i.e. from cathode to anode.

The salt bridge is usually an inverted U-tube filled with a concentrated solution of an inert electrolyte. The inert electrolyte is neither involved in any chemical change, nor does it react with the solutions in the two half cells. Generally salts like KCl, KNO_3, Na_2SO_4 and NH_4NO_3 are used as the electrolytes.

To prepare salt bridge, agar-agar or gelatin is mixed with a hot concentrated solution of electrolyte and is filled in the U-tube. On cooling, the solution sets in the form of a gel inside the U-tube and thus prevents the inter mixing of the fluids. The two ends of the U-tube are then plugged or stoppered with cotton wool to minimise diffusion.

a. The Significance of Salt Bridge

Its main function is to prevent the potential difference that arises between the two solutions when they are in contact with each other. This potential difference is called the liquid junction potential.

- It completes the electrical circuit by connecting the electrolytes in the two half cells.
- It prevents the diffusion of solutions from one half-cell to the other.
- It maintains the electrical neutrality of the solutions in the two half cells.

b. How is the electrical neutrality of the solutions in the two half cells maintained using a salt bridge?

In the anodic half-cell, there will be accumulation of positive charge when the positive ions that are formed pass into the solution. To maintain the electrical neutrality, salt bridge provides negative ions.

For example, in Daniell cell, zinc oxidizes at the anode and passes into the solutions as Zn^{2+} ions, so there will be accumulation of positive charge in the solution. To maintain the electrical neutrality of the solution, the salt bridge provides negative ions (may be, NO_3^- or Cl^-).

In the cathodic half-cell, there will be accumulation of negative ions formed due to the reduction of positive ions. To maintain the electrical neutrality, salt bridge provides positive ions.

For example, in Daniell cell, Cu^{2+} ions from the $CuSO_4$ solution is reduced by the electrons formed by the oxidation of zinc, and deposited on the copper cathode. As a result, the concentration of Cu^{2+} ions decreases in the solution and that of SO_4^{2-} ions (sulphate ions) increases. So there will be an accumulation of negatively charged sulphate ions around the cathode. To maintain the electrical neutrality, salt bridge provides positive ions (may be, K^+ or NH_4^+).

12.2.3. Daniell Cell

The Daniell cell was invented by a British chemist, John Frederic Daniell. In the Daniell cell, copper and zinc electrodes are immersed in a solution of copper (II) sulphate ($CuSO_{4(aq)}$) and zinc (II) sulfate ($ZnSO_4$ (aq)) respectively. The two half cells are connected through a salt bridge. Here, zinc acts as anode and copper acts as cathode.

At the anode, zinc undergoes oxidation to form zinc ions and electrons. The zinc ions pass into the solution. If the two electrodes are connected using an external wire, the electrons produced by the oxidation of zinc travel through the wire and enter into the copper cathode, where they reduce the copper ions present in the solution and form copper atoms that are deposited on the cathode.

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

The half-reactions are:

- At Anode: Anode: is an electrode at which oxidation occurs. Because it is the source of electrons, in voltaic cell, it is also called the negative electrode.

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

- At Cathode: Cathode: is an electrode at which reduction occurs. Because it is the receiver of electrons, in voltaic cell, it is also called the positive electrode.

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

Total cell reaction is the sum of the two half-cell reactions:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

- Zinc is oxidized to Zn^{2+} and releases 2 electrons; it is the anode of the cell.
- Cu^{2+} is reduced to copper and captures two electrons; it is the cathode where copper metal is deposited.
- In half-Zn cell, Zn^{2+} ions are produced, which means that the solution is positively charged.
- In half-cell of Cu, Cu^{2+} ions are deposited and there is an excess of SO_4^{2-} ions, so that the solution becomes negatively charged.

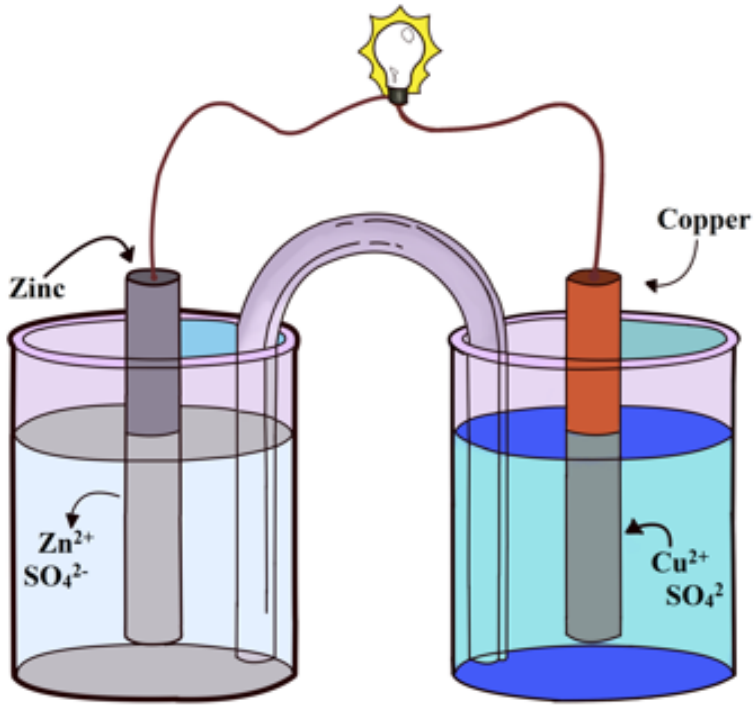


Figure 12.2: Daniell cell

The flow of electrons takes place through the external circuit. As electrons leave

one half of a galvanic cell and flow to the other, a difference in charge is established. If no salt bridge were used, this charge difference would prevent further flow of electrons.

The ***salt bridge*** and ***wire*** join the two half cells:

- The salt bridge connects the two solutions, allowing ions to be transferred between the half cells.
- The wire connects the two metals, allowing the electrons to be transferred between the two half cells.

The two equilibria which are set up in the half cells are:

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $E^o = -0.76$ V

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $E^o = +0.34$ V

The negative sign of the zinc E^0 value shows that it releases electrons more readily than hydrogen does while the positive sign of the copper E^0 shows that it releases electrons less readily than hydrogen.

Taking the apparatus as a whole, there is a chemical reaction going on, in which zinc is going into solution as zinc ions, and is giving electrons to copper (II) ions to turn them into metallic copper. This is exactly the same reaction that occurs when you drop a piece of copper into some copper (II) sulphate solution. The blue colour of the solution fades as the copper (II) ions are converted into brown copper metal. The final solution contains zinc sulphate (where the sulphate ions are spectator ions).

You can add the two electron-half-equations above to give the overall ionic equation for the reaction.

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ Oxidation to anode electrode

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ Reduction to cathode electrode

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ Overall reaction

12.2.4. Description of standard hydrogen electrode as used to determine standard electrode potentials

Activity 12.2 (b)

Some electrode potentials experimentally measured are found in the *table 12.3*. Use any document to:

1. Suggest a reason why these potentials are called "standard".
2. Describe the way the electrode potential given for an atom can be measured.

When a metal electrode is dipped in a solution containing its metal ions, a potential difference is developed at the metal /solution interface. This potential difference is called the electrode potential.

For example, when a copper rod is dipped in a solution containing Cu^{2+} ions, the Cu^{2+} ions gain electrons from the copper rod leaving positive charge on the copper rod. As a result, a potential difference is set up between the copper rod and the solution and is called the electrode potential of copper.

In a galvanic cell, the anode has a negative potential and cathode has a positive potential. The potential of each individual half-cell cannot be measured. We can measure only the difference between the potential of the two half cells. While it is impossible to determine the electrical potential of a single electrode, we can assign an electrode the value of zero and then use it as a reference.

The electrode chosen as having the value of "zero" is called the Standard Hydrogen Electrode (SHE). The SHE consists of 1 atm of hydrogen gas bubbled through a 1 M strong acid solution, usually at room temperature. Platinum or graphite, which is chemically inert, is used as the electrode.

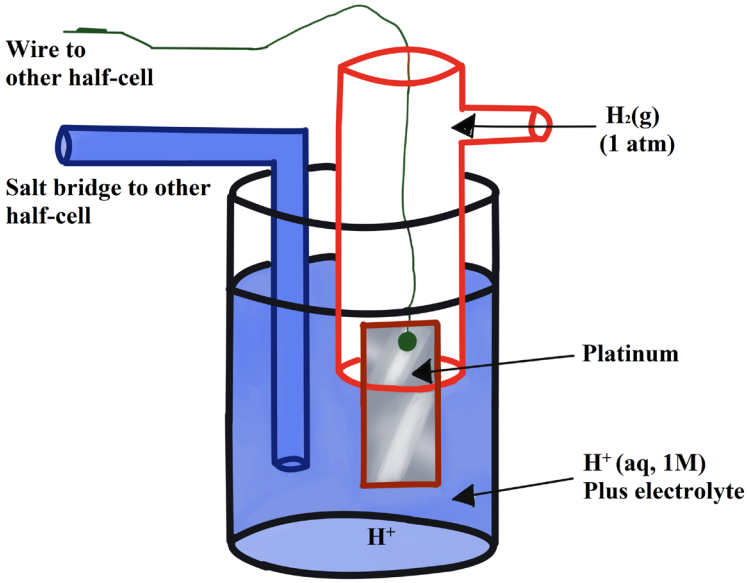


Figure 12.3: Standard Hydrogen Electrode

Thus, electrode potential at standard conditions (temperature of 25°C, pressure of 1 atm and concentration of 1 M concentration for the electrolyte) is called the "standard electrode potential". It is denoted by the symbol E^0 where the superscript "0" on the E denotes standard conditions.

Other standard electrode potentials can be determined using the SHE. The standard reduction (electrode) potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. Here, the minus sign is necessary because oxidation is the reverse of reduction.

$$E^0_{cell} = E^0_{Cathode} - E^0_{Anode}$$

$$= E^0_{Cu^{2+}/Cu} - E^0_{Zn^{2+}/Zn} = 0.34V - (-0.76V) = 1.10V$$

The diagram below shows how the standard potential, E^0 of copper can be determined.

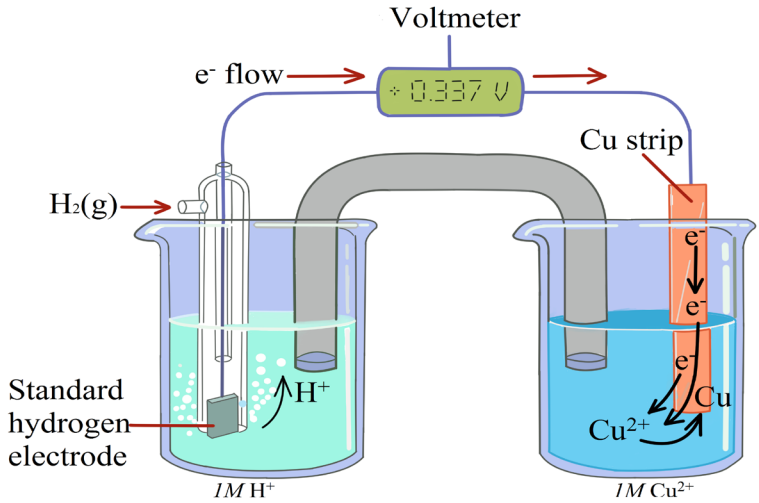


Figure 12.4. Measuring the electrode potential of copper

The copper electrode contains Cu^{2+} ions in equilibrium with copper metal. The hydrogen electrode is linked via a salt bridge to the solution in which the copper electrode is immersed. This permits charge transfer and potential measurement but not mass transfer of the acid solution in the electrode.

The oxidation and reduction at the electrodes leads to a standard electrode potential between the electrode and ions in solution. The standard electrode potential is expressed in Volts (V).

Volt is the measure of electromotive force (e.m.f.) produced by a cell. Standard electrode potentials refer to redox potentials as well. A voltmeter measures a difference in electric potential between two points in an electrical circuit.

If the two points are the electrodes in voltaic cells, the potential difference is the driving force that propels electrons from the anode to the cathode. It is also called the cell potential (E_{cell}). Since the measurements are in volts, the cell potential is also called the "Cell voltage".

When E^0 are measured relative to the SHE (or some other reference electrode), a voltmeter is used. In order to resist any current flowing between the electrode and the SHE, the voltmeter must have high impedance and if a current were allowed to flow, the electrodes would become polarised and would no longer be at equilibrium.

The hydrogen electrode is not a convenient reference electrode to use in measurements because maintaining a stream of hydrogen at 1 atm takes careful management. It is usual to employ a secondary standard such as the saturated calomel electrode.

This electrode contains mercury and solid mercury (I) chloride (calomel) in contact with a saturated with a solution of potassium chloride. An equilibrium is set up between Hg^+ ions and Hg(l). The emf of a cell composed of a saturated calomel electrode and a standard hydrogen electrode is 0.244 V at 25°C. The saturated calomel electrode is easier to use than the standard hydrogen electrode. It can be combined with electrodes of unknown potential, and from the emf of the cell, the unknown electrode potential can be found.

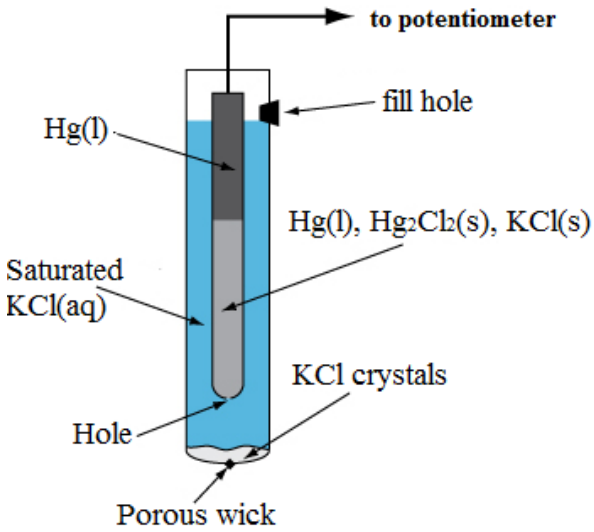


Figure 12.5: Saturated Calomel Electrode

Table 12.1: Standard Reduction Potentials in aqueous solution (at 25 °C).

				$E^0(V)$	
INCREASING STRENGHT OF OXIDISING AGENTS	$F_2(g)+2e^-$	⟶	$2F^-(aq)$	+ 2.870	INCREASING STRENGHT OF REDUCING AGENTS
	$H_2O_2(aq)+2H^+(aq)+2e^-$	⟶	$2H_2O(l)$	+ 1.770	
	$PbO_2(s)+SO_4^{2-}(aq)+4H^+(aq)+2e^-$	⟶	$PbSO_4(s)+2H_2O(l)$	+ 1.685	
	$MnO_4^-(aq)+8H^+(aq)+5e^-$	⟶	$Mn^{2+}(aq)+4H_2O(l)$	+ 1.520	
	$Au^{3+}(aq)+3e^-$	⟶	$Au(s)$	+ 1.500	
	$Cl_2(g)+2e^-$	⟶	$2Cl^-(aq)$	+ 1.360	
	$Cr_2O_7^{2-}(aq)+14H^+(aq)+6e^-$	⟶	$2Cr^{3+}(aq)+7H_2O(l)$	+ 1.330	
	$O_2(g)+4H^+(aq)+4e^-$	⟶	$2H_2O(l)$	+ 1.229	
	$Br_2(l)+2e^-$	⟶	$2Br^-(aq)$	+ 1.066	
	$NO_3^-(aq)+4H^+(aq)+3e^-$	⟶	$NO(g)+2H_2O(l)$	+ 0.960	
	$OCl^-(aq)+H_2O(l)+2e^-$	⟶	$Cl^-(aq)+2OH^-(aq)$	+ 0.890	
	$Hg^{2+}(aq)+2e^-$	⟶	$Hg(l)$	+ 0.855	
	$Ag^+(aq)+e^-$	⟶	$Ag(s)$	+ 0.799	
	$Fe^{3+}(aq)+e^-$	⟶	$Fe^{2+}(aq)$	+ 0.771	
	$I_2(s)+2e^-$	⟶	$2I^-(aq)$	+ 0.535	
	$Cu^+(aq)+e^-$	⟶	$Cu(s)$	+ 0.521	
	$O_2(g)+2H_2O(l)+4e^-$	⟶	$4OH^-(aq)$	+ 0.400	
	$Cu^{2+}(aq)+2e^-$	⟶	$Cu(s)$	+ 0.337	
	$Sn^{4+}(aq)+2e^-$	⟶	$Sn^{2+}(aq)$	+ 0.150	
	$2H^+(aq)+2e^-$	⟶	$H_2(g)$	0.000	
	$Pb^{2+}(aq)+2e^-$	⟶	$Pb(s)$	- 0.126	
	$Sn^{2+}(aq)+2e^-$	⟶	$Sn(s)$	- 0.140	
	$Ni^{2+}(aq)+2e^-$	⟶	$Ni(s)$	- 0.250	
	$V^{3+}(aq)+2e^-$	⟶	$V^{2+}(aq)$	- 0.255	
	$Co^{2+}(aq)+2e^-$	⟶	$Co(s)$	- 0.280	
	$Tl^+(aq)+e^-$	⟶	$Tl(s)$	- 0.340	
	$PbSO_4(s)+2e^-$	⟶	$Pb(s)+SO_4^{2-}(aq)$	- 0.356	
	$Cd^{2+}(aq)+2e^-$	⟶	$Cd(s)$	- 0.403	
	$Fe^{2+}(aq)+2e^-$	⟶	$Fe(s)$	- 0.440	
	$Zn^{2+}(aq)+2e^-$	⟶	$Zn(s)$	- 0.763	
	$2H_2O(l)+2e^-$	⟶	$H_2(g)+2OH^-(aq)$	- 0.828	
	$Al^{3+}(aq)+3e^-$	⟶	$Al(s)$	- 1.660	
	$Mg^{2+}(aq)+2e^-$	⟶	$Mg(s)$	- 2.370	
	$Na^+(aq)+e^-$	⟶	$Na(s)$	- 2.714	
	$K^+(aq)+e^-$	⟶	$K(s)$	- 2.925	
	$Li^+(aq)+e^-$	⟶	$Li(s)$	- 3.045	

(Source: www.chemeddl.org/services/moodle/media/QBank/GenChem/Tables/EStandardTable.htm)

In the above table,

- The best oxidizing agents (the poorest reducing agents) i.e. those most easily reduced appear up (top); for example Au^{3+}, F_2, O_2, etc.
- The poorest oxidizing agents (the best reducing agents) i.e. those most difficult to reduce are on the bottom; for example Na^+, K^+, Li^+, etc.

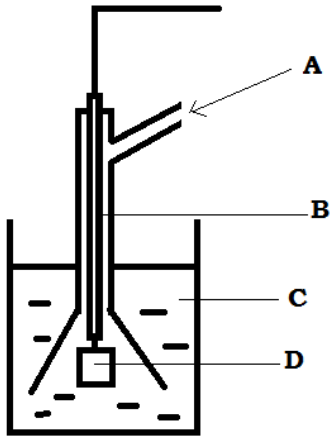
Indeed, Fluorine, F_2, is the most oxidizing agent and Lithium, Li, is the best reducing agent among the elements presented.

Note: The table which shows the standard reduction potentials can be arranged in different manners. The most reducing agent can be shown on the top or at the bottom; it depends on the document used.

Checking Up 12.2 (a)

1. Define standard electrode potential.
2. Is it possible to use another standard electrode than SHE? Justify your answer.
3. Answer by True or False.
   a. Hydrogen electrode which is the reference electrode can be used as Anode or Cathode.

   B. If hydrogen electrode acts as cathode, hydrogen is oxidised.
4. With the aid of a diagram, explain how the standard electrode potential of zinc is measured.
5. Given below is a diagram of hydrogen electrode. Identify A, B, C and D by choosing the words in the text below: Platinum, Inner glass tube, 1M HCl, Hydrogen at 1 atm



12.2.5. Electromotive force (EMF) of a cell and cell notation

Electromotive force (emf) is a measurement of the energy that causes current to flow through a circuit. It can also be defined as the potential difference in charge between two points in a circuit. Electromotive force is also known as cell voltage or cell potential, and it is measured in volts.

a. Calculations of *electromotive force (emf)*

To calculate the standard cell potential for a reaction:

- Write the oxidation and reduction half-reactions for the cell.
- Look up the reduction potential, $E^0_{reduction}$, for the reduction half-reaction in a table of reduction potentials
- Look up the reduction potential for the reverse of the oxidation half-reaction and reverse the sign to obtain the oxidation potential. For the oxidation half-reaction, $E^0_{oxidation} = - E^0_{reduction}$.
- Add the potentials of the half-cells to get the overall standard cell potential.

$$E^0_{cell} = E^0_{reduction} + E^0_{oxidation}$$

Example: Find the standard cell potential for an electrochemical cell with the following cell reaction. $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

1. Write the half-reactions for each process.

   $$\mathbf{Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-}$$

   $$\mathbf{Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)}$$

2. Look up the standard potentials for the reduction half-reaction.

   $$\mathbf{E^o_{reduction}\ of\ Cu^{2+} = + 0.339\ V}$$

3. Look up the standard reduction potential for the reverse of the oxidation reaction and change the sign.

   $$\mathbf{E^o_{reduction}\ of\ Zn^{2+} = - 0.762\ V}$$

   $$\mathbf{E^o_{oxidation}\ of\ Zn = - (- 0.762\ V) = + 0.762\ V}$$

4. Add the cell potentials together to get the overall standard cell potential.

Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$ $\quad E^o_{ox.} = - E^o_{red.} = - (- 0.762\ V) = + 0.762\ V$

Reduction: $Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$ $\quad E^o_{red.} = + 0.339\ V$

Overall: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ $\mathbf{E^o_{cell} = + 1.101\ V}$

How do we know which metal will become oxidized and which metal ion reduced?

By looking at a table of standard reduction potentials! One of the half-reactions must be reversed to yield an oxidation.

- Reverse the half-reaction that will yield the highest (positive) net emf for the cell.
- Remember that when one reverses a reaction, the sign of E^0 (+ or –) for that reaction is also reversed.

Worked example

Consider the following table of standard reduction potentials:

In aqueous solutions at 25 °C	
$Hg^{2+}(aq) + 2e^- \longrightarrow Hg(l)$	E° = 0.86 V
$I_2(s) + 2e^- \longrightarrow 2\,I^-(aq)$	E° = 0.54 V
$2\,H^+(aq) + 2e^- \longrightarrow H_2(g)$	E° = 0.00 V
$Zr^{4+}(aq) + 4e^- \longrightarrow Zr(s)$	E° = – 1.53 V
$Rb^+(aq) + e^- \longrightarrow Rb(s)$	E° = – 2.93 V

The potential generated by a cell constructed from standard **Zr** and $\mathbf{I_2}$ electrodes may be calculated. From the table, we write a balanced reduction half-reaction for each electrode and copy down the reduction potentials:

$I_2(s) + 2e^- \longrightarrow 2\,I^-(aq)$ **E^0 = 0.54 V**
$Zr^{4+}(aq) + 4e^- \longrightarrow Zr(s)$ **E^0 = –1.53 V**

Reversing which reaction will yield most positive standard reduction potential? Let us try both.

Case 1: *Reversing the iodine reduction:* E° = - 0.54 V

Case 2: *Reversing the zirconium reduction:* E° = + 1.53 V

Thus the highest positive potential is found by using the **Zr oxidation** half-reaction because: **+ 1.53 V > - 0.54 V**

Thus the standard cell potential will be $\boldsymbol{E^o_{ox}(Zr) + E^o_{red}(I_2)}$

$$E^{o}_{cell} = (+0.54) + (+1.53)$$

$$E^{o}_{cell} = +2.07\ V$$

Even though we had to multiply the iodine reduction by a factor of 2 so that the electrons consumed would balance with those produced by the zirconium oxidation, we do NOT multiply the iodine reduction potential by this factor. In manipulating potentials, we should only change the signs of the values, not the magnitude.

- A negative reduction potential tells us that the zirconium ion is harder to reduce (is a worse oxidizing agent) than is the hydrogen ion; this also tells us that zirconium metal is a better reducing agent than is hydrogen gas.
- A positive reduction potential tells us that the iodide ion is easier to reduce (is a better oxidizing agent) than is the hydrogen ion; this also tells us that iodine is a worse reducing agent than is hydrogen gas.

In general, the electrode with the more positive value of electrode potential is the cathode (the one which undergoes reduction) and the electrode with more negative value of electrode potential is the anode (easily oxidised).

a. Cell notation

An electrochemical cell consists of two electrodes: Anode and Cathode. The electrolyte solution containing each of these electrodes is called half-cells. When the two half cells are combined, a "cell" is formed.

It is more convenient to represent an electrochemical cell by writing a cell notation than by making a drawing. Cell notation (usually called cell diagram) is shorthand that expresses a certain reaction in an electrochemical cell.

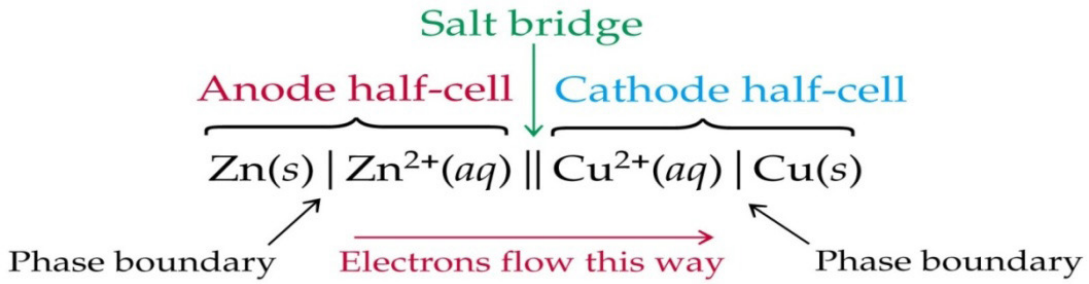
By international agreement, the following conventions are used for electrochemical cell notations:

- Use a single vertical line (I) to represent the boundary between different phases such as between an electrode and a solution.
- Use a double vertical line (II) to represent the salt bridge separating two half–cells.
- Double discontinuous vertical line (ii) would be used to indicate porous barrier separating two half–cells instead of salt bridge.
- Place the anode where oxidation occurs (A-O) on the left side of the diagram. Place the cathode where reduction occurs (C-R) on the right side of the diagram.

- Aqueous solution concentrations are written in parentheses after the symbol

for the ion or molecule.

- A comma is used to show the components that are in the same phase.
- The inert electrode used is specified.



Example 1

The following cell reaction is given: $Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$

Cell Notation: **$Zn_{(s)}$ | $Zn^{2+}_{(aq)}$(1.0 M) || $Cu^{2+}_{(aq)}$(1.0 M) | $Cu_{(s)}$**

Example 2

Ni- $AgNO_3$ cell

Oxidation half reaction $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$

Reduction half reaction $2\ Ag^+(aq) + 2e^- \rightarrow 2\ Ag(s)$

Overall cell reaction $Ni(s) + 2\ Ag^+(aq) \rightarrow 2\ Ag(s) + Ni^{2+}(aq)$

***Cell Notation*: Ni(s) | Ni^{2+}(aq) || Ag^+(aq) | Ag(s)**

Note: In many cases, we use an electrode that does not participate in an oxidation –reduction equilibrium, rather the inert electrode (Pt or graphite) simply furnishes the surface on which an electric potential is established. Consider the following examples.

Example 3

Zn – HCl reaction

Oxidation half reaction $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Reduction half reaction $2\ H^+ + 2\ e^- \rightarrow H_2(g)$

Overall cell reaction $Zn(s) + 2\ H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

Cell Notation: **Zn(s) | Zn^{2+}(aq) || H^+(aq) | H_2(g) | Pt(s)**

Example 4

Pt(s) |Sn^{4+}(aq),Sn^{2+}(aq) ‖ Fe^{2+}(aq),Fe^{3+}(aq) |Pt(s)

Checking Up 12.2 (b)

1. An experiment was carried out to measure the e.m.f. of this cell.

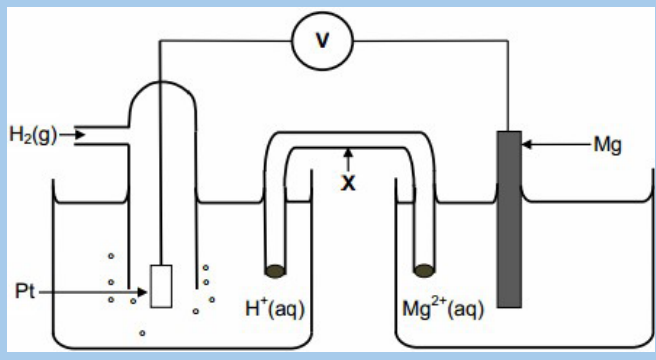
$$Al(s) \mid Al^{3+}(aq) \parallel H^{+}(aq) \mid H_2(g) \mid Pt(s)$$

a. The aluminium used as the electrode is rubbed with sandpaper prior to use. Suggest the reason for this.

b. Draw a labelled diagram of a suitable apparatus for the right-hand electrode in this cell. [You do not need to include the salt bridge or the external electrical circuit].

c. A simple salt bridge can be prepared by dipping a piece of filter paper into K_2CO_3 solution. Explain why such a salt bridge would not be suitable for use in this cell.

2. The electrochemical cell represented below consists of a hydrogen half-cell and a magnesium half-cell at standard conditions.



The reading on the voltmeter is 2.36 V.

a. Apart from concentration, write down two other conditions needed for the hydrogen half-cell to function at standard conditions.

b. Write down the name of the item of apparatus labelled **X**.

c. Is magnesium the anode or cathode in the cell above? Refer to the relative strengths of reducing agents to explain the answer.

d. Write down the cell notation for this cell.

e. Calculate the standard reduction potential of the magnesium half-cell. Show all your working.

f. Write down the balanced net (overall) cell reaction that takes place in this cell. No spectator ions are required.

3. Learners conduct an investigation to determine which combination of two half-cells will provide the largest emf at standard conditions.

Three half-cells, represented as **A**, **B** and **C** in the table below, are available.

HALF-CELL A	HALF-CELL B	HALF-CELL C
Mg/Mg^{2+}	Pb/Pb^{2+}	Al/Al^{3+}

The learners set up galvanic cells using different combinations of the above half-cells.

a. Write down the standard conditions under which these cells operate.

b. Write down the dependent variable in this investigation.

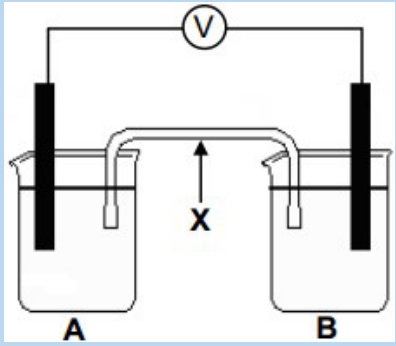
c. Use the Table of Standard Reduction Potentials to determine which one of the three half-cells (A, B or C) contains the:

(i) Strongest reducing agent

(ii) Strongest oxidising agent

d. Without any calculation, write down the combination of two half-cells which will produce the highest emf. Write down only AB, BC or AC.

e. One group of learners set up a galvanic cell using half-cells A and B, as shown below. X represents one of the components of the galvanic cell.



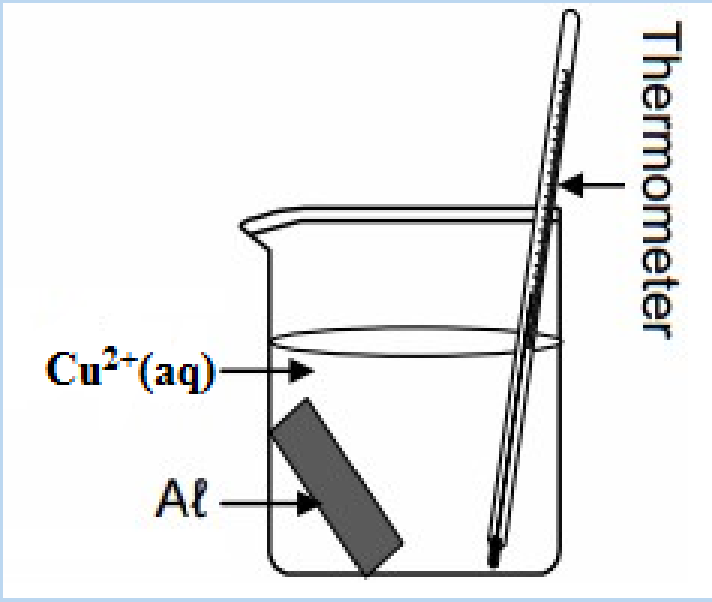
i. Write down the name or symbol of the substance that will act as the anode in this cell. Give a reason for the answer.

ii. Calculate the initial emf of this cell.

iii. How will an increase in the concentration of the electrolyte in half-cell **B** affect the initial emf of the cell? Write down only increases, decreases or remains the same.

iv. Briefly explain how component **X** ensures electrical neutrality while the cell is functioning.

4. A strip of aluminium is placed in a beaker containing a blue solution of a copper (II) salt. After a while the solution becomes colourless.

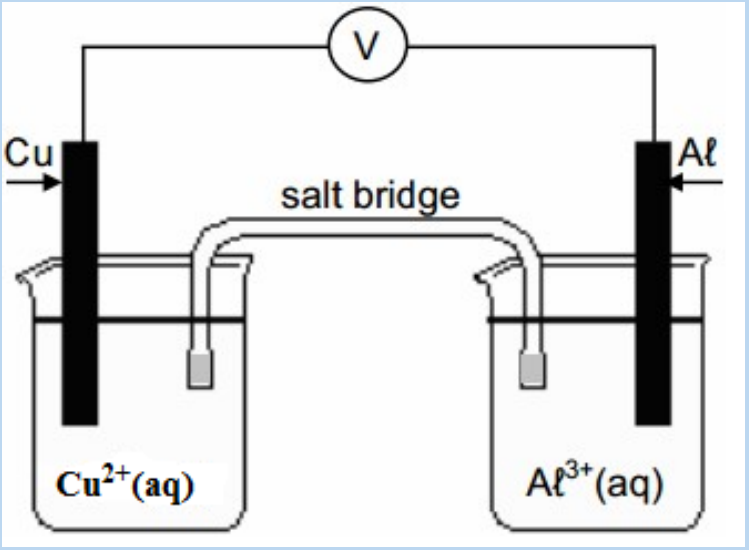


a. How would the reading on the thermometer change as the reaction proceeds? Write down increases, decreases or remains the same. Give a reason for the answer.

b. Refer to the reducing ability of aluminium to explain why the solution becomes colourless.

c. Write down the balanced net ionic equation for the reaction that takes place.

5. The electrochemical cell shown below functions at standard conditions.



a. Which electrode (Cu or Al) is the anode?

b. Write down the cell notation for this cell.

c. Calculate the emf of this cell.

d. What will the reading on the voltmeter be? Give a reason for your answer.

6. Rusting is an unwanted redox reaction. Iron rusts when exposed to oxygen and moisture.

7. The unbalanced ionic equation for one reaction that occurs during rusting is represented below.

$F(s) + O_2 + H_2O \longrightarrow E^{2+}(aq) + H^-(aq)$

Use the Table of Standard Reduction Potentials to answer the following questions for this reaction.

a. Write down the oxidation half-reaction.

b. Write down the name of the substance that is reduced.

c. Perform a calculation to verify that this reaction is spontaneous.

12.3. Prediction of spontaneity of redox reactions

Activity 12.3

Title: Spontaneity of Chemical Reactions (Redox)

Purpose:

To determine if all reactions occur spontaneously.

Materials:

- 4 cleaned strips of each of the following materials , zinc, lead, magnesium and silver (if possible iron may be substituted)
- 0.1 M nitrate solutions of each of the elements above.
- silver nitrate or iron (III) nitrate if you substitute iron
- copper (II) nitrate
- Lead (II) nitrate
- Zinc nitrate

Procedure:

Perform the tests indicated below by adding cleaned strips of the metal element to the solutions in separate test tubes.

Metal / Solutions	$Cu(NO_3)_2$	$AgNO_3$	$Pb(NO_3)_2$	$Zn(NO_3)_2$
Cu (s)				
Ag or Fe (s)				
Pb (s)				
Zn (s)				

Discussion questions:

Indicate with a check mark (√) if there is evidence of a reaction (in the above table).

1. Write the non-ionic and net ionic reaction for each of the single replacement reactions that occur.
2. Indicate if the reaction was spontaneous or not.
3. Label the oxidized and reduced species in each test.
4. Write the half reaction for the reduction of each metal.

5. Label the oxidizing agent and reducing agent.
6. Which metal strip was the best reducing agent?
7. Create a list of the half reactions of the reducing agent from best to least.

12.3.1. Using standard reduction potentials (E^0_{cell})

A positive voltage that forms across the electrodes of a voltaic cell indicates that the oxidation-reduction reaction is a spontaneous reaction for reduction at the cathode and oxidation at the anode.

Conversely, if the potentials of the half-cells are known, then it is possible to predict whether a given redox reaction will be spontaneous (i.e. result in a positive voltage).

A negative voltage indicates that the reaction is not spontaneous, rather the reverse reaction is spontaneous (i.e. oxidation at the cathode, and reduction at the anode).

Basically, any current flow indicates that there is a spontaneous redox reaction occurring in a voltaic cell. The sign of the voltage indicates at which electrode the reduction or oxidation is occurring. As long as we can identify the actual reduction and oxidation processes that will occur in a redox reaction, the general description of the standard reduction potential for any redox reaction would be:

$$\mathbf{E^0 = E^0_{red}\ (reduction\ process) - E^0_{ox}\ (oxidation\ process)}$$

- Thus, E^0 will be positive for the case where the reaction is spontaneous
- E^0 will be zero for a redox reaction at equilibrium
- E^0 will be negative for the case where the reaction is not spontaneous, i.e., the reverse direction reaction is spontaneous

Note that there is no reference here to what is the cathode and what is the anode.

Example: Can copper be oxidized by acid?

This question is asking about the following reaction:

$$\mathbf{Cu(s) + 2\ H^+(\mathit{aq}) \rightarrow Cu^{2+}(\mathit{aq}) + H_2(\mathit{g})}$$

This reaction can be broken down into two half-reactions: an oxidation and a reduction reaction:

- Oxidation: $\mathbf{Cu(s) \rightarrow Cu^{2+}(\mathit{aq}) + 2e^-}$
- Reduction: $\mathbf{2\ H^+(\mathit{aq}) + 2e^- \rightarrow H_2(\mathit{g})}$

Each half-reaction has an associated standard reduction potential:

Reduction potentials refer to the individual ***reduction reaction.*** For the reduction

half-reaction this is straightforward because it is already written to refer to the reduction of hydrogen ion:

$$2\,H^+(aq) + 2e^- \rightarrow H_2(g) \qquad E^0_{red} = 0.00\,V$$

What about the oxidation reaction? The standard reduction potential for copper is listed in tables as copper ion combining with electrons to yield copper metal:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E^0_{red} = +0.34\,V$$

In the oxidation reaction we have copper metal oxidizing to yield copper ion plus electrons. The key point here is that the reverse reaction will have the same voltage magnitude, just an opposite sign. In any case, the expression for the standard reduction potential for the redox reaction requires the reduction potentials for the half reactions.

The standard reduction potential for this reaction is:

$$E^0 = 0\,V - 0.34 = -0.34\,V$$

Since this value is negative, this redox reaction is not spontaneous as written. The reverse reaction (reduction of copper ion by hydrogen gas) is spontaneous.

Worked examples

1. For the reaction: $Ca^{2+}(aq) + Zn(s) \rightarrow Ca(s) + Zn^{2+}(aq) \quad E^o = -2.11\,V$

Is this redox reaction as written spontaneous or non-spontaneous?

Solution:

If $E^o_{(redox\ reaction)}$ is positive, redox reaction is spontaneous

reaction if $E^o_{(redox\ reaction)} > 0$

$E^o_{(redox\ reaction)} = -2.11V$
$E^o_{(redox\ reaction)}$ is negative $(-2.11 < 0)$
Redox reaction as written is ***not spontaneous*.**

2. A strip of magnesium metal is placed in an aqueous 1 mol L^{-1} copper (II) sulphate solution.

   Will a spontaneous redox reaction occur?

Solution:

Given that:

Magnesium in its standard state, that is, as the metal: Mg(s)

Standard aqueous solution of copper (II) sulphate, $CuSO_4(aq)$, contains copper (II) ions, $Cu^{2+}(aq)$, and sulphate ions, $SO_4^{2-}(aq)$.

a. Write the half-equations for the reaction as given in the question:

Oxidation of magnesium metal: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$
Reduction of copper (II) ions: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

b. Use a table of standard reduction potentials to find the value of E^o for each half-reaction:

$Mg_{(s)}$	$\rightarrow Mg^{2+}_{(aq)} + 2e^-$	$E^o = +2.36\ V$
$Cu^{2+}_{(aq)} + 2e^-$	$\rightarrow Cu_{(s)}$	$E^o = +0.34\ V$

c. Add the equations together, and add the E^o value for each half-reaction together

Mg(s)	$\rightarrow Mg^{2+}(aq) + ^-$		$E^o = +2.36\ V$
$Cu^{2+}(aq) + ^-$	$\rightarrow$ Cu(s)		$E^o = +0.34\ V$
$Mg(s) + Cu^{2+}(aq) \rightarrow$	$Mg^{2+}(aq)$ Cu(s)	+	$E^o = +2.36$ + +0.34 $E^o = +2.70\ V$

Decide if the redox reaction as written is spontaneous:

a. Spontaneous reaction if $E^o_{(redox)} > 0$

b. Not a spontaneous reaction if $E^o_{(redox)} < 0$

E^o is positive (+2.70 V), the redox reaction ***is spontaneous.***

12.3.2. Free energy change and electromotive force of a cell

Free energy change, ΔG, is a measure of the spontaneity of a chemical reaction or process. Likewise, the standard reduction potential (E^0_{cell}) for a redox reaction is also a measure of the spontaneity of a redox reaction.

Relationship between *ΔG* and *E*

ΔG has units of J/mole. Reduction potential (electromotive force, E) has units of

Volts. 1 Volt describes the potential difference necessary to impart 1 J of energy to a charge of 1 coulomb (6.24×10^{18} electrons).

We need some way to relate charge in Coulombs (a collection of electrons) to moles of electrons (another collection of electrons)

$$\Delta G = - n F E$$

n = number of moles of electrons transferred in the reaction

F = the quantity of electrical charge (in coulombs) that is contained in 1 mole of electrons (this is the *Faraday* constant).

One Faraday is equal to 96,500 coulombs /mole of electrons. Since 1 volt = 1 Joule/ coulomb, one Faraday also equals 96,500 J/(volt x mole electrons)

F and **n** are positive values. Therefore, **a *positive* value of E** (which indicates spontaneity) is a ***negative* value for ΔG** (which also indicates spontaneity).

In standard conditions

If everything is in the standard state, the relationship is:

$$\Delta G^0 = - n F E^0$$

SUMMARY

- In order for a reaction to proceed spontaneously, ΔG <0, and if ΔG is negative, then E_{cell} must be positive. These lead to some important new ideas concerning spontaneous change.
- If E_{cell} is positive, the reaction in the forward direction (from left to right) is spontaneous.
- If E_{cell} is negative, the reaction in the forward direction (from left to right) is not spontaneous.
- If $E_{cell} = 0$, a system is at equilibrium.
- When a cell reaction is reversed, Ecell and ΔG change signs.
- When we obtain an Ecell value by combining standard electrode potentials from table given previously, we get a standard cell potential E0cel,

Worked example

Calculate the change in Gibbs free energy of an electrochemical cell where the following redox reaction is taking place:

$$Pb^{2+} + Ni \longrightarrow Ni^{2+} + Pb \qquad E^o = 0.12\ V$$

Answer: To solve, we need to use the equation: $\Delta G^0 = -nFE^0$

The number of moles of electrons transferred is 2, while the cell potential is equal to 0.12 V. One volt is 1 Joule/Coulomb.

$\Delta G^0 = -$ 2 moles e^- × 96,485 Coulombs /mole × 0.12 Joules/Coulomb

$\Delta G^0 = -$ 23.156 J = – 2.3 kJ

Because the change in Gibbs free energy is negative, the redox process is spontaneous.

Checking up 12.3

1. The standard electrode potentials for some systems are given below:

	E /V
$Mn^{3+}(aq)\|Mn^{2+}(aq)$	+1.5
$V^{3+}(aq)\|V^{2+}(aq)$	-0.26

   b. Write the convention for the cell formed by combining the two systems.

   c. Write the overall equation for the cell reaction.

   d. Calculate the emf of the cell.

   e. State whether the reaction is possible or not and give a reason for your answer.

2. The standard electrode potential for Daniell cell is 1.1V.

   a. Calculate the standard Gibbs energy for the reaction:
   $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

   b. Will the reaction proceed spontaneously or not? Give a reason for your answer

12.4. Explanation of the effect of concentration on electromotive force (emf) of the cell

Activity 12.4

Consider this copper reduction half-equation:

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $E^0 = +0.34$ V

For this E^0 value to apply, the copper (II) ions would have to have a concentration of 1 mol dm^{-3}. This is an equilibrium we are talking about.

1. Recall the Le Chatelier's Principle.
2. Use this principle to predict what would happen to the electrode potential if the copper (II) ion solution was much more dilute.
3. Use any relevant document to explain clearly the effect of concentration on the electromotive force of the cell.

We have seen that voltaic cells are based on redox reactions which are "spontaneous". We have also seen how the reduction potential (emf) of a cell is calculated when the reactants and products are under standard conditions. However, as a voltaic cell is discharged, the reactants of the reaction are consumed and the products are generated, so the concentrations of these substances change.

The emf progressively drops until E = 0, at which point we say the cell is "dead". At that point the concentrations of the reactants and products cease to change; they are at equilibrium.

In this section we will examine how the cell emf depends on the concentrations of the reactants and products of the cell reaction. The emf generated under non-standard conditions can be calculated by using an equation first derived by Walther Nernst (1864-1941), a German chemist who established many of the theoretical foundations of electrochemistry.

12.4.1. The Nernst equation

The dependence of the cell emf on concentration can be obtained from the dependence of the free-energy change on concentration. Recall that the free-energy change, ΔG, is related to the standard free-energy change, ΔG^o:

$$\Delta G = \Delta G^0 + RT \ln Q$$

The quantity Q is the reaction quotient, which has the form of the equilibrium constant expression except that the concentrations are those that exist in the reaction mixture at a given moment.

Substituting ΔG = - nFE into equation above gives:

$$-nFE = -nFE^0 + RT\ln Q$$

Solving this equation for E gives the Nernst equation:

$$E = E^0 - \frac{RT}{nF}\ln Q$$

This equation is customarily expressed in terms of common (base 10) logarithms:

$$E = E^0 - \frac{2.303RT}{nF}\log Q$$

At T = 298 K the quantity 2.303 RT/F equals 0.0592 V, so the equation simplifies to:

$$E = E^0 - \frac{0.0592V}{n}\log Q \qquad \text{(T = 298 K)}$$

We can use this equation to find the emf produced by a cell under non-standard conditions or to determine the concentration of a reactant or product by measuring the emf of the cell.

As an example of how the equation above might be used, consider the following reaction:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

In this case n = 2 (two electrons are transferred from Zn to Cu^{2+}), and the standard emf is +1.10 V. Thus, at 298 K the Nernst equation gives:

$$E = 1.10V - \frac{0.0592V}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Recall that pure solids are excluded from the expression for Q. From the above equation, it is evident that the emf increases as $[Cu^{2+}]$ increases and as $[Zn^{2+}]$ decreases.

For example, when $[Cu^{2+}]$ is 5.0 M and $[Zn^{2+}]$ is 0.050 M, we have

$$E = 1.10V - \frac{0.0592V}{2}\log\left(\frac{0.050}{5.0}\right)$$

$$= 1.10V - \frac{0.0592V}{2}(-2.00) = 1.16V$$

Notice that we have increased the concentration of the reactant (Cu^{2+}) and decreased the concentration of the product (Zn^{2+}) relative to standard conditions. These concentration changes increase the emf of the cell (***E* = + 1.16 V**) relative to standard conditions (***E°* = + 1.10 V**). We could have anticipated this result by applying ***LeChâtelier's principle***.

In general,

- If the concentrations of reactants increase relative to those of products, the cell reaction becomes more spontaneous and the emf increases.
- If the concentrations of products increase relative to reactants, the emf decreases. As voltaic cell operates, reactants are converted into products and this increases the value of Q and causes the emf to decrease.

Worked Example

Calculate the emf at 298 K generated by the cell described by the following equation when $[Cr_2O_7^{2-}]$ = 2.0 *M*, $[H^+]$ = 1.0 *M*, $[I^-]$ = 1.0 *M*, and $[Cr^{3+}]$ = 1.0 x 10^{-5} *M:*

$$Cr_2O_7^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + 6I^-{}_{(aq)} \rightarrow 2Cr^{3+}{}_{(aq)} + 3I_{2(s)} + 7H_2O_{(l)}$$

Solution:

The standard emf for this reaction was calculated to be $E°$ = 0.79 V and, n = 6. The reaction quotient, ***Q***, is:

$$Q = \frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}[I^-]^6} = \frac{(1.0\times10^{-5})^2}{(2.0)(1.0)^{14}(1.0)^6} = 5.0\times10^{-11}$$

Thus, we have:

$$E = 0.79V - \frac{0.0592V}{6}\log(5.0\times10^{-11})$$
$$= 0.79V - \frac{0.0592V}{6}(-10.30)$$
$$= 0.79V + 0.10V = 0.89V$$

This result is qualitatively what we expect: Because the concentration of $Cr_2O_7^{2-}$ (a reactant) is above 1 M and the concentration of Cr^{3+} (a product) is below 1 M, the emf is greater than E°.

12.4.2. Concentration cells

In each of the voltaic cells that we have looked at before, the reactive species at the anode has been different from the one at the cathode. However, the fact that cell emf depends on concentration means that a voltaic cell with a non-zero emf can be

constructed using the same species in both the anode and cathode compartments as long as the concentrations are different. This is thus "the concentration cell". A concentration cell is "a cell based solely on the emf generated because of a difference in concentrations".

Consider the cell shown in the following figure:

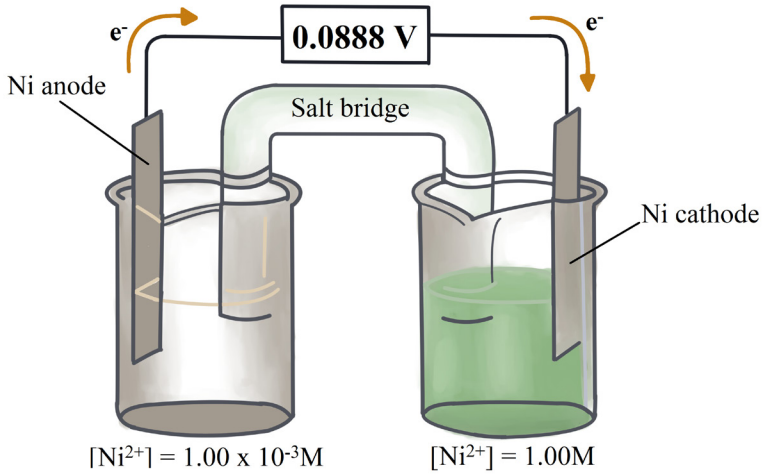


Figure 12.6: A concentration cell based on the Ni^{2+}—Ni cell reaction.

- One compartment consists of a strip of nickel metal immersed in a 1.00 *M* solution of $Ni^{2+}(aq)$.
- The other compartment also has a Ni*(s)* electrode, but immersed in a 1.00 x 10^{-3} *M* solution of $Ni^{2+}(aq)$.

The two compartments are connected by a salt bridge and by an external wire with a voltmeter. The half-cell reactions are the reverse of one another:

Anode: $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^{-} \qquad E^{0}_{Red} = -0.28V$

Cathode: $Ni^{2+}(s) + 2e^{-} \rightarrow Ni(s) \qquad E^{0}_{Red} = -0.28V$

It is apparent that the *standard* emf for this cell is zero:

$$E^{0}_{Cell} = E^{0}_{Red}(cathode) - E^{0}_{Red}(anode) = (-0.28\ V) - (-0.28\ V) = \mathbf{0.00\ V}.$$

But this cell operates under non-standard conditions because of the difference in concentration of Ni^{2+}(aq) in the two compartments.

In fact, the driving force for the cell is provided by the difference in concentration: Operation of the cell tends to equalize the concentrations of Ni^{2+} in both compartments. Thus,

- The compartment with the more dilute solution will be the anode compartment; oxidation of Ni(s) at the anode increases the concentration of $Ni^{2+}(aq)$ in the more dilute solution.
- The compartment with the more concentrated solution will be the cathode compartment, for the reduction of $Ni^{2+}(aq)$ at the cathode decreases the concentration of $Ni^{2+}(aq)$ in that compartment.

The overall cell reaction is therefore:

Anode:	$Ni(s) \rightarrow Ni^{2+}(aq;dilute) + 2e^-$	**Oxidation**
Cathode:	$Ni^{2+}(aq;concentrated) + 2e^- \rightarrow Ni(s)$	**Reduction**
Overall:	$Ni^{2+}(aq;concentrated) \rightarrow Ni^{2+}(aq;dilute)$	

We can calculate the emf of a concentration cell by using the Nernst equation. For this particular cell we see that ***n* = 2.** We also see that the expression for the reaction quotient for the overall reaction is $\mathbf{Q = [Ni^{2+}]_{dilute} / [Ni^{2+}]_{concentrated}}$.

We can calculate the emf at 298 K by the following Nernst Equation:

$$E = E^0 - \frac{0.0592}{n}\log Q$$

$$= 0 - \frac{0.0592}{2}\log\frac{[Ni^{2+}]_{dilute}}{[Ni^{2+}]_{concentrated}} = -\frac{0.0592}{2}\log\frac{1.00\times10^{-3}\,M}{1.00M}$$

$$= +0.0888V$$

This concentration cell generates an emf of nearly 0.09 V even though $E^0 = 0$ for the cell.

The difference in concentration provides the driving force for the cell. As the cell operates the concentration of the dilute solution in the anode compartment increases and that of the concentrated solution in the cathode compartment decreases.

When the concentrations in the two compartments become the same (at equilibrium), the value of Q = 1 and E = 0

The idea of generating a potential by a difference in concentration is the basis for the operation of pH meters. It is also a critical aspect in the regulation of the heartbeat in mammals.

Worked example

A voltaic cell is constructed with two hydrogen electrodes. Electrode 1 has a pressure

of hydrogen (p_{H_2}) = 1.0 atm and an unknown concentration of $H^+(aq)$. Electrode 2 is a standard hydrogen electrode ($[H^+]$ = 1.00 M, p_{H_2} = 1.0 atm). At 298 K, the cell voltage is measured to be 0.211 V and the electrical current is observed to flow from electrode 1 through the external circuit to electrode 2. What is $[H^+]$ for the solution in electrode 1? What is its pH?

Solution

The fact that current flows from electrode 1 to electrode 2 tells us that electrode 1 is the anode of the cell and electrode 2 is the cathode. The electrode reactions are therefore as follows, with the concentration of $H^+(aq)$ in electrode 1 represented with the unknown ***x***:

$$\textbf{\textit{Electrode 1:}} \quad H_2(g;1.00atm) \rightarrow 2H^+(aq;xM) + 2e^- \qquad E^0_{Red} = 0.V$$

$$\textbf{\textit{Electrode 2:}} \quad 2H^+(aq;1.00M) + 2e^- \rightarrow 2H_2(g;1.00atm) \qquad E^0_{Red} = 0.V$$

Because E^0_{Red} is the same for both half-cells, $E^0_{Cell} = 0.0\ V$; **this is a concentration cell**. We recognize that ***n* = 2** for the cell and that the reaction quotient for the overall reaction is given by:

$$Q = \frac{[H^+(electrode1)]^2\, p_{H_2}(electrode2)}{[H^+(electrode2)]^2\, p_{H_2}(electrode1)}$$

$$= \frac{x^2(1.0\ )}{(1.0\ )^2(1.0\ )} = x^2$$

We can solve for the value of ***x*** as follows:

$$E = E^0 - \frac{0.0592}{n}\log Q$$

$$0.211 = 0 - \frac{0.0592}{2}\log x^2 = -\frac{0.0592}{2}(2\log x) = -0.0592\log x$$

$$\log x = \frac{(0.211)}{(-0.0592)} = -3.56$$

$$x = 10^{-3.56} = 2.8\times10^{-4}M$$

Thus, in electrode 1 $[H^+]$ = 2.8 x 10^{-4} M. The concentration of H^+ in electrode 1 is lower than that in electrode 2, which is why electrode 1 is the anode of the cell: The oxidation of H_2 to $H^+(aq)$ increases $[H^+]$ in electrode 1. We essentially calculated the pH of the solution while we were solving the problem: pH = -log(2.8 x 10^{-4}) = 3.56

12.4.3. Cell Electromotive Force (EMF) and chemical equilibrium

The Nernst equation helps us understand why the emf of a voltaic cell drops as it is discharged: As reactants are converted to products, the value of Q increases, so the value of E decreases. The cell emf eventually reaches E = 0. Because ΔG = -nFE, it follows that ΔG = 0 when E = 0.

Recall that a system is at equilibrium when $\Delta G = 0$. Thus, when $E = 0$, the cell reaction has reached equilibrium; no net reaction is occurring in the voltaic cell.

At equilibrium the reaction quotient equals the equilibrium constant: $Q = K$ at equilibrium. Substituting $E = 0$ and $Q = K$ into the Nernst equation gives:

$$0 = E^0 - \frac{RT}{nF} \ln K$$

At 298 K this equation simplifies to:

$$0 = E^0 - \frac{0.0592}{n} \log K \qquad (T = 298\ K)$$

Which can be rearranged to give:

$$\log K = \frac{nE^0}{0.0592} \qquad (T = 298\ K)$$

This useful equation tells us that the equilibrium constant for a redox reaction can be obtained from the value of the standard emf for the reaction.

Worked examples

Calculate the equilibrium constant K, from the following reaction studied at a temperature of 298 K: $Zn^{2+} + Cu \rightarrow Cu^{2+} + Zn$ $E^o = 1.10$ V $\ln K = nFE^oRT$

In this question, 2 moles of electrons are being transferred, F is 96485 Coulombs/mole, R is 8.31Joules K×mole, T is 298 K, and E^o is 1.10 Joules/Coulomb.

Plugging the values into the equation, we get:

ln K = 2×96485×1.10x8.31×298

ln K= 85.7

Solving for K, we get:

$K = e^{85.7}$

$K = 1.68 \times 10^{37}$

This is a particularly high equilibrium constant value, indicating that the equilibrium strongly favors the formation of products (the reaction is effectively irreversible towards the formation of products).

Using the standard reduction potentials (listed in the table 12.3), calculate the equilibrium constant for the oxidation of Fe^{2+} by O_2 in acidic solution, according to the following reaction:

$$O_2\,(g) + 4H^+\,(aq) + 4Fe^{2+}\,(aq) \longrightarrow 4Fe^{3+}\,(aq) + 2H_2O\,(l)$$

Solution:

We observe that O_2 is reduced and Fe^{2+} is oxidized in the reaction. We can determine *E°* in the usual way:

Reduction: $O_2\,(g) + 4H^+\,(g) + 4e^- \longrightarrow 2H_2O\,(l)$ $\quad E^0_{Red}=+1.23V$

Oxidation: $4E^{2+}\,(g) + 4E^{3+}(g$ $\qquad\qquad\qquad\qquad$ $E^0_{Red}=+0.77V$

Thus, E° = (1.23 V) - (0.77 V) = 0.46 V, and n = 4. We have:

$$\log K = \frac{nE^0}{0.0592V} = \frac{4(0.46V)}{0.0592V} = 31$$

$$K = 10^{31}$$

The large magnitude of ***K*** like this (**10^{31}**) indicates that Fe^{2+} ions are unstable in acidic solutions in the presence of O_2 (unless a suitable reducing agent is present).

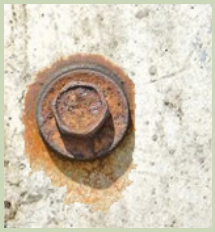
Checking up 12.4

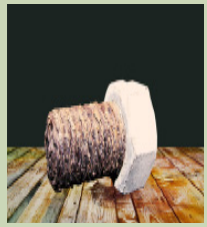
1. A concentration cell is constructed with two Zn(s) $\longrightarrow$ Zn^{2+}(aq) half-cells. The first cell has $[Zn^{2+}]$ = 1.35 M and the second cell has $[Zn^{2+}] = 3.75 \times 10^{-4}$ M.
    a. Which half-cell is the anode of the cell?
    b. What is the emf of the cell?
2. Using standard reduction potentials, calculate the equilibrium constant at 25°C for the reaction: $Br_2(l) + 2Cl^-(aq) \longrightarrow Cl_2\,(g) + 2Br^-(aq)$
3. If the voltage of a Zn-H^+ cell is 0.45 V at 25°C when $[Zn^{2+}]$ = 1.0 *M* and p_{H_2} = 1.0 atm, what is the concentration of H^+?

12.5. Explanation of corrosion and its effects on metallic objects

Activity 12.5

We have seen old metal materials with brown colour coating on their surfaces. Some metal materials are shown here below.





1. we usually call this rust, what is the other name given to this phenomenon?
2. How do metal objects cover themselves with this coat?
3. Suggest some effects of this phenomenon on the metallic objects.

Corrosion is defined as "the degradation of materials by chemical reaction with the environment in which the material resides". This is because of metal oxidation. As metals have a tendency to return to their natural state, it is a natural process which produces either salt or oxides. It requires four elements - anode, cathode, an electrolyte, and a metallic path.

12.5.1. Explanation of metal corrosion

In general, metals have tendency to lose electrons and convert into metal cations through metal oxidation reaction. Metal corrosion is the main cause of metal destruction, like steel rusts due to immersion in seawater. Similarly iron reacts with oxygen to form rust by exposure to moist air, thus the main conditions for rusting are oxygen and water (moisture or humidity).

The most common corrosion process is the rusting of iron which is an electrochemical process. Iron rust is iron oxide $Fe_2O_3 \cdot XH_2O$ where X is the amount of water of hydration which can vary. It shows the colour of rust (yellow-brown).

It is a very complex process which is completed in the following steps.

1. First the iron gets oxidized into ferrous ions [Fe (II)] with the loss of two electrons.

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2\ e^-$$

2. The electrons are conducted through the iron to the cathode where water and oxygen are reduced to OH^-

$$O_2(g) + 2\,H_2O(l) + 4\,e^- \rightarrow 4\,OH^-(aq)$$

3. The ferrous ions [Fe(II)] and the $OH^-(aq)$ ions diffuse from their respective poles and get deposited as iron (II) hydroxide.

$$Fe^{2+}(aq) + 2\,OH^-(aq) \rightarrow Fe(OH)_2(s)$$

4. The iron (II) hydroxide is then oxidised by air to iron (III) hydroxide which is then converted into rust.

$$4\,Fe(OH)_2(s) + O_2(aq) + 2\,H_2O(l) \rightarrow 4\,Fe(OH)_3(s)$$

$$2\,Fe(OH)_3(s) \rightarrow Fe_2O_3.XH_2O(s) + (3\text{-}x)\,H_2O(l)$$

The complete chemical reaction for rust formation is shown below.

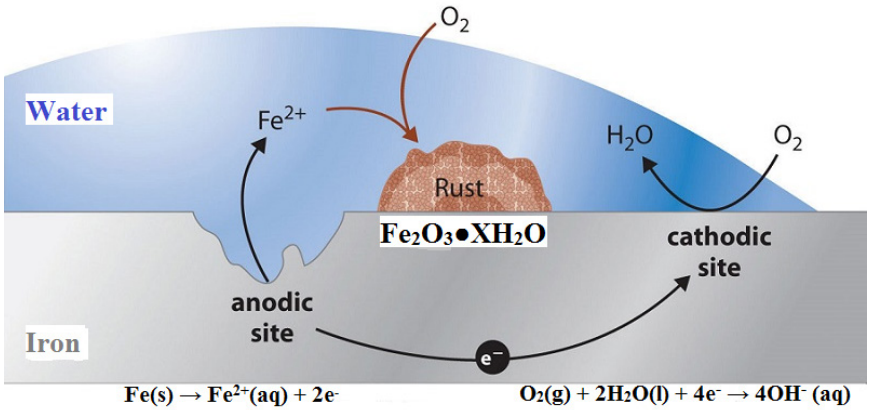


Figure 12.7: Mechanism for the rusting process

The mechanism for the rusting process is similar to the electrochemical cell. The electrons formed during the oxidation of iron are conducted through the metal. Thus, the iron ions diffuse from the water layer to the metal surface where oxygen is present.

This is an electrochemical cell where iron acts as the anode and oxygen gas as the cathode. The aqueous solution of ions behaves like a "salt bridge" as shown in the figure above.

Some of the noble and non-reactive metals like gold, platinum do not react with atmospheric oxygen and do not corrode.

Iron rusts faster under the following circumstances:

- At elevated temperature
- Presence of dissolved electrolytes (especially salts)
- Iron in contact with a less electropositive element (where there are defaults); this is why corrosion accelerates at the contact point of two different metals because it undergoes oxidation.

The presence of salt enhances the conductivity of the aqueous solution formed at the surface of the metal. So the rusting of iron and steel is completed rapidly near the ocean (salty) or with salt.

For instance, in cold countries where the operations of road de-icing are done by spreading salt on the roads, corrosion of car bodies is accelerated.

12.5.2. Harmful effect of corrosion

There are many harmful effects of corrosion. Some of them are listed below.

- The loss of metallic object efficiency
- The product is contaminated by these new impurities.
- Metallic equipments are damaged.
- Accidents due to damage of metallic bridges, cars, aircrafts, etc.
- Pollution due to products from corrosion
- Depletion of natural resources (metals)
- Loss of valuable materials such as blockage of pipes, mechanical damage of underground water pipes, etc.

12.5.3. Protection against corrosion

Since corrosion deteriorate the physical and chemical properties of metals, therefore we always try to protect metal surfaces against corrosion to make the material corrosion resistant.

The common example well known is to use ***anti-rust paints*** which is a physical isolation of the protected surface from contact with oxygen (air) and water.

There are other various ways to protect against corrosion such that:

- **Active corrosion protection:** Developing corrosion-resistant alloys, addition of inhibitors, etc.
- **Passive corrosion protection:** Coating by protective layer or film.
- **Permanent corrosion protection:** Electroplating (like tin plating or copper plating), Galvanization, etc.
- **Temporary corrosion protection:** Anodisation or protective coating.

Galvanisation is the process where the surface of iron is coated with a layer of zinc. Here the zinc acts as the sacrificial anode and undergoes oxidation instead of iron. This method is also called "cathodic protection".

Anodisation is a method of increasing the corrosion resistance of a metal part by forming a layer of oxide on its surface. The part that is being treated forms the anode electrode of an electrical circuit.

Checking up 12.5

The rusting of iron is an electrochemical process. Different regions of the iron act as cathodes and anodes.

a. Write the equation for the reaction of iron at an anodic region.

b. Write the equation for the reaction of oxygen at a cathodic region.

c. Why does the presence of sodium chloride accelerate rusting?

d. Which of the following metals could be used for sacrificial protection of iron: zinc, nickel, tin, magnesium, lead? Explain your answer.

12.6. Applications of electrochemical cells: batteries (dry cells, storage batteries and fuel cells)

Activity 12.6

Electrochemical cells have very important daily applications. Some applications can be illustrated by the following images.

1. Use the images above to describe the main application of electrochemical cells.
2. Use any documents or search engine to answer the following questions.
   a. How do electrochemical cells like simple batteries work?
   b. How do the following work?
      i. Leclanché dry cell
      ii. Alkaline battery
      iii. Mercury cell
      iv. Lead-storage battery
      v. Nickel-cadmium battery
      vi. Lithium ion battery
3. Try to give some explanations of the types of electrochemical cells - primary cells, secondary cells, fuel cells, rechargeable cells and non-rechargeable cells.

Electrochemistry has a number of different uses, particularly in industry. The principles of cells are used to make **electrical batteries**. In science and technology, a battery is a device that stores chemical energy and makes it available in an electrical form. Batteries are made of electrochemical devices such as one or more galvanic cells or fuel cells.

The importance of electrochemical cells or galvanic cells lies in their ability to provide us with a portable source of electrical energy. We have already studied that redox reaction is, primarily, the basis of all the electrochemical cells. Quite often, we use the term "battery" to represent the arrangement of two or more galvanic cells connected in series.

Batteries have many uses including in:

- Torches
- Electrical appliances such as cellphones (long-life alkaline batteries)
- Digital cameras (lithium batteries)
- Hearing aids (silver-oxide batteries)
- Digital watches (mercury/silver-oxide batteries)
- Military applications (thermal batteries)

The galvanic cells can be broadly classified into two categories, namely; primary cells and secondary cells. Here we add also fuel cells.

12.6.1. Primary cells

This type of cells becomes dead over a period of time and the chemical reaction stops. They cannot be recharged or used again. Some common examples are dry cell, mercury cell, etc.

a. DRY CELL

It is a compact form of Leclanché cell known after its inventor, a French chemist, G. Leclanché. In this cell, anode consists of zinc container while cathode is a graphite rod surrounded by powdered MnO_2 and carbon. The space between the electrodes is filled with the paste of NH_4Cl and $ZnCl_2$ (which is the electrolyte).

The arrangement is shown in the figure below.

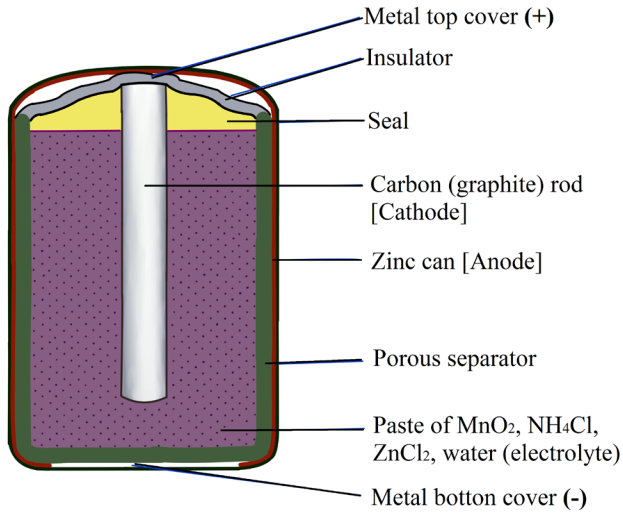


Figure 12.8: Leclanché Dry Cell

The reactions taking place at the electrodes are given in their simplified form as follows:

- ***Cathode:*** $\mathbf{2\ MnO_2(s) + H_2(g) \rightarrow Mn_2O_3(s) + H_2O(l)}$

$$\mathbf{2\ NH_4^+(aq) + 2e^- \rightarrow 2NH_3(g) + H_2(g)}$$

- ***Anode:*** $\mathbf{Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-}$

The zinc ions (Zn^{2+}) so produced combine with ammonia liberated in cathodic reaction to form diammine zinc (II) cation.

$$\mathbf{Zn^{2+}(aq) + 2NH_3(g) \rightarrow [Zn(NH_3)_2]^{2+}(aq)}$$

Dry cells do not have long life as NH_4Cl which is acidic, corrodes the zinc container even if the cell is not in use. The cell potential of dry cells lies in the range **1.25 V** to **1. 5 V.**

b. ALKALINE BATTERIES

Alkaline batteries were developed in the 1950s partly to address some of the performance issues with zinc–carbon dry cells. They are manufactured to be exact replacements for zinc-carbon dry cells. As their name suggests, these types of batteries use alkaline electrolytes.

They consist of Zn powder in the center of the pile as anode and MnO_2 + graphite as cathode. Everything is contained in a steel housing. NH_4Cl is replaced by a solution of about 7 M of KOH, hence the term "alkaline".

The reactions are:

- **Anode: $Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^-$**
- **Cathode: $MnO_2(s) + 2H_2O(l) + 2e^- \rightarrow Mn(OH)_2(s) + 2OH^-(aq)$**

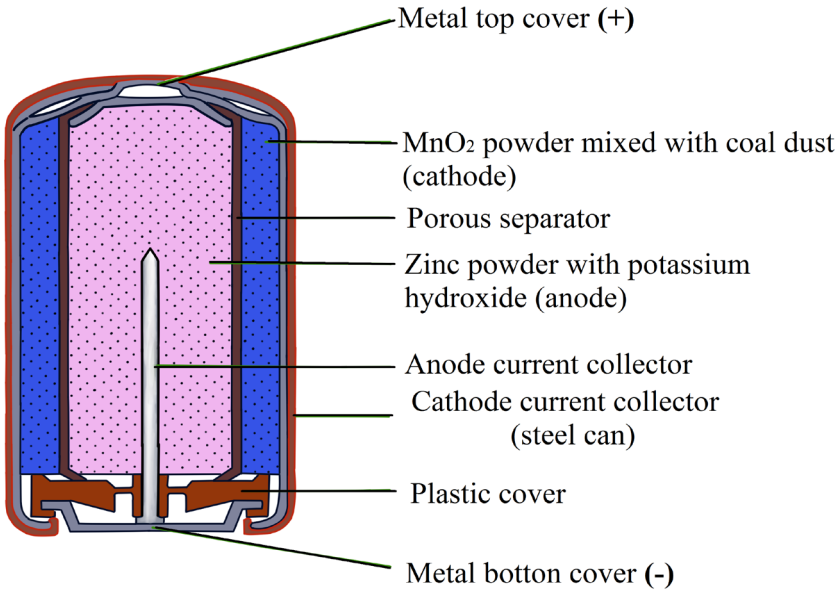


Figure 12.9.: Alikaline battery

Alkaline cells last long than ordinary dry cell. They have a longer shelf life and can be kept in service longer. An alkaline cell has NaOH or KOH in place of NH_4Cl as the electrolyte. It uses essentially the same reduction half-cell reaction as the ordinary dry cell, but in alkaline medium.

Alkaline cells develop a voltage of **1.5 V** as Leclanché cells but have advantage over dry cell.

Attempts to recharge an alkaline battery often lead to rupture of the battery and leakage of the potassium hydroxide electrolyte (this is because it is not rechargeable).

Advantages over the dry cell battery:

- It is more waterproof
- A longer life because it contains more reagents.
- The voltage does not drop rapidly when current is drawn. This is because the concentration of zinc ion does not build up at the anode and the pH remains more nearly constant at cathode.

c. MERCURY CELL

It is miniature cell (used in shape of button cell) which finds a frequent use these days to supply energy for watches, video cameras, hearing aids and other compact

devices. In mercury cell the anode is zinc-mercury amalgam and the cathode is a paste of mercury (II) oxide and carbon. Electrolyte is a moist paste of KOH-ZnO. The arrangement in its simple form is shown in figure below.

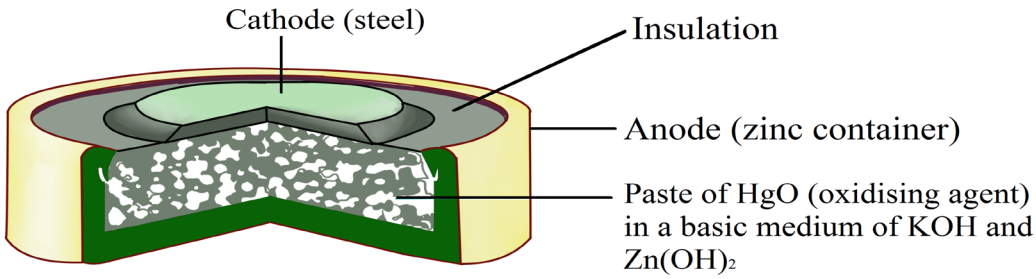


Figure 12.10: Mercury cell

This battery works on the same principle as the *alkaline battery*. The HgO or Ag_2O replaces the MnO_2.

The reactions are:

- **Anode: Zn/Hg *(Amalgam)* + 2 OH^- → ZnO(s) + H_2O(l) + 2 e^-**
- **Cathode: HgO(s) + H_2O(l) + 2 e^- → Hg(l) + 2 OH^-**
- **Overall reaction: Zn/Hg *(Amalgam)* + HgO → ZnO(s) + Hg(l)**

This battery provides a potential difference of 1.35V. Its dimensions are very small and it lasts longer. It contains mercury, which is very toxic (it can be replaced by silver).

12.6.2. Secondary cells

This type of cells can be recharged by passing direct current through them and can be used again and again. These are the types of batteries found in devices such as smart phones, electronic tablets, and automobiles. Some examples are lead-storage battery, nickel-cadmium storage cell, etc.

a. LEAD-STORAGE BATTERY

It is the most frequently used battery in automobiles. It consists of six voltaic cells connected in series. In each cell anode is made of spongy lead and cathode 'is a grid of lead packed with lead dioxide (PbO_2). The lead storage batteries are made of alternating lead electrodes on the one hand, and lead coated PbO_2 on the other. The electrolyte is the aqueous solution of 3M sulphuric acid (38% by mass).

These batteries provide a constant emf of about 12 V. Invented in 1859 by *Gaston Planté*, the lead-acid storage battery is still widely used in cars, trucks, and airplanes. The storage battery consists of a group of cells connected together in series. Each cell consists of a ***lead plate, a lead oxide plate, and an electrolytic solution of***

sulphuric acid.

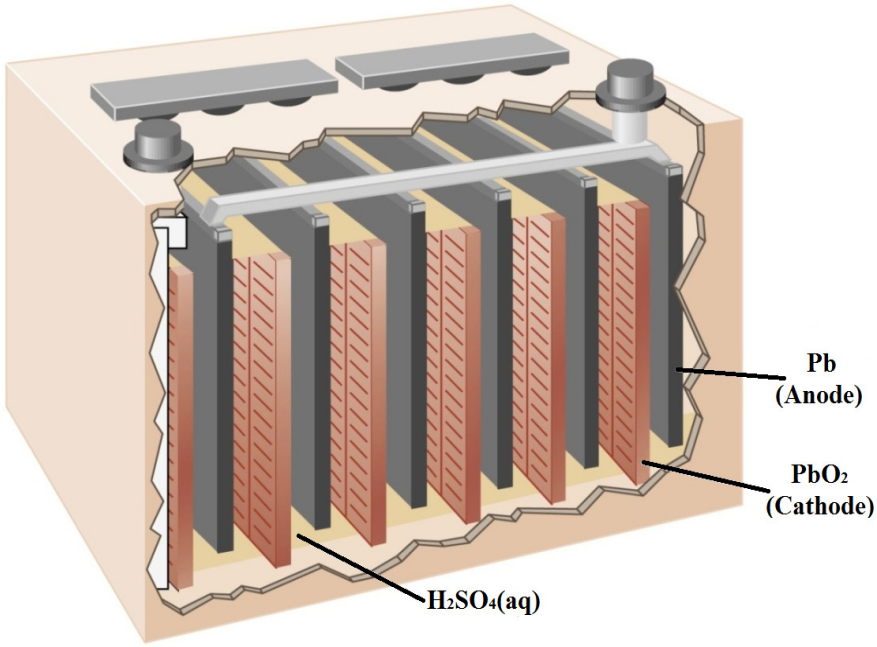


Figure 12.11: Lead storage battery

When these types of batteries run down, they can be recharged by forcing current through the battery in the direction opposite the direction the current flows when the battery is fully charged.

The following reactions occur:

i. Operation during discharge (cell phenomenon):

- Anode (Pb) : $Pb + SO_4^{2-} \rightarrow PbSO_4$
- Cathode (PbO_2) : $PbO_2 + SO_4^{2-} + 4\,H^+ + 2\,e^- \rightarrow PbSO_4 + 2\,H_2O$

- Overall reaction: $Pb + PbO_2 + 2\,H_2SO_4 \rightarrow 2\,PbSO_4 + 2\,H_2O$
  Sulphuric acid is consumed.

ii. Operation when charging (electrolysis phenomenon):

- Anode (Pb) : $\mathbf{PbSO_4 + 2\,H_2O - 2e^- \rightarrow PbO_2 + SO_4^{2-} + 4\,H^+}$
- Cathode (PbO_2) : $\mathbf{PbSO_4 + 2\,e^- \rightarrow Pb + SO_4^{2-}}$

- **Overall reaction: $2\,PbSO_4 + 2\,H_2O \rightarrow Pb + PbO_2 + 2\,H_2SO_4$**

Sulphuric acid is generated

Note: When all of the ***Pb or PbO_2*** is converted to ***$PbSO_4$***, the battery is depleted. But by the electric current, the reaction ***changes direction*** and the battery is charging.

Each cell produces 2 V, so six cells are connected in series to produce a 12-V car battery. Lead acid batteries are heavy and contain a caustic liquid electrolyte, but are often still the battery of choice because of their high current density. Since these batteries contain a significant amount of lead, they must always be disposed of properly.

Their low cost and high current output makes these excellent candidates for providing power for automobile starter motors.

b. NICKEL-CADMIUM STORAGE CELL

The nickel-cadmium (known as **"Nicad"**) battery is another common secondary battery that is suited for low-temperature conditions with a long shelf life. However, their capacity in terms of watt-hours per kilogram is less than that of the nickel-zinc rechargeable batteries.

The anode is made of nickel oxyhydroxide coated by $Ni(OH)_2$ and the cathode of iron or cadmium-covered by $Fe(OH)_2$ or $Cd(OH)_2$ respectively. The electrolyte is a concentrated solution of KOH.

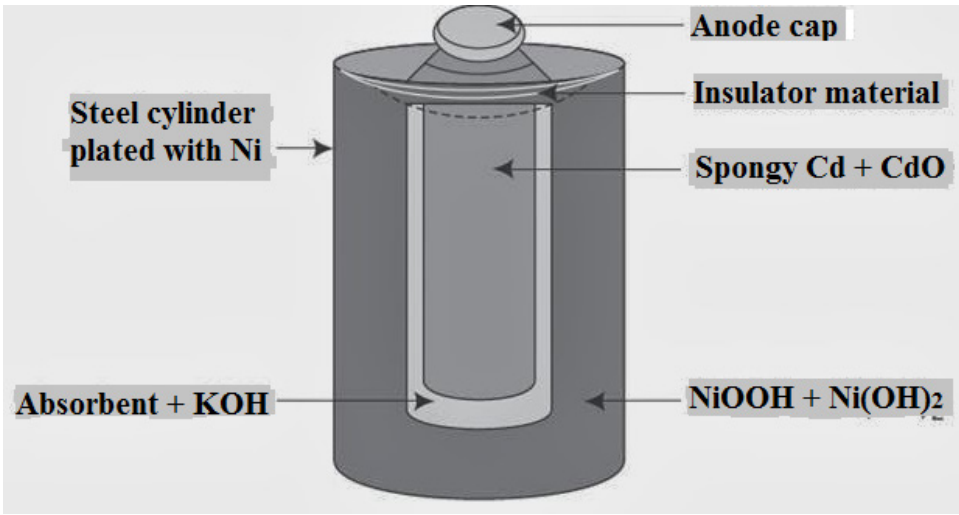


Figure 12.12: A Nickel-Cadmium cell

The reactions are:

- **Operation during discharge:**
  - Anode : $Cd(s) + 2\ OH^-(aq) \rightarrow Cd(OH)_2(s) + 2\ e^-$
  - or **$Fe(s) + 2\ OH^-(aq) \rightarrow Fe(OH)_2(s) + 2\ e^-$**
  - **Cathode: $2\ NiO(OH)(s) + 2\ H_2O(l) + 2\ e^- \rightarrow 2\ Ni(OH)_2(s) + 2\ OH{-}(aq)$**
  - **Overall: $Cd(s) + 2\ NiO(OH)(s) + 2\ H_2O(l) \rightarrow Cd(OH)_2(s) + 2\ Ni(OH)_2(s)$**

- **While charging, the opposite phenomena take place.**

- **Anode : $Cd(OH)_2(s) + 2\ e- \rightarrow Cd(s) + 2\ OH^-(aq)$**
- **Cathode: $2\ Ni(OH)_2(s) + 2OH^-(aq) \rightarrow 2\ NiO(OH)(s) + 2\ H_2O(l) + 2\ e-$**
- **Overall: $Cd(OH)_2(s) + 2\ Ni(OH)_2(s) \rightarrow Cd(s) + 2\ NiO(OH)(s) + 2\ H_2O(l)$**

These batteries provide an emf: **1.42 V** (Fe-Ni) or **1.31 V** (Ni-Cd). The cell is also called **nicad cell**. As is evident, there are no gaseous products, the products formed adhere to the electrodes and can be reconverted by recharging process. This cell is becoming more popular these days and finds use in electronic watches and calculators.

Advantages of the nickel-zinc battery are its long life span, high voltage, and the sufficient energy to mass to volume ratio.

c. LITHIUM ION BATTERIES

Lithium ion batteries are among the most popular rechargeable batteries and are used in many portable electronic devices. The most common lithium-ion cells have an anode of graphite carbon (C) and a cathode of lithium cobalt oxide ($LiCoO_2$). The electrolyte is lithium perchlorate ($LiClO_4$).

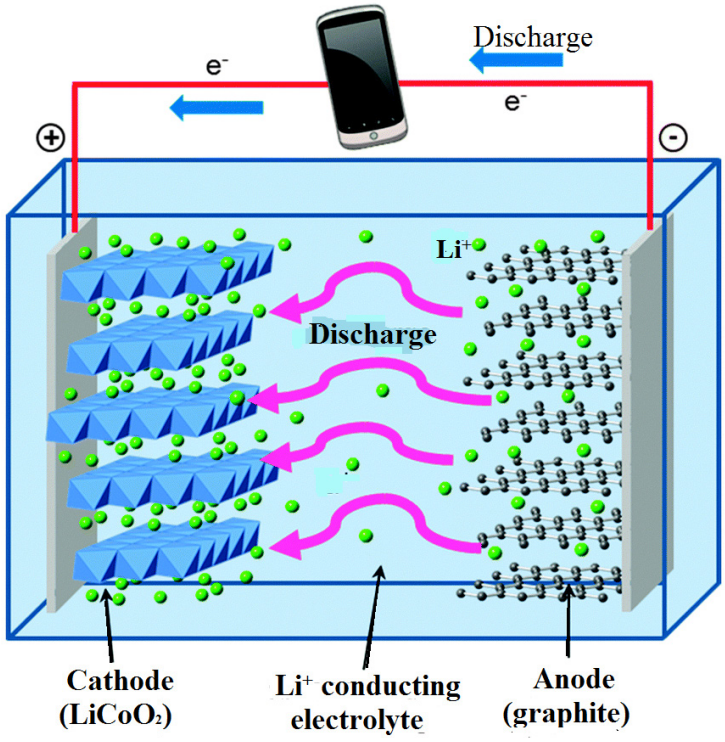


Figure 12.13: Lithium ion battery

- **During discharge**

At the anode, lithium is oxidised. Lithium ions are released from the carbon, along

with electrons: $\mathbf{LiC_6 \rightarrow Li^+ + e^- + 6\ C}$

At the cathode, lithium-ions are absorbed by the lithium dioxide, and the electrode is reduced as it also receives the electrons from the circuit:

$\mathbf{CoO_2 + Li^+ + e^- \rightarrow LiCoO_2}$

The overall reaction is: $\mathbf{LiC_6 + CoO_2 \rightleftharpoons 6\ C + LiCoO_2}$

The structure of $\mathbf{LiC_6}$ involves lithium inserted (intercalated) between the layers of graphite.

- **During recharge**

The opposite action occurs.

In a lithium ion battery, charge flows between the electrodes as the lithium ions move between the anode and cathode. The battery voltage is about **3.7 V**.

Lithium batteries are popular because they can provide a large amount current, are lighter than comparable batteries of other types, produce a nearly constant voltage as they discharge, and only slowly lose their charge when stored.

12.6.3. Fuel cells

Fuel cells work like batteries but they do not run down or need recharging. They produce electricity and heat as long as fuel is supplied. A fuel cell consists of two electrodes: a negative electrode (or anode) and a positive electrode (or cathode) sandwiched around an electrolyte. A fuel, such as hydrogen, is fed to the anode, and air (oxygen) is fed to the cathode.

The anode is porous graphite coated with nickel, the cathode is porous graphite coated nickel and nickel (II) oxide and potassium hydroxide solution is used as electrolyte.

The reactions involved in a fuel cell are as follows:

Anode side (an oxidation reaction): $\mathbf{H_2\ (g) + 2\ OH^-(aq) \rightarrow 2\ H_2O\ (l) + 2\ e^-}$

Cathode side (a reduction reaction): $\mathbf{O_2\ (g) + 2\ H_2O(l) + 4\ e^- \rightarrow 4\ OH^-(aq)}$

Net reaction (the "redox" reaction): $\mathbf{2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)}$

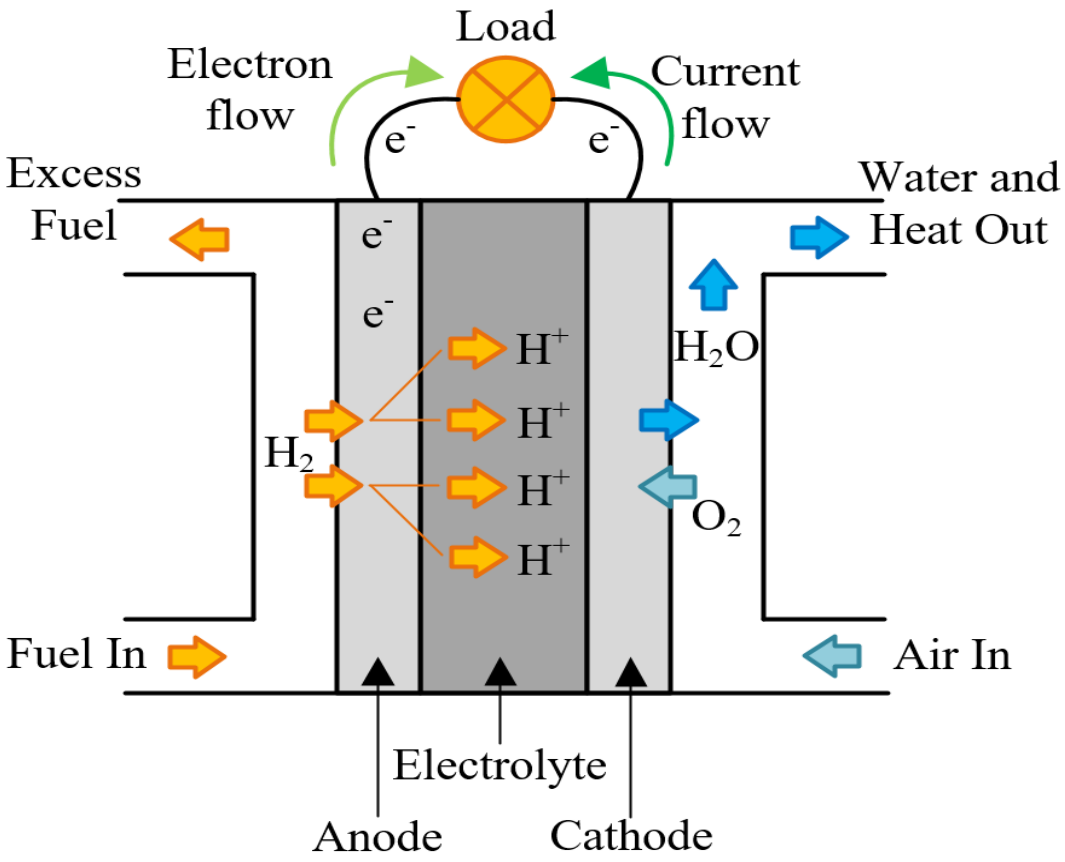


Figure 12.14: Hydrogen fuel cell

In a hydrogen fuel cell, a catalyst at the anode separates hydrogen molecules into protons and electrons, which take different paths to the cathode. The electrons go through an external circuit, creating a flow of electricity. The protons migrate through the electrolyte to the cathode, where they unite with oxygen and the electrons to produce (drinking) water and heat.

Platinum and platinum alloys (like Platinum-Ruthenium) are the most efficient catalysts for speeding up chemical reactions in hydrogen fuel cells.

The reaction in a single fuel cell typically produces only about 0.7 volts. Therefore, fuel cells are usually stacked or connected in some way to form a fuel cell system that can be used in cars, generators, or other products that require power.

Checking up 12.6

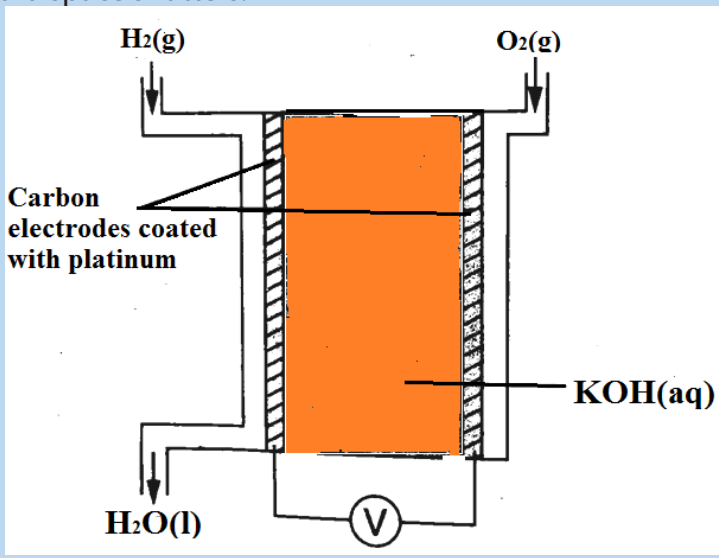
1. A lead-acid battery (car battery) consists of six cells that can provide about 12 V. The half-reactions that take place in each cell and their respective standard reduction potentials are represented below:

$PbSO_4(s) + H^+(aq) + 2e^- \rightarrow Pb(s) + HSO_4^-(aq)$ $\quad E^0 = -0.36\ V$

$PbO_2(s) + HSO_4^-(aq) + 3\ H^+(aq) + 2\ e^- \rightarrow PbSO_4(s) + 2\ H_2O(l)$ $\quad E^0 = +1.7\ V$

   a. Are car batteries primary or secondary batteries? Explain.
   b. Write down the equation for the net (overall) cell reaction that takes place in each cell of this battery.
   c. Calculate the emf of the battery, consisting of six cells, under standard conditions.
   d. State two environmental risks associated with the irresponsible disposal of lead-acid batteries.

2. The following is a simplified diagram for the hydrogen fuel cell used onboard space shutters.



   a. The reaction at the hydrogen compartment is:

$2\ H_2(g) + 4\ OH^-(aq) \rightarrow 4\ H_2O(l) + 4\ e^-$

      i. Write equation to represent the reaction taking place in the oxygen half-cell.
      ii. Write the balanced overall cell reaction.
      iii. Show the direction of flow of electrons.

b. Suggest the function of platinum in the above cell.

c. Give two advantages of fuel cells over those of ordinary batteries.

3. Hydrogen–oxygen fuel cells are used to provide electrical energy for electric motors in vehicles. In a hydrogen–oxygen fuel cell, a current is generated that canbe used to drive an electric motor.

a. Deduce half-equations for the electrode reactions in a hydrogen–oxygen fuel cell.

b. Use these half-equations to explain how an electric current can be generated.

c. Explain why a fuel cell does not need to be recharged.

d. Explain why Hydrogen-oxygen fuel cell can produce drinking water of potable quality.

e. To provide energy for a vehicle, hydrogen can be used either in a fuel cell or in an internal combustion engine.

i. Suggest the main advantage of using hydrogen in a fuel cell rather than in an internal combustion engine.

ii. Identify one major hazard associated with the use of that fuel cell in avehicle.

4. The following half-reactions take place when a non-rechargeable alkaline cell is in use:

$Zn(s) + 2\ OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$ …… ..…. **[1]**

$MnO_2(s) + 2H_2O(l) + 2e^- \rightarrow Mn(OH)_2(s) + 2\ OH^-(aq)$ ……..……... **[2]**

Write down the general name used for non-rechargeable cells.

c. Which one of the above equations (1 or 2) represents the half-reaction that takes place at the cathode? Give a reason for your answer.

d. Give a reason why the cell 'dies' after delivering current for a while.

5. Some cells, such as the nickel-cadmium cell used in calculators and electric shavers, can be recharged. Others, such as those used in watches and torches,cannot be recharged.

a. Are rechargeable cells primary or secondary cells?

b. The half-reactions occurring in a nickel-cadmium cell are shown below

$Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$

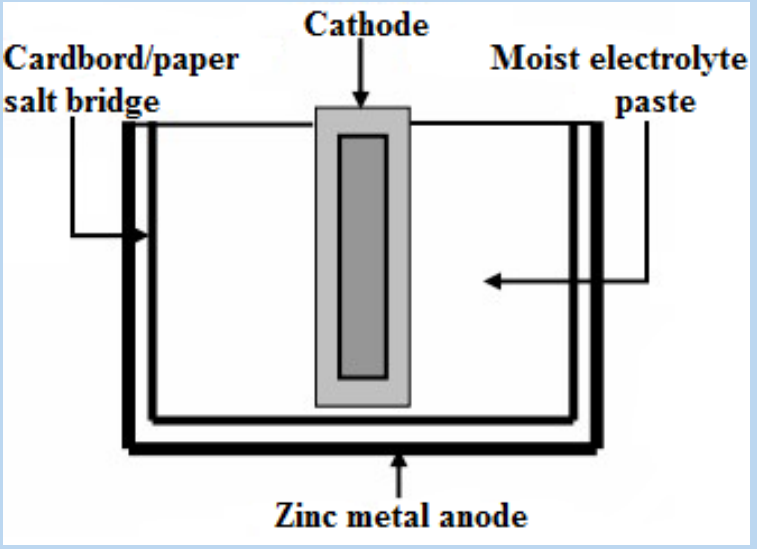
$NiO_2(s) + 2H_2O(l) + 2e\text{-} \rightarrow Ni(OH)_2(s) + 2OH^-(aq)$

The emf of the nickel-cadmium cell is 1.4 V.

c. Which one of these half-reactions occurs at the cathode? Give a reason for your answer.

d. Write down the balanced equation for the overall cell reaction.

6. A sketch of a dry cell, such as the one used in a torch or radio, is shown below.



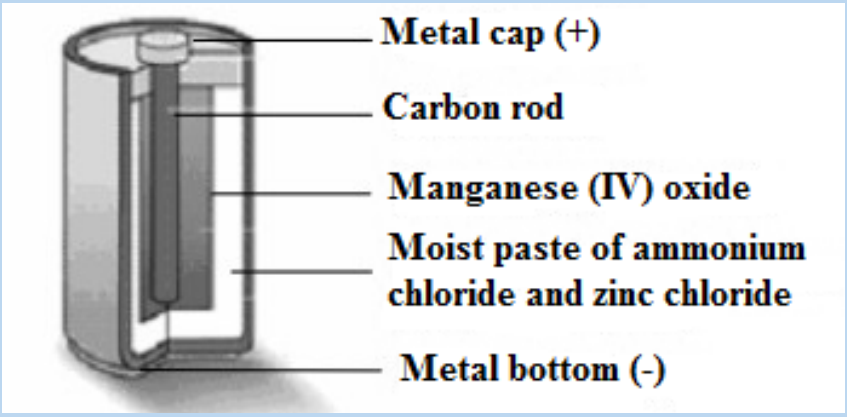
In some types of dry cells, the electrolyte paste is made of ammonium chloride which is acidic. In other types of cells the paste is alkaline, due to an alkali such as potassium hydroxide. The alkaline cells are known to last longer than those containing ammonium chloride.

a. Why is the above cell referred to as a dry cell?

b. Give a reason why alkaline cells last longer than cells that contain acid.

c. Give one reason why rechargeable batteries have less impact on global warming than non-rechargeable batteries.

7. A dry cell, as shown in the diagram below, does not contain a liquid electrolyte. The electrolyte in a typical zinc-carbon cell is a moist paste of ammonium chloride and zinc chloride.



The paste of ammonium chloride reacts according to the following half-reaction:

$$2NH_4^+(aq) + 2e^- \rightarrow 2\,NH_3(g) + H_2(g)$$

Manganese (IV) oxide is included in the cell to remove the hydrogen produced during half-reaction (i), according to the following reaction:

$$2\,MnO_2(s) + H_2(g) \leftrightarrow Mn_2O_3(s) + H_2O(l)$$

The combined result of these two half-reactions can be represented by the following half reaction:

$$2\,NH_4^+(aq) + 2\,MnO_2(s) + 2e^- \rightarrow Mn_2O_3(s) + 2NH_3(g) + H_2O(l)$$

a. Explain why it is important that the hydrogen produced in half-reaction (i) is removed by the manganese (IV) oxide

b. Write down the half-reaction occurring at the anode.

c. Write down the net ionic equation occurring in the zinc-carbon cell.

d. When in use the zinc casing of the dry cell becomes thinner, because it is oxidised. When not in use, it still corrodes. Give a reason for the latter observation.

e. Dry cells are generally discarded when 'flat'. Why is the carbon rod the most useful part of the cell, even when the cell is flat?

12.7. Comparison between galvanic (voltaic) cell and electrolytic cell

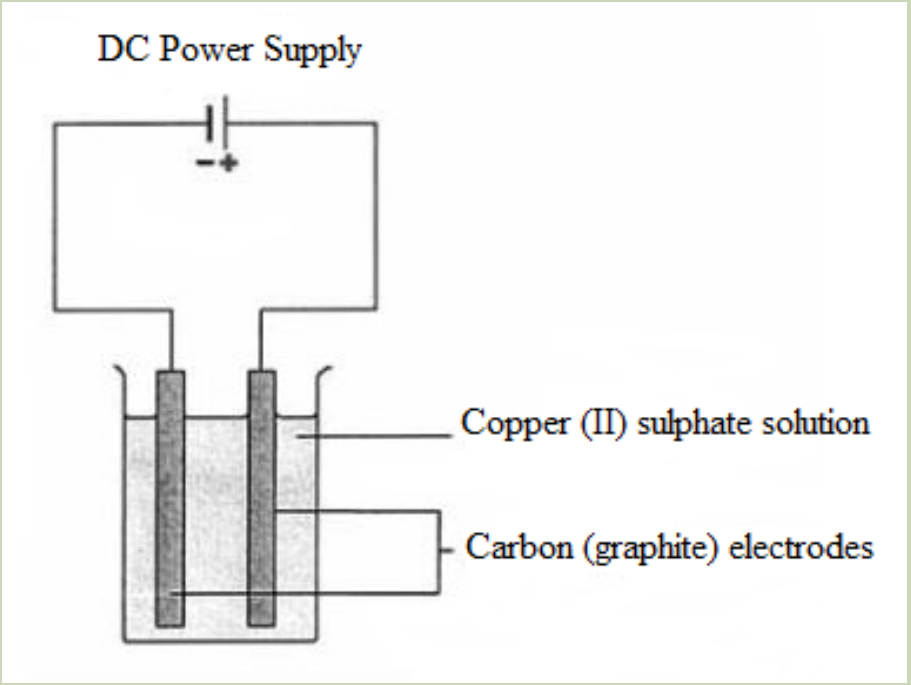
Activity 12.7

1. Electrolysis of copper (II) sulphate solution

Apparatus	Chemicals
• Beaker (250 cm^3) • Graphite electrodes (about 5 mm diameter), • Retort stands and clamps to hold electrodes • DC power supply • Leads and crocodile clips	Aqueous copper (II) sulphate, about 0.5 M, 200 cm^3

Procedure

- Set up the cell as shown in the diagram below.



- Watch for any activity on each of the electrodes,

Discussion questions

a. Write down any observation.

b. Write the reaction equations for the reactions at each electrode.

c. Suggest any role of carrying out this experiment.

2. Give the definition of:

a. Galvanic cell

b. Electrolytic cell.

3. Find out the differences and similarities between galvanic cell and electrolytic cell

We have learnt that there are two types of cells namely galvanic cells and electrolytic cells. Galvanic cell is a device which converts chemical energy into electrical energy. On the other hand, electrolytic cell is a device which converts electrical energy into chemical energy.

For more information about electrolysis and electrolytic cells, see Senior 5 Student Book, Unit 13.

12.7.1. Similarities

Electrolytic cells are very similar to voltaic (galvanic) cells in the sense that both

- Have a cathode and anode side,
- Have a consistent flow of electrons from the anode to the cathode.

12.7.2. Diffrences

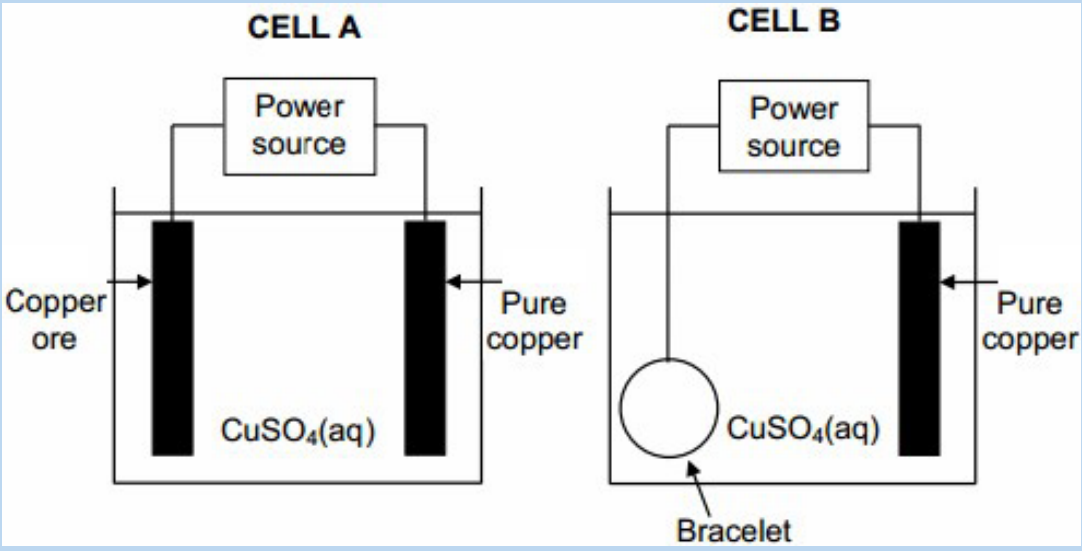
Even though electrolytic and voltaic cells are very similar as we saw, there are also striking differences between the two cells. The main differences are outlined below.

Table 12.2: Differences between galvanic (voltaic) and electrolytic cell

Galvanic Cell	Electrolytic Cell
It converts chemical energy into electrical energy.	It converts electrical energy into chemical energy.
Electrical energy is produced.	Electrical energy is consumed.
It is based upon the redox reactions which are spontaneous.	The redox reactions are non-spontaneous and take place only when energy is supplied.
The chemical changes occurring in the two beakers are different.	Only one chemical compound undergoes decomposition.
Anode (-ve) - Oxidation takes place.	Anode (+ve) - Oxidation takes place.
Cathode (+ve) - Reduction takes place.	Cathode (-ve) - Reduction takes place
Anode is negative and cathode is positive.	Anode is positive and cathode is negative.
The electrons move from anode to cathode in external circuit.	The electrons are supplied by the external source. They enter through cathode and come out through anode.
The two half cells are set up in different containers and are connected through salt bridge or porous partition.	Both the electrodes are placed in the solution or molten electrolyte in the same container.

Checking up 12.7

1. State two differences and two similarities between an electrochemical cell and an electrolytic cell.
2. Which of these is a TRUE statement about voltaic cells?
   a. Voltaic cells convert chemical energy to electrical energy using an oxidation-reduction reaction.
   b. Voltaic cells convert electrical energy to chemical energy using an oxidation-reduction reaction.
   c. Voltaic cells convert chemical energy to electrical energy using a decomposition reaction.
   d. Voltaic cells convert electrical energy to chemical energy using electrolysis.
3. What is the anode in an electrolytic or voltaic cell?
   a. The site of oxidation
   b. The site of reduction
   c. The positive electrode
4. The neutral electrode What is the main difference between voltaic and electrolytic cells?
   a. Voltaic cells only contain a cathode and electrolytic cells only contain an anode.
   b. Voltaic cells convert chemical energy to electrical energy and electrolytic cells convert electrical energy back to chemical energy.
   c. Voltaic cells contain an electrolyte, while electrolytic cells do not.
   d. Electrolytic cells contain an electrolyte, while voltaic cells do not.
5. The simplified diagrams below represent two electrochemical cells, A and B, used in industry. Cell A is used in the purification of copper ore containing silver and platinum impurities. Cell B is used to electroplate a bracelet with a layer of copper.



a. Write down the name of the type of electrochemical cell of which the above two cells are examples.

b. Pure copper is used as one of the electrodes in each of the cells above. In which cell (A or B) is the pure copper the:

   i. Cathode
   ii. Anode

c. Consider cell B. Initially the $CuSO_4(aq)$ has a blue colour.

   i. How will the intensity of the blue colour change whilst the cell is functioning?
   Write down increases, decreases or remains the same. Give a reason for the answer.

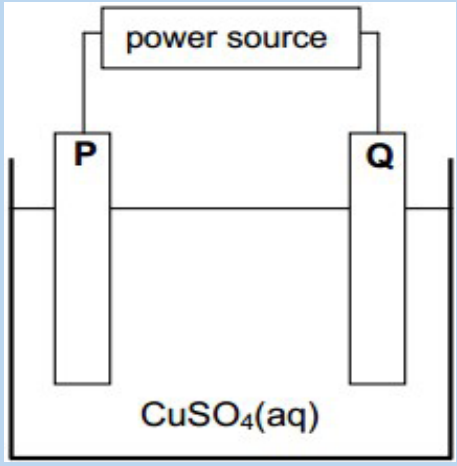
   ii. Write down the half-reaction that takes place at the pure copper electrode.

d. Consider cell A.

   i. Give a reason why the sludge formed in this cell is of economic importance.

   ii. Name one negative impact that the energy usage in this process has on the environment.

6. The simplified diagram below represents an electrochemical cell used in the refining of copper. One of the electrodes consists of impure copper and the other one of pure copper.



a. What type of power source is used to drive the reaction in this cell? Write down only AC or DC.

b. Give a reason why the copper (II) sulphate is dissolved in water before it is used in this cell.

c. When an electric current passes through the solution, electrode **P** becomes coated with copper.

   i. Is electrode **P** the cathode or the anode? Support your answer by writing the half-reaction that takes place at electrode **P**.

   ii. Write down the half-reaction that takes place at electrode **Q**.

d. It is found that the impure copper plate contains platinum. The platinum forms a residue at the bottom of the container during electrolysis.

   i. Refer to the relative strengths of reducing agents to explain why platinum forms a residue at the bottom of the container.

   ii. How will the concentration of the copper (II) sulphate solution change during electrolysis? Write down only increases, decreases or remains the same. Give a reason for the answer.

END UNIT ASSESSMENT

MULTIPLE CHOICE QUESTIONS

1. What is the function of a voltaic electrochemical cell?
   a. To convert electrical energy to light energy
   b. To convert electrical energy to chemical energy
   c. To convert electrical energy to heat energy
   d. To convert chemical energy to electrical energy

2. What is a cathode?
   a. The electrode where reduction takes place and electrons are lost.
   b. The electrode where oxidation takes place and electrons are gained.
   c. The electrode where oxidation takes place and electrons are lost.
   d. The electrode where reduction takes place and electrons are gained.

3. Which of the following statements is FALSE?
   a. Oxidation and reduction half-reactions occur at electrodes in electrochemical cells.
   b. All electrochemical reactions involve the transfer of electrons.
   c. Reduction occurs at the cathode.
   d. Oxidation occurs at the anode.
   e. All voltaic (galvanic) cells involve the use of electricity to initiate non-spontaneous chemical reactions.

4. For a voltaic (or galvanic) cell using Ag, Ag^+ (1.0 M) and Zn,Zn^{2+} (1.0 M) half-cells, which of the following statements is incorrect?
   a. The zinc electrode is the anode.
   b. Electrons will flow through the external circuit from the zinc electrode to the silver electrode.
   c. Reduction occurs at the zinc electrode as the cell operates.
   d. The mass of the zinc electrode will decrease as the cell operates.
   e. The concentration of Ag^+ will decrease as the cell operates.

5. Consider the standard voltaic (or galvanic) cell: Fe, Fe^{2+} versus Au, Au^{3+}. Which answer identifies the cathode and gives the E_o for the cell?

   a. Fe, -0.44 V
   b. Au, 1.94 V
   c. Fe, 1.06 V
   d. Au, 1.06 V
   e. Fe, 1.94 V

6. What is the value of E for the half-cell:

$$MnO_4^-(0.010M) + 8H^+(0.20M) + 5e^- \rightarrow Mn^{2+}(0.020M) + 4H_2O$$

   a. 1.50 V
   b. 1.86 V
   c. 1.44 V
   d. 1.58 V
   e. 1.52 V

7. A concentration cell is constructed by placing identical Cu electrodes in two Cu^{2+} solutions. If the concentrations of the two Cu^{2+} solutions are 1.0 M and 0.0020 M, calculate the potential of the cell.

   a. 0.020 V
   b. 1.2 V
   c. 0.030 V
   d. 1.0 V
   e. 0.080 V

8. What is ΔG^θ per mole of dichromate ions for the reduction of dichromate ions, $Cr_2O_7^{2-}$, to by bromide ions, Cr^{3+}, in acidic solution? (Hint: Use the standard cell potential.)

   a. +26.3 kJ
   b. -145 kJ
   c. +145 kJ
   d. -26.3 kJ
   e. -53.6 kJ

9. Estimate the equilibrium constant for the system indicated at 25°C.

$3\ Mg^{2+} + 2Al \leftrightarrow 3Mg + 2Al^{3+}$

a. ~1069
b. ~1023
c. $\sim 10^{-24}$
d. $\sim 10^{-36}$
e. $\sim 10^{-72}$

10. Which of the following statements is (are) true for all voltaic (or galvanic) cells?

i. Reduction occurs at the cathode.

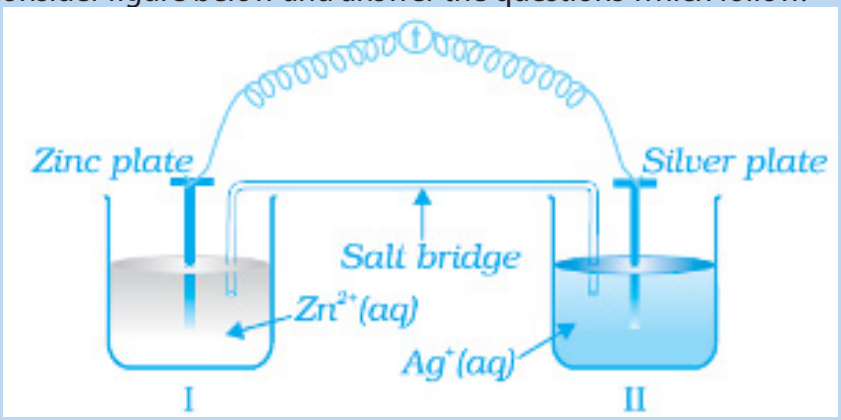
ii. The anode gains mass during discharge (note: this means operation of the cell.)

iii. The voltage is less than or equal to zero.

a. only III
b. only II
c. only I
d. II and III
e. I, II, and III

OPEN QUESTIONS

1. Consider figure below and answer the questions which follow.



a. Redraw the diagram to show the direction of electron flow.

b. Is silver plate the anode or cathode?

c. What will happen if salt bridge is removed?

d. When will the cell stop functioning?

e. How will concentration of Zn^{2+} ions and Ag^{+} ions be affected when the cell functions?

f. How will the concentration of Zn^{2+} ions and Ag^{+} ions be affected after the cell becomes 'dead'?

2. Large blocks of magnesium are bolted onto the hulls of iron ships in an attempt to prevent the iron being converted into iron (II), one of the steps in the rusting process.

Use the data below, where appropriate, to answer the questions which follow.

	E^{θ} / V
$Mg^{2+}(aq) + 2e- \rightleftharpoons Mg(s)$	−2.37
$Fe^{2+}(aq) + 2e- \rightleftharpoons Fe(s)$	−0.44
$O_2(g) + 2H_2O(l) + 4e- \rightleftharpoons 4OH^{-}(aq)$	+0.40

a. Calculate the e.m.f. of the cell represented by $Mg(s)|Mg^{2+}(aq)||Fe^{2+}(aq)|Fe(s)$ under standard conditions.

b. Write a half-equation for the reaction occurring at the negative electrode of this cell when a current is drawn.

c. Deduce how the e.m.f. of the cell $Mg(s)|Mg^{2+}(aq)||Fe^{2+}(aq)|Fe(s)$ changes when the concentration of Mg^{2+} is decreased. Explain your answer.

Calculate a value for the e.m.f. of the cell represented by

$Pt(s)|OH^-(aq)|O_2(g)||Fe^{2+}(aq)|Fe(s)$ and use it to explain why iron corrodes when in contact with water which contains dissolved oxygen.

3. The table below shows some values for standard electrode potentials.

Electrode	Electrode reaction	E^{θ}/ V
A	$Mn^{2+}(aq) + 2e- \rightleftharpoons Mn(s)$	– 1.18
B	$Fe^{2+}(aq) + 2e- \rightleftharpoons Fe(s)$	– 0.44
C	$Ni^{2+}(aq) + 2e- \rightleftharpoons Ni(s)$	– 0.25
D	$Sn^{2+}(aq) + 2e- \rightleftharpoons Sn(s)$	– 0.14
E	$2H^+(g) + 2e- \rightleftharpoons H_2(g)$	?

a. i. Give the name of electrode E and indicate its role in the determination of standard electrode potentials.

ii. What is the value of the standard electrode potential for electrode E?

b. The electrochemical cell set up between electrodes C and D can be represented by the cell diagram:

$$Ni(s) \left| Ni^{2+}(aq) \right|\!\!\left| Sn^{2+}(aq) \right| Sn(s)$$

i. Calculate the e.m.f. of this cell.
ii. State which would be the positive electrode.

iii. Write an equation to show the overall reaction in the cell.

c. Use the standard electrode potential data given in the table above:

i. To explain whether or not you would expect a reaction to occur if a piece of tin were to be added to a test tube containing aqueous iron(II) sulphate;

ii. To predict and explain two observations you would expect to make if a small piece of manganese were to be added to a test tube containing hydrochloric acid of concentration 1 mol dm^{-3}.

4. Calculate the voltage produced by the cell $Sn(s)|Sn^{2+}||Ag^{+}|Ag(s)$ at 25°C given:

$[Sn^{2+}] = 0.15$ M

$[Ag^{+}] = 1.7$ M

5. Hydrogen–oxygen fuel cells are used to provide electrical energy for electric motors in vehicles.

In a hydrogen–oxygen fuel cell, a current is generated that can be used to drive an electric motor.

(a) Deduce half-equations for the electrode reactions in a hydrogen–oxygen fuel cell.

(b) Use these half-equations to explain how an electric current can be generated.

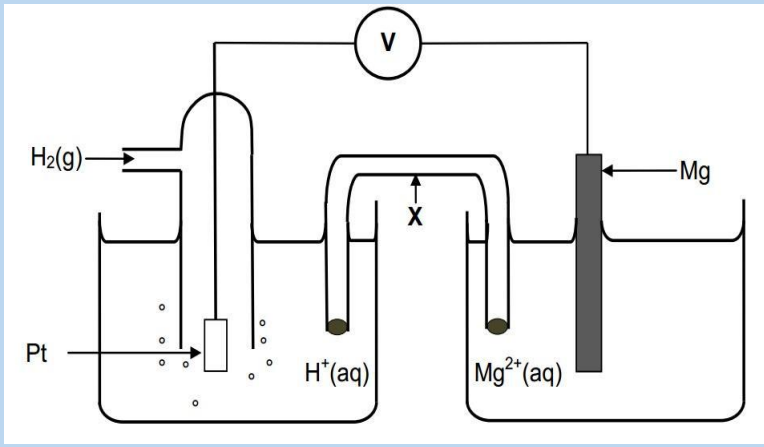
(c) Explain why a fuel cell does not need to be recharged.

(d) To provide energy for a vehicle, hydrogen can be used either in a fuel cell or in an internal combustion engine.

(i) Suggest the main advantage of using hydrogen in a fuel cell rather than in an internal combustion engine.

(ii) Identify one major hazard associated with the use of a hydrogen–oxygen fuel cell in a vehicle.

6. The galvanic cell represented below consists of a hydrogen half-cell and a magnesium half-cell at standard conditions. The reading on the voltmeter is 2.36 V.



a. Apart from concentration, write down two other conditions needed for the hydrogen half-cell to function at standard conditions.

b. Write down the name of the item of apparatus labelled X.

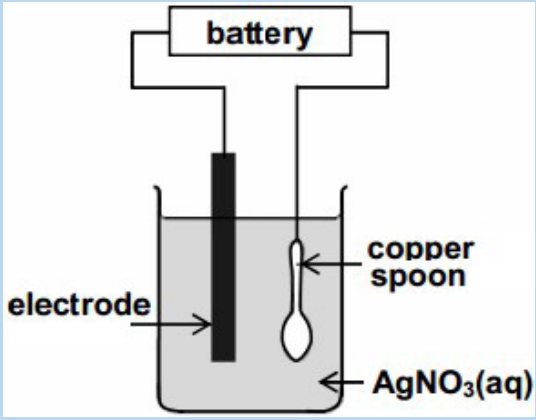
c. Is magnesium the anode or cathode in the cell above? Refer to the relative strengths of reducing agents to explain the answer.

d. Write down the cell notation for this cell.

e. Calculate the standard reduction potential of the magnesium half-cell. Show all your working.

f. Write down the balanced net (overall) cell reaction that takes place in this cell. No spectator ions are required.

7. Electroplating is one of the uses of electrolysis. The diagram below shows an electrolytic cell that can be used to plate a copper spoon with silver.



a. Define the term oxidation in terms of electron transfer.

b. What type of half-reaction takes place at the copper spoon? Write down only oxidation or reduction.

c. Write down a half-reaction that explains the change that occurs on the surface of the copper spoon during electrolysis.

d. Name the metal that is labelled 'electrode'.

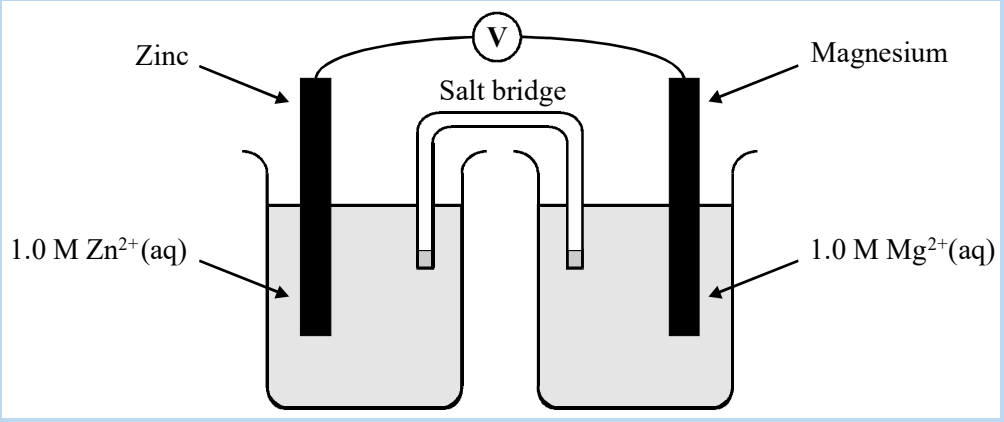
e. Give a reason why the concentration of the AgNO3(aq) remains constant during electrolysis.

8. Use the data given below, where appropriate, to answer the questions which follow.

Standard electrode potentials in acid solution	E^{θ}/V
$Mg^{2+}(aq) + 2e- \longrightarrow Mg(s)$	–2.37
$Zn^{2+}(aq) + 2e- \longrightarrow Zn(s)$	–0.76
$Sn^{4+}(aq) + 2e- \longrightarrow Sn^{2+}(aq)$	+0.15
$VO^{2+}(aq) + 2H^{+}(aq) + e- \longrightarrow V^{2+}(aq) + H_2O(l)$	+0.34
$(aq) + 2H^{+}(aq) + e- \longrightarrow VO^{2+}(aq) + H_2O(l)$	+1.02
$Ce^{4+}(aq) + e- \longrightarrow Ce^{3+}(aq)$	+1.70
	+1.70

a. Give the components of the standard reference electrode used in determining the standard electrode potentials above. State the conditions under which this standard reference electrode has a potential of 0.00 V.

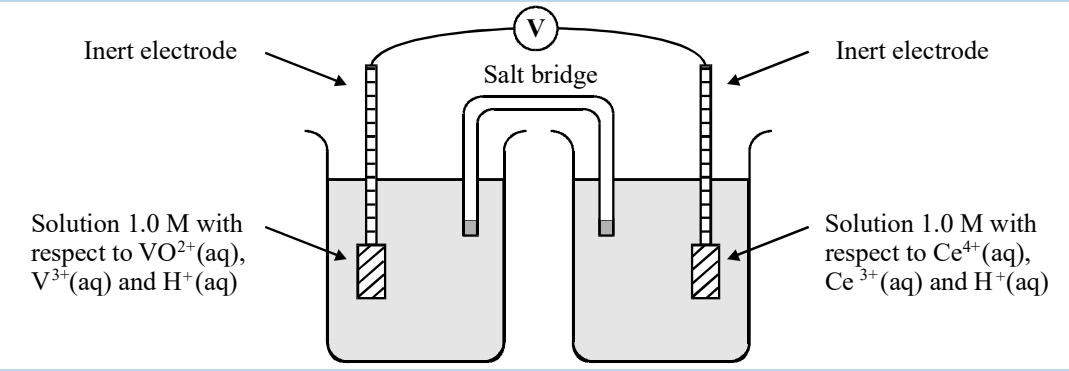
b. A diagram of a cell is shown below.



i. Calculate the overall standard potential of this cell.

ii. State the polarity of the zinc electrode.

c. Another diagram of a cell is shown below.



i. Calculate the overall standard potential of the cell.

ii. Deduce the direction of electron flow in the external circuit when the inert electrodes are connected together.

d. Using data from the table 12.1, derive an equation for the overall redox process which occurs when a solution containing Ce^{4+}(aq) is added to a solution containing V^{3+}(aq).

e. Which, if any, of the four vanadium-containing species, V^{2+}(aq), V^{3+}(aq), VO^{2+}(aq) and VO^{2+}(aq), will convert Sn^{2+}(aq) into Sn^{4+}(aq) in acid solution

UNIT 13

FACTORS THAT AFFECT THE RATE OF REACTIONS

UNIT 13: FACTORS THAT AFFECT THE RATE OF REACTIONS

Key Unit ompetency:

Explain the factors that affect the rate of chemical reaction and use Arrhenius equation to calculate the ratio of rate constant and activation energy with change in the temperature.

Learning objectives

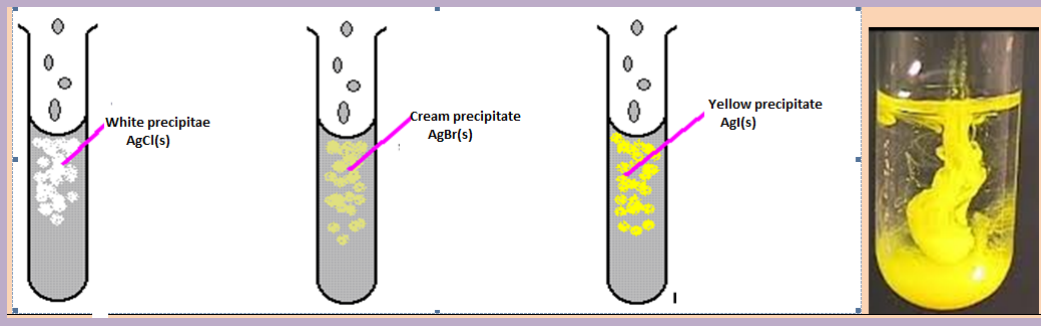
By the end of this unit the learners should be able to:

- Explain the concept of reaction kinetics
- Explain the effect of different conditions on the rate of reaction
- Carry out experiments to show how different factors affect the rate of chemical reactions
- Predict the effect of changing conditions on the rate of reactions
- Appreciate the importance of reaction kinetics.
- Appreciate the importance of different conditions on the reaction rates.

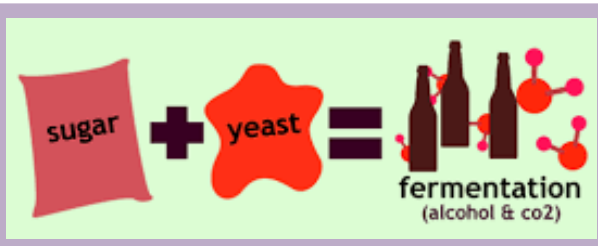
Introductory Activity

Observe the following processes and answer the questions below.

A: RUSTING PROCESS (Oxidation of iron)



B: PRECIPITATION REACTIONS



C: FERMENTATION

D: COMBUSTION

1. Classify the above processes or reactions as slow or fast in the following table.

Slow reactions	Fast reactions

2. Which conditions are necessary for rusting process (corrosion) to take place?
3. During wood combustion, describe what will happen if the amount of air increases.
4. What is the role of yeast in the fermentation process?

Chemistry, by its nature, is concerned with change. It is the study of matter, its composition, properties, and reactivity. Substances having well-defined properties are converted by chemical reactions into other substances with different properties.

One of the features of a chemical reaction is the rate or speed of the reaction and the factors controlling the rate of a chemical reaction. For example, which factors determine how rapidly food gets spoiled? Or what controls the rate at which fuel burns in an auto engine? All these questions can be answered by the branch of chemistry, which deals with the study of reaction rates and their mechanisms, called chemical kinetics.

13.1. Concept of reaction kinetics

Activity 13.1

a. Burn a small amount (about 2 cm^3) of ethanol and record the time taken for this amount of ethanol to be completely burned.

b. Put 4ml of lead (II) nitrate aqueous solution in a test tube and add three drops of aqueous potassium iodide solution, then record the time taken for the yellow precipitate to be formed.

c. Put two or 3 iron nails in an open beaker containing water and predict what will happen to these nails after three weeks or one month.

Questions:

1. Suggest the name of a reaction that takes place in each of the above activities.
2. In the above three activities, indicate the slowest and fastest reaction.
3. Using books or internet describe your understanding on the rate of chemical reaction.

Chemical kinetics is a branch of chemistry mainly dealing with the rates of reaction. The goal of chemical kinetics is to investigate how fast the reactants are consumed or the products are formed. It is important to predict the rate of processes and to find the influencing factors that promote a desired reaction or inhibit an undesired one.

During a chemical reaction, reactants are converted to products by breaking old bonds and formation of new bonds. Some chemical reactions may be slow or fast. For example, the reaction between a solution of lead (II) nitrate and potassium iodide is a fast reaction.

$$Pb(NO_3)_{2(aq)} + 2KI(aq) \longrightarrow \underbrace{PbI_{2(s)}}_{\text{Yellow precipitate}} + 2KNO_{3(aq)}$$

The precipitation of silver chloride is also fast. It occurs instantaneously by mixing aqueous solutions of silver nitrate and sodium chloride.

However, the rusting of iron is a slow process that takes place over many days, even over the years. Similarly, the formation of diamond and other minerals in the earth's crust takes millions of years.

Chemical kinetics is the study of rates and mechanisms of chemical reactions. Any chemical process may be broken down into a sequence of one or more single-step processes known either as elementary processes, elementary reactions, or elementary steps.

The hydrolysis of sucrose was the first chemical reaction whose rate was quantitatively studied by L. Wilhemly in 1850. Since that period, advanced research has been made in the field of chemical kinetics, enabling chemists to study very fast reactions (reactions that occur within less than a second). When we talk about the rate of a chemical reaction, we mean the rate at which reactants are used up, or equivalently the rate at which products are formed.

The rate of a reaction can be defined as the change in concentration of a reactant or product in a given period of time. The reaction rate tells us how fast the reaction is taking place by indicating how much of a reactant is consumed or how much of a product is yielded in a given time.

$$\text{Thus, } \textit{reaction rate} = \frac{\textit{change in amount (or concentration) of a substance}}{\textit{time taken}}$$

For example, if we consider the speed of an automobile, it can be expressed in terms of change in the distance covered in a certain period of time.

In chemical kinetics, the rate of a reaction can be expressed as the initial rate, average rate or instantaneous rate.

The initial rate is the rate of a reaction measured at the beginning of the reaction. It is the change in concentration of a reactant, or product, per unit time at the start of reaction. The initial rate is simply the instantaneous rate at time equal to zero, or at the beginning of the reaction.

The average rate is defined as the change in concentration of a reactant or product of a chemical reaction in a given interval of time.

$$\text{Average rate of reaction} = \frac{\text{change in concentration of reactants or products}}{\text{Time interval}}$$

For example, consider the following reaction:

$$R \longrightarrow P$$

In this reaction, if one mole of the reactant R produces one mole of the product P. If $[R]_1$ and $[P]_1$ are the concentrations of R and P respectively at time t_1 and $[R]_2$, $[P]_2$ are the concentrations of R and P respectively at time t_2 then,

$\Delta t = t_2 - t_1$

$\Delta[R] = [R]_2 - [R]_1$

$\Delta[P] = [P]_2 - [P]_1$

$$\text{The average rate of disappearance of R} = \frac{\text{Decrease in concentration of R}}{\text{Change in time}} = -\frac{\Delta[R]}{\Delta t}$$

By convention, the rate is always expressed as positive quantity. Because the concentration of reactants is decreasing with time, Δ[R] is a negative number. We use the negative sign to make the rate of reaction a positive quantity.

$$\text{The average rate of appearance of P} = \frac{\text{Increase in concentration of P}}{\text{Change in time}} = +\frac{\Delta[P]}{\Delta t}$$

Average rate depends upon the change in concentration of reactants or products and the time taken for that change to occur.

For a better understanding, consider the following examples:

Consider the following reaction at 300 °C: $2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$

If in the first 150 seconds, the concentration of nitrogen dioxide has decreased from 0.0100 mol/L to 0.0055 mol/L, the average rate for the disappearance of nitrogen dioxide for the first 150 seconds is:

$$Rate = -\frac{\Delta[NO_2]}{\Delta t} = -\frac{(0.005mol/L - 0.0100mol/L)}{150s} = \frac{0.0045mol/L}{150s} = 3.0\,x10^{-5}\,mol/L.s$$

Suppose that in the next 150 seconds the concentration of nitrogen dioxide decreases from 0.0055 mol/L to 0.0038 mol/L. The average rate becomes:

$$Rate = -\frac{\Delta[NO_2]}{\Delta t} = -\frac{(0.0038mol/L - 0.0055mol/L)}{150s} = \frac{0.0017mol/L}{150s} = 1.1\,x10^{-5}\,mol/L.s$$

Consider the reaction of the acidified hydrogen peroxide (H_2O_2) added to a solution of potassium iodide (KI) and iodine is liberated.

$H_2O_2(aq) + 2K(aq) + H_2SO_4(aq) \rightarrow 2H_2O(l) + I_2(aq) + K_2SO_4(aq)$

In this reaction, initially the concentration of iodine is zero. But with the passage of time, it increases and the reaction solution becomes brownish. The concentration of iodine can be measured at different intervals of time by titration against sodium thiosulphate. If the concentration of iodine rises from 0 to 10^{-5} mol L^{-1} in 10 seconds, the average rate becomes:

$$Rate = \frac{\Delta[I_2]}{\Delta t} = \frac{10^{-5}mol/L}{10s} = 10^{-6}\,mol\,L^{-1}s^{-1}$$

The instantaneous rate is the change in concentration of a reactant or product of a chemical reaction at a given instant. This rate is measured when the reaction is in progress at any point of time.

It is obtained when we consider the average rate at the smallest time interval dt (i.e. when Δt approaches zero).

Mathematically, for an infinitesimally small dt, the instantaneous rate is given by:

$$Rate, R = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

Where d[R] = small change in concentration of R and dt = small change in time

For the general reaction: $aA + bB \longrightarrow cC + dD$

The rate is given by:

$$Rate = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$$

$$Rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = +\frac{1}{c}\frac{\Delta[C]}{\Delta t} = +\frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Where a, b, c and d are stoichiometric coefficients of reactants and products.
Example:

The decomposition of dinitrogen pentoxide: 2 N_2O_5 (g) → 4 NO_2(g) + O_2(g) was performed in the laboratory and the rate of formation of NO_2 was found to be 0.53 M/s.

a. What was the rate of formation of O_2(g)?

b. What was the rate of consumption N_2O_5(g)?

Answer:

a. First determine the relationship between NO_2(g) and O_2(g) in terms of rate using the coefficients of the balanced equation:

$$Rate = \frac{1}{4}\frac{\Delta[\ O_2\ ]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

Next substitute in the given values and solve the rate of formation of O_2(g):

Rate of formation of O_2(g) = (1/4) (0.53 M/s) = 0.13 M/s

b. First determine the relationship between NO_2(g) and N_2O_5(g) in terms of rate using the coefficients of the balanced equation:

Rate of reaction $Rate = \frac{1}{4}\frac{\Delta[\ O_2\ ]}{\Delta t} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t}$

Next substitute the given values and solve the rate of consumption of $N_2O_5(g)$:

$-\left(\frac{1}{2}\right)$ rate of consumption of $N_2O_5(g)$ = +1/4 rate of formation $NO_2(g)$

Rate of consumption of $N_2O_5(g)$ = $-\left(\frac{1}{2}\right)$ (0.53 M/s) = 0.27 M/s.

The rate of a chemical reaction is important in our daily life as well as in industry. At home, it is interesting to know the rate at which a kind of food is cooked (i.e. boiling an egg or baking a cake). It is interesting to know the rate at which the seeds of maize or beans are growing till the time of harvesting. In the body, chemical reactions must take place at the correct rate to supply exactly the needs of the cells.

The rate of reaction dictates the rate of production of our daily products. In order to meet the demand and safety standards, optimization of rate of reaction is nonetheless the most important subject to control and study. Kinetic studies are important in understanding reactions, and they also have practical implications. In industry, the reactions are conducted in reactors in which compounds are mixed together, possibly heated and stirred for a time, and then moved to the next phase of the process. It will be important to know how long to hold the reaction at one stage before moving on, to make sure that reaction has finished before starting the next one. By understanding how a reaction takes place, many processes can be improved.

Another importance of kinetics is to understand the biological processes, especially enzyme-catalyzed reactions.

Checking up 13.1

1. What is meant by the rate of a reaction?
2. In the following reaction:

The concentration of A decreases from 0.5 mol/L to 0.4 mol/L in 10 minutes. Calculate the rate during this interval?

13.2. Factors that change the rates of reactions

Activity 13.2 (a)

1. Using textbooks and internet (where possible) find out at least six factors that affect the rate of reaction and explain how they affect the reaction rate.
2. Why does bread grow mold more quickly at room temperature than in the refrigerator?

In chemical kinetics, the determination of how quickly or slowly reactants turn into products is a measure of the reaction rate. A reaction that takes long time has low reaction rate while a reaction that occurs quickly has a high reaction rate. Some conditions can be used to speed or to slow down the rate of a chemical reaction.

The rate of reaction is defined as the rate of increase in the molar concentration of the products of a reaction per unit time or the rate of decrease in the molar concentrations of the reactants per unit time.

The factors that influence rate of chemical reaction are:

a. Concentration
b. Temperature
c. Pressure
d. Catalyst
e. Light
f. Surface area

In order to understand how these factors affect the rate of chemical reactions, it is essential to understand how reactions take place based on the collision theory. According to this theory, a chemical reaction takes place only by collisions between the reacting particles; it means that, for a chemical reaction to occur it is necessary for the reacting species (atoms or molecules) to collide with energy equal to or greater than the activation energy and with proper orientation.

In general, a factor that increases the number of collisions between particles will increase the reaction rate and a factor that decreases the number of collisions between particles will decrease the chemical reaction rate.

13.2.1. Effect of concentration

Activity 13.2 (b)

Chemicals and Apparatus: 0.2M sodium thiosulphate, 2.0M hydrochloric acid, distilled water, measuring cylinder, stop clock (or stop watch), conical flask and white paper.

Procedure:

1. Prepare sodium thiosulphate solution (about 0.2M) by adding 2g of sodium thiosulphate solid to 60cm^3 of water in a conical flask.
2. Divide the solution into three equal portions, put them in three different conical flasks and place each conical flask on white paper marked with a cross (X).
3. To one conical flask add 1cm^3 of 2M HCl solution and swirl the mixture gently for uniform mixing, you must start the stop clock immediately you add the acid into the sodium thiosulphate solution. Record the time it takes for sulphur to be precipitated enough to obscure the cross when viewed from the top.
4. To the remaining two conical flasks, add 2cm^3 and 3cm^3 of the 2M HCl respectively. Record the time taken in each case for the cross to be obscured.

Questions:

1. State, in which conical flask, the reaction was fast. Give a reason for your answer.
2. Write balanced equation for the reaction that takes place.

Concentration refers to the number of particles dissolved in a given volume of a solution. The more the reacting particles are present in a given volume, the more opportunities of the collisions involving those particles will occur.

The rates of many reactions depend on the concentrations of the reactants. It has been observed that the rate of chemical reaction is directly proportional to the concentration of the reactants. Thus, increasing the concentration of the reactants usually results in a higher reaction rate. At lower concentrations, there is less chance for collisions between particles. Thus, decreasing the concentrations of reactants results in a lower reaction rate.

At the beginning of a reaction, when the concentration of reactants is maximum, the rate of reaction is also maximum. However, as the reaction proceeds the concentration of the reactants decreases as some amount of reactants is converted into products. The rate of the reaction decreases as the reactants are consumed and

it increases when the products are formed **(Figure 13.1).** The reaction rate is directly proportional to the concentration, i.e it increases with increasing concentration of the reactants.

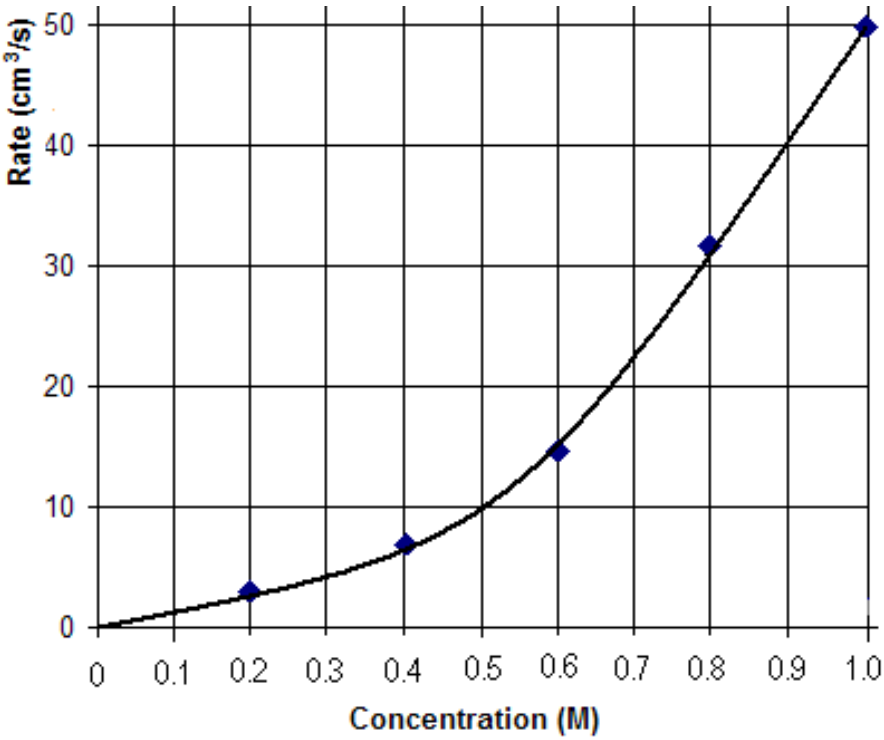


Figure 13.1: Effect of concentration on the rate of reaction

For example, consider the reaction: $\mathbf{2NO + O_2 \rightarrow 2NO_2}$

The rate of this reaction doubles ***when the concentration of oxygen is doubled.*** On the other hand, when the concentration of nitric oxide is ***doubled,*** the rate of reaction ***increases four times.***

13.2.2. Effect of pressure

Pressure is defined as the force per unit area. The units of pressure are Pascals (N/m^2) or atmospheres (1 atm); 1 atm = 101,325 Pascals (Pa). The pressure affects the rate of chemical reactions when the reactants or products are in gaseous state. This is because solids and liquids cannot be compressed, they do not change in volume when pressure is reduced or increased.

Pressure has a similar effect as concentration on the reaction rate. When the pressure increases in the gaseous system, the number of collisions between reactants also increases. Consequently the rate of reaction is increased. At high pressure, the gas particles are closer together which can increase the collision.

13.2.3. Effect of temperature

The temperature is a factor that plays a big role in chemical reactions. In general, the rates of most chemical reactions increase as the temperature rises. When the temperature of a reaction is increased, the heat is supplied to the particles involved in the reaction. Since heat is a form of energy, these particles acquire more energy which enables them to move more quickly and they collide with each other more frequently and with more energy. Therefore more particles will overcome the activation energy barrier to form products. If the temperature is decreased, the particles will move more slowly, therefore decreasing the rate of reaction.

Increasing the temperature of the reactants sometimes provides the activation energy needed to initiate a chemical reaction.

In general, an increase in the temperature increases the rate of reaction or a decrease in temperature decreases the rate of reaction.

Examples:

(i) Some types of food such as meat can spoil quickly when kept out of a refrigerator. However, when they are kept in a refrigerator, the lower temperature inside the refrigerator retards the process of developing microorganisms that can destroy the meat.

(ii) Consider the chemical reaction: $CaCO_3(s) + 2\,HCl(aq) \rightleftharpoons CaCl_2(aq) + CO_2(g) + H_2O(l)$

At 273 K (0 °C), the reaction is extremely slow and the amount of CO_2 produced is very small. When the temperature is raised to 323 K (50 °C), the reaction becomes fast and more quantity of CO_2 is obtained.

(iii) The reaction between zinc and hydrochloric acid can be performed at two different temperatures: 293 K and 308 K. It is found that the volume of hydrogen formed during the same interval time is higher at 308 K than at 298 K.

The temperature dependence of the rate of a chemical reaction can be explained by the following Arrhenius equation.

$$K = Ae^{-\frac{Ea}{RT}}$$

Where:

K is Rate constant
A is Arrhenius constant
Ea is Activation energy
R is Gas constant
T is Temperature

The logarithmic form of the Arrhenius equation is:

$$\ln K = \ln A - \frac{Ea}{RT} \text{ Or } \log K = \log A - \frac{Ea}{R}(\frac{1}{T})$$

$$K = \log A - \frac{Ea}{2.303R}(\frac{1}{T})$$

The Arrhenius equation at the temperature T_1 and T_2 can be written as:

$$\ln \frac{K_1}{K_2} = \frac{Ea}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \text{or} \quad \log \frac{K_2}{K_1} = -\frac{Ea}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Using the above equations, we can calculate the ratio of rate constants or activation energy if we know the rate constant of a reaction at two or more temperatures.

Example:

The rate constant for the reaction: $H_2(g) + I_2(g) \rightarrow 2HI(g)$ is 2.7×10^{-4} at 600 K and 3.5×10^{-3} at 650 K. Calculate the activation energy of the reaction. ($R = 8.31 Jmol^{-1}K^{-1}$).

Solution:

$$\log \frac{K_2}{K_1} = -\frac{Ea}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\log \frac{3.5x10^{-3}}{2.7x10^{-4}} = -\frac{Ea}{2.303x8.31}\left(\frac{1}{650} - \frac{1}{600}\right)$$

With this, Ea = 1.03×10^5 J mol^{-1}

Note: The relationship between temperature and rate constant will be developed in more detail in unit 14.

13.2.4. Effect of Catalyst on rate of reaction

Activity 13.2 (c)

Apparatuses and chemicals: Hydrogen peroxide, test tubes, wooden splint, manganese (IV) oxide, test tube racks, ammonium iron (II) sulphate crystals or iron (II) sulphate crystals, propane-1,2,3-triol.

Procedure

1. Put 2 cm^3 of dilute hydrogen peroxide in a clean test tube and place it in the test tube rack. Observe the test tube from time to time and record your observations.
2. Put another fresh 2cm^3 of dilute hydrogen peroxide in a clean test tube and add a half-spatula of manganese (IV) oxide. Test the gas produced with a glowing splint.
3. Put 50 cm^3 of dilute hydrogen peroxide in a clean beaker and put a very small amount of manganese (IV) oxide. When the reaction starts add about 1cm^3 of propane-1,2,3-triol and shake the contents of the beaker.

Question:

Compare the rate of the progress of gas when peroxide has both manganese (IV) oxide and propane-1,2,3-triol with the peroxide containing (IV) oxide only

For a reaction to take place, the molecules must possess a certain energy called **activation energy**. Activation energy is the minimum amount of energy required for a chemical reaction to take place. If the activation energy is high, the reaction will be slow and a catalyst is required for lowering this activation energy.

A catalyst is a substance that increases or decreases the rate of a chemical reaction by lowering the activation energy without itself being consumed by the reaction. Catalysts reduce the amount of energy required to break and form bonds during a chemical reaction. These substances that slow down the rate of reaction; they are often called negative catalysts or inhibitors. When the reaction is complete, catalysts remain chemically unchanged and they can be reused several times. For example, enzymes are catalysts that allow chemical reactions to occur at relatively low temperatures within the body.

Other examples of catalysts:

The decomposition of hydrogen peroxide (H_2O_2) is relatively slow; however, exposure to light accelerates this process and in the presence of MnO_2 as a catalyst, the reaction goes very fast.

In the manufacture of ammonia, iron is used as a catalyst to increase the rate of reaction. $N_2(g) + 3H_2(g) \rightarrow 2\,NH_3(g)$

Similarly, reaction of Sulphur dioxide and oxygen to produce Sulphur trioxide takes place in the presence of vanadium (V) pentoxide(V_2O_5) catalyst

$2SO_2(g) + O_2(g) \rightarrow 2\,SO_3(g)$

A catalyst increases the reaction rate by providing an alternative pathway (route) or mechanism for the reaction to follow. The effect of adding a catalyst on a reaction can be demonstrated on a Potential Energy Diagram **(Figure 13.2)**

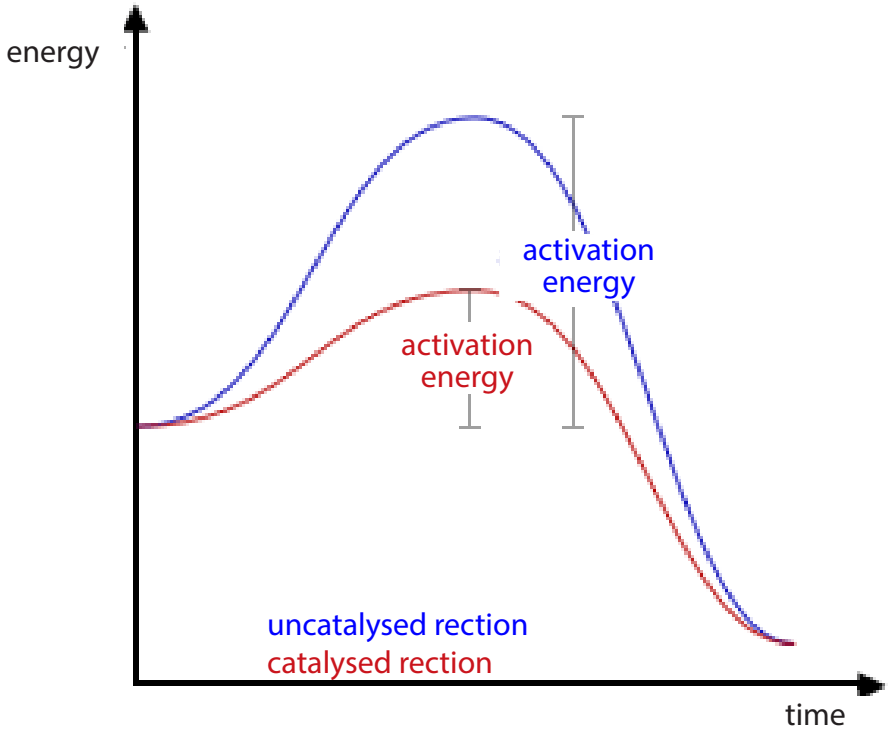


Figure 13.2: Effect of catalyst on the rate of reaction

Most catalysts are highly selective; they often determine the product of a reaction by accelerating only one of several possible reactions that could occur.

Note: Except a catalyst that can lower the activation energy (Ea), increasing the temperature, concentration or surface area has no effect on the activation energy (Ea).

Since a catalyst lowers the activation energy barrier, the forward and reverse reactions are both accelerated to the same degree.

Types of Catalysts

There are two main types of catalysis: homogeneous or heterogeneous catalysis.

a. Homogeneous Catalysis

In a **homogeneous catalysis** the reactants and catalysts are in the same physical state (phase).

Example

- Oxidation of iodide ions by peroxodisulphate ions:

$$S_2O_8^{2-}(aq) + 2I^-(aq) \xrightarrow{Fe^{2+}(aq)} 2SO_4^{2-}(aq) + I_2(aq)$$

b. Heterogeneous Catalysis

Catalysts may be classified as positive and negative catalysts. In heterogeneous catalysis, the reactants and catalyst are in different phases. This process is also known as surface catalysis or contact catalysis.

Examples:

- Haber's Process:

$$N_2(g) + 3H_2(g) \rightleftharpoons^{Fe(s)} 2NH_3(g)$$

- Hydrogenation of alkenes (catalyzed by nickel or platinum):

$$RCH{=}CHR(g) + H_2(g) \xrightarrow{Ni \text{ or } Pt} RCH_2 - CH_2R$$

a. Positive catalyst

The substance which increases the rate of reaction is known as **positive catalyst**. It acts by decreasing the activation energy for reaction.

An example of positive catalyst is the V_2O_5 used in Contact Process:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons^{V_2O_{5(s)}} 2SO_{3(g)}$$

b. Negative catalyst (Inhibitor or retarder)

The substance which decreases the rate of reaction is known as negative catalyst. It acts by increasing the activation energy for reaction.

Example:

Acetanilide prevents oxidation of Na_2SO_3 by air, it acts as negative catalyst. Similarly,

H_3PO_4 prevents the decomposition of H_2O_2 by acting as a negative catalyst for the reaction.

c. Auto catalyst

In this type of catalysis, one of the products of the reaction acts as catalyst.

Example:

In the oxidation of ethanedioic acid (oxalic acid) by potassium permanganate ($KMnO_4$), Mn^{2+} ion formed acts as catalyst and increases the rate of reaction.

$$2MmO^{2-}(aq)_4 + 6H^+(aq) + 5H_2C_2O_4(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(aq)$$

The initial stages of the reaction are slow but as the reaction proceeds, the reaction rate increases. The increase in the rate is caused by the accumulation of the catalyst Mn^{2+} which is formed in the initial stages of the reaction.

Induced catalyst

When a chemical reaction increases the rate of another chemical reaction, it is called induced catalysis.

Example:

Sodium arsenite solution is not oxidized by air but when air is passed through a mixture of the solution of sodium arsenite and sodium sulphite, simultaneous oxidation of both takes place. Thus the oxidation of sodium arsenite is induced by the oxidation of sodium sulphite.

$$Na_2SO_3 \xrightarrow{Air} Na_2SO_4$$

$$Na_2AsO_3 \xrightarrow{Air} \text{No reaction}$$

$$Na_3AsO_3 + \underbrace{Na_2SO_3}_{\text{Induced catalyst}} \xrightarrow{Air} \underbrace{Na_3AsO_4}_{\text{Sodium arsenate}} + Na_2SO_4$$

d. Enzymes

Enzymes are **biological catalysts** which catalyze the chemical reactions occurring in living organisms. Enzymes have high relative molecular masses and are protein molecules. The enzymes are specific in catalyzing only a particular set of reactions. Enzyme activity depends on pH and the temperature.

Examples:

Oxidoreductases: Responsible for catalysis of reduction or oxidation of molecules.

Transferases: Catalyze transfer of functional group from one chemical compound to the other.

Hydrolases: Catalyze the hydrolysis reactions and the reverse reactions.

Note: Enzymes work most effectively at body temperature (37°C). At higher temperatures (above 50-60°C), they are denatured and become ineffective. As the activity of enzyme decreases, the temperature of the body also decreased.

13.2.5. Effect of light on rate of reaction

Activity 13.2 (d)

Procedure:

1. To approximately 10 cm^3 sodium chloride solution in a large test tube add a few cm^3 of silver nitrate solution. An immediate precipitate of silver chloride will be formed.
2. Quickly divide the precipitate formed into three parts, and put them into three separate test tubes.
3. Put one of the test tubes immediately into a dark cupboard, the second may be left out on the bench and the third may be placed near a source of strong light (example: in direct sunshine or near to a lamp).

Question:

Examine the colour of the precipitates at fairly regular intervals and interpret your observations.

Light is a form of energy that can affect the rate of a reaction. The rate of some photochemical reactions, increases with increase in the intensity of suitable light used. With the increase in the intensity, the number of photons in light also increases. Hence more number of reactant molecules gets energy by absorbing more number of photons and undergo chemical change.

Examples:

1. When methane reacts with chlorine in dark, the reaction rate is very low. It can be speeded up when the mixture is put under diffused light. In bright sunlight, the reaction is explosive.

2. The rate of photosynthesis reaction is more on brighter days. At low light ntensities, as light intensity increases, the rate of the light-dependent reaction (photosynthesis) generally, increases. The more photons of light that fall on a leaf, the greater the number of chlorophyll molecules that are ionized and the more ATP and NADPH are generated.

However, some photochemical reactions involving the free radicals, generated in a chain process, are not greatly affected by the intensity of the light. Only one photon is sufficient to trigger the formation a free radical. This, in turn, initiates a chain process in which more free radicals are formed repeatedly in each cycle without the need of extra photons.

When photons strike the reactant molecules, they provide necessary activation energy to the reactant molecules.

There are many reactions influenced by light. For example: photosynthesis and photography. Such reactions are known as **photochemical reactions.** Other examples are:

$$H_2 + Cl_2 \xrightarrow{\text{sunlight}} 2HCl$$

$$2AgCl \xrightarrow{\text{sunlight}} 2Ag + Cl_2$$

$$SO_2 + Cl_2 \xrightarrow{\text{sunlight}} \underbrace{SO_2Cl_2}_{\text{sulphuryl chloride}}$$

$$CO + Cl_2 \xrightarrow{\text{sunlight}} \underbrace{COCl_2}_{\text{phosgene}}$$

13.2.6. Effect of surface area on rate of reaction

Surface area is the measure of how much area of an object is exposed. For the same mass, many small particles have a greater surface area than one large particle. The more surface contact between reactants, the higher the rate of reaction. The less surface contact, the lower the reaction rate.

The rate of chemical reactions increases by increasing the surface area of reactants. For example, a log of wood burns slowly but if it is cut into small wooden chips, the burning takes place rapidly.

The rate of a reaction between two phases depends to a great extent on the surface contact between them. A finely divided solid has more surface area available for reaction than does one large piece of the same substance. Thus a liquid will react more rapidly with a finely divided solid than with a large piece of the same solid.

Examples:

1. Large pieces of iron react slowly with acids; finely divided iron reacts much more rapidly.
2. Large pieces of wood smolder, smaller pieces burn rapidly, and sawdust burns explosively.
3. Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas because the powder has a large total surface area: $2Fe(s) + 6HCl(aq) \longrightarrow 2FeCl_3(aq) + 3H_2(g)$
4. An iron nail reacts more slowly.
5. Powdered calcium carbonate reacts much faster with dilute hydrochloric acid than if the same mass was present as lumps of marble chips or limestone.

$$CaCO_{3(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$$

6. Solid manganese (IV) oxide is often used as the catalyst. Oxygen is given off much faster if the catalyst is present as a powder than as the same mass of granules.

$$2H_2O_{2(aq)} \xrightarrow{MnO_{2(s)}} 2H_2O_{(l)} + O_{2(g)}$$

If one of the reactants is solid, it can be broken into smaller pieces. This increases the surface area for the other reactant to collide with it. In general, the more finely divided a solid reactant is, the greater the surface area per unit volume and the more the number of collisions between reactants. Increasing the collisions increases the rate of reaction.

Checking up 13.2

1. Explain how the following factors affect the reaction rate:
   a. Concentration
   b. Pressure
   c. Temperature
   d. Catalyst
   e. Light
   f. Surface area or particle size
2. The rate constants of a reaction at 500K and 700K are $0.02s^{-1}$ and $0.07s^{-1}$ respectively. Calculate the values of activation energy (Ea) and frequency factor (A).
3. The rate constants of reaction at 700 K and 760 K are $0.011M^{-1}s^{-1}$ and $0.105 M^{-1}s^{-1}$ respectively. What are the values of 'A' and 'Ea'?

END UNIT ASSESSMENT

1. For the following multiple choice questions on the rate of reactions, choose the correct answer.
   Study of rate of chemical reactions is called ……
   a. reaction rate
   b. reaction kinetics
   c. reaction speed
   d. reaction power

2. As the temperature of a reaction is increased, the rate of the reaction increases because the……..
   a. Reactant molecules collide less frequently
   b. Reactant molecules collide more frequently and with greater energy per collision
   c. Activation energy is lowered
   d. Reactant molecules collide less frequently and with greater energy per collision

3. Rate of reaction is change in amount of reactants or products in specific
   a. volume
   b. density
   c. time
   d. area

4. Effect of pressure (in case of gases) is similar to effect of
   a. concentration
   b. molarities
   c. temperature
   d. humidity

5. Factors which affect rate of chemical reaction are
   a. surface area
   b. temperature, catalysts
   c. concentration
   d. All of above

6 The minimum amount of energy needed to start a reaction is called the

a. activation energy.
b. energy of reaction.
c. entropy of reaction
d. reaction mechanism energy

7. Of the following, _____ will lower the activation energy for a reaction.

a. Increasing the concentrations of reactants
b. Raising the temperature of the reaction
c. Adding a catalyst for the reaction
d. Removing products as the reaction proceeds

8. If a piece of beef liver (which acts as manganese (IV) oxide) is dipped in hydrogen peroxide, gas given off is:

a. Hydrogen
b. Ice
c. Carbon monoxide
d. Oxygen

9. Which of the following would NOT increase the rate of reaction.

a. Raising the temperature
b. Adding catalyst
c. Increasing the concentration of the reactants
d. Increasing the volume of the container

10. If the temperature of a reaction is increased by 10°C, the new rate of reaction will be approximately

a. ten times greater
b. doubled
c. unchanged
d. four times greater

11. Aluminium reacts with warm dilute hydrochloric acid to give aluminium chloride solution and hydrogen. Explain why the reaction of dilute hydrochloric acid with aluminium foil is fairly slow whereas the reaction with the same mass of aluminium powder can be extremely vigorous.

12. For the reaction $A \rightarrow B$, the concentration of a reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.

13. The decomposition of dinitrogen pentoxide (N_2O_5) in tetrachloromethane (CCl_4) at 318K has been studied by monitoring the concentration of dinitrogen pentoxide in the solution. Initially, the concentration of dinitrogen pentoxide is 2.33mol/L and after 184 minutes. It is reduced to 2.08mol/L. The reaction takes place according to the equation:

    Calculate the average rate of this reaction in terms of hours, minutes and seconds. What is the rate of production of nitrogen dioxide during this period?

14. Calculate the activation energy for a reaction whose rate constants are $2.15 \times 10^{-1} dm^3 mol^{-1} s^{-1}$ and $7.25 \times 10^{-3} dm^3 mol^{-1} s^{-1}$ at 991K and 500K respectively. ($R = 8.3145\ JK^{-1}mol^{-1}$).

15. How much faster will the reaction be at 781K than 550K if the activation energy of the reaction is 190 kJ/mol? ($R = 8.3145\ JK^{-1}mol^{-1}$)

UNIT 14

RATE LAWS AND MEASUREMENT

UNIT 14: RATE LAWS AND MEASUREMENTS

Key Unit Competency:

Measure the rates of reaction and formulate simple rate equations using the experimental results.

Learning objectives:

By the end of this unit the learners should be able to:

- State and explain kinetic conditions for a chemical reaction to take place.
- Explain the effect of the temperature and catalysts on the rate of the reaction using Boltzmann distribution of energies (and of collision frequency).
- Differentiate between SN_1 and SN_2 mechanisms.
- State and explain the rate determining steps for multi-step reactions.
- Deduce the order of reaction from appropriate experimental data.
- Calculate the initial rates and the rate constants of reactions from the experimental data.
- Perform practical activities to show how different reactions have different rates.
- Interpret the graphs which show the change in activation energy with the catalyst.
- Calculate the half-life of chemical reaction.
- Perform practical activities to measure the rates of reaction by observing the changes in physical quantities (e.g. volume, mass and colour change).
- Use collision theory to predict if the reaction will go faster or slower.
- Construct rate equations of the form (Rate = $k [A]^n[B]^m$) limited to simple cases involving zero, first and second order reactions.
- Interpret graphs of concentration against time and those of concentration against rate for zero and first order reactions.
- Develop a spirit of team work, analysis, and self-confidence while discussing exercises and performing the experiments.
- Appreciate the contributions of Arrhenius and Boltzmann on the effect temperature and activation energy of different substances and number of molecules

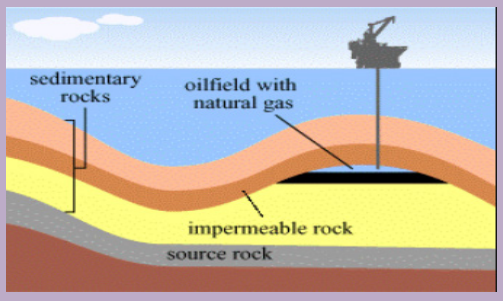
Introductory activity

One of the mission of chemistry consists in making substances from other substances. Referring to the following six figures; some processes are observed during a chemical reaction from each Figure. Observe these figures carefully and answer the related questions.

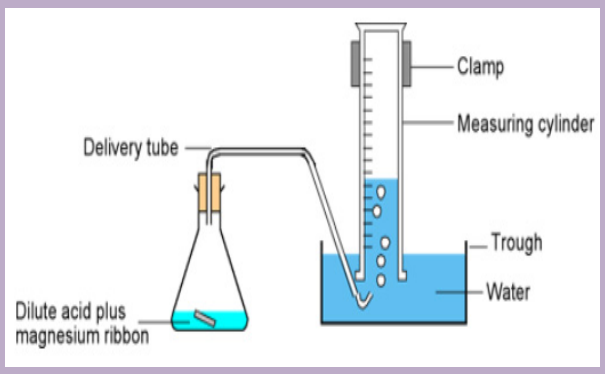
(1)

(2)

(3)



(4)



(5)

(6)

i. Suggest what is happening in each image.

ii. Classify the processes into slow or fast processes, and explain why?

14.1 Theories of reaction rates

Activity 14.1

1. Draw the energy profile diagram for
   a. An exothermic reaction
   b. An endothermic reaction
2. Using textbook or internet read and analyze the content about collision theory of reaction rates and make a summary to be presented to the class. In this work you should be able to explain contribution of Arrhenius and Boltzmann on the effect of temperature and activation energy on rates of reaction.

In the previous unit, the factors that influence the rate of a reaction have been discussed. It is known that during a chemical reaction, the reactant species are converted into the new substances called products. This means that during a chemical reaction, the concentration of reactants decreases as they are consumed and that of products increases as they are in formation. In a chemical reaction, how quickly or slowly reactants turn into products is called the **rate of reaction**. Two theories known as "collision theory" and transition state theory" explain the rate of reaction.

14.1.1. Collision theory

According to the collision theory, a chemical reaction takes place due to the effective collisions of reacting molecules. For an effective collision to happen, the reactant species must be oriented in space correctly to facilitate the breaking of old bonds and forming of new bonds. Molecules which did not participate in effective collisions do not favor the reaction. During a chemical reaction species that collide must possess also a minimum amount of kinetic energy called "activation energy (Ea)". The activation energy varies depending on the reaction. Therefore, the rate of reaction depends on the activation energy; a higher activation energy means that fewer molecules will have sufficient energy to undergo an effective collision.

Consider the reaction: A-A + B-B → 2(A-B)

For the reaction to take place, A-A and B-B must possess the activation energy, Ea that is required for breaking their bonds in order to form the new compound 2(A-B). The energy changes that occur during a chemical reaction can be shown in a Figure 14.1.

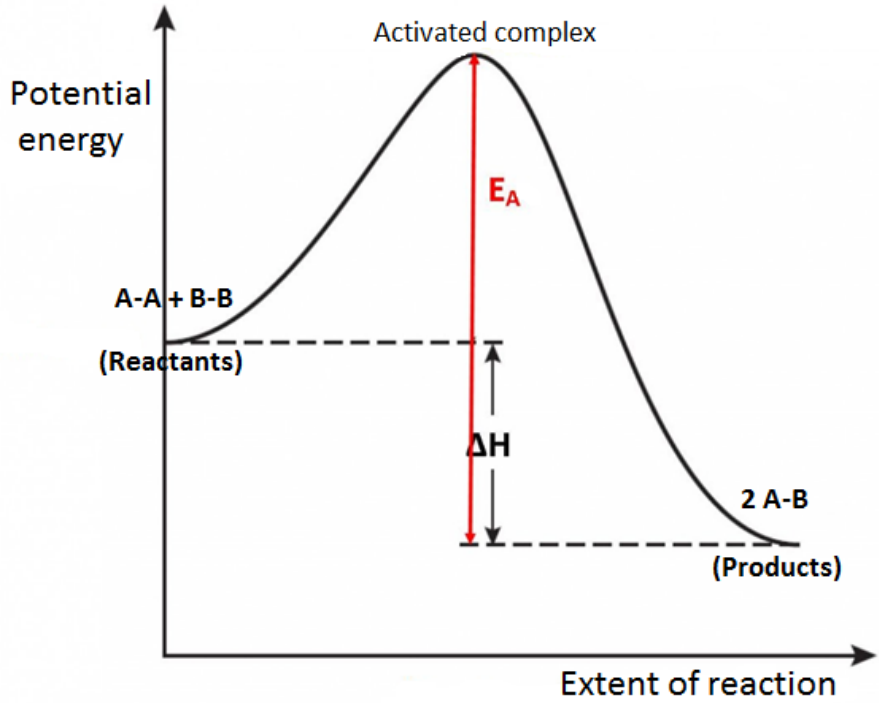


Figure 14.1: The energy profile diagram

The activation energy, (Ea), is the minimum energy required to initiate a reaction. Only colliding molecules with energy greater than or equal to Ea can lead to the reaction process. When two reactant molecules approach one another, their velocity will be slowed down due to the repulsion between their electrons clouds. However, if the initial kinetic energy of the colliding molecules is high, they can overcome the repulsion force and approach one another leading to the formation of products by merging the electron clouds.

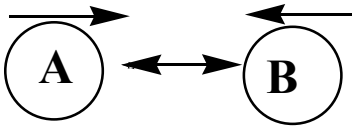
For a chemical reaction to occur, there are three main conditions that must be fulfilled.

i. The reactants must collide: no reaction is observed if there are no collisions between reactant compounds.
ii. The molecules must have sufficient energy (activation energy) to initiate the reaction.
iii. The molecules must have proper orientation. Unless the reactant particles possess this orientation when they collide, the collision will not be an effective one.

Application examples:

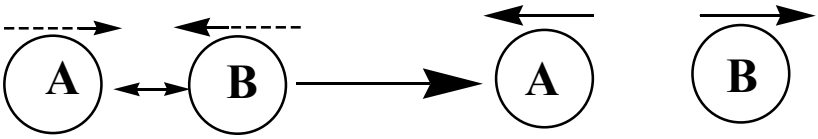
1. Consider the reaction: **A + B→ AB**

As the two reactant molecules approach one another, their velocity will be slowed down due to the repulsion between their electron clouds.



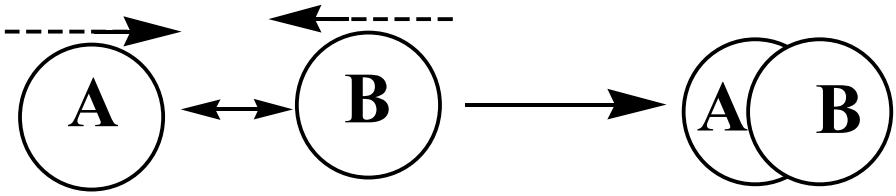
Repulsion between electron clouds

If the initial kinetic energy of the colliding molecules is low, the molecules will repel one another and no product will be formed.



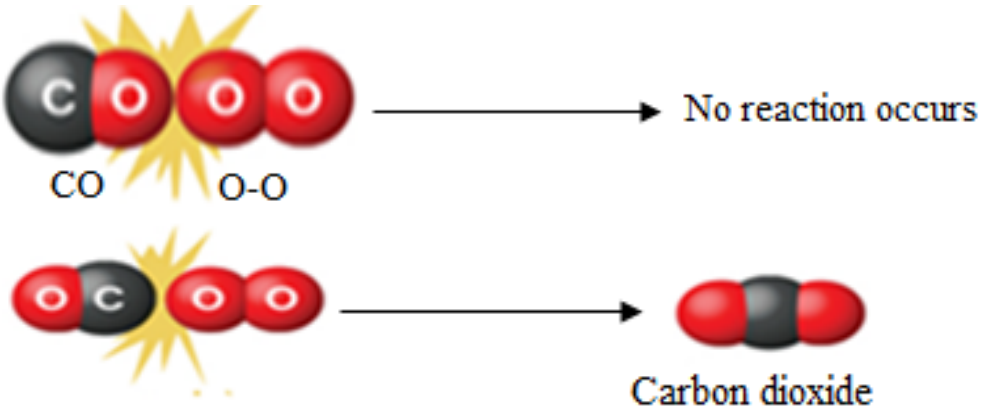
Repulsion collision

If the initial kinetic energy of the colliding molecules is high, they can overcome the repulsion force and approach one another so that electron clouds merge to form the products.



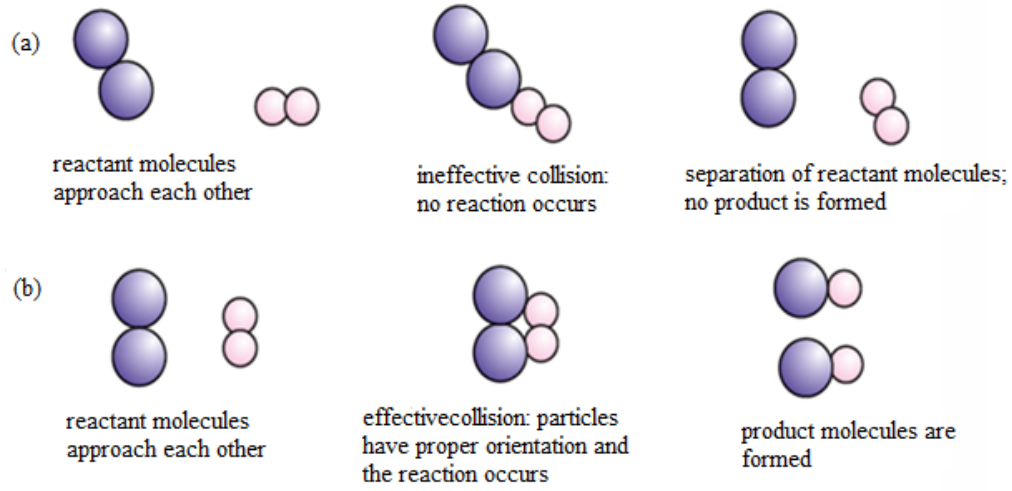
Effective collision

2. Consider the reaction ($CO(g) + O_2(g) \rightarrow CO_2(g)$) represented as follows:



These examples show that when an effective collision requires a proper orientation of the reacting particles to form the products.

3. The following examples (a) and (b) show also that the probability of a reaction to occur depends not only on the collision energy but also on the spatial orientation of the molecules when they collide.



The collision theory is based on the kinetic theory and assumes a collision between reactants before a reaction can take place. It explains how temperature and activation energy affect the rate of reaction.

a. The speed of reaction and theory of collision

The activation energy depends on the nature of chemical bonds, which are broken during the reaction. The stronger the bonds, the greater is the activation energy.

For an elementary reaction, the collision theory shows that the speed (rate, R) of a reaction is given by $R = f \times p \times z$

Where: R = the rate or speed of the reaction

f = the fraction of molecules having kinetic energy that can cause a reaction

p = the probable fraction of collisions with proper (effective) orientation

z = the frequency of collision

b. Effect of increase in temperature on the rate of reaction

An increase in temperature typically increases the rate of reaction. An increase in temperature will raise the average kinetic energy of the reactant molecules. Therefore, a greater proportion of molecules will have the minimum energy necessary for an effective collision. For example, an increase in temperature by 10 °C (or 10 K), doubles the speed of reaction.

From the kinetic theory, it is known that the kinetic energy (K) of a gas is directly proportional to its temperature.

$$K = \frac{1}{2}mv^2 = \frac{3RT}{2N_A}$$

Where: m = mass of the gas

v = speed of the gas molecule

N_A = Avogadro's number = 6.6023 x10^{23} particles for one mole of a gas at standard conditions

$\frac{R}{N_A} = 1.38 \times 10^{-23}$ J K^{-1} =1.38×10^{-16} erg/K

= The Boltzmann constant

T = Absolute temperature in Kelvin (K)

R = Universal (molar) gas constant = 0.08206 L atm/mol K or 8.314 m^3Pa/mol K

The numerical values of the gas constant, R, can be expressed using different units as indicated in Table 14.1.

Table14.1. Gas constant R converted in various units

Units	Numerical value
L-atm/mol-K	0.08206
J/mol-K	8.314
Cal/mol-K	1.987
m^3 Pa/mol-K	8.314
L-torr/mol-K	62.36

When the temperature is increased, there is an increase in the total number of particles with energy equal to or greater than the activation energy (Ea).

The combined effects cause the rate of reaction to increase as illustrated by the Maxwell-Boltzmam distribution curve (Figure 14.2).

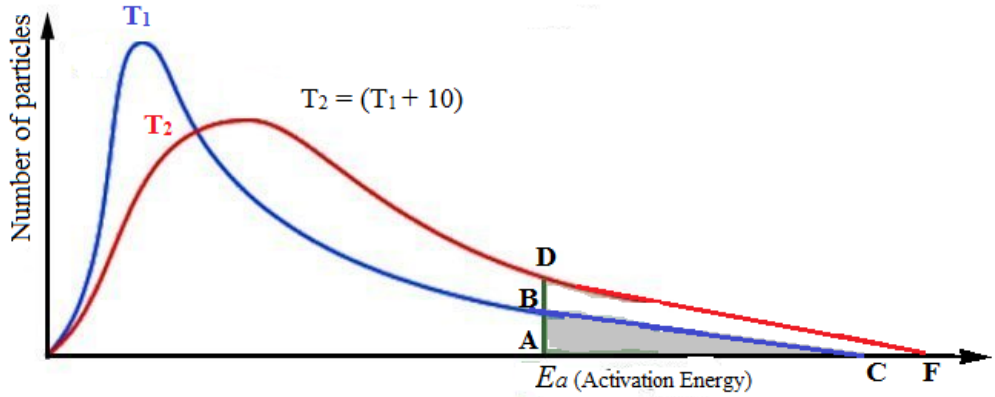


Figure 14.2: The Maxwell-Boltzmann distribution curve

Note:

- The area under the curve is the same in both cases because the number of molecules remains the same.
- All the fractions add up to unity
- The fraction of molecules with energy E ≥ Ea, is greatest at higher temperature, T_2.

That is when temperature increases,

i. the average kinetic energy of the molecules increases resulting in more collisions per unit time,

ii. The fraction of molecules with E ≥ Ea increases

At temperature T_1, the number of particles having energy equal to or greater than the activation energy (Ea) is given by the area ABC (Figure 14.2).

At T_2 the number of particles having energy equal or greater to Ea increases about two times by the area ADF (Figure 14.2).

c. **Temperature, rate of reaction and Arrhenius equation**

The relationship between the rate constant (k) of a reaction and temperature (T) of the system was first proposed by Arrhenius in 1889 and it is commonly known as the Arrhenius equation. It is written as:

$$k = A.\ e^{-Ea/RT} \quad (1)$$

Where: k = rate constant

Ea = activation energy

R is the gas constant = 8.314 (J mol^{-1} K^{-1})

T = absolute temperature in Kelvin degrees (0°C = 273 K)

A = Arrhenius constant or frequency factor

A = p · Z, where Z is the collision frequency and ***p*** is called the steric factor (always less than 1) and reflects the fraction of collisions with effective orientations.

$e^{-Ea/RT}$ represents the fraction of collisions with sufficient energy to produce a reaction.

The Arrhenius equation (1) is often written using the natural logarithm of both sides in order to determine the activation energy (Ea) for a chemical process.

$$\ln k = -\frac{Ea}{RT} + \ln A \qquad (2)$$

From the equation (2), it is possible to determine the activation energy using the ratio of two rate constants (k_1, k_2) and the two corresponding reaction temperatures (T_1, T_2). The following equations may be obtained:

$$\ln k_1 = -\frac{Ea}{RT_1} + \ln A \qquad (3)$$

$$\text{and } \ln k_2 = -\frac{Ea}{RT_2} + \ln A \qquad (4)$$

Subtracting the equation (4) from the equation (3), we have:

$$\ln k_1 - \ln k_2 = \left(-\frac{Ea}{RT_1} + \ln A\right) - \left(-\frac{Ea}{RT_2} + \ln A\right) \qquad (5)$$

Simplifying the equation (5) and rearranging it gives:

$$\ln \frac{k_1}{k_2} = \frac{Ea}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (6)$$

$$\text{Or } \log \frac{k_2}{k_1} = -\frac{Ea}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (7)$$

The equation (7) can be written as:

$$\log \frac{k_2}{k_1} = +\frac{Ea}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (8)$$

The activation energy can be deduced from the equation (8) if k_1, k_2, T_1 and T_2 are known.

Example 1:

For a reaction with activation energy of 55 kJ/mol, by what factor will the rate constant go up with a rise in temperature from 300 K to 310 K?

Solution:

$$\log\frac{k_2}{k_1} = -\frac{55000}{2.303x8.314}\left(\frac{1}{310} - \frac{1}{300}\right)$$

$$\log\frac{k_2}{k_1} = 0.30887 \Rightarrow \frac{k_2}{k_1} = 2.04$$

The above example showed that an increase of the temperature leads to the increase of the rate of the reaction. The rate of the reaction doubles for any 10K rise in temperature.

Example 2:

What is the activation energy of a reaction whose rate quadruples when the temperature is raised from 293 K to 313 K?

Solution:

$$\log\frac{k_2}{k_1} = +\frac{Ea}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\frac{k_2}{k_1} = 4;\ T_1 = 293K \text{ and } T_2 = 313K$$

$$\text{Applying the relation}: \log\frac{k_2}{k_1} = +\frac{Ea}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right), \textit{we have}:$$

$$\log 4 = \frac{Ea}{2.303x8.314}\left(\frac{1}{293} - \frac{1}{313}\right)$$

$$Ea = \frac{(\log 4)x2.303x8.314}{\left(\frac{1}{293} - \frac{1}{313}\right)}$$

$$Ea = 52.85kJ/mol$$

The Arrhenius relation can be plotted to obtain a straight line. The graph of **ln k** versus **1/T** (Figure 14.3) is a straight line with a negative slope. It shows the dependence of the rate of reaction with temperature.

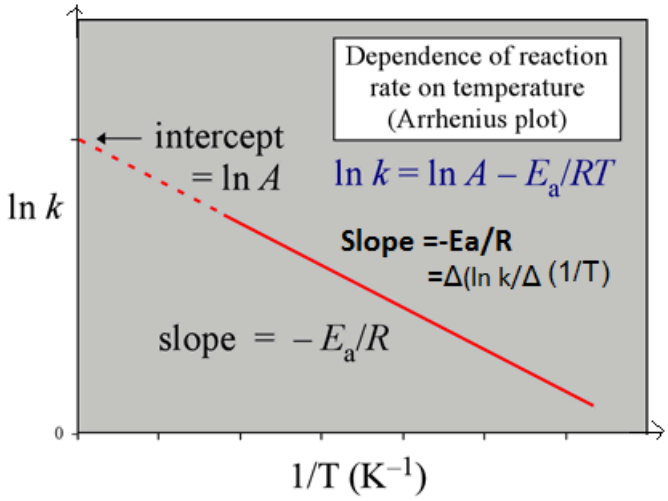


Figure 14.3: The Arrhenius plot of ln k against $\frac{1}{T}$

A part from the collision theory that explain the effect of temperature on the rate of reaction, the transition state theory also is based on the temperature effect on the rate of reaction.

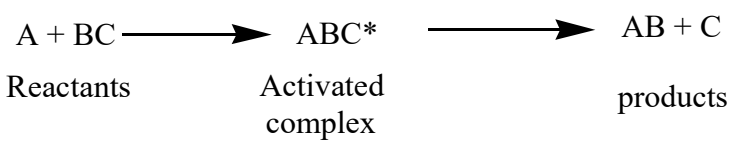
14.1.2 The transition state theory

The transition state theory has been developed by Henry Erying in 1935. The theory supposes that a collision between reactants does not lead immediately to products. This theory supposes that the molecules collide and remain held for a certain interval of time, forming intermediate species or activated complexes (transition state) whose energy is higher than the average energy of the reactants. These activated complexes get then dissociated by generating either the reaction products or the starting reactants.

The activated complex is an unstable grouping of atoms, formed during a fruitful collision that breaks apart to form reaction product(s).

The energy needed to form an activated complex is equal to or greater than the activation energy Ea of the reaction.

Example:



(*) The exponent is used to designate the activated complex.

The transition state theory provides a way to calculate the rate constant for the reaction.

According to the transition state theory:

1. During collision, the attraction between reacting molecules decreases and the kinetic energy of the molecules is converted into potential energy.
2. When the molecules approach, the interaction of the electronic configuration allows the rearrangement of valence electrons.
3. A temporary bond between atoms A and B is formed where as the bond for a bond B-C is weakered, which leads to the formation of activated complex. The activated complex is momentary as it decomposes to give the products (A-B + C)

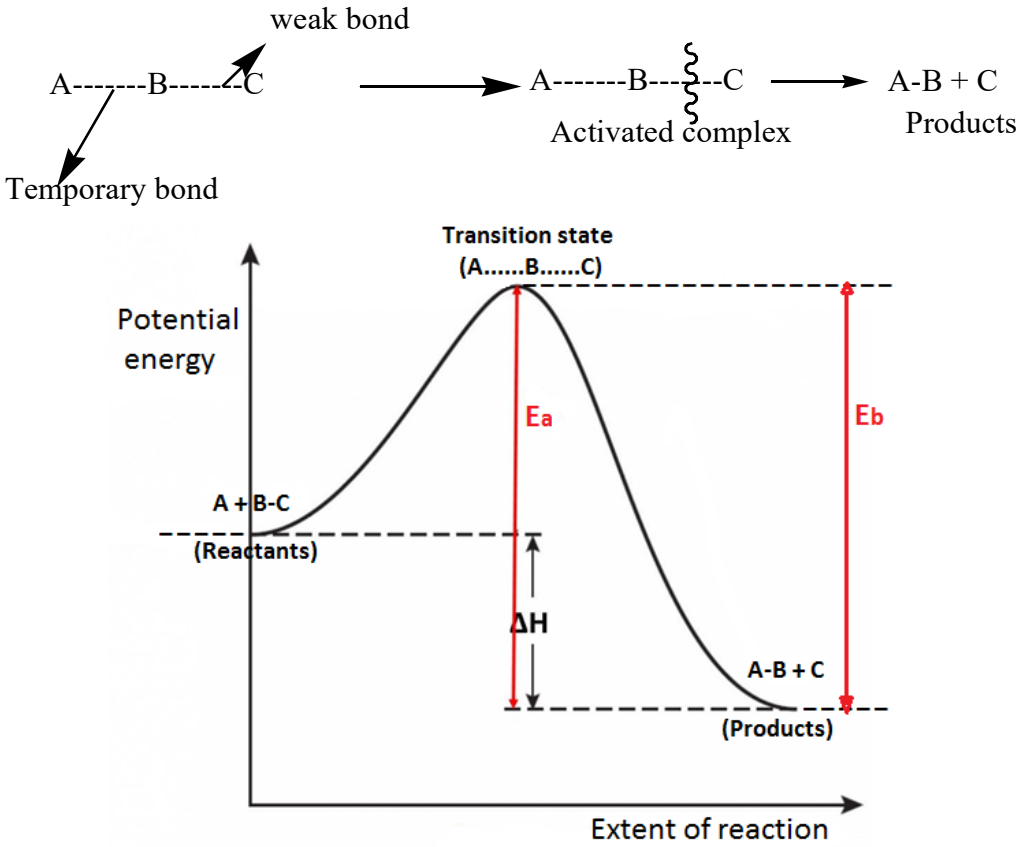


Figure 14.4: The diagram of energy profile for an exothermic reaction

The difference in potential energy between the reactants and the activated complex corresponds to the activation energy of the reactants, Ea

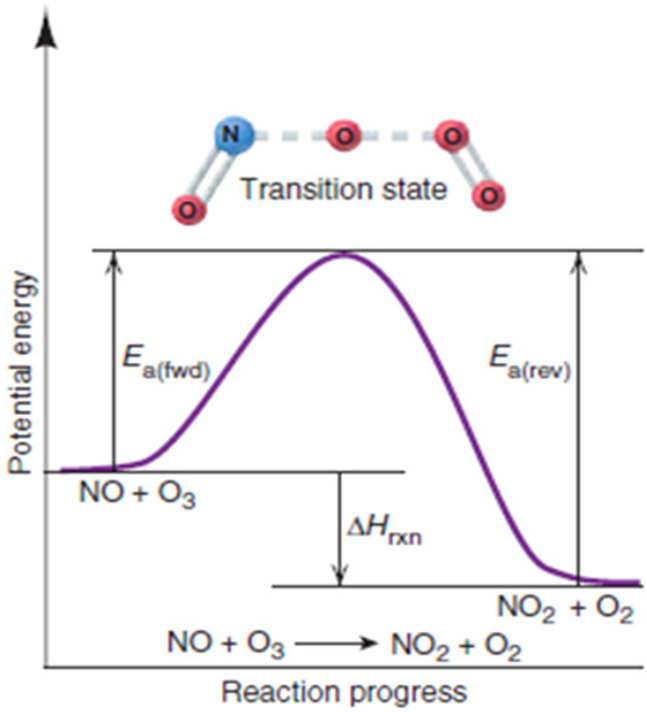
Eb is the energy required for the products to give reactants (for reverse reaction)

The change in enthalpy of the reaction ΔH can be found as follows:

$\Delta H = \sum H_{products} - \sum H_{reactants}$ or $\Delta H = Eb - Ea$

Example: Consider the diagram profile for the following reversible reaction:

$$NO + O_3 \rightleftharpoons NO_2 + O$$



ΔH_{rxn} = Ea (rev) – Ea (fwd) > 0, the reaction is exothermic

If the potential energy of the products is less to the energy of reactants, the obtained energy (for the transition state to change to products will be greater than the activation energy.. Hence the reaction will be exothermic. If the potential energy of products is greater than that of reactants, the energy released for the activated complex to give products will be less than the activation energy. Hence the reaction will be endothermic.

For any reaction, there exist a **barrier of energy** (activation energy) which must be overcome for a reaction to take place.

The use of a catalyst can reduce the activation energy as it provides an alternative reaction pathway with the minimum activation energy as a result, more reactant molecules possess the energy required for a successful collision. As the speed of the reaction is proportional to the effective collisions, the presence of a catalyst increases the speed of both forward and reverse reaction but it is regenerated after reaction.

It should be noted that even if a catalyst lowers the activation energy, the difference in energy, ΔH, between products and reactants remains constant. For an endothermic reaction, the activation energy of the reactants is greater than that of products and ΔH of the reaction is negative (Figure 14.5).

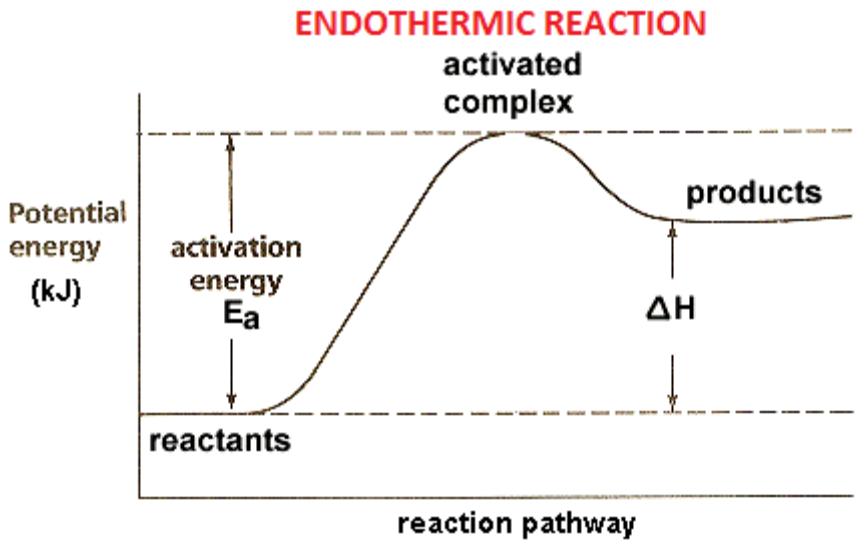
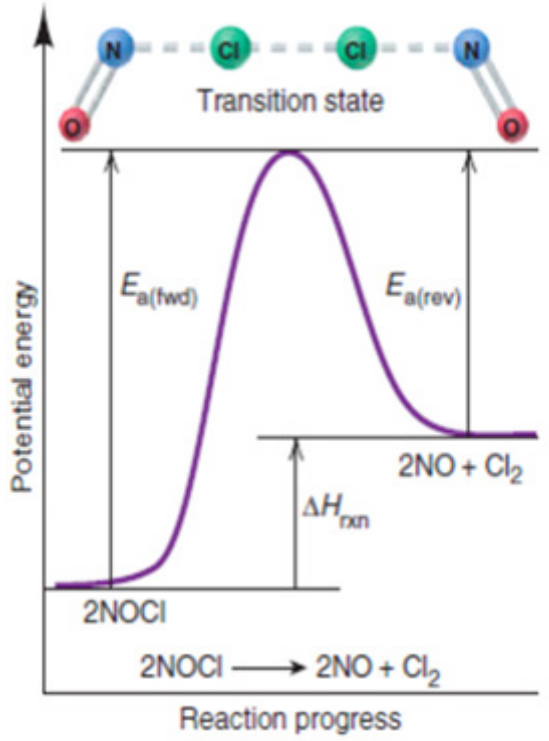


Figure 14.5: Potential energy for an endothermic reaction.

Example:

Consider the following diagram profile of the reaction:

$$2NOCl \longrightarrow 2NO + Cl_2$$



ΔH_{rxn} = Ea (rev) – Ea (fwd) < 0, the reaction is endothermic

Checking up 14.1

1. Given the following equation for the decomposition of nitrous oxide: $2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$ and given that the activation energy for the forward reaction is + 251 kJ and that the change in enthalpy for the reaction is +167 kJ.
   a. Sketch and label a potential energy diagram for the decomposition of nitrous oxide:
   b. What is the activation energy for a reverse reaction?
2. For the reaction between A-A and B-B to give AB +AB
   i.e A-A + B-B → AB +AB, Draw a situation showing effective collision and another situation which is not effective.

14. 2. Measuring the rates of reaction by observing the mass changes, colour changes and volume changes

Activity 14.2

Experiment 1: Measuring the rate of reaction by observing the volume change of the gas produced.

Apparatuses and chemicals: 3.0M HCl, calcium carbonate in form of marble chips, graduated measuring cylinder or flexible graduated syringe, balance, funnel, conical flask, stop clock, stopper for closing the conical flask, retort stand .

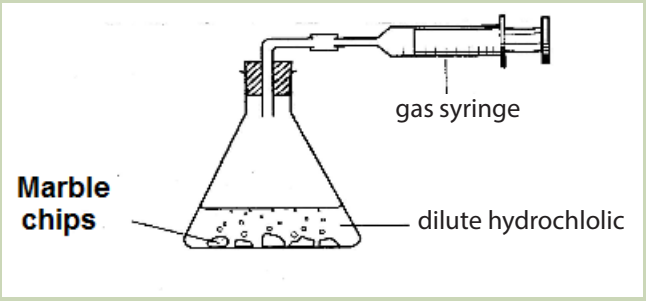
Procedure:

1. Weigh 40g of marble chips (calcium carbonate) and put them in the conical flask

Time taken/ s	**0**	**10**	**20**	**30**	**40**	**50**	**60**	**70**	**80**	**90**	**100**	**110**	**120**
Vcarbon dioxide/cm^3													

2. Measure 100 cm^3 of 3.0M HCl and transfer all the acid into the conical flask using a funnel. Close the mouth of the conical flask with a stopper.
3. Connect the conical flask to a flexible graduated syringe. Clamp the flexible graduated syringe.

Start the stop clock and record the total volume of carbon dioxide collected in the flexible graduated syringe. Record your results in the table below:



Measuring the rate of reaction by observing the volume change

Questions:

a. Plot a graph of gas volume of carbon dioxide evolved on y-axis against time on the x-axis.

b. Determine the rate of evolution of gas at 10 seconds, 20 seconds, and 100 seconds. What can you conclude about the reaction rate as time progresses?

Experiment 2: Measuring the rate of reaction by obsering color change

You are provided with 0.2M HCl(aq) and 0.05M $Na_2S_2O_3$(aq).

By changing the concentration of $Na_2S_2O_3$ and keeping constant the concentration of HCl.

a. On a piece of paper, draw a cross (X) using a marker pen and place this paper under a conical flask.

b. Complete the following table of results:

Volume of $Na_2S_2O_3/cm^3$	Volume of H_2O/cm^3	Volume of HCl/cm^3	time/sec for the cross to disappear	ΔV	Δt	ΔV/ Δt
100		25				
50		25				
25		25				
12.5		25				
6.25		25				

i. Write an equation between $Na_2S_2O_3$(aq) and HCl(aq).

ii. Plot a graph of time for the cross to disappear against volume of Na2S2O3(aq)

iii. Write down the color changes in the reaction above.

iv. Describe the chemical test of a gas produced in the reaction

Measuring the rates of reaction uses different techniques depend on the reaction.

The rate of reaction can be measured by using the change in mass, color change, volume and other properties. By analyzing the reaction mixture at suitable time intervals, one can determine the concentration of both reactants and products at particular time, hence determining the reaction rate. Sometimes it is easier to measure the change in the amount of a reactant that has been used up; sometimes it is easier to measure the change in the amount of a product that has been produced.

The method used to analyze the reaction mixture depends on the reaction under consideration. The concentration is not measured directly in many cases, it is determined based on the signal related to the change in concentration. For example in the case of the reaction producing the colour, the intensity of the colour can be measured and related to the amount of products formed. If a reaction gives off gas, the change in volume or in mass can be measured. In this case, we will discuss about the change in volume or mass and change in color to measure the rate s of the reaction.

14.2.1. Measuring the rates of reaction by observing the volume changes

To measure the reaction rate by change in volume of gas produced is a convenient method if one of the products is a gas. A gas syringe can be used for this purpose (Figure 14.7).

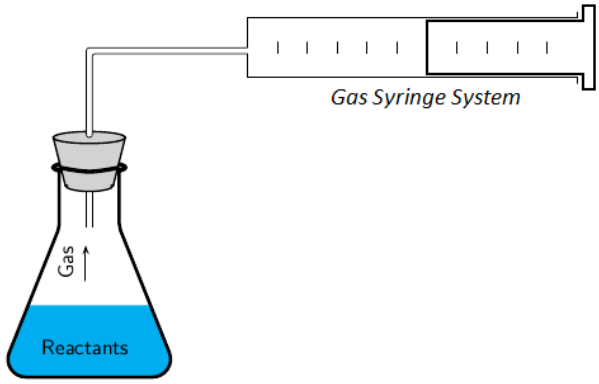


Figure 14.7: The gas syringe method.

This method consists of a ground glass and a plunger, which moves outwards as the gas collects and is calibrated to record the volume directly. As more gas is produced, the plunger is pushed out and the volume of the gas in the syringe can be recorded. By measuring the volume at different time intervals, we can plot the data by following the change in volume against time and hence determine the rate of the reaction (Figure 14.8).

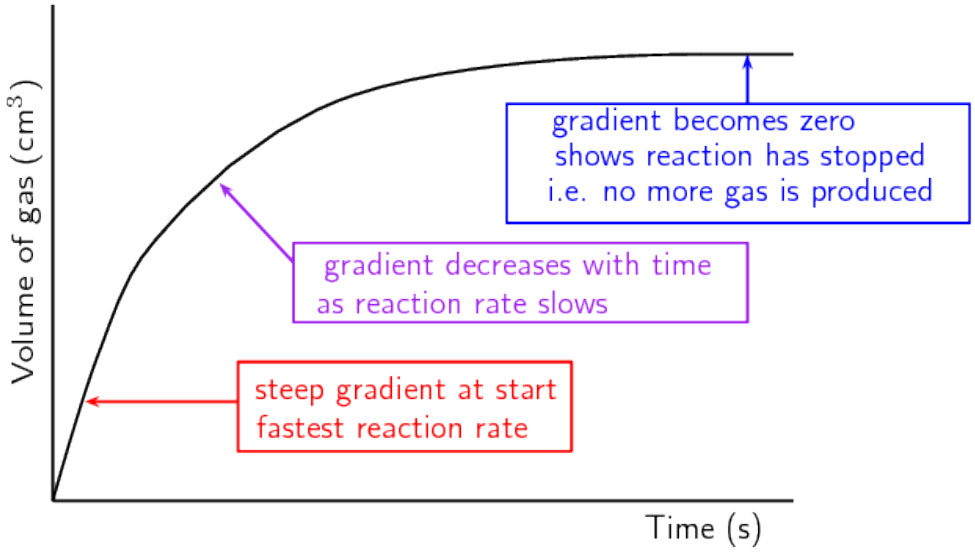


Figure 14.8: Graph showing the volume of gas collected against time.

Examples of reactions that produce gas

i. Reaction that produce hydrogen gas

When a metal reacts with an acid, hydrogen gas is produced. For example, magnesium reacts with sulphuric acid to produce magnesium suphate and hydrogen as follows.

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

The hydrogen can be collected in a test tube. A glowing splint can be used to test the presence of hydrogen. The '**pop**' sound shows that hydrogen is present.

ii. Reaction that produce carbon dioxide

When a carbonate reacts with an acid, carbon dioxide gas is produced. When carbon dioxide is passed through limewater, it turns the limewater milky. A burning splint will also stop burning (be extinguished) in the presence of CO_2 gas. These are simple tests for the presence of carbon dioxide.

The reaction is: $CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

iii. Reaction that produce oxygen

Hydrogen peroxide decomposes in the presence of a manganese (IV) oxide as catalyst to produce oxygen and water.

$$2H_2O_2(aq) \xrightarrow{MnO_2} 2H_2O(l) + O_2(g)$$

14.2.2. Measuring the rate of reaction by observing change in mass

Many reactions involve a change in mass and it may be measured directly. For a reaction that produces gas, the decrease in mass can be measured by standing the reaction mixture directly on a balance (Figure 14.9).The mass loss indicates the amount of gas that has been produced and escaped from the reaction vessel. The method allows continuous reading and a graph can be plotted directly of sample mass and mass lost against time (Figures 14.10 and 14.11), respectively. The release of carbon dioxide from the reaction between a carbonate and a diluted acid can be measured by this method and the rate is determined

$CaCO_3(s) + 2\,HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

To start the reaction, the flask is gently lent to one side, causing the card to fall and the marble chips and acid to mix. A piece of cotton wool placed in the neck of the flask allows carbon dioxide gas to escape. As the gas escapes the mass of the flask reduces within an interval of time. The rate of the reaction can be deduced as the change in mass over the change in time.

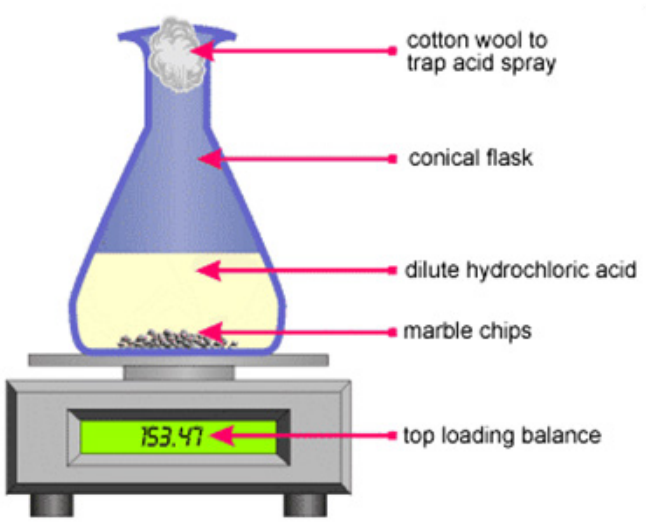


Figure 14.9. Measurement of the reaction rate following change in mass of reactants against time

Since the reaction rate is the change in the amount of a product or a reactant per unit time, any property that is related to amount of product or reactant present can be used to measure the rate of reaction.

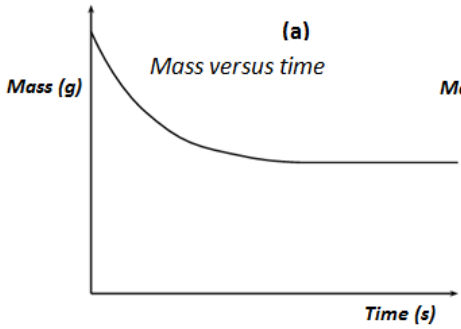


Figure 14.10. A graph of the sample mass versus time

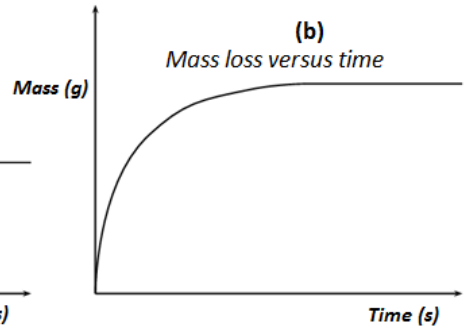


Figure 14.11. A graph of the mass loss versus time.

property that is related to amount of product or reactant present can be used to measure the rate of reaction

14.2.3. Measuring the rate of reaction by observing color change

Measuring the rate of reaction by observing color change can be applied if one of the reactants or products is colored and gives characteristic absorption in the visible region (about 320-380 nm of wavelength). Sometimes, an indicator can be added to generate a coloured substance that can be followed in the reaction. A colorimeter or spectrophotometer can be used to measure the intensity of the light transmitted by the reaction compounds. As the concentration of the coloured substances increases, it means that it absorbs more light and is less transmitted.

Amount of light absorbed depends on the amount of absorbing species present. If a reactant or product absorbs light, then the color intensity will vary as the amount of this species changes. An example is the reaction between sodium thiosulphate and hydrochloric acid.

$$Na_2S_2O_3\,(aq) + HCl(g) \rightarrow SO_2(g) + 2NaCl(aq) + H_2O(l) + S(s)$$

The solution changes its color from colorless to yellow due to sulphur precipitate which is formed, and the concentration of yellow precipitate increases with time as more sulphur is being formed indicating that the reaction has occurred.

14.3. Experimental determination of orders of reaction and rate laws

Activity 14.3

Using this textbook or internet or any other relevant book, read and analyze the content about experimental determination of orders of reactions and rate laws and make summary to be presented in the class. In this work you should also do the exercises of calculation.

- **Rate law or rate equation**

The rate of the reaction changes with time. The rate of reaction does not depend on the choice of substance, but it does depend on the way in which the chemical reaction is written. Therefore, a rate must be specified with a specific time unit (Mole/L. sec or $M.s^{-1}$.

The rate law or rate equation of a chemical reaction is a mathematical equation that links the reaction rate with concentration or pressure of reactants and a constant rate.

In a chemical reaction, the stoichiometric coefficients indicate the reacting mole ratio of the reactant and the number of mole of product that can be obtained.

Let us consider the following equation:

$$aA + bB \rightarrow cC + dD$$

In the reaction, **a** mole of A will combine with **b** moles of B to form **c** moles of C and **d** moles of D.

The rate law of this reaction can be expressed as: $Rate\ law = k[\mathrm{A}]^x[B]^y$

Where:

k: rate constant

x and y are integers: small whole numbers (Usually 0,1 or 2) called orders of reaction

[A] and [B] are molar concentrations of A and B respectively.

The proportionality constant, *k,* is known as the **rate constant** and is specific for the reaction shown at a particular temperature. The rate constant changes with temperature and its units depend on the sum of the concentration term exponents

in the rate law. The exponents (*x* and *y*) must be experimentally determined and do not necessarily correspond to the coefficients in the balanced chemical equation.

Note: When the concentration of A is changed by a factor of x, the rate will increase by a factor of x. A reaction's rate law may be determined by the initial rates method.

- **Reaction order**

The sum of the concentration term exponents in a rate law equation is known as its reaction order. We can also refer to the relationship for each reactant in terms of its exponent as an order. All the concentrations of all reactants taking part in a reaction cannot determine the order of reaction. The order of reaction is given by the number of atoms or molecules whose concentrations vary during the chemical change. In this part, we will be dealing with zero order, first order, and second order reaction.

- For a zero order reaction any change in concentration of reactant does not affect the rate of reaction.
- For a first order reaction, increasing the concentration of reactant two or three times also increase the rate two or three times (i.e. if the concentration of a reactant changes by a given factor, the rate must also change by the same factor) .
- For a second order reaction, doubling or tripling the concentration of a reactant increases the rate four or nine times respectively (i.e. any change in concentration of a reactant by a factor x changes the rate by x^2 times.

Experimental determination of order of reaction

The order of the reaction can be determined using the initial rate method.
Let us consider the following reaction:

$$aA + bB \rightarrow cC + dD$$

The rate law = $k [A]^n [B]^m$

Where **n** and **m** are the order of reactants A and B respectively. The order n can be equal to a or not, and the order m can also be equal to b or not.

As the order of the reaction is determined by experiment, the initial rate method can be used to determine the order of the reaction which is the sum (n + m), n is the partial order with respect to the reactant A and m is the partial order with respect to the reactant B

In order to determine the order with respect to A, two experiments are carried out separately keeping the concentration of B constant in both cases while changing the

concentration of A. The initial rate for both the experiments are then determined.

Any change in the initial rate can only be due to the change in the concentration of A and not B.

To determine the order with respect to B, the concentration of A is taken as constant while the concentration of B is changing.

Application examples:

Example 1: The following results were obtained for Q run between A and B

Run	Concentration ($moldm^{-3}$)		Initial rate ($moldm^{-3}\ s^{1-}$)
	A	B	
1	0.50	1.00	2.00
2	0.50	2.00	8.00
3	0.50	3.00	18.00
4	1.00	3.00	36.00
5	2.0	3.00	72.00

a. What is the order of reaction with respect to A and with respect to B.

b. What is the rate equation for the reaction?

c. Calculate the rate constant.

Solution

A+B →products

The rate of reaction =$k[A]^n[B]^m$

Rate a =$k\ [A]_a^n[B]_a^m$

Rate b = $k\ [A]_a^n[B]_b^m$

Let us compare run (a) and run (b) where [A]is constant

$$\frac{rate\ a}{rate\ b} = \frac{k\ [A]_a^n[B]_a^m}{k\ [A]_a^n[B]_b^m}$$

$$\frac{rate\ a}{rate\ b} = \left(\frac{[B]_a}{[B]_b}\right)^m$$

$$\frac{2}{8} = \left(\frac{1}{2}\right)^m$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^m$$

$$\left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^m$$

$$m = 2$$

The order of reaction with respect to B=2

Let us compare run (c) and run (d) where [B] is constant

$$\frac{rate\ c}{rate\ d} = \left(\frac{[A]_c}{[A]_d}\right)^n$$

$$\frac{18}{36} = \left(\frac{0.5}{1}\right)^n \quad \left(\frac{1}{2}\right)^1 = \left(\frac{1}{2}\right)^n, n = 1$$

The order of reaction with respect to A=1

Rate equation $=k\,[A]^n\,[B]^m$ Then

Rate equation $=k\,[A]^1[B]^2$

Rate $=k[A][B]^2$

$$k = \frac{Rate}{[A][B]^2}$$

$$k = \frac{2mol\ dm^{-3}\ s^{-1}}{(0.5mol\ dm^{-3})(1mol\ dm^{-3})^2}$$

$k = 4mol^{-2}dm^6s^{-1}$

Example 2: P, Q, and R reacted together to form products.

P +Q +R → Products

The table shows the results of the experiments carried out to investigate the kinetics of the reaction.

Experiment	$[P]_0$(moldm^{-3})	$[R]_0$(moldm^{-3})	$[R]_0$(moldm^{-3})	Initial rate (moldm^{-3}s^{-1})
1	1.0 x10^{-3}	6.0 x10^{-3}	6.0 x10^{-3}	8.64 x 10^{-7}
2	5.0 x10^{-3}	6.0 x10^{-3}	6.0 x10^{-3}	8.64 x 10^{-7}
3	1.0 x10^{-3}	3.0 x10^{-3}	6.0 x10^{-3}	8.64 x 10^{-7}
4	3.0 x10^{-3}	3.0 x10^{-3}	3.0 x10^{-3}	8.64 x 10^{-7}

a. Deduce the order of reaction with respect to P, Q and R.

b. Write the rate equation

c. Calculate the rate constant k for the reaction and state the units.

Solution:

a. Let us write the rate as follows:

k = $[P]^x\ [Q]^y\ [R]^z$

For finding the order of reaction with respect to P:

Comparing experiments (1) or (2) where [Q] and [R] are constant, we have,

$$\frac{R_1}{R_2} = \frac{k\,[P]_1^x\ [Q]_1^y\,[R]_1^z}{k[P]_2^x\ [Q]_2^y\ [R]_2^z}$$

$$\frac{R_1}{R_2} = \frac{k\ (1.0\ \text{x}10^{-3})^x\ (6.0\ \text{x}10^{-3})^y\ (6.0\ \text{x}10^{-3})^z}{(5.0\ \text{x}10^{-3})^x\ (6.0\ \text{x}10^{-3})^y\ (6.0\ \text{x}10^{-3})^z}$$

Simplifying the equation we get

$2 = 2^x$

x = 1

For finding the order of reaction with respect to Q:

Comparing experiments (1) or (2) where [P] and [R] are constant, we have:

$$\frac{R_1}{R_2} = \frac{k\,[P]_1^x\ [Q]_1^y\,[R]_1^z}{k[P]_3^x\ [Q]_3^y\ [R]_3^z}$$

$$\frac{R_1}{R_3} = \frac{k\ (1.0\ \text{x}10^{-3})^x\ (6.0\ \text{x}10^{-3})^y\ (6.0\ \text{x}10^{-3})^z}{k\ (1.0\ \text{x}10^{-3})^x\ (3.0\ \text{x}10^{-3})^y\ (6.0\ \text{x}10^{-3})^z}$$

Simplifying the equation we get

$4 = 2^y$

$2^y = 2^2$

y= 2

For finding the order of reaction with respect to R

Comparing experiments (3) or (4) where [P] and [R] are constant,, we have

$$\frac{R_3}{R_4} = \frac{k\,[P]_3^x\ [Q]_3^y\,[R]_3^z}{k[P]_4^x\ [Q]_4^y\,[R]_4^z}$$

$$\frac{R_1}{R_3} = \frac{k\ (1.0\ \text{x}10^{-3})^x\ (3.0\ \text{x}10^{-3})^y\ (6.0\ \text{x}10^{-3})^z}{k\ (3.0\ \text{x}10^{-3})^x\ (3.0\ \text{x}10^{-3})^y\ (3.0\ \text{x}10^{-3})^z}$$

Simplifying the equation we get

$\frac{1}{3} = \frac{1}{3}\ (2)^z$

$1 = 2^z$

$2^0 = 2^z$

z = 0

b) The rate equation,

Rate = k $[P]^1$

c. The rate constant can be found as follows:

From the rate law

$k = \frac{Rate}{[P]^1\ [Q]^2}$

You can use experiment (1)

$k = \frac{8.64\ x10^{-7}}{(1.0\ \text{x}10^{-3})(6.0\ \text{x}10^{-3})^2}$

k = 24 $mol^{-2}\ dm^6\ s^{-1}$

Checking up 14.3

The table below shows the experimental data for the following reaction :

$A+2B \rightarrow C$

Experiment	[A]/ (mol dm^{-3})	[B]/ (mol dm^{-3})	Rate (mol $dm^{-3}S^{-1}$)
1	1.00×10^{-2}	2.80×10^{-3}	2.1
2	5.00×10^{-3}	2.80×10^{-3}	1.10
3	1.00×10^{-2}	5.60×10^{-3}	4.30

a. Determine the order of reaction with respect to A and B.

b. Write the rate equation for the reaction

c. Calculate the rate constant for the reaction and give its units.

d. Calculate the rate of reaction when the concentrations of A and B are 8.50 $x10^{-3}$ and 3.83 $x10^{-3}$ mol dm^{-3}, respectively.

14.4. Relationship between reactant concentrations and time for zero, first and second order reaction

Activity 14.4

1. For hypothetical reaction: $n\ A \rightarrow B$
Write the equation of the:

a. Average rate of reaction in terms of A

b. Rate law for the reaction

c. Compare the equation found in (a) and the equation found in (b)

d. Replace the exponent n by the following figure and in each case integrate from 0 to the figure.

i. 0
ii. 1
iii. 2

2. Using this textbook or internet or any other relevant book, read and analyze the content about relation between reactant concentrations and time for zero order reaction, first order reaction and second order reaction and make summary to be presented to the class. In this work you should do the exercises of calculation and sketch different graphs for order 0, 1, and 2.

Rate laws express the rate as a function of the reactant concentration. Rate laws can also be converted into the equations that express the concentrations of the

reactants or products at any given time during the course of a reaction.

14.4.1. Zero order reaction

In a zero –order reaction, the rate is independent of the concentration of the reactant.

Consider the reaction: A→ Products

The rate law is $R = k[A]^0$

Let us consider $[A]_0$ as the initial concentration of A , $[A]_t$ as the concentration of A at time t and [A] as the concentration of A that has reacted. Therefore $[A] = [A]_0 - [A]_t$

The rate of the reaction is expressed as the change in concentration over time.

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^0$$

$$\frac{-d[A]}{dt} = k[A]^0$$

$$\frac{-d[A]}{dt} = k$$

$$-d[A] = kdt$$

Integrating from the time t = 0 to time t = t, we have:

$$-\int_{[A]_0}^{[A]_t} d[A] = k\int_0^t dt$$

$-[A]_t+[A]_0=kt$

$[A]_t = -kt +[A]_0$

- **Half –life of a zero order reaction**

Half –life of a reaction, $\mathbf{t}_{½}$, is the time required for the concentration of any reactant to reach one half of its initial value.

For a zero order reaction, $[A]_t = [A]_0 - kt$

At a time $t = t_{1/2}$, $[A]_t = [A]_0/2$ and we have:

$$\frac{[A]_0}{2} = kt_{1/2} + [A]_0$$

$$\frac{[A]_0}{2} - [A]_0 = -kt_{1/2}$$

$$\frac{[A]_0 - 2[A]_0}{2} = -kt_{1/2}$$

$$-\frac{[A]_0}{2} = -kt_{1/2}$$

$$\frac{[A]_0}{2} = kt_{1/2}$$

$$t_{1/2} = \frac{[A]_0}{2K}$$

For a zero order reaction, the concentration-time graph is a straight line, showing a constant rate (Figure 14. 12). The gradient of the line = k. The rate-concentration graph is a horizontal line (Figure 14.13).

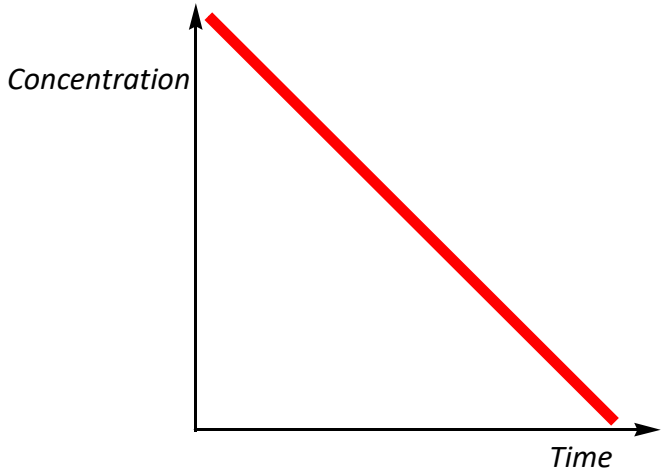


Figure 14.12: Concentration-time graph for a zero order reaction

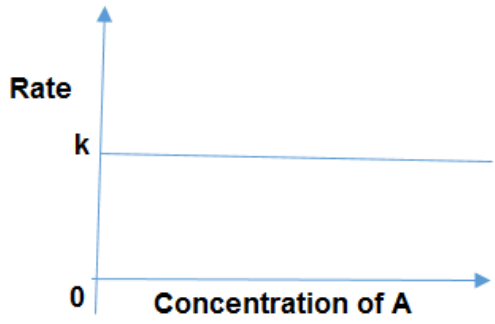


Figure 14.13: Rate-concentration graph for a zero order reaction

Examples of zero order reactions are:

1. **The reaction of the iodination of propanone**

$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$

The reaction is said to be zero order with respect to iodine. The rate law equation can be given as follows: $R = k [CH_3COCH_3]$

2. **The adsorption of gaseous reactants in gaseous reactions:**

Sometimes, reactions between gases are zero order with respect to one of the reactants. This often indicates that this reactant has been adsorbed on the surface of the vessel. The rate of reaction then depends on the frequency with which molecules of the adsorbed gas collide with the inside of the vessel. This frequency is proportional to the concentration of the non-adsorbed reactant.

3. **Reaction of sodium thiosulphate and HCl is zero order with respect to HCl**

14.4.2. First order reaction

A first order reaction is a reaction whose rate depends on the concentration of a single reactant raised to the first power.

Consider the first order reaction A →products

The rate equation can be written as: $R = k [A]$

$$Rate = -\frac{\Delta[A]}{\Delta t} = k[A]$$

$$(-d[A])/dt) = k[A]$$

$$\frac{-d[A]}{d[A]} = kdt$$

Integrating for time t=o to t=t, we have

$$-\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = k\int_0^t dt$$

$$-(ln[A]_t - ln[A]_0) = k(t-0)$$

$$-\ ln\ \frac{[A]_t}{[A]_0} = kt$$

$$ln\ \frac{[A]t}{[A]_0} = -kt$$

$$ln\ \frac{[A]_0}{[A]_t} = kt \text{ or } 2.303log\ \frac{[A]_0}{[A]_t} = kt$$

$$ln[A]_t = -kt + ln\ [A]_0$$

- **Half –life ($t_{1/2}$) of the first order reaction**

At a time $t_{1/2}$,

$$[A]_{t_{1/2}} = \frac{1}{2}[A]_0$$

For the first order reaction, we have:

$$-ln\ \frac{[A]_t}{\frac{[A]_0}{2}} = kt_{1/2}$$

$$-ln\ \frac{2[A]_0}{[A]0} = kt_{1/2}$$

$$ln2 = kt_{1/2}$$

$$\boldsymbol{t_{1/2} = \frac{ln2}{k} = \frac{0.693}{k}}$$

Therefore for all first order reactions, half-life ($t_{1/2}$) is independent of initial concentration $[A]_0$ of the reactant.

For a first order reaction, the graph concentration-time (Figure 14.14) is a curve showing the decreasing rate with concentration while the graph rate-concentration (Figure 14.15) is a straight line passing through the origin.

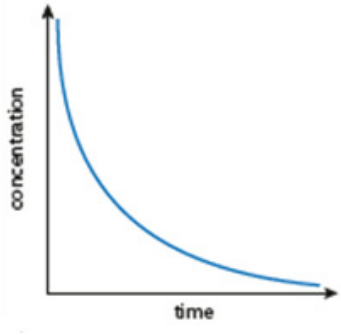


Figure 14.15: Concentration-time graph for graph for a first order reaction

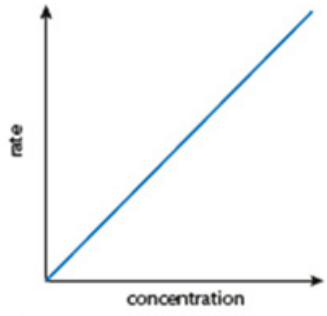


Figure 14.16: Rate-concentration a first order reaction.

14.4.3. Second order reaction

A second order reaction is a reaction involving two reacting species.

For the following reaction: A+B → Products,

$$Rate = \frac{-d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B]$$

If $[A] = [B]$ then $\frac{-d[A]}{dt} = k[A]^2$

$\frac{d[A]}{[A]^2} = -kdt$

Integrating from time, t = 0 to time, t = t:

$$\int_{[A]_0}^{[A]t} \frac{[A]_t}{[A]^2} = -\int_0^t \frac{d[A]}{[A]^2} - kdt$$

$$\left[-\frac{1}{[A]}\right]_{[A]_0}^{[A]_t}$$

$$-\frac{1}{[A]_t} + \frac{1}{[A]_0} = -k[t]_0^t$$

$$-\frac{1}{[A]_t} + \frac{1}{[A]_0} = -k(t-0)$$

$$-\frac{1}{[A]t} + \frac{1}{[A]0} = -kt$$

$1/[A]_t - 1/[A]_0 = kt$

When $t = t_{½}$, $[A]_t = \frac{[A]_0}{2}$

Then $\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$

$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{½}$

$\frac{1}{[A]_0} = kt_{½}$

$t_{½} = \frac{1}{K[A]_0}$

For a second order reaction, the graph concentration-time (Figure 14.17) is curve while the graph rate-concentration is a parabola. Characteristic of the square function (Figure 14.18).

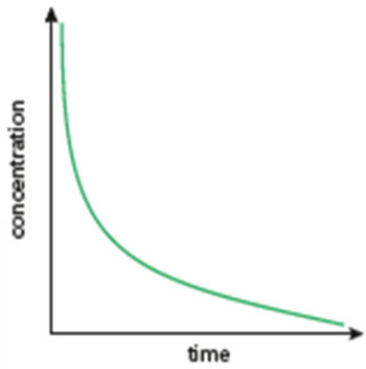


Figure 14.17: Concentration-time graph for graph for a second order reaction.

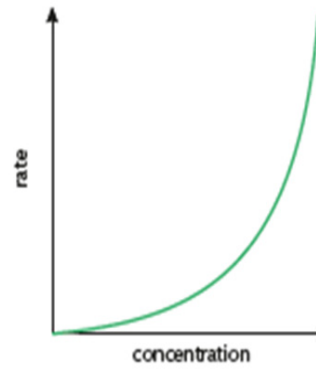


Figure 14.18: Rate-concentration for a second order reaction.

14.4.4. Pseudo-first order reaction

It is known that the order of reaction depends on the dependency of the rate of reaction on the concentration of reactants. If the rate is independent of the concentrations of reactants, the order of reaction is zero. A reaction which is not first-order reaction naturally but made first order by increasing or decreasing the concentration of one or the other reactant is known as Pseudo first order reaction. Pseudo-first order reaction is a reaction dependent upon the concentrations of both the reactants, but one of the components is present in large excess and thus its concentration hardly changes as the reaction proceeds.

Consider the reaction: A + B → Products

This reaction is dependent upon the concentrations of both A and B but if the component B is present in large excess and the concentration of B is very high compared to that of A, the reaction is considered to be pseudo-first order reaction with respect to A. similarly, if the component A is in large excess and the concentration of A is very high as compared to that of B, the reaction is considered to be pseudo first order with respect to B.

i. If [B] is in excess, the rate equation can be written as follows:
Rate =k[A] [B]

The concentration of B practically remains constant during the reaction, and therefore the rate law can be written:

Rate =k'[A]

Where the rate constant, k'= k[B]

The real order of that reaction is 2 but in practice it will be order 1.

Example:

Let us consider the elementary reaction where water is in excess:

$CH_3CH_2COOCH_3$ (l) + H_2O (l) + H^+ (aq) $\rightarrow$ CH_3CH_2COOH(aq) +CH_3OH(aq)

The rate law for the reaction is: Rate = k' [$CH_3CH_2COOCH_3$], where k' = k [H_2O]

At low concentration of H_2O, water is first order. But when water is in excess, water does not affect the rate of reaction.

- **Rate constant and its units**

The rate of the reaction, as seen above, is the change in concentration over the change in time. Therefore, the reaction rate is expressed in Ms^{-1} or mol dm^{-3} s^{-1}. The unit of concentration is mol/dm^3 and that of time is seconds (s).

The units of the rate constant depend on the form of the rate law in which it appears.

Units of k for a zero order reaction

Rate = k $[A]^0$

$$Rate = -\frac{d[A]}{dt} = k[A]^0 \Rightarrow M/t = k$$

$$k\,units: M/s, M/\min, \mathrm{M/hr}, \text{etc}$$

Note: Time can be expressed in seconds, minutes, days, hours, months, years, etc.

$$k = \frac{d[A]}{dt} = \frac{mol}{dm^3} \times \frac{1}{time} = mol\ dm^{-3} time^{-1}$$

Units of k for a first order reaction

$$Rate = -\frac{d[A]}{dt} = k[A] \Rightarrow \frac{M}{t} = k \times M$$

$$k - units: s^{-1}, \min^{-1}, hr^{-1}, etc$$

$$k = \frac{2.303}{t}\ log\ \frac{[A]_0}{[A]_t} = Time^{-1}$$

Units of k for second order reaction

$$Rate = -\frac{d[A]}{dt} = k[A]^2 \ or Rate = k[A][B]$$

$$\Rightarrow \frac{M}{t} = k \times M^2$$

$$k - units: M^{-1}s^{-1}(mol^{-1}dm^3s^{-1}), M^{-1}\min^{-1}, M^{-1}hr^{-1}, etc.$$

$$k = \frac{1}{t}\ log\ \frac{[A]}{[A]_0\,([A]_0 - [A])} = \frac{1}{time} * \frac{[\,]}{[\,]\ [\,]} = \ mol^{-1}\ dm^3 Time^{-1}$$

Checking-up 14.4

1. The half–life of a first-order reaction is 2.5 min, calculate the time taken for the amount of reactant to decrease to10% its original value.
2. Consider the following reaction: A + B → products
   This is first order with respect to A and second order with respect to B.
   a. Write an expression of the reaction.
   b. Draw and label graphs that would allow the rate constant to be determined from a series of experiments in which
      i. [A] is kept constant, but [B] is varied.
      ii. [B] is kept constant, but [A] is varied.

14.5. Difference between order of reaction and molecularity

Activity 14.5

Using this textbook, internet or any other relevant book, read and analyze the content about order of reaction and molecularity and make summary to be presented to the class. In this work you should also do give examples of reactions for each.

Molecularity is the number of reacting species (e.g: molecules, ions) that participate (take part) simultaneously in the formation of the transition state. That is, the number of species involved in the rate determining step for the reactions occurring in stages.

It can be the number of species that participate as reactants simultaneously in an elementary reaction or elementary processes (reaction occurring in single event or step).

If a single molecule is involved simultaneously in an elementary reaction, the reaction is unimolecular.

For example: $N_2O_5 \rightarrow NO_3 + NO_2$, One reactant molecule is decomposed into two product molecules.

If two molecules are involved simultaneously in an elementary reaction, the reaction is bimolecular.

Examples:

i. $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$
ii. Mechanisms for the reactions of primary alkylhalides (1^0 R-X) with nucleophiles, S_N2, involve two molecules in the rate determining step.

If three molecules are involved simultaneously in an elementary reaction, the reaction is termolecular.

Termolecular reactions are less probable than unimolecular or bimolecular reactions and are rarely encountered because the chance that three particles collide at the same time, with proper orientation and sufficient energy, are considered extremely small.

An example of termolecular reaction is thought to occur during the formation of ozone from oxygen in the outer atmosphere:

$$2\,O_2 + N_2 \rightarrow O_3 + O\cdot + N_2^*$$

The rate laws for most reactions have the general form:

Rate $= k[\text{reactant A}]^x[\text{reactant B}]^y$…..

The exponents x and y in a rate law equation are called reaction orders.

For the reaction aA + bB+ cC → Product…….

The **order of a reaction** is the sum of powers to which the concentration terms raised in the rate equation

Rate $= k[A]^x[B]^y[C]^z$

For the reaction rate; x, y, z are the powers of the considered concentration of A, B and C respectively with respect to each reactant.

x is the order of the reaction with respect to A

y is the order of reaction with respect to B

z is the order of reaction with respect to C

The sum of x, y and z gives the overall order of reaction.

x, y, z are obtained through experiments only and not from the number of moles as written in the stoichiometric equation.

The difference between the order and molecularity of reaction are shown in the Table 14.1.

Table 14.1. Differences between order of reaction and molecularity

ORDER OF A REACTION	MOLECULARITY OF A REACTION
It is the sum of the exponents (powers) of the concentrations in the rate law.	It is the number of reacting species (e.g: molecules, ions) that participate simultaneously in the formation of the transition state.
It can be fractional	It is always a whole number.
It can be zero	It cannot be zero
It can be determined experimentally	It can be calculated by simply adding the molecules of the slowest step (It is theoretical)
It can change with conditions such as pressure, temperature, or concentration	It depends to the number of molecules for a chemical equation

Checking-up 14.5

It has been proposed that the conversion of ozone into O_2 proceeds by a two –step mechanism:

$$O_3(g) \rightarrow O_2(g) + O\cdot(g)$$
$$O_3(g) + O\cdot(g) \rightarrow 2O_2(g)$$

a. Describe the molecularity of each elementary reaction in this mechanism.
b. Write the equation for the overall reaction
c. Identify the intermediates

14.6. Reaction mechanisms and kinetics

Activity 14.6

1. a. Five people have to run 100 m. Two of them do not perform well in running (they are slow in running). You are asked to organize them in order to perform that exercise so that the people leave the same place and reach the same destination at the same time.

   b. Differentiate between SN_1 and SN_2 reactions. Show also the mechanism of reaction.

2. Using this textbook or internet or any other relevant book, read and analyse the content about the mechanism of reaction and make summary to be presented to the class

Reaction rates provide information regarding how a chemical process occurs as well as the mechanism by which a reaction happens at molecular level. Most chemical reactions occur via a series of steps called the reaction mechanism. The individual steps, called elementary steps, cannot be observed directly. A reaction mechanism consists of a set of proposed elementary steps involving molecular species – reactants as well as reaction intermediates. A reaction mechanism explains how a given reaction might take place and from which a rate law can be derived, which must agree with the one determined experimentally.

If the mechanism consists of more than one elementary step, the sum of these steps must be equal to the overall balanced equation for the reaction.

A reaction mechanism describes in great detail the order in which bonds are broken and formed and the changes in relative positions of the atoms in the course of the reaction.

The Table 14.2 summarizes the types of elementary steps and the rate laws that they follow. A and B represent the reactants or reaction intermediates. Typically these steps are usually either unimolecular or bimolecular.

Table 14.2. Elementary steps and rate laws

Elementary Reactions	Molecularity	Rate Law
A → product	Unimolecular	Rate = k [A]
2A → product	Termolecular	Rate = k [A]2[B]
2A + B → product	Bimolecular	Rate = k [A][B]
A + B → product	Bimolecular	Rate = k [A]2

Example: N_2 (g) +3H_2 (g) →2NH_3 (g)

Molecularity of reaction is equal to 1+3 = 4 but the order can be derived from the rate determining step. The reaction mechanism is the step-by-step process by which reactants actually become products. In the reaction mechanisms, some steps are fast while others are slow.

A reaction cannot proceed faster than the rate of the slowest elementary step, the slowest step in a mechanism establishes the rate of the overall reaction which is known as the rate determining step. When a proposed mechanism consists of more than one elementary step, the one with the slowest rate will determine the overall rate of reaction.

Examples:

1. Consider the reaction: $NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$
This reaction is believed to take place in two steps.

Step-1: $NO_2 + NO_2 \rightarrow NO_3 + NO$; (slow rate-determining)

Step-2: $NO_3 + CO \rightarrow CO_2 + NO$; (fast)

The overall chemical equation is obtained by adding the two steps and canceling any common species to both sides.

The overall reaction is given by:

$$\begin{array}{l} NO_2\,(g) + NO_2\,(g) \longrightarrow NO_3(g) + NO(g) \quad (slow) \\ NO_3\,(g) + CO(g) \longrightarrow NO_2\,(g) + CO_2\,(g) \quad (fast) \\ \hline NO_2\,(g) + CO(g) \longrightarrow NO(g) + CO_2\,(g) \end{array}$$

If the reaction follows a one elementary step mechanism, the rate law would be:

Rate = $k[NO_2][CO]$

However, the experimentally determined rate law is:

Rate = $k[NO_2]^2$

The rate law for the rate-determining step: Rate = $k_1[NO_2]^2$, which is identical in form to the rate law obtained experimentally. The second step, which occurs very fast, does not influence the overall rate.

An intermediate substance is neither a reactant nor a product in the overall reaction. It is formed in one step and consumed in the next step. In the above example, the intermediate is NO_3 because it is produced in the first step and consumed in the second one.

2. Consider the reaction: $2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$
   The experimental rate law is: Rate = $k[NO_2][F_2]$

The reaction is first order with respect to each reactant. This reaction occurs follow two steps (slow and fast):

$$\text{Step 1: } NO_2(g) + F_2(g) \xrightarrow[k_1]{\text{Slow}} NO_2F(g) + F(g)$$

$$\text{Step 2: } NO_2(g) + F(g) \xrightarrow[k_2]{\text{Fast}} NO_2F(g)$$

$$\text{Overall: } 2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$$

F is an intermediate species, it is produced in the first step and consumed in the next step.

Since the overall rate of the reaction is determined by the slow step, it seems logical that the observed rate law is Rate = $k_1[NO_2][F_2]$.

SN_1 and SN_2 mechanisms and kinetics

Chlorine, bromine, and iodine (X) possess a higher electronegativity than carbon. As a result, the bonding electrons in C-X bond are unevenly distributed. The carbon atom is partially positively charged (δ+) while the halogen atom is partially negatively charged (δ-). The polarity of carbon-halogen bonds forms the basis of two frequently found reaction types of this compound family, namely nucleophilic substitutions (S_N) reactions and elimination reactions.

In a nucleophilic substance, or electron rich species, nucleophile, selectively attack a positive or partially positive charge of an atom or group of an atom or group of atoms to replace the leaving group.

Nucleophilic substitutions (S_N) reactions can be of:

Second-order reactions: Occur with primary alkyl halides.

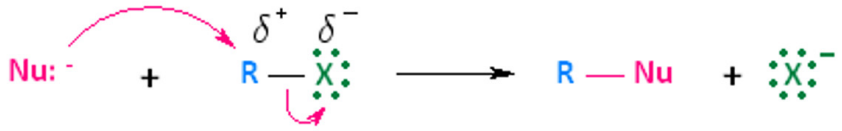
First-order reactions: Occur with tertiary alkyl halides.

Secondary alkyl halides can undergo second-order reactions or first-order reactions. In both kinetic cases of substitutions, a leaving group (halide ion) is substituted by a nucleophile.

1. Second-order nucleophilic substitution (SN^2 reactions)

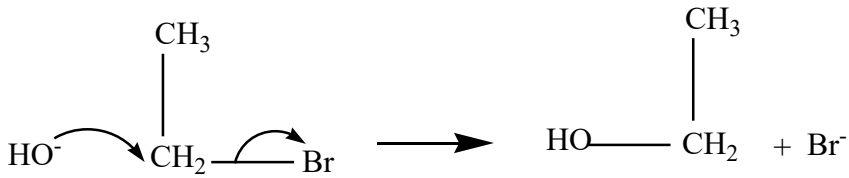
A nucleophile attacks a positively polarized carbon atom. The attack of the nucleophile results in the heterolytic cleavage of the carbon-ligand bond, where the bonding electron pair is completely passed onto the ligand (**X**). The substrate, along with the nucleophile, participates in the rate-determining step. Thus, the reaction

rate depends on both the substrate and the nucleophile's concentration. Therefore, this reaction type is called **bimolecular nucleophilic substitution** reaction **(SN²).**



Example:

$CH_3CH_2Br + HO^- \rightarrow CH_3CH_2OH + Br^-$

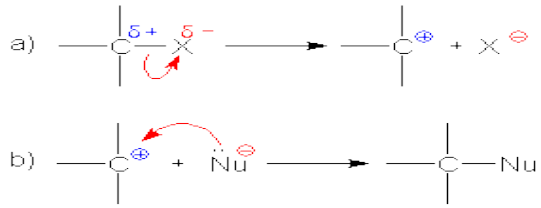


The rate of hydrolysis of a primary alkyl halide is proportional to the concentration of both halogenoalkane and hydroxide ions.

This reaction is second order and its rate expression is, Rate = k[RX] [OH^-]

2. First-order nucleophilic substitution (SN_1 reactions)

The carbon-halogen bond is cleaved and involves the halogenoalkane alone, forming a halide ion and a carbocation. The attack of the nucleophile on the carbocation yields the substitution product. Thus, the reaction rate depends only on the halogenoalkane concentration. Therefore, this reaction type is called unimolecular nucleophilic substitution reaction (SN^1 reaction).

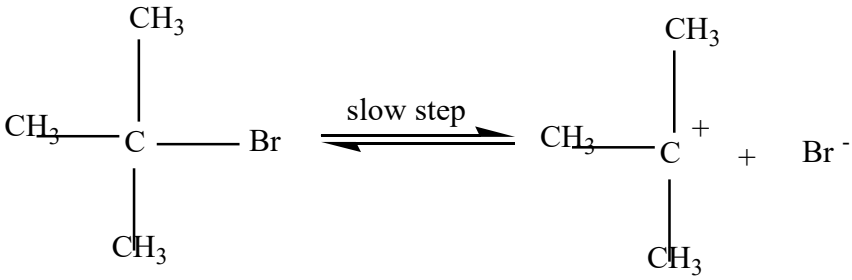


Example:

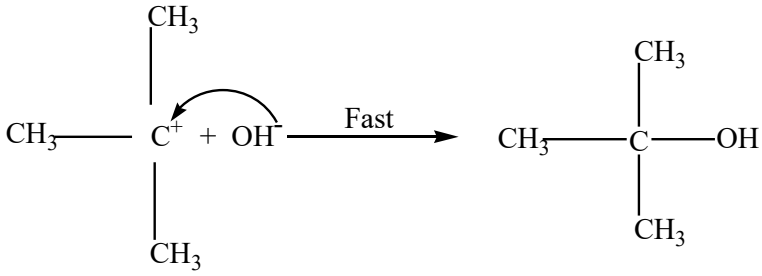
Let us consider a hydrolysis reaction of a tertiary halogenoalkane:

$(CH_3)_3CBr + NaOH \rightarrow (CH_3)_3COH + NaBr$. The experimental results show that the reaction is first order with respect to the halogenoalkane:

Rate=k[$(CH_3)_3CBr$]



[1]



[2]

The rate of hydrolysis of a tertiary alkyl halide is proportional to the concentration of halogenoalkane but does not depend on hydroxide ions. The reaction is 1st order with respect to the halogenoalkane.

Rate $=k[(CH_3)_3CBr]$

Checking-up 14.6

1. Differentiate between SN^1 and SN^2 reactions.
2. The decomposition of nitrous oxide, N_2O ,is believed to occur by two –step mechanism:
   $N_2O\ (g) + N_2(g) + O\cdot\ (g)$ (slow)
   $N_2O(g) + O\ (g) \rightarrow N_2(g) + O_2(g)$ (fast)

   a. Write the equation for the overall reaction.

   b. Write the rate law for the overall reaction.

END UNIT ASSESSMENT

1. Collision theory states that particles must collide with each other in correct orientation and sufficient energy to
   a. attract
   b. repel
   c. react
   d. respond

2. According to Collision theory, particles must
   a. Collide every where
   b. Collide with correct orientation
   c. Must be kept under immense pressures
   d. Shall not be below their melting points

3. Some particles collide but bounce back afterwards it is called
   a. successful collision
   b. unsuccessful collision
   c. successful reaction
   d. unsuccessful reaction

4. The rate law for a reaction is k [A][B]2
   Which one of the following statements is false?
   a. The reaction is first order in A.
   b. The reaction is second order in B.
   c. The reaction is second order overall.
   d. k is the reaction rate constant

5. A reaction was found to be zero order in A. Increasing the concentration of A by a factor of 3 will cause the reaction rate to
   a. remain constant
   b. increase by a factor of 27
   c. increase by a factor of 9
   d. triple

6. The rate law of the overall reaction is k[A][B]0. Which of the following will not increase the rate of the reaction?
   a. increasing the concentration of reactant A
   b. increasing the concentration of reactant B
   c. increasing the temperature of the reaction
   d. adding a catalyst for the reaction

7. When a lit match is touched to the wick of a candle, the candle begins to burn. When the match is removed, the candle continues to burn. The match
   a. behaves as a catalyst

b. Supplies the activation energy
c. Is part of the rate determining step
d. Lowers the activation energy barrier

8. Which step of a reaction is the rate-determining step?
   a. the fastest step
   b. the last step of the reaction mechanism
   c. the first step
   d. the slowest step

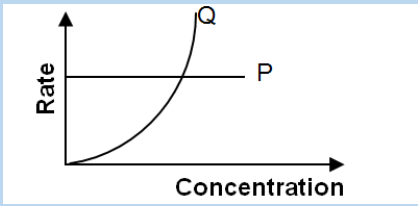
9. Consider the following mechanism:
   Step 1: $Cl. + O_3 \rightarrow ClO. + O_2$
   Step 2: $O. + ClO \rightarrow Cl + O_2$
   The reaction intermediate is
   a. Cl
   b. O_2
   c. O_3
   d. ClO.

10. The table below shows the rates of reaction between substance A and B at different concentrations

Experiment number	[A] /mol dm^{-3}	[B] /mol dm^{-3}	Rate (mol $dm^{-3}s^{-1}$)
1	0.50	0.50	$2.0x10^{-2}$
2	1.00	0.50	$8.0x10^{-2}$
3	1.00	1.00	$1.6x10^{-1}$

   a. Determine the order with respect to A and B.
   b. Write the rate expression or rate law.
   c. Calculate the rate constant indicating clearly its units

11. a. A reaction between two reactants, P and Q, gave the rate-concentration graphs shown below:



   b. The rate equation for a reaction between R and S is Rate = $K[R]^2[S]$
      i. Determine the order with respect to R and S.
      ii. Sketch the rate-concentration graphs for reactants R and S.

12. Consider the following reaction: $A + B \longrightarrow P + R$

Experiment number	[A] /mol dm^{-3}	[B] /mol dm^{-3}	Rate (mol $dm^{-3}s^{-1}$)
1	2.0×10^{-3}	3.0×10^{-3}	3.0×10^{-3}
2	2.0×10^{-3}	6.0×10^{-3}	1.2×10^{-2}
3	4.0×10^{-3}	6.0×10^{-3}	2.4×10^{-2}
4	5.0×10^{-3}	5×10^{-3}	Z

i. Determine the rate equation and the rate constant.
ii. Find the value of Z.

13. In the reaction: P + Q + R → Product (s), deduce the order of reaction with respect to P, Q and R if:
    a. The rate does not change when [R] is doubled.
    b. The rate increases by 9 when [Q] is tripled
    c. The rate doubles when [P] is doubled

14. In the reaction: A + B → C, Rate = $[A][B]^2$. State how the rate will change if:
    a. The concentration of A is halved.also halved
    b. The concentration of A is tripled and that of B is doubled.

15. In the reaction: $2NO + Br_2 \rightarrow 2NOBr$, when the concentration of NO is reduced from 4×10^{-2}M to 2×10^{-2}M the rate falls by a factor of 4. What is the order of reaction with respect to NO? Give a reason to your answer.

16. In the reaction: $2NO_2 \rightarrow 2N_2 + O_2$, when the concentration of NO_2 decreases from 5×10^{-3}M to 2×10^{-3}M, the rate of decomposition falls by a factor of 2.5. What is the order of reaction? Give a reason to your answer.

17. The reaction between 2-bromo–2-methylpropane $(CH_3)_3C–Br$ and aqueous hydroxide ions OH– takes place by the following outline mechanism:

    Step 1 $(CH_3)_3C\text{-}Br \rightarrow (CH_3)_3C^+ + Br^-$ (slow)

    Step 2 $CH_3C^+ + OH^- \rightarrow (CH_3)_3C\text{-}OH$ (fast)

    a. What is the order of reaction with respect to $(CH_3)_3C–Br$?
    b. What is the total order of reaction?
    c. Write the rate equation for this reaction.

18. a. Paracetamol has a biological half-life of 380 seconds. How long will it take for the level of paracetamol in the body to fall to one-sixteenth of its original value?
    b. 50% of a first order reaction is complete in in 23 minutes. Calculate the time

UNIT 15
RADIOACTIVITY

UNIT 15: RADIOACTIVITY

Key Unit Competence:

To be able to explain the importance and dangers of radioisotopes in everyday life.

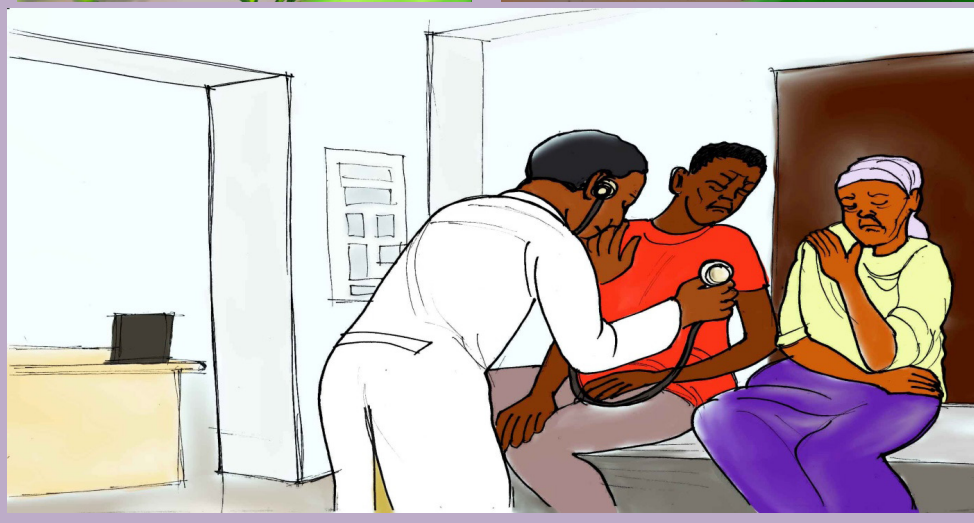
Learning objectives:

- Explain the process of radioactivity.
- Explain the properties of alpha, Beta and Gamma rays.
- Develop awareness of the dangers of radioactive substances and nuclear weapons.
- Write and balance nuclear reaction equations.
- Compare and contrast chemical and nuclear reactions.
- Explain half-lives of radioactive isotopes/radioisotopes.
- Perform calculations involving the half- life of radioactive substances.
- Explain the applications of radioisotopes in medicine, agriculture and industries.
- Apply the calculations of half-life to determine the age of fossils.

Introductory activity:

1. Have you ever heard about Radioactivity?
2. If yes, can you explain what it is?
3. Can you mention some applications of Radioactivity?
4. What is the difference between an ordinary chemical reaction and a nuclear reaction?

You are provided with illustrations which are linked with radioactivity. Observe them and try to analyse them.



The above pictures show different ways through which radiations reach into our body (cells). The most familiar to you is radiation from sun rays! However, everything present in the pictures above, and many others that are not included, emits radiation. Now, discuss on the following points. **Note:** If you get stuck by some points, don't be frustrated! You are allowed to visit any important document (textbook, search engine …) that can help you to find out the required solution.

Point 1: Can you see or feel the presence of radiation?

Point 2: How are we exposed to natural ionizing radiation? (Radiation with the ability to rip out one or several electrons from an atom or molecule is referred to as ionizing radiation and Radiation which does not have sufficient energy to damage atoms or molecules is called non-ionizing radiation).

Point 3: What do you understand by "radioactive materials"? Do you think all of them are natural? Do you think all of them (i.e, radioactive materials) as harmful?

The discovery of the electron towards the end of the nineteenth century was the starting point of new avenues of research in science, which were to give physicists an insight into the structure and nature of the atoms of matter. They discovered that there is a nuclear phenomenon in some elements that pushes them to emit radiations.

This phenomenon was called **radioactivity** as proposed by **Marie Curie** to describe those emissions of nuclear radiation by some of the heavy elements.

Radioactivity is an integral part of our environment. All living beings have been exposed to a constant flux of natural radiation on the surface of our friendly planet, but this radiation has no negative effect.

Particles and rays are emitted when a nucleus of a radioactive isotope of element breaks down. They break down to acquire stability as all atoms want to be stable.

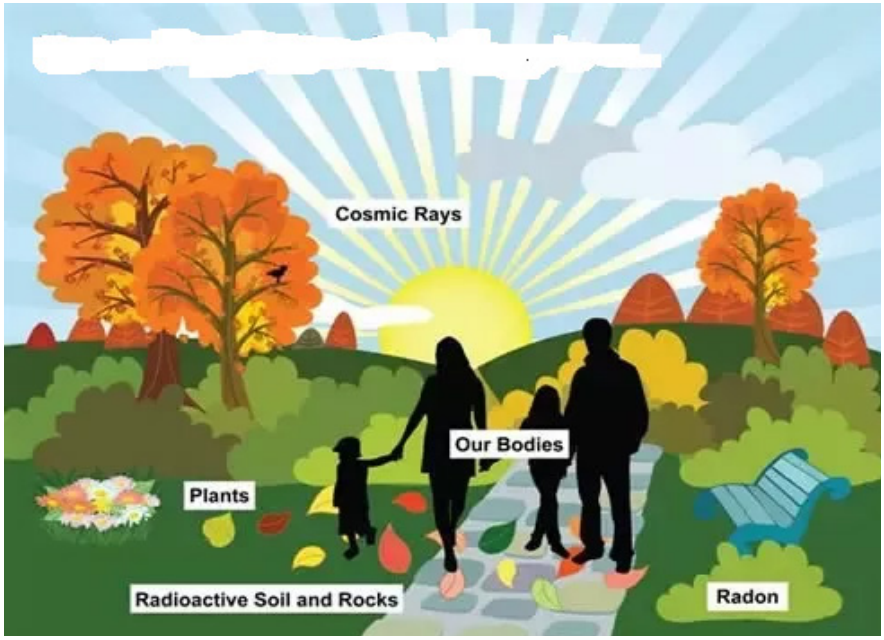


Figure 15.1: Natural sources of radioactivity

We are constantly being bombarded by particles of cosmic radiations: several hundred go through our bodies every second. Rocks like granite, which have become symbols of permanence and durability (hence used in building), contain light traces of radioactive uranium. Sitting on or walking near a block of granite exposes you to many sources of radioactivity. Even the food we eat or the air we breathe contains radioactive elements (such as radon) either formed by the intervention of cosmic rays, or as old as the solar system itself. There is absolutely no way to escape from it: we are even radioactive! Eight thousand atoms of potassium-40 or carbon-14 disintegrate in our bodies every second.

Figure 15.2: Granite as a source of radioactivity

15.1 Definition of radioactivity, radioisotopes and comparison between chemical and nuclear reactions.

Activity 15.1

1. What do you think about the terms 'radioisotopes' and 'radioactivity'? How can you define the two terms from your understanding? From chemical and nuclear equations, describe any differences between these two types of equations
2. Now use a search engine or textbooks (including even this one) to find out appropriate explanations on radioisotopes, radioactivity and nuclear equation, then make a good report to share with others.

15.1.1. Definition of radioactivity and radioisotopes

Radioactivity is a nuclear phenomenon. It is the process by which an unstable atomic nucleus changes into another more stable atomic nucleus by emitting energy in form of radiation. Substances which have the property of emission of radiation are called **radioactive substances**. Radioactivity is also known as **radioactive disintegration** or **radioactive decay.**

A radioactive decay results when an atom with one type of nucleus, called "**the parent radioactive nuclide**" transforms into another atom with a different nucleus. The new product or element is named "**the daughter nuclide**";, and thus the decay process results in "**transmutation**". **Transmutation**, in this case, means creation of an atom of a new element. In this way, the energy or radiation emitted may take the form of particles such as **alpha (α)** or **beta (β) particles**.

During the transmutation process, daughter nuclides are often in metastable or excited state; they lose energy in form of **gamma (γ) ray** to become de-excited. Gamma rays, here, can be compared to the heat of reaction that accompanies an exothermic reaction.

In nuclear chemistry, the term 'nuclide' is used to designate a nucleus of an element.

'Nucleons' is the term used for nuclear particles such as protons and neutrons. In radiochemistry, the nucleon number stands for mass number (sum of protons and neutrons present in the nucleus of a given atom).

Different nuclides, which have the same proton number but different nucleon numbers are called isotopes or isotopic nuclides.

Radioisotopes or radioactive isotopes are the atoms of an element whose atomic nuclei undergo decay by emitting radiation(s).

15.1.2. Comparison between chemical reaction and nuclear reaction

Nuclear reaction and chemical reaction differ as shown in the following table:

***Table 15.1*: Differences between a chemical reaction and a nuclear reaction**

Ordinary chemical reaction	Nuclear reaction
• Valence electrons are used • Atoms do not change their nature • Affected by external factors (temperature, pressure) • Low energy involved	• Nuclei are involved • New atoms are produced • Not affected by external factors • Gigantic energy involved

Checking up 15.1:

1. Explain what is meant by each of the following terms:
   a. Radioactive decay.
   b. Daughter nuclide.
   c. Transmutation.
2. Differentiate between isotopes and radioactive isotopes
3. Describe the following as pertaining to chemical reaction or nuclear reaction:
   a. Isotopes have the same chemical properties as they have the same number of electrons.
   b. Hydrogen nuclei are the reactants.
   c. Large amounts of energy are released.
   d. The mass is strictly conserved.

15.2. Emission of alpha particles, beta particles and gamma rays and their properties and effect of electric and magnetic field on them.

Activity 15.2

1. State the types of radiation as revealed in the previous discussions.
2. Use your search engine or any textbooks available to find out the properties the three types of radiation and the effect of electric and magnetic fields on them.

15.2.1. Alpha particles, beta particles, gamma rays and their properties

Different forms of radiation are emitted from an unstable nucleus as it decays. The main types of emitted particles are alpha particles, beta particles and gamma rays. The detailed information on each particle is provided below.

a. Alpha particles

An alpha particle contains two protons and two neutrons (so, its mass number, A=4 and atomic number, Z=2). Because it has 2 protons, an alpha particle has a charge of 2+ (+2). That makes it identical to helium nucleus. In equations, it is written as the Greek letter "alpha (α)" or as the symbol for helium (^4_2He). The charge of an alpha particle was found experimentally by passing it in an electric field between two plates where it was attracted towards the negative plate.

The main properties of an alpha particle are the following:

- Alpha particle bears a positive charge of +2
- It has a mass of 4 amu
- It is deflected toward the negative pole of electric and magnetic fields. Look at Figure 15.4 below.
- It affects a photographic plate and causes fluorescence on striking a fluorescent material.
- It ionizes the gas through which it passes.
- Not very penetrating; a very thin sheet of aluminium foil or a sheet of paper stops it.
- It can be shielded by paper or clothing.
- It destroys living cells and causes biological damage.
- It is strongly ionizing

The process of α-decay occurs commonly in nuclei with atomic number greater than 83. The nuclei of these elements are extremely unstable due to the large number of

neutrons and protons present. More information about stability of nuclei of atoms is discussed in this unit, **section 15.4.**

When a nuclide decays by alpha emission, it loses 2 atomic number units and 4 mass units; in other words the daughter nuclide is the element located at 2 places before the parent nuclide in the periodic table.

Examples:

$$^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$$

$$^{226}_{88}\text{Ra} \longrightarrow {}^{222}_{88}\text{Ra} + {}^{4}_{2}\text{He}$$

b. Beta particles

A beta particle, which is a high energy electron, has a charge of -1 and because its mass is so much less than that of a proton, it is given a mass number of zero (0). It is represented by the Greek letter "beta (β)" or by the symbol for electron with the charge, -1, written on the lower left "$_{-1}^{0}\text{e}$". Beta particle is deflected toward the positive plate of an electric and magnetic field.

The main properties of a beta particle are the following:

- It bears a negative charge of -1
- It is deflected toward positive plate of an electric and magnetic fields. The deflection is large since a beta particle is lighter than an α-particle. Refer to figure 15.4 for further understanding.
- It affects photographic plates.
- It is ionizing but less than alpha ray.
- It travels at speeds close to that of light (of the order of 10^8 m/s).
- Its penetrating power is 100 times greater than that of α-particles.
- It causes fluorescence on striking a fluorescent material.
- It can be stopped by1/16 inch of lead.
- It causes greater radiation damage as it can easily pass through the skin of the body.

Beta particles are produced from unstable nuclei when a neutron is transformed into a proton and an electron. The high-energy electron is emitted from the nucleus as a "beta radiation"

$$^{1}_{0}\text{n} \longrightarrow {}^{1}_{1}\text{p}\ (\ {}^{1}_{1}\text{H}) + {}^{0}_{-1}\text{e}\ (\beta)$$

Neutron in the nucleus — *New proton remains in the nucleus* — *New electron formed and emitted as beta radiation*

This shows that the number of neutrons decreases by one and the number of protons increases by one.

$$^{A}_{Z}X \rightarrow {}^{A}_{(Z+1)}X + {}^{0}_{-1}e$$

It is noteworthy that a β-emission results in the production of **isobars** (nuclides having the same mass numbers but different atomic numbers). The beta emission produces a new element with 1 more atomic number unit, or the element that directly follows in the periodic table.

Examples: $^{14}_{6}C \rightarrow {}^{14}_{7}N + {}^{0}_{-1}e$

$^{241}_{94}Pu \rightarrow {}^{241}_{95}Am + {}^{0}_{-1}e$

A positron is similar to an electron except that a positron has a positive (+1) charge. A positron is produced by an unstable nucleus when a proton is transformed into a neutron and a positron.

This shows that the number of neutrons increases by one and the number of protons decreases by one; the element just preceding the parent nuclide in the periodic table is formed.

$$^{A}_{Z}X \rightarrow {}^{A}_{(Z-1)}X + {}^{0}_{+1}e$$

Example: $^{49}_{25}Mn \rightarrow {}^{49}_{24}Cr + {}^{0}_{+1}e$

Note that a positron is an example of "**antimatter**", a term physicists use to describe a particle that is the exact opposite of a particle, in this case, an electron. When an electron and a positron collide, their minute masses are completely converted to energy in the form of "**gamma rays**"

$$^{0}_{-1}e + {}^{0}_{+1}e \rightarrow 2\,{}^{0}_{0}\gamma$$

Electron capture: an electron is captured by the nucleus from the same isotope which combines with a proton to form a neutron.

$$^{1}_{1}p + {}^{0}_{-1}e \rightarrow {}^{1}_{0}n$$

Isotopes that undergo electron capture have got fewer neutrons than stable isotopes of the same element and as such a proton must be changed to a neutron. Electron capture results in decreasing of the atomic number by one unit as in positron emission.

$$^{A}_{Z}X + {}^{0}_{-1}e \rightarrow {}^{A}_{(Z-1)}X$$

Examples:

$^{38}_{19}K + {}^{0}_{-1}e \rightarrow {}^{38}_{18}Ar$

$^{37}_{18}Ar + {}^{0}_{-1}e \rightarrow {}^{37}_{17}Cl$

Note that in few cases, both positron emission and electron capture may occur in the same element. For example, zinc-63 can undergo both electron capture and positron emission forming copper-63. Observe the following equations:

$$^{63}_{30}\text{Zn} + {}^{0}_{-1}\text{e} \longrightarrow {}^{63}_{29}\text{Cu}$$

$$^{63}_{30}\text{Zn} \longrightarrow {}^{63}_{29}\text{Cu} + {}^{0}_{+1}\text{e}$$

c. Gamma rays

Gamma rays, **γ**, are high-energy radiation released as an unstable nucleus undergoes a rearrangement of its particles to give a more stable, lower energy nucleus.

Because gamma ray is an electromagnetic radiation, it has no mass and no charge.

The main properties of gamma radiation (gamma ray) are the following:

- It is an electromagnetic radiation of short wavelength and higher frequency, hence high energy
- It is not deflected by electric and magnetic fields. Refer to figure 15.4 for more understanding.
- It affects photographic plates.
- Its ionizing power is very low compared to alpha-particles and beta-particles.
- It travels at the same speed as that of light.
- It has the greatest penetrating ability, 5000-10000 times that of alpha particles.
- It causes fluorescence when they strike a fluorescent material.
- It is diffracted by crystals.
- It can be stopped by several inches (5cm thick piece) of lead or a thick concrete.
- It can easily pass through the human body and cause immense biological damage.

Normally, there are very few pure gamma emitters. In radiology, one of most commonly used gamma emitter is technetium (Tc). The excited state called "*metastable technetium*" is written as technetium-99m, **Tc-99m**. By emitting energy in the form of gamma rays, the excited nucleus becomes more stable.

$$^{99m}_{43}Tc \rightarrow {}^{99}_{43}Tc + \text{Y}$$

Stable nuclides are usually in the state of least energy or ground state. But these nuclides can be excited by particles or photon bombardment. The excited nucleus returns into the ground state by emission of excess energy as ϒ-rays.

$$^{\text{A}}_{\text{Z}}\text{X}^{*} \longrightarrow {}^{\text{A}}_{\text{Z}}\text{X} + \gamma$$

Examples:

$$^{27}_{13}Al^{*} \longrightarrow {}^{27}_{13}Al + \gamma$$

$$^{87}_{38}Sr^{*} \longrightarrow {}^{87}_{38}Sr + \gamma$$

$$^{99}_{43}Mo \longrightarrow {}^{99}_{42}Tc^{*} + {}^{0}_{1}e$$

$$\downarrow$$

$$^{99}_{42}Tc + \gamma$$

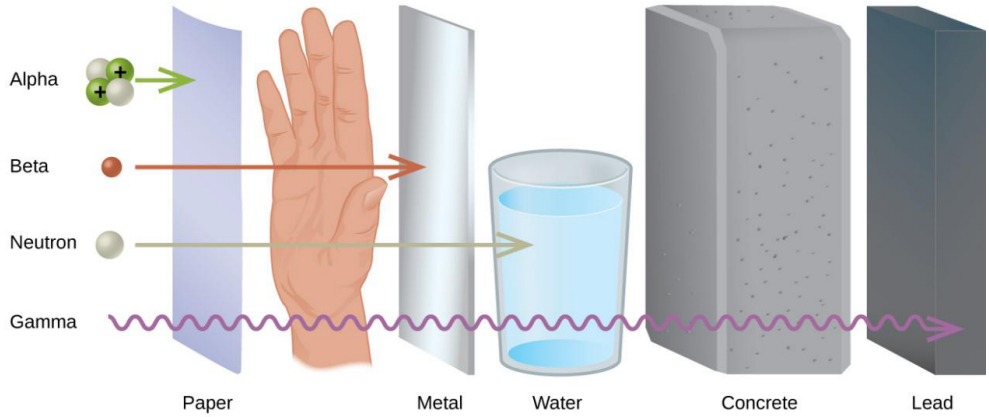


Figure 15.3: Penetration power and shielding of the main radioactive particles

15.2.2. Effect of electric and magnetic fields on nuclear radiations

Experiments involving emissions of radiations cannot be performed in an ordinary school laboratory but can be carried out in research laboratories.

In 1899, the study of radioactivity was taken up by **Ernest Rutherford.** He placed a little radium at the bottom of a small lead box and subjected the rays that emerged from it to the action of a very strong magnetic field at right angles to their direction. He found that the rays separated into three distinct constituents as shown in the figure 15.4 below.

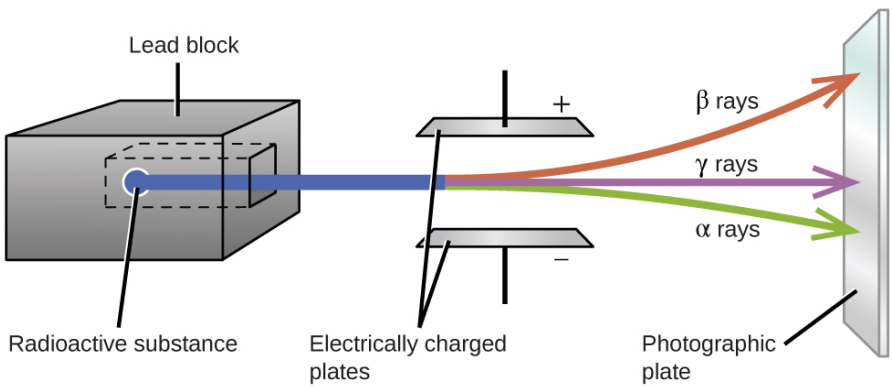


Figure15.4: Effect of magnetic field on radioactive emissions

It is clear that when these radiations pass through a magnetic field or an electric field, they are affected differently. The heavy alpha particles are slightly deflected towards the negatively charged plates; this shows that they bear a positive charge. The lighter beta particles are deflected more sharply towards the positively charged plates, showing that they are bear a negative charge. The gamma rays are not affected by the magnet, showing that they bear no charge. Table 15.2 summarizes the properties of the particles discussed above.

Table 15.2: Distinction between the properties of α, β and γ radiations (summary)

Property	α-particle	β-particle	γ-radiation
Nature	Stream of positively charged particles i.e, helium nuclei	Stream of negatively charged particles i.e, high-energy electrons	Electromagnetic waves i.e, high-energy rays
Speed	Nearly 10^7 ms^{-1}	About 90% of the speed of light or 2.7 x 10^8 ms^{-1}	3 x $l0^8$ ms^{-1} (in vacuum)
Rest mass	4 times the mass of proton i.e., 6.64 x 10^{-27} kg	Mass of electron i.e. 9.1x10^{-31} kg	No mass
Charge	Positive charge +3.2 x 10^{-19} C (+2)	Negative charge -1.6 x 10^{-19}C (-1)	No charge (0)
Effect of electric and magnetic fields	Deflected toward negative plate	Deflected toward positive plate	Unaffected
Ionizing power	Maximum (10,000 times γ)	Less than alpha (100 times of γ)	Minimum
Penetrating power	Small (2-4 cm in air)	High (about 1 mm of lead or about 5 mm of Al) 200-300 cm in air	Very high (about 30 cm of iron) 500 m in air
Biological damage	Cause some damage	Cause more damage	Cause immense biological damage

Checking up 15.2

1. How are an alpha particle and a helium nucleus similar? Different?
2. Naturally occurring potassium consists of three isotopes: potassium-39, potassium-40 and Potassium-41.
   a. Write the atomic symbols for each isotope.
   b. In what ways are the isotopes similar and in what ways do they differ?

3. Give the missing information in the following table:

Medical use	Atomic symbol	Mass number	Number of protons	Number of neutrons
Heart imaging	$^{201}_{81}Tl$			
Radiation therapy		60	27	
Abnormal scan			31	36
Hyperthyroidism				
Leukaemia treatment	$^{131}_{53}I$	32		17

4. Explain why alpha particles are not greatly deflected by an electric or magnetic field as beta particles
5. Briefly describe the effect of a magnetic field on different nuclear radiations

15.3 Nuclear equations and radioactive decay series

Activity 15.3

1. Use your search engine or any available resources to learn about nuclear equations, how they are balanced and radioactive decay series and make a summary to be presented. While carrying out your research try to answer to question number 2 below.
2. Complete the following nuclear equations and balance them:

a) $^{226}_{88}\text{Ra} \rightarrow ? + {}^{4}_{2}\text{He}$

b) $^{241}_{95}\text{Am} \rightarrow ? + {}^{4}_{2}\text{He}$

c) $^{60}_{27}\text{Co} \rightarrow ? + {}^{0}_{-1}\text{e}$

d) $^{118}_{54}\text{Xe} \rightarrow ? + {}^{0}_{+1}\text{e}$

e) $^{4}_{2}\text{He} + {}^{10}_{5}\text{B} \rightarrow ? + {}^{1}_{0}\text{n}$

When a nucleus spontaneously breaks down by emitting radiation, the process is called **natural radioactive decay**. It can be shown as **a nuclear equation** using the symbols for the original radioactive nucleus, the new nucleus and the radiation emitted.

Radioactive nucleus → New nucleus + radiation (α, β, β^+ or γ)

(parent) **(daughter)**

If the first daughter nuclide is stable, the activity of the radioactive source ends there. But in many cases, the daughter nuclide is also radioactive and we obtain a **"decay series (chain)"**.

A → B → C → ... Z (sterile)

More stable

A nuclear equation is balanced when the sum of the mass numbers and the sum of the atomic numbers of the particles and atoms on one side of the equation are equal to their counterparts on the other side.

The changes in mass and atomic numbers of an atom that emits a radioactive particle are shown in the table below.

Table 15.3: Mass number and atomic number changes due to radiation

Decay process	Radiation symbol	Mass number	**Atomic number**	**Charge**
Alpha emission	$^{4}_{2}He$ or α	4	2	+2
Beta emission	$^{0}_{-1}e$ or β	0	-1	-1
Positron emission	$^{0}_{+1}e$ or $^{0}_{+1}\beta$	0	+1	+1
Gamma emission	$^{0}_{0}\gamma$ or γ	0	0	0
Proton	$^{1}_{1}p$	1	1	+1
Neutron	$^{1}_{0}n$	1	0	0

15.3.1. Nuclear equations

A nuclear reaction is represented by a nuclear equation as follows:

Example 1:

Radium-226 emits an alpha particle to form a new isotope whose mass number, atomic number and identity we must determine.

Step 1: Write the incomplete nuclear equation.

$$^{226}_{88}\text{Ra} \longrightarrow {}^{A}_{Z}\text{X} + {}^{4}_{2}\text{He}$$

Step 2: Determine the missing mass number, A.

226 = A + 4

226 – 4 = A

222 = A

Step 3: Determine the missing atomic number, Z.

88 = Z + 2

88 – 2 = Z

86 = Z

Step 4: Determine the symbol of the new nucleus.

Use the periodic table to find out the element with the atomic number corresponding to that obtained in *step 3* above. In this case the element is Radon (Rn). The symbol of this isotope of Radon is written as $^{222}_{86}\text{Rn}$.

Step 5: Write the complete nuclear equation.

$$^{226}_{88}\text{Ra} \longrightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He}$$

Step 6: Check if the equation is balanced, i.e:

i. If the sum of mass numbers at the left side of the equation is equal to the sum of mass number at the right side (226 = 222+4)
ii. If the sum of atomic numbers at the left side of the equation id equal to the sum of atomic numbers at the right side (88 = 86+2)

Example 2:

When a proton bombards Nickel-58, the products are a new nucleus and an alpha particle. Write the balanced nuclear equation for this bombardment reaction.

Step 1: Write the incomplete nuclear equation.

$$^{58}_{28}\text{Ni} + {}^{1}_{1}\text{H} \longrightarrow ? + {}^{4}_{2}\text{He}$$

Step 2: Determine the missing mass number

58 + 1 = ? + 4

59 – 4 =A

55 = A

Thus, the mass number for the new nucleus is 55.

Step 3: Determine the missing atomic number

28 + 1 = ? + 2

29 – 2 = A

27 = A

Step 4: Determine the symbol for the new nucleus.

On the periodic table, the element that has the atomic number of 27 is Cobalt, Co. the symbol of this isotope of Cobalt is written as $^{55}_{27}\mathrm{Co}$.

Step 5: Complete the nuclear equation.

$$^{58}_{28}\mathrm{Ni} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{55}_{27}\mathrm{Co} + {}^{4}_{2}\mathrm{He}$$

Step 6: The equation is balanced.

Note: Nuclear reactions involving hitting a nuclide by a particle such as proton or neutron as in the example 2 are referred to as 'bombardment reactions'. Bombardment reactions are not natural; they are induced (or artificial) nuclear reactions.

For the case of example 1, when a radioactive particle is emitted, the type of nuclear reaction is **emission reaction**; those are natural radioactive isotopes.

15.3.2. Radioactive decay series

Radioactive decay Series is the series of steps by which a radioactive nucleus decays into a non-radioactive nucleus. The element goes from radioactive to non-radioactive.

A radioactive element disintegrates by emission of an α- or β-particle from the nucleus to form a new "daughter element." This again disintegrates to give another "daughter element'. This is why the whole series of elements starting with the parent radioactive element to the stable end-product is called radioactive disintegration series or radioactive decay series as seen above.

Naturally radioactive nuclides disintegrate to acquire stability. In nature there are four radioactive decays, that is, a series starting with a radioactive element and then ending with a reasonable stable element.

The three series are Uranium, Thorium and Actinium series. Uranium series is the most important.

The three series are similar because they all involve losses of alpha and beta particles ending with isotopes of Lead. Uranium series gives Lead-206, the most stable isotope of Lead; Thorium gives Lead-208 and actinium series gives Lead-207.

The fourth series is the Neptunium series which leads to Bismuth-209.

1. The uranium series

It starts with the parent element Uranium-238 and ends with the stable element Lead-206. It derives its name from Uranium-238 which is the starting nuclide of the series and has the longest half-life. In the process 8 alpha and 6 beta particles are emitted before Lead-206 is attained. The whole process is shown belo

$$^{238}_{92}U \xrightarrow{\alpha} {}^{234}_{90}Th \xrightarrow{\beta} {}^{234}_{91}Pa \xrightarrow{\beta} {}^{234}_{92}U \xrightarrow{\alpha} {}^{230}_{90}Th \xrightarrow{\alpha} {}^{226}_{88}Ra \xrightarrow{\alpha} {}^{222}_{86}Rn \xrightarrow{\alpha} {}^{218}_{84}Po$$

$$\xrightarrow{\alpha} {}^{214}_{82}Pb \xrightarrow{\beta} {}^{214}_{83}Bi \xrightarrow{\beta} {}^{214}_{84}Po \xrightarrow{\alpha} {}^{210}_{82}Pb \xrightarrow{\beta} {}^{210}_{83}Bi \xrightarrow{\beta} {}^{210}_{84}Po \xrightarrow{\alpha} {}^{206}_{82}Pb$$

2. The Thorium series

It begins with the parent element thorium-232 and ends with Lead-208 which is stable.

$$^{232}_{90}Th \xrightarrow{\alpha} {}^{228}_{88}Ra \xrightarrow{\beta} {}^{228}_{89}Ac \xrightarrow{\beta} {}^{228}_{90}Th \xrightarrow{\alpha} {}^{224}_{88}Ra \xrightarrow{\alpha} {}^{220}_{86}Rn \xrightarrow{\alpha} {}^{216}_{84}Po \xrightarrow{\alpha}$$

$$^{212}_{82}Pb \xrightarrow{\beta} {}^{212}_{83}Bi \xrightarrow{\beta} {}^{212}_{84}Po \xrightarrow{\alpha} {}^{208}_{82}Pb$$

3. The Actinium series

It starts with the radioactive element Actinium-235. The end-product is the stable element Lead-207.

4. The Neptunium series

This series consists of elements which do not occur naturally. It commences with neptunium-237 and terminates at bismuth-209.

Checking up 15.3

1. Complete the following nuclear equations:
   a. $^{28}_{13}\text{Al} \rightarrow ? + {}^{0}_{-1}\text{e}$
   a. $? \rightarrow {}^{86}_{36}\text{Kr} + {}^{1}_{0}\text{n}$
   b. $^{210}_{83}\text{Bi} \rightarrow ? + {}^{4}_{2}\text{He}$
   c. $^{40}_{18}\text{Ar} + ? \rightarrow {}^{43}_{19}\text{K} + {}^{1}_{1}\text{He}$
   d. $^{238}_{92}\text{U} + {}^{1}_{0}\text{n} \rightarrow ?$
2. Cobalt-60 decays by emitting a beta particle. Write the nuclear equation for its decay.
3. A new isotope is produced by the bombardment of Zinc-66 by a proton. Write the equation for this nuclear bombardment.
4. Complete the Thorium series starting with $^{232}_{90}\text{Th}$. 2 beta particles emitted, then 3 alpha particles; followed by a beta particle; then alpha particle; beta particle and then 2 alpha particles. Note that 2 beta particles are emitted consecutively.

15.4. Stability and instability of nuclei of atoms

Activity 15.4

1. What do you think can influence the stability of the nucleus of a given atom?
1. Use a search engine or any available resources to understand and share everything about stability of nuclei of atoms.

Nuclides can either be **stable** or **unstable** toward radioactivity but a nucleus that is unstable can become stable by undergoing a nuclear reaction or change.

Most isotopes of elements up to atomic number 19 have stable nuclei. Elements with higher atomic numbers (20 to 83) consist of a mixture of isotopes, some may have unstable nuclei. Elements with atomic numbers of 84 and higher consist only of radioactive isotopes. So many protons and neutrons are crowded together in their nuclei that the strong repulsions between the protons make these nuclei unstable.

Nuclear Stability is a concept that helps to identify the stability of an isotope. The **ratio of neutrons to protons (n/p)** is a good indicator to know if an isotope is radioactive or not.

To help you understand this concept, there is a chart of the nuclides known as a **Segre chart** (see figure 15.5)

This chart shows a plot of the number of neutrons versus the number of protons for known stable nuclides and shows the existence of the stability zone or band of stability. It can be observed from the chart that there are more neutrons than protons in stable nuclides with atomic number (Z) greater than 20 (Calcium). These extra neutrons are necessary for stability of the heavier nuclei.

The excess neutrons act somewhat like nuclear glue. Atomic nuclei consist of protons and neutrons, which attract each other through the nuclear force, while protons repel each other via the electric force due to their positive charge. These two forces compete, leading to stability of various nuclei.

Neutrons stabilize the nucleus, because they attract each other and protons, which helps offset the electrical repulsion between protons. As a result, as the number of protons increases, an increasing ratio of neutrons to protons is needed to form a stable nucleus. If there are too many or too few neutrons for a given number of protons, the resulting nucleus is not stable and it undergoes radioactive decay.

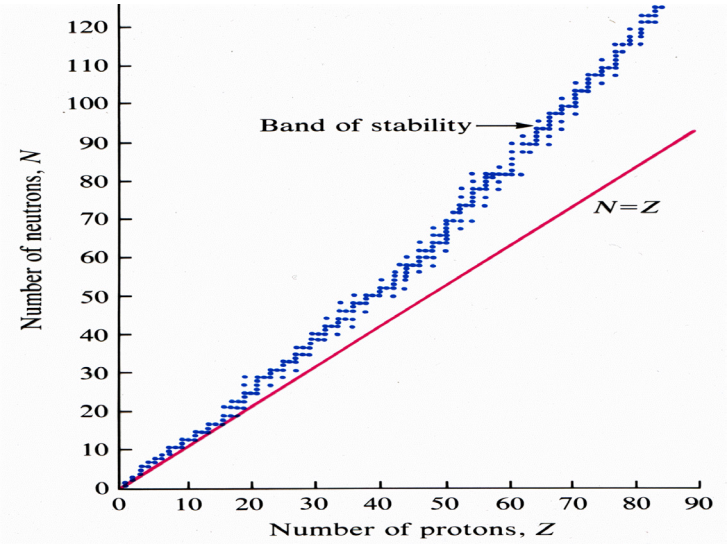


Figure 15.5: Neutron number against proton number (stability of atoms) graph.

From figure 15.5, the blue band is called band of stability or "stability belt"; any nuclide whose n/p ratio is within the stability belt is stable. A nuclide with n/p outside the stability belt is unstable. The red strait line represents n/p = 1 of N=Z.

The stable isotopes of elements with proton number less than 20 have a neutron-proton ratio (n/p) equal to 1. For elements with proton number of 20 or more, the stable isotopes have n/p ratios of greater than 1. Radioactive isotopes will disintegrate until they form the daughter nuclei that lie in the stability belt. Table 15.4 compares some stable non-radioactive isotopes with some radioactive isotopes.

Table 15.4: Stable and radioactive isotopes of some elements

Elements:	Magnesium	Iodine	Uranium
Stable isotopes:	$^{24}_{12}Mg$ Magnesium-24	$^{127}_{53}I$ Iodine-127	None
n/p ratio	1	1.4	
Radioactive isotopes:	$^{23}_{12}Mg$:Magnesium-23 $^{27}_{12}Mg$: Magnesium-27	$^{125}_{53}I$: Iodine-125 $^{131}_{53}I$: Iodine-131	$^{235}_{92}U$: Uranium-235 $^{238}_{92}U$: Uranium-238
n/p ratio	0.9 1.25	1.35 1.47	1.55 1.78

Checking up 15.4

1. What can you take as the basis to predict the stability of nuclei of atoms?
2. Use your periodic table to provide examples (2 in each case) of
   a. Elements with naturally occurring stable isotopes.
   b. Elements with naturally radioisotopes.
   c. Elements with mixtures of both stable and unstable isotopes.

Please specify the atomic number of each element you have provided

15.5. Rate of decay of radioactive substances and half-life of a radioisotope

Activity 15.5:

1. Use your prior knowledge on the reaction kinetics (in the previous unit), answer the following questions:
   a. A little sulphuric acid is added to 1 dm^3 of a solution containing 0.300 mol of methylethanoate. After 120 s, the concentration of the ester decreases to 0.292 mol dm^{-3}. Calculate the average rate of reaction in the first 120 s.
   b. Reaction A takes 2 min 35 s to be completed while reaction B takes 1 min 15 s to be completed. What is the rate of reaction A relative to that of reaction B?
   c. Explain what you understand by the term "half-life of a radioisotope"
2. Use your search engine or any available source to you to carry out a research about rate of decay/disintegration and try to compare this one with that in the previous unit.

15.5.1. Rate of decay of radioactive substances

As seen in units 13 and 14, the time for different chemical reactions to be completed varies. In this unit, we are concerned with the calculation of decay rate for a decay process which is a first order reaction.

Consider a simple case for a first daughter stable. Suppose that at time, t, there are N radioactive nuclides and dN disintegrations in a time dt. The rate of disintegration, dN/dt, is given by:

$$\frac{dN}{dt} = -\lambda N$$

This shows that the rate of disintegration/decay is directly proportional to the number of radioactive nuclides/particles present; **λ** (Lamda, a Geek letter) is the proportionality constant known as "radioactive constant".

The above mathematical expression can be written as: $\frac{dN}{N} = -\lambda dt$

The negative sign shows that the increase in disintegrations is associated with a decrease in the number of radioactive nuclides. Integration of the relation above gives:

$$\int_{No}^{N} \frac{dN}{N} = -\lambda \int_{0}^{t} dt$$

Here, N_0 stands for initial number of radioactive nuclides (radioactive nuclides at time, t = 0).

After integrating, we have: $lnN \Big|_{N_o}^{N} = -\lambda t$

By applying logarithm properties, we get

$$\ln N - \ln No = -\lambda t$$

$$\ln \frac{N}{No} = -\lambda t \quad \text{or} \quad \ln \frac{N}{No} = \lambda t$$

$$\frac{N}{No} = e^{-\lambda t} \quad \text{or} \quad \frac{No}{N} = e^{\lambda t}$$

Thus, finally the following equation is obtained

$N = N_0 e^{-\lambda t}$

The equatuion is known as " radioactive decay law"

The SI unit of the activity is **Becquerel (Bq)** which is defined as one disintegration per second (disintegration or decay or event second^{-1}). Some multiples of Becquerel include mega and giga Becquerel (GBq).

1MBq = 1.0 x 10^6 Bq and 1GBq = 1.0 x 10^9 Bq

The activity can also be expressed in **Curies (Ci)** which is the rate of decay of 3.7 x 10^{10} disintegrations per second (**3.7 x 10^{10} Bq = 37 GBq**).

It can also be expressed in **Rutherford (R).**

1R = 10^6 Bq = 1 MBq.

Worked examples

1) The disintegration constant for the conversion of radioactive sodium into magnesium is 2.85 x 10^{-3} s^{-1}. Calculate the fraction of the original sample left after 150 seconds.

Solution:

Given: disintegration constant, $\lambda = 2.85 \times 10^{-3} s^{-1}$ time, t = 150 s

Need: fraction of the original sample remaining, $\frac{N}{No}$

Solution : $\frac{N}{No} = e^{-\lambda t} = e^{-(0.00285 \times 150)} = 0.65 = \frac{65}{100} = \frac{13}{20}$

Thus, 65% of the original sample is the part left after 150s. The other part has decayed/disintegrated.

2) A sample of phosphorus-32, a beta emitter, has an activity of 2 millicuries (mCi). How many beta particles are emitted by this sample of P-32 in 1s?

Solution:

Given: Activity = Rate = 2 mCi = 2×10^{-3} Ci = $2 \times 10^{-3} \times 3.7 \times 10^{10}$ disintegrations/second (remember that 1 Ci = 3.7×10^{10}disintegrations/second)

Thus, Rate = 7.4×10^{7} disintegrations/second = 7.4×10^{7} β-particles /second (here each disintegration correspond to one β-particle)

Time, t = 1s

Need: Number of β-particles (or disintegrations), N

Solution: N = $7.4 \times 10^{7} \times 1 = 7.4 \times 10^{7}$ β-particles

15.5.2. Half-life of raditive substances and calculations involved

When a radioactive substance disintegrates, there is a time where it reaches half of its original size. As seen previously, the rate of decay of a radioisotope depends also on its half-life.

By definition, the **half-life** of a radioactive isotope is the time taken for a given mass or number of nuclides to decay to half its original mass or activity.

It can also be defined as the time within which half the nuclei in a sample of radioactive material undergoes decay. The half-life time is constant and specific for each element.

Let $\mathbf{N_0}$ be the initial activity for a given radionuclide at time, t = 0; that undergoes nuclear decay. After its half-life it is reduced to half its initial activity which can be written as $\frac{No}{2}$.

Let **N** be the activity of the same nuclide available after **time, t.** As the decay continues indefinitely we can draw the following table and then after draw the graph of mass

or activity against time expressed in terms of half-life times.

Time (t)	0	T	2T	3T	4T	5T	6T	….	….
Activity (N)	N_0	$N_0/2$	$N_0/4$	$N_0/8$	$N_0/16$	$N_0/32$	$N_0/64$	…	…..

Let us use iodine-131 as an example. Its half-life is 8 days. It decays into non-radioactive xenon-131 by emitting a beta particle.

$$^{131}_{53}\mathrm{I} \rightarrow {}^{131}_{54}\mathrm{Xe} + {}^{0}_{-1}\mathrm{e}$$

Suppose that we have a sample that contains 40 g of I-131. In 8 days, one half (i.e, 50%) of all the nuclei in the sample will decay to give Xe-131. That means that after 8 days, there are 20 g of I-131 remaining.

The decay process has also produced 20 g of the product, Xe-131. After another half-life (i.e, 8 days) passes, 10 g of the 20 g of I-131 will decay to Xe-131. At this time there will be 10 g (25%) of I-131 remaining and 30 g of Xe-131 produced. The process may continue until a very small fraction of I-131 remaining.

$$40\text{ g of } {}^{131}_{53}\mathrm{I} \xrightarrow[8\text{ days}]{1\text{ half-life}} 20\text{ g of } {}^{131}_{53}\mathrm{I} \xrightarrow[8\text{ days}]{2\text{ half-lives}} 10\text{ g of } {}^{131}_{53}\mathrm{I}$$

and so on and so forth.

According to the radioactive decay law, the above information can be summarized by plotting the graph iodine-131 percentages against time (half-lives)

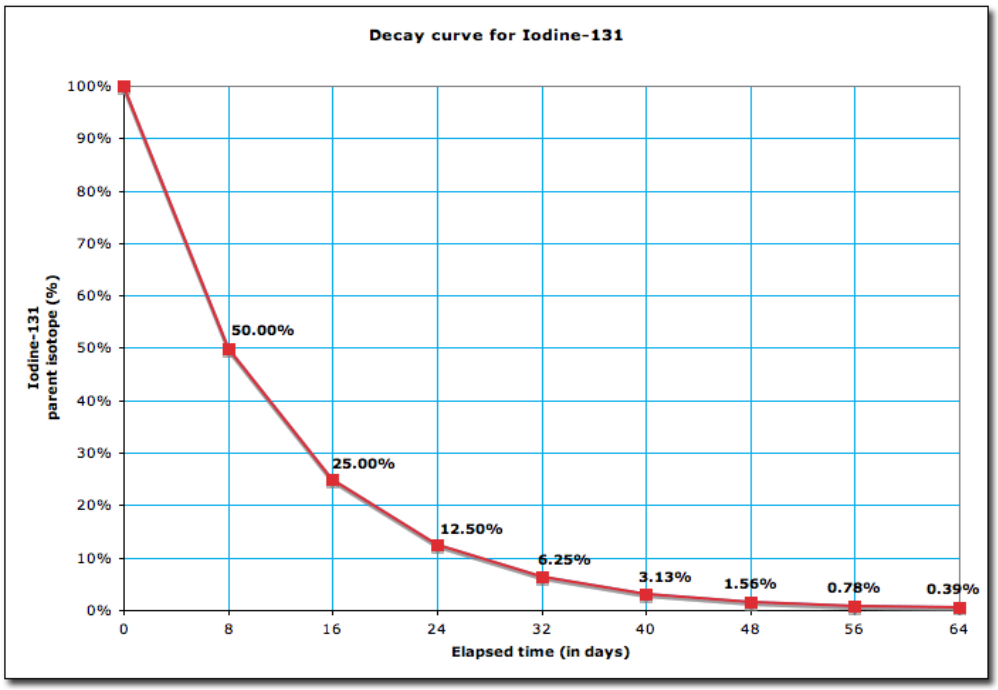


Figure15.6: Disintegration of iodine-131 with time (highlighting half-lives, $t_{½}$)

From the decay curve, we can deduce a generalized formula that expresses how a

fraction of a nuclide decreases rapidly (exponentially) as time increases.

$\mathbf{N = \frac{N_0}{2^n}}$ where, $\mathbf{n = \frac{t}{t_{½}}}$ is the number of decays or number of period or number of half -lives.

At half-life, we normally have:

$t = t_{½}$, $N = \frac{No}{2}$ but $N = No.\ e^{-\lambda t}$ as seen above.

Thus, we have:

$\frac{No}{2} = No.\ e^{-\lambda\ t1/2}$

$\ln\frac{No}{2} = \ln (No.\ e^{-\lambda t1/2})$

$\ln No - \ln 2 = \ln No - \lambda t_{1/2}$

$t_{½} = \frac{\ln 2}{\lambda}$ and $\lambda = \frac{\ln 2}{t½}$

From calculations using a scientific calculator, it is found that ln 2 = 0.693. Thus, we have

$t_{½} = \frac{0.693}{\lambda}$ and $\lambda = \frac{0.693}{t½}$

The value of λ can be found experimentally by finding the number of disintegration per second with the help of some devices like a Geiger-Muller counter.

The half-life for a given isotope is always the same; it does not depend on how many atoms you have or on how long they have been sitting around. Each radioactive isotope decays at its own rate and therefore has its own half-life reason why it ranges from fractions of seconds to millions (and even billions) of years. For example, look at table 15.5.

Table 15.5: Half-lives of some radioisotopes

Nuclide	Half-life (T or $t_{1/2}$)
Polonium-212	2.98×10^{-7} s
Laurencium-257	8 s
Protactinium-234	1.14 min
Thorium-234	24.5 days
Uranium-234	4.5×10^{9} years
Carbon-14	5570 years

Polonium-218	3 min

- The shorter the half-life, the faster the decay of nuclide and the longer the half-life, the slower the decay of the nuclide. Nuclides with short half-lives are often used in medicine as they do not stay in the body for a long time, hence causing minimal damage.
- The rate of radioactive decay is unaffected by any chemical or physical change.

Detection of radioactivity: devices that detect radiation include:

- **Cloud chamber:** detects alpha and beta particles radiation, leaves a trail of ions in the water or ethanol vapor (gas) in the chamber.
- **Bubble chamber:** detects alpha and beta particles radiation, holds a super-heated liquid in which particles leave a path of bubbles if they are present.
- **Electroscope:** Has leaves that repel or attract each other depending on the charge in the air. If the electroscope is given a negative charge the metal leaves separate from each other. A negatively charged electroscope discharges when ions in the air remove electrons from it, and consequently, a positively charged electroscope discharges when it takes electrons from the air around it. The rate of discharge of the electroscope is a measure of ions in the air and can be used as a basis of measurement and detection.
- **Geiger counter:** measures radioactivity by producing an electric current when radiation is present, detects alpha, beta and gamma radiation.

Worked examples

1. If we start with 1.000 grams of Sr-90, 0.953 grams will remain after 2.0 years.
   a. What is the half-life of strontium-90?
   b. How much strontium-90 will remain after 5.00 years?

Solution:

a. Given: No = 1.000 g N = 0.953 g and time, t = 2.0 years

Need: half-life, $t_{1/2}$

Solution: Let us first work out the radioactive decay constant, λ, from the formula,

$N = No.e^{-\lambda t}$

As seen above it can be easily shown that $\ln\left(\frac{N}{No}\right) = -\lambda t$. Now, let us substitute the given data in the formula to find the value of λ.

$\ln(0.953/1) = -2\lambda$

$-0.04814 = -2\lambda$ and $\lambda = 0.0241\ \text{year}^{-1}$

Hence, use the formula, $t_{1/2} = \frac{ln2}{\lambda}$ to find the half-life

$t_{1/2} = \frac{0.693}{0.0241} = 28.8$ years

b) **Given:** No = 1.000 g and time, t = 5.0 years

Need: N

Solution: Let us first work out the radioactive decay constant, λ, from the formula,

$N = No.\ e^{-\lambda t}$ ($\lambda = 0.0241\ \text{year}^{-1}$ is constant for this radioisotope).

By substituting the given data in the formula, we get:

$N = 1 \times e^{-0.0241 \times 5}$

$N = 0.8865$ g

2. f the half-life of 100.0 grams of a radioactive isotope is 8 years, how many grams will remain in 32 years?

Solution:

Given: No = 100.0 g time, t = 32 years and half-life, $t_{1/2} = 8.0$ years

Need: N

Solution: Let us first work out the radioactive decay constant, λ, from the formula, $\lambda = \frac{\ln 2}{t_{1/2}}$

$\lambda = \frac{0.693}{8} = 0.086625\ \text{year}^{-1}$

Now, work out the mass of nuclides at the time given, N, by substituting the given data in the formula, $N = No.\ e^{-\lambda t}$

$N = 100.0 \times e^{-(0.086625 \times 32)} = 6.254$ g

Or there is no need to solve for the radioactive decay equation. If 32 ÷ 8 = 4, then the material will go through 4 half-lives.

$$100.0\ \text{g} \xrightarrow{1^{st}\ \text{half-life}} 50.0\ \text{g} \xrightarrow[\text{or 2 half-lives}]{2^{nd}\ \text{hlf-life}} 25.0\ \text{g} \xrightarrow{3^{rd}\ \text{half-life}} 12.5\ \text{g} \xrightarrow{4^{th}\ \text{half-life}} 6.25\ \text{g}$$

3. What is the decay constant for a radioactive isotope with a half-life of 22.5 hours?

Answer:

At first glance, it may seem that not enough information was provided to solve this problem. However, if the half-life value is given for time (t) then the value of $\frac{Nt}{No} = \frac{1}{2}$ (because only half of the original material remains).

$ln \frac{N}{No} = - \lambda t$

ln 0.5 = - λ (22.5)

- 0.693 = - λ (22.5)

λ = 0.0308 hour^{-1}

4) Calculate how long it will take for 25% of a U-238 sample to radioactively decay.

Answer:

If 25% of the sample has undergone radioactive decay, then the ratio of $\frac{N_0}{N_t} = 0.75$ because 75% of the original sample remains. The rate of decay constant for U-238 will be used from the previous problem.

$ln \frac{N}{No} = - \lambda t$

$\ln 0.75 = -1.55 \times 10^{-10}\ year^{-1} \times t$

T = 1.86 x 10^9 years

Checking up 15.5

1. a) A sample of iodine-131 has an activity of 3.0 Ci. How many disintegrations occur in the Iodine-131 sample in 20 s?

   b) The recommended dosage of iodine-131 is 4.20 μCi/kg of body weight. How many Microcuries of iodine-131 are needed for a 70.0-kg person with hyperthyroidism?

(1 Ci = 1.0 x 10^{-6} μCi)

2. The β-activity of an archeological artifact is 6.5 disintegration per minute per gram of carbon. Given that the β-activity of a living specimen is 15.3 disintegration per minute per gram of carbon. What is the age of the artifact? (the decay constant for this artifact = 1.21 x 10^{-4})

3. Explain what is meant by "half life" and suggest a reason why radioisotopes with short half- lives used for diagnosis in nuclear medicine.

4. Calculate the rate of decay constant for U-238 if its half-life is 4.468 × 10^9 years.

5. The radioisotope caesium-137 has a half-life of 30 years. A sample of this radioisotopes decays at the rate of 544 counts per minute in 2011. In what year will the decay rate be 17 counts per minute?

15.6. Uses of some radioisotopes

Activity 15.6:

1. According to your own understanding, how do you think radioactivity is important in daily life?
2. Consult different sources (textbooks and search engines) to carry out a deep research on the uses of radioisotopes. Please take care because you will have to present your findings!

Radioactive isotopes have a variety of applications. Generally, they are useful because either we can detect their radioactivity or we can use the energy they release.

Radioactive isotopes are effective tracers because their radioactivity is easy to detect. A tracer is a substance that can be used to follow the pathway of that substance through some structures. For instance, leaks in underground water pipes can be discovered by running some tritium-containing water through the pipes and then using a Geiger counter to locate any radioactive tritium subsequently present in the ground around the pipes.

Tracers can also be used to follow the steps of a complex chemical reaction. After incorporating radioactive atoms into reactant molecules, scientists can track where the atoms go by following their radioactivity. One excellent example of this is the use of carbon-14 to determine the steps involved in photosynthesis in plants.

1. Radioactive Dating

Radioactive isotopes are useful for establishing the ages of various objects. The half-life of radioactive isotopes is unaffected by any environmental factors, as seen above, so the isotope acts like an internal clock.

For example, if a rock is analyzed and is found to contain a certain amount of uranium-235 and a certain amount of its daughter isotope, we can conclude that a certain fraction of the original uranium-235 has radioactively decayed. If half of the uranium has decayed, then the rock has an age of one half-life of uranium-235, or about 4.5×10^9 years. Many analyses like this, using a wide variety of isotopes, have indicated that age of the earth itself is over 4×10^9 years.

In another interesting example of radioactive dating, hydrogen-3 dating has been used to verify the stated vintages of some old fine wines.

One isotope of carbon, carbon-14, is particularly useful in determining the age of once-living artifacts. A tiny amount of carbon-14 is produced naturally in the upper reaches of the atmosphere, and living things incorporate some of it into their tissues, building up to a constant level. Once a living thing dies, it no longer acquires carbon-14. As time passes the carbon-14 that was in the tissues decays. The half-life

of carbon-14 is 5,730 years. If an artifact is discovered and analyzed many years after its death and the remaining carbon-14 is compared to the known constant level, an approximate age of the artifact can be determined.

Radiocarbon dating is used in many fields to learn information about the past conditions of organisms and the environments present on Earth.

2. **In Medicine**

Radioactive isotopes have many medical applications in diagnosing and treating illness and diseases.

When a radiologist wants to determine the condition of an organ in the body, the patient is given a radioisotope that is known to concentrate in that organ. After a patient receives a radioisotope, a scanner produces an image of the organ. The scanner moves slowly across the region of the body where the organ containing the radioisotope is located. The gamma lays emitted from the radioisotope in the organ are used to expose a photographic plate with a scan of the organ.

One example of a diagnostic application is using radioactive iodine-131 to test for thyroid activity. The thyroid gland in the neck is one of the few places in the body with a high concentration of iodine.

To evaluate thyroid activity, a measured dose of ^{131}I is administered to a patient, and the next day a scanner is used to measure the amount of radioactivity in the thyroid gland. The amount of radioactive iodine that collects there is directly related to the activity of the thyroid, allowing radiologists to diagnose both hyperthyroidism and hypothyroidism.

image from a scanner of a patient suffering from the thyroidism disorder

Figure 15.7: Examination of thyroid activity in radiography

Iodine-131 has a half-life of only 8 days. So, it has low cell damage due to the minimum exposure. Technetium-99 can also be used to test thyroid function. Bones, the heart, the brain, the liver, the lungs, and many other organs can be imaged in similar ways by using the appropriate radioactive isotope.

Other medical applications of radioisotopes include:

- Radiation from Co-60 (γ-rays) is used to irradiate the tumours (for instance, diagnosis and treat thyroid disorders).
- Iodine-125 (I-125) is used in treatment of brain cancer and in osteoporosis (a disease which causes bones to become weaker and easily broken) detection.
- Iodine-131 (I-131) is used to diagnose and treat thyroid disorders, in treatment of Graves' disease, goiter and prostate cancer.
- Phosphorus-32 (P-32) is used in the treatment of leukaemia, excess red blood cells (tumours) and pancreatic cancer.
- Technetium-99m is used in imaging of skeleton and heart muscle, brain, liver, heart, lungs, bones, spleen, kidney and thyroid. This is the most widely used radioisotope in nuclear medicine.
- Cerium-141 (Ce-141) is used in gastrointestinal tract diagnosis and in measuring blood flow to the heart.
- Sodium-24 (Na-24) in the form NaCl is used as a tracer in blood.
- Strontium-85 (Sr-85) is used in detection of bone lesions and brain scans
- Radio Gold (Au-198) is used in Liver disease diagnosis.
- Radio iron (Fe-59) is used in Anemia diagnosis.
- In addition, radioisotopes are also used in sterilization of medical devices.

3. **In Agriculture**

Obviously, we obtain **food to eat and some drinks** as a result of agriculture. But contaminated food causes some diseases. Thus, there are some radioisotopes that kill dangerous microorganisms present on food by "**irradiation"**.

The radiation emitted by some radioactive substances can be used to kill microorganisms on a variety of foodstuffs thereby increasing the shelf life of these produces. Produces such as tomatoes, mushrooms, sprouts, and berries are irradiated with the emissions from cobalt-60 or caesium-137. This exposure kills a lot of the bacteria that could cause spoilage and so the produce stays longer. Eggs and some meat, such as beef, pork, and poultry, can also be irradiated. Normally, irradiation of food does not make it radioactive.

By using known vintages (qualities of wines), oenologists (wine scientists) can construct a detailed analysis of the cesium-137 of various wines through the years.

The verification of a wine's vintage requires the measurement of the activity of cesium-137 in the wine. By measuring the current activity of cesium-137 in a sample of wine (the gamma rays from the radioactive decay pass through glass wine bottles easily, so there's no need to open the bottle), comparing it to the known amount of cesium-137 from the vintage, and taking into account the time passed, researchers can collect evidence for or against a claimed wine vintage.

In addition in plant research, radiation is used to develop new plant types to speed

up the process of developing large amount of agricultural products. This involves insect control, drastic reduction of pest populations and, in some cases, elimination of insects by exposing the male ones to sterilizing doses of radiation. Radiation pellets are used in grain elevators to kill insects and rodents. Irradiation prolongs the shelf-life of foods by destroying bacteria, viruses, and molds as seen above.Other agricultural uses of radioisotopes include the following:

- Radioactive phosphorus (P-32) is used in the study of metabolism of plants.
- Radioactive sulphur (S-35) helps to study advantages and disadvantages of fungicides.
- Pests and insects on crops can be killed by gamma - radiations.
- Gamma - rays are used for preservation of milk, potatoes etc.
- Yield of crops like carrot, root, apples or grapes can be increased by irradiation with radioisotopes.

4. **In Industry**

The applications of radioisotopes in industry are so many. Many types of thickness gauges exploit the fact that gamma rays are attenuated when they pass through the material. By measuring the number of gamma rays, the thickness can be determined. This process is used in common industrial applications such as:

a. **The automobile industry**: to test steel quality in the manufacture of cars and to obtain the proper thickness of tin and aluminum

b. **The aircraft industry**: to check for flaws in jet engines

c. **Road construction**: to gauge the density of road surfaces and sub surfaces

d. **Pipeline companies**: to test the strength of welds and leakage

e. **Oil, gas, and mining companies**: to map the contours of test wells and mine bores, and

f. **Cable manufacturers**: to check ski lift cables for cracks.

The isotope ^{241}Am is used in smoke detectors , in thickness gauges designed to measure and control metal foil thickness during manufacturing processes, to measure levels of toxic lead in dried paint samples, and to help determine where oil wells should be drilled.

The isotope ^{252}Cf (a neutron emitter) is used for neutron activation analysis, to inspect airline luggage for hidden explosives, to gauge the moisture content of soil and other materials, in bore hole logging in geology, and in human cervix-cancer therapy.

Checking up 15.6

1. Define radioactive tracer and give an example of how these tracers work.
2. Explain how radioactive dating works.
3. Name two isotopes that have been used in radioactive dating.
4. The current disintegration rate for carbon-14 is 14.0 Bq. A sample of burnt wood discovered in an archeological excavation is found to have a carbon-14 disintegration rate of 3.5 Bq. If the half-life of carbon-14 is 5,730 years, approximately how old is the wood sample?
5. Bone and bony structures contain calcium and phosphorus.
   a. Explain why the radioisotopes of calcium-47 and phosphorus-32 would be used in the diagnosis and treatment of bone diseases.
   b. During nuclear tests, scientists were concerned that strontium-85, a radioactive product, would be harmful to the growth of bone in children. Explain

15.7. Nuclear fission and fusion and their applications

Activity 15.7:

1. Have you ever heard about nuclear fission and fusion? If yes, explain the two terms and state any use of one of/both these processes
2. From your prior knowledge, explain what you think about the difference between fission and fusion.
3. Use your search engine, or any available source to read about nuclear fission and fusion and then make a summary to be presented to your colleagues.

While many elements undergo radioactive decay naturally, some nuclear reactions are not spontaneous but are brought about when stable isotopes are bombarded with high-energy particles (like neutrons, α-particles, protons ...). Nuclear fission and fusion are good examples **artificial radioactivity** as they do not take place spontaneously.

15.7.1. Nuclear fission and fusion

1. **NUCLEAR FISSION**

Nuclear fission is a process in which a large atomic nucleus is split into two smaller

nuclei. Large nuclei obviously have a large number of protons. The close proximity of so many protons makes these nuclei unstable due to the repulsion forces between protons. Thus, the nucleus of the unstable isotope splits to form smaller atoms by bombardment with a suitable sub-atomic particle. Those stable isotopes that are bombarded by a neutron to undergo fission reactions (to become fissionable) are known to be "fertile radioisotopes".

Among the three natural isotopes of uranium $^{238}_{92}\mathbf{U}$, $^{235}_{92}\mathbf{U}$ **and** $^{234}_{92}\mathbf{U}$, the $^{235}_{92}\mathbf{U}$ nucleus undergoes nuclear fission when bombarded with slow neutrons. Uranium-236 is formed which being unstable, further breaks up in several different ways.

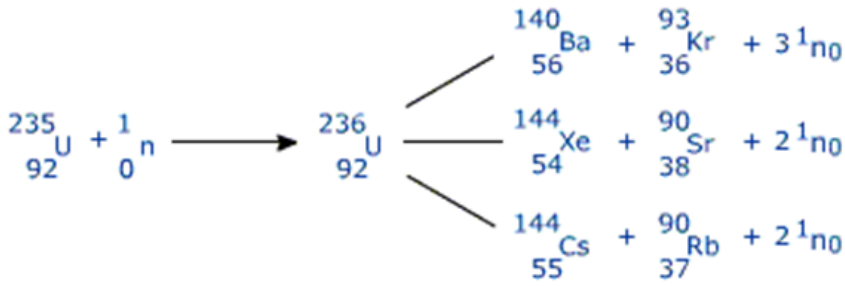


Figure 15.8: Nuclear fission of Uranium-235 nucleus

The neutrons emitted, in this fission reaction, bombard more uranium nuclei available to form a "reaction chain". This chain reaction is the basis of nuclear power. As uranium atoms continue to split, a significant amount of energy is released, in form of heat, from the reaction. This heat released is used to produce electricity (in a nuclear plant) or used in atomic/nuclear bombs.

Other examples: nitrogen-14 and oxygen-16 undergoing alpha and neutron bombardment respectively.

$$^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H}$$

$$^{16}_{8}\mathrm{O} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{13}_{6}\mathrm{O} + {}^{4}_{2}\mathrm{He}$$

The tremendous amount of energy released during nuclear fission results from the principle of mass-energy equivalence; during the nuclear reaction, there is loss of mass but the mass lost is transformed into energy. Thus, the sum of the masses of the fragments produced and particles released as a result of fission is less than the sum of the masses of the starting materials. The loss in mass gets converted into energy according to Einstein equation:

$$\mathbf{E = \Delta mc^2}$$

Where,

E = energy produced

Δm = mass defect or mass lost (which is given by the sum of masses of particles present in reactants minus masses of particles present in products)

c = velocity of light (3×10^8 ms^{-1})

This gives us the energy generated when the mass lost is converted into energy. Since the term c^2 is so large, a small mass produces a great deal of energy.

Note: Protons are not used for bombardment for fission because of the repulsion between positively charged nucleus and positively charged proton and make fission difficult.

2. NUCLEAR FUSION

Nuclear fusion is a process that consists of joining two atomic nuclei of smaller masses to form a single nucleus of a larger mass.

A good example is the fusion of two "heavy" isotopes of hydrogen (deuterium, Hydrogen-2, and tritium, Hydrogen-3) into the element helium.

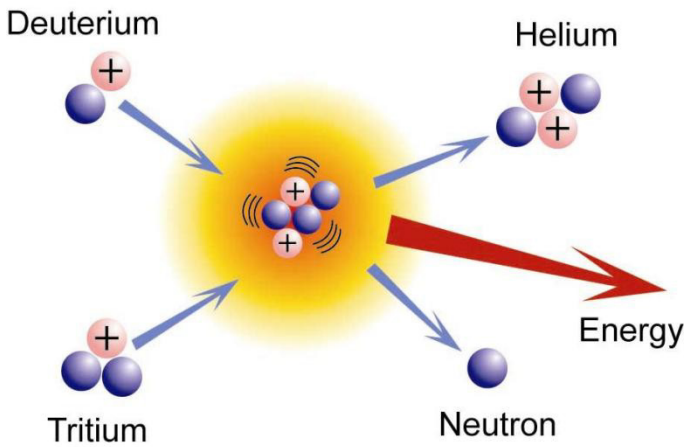


Figure 15.9: Nuclear fusion of deuterium (^2H) and tritium (^3H) nclei

Similarly, when two atoms of deuterium (hydrogen-2) collide at high speed, they might combine (fuse) to form a helium atom (He-3).

$$2\ {}^{2}_{1}H \rightarrow {}^{3}_{2}He + {}^{1}_{0}n$$

However, very high temperatures and pressures are required for the fusion to take place because of the repulsion between the positive nuclei. Thus, for the fusion to take place the nuclei must have enough kinetic energy to overcome these repulsion forces between like charges.

Like fission, in the fusion process large quantity of energy is liberated in the form of

heat. This energy is also used in atomic/nuclear bombs (Hydrogen bomb).

Note that it is very difficult to carry out nuclear fusion between two large nuclei due to the highly strong repulsion forces that are between their positively charged nuclei. Table 15.6 provides the differences between nuclear fission and nuclear fusion.

Table 15.6: Differences between nuclear fission and nuclear fusion

Nuclear fission	Nuclear fusion
• A bigger (heavier nucleus) splits into smaller nuclei. • It does not require extreme high temperature and pressure as the nuclear fission • A chain reaction sets • It can be controlled and energy released can be used for producing electricity in nuclear power reactors • The products of the reaction are radioactive; hence high risks of radioactive pollution.	• Lighter nuclei fuse together to form the heavier nucleus. • Extremely high temperature and pressure are required. • It is not a chain reaction. • Up to now it has not been controlled to produce electricity • The products of fusion reaction are non-radioactive in nature; hence non-pollutant

15.7.2. Applications of fission and fusion

Both fission and fusion are nuclear reactions that produce energy as described above. Fission is used in nuclear power reactors since it can be controlled, while fusion is not utilized to produce power since the reaction has not yet controlled up to now. The two processes have an important role in the past, present and future in energy creation.

Example of nuclear energy calculation:

Consider the following nuclear reaction:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{144}_{56}\mathrm{Ba} + {}^{90}_{36}\mathrm{K} + 2\,{}^{1}_{0}\mathrm{n}$$

The exact masses are:

U = 235.04393u

Ba = 143.923u

Kr = 89.9197u

n = 1.008665u

Where,

u = atomic mass unit (amu)

1u = 1/12 of the mass of carbon-12 atom and is equal to 1.66033 x 10^{-27} kg.

Let us work out the total mass (m_r: mass of reactants) before the reaction:

m_r = 235.04393 + 1.008665 = 236.052595u

and the total mass (m_p: mass of products) after reaction:

m_p = 143.923 + 89.9197 + (2 x 1.008665) = 235.86003u

Now, the mass lost (or mass defect, m) is given by the difference in the two masses calculated above.

Δm = 236.052595 - 235.86003 = 0.192565u

Converting this mass defect into kilograms, we get m = 0.192565 x 1.66033 x 10^{-27} x 6.02 x 10^{23} = 1.924723 x 10^{-4} kgmol^{-1}

The loss in mass is converted into energy. The amount of energy is calculated by using Einstein's equation, $E = \Delta mc^2$.

E = 1.924723 x 10^{-4} x (3 x10^8)^2 = 5.774 x 10^{12}J mol^{-1} or 1.73 x 10^9kJ mol^{-1}.

This energy is equivalent to the energy that can be produced by burning 300,000 tonnes of petrol!

Like other forms of energy, nuclear energy can be either renewable (nuclear fusion) or non-renewable (nuclear fission).

- Nuclear fission is non-renewable because uranium or other fissile nuclides needed for this process are not renewable.
- For example: In Atomic Bomb, there are fission reactions of uranium. The energy produced is uncontrolled and this principle is used to manufacture the bombs and missiles. When controlled, the nuclear fission is also useful in the production of electricity.
- Nuclear fusion energy (if mastered) could be renewable because hydrogen needed for this process is available in nature in large amount.
- For example: In Hydrogen Bomb, the nuclear reaction involves the fusion of deuterium and tritium nuclei to form helium.

$$_1^2\mathrm{H} + {}_1^3\mathrm{H} \rightarrow {}_2^4\mathrm{He} + {}_0^1\mathrm{n}$$

The deuterium comes from the ocean and has a near infinite supply and will not run out in the next few million years. With advancements in technology, we might be able to fuse protium itself. As it comes from water, the fuel supply is also near infinite and thus nuclear fusion is a renewable source of energy.

Checking up 15.7:

1. Classify the following as pertaining to nuclear fission, nuclear fusion, or both:
   a. Small nuclei combine to form larger nuclei.
   b. Large amounts of energy are released.
   c. Very high temperatures are needed for the reaction.
2. In a fission reaction, U-235 bombarded with a neutron produces Sr-94, another small nucleus and 3 neutrons. Write the complete equation for this fission reaction

15.8. Health hazards of radioactive substances

Activity 15.8:

1. Have you ever heard about health risks associated with nuclear radiations? If yes, state and explain them.
2. Use your search engine or any available resources to you to find out how we are all exposed to radiation and the hazards that are brought to us by radiation.

Radioactive materials in the environment, whether natural or artificial, do expose people to risks.

This can happen in two ways:

- The radiation from the material can damage the cells of the person directly. This is damage by ***irradiation*.**
- Some of the radioactive materials can be swallowed or breathed in. While inside the body, the radiation it emits can produce damage. This is damage by **contamination.**

Some health Hazards are: **radiation burns, hair loss** (temporary or permanent), **cancer, reproductive sterility, mutations in offspring, etc.**

We are all exposed to low levels of radiation every day. Naturally occurring radioisotopes are part of atoms of wood, brick and concrete in our homes and the buildings of schools, hospitals, supermarkets, etc. This radioactivity is called "background radiation" and is present in the soil, in the food we eat, in the water we drink, and the air we breathe. For instance, one of the naturally occurring isotopes of potassium, potassium-40, is radioactive. This one is found in the body because it is

present in any potassium-containing food. Other naturally occurring radioisotopes in air and food are carbon-14, radon-222, strontium-90 and iodine-131.

In addition to naturally occurring radiation from construction materials in our homes, we are constantly exposed to radiation (cosmic rays) produced in space by the sun.

The larger the dose of radiation received at one time, the greater the effect on the body. Exposure to low amount of radiation cannot be detected, but at medium levels the whole-body exposure produces a temporary decrease in number of white blood cells. If the exposure is very high, the person suffers the symptoms of radiation sickness such as nausea, vomiting, fatigue, and a reduction of white-cell count which can even be lowered to zero. So the victim suffers from diarrhea, hair loss, hair loss and infection. Too much exposure is expected to cause death.

You can ask yourself how radiation (which is in the air all around you) might lead to lung cancer. This is explained by the presence of Radon gas (mainly from granite rock) which is the main source of background radiation, and which is in turn responsible for almost all the radiation we get exposed to over our lifetime. When we breathe in; some of the radioactive atoms in the air undergo radioactive decay and emit alpha, beta or gamma radiation. These radiations can collide with and ionize atoms in our lung tissue, which could ultimately lead to lung cancer.

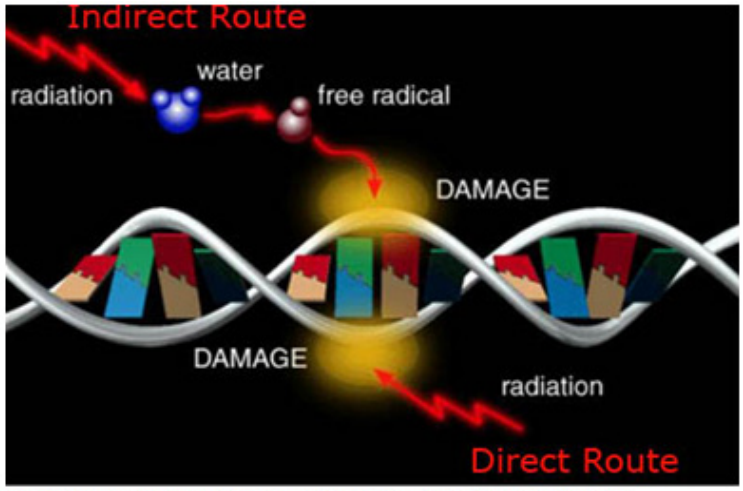


Figure 15.10: Ways through which radiations reach the body cells

Checking up 15.8:

1. List any three sources of natural radiation.
2. What are some symptoms of radiation sicknesses?

END UNIT ASSESSMENT

I. MULTIPLE CHOICE QUESTIONS. Choose the letter corresponding to the appropriate answer

1. Elements which emit natural radioactivity are known as:
   a. radio elements
   b. active elements
   c. radioactive elements
   d. nuclear elements

2. Spontaneous emission of radiation by unstable nuclei is called
   a. positive radioactivity
   b. artificial radioactivity
   c. natural radioactivity
   d. nuclear elements

3. The half-life of technetium-99 is 6 hours. How much of a 100 milligram sample of technetium-99 will remain after 30 hours?
   a. 12.5 mg
   b. 3.125 mg
   c. 6.25 mg
   d. 1.56 mg

4. What change occurs in the nucleus of an atom when it undergoes beta emission?
   a. The outer shell of electrons is filled.
   b. The number of neutrons decreases by one.
   c. A high speed electron is produced.
   d. A proton is produced.
   e. There is a release of energy.

5. Which one of the following does not occur in nuclear reaction?
   a. Nuclear radiation is released.
   b. There is a change in mass.
   c. It involves a rearrangement of electrons.
   d. New elements are made

6 When beta decay occurs in a radioactive isotope, the atomic number (Z) always

a. Increases by one
b. Stays the same
c. Increases by two
d. Decreases by one

7. Which of the following statements is not correct concerning alpha-particles?

a. They are composed of helium nuclei
b. They are emitted from unstable nuclei
c. They have a positive charge
d. They can penetrate thick sheets of lead

8. Which one of the following is true when a nucleus undergoes radioactive decay?

a. A new element is always formed
b. Alpha-particles are always emitted
c. Beta-particles are always emitted
d. The unstable nucleus loses energy

9. Why would the occupants of a house fitted with smoke detectors containing americium–241 not be at risk from alpha radiation emitted by these devices?

a. It has very low penetrating power through the air.
b. Alpha radiation has very low ionizing power.
c. The occupants wear protective clothing at all times
d. Alpha radiation is not harmful

10. Which of these metals is used as a shield against radioactive emissions?

a. Uranium
b. Lead
c. Radium
d. Gold

11. Which one of the following reactions is not correct?

A. $^{238}_{92}U - {}^{4}_{2}He \rightarrow {}^{234}_{90}Th$

B. $^{24}_{11}Na \rightarrow {}^{20}_{9}F + {}^{0}_{-1}e$

C. $^{198}_{79}Au \rightarrow {}^{198}_{80}Hg + {}^{0}_{-1}e$

D. $^{14}_{6}C \rightarrow {}^{14}_{7}N + {}^{0}_{-1}e$

12. Polonium-210 decays by emitting an alpha particle. What are the values of x, y and Z in the equation? Refer to .

a. x = 206, y = 82, Z = Pb
b. x = 82, y = 206, Z = Pb
c. x = 83, y = 206, Z = Bi
d. x = 82, y = 204, Z = Pb

13. Radium-226 may decay by the emission of an alpha-particle. Which one of the following sets of products would result in such decay? (Radium has an atomic number of 88).

A. $^{226}_{89}Ac + {}^{0}_{-1}e$

B. $^{230}_{90}Th + {}^{4}_{2}He$

C. $^{222}_{86}Rn + {}^{4}_{2}He$

D. $^{227}_{88}Ra + {}^{0}_{-1}e$

14. Which of the following would not be the use of radioisotopes?

a. Dating of silverware found in an archaeological site
b. Putting a date on the remains of a dinosaur
c. Irradiation of tropical fruits before consuming them
d. Tracing leaks from underground pipes

15. How much of a radioisotope will have decayed after two half-lives?

a. 12.5%
b. 50%
c. 75%

II. Matching: Choose the letter of the correct word for each of the questions below. Each letter will be used only once

a. Decay series
b. Half-life
c. Helium
d. Longer
e. Nuclear fission
f. Nuclear fusion
g. Radioactive
h. Radioactive decay
i. Radioactivity
j. Transmutation

1. An element that gives off nuclear radiation is known to be ….
2. When an element changes to another, more stable element, there is …
3. The amount of time for half the atoms in a radioactive sample to decay is referred to as …
4. The more stable a nucleus is, the _____ its half-life.
5. The process in which the nucleus of an unstable atom releases radiation in order to become stable is known as …
6. The changing of an atom into another, more stable atom during decay is …
7. The splitting of an atom into 2 smaller nuclei (nuclear power plant) is known as …
8. An alpha particle is actually a nucleus of _____.
9. The name given to the several steps required to get a radioactive element to a stable element is the …
10. The joining of 2 atoms to form a single, larger nucleus is known as …

III. Short and long answer open questions

1. Define radioactivity.
2. Describe an alpha particle. What nucleus is it equivalent to?
3. Plutonium has an atomic number of 94. Write the nuclear equation for the alpha particle emission of plutonium-244. What is the daughter isotope?
4. Francium has an atomic number of 87. Write the nuclear equation for the alpha particle emission of francium-212. What is the daughter isotope?

5. Write balanced equations for the following nuclear reactions:

   a. Nuclide carbon-14 undergoes beta decay
   b. Uranium-238 decays by alpha particle emission
   c. Carbon-11 decays by position emission
   d. Cobalt-60 decays by gamma radiation
   e. Gold-195 decays by electron capture

6. a) Give values for a, b, c and d in the following nuclear equations:

   i) $^{35}_{17}Cl + {}^{1}_{0}n \rightarrow {}^{a}_{b}X + {}^{1}_{1}H$

   ii) $^{7}_{3}Li + {}^{2}_{1}H \rightarrow 2{}^{c}_{d}Y + {}^{1}_{0}n$

   b) $^{238}_{92}U$ undergoes radioactive decay as shown below:

   $$^{238}_{92}U \xrightarrow{\alpha-emission} A \xrightarrow{\beta-emission} B \xrightarrow{\beta-emission} X \xrightarrow{\alpha-emission} Y$$

   Calculate the mass number and atomic number of element Y.

7. If radium-226 undergoes a series of decays that produce five α and four β particles, what is the final product?

8. Strontium-90 is a beta particle emitter and has a half-life of 28.1 yrs.

   a. Write the decay equation for strontium-90.

   b. Calculate the decay constant

9. A sample of a particular radioactive isotope is separated and monitored over a period of 15 hours. If it is found that 12.0 grams of the isotope remain after 4.2 hours and that 10.8 grams remain after 11.3 hours, what is the half-life of the isotope?

10. What is the age BP of a bone fragment that shows an average of 2.9 dpm/gC in 2005? The carbon in living organisms undergoes an average of 15.3 dpm/gC, and the half-life of ^{14}C is 5730 years. (BP = Before Present, with the year 1950 used as the reference; dpm/gC = disintegrations per min. per gram Carbon)

11. How much energy is released (in kJ) in the following fusion reactions to yield 1 mol of ^{4}He or ^{3}He?

    a. $^{2}H + {}^{3}H \rightarrow {}^{4}He + {}^{1}n$

    b. $^{2}H + {}^{2}H \rightarrow {}^{3}He + {}^{1}n$

    (The atomic masses are: ^{1}H = 1.00782 u; ^{2}H = 2.01410 u; ^{3}H = 3.01605 u; ^{3}He = 3.01603 u; ^{4}He = 4.00260 u and ^{1}n = 1.008665 u)

12. It has been estimated that 3.9 x 1023 kJ/s is radiated into space by the sun. What is the rate of the sun's mass loss in kg/s?

13. How much energy (in kJ) is produced in the fission reaction of 1.0 mol of uranium-235 according to the following equation?

    $^{235}U + 1n \rightarrow {}^{142}Ba + {}^{91}Kr + {}^{31}n$

    (The atomic masses are: ^{235}U = 235.0439 u; ^{142}Ba = 141.9164 u, ^{91}Kr = 90.9234 u; ^{1}n = 1.00867 u

14. a. State four uses of radioactive isotopes

    b. The half-life of cobalt-60 is 5.2 years. What fraction of cobalt-60 would remain after 26 years?

    c. The half-life of carbon-14 is 5600 years. Analysis of a fossil from a historical site showed that 6.25% of carbon-14 was present compared to living material. Calculate the age in years of the fossil.

15. The half-life of uranium-238 is 4.5 billion years. What will be the $^{238}U/^{206}Pb$ atomic ratio in a rock that is 5.0 billion years old? (Assume that isotope lead-206 was not present initially)

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