G.C.E. (Advanced Level)

CHEMISTRY

Teacher's Instructional Manual (Revisited)

Grades 12 & 13

2012

(To be implemented from 2012)



Department of Science Faculty of Science and Technology National Institute of Education

Chemistry

Teacher's Instructional Manual (Revisited)

Grades 12 & 13 – 2012

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Department of Science Faculty of Science & Technology National Institute of Education

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Director General's Message

The new G.C.E. Advanced Level Chemistry Syllabus was introduced to the school system in 2009 and subsequently the Teacher's Instructional Manuals were published in the same year for Grade 12 and in 2010 for Grade 13.

As per the requests of the schools and universities, the G.C.E. Advanced Level Chemistry Syllabus was revised in 2012 with a follow-up. This new book has been prepared by revising the two instructional manuals conforming to the syllabus.

This book comprehensively presents the details as regard the competencies and competency levels expected to be achieved by the students. We believe that this information is of utmost importance to teachers when designing learning teaching events in Chemistry.

Three aspects need to be taken into consideration by teachers when using this book. They are, the coherence of the Teacher's Instructional Manual and the syllabus, its building up founded on the vision of the syllabus and the expected competencies and its preparation taking into consideration the expected achievement level of grades 12-13 students. Thus the use of this book meaningfully is an indispensable task and a responsibility on the part of teacher.

With a view to bringing the three aforesaid matters to your attention, the National Institute of Education is in the process of giving the necessary training to all the teachers teaching G.C.E. Advanced Level classes. Participation of the relevant teachers in these training sessions is extremely important because it is a great underpinning to understand the learning teaching principles and processes set out here. Especially the school-based assessment is expected to be applied to develop the student competencies. We all involved in the process of education and evaluation should discern that these interventions are essential to realize the task of promoting the students' skills without limiting merely to the transmission of subject matter.

I wish to extend my special thank to all the staff of the National Institute of Education including the officers of the academic sections and all the external scholars who shouldered the arduous task of compiling this manual.

Prof. W.M. Abeyrathna Bandara Director General National Institute of Education

Foreword

This Teacher's Instructional Manual is useful to organize the learning and teaching process for the students of grades 12 and 13 from 2012. It is compulsory to cover the competency levels and the content during the given time period. When planning the school based assessment tools, it is important to consider the learning outcomes given under each competency level. It is advised to encourage the students to use websites and additional resources relevant to the subject matter to get a clear understanding of the subject.

In this modern era where the technology is developed to facilitate education, the teacher has a responsibility to organize the teaching learning environment to get the best use of the technology to make learning a pleasurable and a meaningful activity to the student.

I would like to thank the subject specialists of the National Institute of Education and external resource persons who contributed their time and expertise in performing this Teacher's Instructional Manual.

Sydney Jayawardana Assistant Director General Faculty of Science and Technology

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Competency 1.0 : Uses electronic arrangements and energy transactions in determining the nature of matter.

Competency Level 1.1 : Reviews the models of atomic structure.

Periods : 06

Learning Outcomes

- Presents information on sub-atomic particles, isotopes and radioactivity.
- Describes characteristics of cathode rays.
- Describes radioactivity.
- Describes gold foil experiment.
- Reviews the models of atomic structure comparatively.

Guidance for teacher elaboration :

- Some information about sub-atomic particles (History of the discovery of proton and neutron is not necessary)
- Discovery of cathode rays and their properties

	electron	proton	neutron
Symbol of the particle	e	р	n
Mass of the particle / kg	9.107 × 10 ⁻³¹	1.6725×10^{-27}	1.6742×10^{-27}
Relative mass of the particle	$\frac{1}{1840}$	1	1
Charge of the particle /C	1.602 × 10 ⁻¹⁹	1.602×10^{-19}	0
Relative charge of the particle	-1	+1	0

• Isotopes

The atoms which have the same atomic number and different mass numbers are defined as isotopes of that element. (Calculations based on relative isotope masses and their relative abundance are not necessary)

• Nuclides

Atomic species of which the proton number and nucleon number is specified.

 $^{
m Nucleon}_{
m Proton} X$

Type of nuclides										
1.	Stable nuclides existing in nature									
2.	Unstable nuclides existing in nature									
3.	Artificial radioactive nuclides									

• Radioactivity

Emission of radiation by unstable nuclei or particles spontaneously for the sake of stability of the nucleus is called radioactivity. These can penetrate and ionize gases.



Properties of alpha, beta and gamma rays

Туре	Alternative	Charge	Penetrating	Stopped by
	name		power	
Alpha, α	Helium nucleus (2 protons + 2 neutrons)	+2	Low	Air or paper
Beta, β	Electron	-1 %	Medium	Thin aluminium
Gamma, Y	High energy electromagnetic radiation	0	High	Thick lead

• Geiger and Marsden experiment which was the basis for presenting the nuclear models of the atom.



• Explanation of the observation made in Geiger and Marsden experiment

• Bohr model and postulates

Bohr model is based on three postulates.

- 1. Only orbits of certain radii, corresponding to certain definite energies, are permitted for the electron in a hydrogen atom.
- 2. An electron in a permitted orbit has a specific energy and is in an "allowed" energy state. An electron in an allowed energy state will not radiate energy and therefore will not spiral into the nucleus.
- 3. Energy is emitted or absorbed by electron only as the electron transfers from one allowed energy state to another. This energy is emitted or absorbed as a photon, E = h.



The nucleus of the hydrogen atom and the first four shells containing the electron according to the Bohr model

Suggested learning teaching activities :

• Discuss the contradictions between present knowledge and facts presented by Dalton through his atomic theory.

υ

- Review prior knowledge about sub-atomic particles.
- Review prior knowledge about atomic number and mass number.
- Introduce isotopes.
- Describe how relative isotope masses affect relative atomic mass.
- Conduct a discussion on models for the atom presented by Thomson, Rutherford and Bohr.
- Conduct a group discussion subjecting those models to a comparative review.

Competency 1.0	:	Uses electronic arrangements and energy transactions in
		determining the nature of matter.
Competency Level 1.2	:	Investigates different types of electromagnetic radiation.
Periods	:	03

Learning outcomes

- Name physical quantities that describes the properties of waves and expresses relationships among them.
- Describes what is an electromagnetic radiation.
- Identifies the different ranges in the electromagnetic spectrum and provides examples for the uses of radiations belonging to those ranges.
- Observes the visible range by using appropriate methods and reports its nature.

Guidance for teacher elaboration:

- Energy is transmitted as electromagnetic radiation through the space.
- They consist of both electric and magnetic fields which are perpendicular to each other.
- Velocity of all the electromagnetic radiation in vacuum is;

 $3.00 \ x \ 10^8 \ m \ s^{-1}$ which is the velocity of light.

- When λ is the wave length and υ is the frequency, the velocity of an electromagnetic wave- $C = \upsilon \lambda$.
- The energy of an electromagnetic wave $E = h \upsilon$ (E is the energy of a photon.) where h is a constant. It is named as Planck's constant.

Planck constant = 6.624 x 10⁻³⁴ J s Hence $E = \frac{hc}{\lambda}$

• Arrangement of the electromagnetic radiations in the ascending order of the frequency produces the electromagnetic spectrum.



Electromagnetic spectrum

• Uses of the radiations belonging to different ranges of the electromagnetic spectrum

•	Radio waves	:	Used for communication through television and radio
			media.
•	Radar waves	:	Used in naval and aeronautical security systems.
•	Micro waves	:	Microwave ovens function due to these waves. Used in
			cellular phones.
•	Infrared waves	:	Used in physiotherapy treatments. Used in sending signals
			by remote control devices and also in analytical work using
			spectroscopic methods.
•	Visible waves	:	Vision and photography are due to waves in this range.
			Used in colorimetric analysis.
•	Ultraviolet waves	:	Used for sterilization and to read confidential symbols in
			currency notes etc. Also used in spectroscopic analysis.
•	X- rays	:	Used in X ray photography and in studies of the structure
			of crystals etc.
•	γ- rays	:	Used in the treatment of cancer.

Suggested learning - teaching activities

- Allow a beam of white light to be seperated using a prism and project it on to a screen. Allow students to observe how the colours are separated in it.
- Give prior notice to students to come prepared with the uses of radiations belonging to different ranges in the electromagnetic spectrum.
- Ask small groups of students to conduct a whole class presentation on the uses of the radiations belonging to each range of the electromagnetic spectrum.
- Solve simple problems using Planck equation.
 - eg. Wave length of yellow light is 589 nm. Calculate the energy of one mole of photon of this radiation.

Competency 1.0 : Uses electronic arrangements and energy transactions in determining the nature of matter.

Competency Level 1.3: Analyses evidences for electronic energy levels of atoms.

Periods : 08

Learning outcomes

- Presents evidences for the presence of electrons of atoms in main energy levels and sub energy levels using graphs of successive ionisation energies.
- Explains qualitatively the series of lines in the atomic hydrogen spectrum using the Bohr model.
- States that the identity of an electron situated in a certain atom is described by the relevant set of quantum numbers.
- Describes wave-particle duality of electron with examples.
- States the information given by four quantum numbers.
- Explains quantization of energy.
- Illustrates the shapes of *s* and *p* orbitals.

Guidance for teachers elaboration :

• Variation of successive ionisation energies for phosphorus, carbon and oxygen.



• The above graph illustrates all the successive ionization energies of those elements. The number of successive ionisation energies is equal to the number of electrons in the atom. When attention is paid to sudden increase in successive ionisation energies it is proved that electrons exist as groups in various energy levels. • Absorption spectrum



• Explanation for the formation of lines in the emission spectrum of hydrogen by Bohr model.



• Limitations of Bohr model

While the Bohr model explains the line spectrum of the hydrogen atom, it cannot explain the spectra of other atoms, except in a rather crude way. Bohr also avoided the problem why the negatively charged electrons would not just fall into the positively charged nucleus by simply assuming it would not happen. Therefore, there is a problem with describing an electron merely as a small particle circling about the nucleus.

• *s*, *p*, *d* and *f* sub-energy levels

Sub energy level	Number of orbitals	Maximum number of electrons that can exist
S	1	2
р	3	6
d	5	10
f	7	14

• Wave - particle nature of electrons

- Wave properties : While passing through an ionic crystal a beam of electrons gets diffracted in the same way as a beam of X-rays does. A beam of electrons also show interference patterns.
- Particle properties : A beam of electrons has ability to do work (due to the

momentum) and also it has a charge.

Shapes of orbitals









s orbital

p orbital

• Quantization of energy

- Atoms absorb or emit energy in the form of definite small quantities.
- The smallest quantity of energy is referred as 'quantum' or 'photon'.
- According to Planck, matter absorbs or emits energy in the form of photons or whole number multiples of it.
 - eg. $h \upsilon$, 2 $h \upsilon$, 3 $h \upsilon$,
- Hence, it is considered as energy is quantized.

• Quantum numbers

• Principal quantum number (n)

The main energy level to which the electron belongs is represented by this quantum number.

n = 1, 2, 3,

• Azimuthal quantum number (*l*)

The sub - energy level (s,p,d,f....) to which the electron belongs is represented by this quantum number.

 $l = 0, 1, 2, \dots, (n-1)$

• Magnetic quantum number (m_1)

The orbital (Eg. p , p , p) in which the electron exists in a certain sub- energy level is represented by this quantum number

 $m_l = -l, (-l+1), \dots, 0, \dots, (l-1), l$

• Spin quantum number (m_s) The direction of spin of an electron present in a certain orbital is represented by this quantum number.

$$m_s = \pm \frac{1}{2}$$

Assignment of the four quantum numbers n, l, m_l and m_s for electrons in the first three energy levels of an atom

Principal quantum number	Azimuthal quantum number <i>l</i>	Relavent sub energy	Magnetic quantum number m _l	Spin quantum number m _s	Maximum number of electrons in the orbitals	Maximum number of electrons belonging to
1	0	1s	0	+ 1/2 - 1/2	} 2	2
2	0	2s	0	+ 1/2 - 1/2	}- 2	
	1	2р	-1	+ 1/2 - 1/2		
			0	+ 1/2 - 1/2	6	8
			+1	+ $1/2$ - $1/2$	J	
	0	3s	0	+ 1/2 - 1/2	} 2	
	1	3р	-1	+ 1/2 - 1/2	ן	
			0	+ 1/2 - 1/2	6	
			+1	+ 1/2 - 1/2	J	

Principal quantum number n	Azimuthal quantum number <i>l</i> (0 to n-1)	Relavent sub energy level	Magnetic quantum number m _l (-l to +l)	Spin quantum number m _s (+1/2, -1/2)	Maximum number of electrons in the orbital	Maximum number of electrons belonging to the main energy level
	2	3d	-2 -1 0 +1 +2	$\begin{array}{r} + 1/2 \\ - 1/2 \\ + 1/2 \\ + 1/2 \\ - 1/2 \\ + 1/2 \\ - 1/2 \\ + 1/2 \\ - 1/2 \\ + 1/2 \\ - 1/2 \end{array}$		18

• The ability to write the set of quantum numbers of a certain electron situated in an atom is not measured at the G.C.E. (A/L) Examination. The above table is presented only to show that the set of quantum numbers for a certain electron is exclusive for it.

Suggested learning - teaching activities :

- Draw graph of the successive ionization energies of a given element against the number of electrons removed.
- Build up the above table along with the students.

Competency 1.0	:	Uses electronic arrangements and energy transactions in
		determining the nature of matter.
Competency Level 1.4	:	Analyses the ground state electronic configuration of
		isolated gaseous atoms and ions.
Periods	:	04

Learning outcomes

- States the principles and rules relevant to the filling up pattern of electrons.
- Writes the electronic configuration of isolated gaseous atoms and ions of elements of atomic number from 1 to 38 according to the standard form.
- Explains the variation of successive ionization energies and first ionization energies of elements considering the stable electronic configurations of energy levels and sub energy levels.

Guidance for teacher elaboration :

• Principles and rules relevant to the filling up pattern of electrons **Hund's rule**

Orbitals of the same energy (degenerate) are occupied by electrons singly so that their spins are parallel to make the maximum number of unpaired electrons and then doubly with their spins anti parallel.

Pauli's exclusion principle

This principle states that no orbital can accommodate more than two electrons (In other words the set of quantum numbers for a certain electron of an atom is exclusive for it or no two electrons in an atom can have the same set of quantum numbers.)

Aufbau principle

It states that the filling up of electrons in the orbitals takes place according to the increasing order of energy of the orbitals in accordance with the Pauli exclusion principle.

• Ascending order of energy in the sub energy levels





Graph showing the variation of first ionization energies of elements of atomic number from 1 to 20

• Anomalous behaviour seen from group II to III and from group V to VI is due to extra stability of half-filled (p³) and completely-filled shells (s², p⁶). Electronic configurations d⁵ and d¹⁰ also exhibit extra stability.

Atomic number

Suggested learning - teaching activities :

- Direct the students in groups to build up the electronic configuration of a few assigned elements with atomic numbers 1 to 38 and their ions using the relevant rules and principles.
- Allow the identification of elements with more stable configurations among the assigned elements by comparing their electronic configurations.
- Illustrate the filling of electrons to atomic orbitals according to Hund's rule.
- Direct the students to explain the variation of successive ionization energies and first ionization energies on the basis of the stability of electronic configurations.

Competncy 1.0	:	Uses electronic arrangements and energy transactions in determining the nature of matter.
Competency Level 1.5	•	Analyses the electronic configuration of elements to verify their placement in the periodic table and relates atomic properties to electronic configuration.
Periods	:	08

Learning Outcomes :

- Builds up the periodic table on the basis of electronic configuration
- Classifies the elements under s, p, d and f blocks
- Identifies elements belonging to *s*, *p* and *d* blocks and the elements belonging to groups 1 to 18.
- Describes trends shown by *s* and *p* block elements accross the period and down the group.

Guidance for teacher elaboration :

• Periodic table is given in page 14.

Trends shown by s and p block elements across the period and down the group

- Formation of cations and anions
 - Formation of anions and cations depends on the number of electrons in the valency shell and ionization energy.
 - The elements of the group I(1), II(2) and III(13), form cations while the elements of the groups V(15), VI(16) and VII(17) form anions.
 - The elements in the group IV(14) generally do not form free M⁴⁺ ions. The reason is the high aggregate of first, second, third and fourth ionization energies.

• Oxidation states

- In the elemental state oxidation number of any element is considered as zero.
- Oxidation state is a measure of the electron control that an atom has in a compound compared to its elemental state.
- The highest oxidation number that an element can have in a compound is equal to its number of valency electrons.
- In combined state certain elements have variable oxidation states.

• Reducing ability / Oxidizing ability

- In general oxidizing ability of elements decreases across the period up to group 17.
- In general oxidizingf elements increases down the group.

 $\mathrm{ns}^2\,\mathrm{np}^6$

																		18/VIII
	ns ¹	ns^2						1					ns ² np	$ns^2 np^2$	$ns^2 np^3$	$\mathrm{ns}^2\mathrm{np}^4$	$\mathrm{ns}^2\mathrm{np}^5$	2
	1/I	2/II	_					1.00	79				13/III	14/IV	15/V	16/VI	17/VII	He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 0 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.30	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.35	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Šr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92,91	42 Mo 195.94	43 Tc 98 91	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag	48 Cd	49 In 114.8	50 Sn 118.7	51 Sb	52 Te 127.6	53 126.0	54 Xe 121.2
6	55 Cs	56 Ba	La- Lu	72 Hff 178.5	73 Ta	74 W	75 Re	76 Ös	77 Ir 192.2	78 Pt	79 Au	80 Hg	81 TI	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr 223.0	88 Ra 226.0	Ac- Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uut	113 Uut	201.2	203.0	2.10.0	210.0	222.0
	s block	k	d bloc	k									p bloc	k				
Lanthanides Latinides Actinides 257 58 59 La Ce Pr 138.9 140.1 140.9 89 90 91 Ac Th Pa 227.0 232.0 231.0					69 6 7 N 0.9 14 91 9 10 23	0 6 d P 4.2 14 2 9 J N 8.0 23	m S 6.9 15 3 3 1p F 7.0 23	62 E 60.4 19 94 E Pu A 19.1 24	63 Eu 52.0 1 95 Vm 0 41.1 2	64 Gd 57.2 96 Cm 244.1	65 6 Tb D 158.9 16 97 5 Bk (249.1 25	6 6 Dy H 2.5 16 8 9 Df E 2.1 25	7 (6 E 4.9 16 9 1 5 F 2.1 25	88 (7.3 16 00 1 m N 7.1 25	89 17 18.9 17 01 1 1d P 6.1 25	70 71 70 Lu 13.0 175.0 02 103 10 Lr 19.1 260.1		
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• Electronegativity

- The ability of an element to attract electrons in a bond of a molecule towards itself varies from one element to the other. When expressed quantitatively, this ability is known as the electronegativity of an element.
- Electronegativity is expressed according to various scales. The following table gives the electronegativity values for different elements according to the Pauling scale in their most common oxidation state.

	10 1	auning	scare			Н 2.1
Li	Be	В	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	Р	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K	Ca	Ga	Ge	A s	Se	Br
0.8	1.0	1.6	1.8	2.0	2.4	2.8
Rb	Sr	In	Sn	Sb	Te	I
0.8	1.0	1.7	1.8	1.9	2.1	2.5
Cs	Ba	Tl	Pb	Bi	Po	At
0.7	0.9	1.8	1.9	1.9	2.0	2.2

Electronegativity values for different elements according to Pauling scale

• Although a different value for the electronegativity of each element is stated according to the Pauling scale, the electronegativity of an atom of an element changes according to its environment (Hybridization, Charge, Oxidation number).

Example : In the species NH_2^+ , NH_3 and NH_4^+ the electronegativity of N varies in the order $NH_2^- < NH_3 < NH_4^+$.

• Electron affinity

- It is the change in energy that takes place when a mole of uni- negative ions are formed in the gaseous state when electrons are given to a mole of atoms in the gaseous state.
- The first electron affinity of many elements takes a negative value. It is because the added electron gets attracted by the nucleus. The second electron affinity always takes a positive value. It is because an electron is added to an already negative ion.

• The first electron affinities of elements belonging to the second and third periods

Element	Li	Be	В	С	Ν	0	F
Electron	-59.6	+66	-26.'7	-122	+31	-141	-318
affinity /kJ mol ⁻¹							
Element	Na	Mg	Al	Si	Р	S	Cl
Electron	-53	+67	-30	-135	-60	-200	-364
affinity /kJ mol ⁻¹							

- Across a period from left to right the nuclear charge increases and atomic radius decreases. Hence, the ionization energy increases. Therefore, the tendency to form cations decreases and also the ability to act as reducing agents decreases across a period.
- Similarly the ability to form anions increases and also the ability to act as oxidizing agent increases from left to right across a period.
- Atomic radius
 - In general, the atomic radius is referred as the distance between the nucleus and the outermost energy level occupied by electrons.
 - However, the position of an electron is uncertain and consequently it is difficult to express the radius of an atom.
 - Therefore, atomic radius is expressed in different ways.
 - Attraction towards outermost electrons from the nucleus is hindered to a certain extent by the electrons existing in inner energy levels. This effect is referred as 'shielding effect'.
 - Protons in the nucleus attract the electron cloud. The resultant effect of this attraction and shielding effect is referred as 'effective nuclear charge'.
 - Shielding effect affects the atomic radius and ionization energy.

Covalent radius



When two atoms of the same element are covalently bonded, half the internuclear distance of these two atoms is called its covalent radius.

Covalent radius = d/2

• The covalent atomic radius increases down a group and decreases from left to right along a period up to group 18.

Van der Waals radius

When two molecules or atoms are placed as close together as possible, half the distance between the two nuclei which are close to each other is called the Van der waals radius.



Metallic radius

Half the distance between two adjacent cation nuclei in the metallic lattice is the metallic radius.

$$d metallic radius = d/2$$

• Ionization energy is determined by nuclear charge, radius and shielding effect.

Ionic radius

- A value assigned to the radius of an ion in a crystalline solid, based on the assumption that the ions are spherical with a definite size. X-ray diffraction can be used to measure the inter-nuclear distance in crystalline solids. Ionic radius can be calculated according to the inter-nuclear distance.
- In general, negative ions have larger ionic radii than their neutral atoms and positive ions have smaller ionic radii than their neutral atoms.

Suggested learning-teacing process:

- Exhibit a large periodic table and recall the prior knowledge about groups and periods
- Assign few elements each from s block, p block and d- block to student groups without mentioning the block to which they belong.
- Direct them to write the electronic configuration of the elements and to identify the sub energy levels lastly filled with electrons.
- Allow them to find out the due place for these elements in the periodic table.
- Direct groups of students to reveal the relationships shown by the electronic configuration of element with the group, the period and the block of the periodic table to which the element belongs.
- Discuss the difference in electron affinity between N and P, F and Cl.
- Discuss the anomalous values of electron affinity of Be, Mg and N.
- Discuss the effect of following factors on ionization energy.
 - Charge of the nucleus
 - Distance from the nucleus (atomic radius)
 - Shielding effect
 - Electronic configuration (Whether electrons occupy singly or doubly in the orbitals)

Competency 2.0	:	Relates bonding and structure to properties of matter.
Competency Level 2.1	:	Analyses the primary interactions of polyatomic systems
		as a means of determining the structure and properties
		of matter.
Periods	:	06

Learning outcomes :

- States that covalent bonds are formed by the overlapping of atomic orbitals
- Introduces the valence bond theory.
- Separates the bonds into non- polar covalent bonds, polar covalent bonds and ionic bonds depending on the difference of electronegativity of the atoms which are involved in the bond.
- Explains the formation of dative-covalent bond and metallic bond.

Guidance for teacher elaboration :

- The electrons in the valence shell of the atom are involved in the formation of bonds.
- The attraction present between the atoms so as to minimize the energy in a polyatomic system is called a chemical bond.

Ionic bonds

- The electrostatic attraction between positive and negative ions that are formed when the valence electrons of one atom are given to another atom during the formation of a bond between a pair of atoms with a high difference in electronegativity, is called the ionic bond.
- When sodium chloride in the solid state is considered, the ions are attracted electrostatically and packed in a definite pattern. Therefore, when an ionic compound exists in the solid state, ions do not have the ability for movement. Particles can only vibrate while being in the places where they are situated. Accordingly, an ionic crystal does not conduct electricity.
- When sodium chloride in the liquid state is considered, the ions exist separately. An ionic compound in the molten state conducts electricity because ions have the ability of movement.

Polarization-Polarizing power of a cation and polarizability of an anion

• When an ideal ionic compound is considered, the anion and cation which are its components are regarded as existing in the form of regular solid spheres. But depending on the nature of the cation and the anion which are the constituents of the ionic compound, the cation attracts the electron cloud (polarizing power of the cation) of the anion and at the same time repels the nucleus thus distorting or polarizing the anion and as a result distortion occurs in the electron cloud of the anion (polarizability and tendency to undergo polarization). If the degree of polarization is insignificant the bond remains ionic whereas if it significant electron cloud will be pulled towards the cation resulting in a considerable degree of covalent character.

Example : Complete ionic bond



No Polarization

Increase in polarization of the anion

Distortion

Showing Covalent character to a considerable extent.

- Cation : Smaller in size Highly charged or both
 Polarizing power is high.
- Anion : Larger in size Highly charged or both
 Polarizability is high (Tends to distort or polarize)

Examples

In AgF, AgCl, AgBr and AgI the ionic properties vary as follows.

When the anion becomes larger the polarizability increases with the resulting increase of covalent character.

CsI > KI > NaI > LiI

When the cation becomes smaller the polarizing power increases with the resulting increase of covalent character.

 $MCO_3 \longrightarrow MO + CO_2$

Breaking up of the $CO_3^{2^*}$ group into O^{2^-} and CO_2 is influenced by the polarizing power of the M^{2+} ion. The polarizing power of the cations in Group II varies in the order, Be>Mg>Ca. Therefore the thermal decomposition temperatures of group two carbonates vary in the order BeCO₃ < MgCO₃ < CaCO₃.

Covalent bonds

- Covalent bonds are formed by keeping the bond pair of electrons common to both the atoms. Covalent bonds are formed by the overlapping of atomic orbitals.
- If the electronegativity difference between two covalently bonded atoms is zero, the bond is referred as a non-polar covalent bond. Other covalent bonds are referred as polar covalent bonds.
- A bond can be formed by the overlapping of an orbital containing lone pair of electrons with the empty orbital of the valance shell of another atom. The bond formed in this way is called the dative bond. There, the species which give the lone pair of electrons is called the donor group (Lewis base) and the species that receives the electrons to form the bond is called the acceptor group (Lewis acid).



Metallic bonds

• The electrons in the valence shell of metallic atoms are loosely bonded to the atom. Therefore, there is a tendency for the metallic atoms to release the electrons in valence shell and exist as positive ions. As a result a system is formed in which positive ions are immersed in a sea of electrons which were released from the metal atoms. The positive ions and the sea of electrons get attracted electrostatically to form metallic bonds.



- Metals conduct electricity due to the presence of free electrons.
- Strong metallic bonds are formed when the size of the metal ion decreases, when the charge of the metal ion increases and when the number of electrons contributing to the metallic bond increases.
- When the strength of metallic bond increases melting point of the metal also increases.
- Attractions that exist in covalently bonded molecules or in ionic compounds or in metalic latices are referred as primary interactions.

Suggested learning – teaching activities :

- Give each group of students a collection of molecules and ionic systems which are examples for various primary interactions and direct them to discuss the following.
 - How the primary interactions have taken place.
 - The properties shown according to the nature of primary interactions and the difference in electronegativity.

Competency 2.0 : Relates bonding and structure to properties of matter.

Competency Level 2.2 : Analyses the shapes of covalent and polar covalent molecules and simple ion groups.

Periods : 10

Learning outcomes :

- Draws Lewis structures of covalent molecules and groups of ions which are commonly encountered and containing up to a maximum of ten atoms.
- Predicts using the valence shell electron pair repulsion theory, how the pairs of electrons are oriented around the central atom of covalent molecules and ions and thereby shapes of the molecule/ion.
- Describes using suitable examples how sp, sp^2 and sp^3 hybridizations take place.
- Draws all the resonance structures which are possible for the existence of a given molecule or an ion group and subjects their stability to a comparative review.
- Describes σ and bonds in relation to linear and lateral overlapping of atomic orbitals.

Guidance for teacher elaboration :

• A structure where the covalent bonds in a covalent molecule or an ion group are represented by Lewis dot symbols, with shared pairs of electrons shown by a short line or a pair of dots for a pair of dot – cross), and the lone pair of electrons on each atom by pairs of dots or pairs of crosses, is called a Lewis structure. In the Lewis structure only the valence electrons are shown.

Example (i) Consider H₂O molecule.

Lewis symbol of oxygen	• () •
Lewis symbol of hydrogen	Η×
Lewis dot - cross structure of the molecule of water	$H^{\star} O^{\star} H$
Lewis structure of the molecule of water	Н-О-Н
Example (ii) Consider chloride ion.	Cl
Example (iii) Consider ammonium ion.	$ \begin{array}{c} H \\ \times \times_{+} \\ H \\ \times \\ N \\ \bullet \times \\ H \end{array} $

• From a Lewis structure information can be obtained about the way that atoms are attached in a molecule, how the number of electrons in the valence shells are distributed and also about the type of the bonds formed. But the Lewis structure does not give information about the shape. By obtaining the number of bond electron pairs and the number of lone pairs situated around the central atom of a molecule from the Lewis structure, the shape of the molecule can be predicted by applying the valence shell electron pair repulsion(VSEPR) theory .



Tetrahedral

Octahedral

Orientation of the electron pairs of the central atom in space depending on their number

Electron pairs		airs	Electron pair geometry /	Shape of the	
Total	Bonding	Lone	Electron pair domain	molecule	
2	2	0	Linear	Linear	5
3	\int^{3}	٥	Trigonal planar	Trigonal planar	
	2	1		Angular	oÖo
	¢	ر ا		Tetrahedral	
4	3		Tetrahedral	Trigonal pyramidal	e B
	2	2		Angular	9 ⁶ 9



There are occasions where two or more Lewis structures exist for a given same molecule or the ion group which differ from one another only due to differences in the electron arrangement. Such structures that exist for a certain molecule are known as resonance structures. The actual structure of the molecule is not the same as any of these but is a more stable different structure formed by the hybridization of resonance structures. The resonance structures/resonance forms/canonical structures do not have independent existence, but merely drawn for convenience.



Suggested learning - teaching activities :

- Discuss the nature of bonds (and) in molecules such as O_2 , O_3 and N_2 .
- Give instructions to draw the Lewis structures of the following molecules/ions and to determine the geometrical shapes provided (Other suitable examples also should be provided).

BeCl₂, BF₃, CH₄, NH₃, H₂O, PCl₃, NH₄⁺, SF₆, SF₄, ClF₃, XeF₂, IF₅, XeF₄, NO₃⁻, CO₃²⁻, SO₄²⁻

- Allow the students to determine the hybridization of the central atom in the following molecules/ions (sp, sp² and sp³ only)
 BeCl₂, BF₃, CH₄, NH₃, H₂O, PCl₃, NH₄⁺, (Other suitable examples also should be
- BeCl₂, BF₃, CH₄, NH₃, H₂O, PCl₃, NH₄⁺, (Other suitable examples also should be provided)
- Give instructions to draw the resonance structures of the following (Other suitable examples should also be provided). O₃, NO₃, CO₃², SO₄², N₂O

Competency 2.0	: Relates bonding and structure to properties of matter.
Competency Level 2.3	: Analyses the secondary interactions existing in various systems as a means of determining the structure and properties of matter
Periods	: 06

Learning outcomes

- Describes the concepts, polarization, dipole moment and polarizability giving suitable examples.
- Describes the types of secondary interactions included in the syllabus using suitable examples.
- Highlights the relationship between the nature of secondary interactions present in a certain substance and the physical properties of that substance.

Guidance for teacher elaboration :

:

• The asymmetrical distribution of electron clouds between two atoms involved in a chemical bond due to the difference in electronegativities of the two atoms concerned or due to another external influence is known as polarization. Example :



• The product of the charge () present on individual atoms in such a molecule and the length of the bond between the atoms is called the dipole moment

() of the bond. In polyatomic molecules, the dipole moment is considered for each bond. Their resultant is taken as the dipole moment of the molecule.



- The resultant of the dipole moments of all the N- H bonds gives the dipole moment of the NH₃ molecule.
- For some symmetric molecules the dipole moment is zero. Example:



• For polarizability refer 2.1.

• Secondary interactions

All types of intermolecular interactions exist among molecules are commonly referred as van der Waals interactions. Those interactions can be categorized into five types.

- Ion dipole interactions
- Dipole dipole interactions and hydrogen bonds
- Ion induced dipole interactions
- Dipole induced dipole interactions
- Dispersion (London) forces

• Ion - dipole interactions

These interactions are said to take place when polar molecules are attracted to a cation or an anion. The strength of these interactions depend on the charge and size of the ions and on the magnitude of the dipole.



• Dipole – dipole interactions

These forces are found in polar molecules which have permanent dipole,



Examples : $I^{\underline{5+}} Cl^{\underline{5}} \cdots I^{\underline{5+}} Cl^{\underline{5}}$

$$\mathrm{H}^{\mathrm{b} \mathrm{t}} = \mathrm{Cl}^{\mathrm{b}} \cdot \cdots \cdot \mathrm{H}^{\mathrm{b} \mathrm{t}} = \mathrm{Cl}^{\mathrm{b}}$$

• Hydrogen bonds

Hydrogen bond is a special type of electrostatic interaction between a hydrogen atom covalently bonded to an electronegative element (X) and another electronegative element (Y) such as fluorine or oxygen or nitrogen which has one or more lone pairs. This interaction can be represented by $X^{\mathfrak{F}}$ — $H^{+\mathfrak{F}}$ —– $Y^{\mathfrak{F}}$.

Bond type	Bond energy/kJ mol ⁻¹
H bonding	10 - 40
Other inter molecular interactions	0.1 - 10

Examples:

(i) HF





Existence of hydrogen bonding can be proved by referring to the variation of boiling temperatures of group 15, 16 and 17 hydrides.



Variation of boiling points of group 15, 16 and 17 hydrides

Ion - induced dipole interactions

When a charged particle such as an ion is introduced into the neighbourhood of an uncharged non-polar molecule (eg. an atom of a noble gas) it will distort the electron cloud of the atom or molecule.

eg. I_2 dissolved in aqueous KI to form ion

Dipole - induced dipole interactions

This type of attraction is found between an uncharged non-polar and a polar species. eg. Dissolving non-polar species such as O_2 , I_2 , Xe, etc. in water.

Dispersion forces (London forces or London dispersion forces)

Interactions between non-polar molecules or atoms are referred as dispersion forces. Any non-polar molecule can be temporary polarized due to an instantaneous deformation of its electron cloud. Due to the polarity of a such molecule another non polar molecule can also be temporary polarized. Interactions between such molecules are referred as dispersion forces. Such forces exist between any molecules. Generally dispersion forces are the weakest among all types of van der Waals forces. However, there are instances where strength of dispersion forces exceeds dipole - dipole interactions.

Compound	Melting point	Nature of secondary interaction
CH ₃ F	-142 °C	Dipole-dipole interactions and dispersion forces
CCl ₄	-23 °C	Dispersion forces

Suggested learning-teaching process :

- Display the graph showing the variation of boiling points of group 15, 16 and 17 hydrides and ask reasons for the variation.
- Assign students with several simple molecules and ask them to discuss whether they are polar or non-polar and the strength of their dipole moment.
- Assign students with suitable molecular/ionic systems and ask them to discuss the possible secondary interaction that can exist and related properties.

Competency 2.0	:	Uses electronic arrangements, electronic interactions and
		energy transactions in determining the nature of matter.
Competency Level 2.4	:	Analyses how the structure of the solid state of substances
		relates to their physical properties.
Periods	:	04

Learning outcomes

- Classifies substances according to the lattice arrangement.
- Predicts the physical properties of a given substance as shown by its lattice arrangement.
- Compares the physical properties of substances with lattice structures different from one another.

Learning teaching process :

- A formation where the building units are attached to one another in an orderly pattern can be described as a lattice.
- Presence of a formal pattern and the formation from a repetitive basic unit is a common feature of the lattices.
- Various substances with lattice like structures exist in nature.
- substances with atoms or molecules or ions arranged in orderly lattice patterns exist.
- Substances with lattice arrangements can be classified according to their building units as follows.
 - Homoatomic lattices
 - Heteroatomic lattices
- Polar molecular lattices
- Ionic lattices
- Non polar molecular lattices
- Bonding formed during the formation of the lattice are different, depending on the nature of the building unit of the lattice substance.
- the nature of the bonding formed during the formation of the lattice affects the physical properties of the lattice.

• Homoatomic lattices

Diamond and graphite lattices which are formed from homogeneous atoms are examples for homoatomic lattices.



Figure 2.4.1 : Lattice arrangement of diamond



Figure 2.4.2 : Lattice arrangement of graphite
• Heteroatomic lattices

silicon dioxide which is formed from heterogeneous atoms is an example for heteroatomic lattices.



Latice arrangement of SiO₂

- Homogeneous and heterogeneous atomic lattices are formed by atoms covalently bonding with one another.
- Substances composed of homogeneous and heterogeneous atomic lattices have a high hardness and also higher melting points/ boiling points because such lattices are formed by strong covalent bonds.
- There is no tendency to go into solution because the covalent bonds present in atomic lattices are very strong.
- Electricity is not conducted through atomic lattices as they lack mobile electrons. (Graphite is an exception)
- Non-polar molecular lattice
 - Iodine crystals which are formed from nonpolar iodine molecules are examples for non-polarized molecular lattices.



Figure 2.4.4 : Lattice arrangement of iodine

- Non polar molecular lattices are built by the bonding of non polar molecules to one another by attractive forces formed between induced dipoles.
- the substances with nonpolar molecular lattices consisting of molecules bonded to one another by weak Van der Waals forces have a low hardness and their melting points/ boiling points are also low relative to substances formed by other lattices.
- the substances formed by nonpolar molecular lattices dissolve in nonpolar solvents because they consist of nonopolar molecules and they do not conduct electricity as they do not possess mobile electrons.

- Polar molecular lattice
 - Ice which is formed from polar molecules is an example for polar molecular lattice.



Figure 2.4.5 : Latice arrangement of ice

- polar molecular lattices are formed by the bonding together of polar molecules to one another by attractive forces developed between permanent dipoles.
- Substances formed by polar molecular lattices show a high tendency to dissolve in polar solvents but do not conduct electricity due to the lack of mobile electrons
- Substances formed by polar molecular lattices consisting of molecules bonded by permanent dipole permanent dipole attractive forces (or hydrogen bonds) have a high hardness and also higher melting points / boiling points compared to substances formed by nonpolar molecular lattices.
- Ionic lattice
 - Sodium chloride which consists of sodium ions and chloride ions is an example for ionic lattice.



Figure 2.4.6 : Lattice arrangement of NaCl

• Ionic lattices are formed by the bonding together of ions by strong electrostatic attractions developed between positively charged and negatively charged ions.

- Substances formed by ionic lattices bonded by strong electrostatic attractions show higher melting points/boiling points and also a high hardness.
- the substances with ionic lattices show a tendency to dissolve in polar solvents.
- the substances consisting of ionic lattices do not conduct electricity in the solid state due to the lack of mobile electrons or mobile ions.
- the substances with ionic lattices conduct electricity in the molten state or in solution because of the presence of mobile ions.
- For metallic lattice refer 2.1.

Suggested learning - teaching activities :

- Exhibit a picture of a lattice to the class.
- Present the following problems to the class.
 - What is meant by a lattice?
 - What are the common properties seen in lattices?
 - Are there substances with lattice arrangement?
 - What is the nature of the bonding in substances formed with lattice arrangements?
- Divide the class into five groups and assign each group with one type of secondary interaction.
- Ask each group to relate the following of properties with the nature of a lattice which has the assigned type of secondary interaction.
 - Melting/boiling points
 - Electric conductivity
 - Hardness
 - Solubility

Competency 3.0	:	Works out chemical calculations accurately.
Competency Level 3.1	:	Formulates chemical formulae using physical quantities related to atoms and works out relevant calculations using relevant constants.
Periods	:	06

Learning – outcomes

- States the values of Avogadro constant (L) and Faraday constant (F) with the units.
- Works out calculations related to Avogadro constant and Faraday constant.
- Defines the term composition.

:

- Defines the terms mass fraction, volume fraction and mole fraction.
- Solves problems related to mass fractions, volume fractions and mole fractions.
- Defines concentration as the composition expressed in terms of moles per volume.
- Derives relationships between compositions expressed in terms of mass/mass, mass/ volume, moles/volume and moles/mass.
- Calculates and expresses the compositions in terms of mass/volume, moles/volume and moles/mass.
- Determines the empirical formula when the percentage compositions are known and the molecular formula when the empirical formula and the molecular mass are known.

Guidance for teacher elaboration :

• Avogadro constant (L) is given by the equation $L = \frac{N}{n}$ where

N = number of particles

n = amount of substance

Avogadro constant (L) = $6.022 \times 10^{23} \text{ mol}^{-1}$

• Faraday constant (F)

Faraday constant is defined as the molar charge of the proton. (Refer 14.5)

F = e L

L-Avogadro constant

 $e-Charge \ of the \ electron$

Faraday constant (F) = 96500 C mol⁻¹

- There are various ways in which the composition can be expressed. They are;
 - Mass fraction
 - Volume fraction
 - Mole fraction
 - Mass/volume
 - Moles/volume
- When the composition is expressed in terms of moles / volume it is called as concentration.
- Composition of a mixture can be expresed as a fraction
- In a mixture of A and B,

Mass fraction of
$$A = \frac{Mass \text{ of } A}{Mass \text{ of } A + Mass \text{ of } B}$$

Volume fraction of
$$A = \frac{V \text{olume of } A}{T \text{otal volume of mixture } A \text{ and } B}$$

$$Mole fraction of A = \frac{Number of moles of A}{Number of moles of A + Number of moles of B}$$

- Composition stated as the number of parts per million of parts (ppm) = fraction $x \, 10^6$
- Composition stated as the number of parts per billion of parts (ppb) = fraction x 10⁹ Example:

0.020 g of a substance is present in 20.00 g of an aqueous solution

- (i) Mass fraction of the substance $=\frac{0.020 \text{ g}}{20.000 \text{ g}} = \frac{20}{20000} = \frac{1}{1000}$ Its value in ppm is $\frac{1}{1000} \times 1000000 = 1000$
- Composition of substances present in very small amounts is commonly expressed in terms of parts per millions (ppm) and parts per billion (ppb).
- Density of water is 1000 g dm⁻³. Density of a dilute aqueous solution can be considered as approximately equals to the density of water. Therefore,

mass of 1 dm³ of a solution = 1 kg = 1000 g = 1000000 mg

For such instances, mass/volume ratio can also be expressed in ppm. As a mass fraction, 1 ppm means that 1 000 000 mg of the mixture contains 1 mg of the particular substance. For dilute solutions,

 $1ppm = 1 mg kg^{-1} = 1 mg dm^{-3}$ $= 1 \ \mu g g^{-1}$ $= 1 \ \mu g cm^{-3}$

Example:

Composition of Fe^{3+} in a solution is 1.5 ppm. Express that composition in moles per cubic decimeter.

1.5 ppm = 1.5 mg dm⁻³
= 1.5 x 10⁻³ g dm⁻³
=
$$\frac{1.5 x 10^{-3} g dm^{-3}}{56 g mol^{-1}}$$

= 2.7 x 10⁻⁵ mol dm⁻³

• Percentage composition

Examples: $158.04 \text{ g of KMnO}_4$ contains 39.10 g of K, 54.94 g of Mn and 64.00 g of O.

Percentage mass of K = $\frac{39.10}{158.04} \times 100 = 24.74\%$

Percentage mass of Mn = $\frac{54.94}{158.04} \times 100 = 34.76\%$

Percentage mass of O =
$$\frac{64.00}{158.04} \times 100 = 40.50\%$$

Empirical formula : The formula that shows the simplest whole number ratio between the number of atoms in agreement with the composition of a compound is its empirical formula eg. : Empirical formula of benzene is CH
 Molecular formula : The formula that shows the exact number of atoms in a molecule of a compound is its molecular formula. eg : Molecular formula of benzene is C₆H₆

The ratio between the empirical formula mass and the molecular formula mass of a compound is a whole number.

 $\frac{\text{Relative molecular mass}}{\text{Relative empirical formula mass}} = n$

Molecular formula = (Empirical formula)_n

Example:	An organic compound contains	48.12% of	C, 8.32 % of	fH and 21.	20% of N by					
	weight. The rest is oxygen.									
	(i) Determine the empirical formula of the compound									
	(ii) If relative molecular mass of the compound is 155 find the molecular formula of the compound. H = 1.01, C = 12.00, N = 14.00, O = 16.00									
	Total percentage masses of (Total percentage masses of C, H and $N = 48.12 + 8.32 + 21.20$								
		=	77.64%							
	Therefore, the percentage ma	uss of O =	= 100 - 77.6	4						
~		=	= 22.36%							
Con	sidering 100 g of the substance,									
		С	Н	Ν	0					
Con	nposition (mass)	48.12	8.32	21.20	22.36					
Con	position (molar)	48.12	8.32	21.20	22.36					
		12.00	1.01	14.00	16.00					
Sim	nla ratio batwaan tha malas	4.01 4.01 ·	8.32 8.32 ·	1.51	1.40					
(By	dividing by the smallest number)	4.01 . 1.40	0. <i>32</i> . 1.40	1.31 .	1.40					
(Ву	arviang by the smallest number)	2.9 ·	5.9 ·	1. 4 0	1.40					
Mol	ar ratio (Whole number)	3 :	6 :	1 :	1					
Emp	pirical formula = C_3H_6NO									
Rela	tive empirical formula mass	= 3(C) + 6(H) + 1(N) + 1(O)								
		=3(12)+6(1)+1(14)+1(16)								
		=72								
Rela	tive molecular mass of the compoun	d = 155								
Ther	refore, n	= 155								
		= 2.15								
		2.10								
As r	n is a whole number, n	= 2								
Ther	refore, the molecular formula	$= (C_3 H_6 NO)_n$								
		$= (C_3H_6N0)$	D) ₂							
		$= C_6 H_{12} N_2$	$_{2}O_{2}$							

Suggested learning – teaching activities :

- Divide the students into groups and direct them to discuss information on Avogadro constant, and Faraday constant.
- Present simple problems related to these and allow the students to practice them.
- Present quantitative information about the components of systems in different ways.
- Direct them to express the composition of these systems using mass fraction, volume fraction and mole fraction in a suitable manner.
- Guide them to express composition by choosing pph, ppt and ppm appropriately.
- Present the problems related to calculation of composition to the student groups and instruct them to calculate.
- Direct to obtain empirical formula and molecular formula of compounds using provided percentage compositions.

Competency 3.0	:	Works out chemical calculations accurately.
Competency Level 3.2	:	Carries out calculations associated with balanced chemical equations.

Periods : 09

Learning outcomes :

- Examines the balance in a chemical equation considering the mass and charge conservation.
- Balances given nuclear equations.
- Balances equations by using inspection method and oxidation / reduction half reactions.
- Solves problems related to gravimetry.
- Experimentally determines the concentration of sulphate ions in a solution using Ba²⁺.

Guidance for teacher elaboration:

- A chemical equation should be balanced with respect to mass and charges of ions in order to get quantitative information from it.
- $Cr^{3+}(aq) + 3NaOH(aq) \rightarrow Cr(OH)_3(s) + 3Na^{+}(aq)$ In the above equation atoms and charges are balanced.
- It is expected to balance simple nuclear equation as given below.

$$\begin{array}{ccc} {}^{235}_{92}\mathrm{U} + {}^{4}_{2}\alpha \ \rightarrow \ {}^{239}_{94}\mathrm{Pu} \\ {}^{87}_{30}\mathrm{Kr} \ \rightarrow {}^{87}_{37}\mathrm{Rb} + {}^{0}_{-1}\beta \end{array}$$

• Inspection method

Balancing an equation by balancing the number of atoms of each kind in the reactants and products is called inspection balancing.

• Balancing redox equations by checking the changes in oxidation number

Example: Cu reacts with dilute HNO_3 to form $Cu(NO_3)_2$, NO and H_2O . (i) Find the changes in oxidation states.

 $\underset{0}{\overset{\text{Cu}}{\underset{+5}{\text{U}}}} + \underset{+5}{\overset{\text{NO}}{\underset{+5}{\text{NO}}}} \rightarrow \underset{+2}{\overset{\text{Cu}}{\underset{+2}{\text{U}}}} (\text{NO}_3)_2 + \underset{+2}{\overset{\text{NO}}{\underset{+2}{\text{NO}}}} + \underset{+2}{\overset{\text{NO}}{\underset{+2}{\text{NO}}}} + \underset{+2}{\overset{\text{NO}}{\underset{+2}{\text{NO}}}}$

(ii) Add coefficients to the relavent atoms so the exchange of electrons is balanced.

 $3Cu + 2HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + H_2O$

(iii) Balance the remaining atoms.

 $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

(Extra six HNO₃ molecules are added to the left hand side to balance six nitrate ions in the right hand side.)

• Balancing equations using oxidation / reduction half reactions

Example: Cu reacts with dilute HNO_3 to form $Cu(NO_3)_2$, NO and H_2O .

Reduction half reaction

 $4H^+ + NO_3^- + 3e \rightarrow NO + 2H_2O$

Oxidation half reaction

 ${\rm Cu}\ \rightarrow\ {\rm Cu}^{2*}+2e$

Balanced ionic equation

 $3\mathrm{Cu}+8\mathrm{H}^{*}+2\mathrm{NO}_{3}^{-}\rightarrow 3\mathrm{Cu}^{2*}+2\mathrm{NO}+4\mathrm{H}_{2}\mathrm{O}$

Balanced chemical equation

 $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

Suggested learning – teaching activities :

- Introduce oxidation number and assign students to find the oxidation state of elements in different compounds.
- Direct students to solve problems related to gravimetry.
- Present for balancing the equations encountered during the teaching of *p*-block and *d* block.
- Give an assignment to the students to solve problem related to inspection method and oxidation reduction method.

Competency 4.0	:	Investigates the behaviour of the gaseous state of matter
Competency Level 4.1	:	Uses organization of particles in three principal states of matter to explain their typical characteristics.

Periods : 01

Learning outcomes :

- Investigates the organization of particles in solids, liquids and gases, the principal states of matter.
- Compares the properties such as volume, density, shape and compressibility of solids, liquids and gases in relation to the arrangement of particles.

Guidance of teacher elaboration :

Property	Solids	Liquids	Gases
Volume	Definite	Definite	Occupy the volume of the container
Shape	Definite	Take up shape of the container but do not spread throughout the entire volume of the container	Take up the shape of the container and occupy the entire volume of the container
Compressibility	Extremely hard to compress	Extremely hard to compress	Can be compressed to a great extent
Density	Have high values	Have high values	Have low values

Suggested learning - teaching activities :

- Bring up evidences for the discontinuous nature of matters using relevant examples.
- Show evidence for the discontinuous nature of matter by demonstrating a few relevant simple activities.
- Recall the prior knowledge of students about the organization of particles in solids, liquids and gases.
- Describe the organization of particles in solids, liquids and gases and direct the students to compare the properties such as volume, shape, compressibility and relative density in relation to it.

Competency 4.0	:	Investigates the behaviour of the gaseous state matter.
Competency Level 4.2	:	Uses the model of ideal gas as a means of describing the behavioural patterns of real gases
Periods	:	08

Learning outcomes

- States the ideal gas equation and explains the terms in it.
- Describes an ideal gas.
- States Boyle, Charles and Avogadro laws.
- Derives Boyle, Charles and Avogadro laws from the ideal gas equation.
- Determines experimentally the molar volume of a gas and makes a report.
- Solves problems related to the ideal gas equation.

Guidance for teacher elaboration :

• The temperature, pressure, volume and the amount (moles) of substance of a gas are the factors that affect the behaviour of a gas. The ideal gas equation can be described as a relationship of the above four variables regarding a gas.

PV = nRT The constant R = 8.314 J K⁻¹ mol⁻¹

• Any gas which obeys the above relationship under any given temperature and pressure is referred as an ideal gas.

• Derivation of Boyle law from the ideal gas equation PV= nRT

For a fixed mass of gas at constant temperature the product nT is constant. As R is constant nRT = k (a constant)

$$PV = k \text{ (or } P = \frac{k}{V} \text{ or } p \alpha \frac{1}{V} \text{)}$$

That is the pressure of a fixed mass of gas at constant temperature is inversely proportional to the volume of the gas (Boyle Law).

• Derivation of Charles law from the ideal gas equation

$$PV = nRT$$
$$V = \frac{nRT}{P}$$

When the pressure of a fixed mass of gas is constant, $\frac{nR}{P}$ is constant.

$$\frac{V}{T} = k \qquad (\text{or } V = kT \text{ or } V \alpha T)$$

That is, the volume of a fixed mass of gas under constant pressure is directly proportional to the absolute temperature of the gas (Charles Law).

• Derivation of Avogadro's law from the ideal gas equation

$$PV = nRT$$
$$V = \frac{RT}{P} \times n$$
$$V = \frac{RT}{P} \times \frac{N}{L} = \frac{RT}{PL} \times N$$

Here N and L are the number of molecules of the gas and the Avogadro constant respectively. By applying the above relationships to equal volumes of gases A and B which are with the same volume at the same temperature and pressure,

$$V = \frac{RT}{PL} \times N_A \quad \dots (1)$$
$$V = \frac{RT}{PL} \times N_B \quad \dots (2)$$
$$(1) = (2) \quad \Rightarrow N_A = N_B$$

That is, equal volumes of different gases under the same conditions of temperature and pressure contain the same number of molecules. (Avogadro's Law)

• Molar volume

The molar volume of a gas is the volume of one mole of gas. Molar volume of a gas varies with temperature and pressure. Volume of one mole of a gas at 0 °C and 1 atm is defined as the molar volume of a gas at standard temperature and pressure.

Suggested learning - teaching activities :

- Introduce absolute temperature.
- Direct the students to obtain the value of the gas constant by substituting information to the ideal gas equation about one mole of an ideal gas at the standard temperature and pressure.
- Direct the students to state Boyle, Charles and Avogadro laws and derive them using the ideal gas equation.
- Direct students to solve problems based on ideal gas equation and its alternative forms $(PV = \frac{W}{M}RT, PM = dRT, P = cRT).$

Competency 4.0	:	Investigates the behaviour of the gaseous state of matter
Competency Level 4.3	:	Uses molecular kinetic theory of gases as a means of
		describing the behaviour of real gases.
Periods	:	04

Learning outcomes:

- States the assumptions of the molecular kinetic theory of gases.
- States the molecular kinetic equation and describes its terms.
- Describes the factors affecting diffusion of gases.
- Describes the information given by Maxwell Boltzmann curves for gases.

Guidance for teacher elaboration

- Assumptions of the molecular kinetic theory of an ideal gas
 - Molecules move randomly in straight lines in all directions and at various speeds.
 - Gas molecules in random motion collide with each other and with the wall of the container. Such collisions are completely elastic.
 - There are no attractions or repulsions between molecules.
 - When compared with the distance between molecules, volume of molecules is considered as negligible.
 - When molecules collide with one another and bounce off the total kinetic energy of the system remains the same.
 - The pressure exerted by a gas is the result of collisions of the molecules on the walls of the container.

• Molecular kinetic equation is
$$PV = \frac{1}{3}mN\overline{c^2}$$

- P = pressure
- V = volume of gas
- m = mass of a gas particle/molecule
- N = number of gas particles/molecules

 $\overline{C^2}$ = mean square speed

If the speeds of gas molecules 1, 2,,N are c_1, c_2 c_N respectively,

$$\overline{C^2} = \frac{c_1^2 + c_2^2 + \dots + c_N^2}{N}$$

Root mean square speed = $\sqrt{c^2}$

Average speed $\overline{C} = \frac{c_1 + c_2 + \dots + c_N}{N}$

- The spreading of a certain type of molecules throughout space occupied by another type of molecules is called diffusion.
 - Example :- When a substance with a scent is kept inside a room, diffusion takes place until the scent is distributed uniformly throughout the room.

Rate of diffusion - solids < liquids < gases

It has been experimentally found that different gases diffuse at different rates. The production of ammonium chloride by the diffusion of ammonia and hydrogen chloride molecules through air can be demonstrated by the following apparatus. From this it is clear that the rate of diffusion of ammonia molecules with a low molecular mass is higher than that of hydrogen chloride molecules.



- Factors affecting the rate of diffusion of a gas It is sufficient to state molar mass, area, concentration gradient and temperature.
- Variation of the mean speed of a gas with temperature is shown by the following Maxwell Boltzmann curves.



Suggested learning - teaching activities :

- Introduce the molecular kinetic equation and discuss the assumptions of the molecular kinetic theory of an ideal gas.
- Present the Maxwell Boltzmann curves and direct the student groups to discuss the information given by them about the behaviour of gases.
- Demonstrate diffusion by adding a drop of bromine into a reagent bottle, closing it and allowing the students to observe.

Competency 4.0	:	Investigates the behaviour of the gaseous state of matter.
Competency Level 4.4	:	Uses Dalton's law of partial pressure to explain the behaviour of a gas mixture.

_ ____

Periods

Learning outcomes

- Explains the term partial pressure and states Dalton's law of partial pressures.
- Derives Dalton's law of partial pressures from the ideal gas equation.
- Solves problems related to Dalton's law of partial pressures.

Guidance for teacher elaboration :

- The contributions made by the constituent gases towards the total pressure of a mixture of gases is called their partial pressures.
- The pressure that a constituent gas of a mixture of gases would exert if it alone occupies the volume of the container of the mixture is equal to the partial pressure of that gas.

• Dalton's law of partial pressures

: 03

In a mixture of gases which do not react with each other the total pressure is equal to the sum of the partial pressures of each of the constituent gases.

- If the partial pressures of individual gases in a mixture of gases A, B and C are P_A , P_B and P_C respectively, total pressure of the mixture $P_t = P_A + P_B + P_C$
- Derivation of Dalton's law of partial pressure from the ideal gas equation. In a mixture of gases A and B there are n_A and n_B moles of each gas respectively.

PV = nRT

For the gas A

$$P_{A}V = n_{A}RT$$

$$\therefore n_{A} = \frac{P_{A}V}{RT}$$

For the gas B

$$P_{B}V = n_{B}RT$$

$$\therefore n_{B} = \frac{P_{B}V}{RT}$$

For the mixture of gases

$$P_{toal}V = n_{total}RT$$

$$\therefore n_{total} = \frac{P_{toal}V}{RT}$$

$$n_{total} = n_A + n_B$$

$$\frac{P_{total}V}{RT} = \frac{P_AV}{RT} + \frac{P_BV}{RT}$$

$$\therefore P_{total} = P_A + P_B$$

Suggested learning - teaching activities :

- Remind that the atmosphere is a mixture of various gases and then conduct a brainstorming session on the contribution of each gas towards the atmospheric pressure.
- Divide the class into groups and direct them to solve simple problems such as follows.
 - Determination of the composition of a mixture of gases and the total pressure when the partial pressure of each gas in a mixture of gases is given.
 - Determination of the partial pressure of each gas when the composition and the total pressure of a mixture of gasses are given.
 - Determination of the composition when the total pressure and partial pressures of gases in a mixture are given.

 $(P_A = Mole \text{ fraction of gas A x } P_{total})$

Competency 4.0	:	Investigates the behaviour of three principal states of matter.
Competency Level 4.5	:	Analyzes amendments to the ideal gas equation enable it to be applied for real gases.
Periods	:	02

Learning outcomes

- Defines the compressibility factor and graphically presents how this value varies with respect to real and ideal gases.
- Describes the reasons for the deviation of real gases from the behaviour of ideal gases by citing assumptions of the molecular kinetic theory.
- Presents Van der Waals equation as an equation constructed taking into consideration the deviation of real gasses from the ideal behaviour.

Guidance for teacher elaboration :

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•
$$z = \frac{PV}{nRT}$$

z is the compressibility factor. For ideal gases z = 1. But the fact that this value is not a constant for real gases is revealed by experimental data.

• The graph of the product PV against P for different gases at the temperature 273 K



• According to this graph it is clear that real gases approach ideal behaviour under conditions of low pressure.

• The graph of *PV/RT* against *P* for a mole of hydrogen at various temperatures.



• It is clear from the above graph that at high temperatures the real gases approach ideal behaviour.

Van der Waals equation

$$\left(P + \frac{n^2 a}{V^2}\right) (V - nb) = nRT$$

P = Pressure

V = Volume

n = Amount (moles) of substance

R =Universal gas constant

T = Absolute temperature

a and b are constants (Van der Waals constants) for real gases

$$n^2a$$
 .

 $\frac{1}{V^2}$ is the correction for pressure drop due to Van der Waals interactions.

nb is the correction for the volume of gas molecules.

N.B. Calculations using Van der Waals equation are not necessary.

Suggested learning - teaching activities

- Allow to study of the variation of the compressibility factor in relation to real gases using the graph.
- Direct the students to discuss the reasons for the real gases to deviate from ideal behaviour and the conditions for approaching ideal behaviour.
- Discuss how amendments have been included in the Van der Waals equation so as to apply it for real gasses.

Competency 5.0 : Predicts the stability of chemical systems and feasibility of conversions by investigating associated changes in enthalpy and entropy.

Competency Level 5.1 : Explores concepts related to enthalpy.

Periods : 04

Learning outcomes

- Defines the terms system, surrounding, boundary, closed system, open system and isolated system.
- Describes both enthalpy and entropy as functions of state and thermodynamic properties.
- Calculates the enthalpy changes associated with reactions using tabulated enthalpy data.

Guidance for teacher elaboration

- The portion of the universe selected for study is called the **system**.
- Rest of the universe other than the portion selected for study is called the **environment.**
- The surface that separates the system and the environment is called the **boundary**.

system environment boundary

• Systems where there is an exchange of energy, matter and work across the boundary are called **open systems**.



• Systems where only energy and work can exchange across the boundary are called **closed systems.** (i.e. Boundary is impermeable to matter.)



- Systems where there is no exchange of energy, matter or work across the boundary are called **isolated** systems.
- The properties that depend upon the amount of matter are named **extensive properties.**

Examples- mass, volume, heat capacity

• The properties that are independent of the amount of matter are named **intensive properties.**

Examples : temperature, pressure, density, viscosity, molar volume, molar heat capacity

- Description of the temperature, pressure and composition of the system is called the state of the system. This information is specific for a particular system.
- The properties with specific values for the state in which a system exits are called state functions. These properties do not depend on the history of the system.
- The change in a function of state depends only on its initial state and final state. It is independent of the route followed.
- Volume, temperature, density, refractive index, enthalpy, entropy, etc. are examples for functions of state.
- The quantity of heat supplied to a system or given out from a system under the condition of constant pressure is called the enthalpy change (ΔH). This is a thermodynamic property and a function of state.
- The enthalpy change (ΔH) associated with a reaction is given by the difference in enthalpy of the products and reactants.

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

- Enthalpy change associated with a reaction ; if $\Delta H < 0$ the reaction is exothermic and if $\Delta H > 0$ the reaction is endothermic.
- According to IUPAC convention, enthalpy changes are reported for unit extent of reaction in kJ mol⁻¹. It is recommended to follow IUPAC convention.

Suggested learning - teaching activities

• Provide the standard enthalpy values for reactants and products (that is the standard enthalpy of formation of these substances) related to various reactions to groups of students and direct them to calculate the enthalpy changes of these reactions

using $\Delta H^{\theta} = H^{\theta}_{\text{products}} - H^{\theta}_{\text{reactants}}$.

Competency 5.0	:	Predicts the stability of chemical systems and feasibility
		of conversions by investigating associated changes in enthalpy and entropy.
Competency Level 5.2	:	Predicts the feasibility of conversions by analysing the enthalpy changes associated with them.
Periods	:	14

Learning outcomes

:

- Defines enthalpy changes and standard enthalpy changes given in the syllabus.
- Calculates enthalpy changes associated with various processes using enthalpy diagrams and thermochemical cycles.
- Determines experimentally the enthalpy of dissolution of various substances and reports them.
- Determines experimentally the enthalpy of neutralization of acids and bases and reports them.
- Determines experimentally the enthalpy of a displacement reaction and reports it.
- Tests the validity of Hess's law by a suitable experiment and reports it.

Guidance for teacher elaboration :

ΔH of a reaction changes with pressure. In order to make comparisons of ΔH values, it is important that everyone knows what pressure is used for that purpose. The convention is to use a pressure of 1 atmosphere (in non SI units), 101.325 kPa in SI units, as the *standard pressure*. Values of enthalpy changes that are measured at the standard pressure (or corrected to apply to this condition) are called standard enthalpy changes. Standard enthalpy changes are given a special symbol ΔH^θ.

• Standard enthalpy of formation (ΔH_f^{θ})

It is the enthalpy change that occurs when one mole of the compound is formed in the standard state from the constituent elements in the standard state.

Example: Standard enthalpy of formation of $H_2O(1)$ is = -286 kJ mol⁻¹.

It can be shown as follows.

$$\begin{split} & \operatorname{H}_2(\mathbf{g}) + \frac{1}{2} \operatorname{O}_2(\mathbf{g}) \longrightarrow \operatorname{H}_2 \operatorname{O}(\mathbf{l}) \\ & \Delta H_f^{\theta} = -286 \ \mathrm{kJ \ mol^{-1}} \end{split}$$

• Standard enthalpy of combustion (ΔH_{c}^{θ})

It is the enthalpy change that occurs when one mole of an element or a compound in the standard state undergoes complete combustion in an excess amount of oxygen.

CH₄(g) + 2O₂(g) → CO₂(g) + 2H₂O(l)

$$\Delta H^{\theta}_{C(CH_1)} = -892 \text{ kJ mol}^{-1}$$

• Standard enthalpy of bond dissociation (ΔH^θ_D)

It is the enthalpy change that occurs when a gaseous species in the standard state is converted into gaseous components by breaking a mole of bonds (This is stated with respect to a specified bond in a specified element or a compound).

$$\begin{split} \mathrm{H}_{2}(\mathrm{g}) &\rightarrow \mathrm{2H}(\mathrm{g}) & \Delta H_{\mathrm{D}}^{\theta} = 432 \ \mathrm{kJ \ mol}^{-1} \\ \mathrm{CH}_{4}(\mathrm{g}) &\rightarrow \mathrm{CH}_{3}(\mathrm{g}) + \mathrm{H}(\mathrm{g}) & \Delta H_{\mathrm{D}}^{\theta} = 428 \ \mathrm{kJ \ mol}^{-1} \\ \mathrm{CH}_{3}(\mathrm{g}) &\rightarrow \mathrm{CH}_{2}(\mathrm{g}) + \mathrm{H}(\mathrm{g}) & \Delta H_{\mathrm{D}}^{\theta} = 441 \ \mathrm{kJ \ mol}^{-1} \\ \mathrm{CH}_{2}(\mathrm{g}) &\rightarrow \mathrm{CH}(\mathrm{g}) + \mathrm{H}(\mathrm{g}) & \Delta H_{\mathrm{D}}^{\theta} = 454 \ \mathrm{kJ \ mol}^{-1} \\ \mathrm{CH}(\mathrm{g}) &\rightarrow \mathrm{C}(\mathrm{g}) + \mathrm{H}(\mathrm{g}) & \Delta H_{\mathrm{D}}^{\theta} = 344 \ \mathrm{kJ \ mol}^{-1} \end{split}$$

Average of the above values is considered as average bond dissociation enthalpy of C-H bond in CH_4 .

• Standard enthalpy of neutralization $(\Delta \mathcal{H}_{mu}^{\theta})$

It is the enthalpy change that occurs when a mole of H^+ ions in an aqueous solution reacts with a mole of OH^- ions in an aqueous solution under the standard state to form a mole of H_2O .

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(1) \quad \Delta H^{\theta}_{--} = -57 \text{ kJ m ol}^{-1}$$

• Standard enthalpy of solvation (ΔH_{xi}^{θ})

It is the enthalpy change that occurs when a mole of gaseous ions under the standard state changes into the solution form in the presence of an excess of the solvent.

 $M^{n+}(g) + \text{ excess of } \rightarrow M^{n+}(\text{solvent})$ solvent

• Standard enthalpy of hydration $(\Delta H_{kyd}^{\theta})$

It is the enthalpy change that occurs when a mole of gaseous ions under the standard state changes into the solution form in the presence of an excess of water.

 $Na^{+}(g) + (aq) \rightarrow Na^{+}(aq); \qquad \Delta H^{\theta}_{kyd} = -406 \text{ kJ mol}^{-1}$

• Standard enthalpy of dissolution $(\Delta H^{\theta}_{dissolution})$

It is the enthalpy change that occurs when a mole of a substance under the standard state is dissolved in an excess of solvent to form a solution.

eg. NaCl(s) + (aq) \rightarrow NaCl(aq) ; $\Delta H^{\theta}_{disolution} = 1$ kJ mol⁻¹

Hess's law

The enthalpy change that takes place in a chemical reaction where the reactants and products are at specified states is independent of the route of the reaction.



According to Hess's law

 $\Delta H_1 = \Delta H_2 + \Delta H_3$

Thermochemical cycle



$$\Delta H^{\circ} = +184 - 277.$$

= -93 kJ mol⁻¹



Suggested learning - teaching activities :

- Demonstrate an exothermic reaction and an endothermic reaction.
- Carry out the suggested practical activities.
- Direct the students to solve problems in groups using thermochemical cycles and enthalpy diagrams.

Competency 5.0	:	Predicts the stability of chemical systems and feasibility of conversions by investigating associated changes in enthalpy and randomness.
Competency Level 5.3	:	Predicts the stability of ionic systems using Born-Haber cycles.

Periods : 04

Learning outcomes

- Defines the enthalpy changes included in the syllabus which are used in the determination of the enthalpy of formation of ionic compounds.
- Develops the Born Haber cycle related to the formation of an ionic compound.
- Calculates the standard enthalpy of lattice using Born Haber cycle.

Guidance for teacher elaboration :

• Standard enthalpy of sublimation (ΔH_{sb}^{θ})

It is the change in enthalpy that occurs when a mole of a solid element or a mole of a solid compound at the standard state is converted completely into a gas at its standard state.

 $Ca(s) \rightarrow Ca(g) \qquad \Delta H_{ab}^{\theta} = 193 \text{ kJ mol}^{-1}$

:

Standard enthalpy of evaporation (ΔH^θ_{vm})

It is the change in enthalpy that takes place when a mole of a liquid compound or element at the standard state is converted into a mole of a gaseous compound/ element at its standard state.

 $Br_2(l) \rightarrow Br_2(g) \qquad \Delta H_{wap}^{\theta} = 30.91 \text{ kJ mol}^{-1}$

• Standard enthalpy of fusion $(\Delta H_{fis}^{\theta})$

It is the change in enthalpy that takes place when a mole of a solid compound or element at the standard state is converted into a mole of liquid compound/element at standard state.

 $A1(s) \rightarrow A1(l) \quad \Delta H_{fis}^{\theta} = 10.7 \text{ kJ mol}^{-1}$

• Standard enthalpy of atomization $(\Delta H_{\rm at}^{\theta})$

It is the change in enthalpy that takes place when an element or a compound at the standard state is converted into a mole of gaseous atoms at the standard state. $1/2 \operatorname{Cl}_2(g) \rightarrow \operatorname{Cl}(g) \quad \Delta H_{\mathrm{st}}^{\theta} = 121 \text{ kJ mol}^{-1}$ • Standard enthalpy of first ionization $(\Delta H^{\theta}_{IB_{1}})$

It is the change in enthalpy that takes place when a mole of gaseous uni-positive ions are formed by removing an electron from each atom that is most weakly bonded to the nucleus from a mole of gaseous atoms of an element at standard state.

 $\operatorname{Na}(g) \rightarrow \operatorname{Na}^{+}(g) + e \qquad \Delta H^{\theta}_{L\!\!E_{1}} = 496 \text{ kJ mol}^{-1}$

• Standard enthalpy of electron affinity (or electron gain) $\left(\Delta H^{\theta}_{EA} \right)$

It is the change in enthalpy that takes place when a mole of uni- negative ions are formed in the gaseous state when electrons are given to a mole of atom in the gaseous state under standard state.

 $Cl(g) + e \rightarrow Cl^{-}(g) \qquad \Delta H_{EA}^{\theta} = -349 \text{ kJ mol}^{-1}$

• Standard lattice enthalpy of an ionic compound (ΔH_L^{θ})

It is the change in enthalpy that takes place when one mole of an ionic compound in the solid state is formed from gaseous positive ions and negative ions at the standard state.

 $\operatorname{Na}^{+}(g) + \operatorname{Cl}^{\cdot}(g) \rightarrow \operatorname{NaCl}(s) \quad \Delta H_{L}^{\theta} = -788 \text{ kJ m ol}^{-1}$

• Born – Haber cycle

The thermochemical cycle that is developed to find the enthalpy change of lattice formation of an ionic compound is called the Born-Haber cycle.



Born - Haber cycle for the formation of solid NaCl

Suggested learning - teaching activities

- Define the relevant enthalpy changes.
- Assign various ionic compounds to student groups and ask them to find the enthalpy of lattice of those compounds using the given relevant enthalpy values.
- Ask the students to calculate the enthalpy of formation of a given ionic compound using the Born Haber cycle.

Competency 5.0 : Predicts the stability of chemical systems and feasibility of conversions by investigating associated changes in enthalpy and randomness.

Competency Level 5.4 : Predicts the spontaneity of chemical reactions.

Periods : 04

Learning outcomes

- Explains the terms entropy (S) and Gibbs energy (G).
- Understands that *S* and *G* are state functions.
- States the relationship among ΔG , ΔH and ΔS .
- Predicts using ΔG the spontaneity of a certain reaction or an event occuring under constant pressure and temperature.
- Knows that ΔG and ΔS are reported for a unit extent of reaction.

 ΔG (kJ mol⁻¹), ΔS (kJ mol⁻¹ K⁻¹)

Guidance for teacher elaboration :

- Entropy of a system is a measure of the randomness of the system.
- Entropy is a function of state and it depends only on the initial and final state of the system and is independent of the path of the change.
- Entropy is also a factor affecting both chemical and physical changes.
- Spontaneous changes in an isolated system takes place with an increase in entropy.
- As the entropy related to a certain system is a function of state, the change in entropy can be calculated by subtracting the initial value of entropy from the final value of entropy.

$$\Delta S = S_{final} - S_{initial}$$

$$\Delta S = S_{products} - S_{reactants}$$

• If this change is measured under the standard conditions

$$\Delta S^{ heta} = S^{ heta}_{products}$$
 - $S^{ heta}_{reactants}$

• The total influence of ΔH and ΔS on a change is given by the Gibbs energy change which is ΔG . The relationship among these at constant temperature (*T*) is as follows.

 $\Delta G = \Delta H - T \Delta S$

At a constant temperature and pressure;

for a spontaneous reaction $\Delta G < 0$

for a reaction which is not spontaneous $\Delta G > 0$

for a reaction at equilibrium $\Delta G = 0$

• Spontaneity of a system with a constant entropy ($\Delta S = 0$) is decided by ΔH and the spontaneity of a change that takes place under a constant enthalpy ($\Delta H = 0$) is decided by ΔS .

Suggested learning - teaching activities

• Give examples to show that enthalpy change is not the only factor that determines the feasibility of a reaction.

eg. Instances where reactions occur spontaneously when $\Delta H > 0$.

Instances where reactions do not occur spontaneously when $\Delta H < 0$.

- State that the feasibility or non-feasibility of a reaction or a process depends on the change in randomness associated with the relevant system.
- Explain quantitatively the concept entropy that is used to explain randomness and designate it quantitatively.
- Give examples for reactions which occur spontaneously though $\Delta H > 0$ and show how entropy has increased in them.
- Show that the randomness of elements and compounds has been determined and tabulated.
- Guide the students to decide whether a reaction is spontaneous or not when the values of ΔS , ΔH and ΔG are given. Also direct them to use the equation
 - $\Delta G = \Delta H$ $T\Delta S$ when necessary.

Competency 6.0	:	Investigates the elements and compounds of <i>s</i> , <i>p</i> and <i>d</i> blocks to be familiar with their properties.
Competency Level 6.1	:	Investigates chemical properties of elements in <i>s</i> block.
Periods	:	06

Learning outcomes

- Compares the reactions of the *s* block elements (except H and He) with air/ O₂, water, acids, N₂ and H₂.
- Describes the nature of the reactions of elements of the first and second groups with air/O₂, water, acids, N₂ and H₂.
- States by means of balanced chemical equations the reactions of elements belonging to the first and second groups with air/O₂, water, acids, N₂ and H₂.
- Observes reactions of Na and Mg with air/O₂, water, acids taking them as representative elements.
- Explains that *s* block elements can function as reducing agents by forming stable cations with noble gas configuration by giving up electrons which are loosely bonded to the nucleus.

Guidance for teacher elaboration :

- With water
 - All the elements of the first group react with water liberating hydrogen and become hydroxides.

Example : Na reacts rapidly with water liberating hydrogen.

 $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$

- When a small piece of K is added into water it reacts while burning. As K reacts with water more rapidly than Na, it can be concluded that the rate of reaction with water increases down the group.
- A reaction is not seen when a clean piece of Mg is added into water. When the water with Mg is warmed, it is seen to react slowly.

 $Mg(s) + 2H_2O(l) \rightarrow Mg(OH)_2(s) + H_2(g)$

• As the reactivity shown by Mg with water is lower compared to Na, it can be said that the metals of group II compared to metals of group I show a lower reactivity. Be does not react with water. Ca, Sr, and Ba react with water liberating hydrogen and forming the hydroxides.

 $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$

• Be and Mg react with steam to form the oxides.

$$\begin{array}{rll} \operatorname{Be}(s) &+& \operatorname{H_2O}(g) \rightarrow &\operatorname{BeO}(s) &+& \operatorname{H_2}(g) \\ \operatorname{Mg}(s) &+& \operatorname{H_2O}(g) \rightarrow &\operatorname{MgO}(s) &+& \operatorname{H_2}(g) \end{array}$$

• With air/ O_2

- There are several reactions of group I metals with air/O_2 .
 - $4Na(s) + O_{2}(g) \rightarrow 2Na_{2}O(s)$ $2Na(s) + Excess O_{2}(g) \xrightarrow{a} Na_{2}O_{2}(s)$ $2Na(s) + 2H_{2}O(g) \rightarrow 2NaOH(s) + H_{2}(g)$

K, Rb and Cs readily react with O₂ forming superoxides.

 $\begin{array}{rcl} & & & & \\ & & & \\ K(s) \ + & O_2(g) & \underline{\quad} & & & \\ & & & & \\ & & & & \\ \end{array} \quad KO_2(s)$

• When heated in air only Li of Group I reacts with nitrogen.

$$6Li(s) + N_2(g) \longrightarrow 2Li_3N(s)$$

- When a clean piece of Mg ribbon and a small cut piece of Na are exposed to air Na tarnishes faster than Mg. Hence it is clear that the reactivity of Mg is lower than Na.
- Accordingly it can be said that relative to metals of group I, the reactivity of group II metals with air is lower.
- Metals of the Group II when heated in air burn forming oxides and nitrides.

 $2Mg(s) + O_2(g) \xrightarrow{\bullet} 2MgO(s)$ $3Mg(s) + N_2(g) \xrightarrow{\bullet} Mg_3N_2(s)$

For Be to react it should be heated to a very high temperature.

• With acids

• As the metals of the group I react with acids liberating large quantity of heat, an explosion takes place. Therefore it should not be tested.

$$2 \operatorname{Na(s)} + \operatorname{H}_2^{\operatorname{del}}(\operatorname{aq}) \rightarrow \operatorname{Na}_2^{\operatorname{SO}_4}(\operatorname{aq}) + \operatorname{H}_2(\operatorname{g})$$

- Group II metals reacts with dilute acids to liberate H_2 rapidly. $Mg(s) + H_2SO_4 (aq) \rightarrow MgSO_4 (aq) + H_2(g)$
- Group II metals can be oxidised by concentrated acids.

$$\begin{split} \mathrm{Mg}(\mathrm{s}) &+ 2\mathrm{H}_{2}^{\mathrm{conc.}}(\mathrm{aq}) \rightarrow \mathrm{MgSO}_{4}(\mathrm{aq}) + \mathrm{SO}_{2}(\mathrm{g}) + 2\mathrm{H}_{2} \bigcirc (\mathrm{l}) \\ \mathrm{Mg}(\mathrm{s}) &+ 4\mathrm{HNO}_{3}(\mathrm{aq}) \rightarrow \mathrm{Mg}(\mathrm{NO}_{3})_{2}(\mathrm{aq}) + 2\mathrm{NO}_{2}(\mathrm{g}) + 2\mathrm{H}_{2} \bigcirc (\mathrm{l}) \end{split}$$

• With N₂

Lithium and Group II metals form metal nitrides by reacting with N_2 gas or N_2 presents in air.

 $6Li(s) + N_2(g) \rightarrow 2Li_3N(s)$

 $3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$

- With H,
 - s Block elements form metal hydrides by reacting with H_2 gas.

 $2\text{Li}(s) + \text{H}_2(g) \rightarrow 2\text{LiH}(s)$

 $2Na(s) + H_2(g) \rightarrow 2NaH(s)$

 $Mg(s) + H_2(g) \rightarrow MgH_2(s)$

- Because *s* block elements easily remove their electrons and form cations they are considered as good reducing agents.
- While atomic radius increases down the group nuclear attraction decreases. Consequently, reducing ability of the elements also increases.

Suggested learning - teaching activities

- Discuss the observations made when a small piece of sodium is added into a beaker of water with little of phenolphthalein.
- Add a clean piece of Mg ribbon into a boiling tube of water containing a drop of

Competency 6.0	:	Investigates the elements and compounds of <i>s</i> , <i>p</i> and <i>d</i> blocks to be familiar with their properties.
Competency Level 6.2	:	Investigates the properties of compounds and their trends associated with <i>s</i> and <i>p</i> block elements.
Periods	:	08

Learning outcomes

- Compares the solubility of the salts of *s* block salts in water.
- Compares the thermal stability of the nitrates, carbonates and bicarbonates of *s* block salts.
- States how the acidic / basic/ amphoteric nature of the halides, oxides, hydrides and hydroxides of *s* and *p* blocks vary along the periods and down the groups.

	Cl	Br	Ŀ	OH-	CO3-	HCQ	NO_2^{-}	NO_3^{-}	S^{2-}	SO ₃ ²⁻	SO4-
Na ⁺	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
K ⁺	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
Be ²⁺	Soluble	Soluble	Soluble	Insoluble	Insoluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
Mg ²⁺	Soluble	Soluble	Soluble	Insoluble	Insoluble	Soluble	Soluble	Soluble	Soluble	Sparingly soluble	Soluble
Ca ²⁺	Soluble	Soluble	Soluble	Sparingly	Insoluble	Soluble	Soluble	Soluble	Soluble	Insoluble	Sparingly
Sr ²⁺				soluble							soluble
51	Soluble	Soluble	Soluble	Sparingly	Insoluble	Soluble	Soluble	Soluble	Soluble	Insoluble	Insoluble
Ba ²⁺	Soluble	Soluble	Soluble	soluble soluble	Insoluble	Soluble	Soluble	Soluble	Soluble	Insoluble	Insoluble

Guidance for the teacher elaboration :

- Variation of solubility of sulphates and hydroxides down the group can be explained by using lattice enthalpy and hydration enthalpy values.
- Variation of thermal stability of *s* block carbonates, bicarbonates and nitrates down a group can be explained by using electronegativity values of elements and ionic nature of those compounds. Relevant balanced equations are needed.
- Acidic/basic/amphoteric nature of halides (eg. chlorides) of third period

NaCl	MgCl ₂	AlCl ₃	SiCl ₄	PCl ₅	SCl ₂ /S ₂ Cl ₂
Neutral	very weakly	acidic	acidic	acidic	acidic
	acidic				

• Acidic/basic/amphoteric nature of oxides of elements of the 3rd period

Na ₂ O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_2/SO_3	Cl_2O_7
Strongly	Basic	Amphoteric	Very	Weakly	Acidic	Strongly
basic			weakly	acidic		acidic
			acidic			

• Nature of oxides down the group 15

 N_2O_3 – acidic

- P_2O_3 weakly acidic
- As_2O_3 amphoteric
- Sb_2O_3 amphoteric
- Bi_2O_3 basic
- Acidic/basic/amphoteric nature of hydroxides of elements of the 3rd period

NaOH	Mg(OH) ₂	Al(OH) ₃	Si(OH) ₄	P(OH) ₅	S(OH) ₆	Cl(OH) ₇
			-H ₂ O	-H ₂ O	-2H ₂	O -3H ₂ O
NaOH	Mg(OH) ₂	Al(OH) ₃	H ₂ SiO ₃	H ₃ PO ₄	H_2SO_4	HClO ₄
Strongly	Basic A	Amphoteric	Very	Weakly	Strongly	Very
basic			weakly	acidic	acidic	strongly
			acidic			acidic

• Acidic/basic/amphoteric nature of hydrides of the 3rd period

NaH	MgH ₂	AlH,	SiH4	PH ₃	H,S	HCl
Strongly	Weakly	Amphoteric	Very	Very	Weakly	Very
basic	basic		weakly	weakly	acidic	strongly
			acidic	basic		acidic

Suggested learning - teaching activities:

- Give opportunities for the student groups to examine the solubility of salts formed by *s* block elements.
- Direct the students to examine the thermal stability of the nitrates, bicarbonates and carbonates formed by *s* block elements.
- Discuss acidic, basic and amphoteric nature of oxides, halides, hydrides and hydroxides by using electronegativity difference and hydrolyzing ability.

Competency 6.0	:	Investigates the elements and compounds of s, p	and
		d blocks to be familiar with their properties.	
Competency Level	6.3:	Investigates elements and compounds of <i>p</i> block	to
		identify their variety.	

Periods	:	16
Periods	:	16

Learning outcomes

- Describes reactions of aluminium and electron deficiency of AlCl₃.
- Presents information about the allotropic forms of oxygen, sulphur and carbon.
- Presents structures of the oxoacids of carbon, nitrogen, sulphur and chlorine.
- Presents with the aid of balanced chemical equations, instances where H₂O₂, H₂S and SO₂ behave as oxidizing agents and reducing agents.
- Describes the thermal decomposition of ammonium salts.
- Describes giving suitable examples, the acidity of hydrogen halides in an aqueous medium, hydrolysis of chlorides, disproportionation of chlorine and chlorate(I) ions and the relative oxidation powers of the halides.
- States the properties of the noble gases and gives examples of some compounds they form.
- Carries out the suggested practical under the competency level 6.3 and reports them.

Guidance for teacher elaboration :

• Aluminium

Al is an amphoteric metal. It reacts with acids and strong bases.

$$2A1(s) + 6HCI(aq) \rightarrow 2A1CI_3(aq) + 3H_2(g)$$
 or

$$2Al(s) + 6HCl(g) \rightarrow Al_2Cl_6(s) + 3H_2(g)$$

 $2\mathrm{Al}(\mathrm{s}) + 2\mathrm{H}_2\mathrm{O}(\mathrm{l}) + 2\mathrm{Na}\mathrm{OH}(\mathrm{aq}) \rightarrow 2\mathrm{Na}\mathrm{Al}\mathrm{O}_2(\mathrm{aq}) + 3\mathrm{H}_2(\mathrm{g}) \quad \text{ or } \quad$

$$2 \text{Al}(\text{s}) + 6 \text{H}_2 \text{O}(\text{l}) + 2 \text{NaOH}(\text{aq}) \rightarrow 2 \text{NaAl}(\text{OH})_4(\text{aq}) + 3 \text{H}_2(\text{g})$$

 $AlCl_3$ is an electron defficient compound and also highly covalent when anhydrous. AlCl_3 exists as a dimer thus attaining an octet of electrons.

$$2A1(s) + 3Cl_2(g) \rightarrow 2A1Cl_3(s) \rightarrow Al_2Cl_6(s)$$



• Carbon

Carbon is a non-metal. Carbon exists in various allotropic forms such as graphite, diamond, C_{60} (Fullerene). For the structures of allotropes refer 2.4

• Oxides of carbon

CO is a colourless, neutral, and poisonous gas. CO is used as an industrial fuel. CO is a Lewis acid.

Lewis structure of CO

$$C = O^{+}$$

 CO_2 is a colourless acidic gas and a non polar molecule. Solid CO_2 (dry ice) contains dispersion interactions. Dry ice is used as a freezing agent in food industry, in causing artificial rain, etc.

• Carbonic acid

Carbonic acid is weak diprotic acid. There are two salts derived from H₂CO₃.

 $CO_{2}(g) + H_{2}O(1) \square H_{2}CO_{3}(aq)$ $H_{2}CO_{3}(aq) \square H^{+}(aq) + HCO_{3}^{-}(aq)$ $HCO_{3}^{-}(aq) \square H^{+}(aq) + CO_{3}^{2-}(aq)$

• Nitrogen

 N_2 is a colourless gas. It contains a triple bond, $N \equiv N$, with a short bond length of 1.09 °A. It has high dissociation bond energy 946 kJ mol⁻¹ and it is an inert gas.

- Liquid N₂ (boiling point -196 °C) is used as a coolant. N₂ gas is used in the manufacture of ammonia. (Refer 15 .2)
- Nitrogen shows variable oxidation states.

• Oxoacids of nitrogen

Nitrous acid (HNO_2) is unstable except in dilute solutions. HNO_2 is formed when acid reacts with metal nitrites.

 $NaNO_2(s) + HCl(aq) \rightarrow HNO_2(aq) + NaCl(aq)$

Nitric acid (HNO₃) is a colourless liquid which boils at 86 $^{\circ}$ C. HNO₃ a stable, strong acid as well as a strong oxidizing agent. Concentrated HNO₃ acid is usually yellow. In the light, it decomposes to form nitrogen dioxide and oxygen.

 $4\mathrm{HNO}_3(\mathrm{l}) \ \rightarrow \ 4\mathrm{NO}_2(\mathrm{g}) + \mathrm{O}_2(\mathrm{g}) + 2\mathrm{H}_2\mathrm{O}(\mathrm{l})$

Manufacture of nitric acid, HNO₃ is discussed under 15.2.

• Ammonia and ammonium salts

 NH_3 colourless, poisonous basic gas with pungent odour. It dissolves readily in water and forms a basic solution. Production of NH_3 is discussed under 15.2.

• Reactions of ammonia

NH₃ acts as an oxidizing agent and as well as an acid.

$$\begin{split} &2\mathrm{Na}(\mathrm{s})+2\mathrm{NH}_3(\mathrm{l}) \ \rightarrow \ &2\mathrm{Na}\mathrm{NH}_2(\mathrm{s})+\mathrm{H}_2(\mathrm{g}) \\ &3\mathrm{Mg}(\mathrm{s})+2\mathrm{NH}_3(\mathrm{l}) \ \rightarrow \ &\mathrm{Mg}_3\mathrm{N}_2(\mathrm{s})+3\mathrm{H}_2(\mathrm{g}) \\ &6\mathrm{Li}(\mathrm{s})+2\mathrm{NH}_3(\mathrm{l}) \ \rightarrow \ &2\mathrm{Li}_3\mathrm{N}(\mathrm{s})+3\mathrm{H}_2(\mathrm{g}) \end{split}$$

NH₃ acts as a weak reducing agent.

$$\begin{aligned} 3\mathrm{Cl}_2(\mathrm{g}) + 2\mathrm{NH}_3(\mathrm{g}) &\to 2\mathrm{N}_2(\mathrm{g}) + 6\mathrm{HCl}(\mathrm{g}) \\ 3\mathrm{CuO}(\mathrm{s}) + 2\mathrm{NH}_3(\mathrm{g}) &\to \mathrm{N}_2(\mathrm{g}) + 3\mathrm{Cu}(\mathrm{s}) + 3\mathrm{H}_2\mathrm{C}(\mathrm{g}) \\ 3\mathrm{O}_2(\mathrm{g}) + 4\mathrm{NH}_3(\mathrm{g}) &\to 2\mathrm{N}_2(\mathrm{g}) + 6\mathrm{H}_2\mathrm{O}(\mathrm{l}) \end{aligned}$$

NH₃ acts as a base.

$$\mathrm{HCl}(g) + \mathrm{NH}_{3}(g) \rightarrow \mathrm{NH}_{4}\mathrm{Cl}(s)$$

Ammonium salts

Ammonium salts decompose quite readily on heating. -

$$\begin{split} (\mathrm{NH}_{4})_{2}\mathrm{CO}_{3}(\mathrm{s}) & \xrightarrow{\mathbb{A}} 2\mathrm{NH}_{3}(\mathrm{g}) + \mathrm{CO}_{2}(\mathrm{g}) + \mathrm{H}_{2}\mathrm{O}(\mathrm{g}) \\ \mathrm{NH}_{4}\mathrm{Cl}(\mathrm{s}) & \xrightarrow{\mathbb{A}} \mathrm{NH}_{3}(\mathrm{g}) + \mathrm{HCl}(\mathrm{g}) \\ \mathrm{NH}_{4}\mathrm{NO}_{2}(\mathrm{s}) & \xrightarrow{\mathbb{A}} \mathrm{N}_{2}(\mathrm{g}) + 2\mathrm{H}_{2}\mathrm{O}(\mathrm{g}) \\ \mathrm{NH}_{4}\mathrm{NO}_{3}(\mathrm{s}) & \xrightarrow{\mathbb{A}} \mathrm{N}_{2}\mathrm{O}(\mathrm{g}) + 2\mathrm{H}_{2}\mathrm{O}(\mathrm{g}) \\ \mathrm{NH}_{4}\mathrm{NO}_{3}(\mathrm{s}) & \xrightarrow{\mathbb{A}} \mathrm{N}_{2}\mathrm{O}(\mathrm{g}) + 2\mathrm{H}_{2}\mathrm{O}(\mathrm{g}) \\ (\mathrm{NH}_{4})_{2}\mathrm{Cr}_{2}\mathrm{O}_{7}(\mathrm{s}) & \xrightarrow{\mathbb{A}} \mathrm{N}_{2}(\mathrm{g}) + \mathrm{Cr}_{2}\mathrm{O}_{3}(\mathrm{s}) + 4\mathrm{H}_{2}\mathrm{O}(\mathrm{g}) \end{split}$$

• Oxygen

It is a colourless and odourless gas. Oxygen exists in two allotropic forms.

• Allotropic forms of oxygen


• Sulphur

Sulphur is a non metal and shows different oxidation states.

- + VI SO_3 , H_2SO_4 + IV - SO_2 , H_2SO_3 + II - SCl_2 0 - S_8 -II - H_2S
- Reactions of sulphur
 - $$\begin{split} &\mathrm{S}(s) + \mathrm{Hot}\ \mathrm{conc.}\ 2\mathrm{H}_2\mathrm{SO}_4(\mathrm{aq}) \ \rightarrow \ 3\mathrm{SO}_2(\mathrm{g}) + 2\mathrm{H}_2\mathrm{O}(\mathrm{l}) \\ &\mathrm{S}(s) + \mathrm{Hot}\ \mathrm{conc.}\ 6\mathrm{HNO}_3(\mathrm{aq}) \ \rightarrow \ \mathrm{H}_2\mathrm{SO}_4(\mathrm{l}) + 2\mathrm{H}_2\mathrm{O}(\mathrm{l}) + 6\mathrm{NO}_2(\mathrm{g}) \\ &\mathrm{S}(s) + \mathrm{Cu}(\mathrm{s}) \ \rightarrow \ \mathrm{CuS}(\mathrm{s}) \\ &\mathrm{4S}(\mathrm{s}) + 6\mathrm{NaOH}(\mathrm{aq}) \ \rightarrow \ 2\mathrm{Na}_2\mathrm{S}(\mathrm{aq}) + \mathrm{Na}_2\mathrm{S}_2\mathrm{O}_3(\mathrm{aq}) + 3\mathrm{H}_2\mathrm{O}(\mathrm{l}) \end{split}$$

• Allotropic forms of sulphur

Allotropic forms of sulphur exist in two forms namely crystalline and amorphous. Crystalline forms of sulphur consist of S_8 molecules.



• Crystalline sulphur



Rnombic sulphur Transparent yellow crystals $T_m = 113 \ ^{\circ}C$ Monoclinic sulphur Brown needle shaped crystals $T_m = 119$ °C

• Amorphous sulphur

Examples are plasitic sulphur and colloidal sulphur.

Oxo - acids of sulphur •



• Dilute acids show acidic properties.

eg.
$$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$$

• Concentrated acids show oxidizing properties.

eg.
$$Cu(s) + 2H_2SO_4(aq) \rightarrow CuSO_4(aq) + SO_2(g) + H_2O(l)$$

• Concentrated acids also show dehydartion properties.

$$\mathrm{eg.}\qquad \mathrm{C_6H_{12}O_6(s)+H_2SO_4(aq)}\ \rightarrow\ \mathrm{6C(s)+H_2SO_4\cdot 6H_2O(aq)}$$

• Hydrogen peroxide (H_2O_2) H_2O_2 is a viscous liquid having inter molecular hydrogen bonds. Melting point and boiling point of H₂O₂ are 0.43 °C and 150 °C respectively.



Structure of gaseous hydrogen peroxide

• H_2O_2 as a reducing agent

$$\begin{split} & 2\mathrm{MnO}_4^{\text{-}}(\mathrm{aq}) + 5\mathrm{H}_2\mathrm{O}_2(\mathrm{aq}) + 6\mathrm{H}^{\text{+}}(\mathrm{aq}) \rightarrow 2\mathrm{Mn}^{2\text{+}}(\mathrm{aq}) + 8\mathrm{H}_2\mathrm{O}(\mathrm{l}) + 5\mathrm{O}_2(\mathrm{g}) \\ & \mathrm{MnO}_2(\mathrm{s}) + \mathrm{H}_2\mathrm{O}_2(\mathrm{aq}) + \mathrm{H}_2\mathrm{SO}_4(\mathrm{aq}) \rightarrow \mathrm{MnSO}_4(\mathrm{aq}) + \mathrm{O}_2(\mathrm{g}) + 2\mathrm{H}_2\mathrm{O}(\mathrm{l}) \\ & \mathrm{Ag}_2\mathrm{O}(\mathrm{s}) + \mathrm{H}_2\mathrm{O}_2(\mathrm{aq}) \rightarrow 2\mathrm{Ag}(\mathrm{s}) + \mathrm{O}_2(\mathrm{g}) + \mathrm{H}_2\mathrm{O}(\mathrm{l}) \end{split}$$

• H_2O_2 as an oxidizing agent

$$2H^{+}(aq) + H_{2}O_{2}(aq) + 2I^{-}(aq) \rightarrow I_{2}(aq) + 2H_{2}O(l)$$

$$4H_{2}O_{2}(aq) + PbS(s) \rightarrow PbSO_{4}(s) + 4H_{2}O(l)$$

$$2FeSO_{4}(aq) + H_{2}O_{2}(aq) + H_{2}SO_{4}(aq) \rightarrow Fe_{2}(SO_{4})_{3}(aq) + 2H_{2}O(l)$$

Water (H,O)

Due to amphiprotic properties of water it can act as both an acid and a base.

$$\begin{split} &H_2O(l) + NH_3(aq) \quad \Box \quad NH_4^+(aq) + OH^-(aq) \\ &H_2O(l) + HCl(aq) \quad \Box \quad H_3O^+(aq) + Cl^-(aq) \end{split}$$

• Sulphur dioxide (SO,)

It is a colourless gas with a higher density than air and with a pungent smell. It is very soluble water. 'n

- SO, dissolves in water to form sulphuric(IV) acid. It is a weak acid.
- $SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$ SO_2 as an oxidizing agent $2Mg(s) + SO_2(g) \longrightarrow 2MgO(s) + S(s)$ $3Mg(s) + SO_2(g) \rightarrow 2MgO(s) + MgS(s)$ • SO₂ as a reducing agent $SO_2(g) + 2H_2O(l) \xrightarrow{a} 4H^+(aq) + SO_4^{2-}(aq) + 2e$ (i) with $H^+/KMnO_4$ $5\mathrm{SO}_2(g) + 2\mathrm{H}_2\mathrm{O}(l) + 2\mathrm{KMnO}_4(\mathrm{aq}) \rightarrow \mathrm{K}_2\mathrm{SO}_4(\mathrm{aq}) + 2\mathrm{MnSO}_4(\mathrm{aq}) + 2\mathrm{H}_2\mathrm{SO}_4(\mathrm{aq})$ (ii) with $H^+/K_2Cr_2O_7$ $K_2Cr_2O_7(aq) + H_2SO_4(aq) + 3SO_2(g) \rightarrow K_2SO_4(aq) + Cr_2(SO_4)_3(aq) + H_2O(l)$ (iii) with aqueous FeCl₃ $2FeCl_{a}(aq) + SO_{b}(g) + 2H_{b}O(l) \rightarrow H_{b}SO_{a}(aq) + 2FeCl_{b}(aq) + 2HCl(aq)$ (iv) with halogens $SO_2(g) + Cl_2(g) + 2H_2O(l) \rightarrow H_2SO_4(aq) + 2HCl(aq)$ (v) with H₂O₂ $H_2O_2(aq) + SO_2(g) \rightarrow H_2SO_4(aq)$ As a bleaching agent $SO_2(g)+H_2O(l) \rightarrow H_2SO_3(aq)$ -----(1) $H_2SO_3(aq) + H_2O(l) \rightarrow H_2SO_4(aq) + 2H$ -----(2) $2H \rightarrow 2H^+ + 2e$ -----(3) (1) + (2) + (3); $SO_2(g) + 2H_2O(l) \rightarrow H_2SO_4(aq) + 2H^+(aq) + 2e$ \mathbf{H}_{n}

$$X + nH^+ + ne \rightarrow XH$$

Coloured dye Colourless compound

• Sulphur trioxide (SO₃)

SO₂ is a powerful acidic oxide, thus it fumes in moist air and react explosively with water to form sulphuric acid. For manufacture of sulphuric acid refer 15.2.

 $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$; Exothermic reaction

• Hydrogen sulphide (H₂S)

It is a colourless gas slightly soluble in water. It has the smell of rotten eggs. An aqueous solution of H_2S is somewhat acidic.

 $\begin{array}{rrr} H_2S(aq) & \square & H^+(aq) + HS^{-}(aq) \\ HS^{-}(aq) & \square & H^+(aq) + S^{2-}(aq) \end{array}$

- Evidence for the acidic nature
 - (i) Reactions with sodium

Excess $2Na(s) + 2H_2S(g) \rightarrow 2NaHS(s) + H_2(g)$ $2Na(s) + H_2S(g) \rightarrow Na_2S(s) + H_2(g)$

- (ii) Reaction with sodium hydroxide
 - When the base is in excess $2NaOH(aq) + H_2S(g) \rightarrow Na_2S(s) + 2H_2O(l)$
 - When H_2S is in excess $H_2S(g) + NaOH(aq) \rightarrow NaHS(s) + H_2O(l)$
- H₂S reacts with many metal ions such as Cu²⁺, Hg²⁺, Sn²⁺, Sb³⁺, Cd²⁺, Bi²⁺, Pb²⁺ to give sulphides. This is used as a test for identification of metal ions.

$$Pb^{2+}(aq) + H_2S(g) \rightarrow PbS(s) + 2H^+(aq)$$
$$Cu^{2+}(aq) + H_2S(g) \rightarrow CuS(s) + 2H^+(aq)$$

• H₂S as a reducing agent

(i) $2KMnO_4(aq)+3H_2SO_4(aq)+5H_2S(g) \rightarrow K_2SO_4(aq)+5S(s)+2MnSO_4(aq)+8H_2O(l)$ (ii) $K_2Cr_2O_7(aq)+4H_2SO_4(aq)+3H_2S(g) \rightarrow K_2SO_4(aq)+Cr_2(SO_4)_3(aq)+3S(s)+7H_2O(l)$ (iii) AsO_4^3 (aq) + 6H⁺(aq) + H_2S(g) $\rightarrow S(s) + As^{3+}(aq) + 4H_2O(l)$ As^{3+} reacts with aqueous S²⁻ ions to form a yellow precipitate. $2As^{3+}(aq) + 3S^{2-}(aq) \rightarrow As_2S_3(s)$

• H₂S as an oxidizing agent

 $Cu(s) + H_2S(g) \xrightarrow{a} CuS(s) + H_2(g)$

- Distinguishing between SO₂ and H₂S
 - (1) When the gases are passed through aqueous $H^+/K_2Cr_2O_7$, SO_2 and H_2S turn the orange colour to green but due to the formation of S with H_2S the solution will not be clear.
 - (2) A filter paper moistened with aqueous $Pb(CH_3COO)_2$ turns glistening black with H_2S .
 - (3) When passed through aqueous H⁺/KMnO₄ both gases turn the purple color to colorless but with H₂S the solution will not be clear due to S formed.
 - (4) Wet petals of flowers are bleached by SO_2 but not by H_2S .

• Halogens

- F₂ Pale yellow poisonous gas
 Cl₂ Yellowish light green poisonous gas
- I, - Shining greyish black solid. Sublimes and forms a violet vapour.
- A radioactive element At
- Reactions of chlorine
 - (i) Oxidizing property

$$\begin{split} & 2\mathrm{Cu}(s) + \mathrm{Cl}_2(g) \to 2\mathrm{Cu}\mathrm{Cl}(s) \\ & 2\mathrm{Cu}\mathrm{Cl}(s) + \mathrm{Cl}_2(g) \to 2\mathrm{Cu}\mathrm{Cl}_2(s) \\ & \mathrm{Fe}(s) + \mathrm{Cl}_2(g) \to \mathrm{Fe}\mathrm{Cl}_2(s) \\ & 2\mathrm{Fe}\mathrm{Cl}_2(s) + \mathrm{Cl}_2(g) \to 2\mathrm{Fe}\mathrm{Cl}_3(s) \\ & 2\mathrm{NH}_3(g) + 3\mathrm{Cl}_2(g) \to \mathrm{N}_2(g) + 6\mathrm{H}\mathrm{Cl}(g) \\ & 2\mathrm{KI}(\mathrm{aq}) + \mathrm{Cl}_2(g) \to \mathrm{KCl}(\mathrm{aq}) + \mathrm{I}_2(\mathrm{aq}) \\ & \mathrm{Oxidizing\ ability\ of\ halogen\ decreases\ down\ the\ group.} \end{split}$$

(ii) Bleaching property

$$\begin{aligned} \mathrm{H}_{2}\mathrm{O}(\mathrm{l}) + \mathrm{Cl}_{2}(\mathrm{g}) &\rightarrow \mathrm{HCl}(\mathrm{aq}) + \mathrm{HOCl}(\mathrm{aq}) \\ 4\mathrm{HOCl}(\mathrm{aq}) &\rightarrow 2\mathrm{Cl}_{2}(\mathrm{aq}) + \mathrm{O}_{2}(\mathrm{g}) + 2\mathrm{H}_{2}\mathrm{O}(\mathrm{l}) \end{aligned}$$

(iii) Disproportionation property

When chlorine gas dissolves in NaOH at or below room temperature a reasonably pure solution of NaOCl and NaCl is obtained.

$$Cl_2 + 2 \operatorname{NaOH}(aq) \rightarrow \operatorname{NaCl}(aq) + \operatorname{NaOCl}(aq) + H_2O(1)$$

With hot NaOH;

$$3Cl_2 + 6 \operatorname{NaOH}(aq) \longrightarrow 5\operatorname{NaCl}(aq) + \operatorname{NaClO}_3(aq) + 3H_2O(1)$$

However, in hot solution (above 80 °C) NaOCl disproportionates rapidly and gives a good yield of NaClO₃.

$$3NaOCl(aq) \rightarrow 2NaCl(aq) + NaClO_3(aq)$$

NaOBr and NaOI are not stable even at low temperatures.

• Oxo acids of chlorine





HOCl < HClO₂ < HClO₃ < HClO₄

Oxidation number and acidity increase. Therefore, oxidising ability also increases.

• Hydrogen halides (HX)

	Standard enthalpy	Standard bond disso	ociation
	(∆H [*])/kJ mol ⁻¹	(△H [*] _D)/kJ mol ⁻¹	Bond length increases.
HF	-273	562	Bond becomes weak.
HCl	-92	431	Stability decreases.
HBr	-36	366	Acidity increases.
HI	27	299	

Acidity of hydrogen halides in aqueous solution

Under dry conditions gaseous hydrogen halides are not forming ions. However, their aqueous solutions are acidic.

 $HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

Aqueous hydrofluoric acid is a weak acid due to its strong HF bond. All the other hydrogen halides are strong acids.

• Hydrolysis of the chlorides of groups 14 and 15

$$\begin{split} & \operatorname{CCl}_4 \operatorname{does} \operatorname{not} \operatorname{hydrolyze.} \\ & \operatorname{SiCl}_4(1) + 2\operatorname{H}_2 O(1) \rightarrow 4\operatorname{HCl}(\operatorname{aq}) + \operatorname{SiO}_2(s) \\ & \operatorname{SiCl}_4(1) + 3\operatorname{H}_2 O(1) \rightarrow 4\operatorname{HCl}(\operatorname{aq}) + \operatorname{H}_2 \operatorname{SiO}_3(\operatorname{aq}) \\ & \operatorname{NCl}_3(1) + 3\operatorname{H}_2 O(1) \rightarrow \operatorname{NH}_3(\operatorname{aq}) + 3\operatorname{HOCl}(\operatorname{aq}) \\ & \operatorname{PCl}_3(1) + 3\operatorname{H}_2 O(1) \rightarrow \operatorname{H}_3 \operatorname{PO}_3(\operatorname{aq}) + 3\operatorname{HCl}(\operatorname{aq}) \\ & \operatorname{PCl}_5(1) + \operatorname{H}_2 O(1) \rightarrow \operatorname{POCl}_3(\operatorname{aq}) + 2\operatorname{HCl}(\operatorname{aq}) \\ & \operatorname{PCl}_5(1) + 4\operatorname{H}_2 O(1) \rightarrow \operatorname{H}_3 \operatorname{PO}_4(\operatorname{aq}) + 5\operatorname{HCl}(\operatorname{aq}) \\ & \operatorname{PCl}_5(1) + 4\operatorname{H}_2 O(1) \rightarrow \operatorname{H}_3 \operatorname{PO}_4(\operatorname{aq}) + 3\operatorname{HCl}(\operatorname{aq}) \\ & \operatorname{AsCl}_3(s) + 3\operatorname{H}_2 O(1) \rightarrow \operatorname{H}_3 \operatorname{AsO}_3(\operatorname{aq}) + 3\operatorname{HCl}(\operatorname{aq}) \\ & \operatorname{SbCl}_3(\operatorname{aq}) + \operatorname{H}_2 O(1) \bigoplus \operatorname{H}_3 \operatorname{BoCl}(s) + 2\operatorname{HCl}(\operatorname{aq}) \\ & \operatorname{BiCl}_3(\operatorname{aq}) + \operatorname{H}_2 O(1) \bigoplus \operatorname{BiOCl}(s) + 2\operatorname{HCl}(\operatorname{aq}) \end{split}$$

• Noble gases and their compounds



Boiling points are very low. The boiling points increase with the increase in atomic number. Polarizability appears in large atoms. Xe forms compounds with fluorine and oxygen.

eg. XeF₂, XeF₄, XeF₆, XeO₃

Due to the ability of forming compounds, electronegativity values have also been assigned to noble gases.

Suggested learning - teaching activities:

- Direct students to draw and name structures of oxoacids of sulphur.
- Give examples for the reactions in which hydrogen peroxide, sulphur dioxide and hydrogen sulphide react as oxidizing agents and reducing agents.
- Write balanced equations to show oxidizing ability of HNO₃ and H₂SO₄.
- Give examples for four types of oxides.

Competency 6.0		Investigates the elements and compounds of s , p and d blocks to be familiar with their properties.
Competency Level 6.4	:	Investigates properties of elements of <i>d</i> block to identify their variation across the period.
Periods	:	05

Learning outcomes :

- States the variable oxidation states shown by the *d* block elements of the fourth period and compares this property with that of the *s* and *p* block elements.
- Compares the pattern of variation of the electronegativity, first ionization energy, metalic nature and ionic radii of the *d* block elements.
- Describes giving suitable examples the ability of the elements and compounds of the *d* block to function as catalysts and also the property of forming coloured compounds.

Guidance for teacher elaboration :



First ionization energy graph of elements from H to Cs

Variation of metalic	radius, e	lectronne	gativity	and ionisa	ation energ	gy from So	c to Zn			
		1. 1		Cr	, Ma	. Fe	. Co	Ni	Cu	2n
Metalic (atomic) radius / nm	0.16	0.15	0.14	0.13	0.14	0.13	0.13	0.13	0.13	0.13
Electronegativity	1.2	1.3	1.45	1.55	1.6	1.65	1.7	1.75	1.75	1.6
First Ionisation Enegy / kJ mol ⁻¹	+630	+660	+650	+650	+720	+760	+760	+740	+750	+910
Second Ionization Energy / kJ mol-1	+1240	+1310	+1410	+1590	+1510	+1560	+1640	+1750	+1960	+1700
Third Ionisation Energy / kJ mol ⁻¹	+2390	+2650	+2870	+2990	+3260	+2960	+3230	+3390	+3560	+3800

			d - Block elements									
S	- block ele	ements										
,			<i>c</i>					~				
Elements			Sc	1	12		TRANS IN CONSIST		the state	高加斯方	u)	
Atomic radius/ nm	0.24	0.20	0.16	0.15	0.14	0.13	0.14	0.13	0.13	0.13	0.13	0.13
Melting point /ºC	64	850	1540	1680	1900	1890	1240	1540	1500	1450	1080	420
boling point /0C	770	1490	2730	3260	3400	2480	2100	2000	2000	3730	2600	420
Density /g cm ⁻³	0.86	1.54	3.0	4 5	6 1	7.9	7 (7.0	2300	2730	2000	910
Ionic radius /nm					0.1	1.2	1.4	7.9	8.9	8.9	8.9	7.1
M*	0.130											
W ²⁺	1110	0.004		0.000	0.000							
		0.094		0.090	0.088	0.084	0.080	0.076	0.074	0.072	0.070	0.074
			0.081	0.076	0.074	0.069	0.066	0.064	0.063	0.062		

Physical properties of elements from K to Zn

s elements. According to the given data density values of *d* elements are comparatively higher than Therefore, all *d* elements are considered as heavy metals.

		Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn
Common oxides	{	Sc ₂ O ₃	Ti ₂ O ₃ TiO ₂	V ₂ O ₃ V ₂ O ₅	Cr ₂ O ₃ CrO ₃	MnO MnO ₂ Mn ₂ O ₇	FeO Fe ₂ O ₃	CoO Co ₂ O ₃	NiO	Cu ₂ O CuO	ZnO
Common chlorides	{	ScCl ₃	TiCl ₃ TiCl ₄	VCl ₃	CrCl ₂ CrCl ₃	MnCl ₂	FeCl ₂ FeCl ₃	CoCl ₂	NiCl ₂	CuCl CuCl ₂	ZnCl ₂
Oxidation numbers shown in the compounds	,	III	II III IV	II III IV V	(I) II III IV V V VI	II III IV V VI VI VII	II III IV V VI	II III IV V	II III IV	І 11 111	п

Oxidation numbers of elements from **Sc** to **Zn** (Common oxidation numbers are shown in bold letters)

Instances where *d* block elements and their compounds are used in industry as catalysts.

d block	substances used	Reaction that is
elements	as catalysts	catalyzed
Ti	TiCl ₃ /Al ₂ (C ₂ H ₅) ₆	$nC_2H_4 \rightarrow \begin{pmatrix} H & H \\ I & I \\ C - C \\ I & H \\ H & H \end{pmatrix}_n$
		Polymerization of ethene
V	V_2O_5 or vanadate (VO_3^2)	$2SO_2 + O_2 \blacksquare \blacksquare 2SO_2$
	2 5 . 2.	Contact process
Fe	Fe or Fe ₂ O ₃	$N_2 + 3H_2$ 1 1 2 NH_3 Haber process
Ni	Ni	$RCH = CH_2 + H_2 \rightarrow RCH_2CH_3$ Production of margarine
Cu	CuCl	Sand Mayer reaction (Refer 11.3)
Pt	Pt	$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ $NO \rightarrow NO_2 \rightarrow HNO_3$ Preparation of nitric acid from ammonia (Refer 15.2)

• Formation of coloured compounds

Transition ions formed by d block metals have partially filled d orbitals. These ions absorb selected range of wave length in white light and get excited and shows the complementary colours. However, d^0 and d^{10} confingurations are colourless.

- $Sc^{\rm 3+}$ Colourless
- Ti^{4+} Colourless
- Ti³⁺ Purple
- V³⁺ Green
- V²⁺ Violet
- Cr^{3+} Purple
- Mn^{3+} Violet
- Mn²⁺ Pale pink
- Fe^{3+} Brown yellow
- Fe^{2+} Pale green

Colours of some oxoanions: Usually, d element oxoanions are coloured.

- MnO_4^{-} Purple/Violet
- $\mathrm{Mn} \bigcirc_4^{2\text{-}}$ Green
- ${\mathbb C}r{\mathbb O}_4^{2\text{-}}$ -Yellow
- $Cr_2O_7^{2-}$ Orange

Suggested learning - teaching activities

- Exhibit several coloured compounds of d block elements and their aqueous solutions.
- Emphasis the formation of various coloured compounds and oxidation number of metals in them.
- Provide group of students with graphical and tabulated data and direct to explore the variation of an assigned property from Sc to Zn.
- Direct group of students to compare the assigned property with those of the of *s* and *p* block elements.

- Co^{2+} Pink
- Ni^{2+} Green Cu^{2+} - Blue
- Cu^+ Colourless

Zn^{2+} - Colourless

Competency 6.0		Investigates the elements and compounds of <i>s</i> , <i>p</i> and <i>d</i> blocks to be familiar with their properties.				
Competency Level 6.5	:	Investigates properties of compounds of <i>d</i> block.				
Periods	:	06				

Learning outcomes

- Expresses acidic/basic/amphoteric nature of oxides of vanadium chromium and manganese.
- Gives examples for reactions in which oxo-anions of chromium and manganese act as oxidizing agents.

Guidance for teacher elaboration :

Oxides of manganese	Oxidation number	Nature of the oxide
MnO	$+\Pi$	Basic
Mn ₂ O ₃	+III	Weakly basic
MnO ₂	+IV	Amphoteric
MnO ₃	+VI	Weakly acidic
Mn ₂ O ₇	+VII	Acidic

Oxides of chromium	Oxidation number	Nature of the oxide
CrO	+II	Weakly basic
Cr ₂ O ₃	+III	Amphoteric
CrO ₂	+IV	Weakly acidic
CrO ₃	+VI	Acidic

Oxides of vanadium	Oxidation number	Nature of the oxide
VO	$+\Pi$	Basic
V ₂ O ₃	+III	Basic
VO ₂	+IV	Amphoteric
V ₂ O ₅	+V	Acidic

- Using the solubility in acids and bases of the types of oxides stated above, they can be classified as acidic, basic or amphoteric.
- The reaction of MnO_4^{-} in an acidic medium as an oxidizing agents with SO_2^{-} , H_2S^{-} , Fe^{2+} , Γ , Br etc.

eg. With SO_2 ;

Reduction half reaction

$$\begin{split} & \mathrm{MnO}_4^{\text{-}}(\mathrm{aq}) + 5\mathrm{e} + 8\mathrm{H}^{\text{+}}(\mathrm{aq}) \rightarrow \mathrm{Mn}^{2\text{+}}(\mathrm{aq}) + 4\mathrm{H}_2\mathrm{O}(\mathrm{l}) \\ & (\mathrm{+VII}) & (\mathrm{+II}) \end{split}$$

Oxidation half reaction

 $\begin{array}{rll} \mathrm{SO}_2(g) &+ \ 2\mathrm{H}_2\mathrm{O}(l) \rightarrow & \mathrm{SO}_4^2 \ (\mathrm{aq}) \ + \ 2\mathrm{e} \ + \ 4\mathrm{H}^+(\mathrm{aq}) \\ (\mathrm{+IV}) & (\mathrm{+VI}) \end{array}$

Balanced ionic equation

$$2 \operatorname{MnO}_{4}^{\cdot}(aq) + 5 \operatorname{SO}_{2}(g) + 2 \operatorname{H}_{2}O(l) \rightarrow 2 \operatorname{Mn}^{2+}(aq) + 5 \operatorname{SO}_{4}^{2+}(aq) + 4 \operatorname{H}^{+}(aq)$$
(+VII) (+IV) (+IV) (+VI)

• The reaction of MnO_4^- as an oxidizing agent in a basic medium with SO_2^- Reduction half reaction

$$MnO_{4}^{-}(aq) + 3e + 2H_{2}O(l) \rightarrow MnO_{2} + 4OH^{-}(aq)$$
(+VII) (+IV)

Oxidation half reaction

$$SO_{2}(g) + 4OH^{-}(aq) \rightarrow SO_{4}^{2}(aq) + 2H_{2}O(l) + 2e$$
(+IV)
(+VI)

Balanced ionic equation

$$2\operatorname{MnO}_{4}^{-}(\mathrm{aq}) + 3\operatorname{SO}_{2}(\mathrm{g}) + 4\operatorname{OH}^{-}(\mathrm{aq}) \rightarrow 2\operatorname{MnO}_{2} + 3\operatorname{SO}_{4}^{2}(\mathrm{aq}) + 2\operatorname{H}_{2}\operatorname{O}(\mathrm{I})$$
(+VII) (+IV) (+VI)

The reaction of $Cr_2O_7^{-2}$ as an oxidzing agent in an acidic medium

$$\begin{aligned} & \mathbb{C}r_{2} \bigcirc_{7}^{2} (aq) &+ 14 \mathrm{H}^{\scriptscriptstyle +}(aq) + 6e &\to 2 \mathrm{C}r^{3+}(aq) + 7\mathrm{H}_{2}\mathrm{O}(l) \\ & \mathrm{SO}_{2}(g) + 2\mathrm{H}_{2}\mathrm{O}(l) \to 4\mathrm{H}^{\scriptscriptstyle +}(aq) + \mathrm{SO}_{4}^{2} (aq) + 2e \\ & \mathbb{C}r_{2} \bigcirc_{7}^{2} (aq) + 2\mathrm{H}^{\scriptscriptstyle +}(aq) + 3\mathrm{SO}_{2}(g) \to 2 \mathrm{C}r^{3+}(aq) + \mathrm{H}_{2}\mathrm{O}(l) + 3 \mathrm{SO}_{4}^{2} (aq) \end{aligned}$$

Suggested learning - teaching activities

- Inquire about the formulae for the oxides that can exist for V, Cr and Mn according to the variable oxidization states shown.
- Give opportunities to develop balanced ionic equations for the reactions of CrO_4^2 , $Cr_2O_7^2$, and MnO_4^- with various reducing agents (like SO_2 and H_2S) in acidic and basic media using separate ionic half reactions.

Competency 6.0	: Investigates the elements and compounds of <i>s</i> , <i>p</i> and <i>d</i>
	blocks to be familiar with their properties.

Competency Level 6.6 : Investigates properties of complex compounds of *d* block to be familiar with their variety.

Periods : 10

Learning outcomes

- States the colours of complex compounds of the elements Cr, Mn, Fe, Co, Ni and Cu formed with the ligands H₂O, NH₃, OH⁻ and Cl⁻.
- Shows by giving suitable examples how the central atom, the oxidation state and the ligand system of a complex ion affect the colour of a complex compound.
- Observes the reactions of copper(II), cobalt(II) and nickel(II) salts with hydrochloric acid and ammonia and reports them.
- Observes the colours relevant to the oxidation states +2, +4, +6 and +7 of manganese and reports them.

Guidance for the teacher elaboration :

• Complex ions formed by the elements Cr, Mn, Fe, Co, Ni and Cu with the ligands H₂O, NH₃ and Cl⁻

Ligand	Central metal ion								
system	Cr ³⁺	Mn ²⁺	Fe ³⁺	Co ²⁺	Ni ²⁺	Cu^{2+}			
H ₂ O	$[Cr(H_2O)_6]^{3+}$	[Mn(H ₂ O) ₆] ²⁺	$[Fe(H_2O)_6]^{3+}$	[Co(H ₂ O) ₆] ²⁺	$[Ni(H_2O)_6]^{2+}$	$[Cu(H_2O)_6]^{2+}$			
	Blue - violet	Pale pink	Yellow	Pink	Green	Blue			
NH ₃	$[Cr(NH_3)_6]^{3+}$ Yellow (formed in liquid	Complex ion is not formed. But hydroxide is formed.	Complex ion is not formed. But hydroxide is formed.	$[Co(NH_3)_6]^{2+}$ Yellow brown	$[Ni(NH_3)_6]^{2+}$ Deep blue	$[Cu(NH_3)_4]^{2+}$ Deep blue			
	NH ₃)								
Cŀ	[CrCl ₄] ⁻	$[MnCl_4]^2$ -	[FeCl ₄] ⁻	[CoCl ₄] ²⁻	[NiCl ₄] ²⁻	$[CuCl_4]^{2-}$			
	Blue violet	Greenish yellow	Yellow	Blue	Yellow	Yellow			

• OH⁻ acts as a ligand in few *d* block cations.

eg. $[Fe(H_2O)_5OH]^{2+}$ formed by the hydrolysis of hydrated Fe³⁺ ions. However, most metal ions with NaOH or NH₃ give insoluble hydroxides and not hydroxo complexes. Hydroxides of some elements has to be discussed,

- eg. $Cr(OH)_3$ Green, $Fe(OH)_3$ Reddish brown, $Fe(OH)_2$ Dirty green, $Cu(OH)_2$ - Blue, $Mn(OH)_2$ - White
- The colour of the complex varies depending on the central metal atom.
 - eg. $[Cr(H_2O)_6]^{3+}$ Blue violet $[Fe(H_2O)_6]^{3+}$ Yellow

• The colour of the complex varies depending on the oxidation state of the central metal atom.

eg.	$[Fe(H_2O)_6]^{2+}$ - Pale green	$[Fe(H_2O)_6]^{3+}$ - Yellow
	$[Mn(H_2O)_6]^{2+}$ - Pale pink	$[Mn(H_2O)_6]^{3+}$ - Violet

- The colour changes also when the ligands change.
 eg. [Co(H₂O)₆]²⁺ Pink [Co(NH₃)₆]²⁺ Yellow brown
- The reaction of aqueous Cu^{2+} ions with HCl(aq) $Cu^{2+}(aq) + 4HCl(aq) \rightarrow [CuCl_4]^{2-}(aq) + 4H^+(aq)$ Blue Yellow
- The reaction of aqueous Co²⁺ ions with HCl(aq)

$$Co^{2+}(aq) + 4HCl(aq) \rightarrow [CoCl_4]^{2-}(aq) + 4H^{+}(aq)$$

Pink Blue

• Oxo- anions of chromium and their conversion

$$2CrO_4^{2-}(aq) + 2H^+(aq) \blacksquare m Cr_2O_7^{2-}(aq) + H_2O(1)$$

Yellow

Orange

 $\operatorname{Cr}_2 \bigcirc_7^2 (\operatorname{aq}) + 2 \bigcirc H^-(\operatorname{aq}) \nexists \textcircled{P} 2 \bigcirc 2 \operatorname{Cr} \bigcirc_4^{2-}(\operatorname{aq}) + \operatorname{H}_2 \bigcirc (1)$

Orange

Yellow

• NH₃ acts as a ligand.

 $\begin{array}{ll} \operatorname{Cu}^{2^{+}}(\operatorname{aq}) + 4\operatorname{NH}_{3}(\operatorname{aq}) \rightarrow \left[\operatorname{Cu}(\operatorname{NH}_{3})_{4}\right]^{2^{+}}(\operatorname{aq}) \\ & \text{Pale blue} & \text{Deep blue} \\ & \operatorname{Co}^{2^{+}}(\operatorname{aq}) + 6\operatorname{NH}_{3}(\operatorname{aq}) \rightarrow \left[\operatorname{Co}(\operatorname{NH}_{3})_{6}\right]^{2^{+}}(\operatorname{aq}) \\ & \text{Pink} & \text{Yellow brown} \\ & \operatorname{Nh}^{2^{+}}(\operatorname{aq}) + 6\operatorname{NH}_{3}(\operatorname{aq}) \rightarrow \left[\operatorname{Nh}(\operatorname{NH}_{3})_{6}\right]^{2^{+}}(\operatorname{aq}) \\ & \text{Green} & \text{Blue} \end{array}$

Suggested learning - teaching activities

- Exhibit samples of complex compounds which are examples for the variation of colour due to the central atom, oxidation state and ligand system.
- Give opportunities for the students to engage in the given practical activities in groups.
- Give opportunities to observe colours of various oxidation states of manganese.

Competency 6.0: Investigates the elements and compounds of s, p and d
blocks to be familiar with their properties.Competency Level 6.7: Names simple inorganic compounds and complex compounds
of the d block elements.

Periods: 03

Learning outcomes :

- Names simple inorganic compounds.
- States the importance of IUPAC nomenclature.
- Names complexes with simple cations and complex anions and those with simple anions and complex cations according to the IUPAC nomenclature.
- Presents the structure when the IUPAC name of a compound is given.

Guidance for teacher elaboration :

IUPAC nomenclature of complexes

• Here, the information required to develop the IUPAC name of a complex and to write the structural formula when the IUPAC name is given will be discussed. Only complexes formed by elements of the *d* block are considered.

The complexes are considered simply under two categories.

- (i) Cations are simple while the anions are complex.
- (ii) Cations are complex while the anions are simple.
- Whatever the complex considered, a common set of rules has to be followed stepwise in their nomenclature.

Writing the name of a complex

- (1) As in the case of a simple inorganic compound, first the cation is named and then the anion. A space is left between the name of the cation and the name of the anion.
- (2) The complex ion in the compound can be either positively charged or negatively charged. First, identify the metal ion and the ligand/s in the complex ion.
- (3) The ligands could be negatively charged, neutral or positively charged (rarely). When naming the ligands, the charge of the ligand is considered.
 - (i) Neutral ligands have no special ending.
 - (ii) Some ligands have special names.

Examples: H₂O aqua NH₃ ammine CO carbonyl NO nitrosyl (iii) For negatively charged ligands an "o" is added to their English name.

Examples:	Cl	chlorido
	CN-	cyanido
	NO_2^-	nitrito
	OH-	hydroxido
	SCN-	thiocyanato
	H	hydrido
	O ²⁻	oxido

(iv) For positively charged ligands the suffix" ium" is added to their English name.

Example: ⁺NH₃-NH₂ hydrazinium

(4) When there is more than one ligand of the same type, in order to indicate the number of such ligands, the name of the relevant number is used as a prefix to the name of the ligand.

When there are 2, 3, 4, 5 and 6 ligands of the same type, the prefixes di-, tri,- tetrapenta- and hexa- are used respectively.

Note: Organic ligands need not be considered.

- (5) When several ligand types are present in a complex ion, in naming the ligands they are listed in the alphabetical order (English) of the first letter of the **ligand**.
 - **Note:** The first letter of the prefix used to denote the number of ligands is NOT considered when deciding the alphabetical order.

No space is left between the names of the ligands.

Example: $[Fe(CN)_2(NH_3)_4]^+$

Ligands are named as; tetraamminedicyanido

(6) When writing the name of the complex ion, the ligands are named first and then the metal ion. The oxidation number of the metal ion is given in capital Roman numerals, within parentheses, after the name.

No space is left between the words when writing the name.

Examples:

$[Co(NH_3)_6]^{3+}$	hexaamminecobalt(III) ion
$[Fe(H_2O)_6]^{2+}$	hexaaquairon(II) ion
$[Cu(NH_3)_4]^{2+}$	tetraamminecopper(II) ion

- (7) The complex may be positively charged, negatively charged or neutral. Depending on this, the name also changes.
 - (i) When the complex is positively charged or neutral, the name of the complex ends with the name of the metal.

Reminder:

The name of the metal is followed by the oxidation number of the metal ion, in capital Roman numerals, within parentheses. No space is left between the name of the metal ion and the oxidation number given in parantheses.

Example:

 $[Fe(CN)_3(NH_3)_3]$

The complex is neutral. Hence, its name is triamminetricyanidoiron(III).

Example:

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

The complex is positively charged. Its name is hexaaquacopper(II) ion.

(ii) When the complex ion is negatively charged, the suffix 'ate' is added to the end of the name of the metal. Here also the oxidation number of the metal ion should be indicated in capital Roman numerals within parentheses. No space is left between the name of the metal ion and the oxidation number given in parentheses.

Examples:

$[\operatorname{CoCl}_4]^{2-}$	tetrachloridocobaltate(II) ion
$[Co(CN)_{6}]^{3-}$	hexacyanidocobaltate(III) ion
$[CuCl_4]^{2-}$	tetrachloridocuprate(II) ion
$[Fe(CN)_{6}]^{4-}$	hexacyanidoferrate(II) ion
$[Fe(CN)_{6}]^{3-}$	hexacyanidoferrate(III) ion
$[Ag(CN)_2]^-$	dicyanidoargentate(I) ion
$[Cr(Br)_{6}]^{3-}$	hexabromidochromate(III) ion

The IUPAC name of any compound can be developed by systematically following the rules studied so far.

(8) When writing the name of a coordination compound, a space should be left between the name of the positively charged species and the negatively charged species.
Examples :

Examples:

• Simple cation and complex anion

$K_{3}[Fe(CN)_{5}NO]$	potassium pentacyanidonitrosylferrate(II)
$Na_{2}[ZnCl_{4}]$	sodium tetrachloridozincate(II)

• Complex cation and simple anion

$[Ag(NH_3)_2]Cl$	diamminesilver(I) chloride
[Fe(OH) ₂ (H ₂ O) ₄]Br	tetraaquadihydroxidoiron(III) bromide
$[\text{CoCl}(\text{NH}_3)_5](\text{NO}_3)_2$	pentaamminechloridocobalt(III) nitrate
$[\text{CoCl(NH}_3)_5](\text{NO}_2)_2$	pentaamminechloridocobalt(III) nitrite

Writing formula of a complex when its name is given

- 1. The positively charged species is written first, followed by the negatively charged species. No space is left between them.
- 2. The complex part of the compound is always written within square brackets.
- 3. When the formula of the complex ion is written, the metal should be indicated first and then the ligands. In writing the ligands, the charge on the ligand is NOT considered. The ligands are written in the alphabetical order of the ligating atoms.

(*i.e.* Atom through which the ligand coordinates to the metal ion).

Note: In multiatomic ligands, where possible, it is recommended that the ligating atom is placed first followed by the other atoms in the ligand.

Example : $(:OH_2)$ rather than H_2O

- 4. Multi atomic ligands are given in parentheses. The number of each type of ligand is given in Arabic numerals as a subscript on the right hand side immediately after the symbol of the ligand. If parentheses are present, this number is written as a subscript on the right hand side without leaving a space, just outside the parentheses.
- 5. The formula of a complex ion should be written within square brackets. If the complex ion has a charge, it should be indicated outside the square bracket as a superscript on the right side. The numerical value should be given first followed by the sign of the charge.
 - **Note:** No space is left between the formulae of the ligands or between the formulae of the ligands and symbol of the metal ion.

Example 1

Write the chemical formula of pentacyanidonitrosylferrate(II) ion.

Step 1: Write the symbol of the metal.

Fe

Step 2: Decide on the order of the ligands. Include the number of ligands of each type when writing their symbols/formulae. Then write the symbols / formulae of the ligands after the symbol of the metal.

The ligands are CN^{-} (ligating atom is C) and NO (ligating atom is nitrogen) hence, the order is CN^{-} followed by NO. Both ligands are multi-atomic. Hence, their formulae are placed within parentheses. The presence of five CN^{-} ligands are indicated.

 $Fe(CN)_{5}(NO)$

Step 3: Place the symbol of the metal ion and the formulae of the ligands within square brackets and show charge of complex.

Oxidation number of metal is +II. Overall charge of the complex ion is

+2+(-5)=-3

Chemical formula is [Fe(CN)₅NO]³⁻

Example 2

Write the chemical formula of pentaamminechloridocobalt(III) ion.

Step 1: Write the symbol of the metal.

Co.

Step 2: Decide on the order of the ligands. Include the number of ligands of each type when writing their symbol/formula. Then write the symbols/ formulae of the ligands after the symbol of the metal.

Ligands are Cl⁻ (ligating atom is Cl) and NH₃ (ligating atom is N). Considering the alphabetical order of the ligating atoms, Cl⁻ is written first followed by NH₃. The NH₃ ligand is multi-atomic and hence the formula is placed within parentheses. The presence of five NH₃ ligands is indicated.

CoCl(NH₃)₅

Step 3: Place the symbol of the metal and the formulae of the ligands within square brackets and show charge of complex.

Oxidation state of the metal ion is +III. Therefore, overall charge of the complex is

+3 + (-1) = +2

Chemical formula is; [CoCl(NH₃)₅]²⁺

Example 3

Write the chemical formula of pentaamminechloridocobalt(III) bromide.

As shown in Example 2, the chemical formula of the complex ion is;

 $[CoCl(NH_3)_5]^{2+}$.

Two Br ions are required to neutralize the charge on this complex ion. Therefore, the formula is; $[CoCl(NH_3)_5]Br_2$

Suggested learning - teaching activities

- Take several simple compounds such as NaCl, AlH₃. Mg₃N₂, CuCl₂, Na₂SO₃, Fe(NO)₃, etc. and name them.
- Divide the class into groups. Give the students names of compounds with simple anions and complex cations and also those with simple cations and complex anions.
- Instruct the students to write their formulae.

Competency 6.0	:	Investigates the elements and compounds of <i>s</i> , <i>p</i> and <i>d</i> blocks to be familiar with their properties.	
Competency Level 6.8		Identifies cations by qualitative analysis.	
Periods	:	10	
Learning outcomes	:	 Identifies the cations using flame test. Explains the colour of the flame using the corresponding emission spectrum. Identifies the cations by precipitation methods and subsequent solubility of the precipitate in different reagents. Identifies the ammonium ion (NH₄⁺) by adding a solution of an alkali. Divides the cations listed into five groups, based on the solubility products of the ionic compounds of the cations. 	

Guidance for teacher elaboration :

Flame Test

• Almost all cations form atoms in a flame test. The colour of the flame in the flame test is associated with elements possessing low energy gaps.

$$\Delta E = \frac{hc}{\lambda}$$
M* excited atom
$$M = \frac{hc}{\lambda}$$
M ground state atom

Cations identified by precipitation

 The precipitates of the cations having d⁷, d⁸, d⁹ and d¹⁰ electronic configurations are soluble in excess ammonia and form the respective stable complex ions.
 M²⁺(aq) + X²⁻(aq) → MX(s)

- (d^7) $[Co(NH_3)_6]^{2+}$ Yellow brown (d^{10}) $[Zn(NH_3)_4]^{2+}$ colourless
- (d^8) [Ni(NH₃)₆]²⁺ Deep blue (d^{10}) [Ag(NH₃)₂]⁺ colourless
- (d^9) [Cu(NH₃)₄]²⁺ deep blue (d^{10}) [Cd(NH₃)₄]²⁺ colourless

Identification of NH₄⁺

• Ammonium salts give ammonia gas with solutions of alkali(NaOH, KOH, Ca(OH)₂ etc). eg. $NH_4Cl(s) + NaOH(aq) \rightarrow NH_3(g) + Na^+(aq) + Cl^-(aq) + H_2O(l)$

The evolved NH_3 gas can be tested with Nessler's reagent or moist red litmus paper. $NH_3(g)$ + Nerssler's reagent \rightarrow brown precipitate/colouration

Separation procedure of a mixture of cations (Refer 13.4)

• Qualitative analysis of a mixture of cations involves the separation of them to five groups. The scheme of qualitative analysis is based on the principle of selective precipitation. The precipitation of cations from a solution one at a time is called selective precipitation.

Group I

Cold, excess dilute HCl is added to a solution containing a mixture of cations. Only Ag⁺, Pb²⁺ and Hg₂²⁺ will be precipitated as insoluble chlorides (AgCl, PbCl₂, Hg₂Cl₂).

Group II

• After the separation of the insoluble chlorides in Group I, the filtrate is still acidic. When H₂S is passed through the solution, only insoluble sulphides get precipitated.

$Pb^{2+}(aq) \rightarrow PbS(s)$	$As^{3+}(aq) \rightarrow As_2S_3(s)$
(black)	(yellow)
$Cu^{2+}(aq) \rightarrow CuS(s)$	$\mathrm{Sn}^{4+}(\mathrm{aq}) \rightarrow \mathrm{SnS}_2(\mathrm{s})$
(black)	(yellow)
$Hg^{2+}(aq) \rightarrow HgS(s)$	$Sb^{3+}(aq) \rightarrow Sb_2S_3(s)$
(black)	(orange)
$Cd^{2+}(aq) \rightarrow CdS(s)$	$\operatorname{Sn}^{2+}(\operatorname{aq}) \to \operatorname{SnS}(\operatorname{s})$
(yellow)	(brown)
$\mathrm{Bi}^{3+}(\mathrm{aq}) \rightarrow \mathrm{Bi}_{2}\mathrm{S}_{3}(\mathrm{s})$	
(black)	

• The concentration of sulphide ion is relatively low because of the higher concentration of H⁺ ions. Other cations such as Mn^{2+} , Zn^{2+} , Ni^{2+} and Co^{2+} with higher K_{sp} values of their respective sulphides will remain in the solution.

Group III

• The filtrate from Group II is boiled for a few minutes to expel all the dissolved H_2S . Then boil the filtrate for a few minutes with conc.HNO₃ to oxidise Fe²⁺ to Fe³⁺. The solution is treated with NH₄Cl and NH₄OH.

$Fe^{3+}(aq)$	$Fe(OH)_3(s)$	(reddish brown)
$Al^{3+}(aq)$	$Al(OH)_3(s)$	(white gelatinous)
Cr ³⁺ (aq)	$Cr(OH)_3(s)$	(green)

Group IV

• The filtrate from Group III contains OH^2 ions and is basic. H_2S is passed through this solution in the presence of OH^2 ions. Then H^2 ions produced from H_2S are neutralised by hydroxyl ions.

• The above equilibrium shifts to the right and the concentration of S²⁻ ions increases.

Group V

Boils off H₂S from Group IV filtrate and add a little amount of NH₄Cl and NH₄OH in excess. Heat the solution, then add (NH₄)₂CO₃ solution. Here Ca²⁺, Sr²⁺ and Ba²⁺ ions are precipitated as carbonates.

$$\begin{array}{c} \operatorname{Ca}^{2+}(\operatorname{aq}) & \xrightarrow{(\operatorname{NH}_4)_2 \operatorname{CO}_3(\operatorname{aq})} \to \operatorname{CaCO}_3(s) \\ & (\text{white}) \\ \operatorname{Sr}^{2+}(\operatorname{aq}) & \xrightarrow{(\operatorname{NH}_4)_2 \operatorname{CO}_3(\operatorname{aq})} \to \operatorname{Sr}\operatorname{CO}_3(s) \\ & (\text{white}) \\ \operatorname{Ba}^{2+}(\operatorname{aq}) & \xrightarrow{(\operatorname{NH}_4)_2 \operatorname{CO}_3(\operatorname{aq})} \to \operatorname{BaCO}_3(s) \\ & (\text{white}) \end{array}$$

• Applications of solubility product will be discussed at lenght under 13.4.

Suggested learning-teaching activities:

- Let students to identify cations in a given mixture by flame tyest.
- Assign students to identify cations in a given mixture by other methods.

Competency 6.0 Competency Level 6.9 Periods		Investigates the elements and compounds of <i>s</i> , <i>p</i> and <i>d</i> blocks to be familiar with their properties.	
		Identifies anions by qualitative analysis.	
		05	
Learning outcomes	:	 Identifies the anions using precipitation method or other methods. Explains the solubility of the precipitates in acids based on the nature of the anions. Explains the solubility of precipitates due to complexing of cations with ammonia. 	
Guidance for teacher ela	abo	ration :	

• The anions Cl⁻, Br⁻, I⁻, S²⁻, SO₄²⁻, SO₃²⁻, S₂O₃²⁻, CO₃²⁻, NO₂⁻, NO₃⁻ and PO₄³⁻ can be identified by the specific tests.

Tests for Cl⁻, Br⁻ and I⁻

• To a solution of the halide ions add dil. HNO_3 and $AgNO_3(aq)$. Silver halides will be precipitated. To identify the halide ion the solubility of the precipitate in ammonia solution is used.

$$Cl^{-}(aq) \xrightarrow{dd.HNO_{3}} AgCl(s) \xrightarrow{ddLNH_{3}} dissolves completely giving [Ag(NH_{3})_{2}]^{+} ion$$
(white)

$$Br^{-}(aq) \xrightarrow{dal.HNO_{3}} AgBr(s) \xrightarrow{conc.NH_{3}} dissolves completely giving [Ag(NH_{3})_{2}]^{+} ion$$
(pale yellow)
$$I=(aq) \xrightarrow{dal.HNO_{3}} AgBr(s) \xrightarrow{conc.NH_{3}} dissolves completely giving [Ag(NH_{3})_{2}]^{+} ion$$

$$I^{-}(aq) \xrightarrow{\operatorname{dil} HNO_{3}} AgI(s) \xrightarrow{\operatorname{conc} NH_{3}} In soluble$$
(yellow)

• Double layer test (halides with Cl₂ water)

Tests for S²⁻, SO₃²⁻, CO₃²⁻ and NO₂⁻

• Following tests are listed for the above anions.

$$S^2(aq) \xrightarrow{dil HCl} H_2S(g) \xrightarrow{(CH_1COO)_2Pb(aq)} PbS(s)$$

black ppt

$$\begin{split} & \mathrm{SO}_3^{2-}(\mathrm{aq}) \xrightarrow{\mathrm{dd}.\mathrm{HCl}} \mathrm{SO}_2(\mathrm{g}) \xrightarrow{\mathrm{H}^+ \Lambda \mathrm{Cr}_2 \mathrm{O}_7^{2-}(\mathrm{aq})} \mathrm{Colour \ changes \ from \ orange \ to \ green} \\ & \mathrm{Cr}_2 \mathrm{O}_7^{2-}(\mathrm{aq}) + 3 \, \mathrm{SO}_3^{2-}(\mathrm{aq}) + 8\mathrm{H}^+(\mathrm{aq}) \xrightarrow{} 2 \, \mathrm{Cr}^{3+}(\mathrm{aq}) + 3 \, \mathrm{SO}_4^{2-}(\mathrm{aq}) + 4\mathrm{H}_2\mathrm{O}(\mathrm{l}) \\ & (\mathrm{Orange}) & (\mathrm{Green}) \end{split}$$

• $CO_3^{2-}(aq) \xrightarrow{\text{dl } HC1} CO_2(g) \xrightarrow{\text{Line water}} Milky colour precipitate will form and become colourless when passing <math>CO_2(g)$ continuously.

$$CO_{2}(g) + Ca(OH)_{2}(aq) \longrightarrow CaCO_{3}(s) + H_{2}O(l) \xrightarrow{CO_{2}(g)} Ca(HCO_{3})_{2}(aq)$$
(White) (Colourless)

• $NO_2^{-}(aq) \xrightarrow{\text{dil HC1}} NO_2(g)$ (Reddish brown fumes will be formed)

Tests for SO₃²⁻ and SO₄²⁻

On addition of $BaCl_2$ to a solution containing these ions, a white precipitate will form. Solubility of these precipitates in acids (dil. HCl or dil. HNO₃) can be used to identify them.

• $SO_3^{2}(aq) \xrightarrow{BaCl_3(aq)} BaSO_3(s) \xrightarrow{dl HCl} dissolves$ (White) $BaSO_3(s) \bigoplus Ba^{2+}(aq) + SO_3^{2+}(aq)$ $H^+(aq) + SO_3^{2+}(aq) \bigoplus HSO_3^{-}(aq)$ $H^+(aq) + (aq) \bigoplus H_2SO_3(aq)$ (weak acid)

Here the \mathbb{SO}_3^2 ions are removed by H⁺ ions, since it forms a weak acid.

•
$$SO_4^2$$
 (aq) $\xrightarrow{\text{BaCl}_2(\text{aq})} \text{BaSO}_4(s) \xrightarrow{\text{dil HCl}} \text{Insoluble}$
(White) HSO_3^2

$$BaSO_4(s)$$
 Ba²⁺(aq) + SO_4^2 (aq)

Here the SO_4^2 ions are not removed by H⁺ ions, since it forms a strong acid.

Tests for S,O₃²⁻

$$S_2O_3^{2-}(aq) \xrightarrow{dd.HCl} SO_2(g) + S(s)$$
 (A milky colour precipitate and a pungent smell)
 $S_2O_3^{2-}(aq) \xrightarrow{AgNO_1(aq)} Ag_2S_2O_3(s) \rightarrow Ag_2S(s)$ (black)
 $S_2O_3^{2-}(aq) \xrightarrow{Pb(NO_1)_2(aq)} PbS_2O_3(s)$ (white) $\xrightarrow{A} PbS(s)$ (black)

Tests for NO₃

- Brown ring test
- To a solution of the nitrate ions add cold aqueous $FeSO_4$ solution and carefully pour a few drops of conc . H_2SO_4 down the side of the test tube. Brown ring can be seen between the layers of nitrate solution and H_2SO_4 .

Ammonia Test

• When heated with Al and aqueous NaOH, nitrate ions are reduced to ammonia.

$$NO_{3}^{\cdot}(aq) + 6H_{2}O(l) + 8e \longrightarrow NH_{3}(g) + 9OH^{\cdot}(aq)$$

Al(s) + 4OH^{\cdot}(aq) $\longrightarrow AlO_{2}^{\cdot}(aq) + 2H_{2}O(l) + 3e$
 $3 NO_{3}^{\cdot}(aq) + 2H_{2}O(l) + 8 Al(s) + 5OH^{\cdot}(aq) \longrightarrow 3NH_{3}(g) + 8 AlO_{2}^{\cdot}(aq)$

Test for PO₄³⁻

To a solution of PO₄³⁻ add conc. HNO₃, excess of ammonium molybdate and warm. A yellow precipitate will be formed.

Suggested learning teaching activities :

- Allow the students to identify the anions in the given sample using precipitation method.
- Ask them to write the balanced equations for the observations.
- Explain the solubility of the precipitate in acids based on the nature of anions..

Competency 7.0 : Investigates the variety of organic compounds.

Competency Level 7.1 : Investigates the importance of organic chemistry as a special field of chemistry.

Periods : 02

Learning outcomes :

- States that there are a large number of natural and synthetic compounds containing carbon as the main constituent element.
- Explains giving the relevant facts the ability of carbon to form a large number of compounds.
- Shows the importance of organic chemistry in daily life by giving examples from various fields.

Guidance for teacher elaboration:

- Some features of carbon that contribute to the formation of a large number of organic compounds are given below.
- Between two C atoms strong single bonds, double bonds and triple bonds can be formed. It has been observed thæt compared to Si which is in the fourth group to which C belongs, the C C, C = C, C = C and C H and other bonds that C forms possess higher bond energies. The relevant information is given in the following table.

Dond	Bond energy
Bolid	/kJ mol ⁻¹
C - C	346
C = C	610
C C	835
С-Н	413
Si - Si	226
Si - H	318

- Carbon can form chains containing thousands of atoms and also rings of all sizes.
- A carbon atom can form 4 covalent bonds. Hence, it is seen that a large number of other atoms/groups can get attached to a carbon atom in a chain or ring and that this property contributes to the existence of a large variety of compounds.
- Carbon forms strong covalent bonds not only with other carbon atoms and hydrogen atoms, but also with other non metal atoms such as O, S, P, N, and halogens.

Suggested learning - teaching activities:

- Ask the students about the basic constituent elements in foods, fuels, medicines, paints, plastics, clothes, dyes, etc. Introduce organic compounds in this way.
- Divide the students in the class into a number of groups. Assign the student groups to discuss examples of organic compounds used in various fields in day to day life and their importance.

Competency 7.0	:	Investigates the variety of organic compounds.
Competency Level 7.2	:	Investigates the variety of organic compounds in terms of the functional groups.
Periods	:	04

Learning outcomes

:

- Identifies the names and symbols of functional groups that are included in the syllabus.
- Identifies the variety of organic compounds in terms of the functional groups present.
- Names the homologous series of compounds containing each of the functional groups and presents examples.

Guidance for teacher elaboration:

- Some organic compounds contain only C and H as the constituent elements. They are known as hydrocarbons.
- On the basis of the structure, hydrocarbons are divided into two main groups called aliphatic and aromatic.
- The set of hydrocarbons consisting of open carbon chains only are named as acyclic aliphatic hydrocarbons.
- The aliphatic hydrocarbons are classified as alkanes, alkenes, and alkynes.
- The cyclic organic compounds which are stabilized by forming a cyclic delocalized cloud of π electrons are called aromatic compounds.
- Benzene which is indicated by the molecular formula C_6H_6 is the simplest of aromatic hydrocarbon compounds.
- Compounds formed by replacing a hydrogen atom of an aliphatic hydrocarbon by a halogen atom are referred to as alkyl halides.
- Compounds formed by replacing a hydrogen atom of a benzene ring by a halogen atom are referred to as aryl halides.
- In many organic compounds, when hetero atoms such as nitrogen and oxygen combine with the carbon chain, due to the difference in electro negativity between the carbon and the combined atoms, this group of atoms will impart to the compound a characteristic reactivity. Such a group of atoms is called a functional group. The compounds are classified according to the functional group present in a molecule.
- Common functional groups and the names of the corresponding homologous series are given below.

Functional group	Name of the homologous series	Example
— ОН	Alcohol	CH ₃ CH ₂ OH (Ethanol)
	Aldehyde	CH ₃ CHO (Ethanal)
$-c^{0}$	Ketone	CH ₃ COCH ₃ (Propanone)
	Carboxylic acid	CH ₃ COOH (Ethanoic acid)
	Acid chloride	CH ₃ COCl (Ethanoyl chloride)
$-c_{O-R}^{0}$	Ester	CH ₃ COOCH ₃ (Methyl ethanoate)
— NH ₂	Amine	CH ₃ CH ₂ NH ₂ (Ethylamine)
	Amide	CH ₃ CONH ₂ (Ethanamide)
COOH – C – NH ₂	Amino acids	CH ₃ CHNH ₂ COOH (2-Aminopropanoic acid)
—x*		CH ₃ CH ₂ Cl (Chloroethane)

* In the IUPAC nomenclature, halogen is not considered a functional group.

Suggested learning - teaching activities:

- Present the students with structural formulae of organic compounds containing various functional groups and direct them to identify these.
- Give a list of chemical compounds to the student groups. Give them the opportunity to select and put compounds belonging to a particular homologous series from it into a table form and also to build up the relevant homologous series.

Competency 7.0	:	Investigates the variety of organic compounds.
Competency Level 7.3	:	Names simple aliphatic organic compounds to facilitate investigations.

Periods : 06

:

Learning outcomes

- States the trivial names of the common organic compounds and recognizes the need for a standard nomenclature.
- Names the given organic compounds which are structurally within the limit stated in the syllabus, using the IUPAC rules.
- Draws the structural formula of a compound when the IUPAC name is stated.

Guidance for teacher elaboration:

- The International Union of Pure and Applied Chemistry -IUPAC has developed a method for systematically naming organic compounds.
- The name given to a compound according to the IUPAC nomenclature consists of several parts.
 - 1. The suffix that is used to indicate the main functional group of the structure
 - 2. Name of the chain that is used to identify the main carbon chain of the compound
 - 3. The prefixes that are used to indicate the substituent groups
 - 4. The numbers that are used to indicate the places at which the substituent groups, additional groups and the main functional groups are attached to the chain
- The IUPAC name of an aliphatic compound can easily be developed by following the steps stated below in the given order.
 - 1. Identifying the principal functional group
 - 2. Selecting the main chain
 - 3. Selecting the root name for the principal chain
 - 4. Addition of the suffix for the double/triple bond in the main carbon chain to the name of the chain
 - 5. Addition of the suffix used to indicate the principal functional group to the name of the chain
 - 6. Naming the substituent groups
 - 7. Adding the names of the substituent groups to the name of the chain
 - 8. Numbering the carbon chain
 - 9. Writing the numbers that are used to indicate the positions of the main functional group and the substituent groups in front of these groups.

Group	Name as	Name as
	the principal	the substituent
	functional group	group
— СООН	oic acid	
- COOR	oate	
- CONH ₂	amide	carbamoyl
— C ≡ N	nitrile	cyano
— сно	al	formyl
	one	οχο
-он	ol	hydroxy
$- NH_2$	amine	amino
- C ≡ C -	yne	
– C=C–	ene	
– x		halo
$-NO_2$		nitro

Table 1 : The series of functional groups arranged in the decreasing order of their priority

Table 2 : The root names used for the compounds according to the numberof carbon atoms and the name of the corresponding hydrocarbon

Number of carbon atoms	Root name	Name of the corresponding hydrocarbon
1	meth	Methane
2	eth	Ethane
3	prop	Propane
4	but	Butane
5	pent	Pentane
6	hex	Hexane

Drawing the structural formula of a compound according to the IUPAC nomenclature

- Drawing the structural formula of a compound according to the IUPAC nomenclature can be done by following the steps given below.
 - 1. Identifying the chain and drawing the chain according to that name
 - 2. Numbering the chain
 - 3. Identifying the principal functional group and the remaining groups according to the IUPAC name given and joining these groups to the correct places of the chain according to the number in front of these groups
 - 4. Placing hydrogen atoms in the chain structure so that each carbon atom has a valency of four

Suggested learning - teaching activities

- Give the structures of a few compounds within the limits of the syllabus and direct the students to name them according to the IUPAC system.
- When the IUPAC name of a compound within the limits of the syllabus is given, direct the students to write its structure.
- Present the above assignments as group activities.

Competency 7.0	:	Investigates the variety of organic compounds.
Competency Level 7.4	:	Investigates the different possible arrangements of atoms in molecules having the same molecular formula.

Periods : 05

:

Learning outcomes

- Draws all the possible structural formulae for a given molecular formula.
- Classifies all the structural formulae that can be drawn for a given molecular formula as structural isomers and stereoisomers.
- Draws the structural formulae for the isomers having specified features out of the isomers that can exist for a given molecular formula.

Guidance for teacher elaboration:

- The phenomenon of the existence of compounds with different atomic arrangements while having the same molecular formula is called isomerism.
- The isomers of a compound can show different physical and chemical properties from one another.
- The isomerism of organic compounds can be classified as follows.



Structural isomerism

Structural isomerism is the phenomenon of having compounds with different structural formulae (without considering the spatil orientation of bonds) for the same molecular formula.

• Chain isomerism

Chain isomerism occurs when the nature of the carbon chain changes for the same molecular formula in the same homologous series.

CH.

Examples :

$$\begin{array}{c} CH_3-CH_2-CH_2-CH_3 \\ Butane \end{array} \quad and \quad CH_3-CH_3-CH_3 \\ 2-Methyl propane \end{array}$$

Position isomerism

•

Though there is the same molecular formula, the same functional group/substituent and the same carbon chain when there is a change in the carbon atom to which the functional group/substituent is attached or a change in the location of the active position, then there occurs position isomerism.

Examples :

СH₃ - CH₂ - CH₂ - OH Propan-1-ol

$$CH_{3} - CH - CH_{3}$$

Propan-2-ol

(ii) $CH_3 - CH_2 - C \equiv CH$ But-1-yne

(iii) Cl

1,2-Dichlorobenzene

 $CH_{3} - C \equiv C - CH_{3}$ But-2-yne



1,3-Dichlorobenzene

Functional group isomerism

Functional group isomerism is the existence of structures with different functional groups for the same molecular formula.

Examples :





Propanoic acid

CH₃-CCH₃ Propanone

CH₃-C

Methyl ethanoate

Stereoisomerism

•

Stereoisomerism is the existence of compounds whose structures differ from each other only in the orientation of bonds in three dimensional space (*i.e.* they have the same molecular formula and the same structural formula). A pair of stereoisomers whose 3D - structures are mirror images of each other are **enantiomers** of each other. A pair of stereoisomers whose 3-D structures are not mirror images of each other are **diastereomers** of each other.

Diastereomerism

Geometric isomerism is one occasion where diastereomerism is seen. In a C=C double bond due to the π bond which exists in addition to the bond, these carbon atoms cannot freely rotate about the bond. It is possible to have different spatial arrengements of the groups joined to the two carbon atoms. These different arrangements which cannot be interconverted by rotation around carbon - carbon bond axis are known as geomentrical isomers. For geometrical isomers to exist, the two groups attached to each carbon atom of the double bond should not be identical.

For example,



The words *cis* and *trans* are used to indicate the geometrical relationship of two groups attached to different carbon atoms in the same double bond. If the two groups are σ on the same side with reference to the plane which is perpendicular to the plane of the molecule going through the carbon - carbon axis of the double bond, then the relationship is *cis*. If the two groups are on opposite sides of the plane then the realtionship is *trans*. For example, in structure (i) *a* and *p* are *cis* to each other while *a* and *q* are *trans* to each other. Thus the two geometrical isomers of but-2-ene are labled as shown below.

Examples:--But-2-ene



Cis isomer

Trans isomer

When all four groups a, b, p and q are different from each other it is not possible to use the cis trans nomenclature.

Enantiomerism

The isomers of which one is the mirror image of the other are known as enantiomers. A compound having a carbon atom which is joined to four different groups shows enatiomerism. Such a carbon atom is known as an asymmetric or chiral carbon atom.
When plane - polarized light is passed through a solution containing only one enantiomer, the plane of polarization rotates. One enantiomer rotates the plane of polarization in one direction and the other enantiomer in the opposite direction. As the enantiomers rotate the plane of polarization, they are also known as optically active isomers.

Enantiomers of bromochlorofluoromethane



Mirror

Suggested learning- teaching activities:

- Ask students to present all the structural formulae that can be drawn for the molecular formula C_4H_8 and C_5H_{12} and explain the terms isomerism, structural isomerism and stereoisomerism.
- Divide the class into groups and give molecular formulae to the students so as to cover all the aspects of isomerism that are included in the syllabus. Instruct the students to present all the structural formulae that can be drawn for those moleculae formula and to classify them.
- Direct the students to make models for the geometrical shapes of molecules using suitable materials and to identify their differences.

Competency 8.0	:	Investigates the relationship between structure and properties of hydrocarbons.
Competency Level 8.1	:	Investigates the structure, physical properties and nature of bonds of aliphatic hydrocarbons.
Periods	:	04

- Describes the nature of the bonds in alkanes, alkenes, and alkynes using suitable examples.
- Explains the variation of physical properties along the homologous series of alkanes, alkenes and alkynes.
- Relates the geometrical shapes of the simple alkanes, alkenes and alkynes to the hybridization of carbon atoms.

Guidance for teacher elaboration:

:

- If two consecutive members differ only by a CH₂ unit, such a series of compounds is called a homologous series.
- An alkane molecule is non polar or very weakly polar. The attractive forces between two non -polar molecules are the weak dispersion forces. While the first few members of the series are gases at room temperature, the higher members are liquids and solids. As a result of increase in surface area down the series dispersion forces also increase. This leads to the aforesaid variation in the physical states.
- With branching of the carbon chain the surface area of a molecules decreases and consequently dispersion forces become weaker and the boiling point decreases. Boiling points of alkanes with five carbon atoms are given below.

Compound	Boiling point / ⁰ C
Pentane	36
2 - Methylbutane	28
2,2 - Dimethylpropane	9

- In alkenes, the physical properties are very much similar to those of alkanes.
- As the polarity of alkynes is also low, their physical properties are very similar to those of the corresponding alkanes and alkenes.
- During the formation of carbon carbon bonds, the carbon atom undergoes hybridization as sp, sp² and sp³. Some examples are given below.



- The electronic configuration of C in its ground state is $1s^2 2s^2 2p^2$. According to the electronic configuration of C in its ground state, the carbon atom has only two unpaired electrons.
- But when a C atom form CH₄, it makes four bonds which are all equivalent. To understand this, it is considered that the electrons of the C atom attain the excited state and then proceed to the process of hybridization.
- Here, the hybridization takes place after an electron from the 2*s* sub energy level of C transits into an empty 2*p* orbital.
- How the C-C single bonds, C = C double bonds and $C \equiv C$ triple bonds are formed can be explained using the C atom with excited electrons undergoing sp^3 or sp^2 or sp hybridizations respectively.
- The differences in energy among the various orbitals of the valency shell of the carbon atom in the ground state, excited state and in hybridized state are given below comparatively.







 CH_4 molecule - Hybridization of the carbon atom is sp^3 .



 C_2H_4 molcule - Hybridization of the carbon atoms is sp^2 .



 C_2H_2 molcule - Hybridization of the carbon atoms is sp

• The percentage of s character in a hybrid orbital affects the bond length and bond energy. Examples are given below.

Hybridization	C-H bond length/ ⁰ A	Bond energy/kJ mol ⁻¹
sp ³	1.112	436
sp^2	1.103	445
sp	1.079	508

Suggested learning- teaching activities:

- Introduce the general formulae for alkanes, alkenes and alkynes to the students. Give an opportunity for students to write one relevant compound for each general formula. From these, explain the structure of a simple alkanes, alkenes and alkynes in terms of the hybridizations they have already learned.
- Divide the class into three groups and give them an opportunity to present in a logically developed manner the type of hybridization, geometrical shape and the physical properties of the carbon atoms of methane, ethene and ethyne.
- Give an opportunity to make models using easily available materials and to describe the shapes of molecules.

Competency 8.0	:	Investigates the relationship between structure and properties of hydrocarbons.
Competency Level 8.2	:	Investigates the nature of bonding in benzene.
Periods	:	04

• Gives reasons why the structure for benzene first presented by Kekule does not explain all the properties of benzene.

Guidance for teacher elaboration:

:

- Under normal conditions benzene does not answer the tests for unsaturation. Therefore, benzene cannot have a structure similar to that of a simple alkene or an alkyne.
- Although the structure proposed for benzene by Kekule shows three double and three single bonds for the molecule, the bond length between any two adjacent carbon atoms in benzene is the same.
- The carbon carbon bond length of benzene is 1.39×10^{-10} m which is in between the length of carbon carbon double bond (1.34×10^{-10} m) and the length of carbon carbon single bond (1.54×10^{-10} m).
- Therefore, the structure of benzene is considered to be a hybrid of the resonance structures given below.



Resonance structures of benzene

- The double headed arrow, ↔ does not indicate that benzene changes between these two structures or that it is in equilibrium. It shows resonance.
- Explain the difference between \leftrightarrow and \Box
- The structure of benzene can be explained by molecular orbital theory. All its C atoms have undergone sp² hybridization. Each carbon bears an unhybridized p orbital which can overlap with the unhybridized p orbitals on either sides of it.

- From this, a cyclic delocalized electron cloud is formed.
- Hence, the real structure of benzene is considered to be a hybrid of two Kekule structures.
- The real structure of benzene with delocalized electrons is more stable than the Kekule structure with three double bonds.
- The data for the standard enthalpy of hydrogenation helps to illustrate the stability of a benzene molecule.

But if benzene possesses three double bonds, its standard enthalpy of hydrogenation should be 3 x (-120 kJ mol⁻¹), that is -360 kJ mol⁻¹. Hence, benzene is more stable than its Kekule structures by an amount equal to (360-208) = 152 kJ mol⁻¹.



Suggested learning- teaching activity :

- Ask the students to draw a possible open chain structure for the molecular formula C_6H_6 . Stress the fact that in these structures there are double bonds, triple bonds or both and therefore, should answer the tests for unsaturation.
- Mention that although a single Kekule structure does not represent the real structure of benzene, in writing reaction mechanisms it is convenient to use a Kekule structure to represent benzene.

Competency 8.0	:	Investigates the relationship between structure and properties of hydrocarbons.
Competency Level 8.3	:	Investigates and compares the chemical reactions of alkanes, alkenes and alkynes in terms of their structures.
Periods	:	10

- Relates the characteristic reactions of alkanes, alkenes and alkynes to their structures.
- Explains the reaction mechanisms of chlorination of methane and the addition of bromine and hydrogen halides to ethene.

Guidance for teacher elaboration:

 In alkanes all the bonds are either C-C or C-H bonds. The polarity of those C-C and C-H bonds are low. Therefore, they do not react with common polar reagents (eg. OH⁻, CN⁻, H⁺) under normal conditions.

Chlorination

Alkanes react with the reagents such as Cl_2 and Br_2 that undergo easy homolytic cleavage to generate free radicals. The mechanism of the chlorination of methane is given below.

• Initiation step:
$$c_1 \xrightarrow{h_U} c_1 \xrightarrow{h_U} c_1 + c_1$$

• Chain propagation steps:

The Cl[•] free radical generated in the initiation step abstracts a H atom from the methane molecule by homolysis of the C-H bond.

$$C_1 \xrightarrow{H^-} CH_3 \longrightarrow HCl + \dot{C}H_3$$

The CH_3 free radical then reacts with a Cl_2 molecule forming CH_3Cl and generate another Cl free radical which can continue the chain reaction.

$$\dot{C}$$
 \dot{C} \dot{C}

• Chain termination steps

Combination of free radicals in the reaction mixture to form stable molecules, results in the termination of chains. $(\sum a)$

Reactions of alkenes

- The loosely bound π electron cloud which lies above and below the plane of the ethylene molecule is capable of attracting electrophilic reagents.
- A molecule or an ion that can accept a pair of electrons is referred to as an electrophile.

Addition of hydrogen halides

• Here, the hydrogen atom which is the electron deficient pole of HBr molecule acts as an electrophile and attacks the double bond. During these electrophilic addition reactions, intermediate carbocations are formed.



• Stability of carbocations follows the following order.



- When alkyl groups are attached to the positively charged C atom of the carbocation, the stability of the cation increases. The reason for this is the release of electrons by the alkyl groups through C-C σ bonds towards the positively charged carbon atom to which they are attached. This results in spreading the positive charge thereby stabilizing the ion.
- In the electrophilic addition reactions of hydrogen halides to asymmetric alkenes, two different carbocations can be formed after the bonding of the electrophile. Out of these the more stable carbocation forms more easily.

Protonation on ²C
³CH₃ - ²CH = ¹CH₂
Protonation on ¹C

$$CH_3 - CH_2 - {}^+CH_2$$

Primary carbocation
 $CH_3 - {}^+CH - CH_3$
Secondary carbocation
(more stable)

- The more stable carbocation is obtained when the electrophile gets attached to the carbon atom to which the highest number of hydrogen atoms are attached.
- After studying reactions of a large number of alkenes, this observation has been generalized as Markownikoff's rule.

Mechanism



• Hydrogen bromide adds in the opposite way to this rule when there are peroxides in the reaction medium. The reason for this is that in the presence of peroxides the reaction of hydrogen bromide and the alkenes takes place via a free radical mechanism. It is not expected to describe this mechanism.

Examples:

$$CH_3 - CH = CH_2 \xrightarrow{HBr} CH_3 - CHBr - CH_3$$

 $CH_3 - CH = CH_2 \xrightarrow{HBr} CH_3 - CH_2 - CH_2 - Br$

This change of the direction of addition (Anti-Markownikoff's addition) is not exhibited by the other hydrogen halides.

Addition of bromine to alkenes

$$CH_2 = CH_2 \xrightarrow{Br_2/CCl_4} \mathcal{T}_{\pi}CH_2BrCH_2Br$$

Mechanism

- When a molecule of Br_2 approaches the electron cloud of an alkene molecule, it gets polarized $(Br^{+\delta} Br^{-\delta})$. The positive end of the dipole then reacts with the alkene, transferring a Br^+ ion to it during the reaction (by heterolytic cleavage of the Br-Br bond) forming a cyclic bromonium ion.
- In the second step of the reaction, a Br⁻ ion acting as a nucleophile, forms a bond to one of the carbon atoms bonded to Br⁺. The bond formed by that carbon atom to Br⁺ is broken during this step, giving an open chain structure again.



Addition of sulphuric acid to alkenes and the hydrolysis of the product obtained.

• Here, proton acts as an electrophile and HSO_4^{-1} ion acts a nucleophile

$$CH_{2} = CH_{2} + H_{2}SO_{4} \longrightarrow H - C - C - H$$
$$H - C - C - H$$

Reaction of alkenes with cold alkaline KMnO₄

Catalytic hydrogenation

• In the presence of catalysts such as finely powdered Pt, Pd or Ni, alkenes react with hydrogen and produces alkanes.

$$CH_2 = CH_2 + H_2 \xrightarrow{Ni}{a} CH_3 - CH_3$$

Reactions of alkynes

• Alkynes have two bonds which react independantly and undergo electrophilic addition reactions with reagents that add to alkenes.

Addition of bromine

$$CH \equiv CH \xrightarrow{\mathbf{k}_{2}/CCl_{4}} CH = CH$$
$$Br Br$$
$$CH = CH \xrightarrow{\mathbf{k}_{2}/CCl_{4}} CHBr_{2}-CHBr_{2}$$
$$Br Br$$

Addition of hydrogen halides

Addition of water

In the presence of Hg²⁺ and dilute sulphuric acid, one molecule of water gets added on to alkynes.

$$CH = CH \xrightarrow{H_2O} H \xrightarrow{-C} C = C \xrightarrow{-OH} CH_3 \xrightarrow{-C} C \xrightarrow{-H}$$
(Enol)

• The rapid rearrangement of the enol to the aldehyde is due to the high stability of C = O.

Catalytic hydrogenation of alkynes

• In the presence of catalysts such as finely powdered Pt, Pd or Ni alkynes react with hydrogen to give alkanes. The reaction can be stopped at the intermediate alkene stage by using a Pd/BaSO₄ catalyst poisoned by quinoline.



In the alkynes, H-C = C-H and R-C = C-H the H attached to the C that forms the triple bond (terminal hydrogen) shows acidic properties.

The acidic H in these alkynes can be displaced by metals.

$$CH_{3} - C \equiv C - H \xrightarrow{Na(1)} CH_{3} - C \equiv C - Na^{+} + H_{2}$$

$$CH_{3} - C \equiv C - H \xrightarrow{NaNH_{2}} CH_{3} - C \equiv C - Na^{+} + NH_{3}$$

$$CH_{3} - C \equiv C - H \xrightarrow{NH_{3}/Cu_{2}Cl_{2}} CH_{3} - C \equiv C - Cu$$

$$CH_{3} - C \equiv C - H \xrightarrow{NH_{3}/AgNO_{3}} CH_{3} - C \equiv C - Ag$$

Suggested learning – teaching activities:

- Show the demonstration models of CH₄, C₂H₄ and C₂H₂ molecules and explain the stability of the carbon- carbon bonds in terms of hybridization.
- Divide the students into three groups. Assign each group to study the reactions respectively of alkanes, alkenes, and alkynes given in the syllabus and report on them.
- Introduce the terms mechanism, homolytic cleavage, heterolytic cleavage and free radical chain reactions. Using these terms discuss the reaction mechanisms of the above mentioned reactions.
- Show that alkynes also answer the tests for unsaturated nature of alkenes.

Competency 8.0	:	Investigates the relationship between structure and prop- erties of hydrocarbons.
Competency Level 8.4	:	Analyses the stability of benzene in terms of its character- istic reactions.
Periods	:	07

- Shows using suitable examples the tendency of benzene to undergo substitution reactions rather than addition reactions.
- Describes the electrophilic substitution reactions as characteristic reactions of benzene using the mechanisms of nitration, alkylation, acylation and halogenation.
- Compares the reactions of benzene with those of alkanes alkenes, and alkynes.

Guidance for teacher elaboration:

Electrophilic substitution reactions of benzene

:

• There is a loosely bound cloud of electrons on both faces of the planar benzene molecule. As with alkenes, this makes benzene reactive towards electrophiles. The first step in this reaction is for the electrophile (E⁺) to form a bond with a carbon atom in the benzene ring.



• The intermediate carbocation so formed is stabilized by the delocalization of the positive charge by conjugation with the two π bonds. This can be shown by resonance.



- However, in going from benzene to the carbocation the cyclic delocalization of π electrons is broken, and the aromatic stabilization energy is lost. Therefore, the intermediate carbocation prefers to lose a proton and re-established the cyclically delocalized electron cloud, rather than reacts with a nucleophile and give an addition product as in the case of alkenes.
- The proton is usually taken up by one of the bases (B:-) present in the reaction mixture. Thus, the result is the substitution of a H atom on the benzene ring with E.



(i) Nitration

In the presence of the nitration mixture composed of conc. HNO_3 and conc. H_2SO_4 , nitrobenzene is formed by the substitution of H by a nitro group.



The electrophile here is ${}^{+}NO_{2}$ generated in the medium by the dehydration of nitric acid by sulphuric acid.



The base which takes up the proton in the final step is HSO_4^- .

(ii) Friedel – Crafts alkylation

During the reaction of benzene with alkyl halides in the presence of a Lewis acid like anhydrous AlCl₂, substitution by an alkyl group takes place.



The electrophile here is R⁺.

$$R-C1 + A1Cl_3 \rightarrow R^+A1Cl_4^-$$

In cases where R^+ is not very stable (*eg*. ⁺CH₃) the species actually reacting with the benzene molecule may be a R-Cl molecule polarized by coordination to AlCl₃, which will transfer R^+ to the benzene molecule during the reaction by cleavage of the R-Cl bond.



The base which takes up the proton in the final step is $AlCl_4^2$.

$$A1Cl_4^{-} + H^+ \rightarrow A1Cl_3 + HCl_3$$

(iii) Friedel – Crafts acylation

During the reaction of benzene with acid chlorides in the presence of a Lewis acid like anhydrous AlCl₃, substitution by an acyl group takes place.



The electrophile here is R-C⁺=O.



The base which takes up the proton in the final step is

$$AlCl_4^{+} + H^{+} \rightarrow AlCl_3^{+} + HCl_3^{+}$$

(iv) Halogenation

When benzene reacts with halogens $(Cl_2 \text{ or } Br_2)$ in the presence of a Lewis acids (such as FeCl₃, AlCl₃) substitution by a halogen group takes place in the benzene ring.



The efective electrophile here is Cl⁺. It is transferred to the benzene ring from the complex during the reaction.

$$A1Cl_3 + Cl_2 \rightarrow Cl_3Al' - {}^+Cl - Cl$$

The base which takes up the proton in the final step is AlCl₄.

$$A1Cl_4^{-} + H^+ \rightarrow A1Cl_3 + HCl$$

Oxidation

Benzene does not get oxidized by normal oxidizing agents like H⁺/KMnO₄. However, the alkyl group in alkyl substituted benzene can be oxidized by H⁺/KMnO₄ to a carboxylic acid group. The benzene ring does not oxidize easily due to its stability. H⁺/K₂Cr₂O₇ can also be used for this reaction.



Tertiary alkyl groups do not get oxidized under the conditions in which primary and secondary alkyl groups get oxidized. More vigorous conditions under which tertiary alkyl groups can be oxidized also result in cleavage of the benzene ring.

Catalytic hydrogenation

Although benzene does not undergo electrophilic addition reactions, like alkenes, they can add hydrogen in the presence of suitable catalysts. The temperatures used are higher than for alkenes.



Suggested learning – teaching activities:

- Direct the students to state giving reasons as to what sort of characteristic reactions will benzene would show.
- Divide the students into four groups and assign them to describe one of the following mechanisms in front of the class.
 - Nitration and its mechanism
 - Alkylation and its mechanism
 - Acylation and its mechanism
 - Halogenation in the presence of FeX₃ and its mechanism.

Competency 8.0	:	Investigates the relationship between structure and
		properties of hydrocarbons.
Competency Level 8.5	:	Analyses the directing ability of substituent groups of
		mono substituted benzene.
Periods	:	01

Periods

Learning Outcomes

- Identifies the substituent groups of mono substituted benzene as ortho, para or meta directing groups.
- States the place where a second substituent group attaches to a mono-substituted benzene on the basis of the directing property of the first substituent group.

Guidance for teacher elaboration:

- When a mono substituted benzene undergoes an electrophilic substitution reaction, the place where the second substituent group attaches will be determined by the nature of the first substituent group.
- Substituent groups can be categorized into two basic types.
 - 1. Ortho para directing groups

-OH, -R, -NH₂, -NHR, -OCH₃, Halogens eg.

Other than halogen, the ortho para directing groups activate the benzene ring towards electrophilic substitution by making it more electron rich than benzene. Example:



2. Meta directing groups

- NO,, - CHO, -COR, -COOH, -COOR eg. Meta directing groups deactivate the benzene ring towards electrophilic substitution by withdrawing electrons from it.

Example:



Suggested learning – teaching activities :

- Divide the students of the class into two groups.
- Give a list of substituent groups and direct one group of students to highlight the specific features of ortho, para directing groups and the other group to highlight those of the meta directing groups.

Competency 9.0	:	Investigates the relationship between the structure and
		properties of alkyl halides.
Competency Level	9.1:	Investigates the structure, polar nature of C-X bond and
		reactions of alkylhalides.
Periods	:	11

Learning Outcomes :

- Classifies alkyl halides as primary, secondary and tertiary.
- Relates the tendency of alkyl halides to undergo nucleophilic substitution reactions with the polar nature of the C – X bond.
- Notes the non-reactivity of chlorobenzene and vinyl chloride towards nucleophilic substitution reactions.
- Describes the preparation and the properties of Grignard reagent.

Guidance for teacher elaboration :

• Alkyl halides are named as primary, secondary or tertiary depending on the number of H atoms attached to the carbon atom which carries the halogen atom.

- Alkyl halides are polar compounds.
- Although they are polar, the solubility of alkyl halides in water is very low. One reason for this is that they do not form hydrogen bonds with water.
- Due to the high electronegativity of the halogen atom relative to the carbon atom, the C X bond is polarized. As a result, there is a deficiency of electrons in that carbon atom. Therefore, nucleophiles attack this position. Nucleophiles are reagents which show a tendency to attack carbon nuclei and which are basic and rich in electrons. A nucleophile will bring a pair of electrons to form a bond with carbon.

Examples: $OH^{*}, CN^{*}, R-C \equiv C^{*}, R-O^{*}$

• Nucleophilic substitution reactions are characteristic of alkyl halides. Here, the carbon atom forms a new bond with the nuclephile and the halogen atom leaves as a halide ion.

Example:

$$Nu^{-} + \bigcup_{i}^{\delta + /} X^{\delta -} \longrightarrow - \bigcup_{i}^{l} Nu + X^{-}$$

 $Nu^{\bullet \bullet}$ is a nucleophile.

• As a nucleophile possesses a pair of electrons available to form a new bond any nucleophile can also act as a base by forming a bond with H⁺. Therefore, when an alkyl halide is reacted with a reagent such as :OH⁻, it can also undergo an elimination reaction by the mechanism shown below.

$$\dot{O}H^- + \dot{-}C - C - X$$
 $C = C + H_2O + X^-$

Here, :OH⁻ instead of reacting as a nucleophile with carbon, reacts as a base and removes a H⁺ from the carbon atom adjacent to the carbon atom bearing halogen. The hydrogen atoms attached to the carbon atom adjacent to the carbon atom bearing the halogen atoms, have a low acidity due to the polarization of the

C-X bond. Thus substitution and elimination are competing reactions in alkyl halides.

• Alkyl halides react with Mg in the medium of dry ether to form the Grignard reagent.

• When an alkyl halide forms a Grignard reagent the polaritiy of the carbon atom originally joined to halogen, changes as shown below.

$$C^{\delta +} X^{\delta -} \rightarrow - C^{\delta -} MgX$$

• Due to the polarization of bonds in RMgX, the carbon attached to magnesium acts as a strong nucleophile and a very strong base.

• The strong basic character of the Grignard reagent can be shown by the following reactions.

$$\begin{split} & \operatorname{RMgX} + \operatorname{CH}_3\operatorname{COOH} \ \rightarrow \ \operatorname{RH} + \operatorname{Mg}(\operatorname{CH}_3\operatorname{COO})X \\ & \operatorname{RMgX} + \operatorname{CH}_3\operatorname{OH} \longrightarrow \operatorname{RH} + \operatorname{Mg}(\operatorname{OCH}_3)X \\ & \operatorname{RMgX} + \operatorname{RNH}_3 \longrightarrow \operatorname{RH} + \operatorname{Mg}(\operatorname{RNH})X \\ & \operatorname{RMgX} + \operatorname{H-C} \equiv \operatorname{CR} \rightarrow \operatorname{RH} + \operatorname{Mg}(\operatorname{C} \equiv \operatorname{CR})X \\ & \operatorname{R-MgX} + \operatorname{NH}_3 \rightarrow \operatorname{RH} + \operatorname{Mg}(\operatorname{NH}_3)X \end{split}$$

Suggested learning – teaching activities :

- Get the students to draw the structures of all the alkyl halides that can exist for the molecular formula C_4H_9Cl .
- Direct the student to classify them as primary, secondary and tertiary.
- Direct the students to write the structure of isomers and also those of the products formed by them in the presence of acids, alcohols and amines.

Competency 9.0	:	Investigates the relationship between the structure and properties of alkyl halides.
Competency Level 9.2	:	Investigates the nucleopilic substitution reactions of alkyl halides in terms of the timing of bond making and bond breaking steps
Periods	:	01

- Recognizes that there are two possible pathways for the nucleopilic substitution reactions of alkyl halides.
- Describes the nucleophlic substitution reaction of alkyl halides as a one step reaction where bond breaking and bond making take place simultaneously.
- Describes the nucleophilic substitution reaction of alkyl halides as a two step reaction when the formation of the new bond takes place after the breaking of the bond.
- Describes how the nature of the alky halide affects the choice of reaction pathway (one step or two steps).
- Explains the non-reactivity of chlorobenzene and vinyl chloride towards nucleophilic substitution reactions.

Guidance for teacher elaboration

- To explain the nucleophilic substitution reaction of alkyl halides, the time interval between bond breaking and bond making steps can be considered.
- When the breaking of the C-X bond and the formation of the new bond to the nucleophile takes place simultaneously, the nucleophilic substitution reaction of the alkyl halide takes place as a one step reaction.
- Accordingly, the one step reaction can be presented as follows:



• When the formation of the new bond to the nucleophile takes place after the breaking of the C-X bond the nucleophile substitution reaction of the alkyl halide takes place as a two step reaction.

• Accordingly, the reaction that takes place by two steps can be presented as follows.



- The reaction that takes place by two steps goes through an intermediate carbocation. On considering the stability of the carbocation formed, the tertiary alkyl halides (R¹, R², R³ = alkyl) which are able to form a more stable tertiary carbocations undergo nucleophilic substitution in two steps. The primary alkyl halides (R¹, R² = H, R³ = H or alkyl) undergo nucleophilic substitution reactions in one step as they are unable to form a stable intermediate carbocation.
- The pathway taken by the secondary alkyl halides (R¹ = H, R², R³ = alkyl) depend on the reaction conditions.
- Vinyl and phenyl carbocations are unstable and therefore, they do not react by the two step pathway. They also do not react by the one step path because the C-X bond is stronger than in alkyl halides due to its double bond character. This can be shown by resonance.



Suggested learning – teaching activities :

• Direct the students to prepare as group activities suitable models to explain how the nucleophilic substitution of alkyl halides takes place in one step and in two steps.

Competency 10.0 :		Investigates the relationship between the structure and properties of oxygen containing organic compounds.		
Competency Level 10.1	:	Investigates the structure, polar nature of carbon-oxygen bond and oxygen-hydrogen bond and reactions of alcohols.		
Periods	:	08		

• Classifies alcohols as primary, secondary and tertiary.

:

- Describes the polar nature of the O- H bond and C- O bond.
- Relates the physical properties of alcohols with their ability to form H bonds.
- Relate the breaking of O-H bond, the breaking of C-O bond and the elimination and oxidation reactions of alcohols with the structure.
- Tests the properties of alcohols and reports on them .

Guidance for teacher elaboration :

• Monohydric alcohols can be classified into three types as primary, secondary and tertiary (As in alky halides).

$$\begin{array}{cccc} H & & & R \\ I & & \\ R & - \begin{array}{c} C - OH \\ | & Primary \, alcohol \\ H \end{array} & & \\ \end{array} \begin{array}{c} R & - \begin{array}{c} C - OH \\ | & Secondary \, alcohol \\ H \end{array} & & \\ \end{array} \begin{array}{c} R & - \begin{array}{c} C - OH \\ | & C - OH \\ | & Secondary \, alcohol \\ R \end{array}$$

• Physical properties

In alcohols the –OH bond is polarized as $R - O^{\delta} - H^{\delta+}$. Hence, due to the inter molecular hydrogen bonds formed between alcohol molecules, their boiling points have higher values compared to the alkanes and ether with comparable relative molecular masses. The boiling point increases in going down the series of alcohols.



The above diagram shows how the inter- molecular hydrogen bonds exist in ethanol. Alcohols which have low relative molecular mass are soluble in water. The solubility of alcohols in water is due to the - OH group which can forms H - bonds with water molecules. The non polar alkyl group in the alcohol molecule is a hindrance to the

solubility in water. In going down the homologous series of alcohols the size of the non-polar alkyl group gradually increases relative to the –OH group. Accordingly the solubility in water gradually decreases, as shown in the table below.

Trivial name	Formula	Boiling point ⁰ C	Solubility in water/g
			(Weight of the alcohol that
			dissolves in 100 g of water)
Methyl alcohol	CH ₃ OH	64.5	ω
Ethyl alcohol	CH ₃ CH ₂ OH	78.3	ø
n - Propyl alcohol	CH ₃ CH ₂ CH ₂ OH	97	ω
n - Butyl alcohol	CH ₃ (CH ₂) ₂ CH ₂ OH	118	7.9
n - pentyl alcohol	CH ₃ (CH ₂) ₃ CH ₂ OH	123.8	2.3
n - Hexyl alcohol	CH ₃ (CH ₂) ₄ CH ₂ OH	136.5	0.6
n - Heptyl alcohol	CH ₃ (CH ₂) ₅ CH ₂ OH	176	0.2
n - Octyl alcohol	CH ₃ (CH ₂) ₆ CH ₂ OH	195	0.05

• - Miscible in any proportion

• Reactions involving cleavage of the O-H bond

(i) Reaction with sodium

 $R - O H + Na \longrightarrow R - O Na^+ + H_2$

Alcohols behave as acids and react with sodium liberating hydrogen and forming sodium alkoxides. The alkoxide ion is a strong nucleophile and also a strong base.

(ii) Reaction with carboxylic acids (Acylation of alcohols)

C2H5OH + CH3COOH ₽₩₩₩₩ CH3COOC2H5 + H2O

Alcohols react with carboxylic acids to form esters. For this esterification reaction, concentrated H_2SO_4 acid acts as a catalyst.

• Nucleophilic substitution reactions that take place by the cleavage of C-O bond

(i) Alcohols react with PCl₃ or PCl₅ to give alkyl chlorides.

$$3R - OH + PCl_{3} \rightarrow 3RCl + H_{3}PO_{3}$$

R - OH + PCl_{5} \rightarrow RCl + POCl_{3} + HCl

(ii) Reaction with hydrogen halides

R-OH $\xrightarrow{\text{HBr}}$ R-Br + H₂O

Alcohols under go nucleophilic substitution reaction with HBr to give the corresponding alkyl bromides. Protonation of the O atom converts the -OH group into a better leaving group.



In this reaction Br⁻ ion acts as a nucleophile and the leaving group is H₂O.

(iii) Reaction with anhydrous ZnCl, and conc. HCl (Lucas test)

In this reaction, R-OH is converted to R-Cl. $ZnCl_2$ is used as a catalyst. Because alkyl halides are insoluble in water, as the raction proceeds the reaction mixture becomes cloudy and turbid. The time taken for the turbidity to appear, after the mixing of reagents, can be used to distinguish between primary, secondary and tertiary alcohols. Under the provided reaction conditions the above nucleophilic substitution reaction takes place in two steps. Tertiary alcohols form stable intermediate tertiary carbocations and therefore, tertiary alcohols in the presence of the Lucas reagent forms a turbidity in a very short time. Secondary alcohols take longer time and primary alcohols react very slowly.

• Elimination reactions

Alcohols undergo an elimination reaction when treated with conc. H_2SO_4 or when heated with alumina to a higher temperature. The reaction in which a molecule of water is eliminated from an alcohol is the dehydration of alcohols. Here, an alkene is formed as the product of the reaction.



• Oxidation of alcohols

The product of oxidation depends on primary, secondary or tertiary nature of the alcohol.

Oxidation of alcohols can be carried out with H⁺/KMnO₄ or H⁺/K₂Cr₂O₇ or H⁺/CrO₃.

(i) Primary alcohols

$$R - CH_2 - OH \xrightarrow{[O]} R - C \xrightarrow{[O]} R - C \xrightarrow{[O]} OH$$

In the presence of the above mentioned oxidizing agents primary alcohols first give aldehydes. These are further oxidized to carboxylic acids. If pyridinium chlorochromate $[C_5H_5NH^+CrO_3Cl]$ is used, the reaction can be stopped at the stage where aldehyde is formed.



(ii) Secondary alcohols are oxidized to give ketones.

$$R \xrightarrow[R']{} CH \xrightarrow[]{OH} OH \xrightarrow[]{OH} OFPCC R \xrightarrow[R']{O} R \xrightarrow[R']{O}$$

(iii) Tertiary alcohols

Normally the tertiary alcohols do not undergo oxidation under conditions that primary and secondary alcohols are oxidized.

Suggested learning – teaching activities :

- Instruct the students to present the structures for all the alcohols that can be written for the molecular formula, C_4H_9OH and to classify them as primary, secondary and tertiary.
- Direct a discussion to identify the nature of inter-molecular attractions present in alcohols and on the resulting physical properties.
- Direct the students to discuss the melting points, boiling points and the solubility of alcohols in water.
- Give opportunities for students to present giving examples and by demonstrations, the reactions that take place by the cleavage of the O-H bond the elimination reactions and the oxidation reactions of alcohols.

Competency 10.0		:	Investigates the relationship between the structure and properties of oxygen containing organic compounds.
Competency Level	10.2	:	Analyses the reactions of phenol in terms of its carbon- oxygen bond and oxygen-hydrogen bond.
Periods		:	04

- Explains why phenols are more acidic than alcohols.
- Explains why phenols do not undergo nucleophilic substitution reactions undergone by alcohols.

Guidance for teacher elaboration :

• Aromatic compounds, in which an -OH group is joined directly to a carbon atom of a benzene ring are called phenols. Alcohols and phenols dissociate in aqueous solutions as shown below.

 $ROH + H_2O \square RO^- + H_3O^+$

 $C_6H_5OH + H_2O \square C_6H_5O^- + H_3O^+$

Phenols are more acidic than alcohols. This means that in the above equilibria, the equilibrium point for phenols is more towards the right than alcohols. The reason for this is that the stability of phenate ion relative to phenol is greater than the stability of the alkoxide ion relative to the alcohol. The phenate ion is more stable because its negative charge gets delocalized by resonance. In the alkoxide ion there is no such charge dispersion.

Reactions involving cleavage of the O-H bond

• The higher acidity of phenols is confirmed by the following examples too. Although an alcohol reacts with sodium it does not react with NaOH. But phenol reacts with sodium as well as with NaOH. However, phenol is not acidic enough to react with Na₂CO₃.

$$2 C_6H_5OH + 2Na \rightarrow 2C_6H_5O^-Na^+ + H_2$$
$$C_6H_5OH + NaOH \rightarrow C_6H_5O^-Na^+ + H_2O$$

Non occurance of nucleophilic substitution reactions by breaking C-O bond

Unlike alcohols phenols do not undergo nucleophilic substitution reactions because,
 (i) the C-O bond is shorter and stronger due to delocalization of lone pair of electrons on the oxygen atom into the benzene ring. This can be shown by resonance.



(ii) phenyl cation is unstable.

Suggested learning – teaching activities

- Direct the students to do the following experiments.
 - Take some phenol into a test tube.
 - Add about 1cm³ of water. Shake well and put a piece of pH paper into it.
 - Add about 1 cm³ of sodium hydroxide solution, shake well then add about 1 cm³ of dilute HCl.
 - Note down the observation.
- According to the observation made in the above experiments, discuss the conclusions arrived at about phenols.

Competency 10.0		Investigates the relationship between the structure and	
		properties of oxygen containing organic compounds.	
Competency Level 10.3	:	Investigates the effect of the -OH group on the reactivity of the bonzone ring in phonol	
		of the benzene ring in phenoi.	
Periods	:	02	

- States that in the substitution reactions of phenol, the constituent gets attached to the ortho (2,6) and para (4) positions relative to the –OH group.
- Explains why the benzene nucleus of phenol is more reactive towards electrophiles than benzene itself.

Guidance for teacher elaboration :

- Due to the delocalization of the lone pairs of electrons which were on the oxygen atom with the benzene ring, the ring is rich with electrons. It has become very reactive towards electrophilic reagents. The O-H group of phenol is ortho, para directing. (It is not necessary to explain why the -OH group is ortho, para directing)
- When the electrophilic substitution reactions of phenol are compared with the corresponding reactions of benzene along with the relevant conditions, it is clear that the benzene ring of phenol, had become more reactive towards electrophiles. Consider the following examples.
 - (i) Reacts immediately with bromine water to give a white precipitate of 2,4,6-tribromophenol.



(ii) For nitration of phenol even dilute HNO_3 is sufficiently reactive.



Suggested learning – teaching activities :

- Direct the students to the following tests and to get the observations
 - Take about 1cm³ of bromine water into a test tube and add a crystal (one or two drops) of phenol into it.

Competency	10.0	:	Investigates the relationship between the structure and properties of oxygen containing organic compounds.
Competency Level 10.4		:	Investigates the polar nature and unsaturated nature of >C=O bond in aldehydes and ketones as exemplified
			by their reactions.
Periods		:	08

• Explains the unsaturated nature of the carbonyl group.

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- Explains nucleopiblic addition reactions as the characteristic reactions of aldehydes and ketones.
- Presents the mechanisms of a few reactions which are examples for the nucleophilic addition reactions.
- Uses the property of aldehydes to undergo oxidation very easily relative to the ketones to distinguish between them.
- Tests the properties of aldehydes and ketones and reports on them.

Guidance for teacher elaboration :

• Mechanism of the addition of HCN to aldehydes and ketones. This reaction is carried out by adding a dilute mineral acid into a mixture of the carbonyl compound and an aqueous solution of sodium cyanide. Here the CN-ion acts as the nucleophile.



• Mechanism of the reaction with Grignard reagent (RMgX)





R group of Grignard reagent together with the electron pair of R-Mg bond reacts as a nucleophile with carbonyl carbon.

- Mechanism of the reaction with Brady's reagent (2,4-DNP)
 - (i) Nucleophilic addition



(ii) Dehydration

The above intermediate product undergoes dehydration as soon as it is formed to give the final product, which is 2,4–dinitrophenylhydrozone.



2,4–dinitrophenylhydrozone (Dark yellow or orange precipitate)

This reaction is used as a test to identify aldyhydes and ketones.

Reduction

(i) Reduction by $LiAlH_4$ or $NaBH_4$

Here, the aldehydes and ketones get reduced to alcohols.

$$R \sim C = O \xrightarrow{(i) \text{ LiAlH}_4} R \xrightarrow{H} C = O \xrightarrow{(i) \text{ H}_2O/H^+} R \xrightarrow{H} C = OH$$



(iii) Reduction by Zn(Hg)/conc. HCl (Clemenson reduction)Here, the aldehydes and ketones can be reduced to the corresponding hydrocarbons.



• Oxidation of aldehydes

Aldehydes are oxidized to carboxylic acids even by mild oxidizing agents such as Tollen's reagent and Fehling solution.

(i) Oxidation by Tollen's reagent

Tollen's reagent, $[Ag(NH_3)_2]^+$ is prepared by adding dilute ammonium hydroxide to the precipitate of silver oxide formed by the addition of a few drops of dilute sodium hydroxide to an aqueous solution of silver nitrate.

$$R = O + 2[Ag(NH_3)_2]^+ + 3OH^- R = R - C + 2Ag + 4NH_3 + 2H_2O$$

$$O^- Silver mirror$$

Oxidation by Tollen's reagent or the silver mirror test is used to distinguish between aldehydes and ketones.

(ii) Oxidation by Fehling solution

A solution of basic cupric tartarate is known as Fehling solution. This is a dark blue aquous solution. When a few drops of an aldehyde are added to this reagent and heated, the blue colour of the solution gradually disappears and a brick red precipitate of cuprous oxide is formed.



Aldehydes and ketones can be distinguished from each other by Fehling solution.

(iii) Aldehydes get oxidised to carboxylic acids by oxidizing agents such as acidified potassium dichromate or acidified chromic oxide or acidified potassium permanganate.



In the presence of aldehydes the pink colour of $H^+/KMnO_4$ solution become colourless. The orange colour of $H^+/Cr_2O_7^{2-}$ solution turns green. By using these reagents also aldehydes and ketones can be distinguished from each other.

Suggested learning – teaching activities

- Assign various aldehydes and ketones to groups of students and direct them to write down the structures of organic compounds formed by their reactions with the reagents specified in the syllabus.
- Show comparatively that ketones do not undergo oxidation under the conditions in which aldehydes undergo oxidation.
- Test to distinguish between aldehydes and ketones in the laboratory.

Competency 10.0	: Investigates the relationship between the struct	
		properties of oxygen containing organic compounds.
Competency Level 10.5		Recognizes the reactivity of the alpha position of
		aldehydes and ketones as exemplified by self-
		condensation reactions.
Periods	:	04

- Shows using suitable examples the reactivity of the position in carbonyl compounds.
- Presents the condensation reactions of aldehydes and ketones in the presence of sodium hydroxide.

Guidance for teacher elaboration :

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• Due to the strong electron withdrawing nature of the carbonyl group, H atoms attached to the carbon atoms directly bound to the carbonyl carbon (the α - H) become acidic. The α - H can be abstracted as a proton by base (*eg*. OH⁻). The carbanion so formed is stabilized by resonance as shown below.

$$\begin{array}{c} H & H \\ | & | \\ R - C_{\alpha} - C^{\delta +} = O^{\delta -} + OH^{-} \rightleftharpoons R - C - C = O + H_{2}O \\ | & H \end{array}$$

The above carbanion attacks the carbon atom of the carbonyl group of an unionized aldehyde molecule as a nucleophile.

Hence aldehydes and ketones with α hydrogens undergo self - condensation reactions.

Example:

Reaction of acetaldehyde in the presence of aqueous NaOH

$$2CH_{3} - C = O \xrightarrow{\text{NaOH(aq)}} CH_{3} - CH_{2} - CH_{2} - CH_{2} - H_{1}$$

Condensation of acetone

$$2CH_{3} - C = O \xrightarrow{\text{NaOH(aq)}} CH_{3} - CH_{2} - CH_{2} - CH_{3} = O$$

The addition products obtained above undergo dehydration easily. Examples :

$$CH_{3} - CH - CH_{2} - C = O \xrightarrow{H^{+}/\Delta} CH_{3} - CH = CH - C = O + H_{2}O$$

$$CH_{3} - CH_{2} - CH_{2} - CH_{2} - C = O \xrightarrow{H^{+}/\Delta} CH_{3} - CH_{3} - CH_{3} - CH_{3} + H_{2}O$$

$$CH_{3} - CH_{3} - CH_{2} - CH_{2} - C = O \xrightarrow{H^{+}/\Delta} CH_{3} - CH_{3} - CH_{3} + H_{2}O$$

Suggested learning – teaching activities

• Direct the students to select aldehydes and ketones containing hydrogens from the following ones. Accordingly direct the students to select those aldehydes and ketones will undergo self - condensation and to write down the condensation products. α

Competency 10.0	:	Investigates the relationship between the structure and
		properties of oxygen containing organic compounds.
Competency Level 10.6	:	Compares the structure and properties of carboxylic acids with the other oxygen containing organic compounds.
Periods	:	06

• Relates the physical properties of carboxylic acids to their structure.

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- Compares the reactivity pattern of the carboxyl (-COOH) group with that of the carbonyl group in carbonyl compounds and the OH group in phenols and alcohols.
- Compares the acidic properties of carboxylic acids, alcohols and phenol using the reactions with Na, NaOH and Na₂CO₃.
- Presents examples for reactions involving the cleavage of the C-O bond.
- Tests the properties and reactions of carboxylic acids and reports on them.

Guidance for teacher elaboration :

The functional group of the carboxylic acids is the carboxyl group. In the carboxyl group there is a carbonyl group and a hydroxyl group attached to that carbon atom.

- Carboxyl group is a polar functional group. Due to the polarity of C O and O H groups it forms intermolecular hydrogen bonds. Relative to the aldehydes and ketones with equal relative molecular masses, the boiling points of carboxylic acids are higher.
- Carboxylic acids of C_1 to C_4 dissolve well in water. When the number of carbon atoms increases solubility decreases. Aromatic carboxylic acids are water insoluble and exist as solid crystalline substances. Almost all the carboxylic acids are soluble in organic solvents.
- The ability to form dimeric structures where carboxylic acid molecules are attached by hydrogen bonds as pairs is also a reason for the high boiling points of carboxylic acids.

Existence of carboxylic acids as dimer structures attached by hydrogen bonds is shown below.

$$\mathbf{R} - \mathbf{C} = \mathbf{C} - \mathbf{R}$$

Reactions of carboxylic acids

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• Reactions involving the cleavage of O – H bond

 $\begin{array}{l} 2\text{RCOOH} + 2\text{Na} \rightarrow \text{R-COO'Na}^{+} + \text{H}_2 \\ \text{RCOOH} + \text{NaOH} \rightarrow \text{R-COO'Na}^{+} + \text{H}_2 \\ \text{RCOOH} + \text{NaHCO}_3 \rightarrow \text{R-COO'Na}^{+} + \text{CO}_2 + \text{H}_2 \\ \end{array}$

A comparison of the reactions of alcohols, phenols and carboxylic acids with sodium, sodium hydroxide and sodium bicarbonate is given in the table below.

Compound	With Na metal	With NaOH solution	With NaHCO ₃
R - OH	Reacts to form R -O ⁻ Na ⁺ liberating H ₂	No reaction	No reaction
ОН	Reacts to form C_6H_5O -Na ⁺ liberating H_2	Reacts to form $C_6H_5O^-Na^+$ and disolves in the NaOH solution	No reaction
R—С_О-н	Reacts to form RCO_2 -Na ⁺ liberating H_2	Reacts to form RCOO ⁻ Na ⁺ and disolves in the NaOH Solution	Reacts to form RCOO ⁻ Na ⁺ liberating CO_2 gas

The above compounds react with Na_2CO_3 in the same way that they react with $NaHCO_3$.

The acidic strengths of alcohols, phenols and carboxylic acids vary as follows. Alcohols < Phenols< Carboxylic acids

The carboxylic acids attain the following equilibrium in an aqueous solution

$$\mathbf{R} - \mathbf{C} \underbrace{\bigvee_{\mathbf{OH}}^{\mathbf{O}}}_{\mathbf{OH}} \mathbf{R} - \mathbf{C} \underbrace{\bigvee_{\mathbf{O}}^{\mathbf{O}}}_{\mathbf{O}^{-}} + \mathbf{H}_{3}\mathbf{O}^{+}$$

The equilibrium point of the above equilibrium is situated more shifted towards the right side relative to the corresponding equilibrium attained by the phenols. The reason for this is that the stability of the carboxylate ion relative to the carboxylic acid is greater than the stability of the phenoxide ion relative to phenol. The carboxylate ion is a resonance hybrid of the following structures.

$$R - C \underbrace{\bigcirc}_{0}^{0} \xrightarrow{R} - C \underbrace{\bigcirc}_{0}^{0}$$
The stability of the carboxylate ion is due to the delocalization of the negative charge between two equivalant electronegative oxygen atoms.

- Reactions involving cleavage of the C O bond
 - With PCl_3/PCl_5



With alcohols

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$$CH_3 - C \subset O + C_2H_5OH$$

Reduction of carboxylic acids with $LiAlH_4$

Carboxylic acids give alcohols when reduced with $LiAlH_4$ which is a very strong reducing agent. Carboxylic acids and their derivatives are not reduced by $NaBH_4$.

$$CH_{\overline{3}}-CH_{2} - C \xrightarrow{O}_{O-H} \xrightarrow{(i) \text{LiAIH}_{4}} CH_{3}- CH_{2}- CH_{2}- OH$$

Suggested learning – teaching activities :

• Conduct a discussion to explain the nature of bonds in the carboxyl group and hence to discover the physical properties of carboxylic acids.

Competency 10.0	:	Investigates the relationship between the structure and
		properties of oxygen containing organic compounds.
Competency Level 10.7	:	Investigates the characteristic reactions of acid
		derivatives.
Periods	:	03

Learning outcomes

- States that the characteristic reactions of the acid derivatives are nucleophilic • substitution reactions.
- Writes down examples for the characteristic reactions of acid chlorides.
- Writes down examples for the characteristic reactions of esters.

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- Writes down examples for the characteristic reactions of amides.
- Recognizes that the first step in all the reactions in this section is an attack by a • nucleophile on the carbon atom of the carbonylgroup.

Guidance for teacher elaboration :

- Reactions of acid chlorides
 - Reaction with sodium hydroxide (i) Acid chlorides react with NaOH to form the corresponding carboxylic acid which reacts with excess NaOH to form its sodium salt.

$$R - C \xrightarrow{O}_{Cl} \xrightarrow{NaOH} R - C \xrightarrow{O}_{OH} R - C \xrightarrow{O}_{O} \xrightarrow{NaOH} R - C \xrightarrow{O}_{O} \xrightarrow{NaOH}$$

Mechanism of the reaction



Reaction with water (ii)

> Acid chlorides also react with water by a similar mechanism to form the corresponding carboxylic acid.

$$R - C \xrightarrow{O}_{Cl} R - C \xrightarrow{O}_{OH}$$

(iii) Reaction with alcohols

Acid chlorides react with alcohols to form esters

$$R - C \bigvee_{Cl}^{O} + C_2 H_5 - OH \longrightarrow R - C \bigvee_{O-C_2 H_5}^{O}$$

(iv) Reaction with phenol

Acid chlorides react with phenol to form phenyl esters.



(v) Reaction with NH_3

Acid chlorides react with ammonia to form amides

$$R - C \xrightarrow{O}_{NH_3} R - C \xrightarrow{O}_{NH_4} NH_4$$

(vi) Reaction with primary amines

Acidchlorides react with amines to form alkyl amines.

$$\mathbf{R} - \mathbf{C} \stackrel{\mathbf{O}}{\searrow} + \mathbf{H} - \stackrel{\mathbf{H}}{\mathbf{N}} - \mathbf{R} \longrightarrow \mathbf{R} - \stackrel{\mathbf{O}}{\mathbf{C}} - \stackrel{\mathbf{H}}{\mathbf{N}} - \mathbf{R}$$

• Reactions of esters

(i) Esters undergo hydrolysis with dilute acids to form the corresponding carboxylic acid and the alcohol.

$$R - C O C_{2H_{5}} \blacksquare \blacksquare \blacksquare \blacksquare R - C O + C_{2H_{5}}OH$$

(ii) Esters when reacted with aqueous NaOH form the sodium salt of corresponding carboxylic acid and the alcohol.

$$R - C \xrightarrow{O}_{OC_2H_5} \xrightarrow{\mathbf{NtOH}} R - C \xrightarrow{O}_{O'Na^+} C_2H_5OH$$

(iii) With Grignard reagent
 Esters react with Grignard reagents to give tertiary alcohols. Here, the ester is first converted to a ketone which reacts rapidly with the Grignard reagent again to give the product.

$$R \longrightarrow C \longrightarrow OC_{2}H_{5} + 2CH_{3}MgBr \rightarrow R \longrightarrow C \longrightarrow CH_{3} \longrightarrow R \longrightarrow C \longrightarrow CH_{3} \longrightarrow R \longrightarrow CH_{3}$$

(iv) Reduction by LiAlH₄

$$\begin{array}{c} O \\ || \\ R - C - OC_2H_5 \xrightarrow{(i) \text{ LiAlH}_4 \cdot Dry \text{ efter}} RCH_2 - OH + C_2H_5OH \end{array}$$

• Reactions of amides

(i) With NaOH

When amides are warmed with an aqueous solution of NaOH, NH_3 is liberated and the sodium salt of the corresponding carboxylic acid is formed.

$$R - C \xrightarrow{O}_{NH_2} \xrightarrow{Aqueous NaOH} R - C \xrightarrow{O}_{O^-Na^+} + NH_3$$

(ii) With LiAlH₄

Amides are reduced to the corresponding primary amine with LiAlH₄.

$$R - C \underbrace{\bigvee_{\text{NH}_{2}}^{\text{O}}}_{\text{NH}_{2}} \underbrace{\stackrel{\text{(i) LiAlH}_{4}}{\underset{\text{(ii) H^{+}/\text{H}_{2}\text{O}}}} R - CH_{2} - NH_{2}$$

Suggested learning – teaching activities :

• Assign the characteristic reactions of acid chlorides, esters and direct them to study those.

Competency 11	:	Investigates the relationship between structure and
		properties of nitrogen containing organic compounds.
Competency Level 11.1	:	Analyses amines and aniline in terms of their characteristic
		reactions and properties.
Periods	:	06

Learning outcomes

- Identifies the types of alkyl amines.
- Studies the reactions of primary amines.

Guidance for teacher elaboration :

 Amines can be defined as compounds where alkyl or aryl groups are attached to nitrogen in place of hydrogen atoms in ammonia. Amines are classified as primary, secondary and tertiary. Unlike the alkyl halides and alcohols, the amines are classified according to the number of alkyl or aryl groups attached to the nitrogen atom. The compounds in which an alkyl or an aryl group is attached in place of one of the three atoms of hydrogen in ammonia are called primary amines. The compounds in which two alkyl or aryl groups are attached in place of two atoms of hydrogen in ammonia are called secondary ammines and the compounds in which three alkyl or aryl groups are attached in place of the three atoms of hydrogen are called tertiary amines.

Examples:

$$\begin{array}{c} CH_{3}NH_{2} \\ H_{3}NH_{2} \\ H_{3}NH_$$

Primary amine

• The compounds in which at least one aryl group is attached to the nitrogen atom are called aryl amines.



• Aniline readily reats with bromine water to give a white precipitate as -NH₂ group activates benzene ring.



• Amines act as nucleophiles due to the lone pair of electrons on the nitrogen atom. The following are some of the reactions of primary amines with various reagents where the amine acts as a nucleophile.

(i) With acid chlorides

$$R - NH_2 + R - COC1 \longrightarrow R' - C - NH - R$$

(ii) With aldehydes and ketones

$$R-NH_{2} + R'-C-H \longrightarrow R-N = C-H + H_{2}O$$

$$H R - N-C-H$$

$$H R - H_{2}O$$

The above reaction corresponds to the reaction of aldehydes and ketones with the Brady's reagent.

(iii) With alkyl halides

$$CH_3NH_2 + RCl \longrightarrow CH_3 - N - H$$

The secondary amine thus formed reacts further with alkyl halide to form a tertiary amine and a quaternary ammonium salt.

$$\begin{array}{c} \mathrm{CH}_{3}-\mathrm{N}-\mathrm{H}+\mathrm{RC1}\longrightarrow\mathrm{CH}_{3}-\mathrm{N}\\ \mathrm{R}\\ \mathrm{CH}_{3}-\mathrm{N}\\ \mathrm{R}+\mathrm{RC1}\longrightarrow \left[\begin{array}{c}\mathrm{CH}_{3}-\mathrm{N}-\mathrm{R}\\ \mathrm{R}\end{array}\right]^{*}\mathrm{C1}\end{array}$$

Accordingly, a mixture of products is obtained in the above reaction.

(iv) With NaNO₂/HCl (Nitrous acid)

Primary amines react with nitrous acid to form diazonium salts. As alkyl diazonium salts are unstable they rapidly convert to alcohols with the evolution of nitrogen gas.

 $R-NH_2 \xrightarrow{NaNO_2/dal.HCl} R-N_2^+Cl^- \xrightarrow{H_2O} R-OH + N_2 + HCl$

Alkyl diazonium chloride

Aromatic diazonium salts formed from aryl amines are more stable particularly at low temperatures.

Suggested learning – teaching activities :

- Assign the students to present structures for the possible alkyl amines for a given molecular formula.
- Discuss the reactions of primary amines.

Competency 11		:	Investigates the relationship between structure and properties of nitrogen containing organic compounds.
Competency Level	11.2	:	Compares and contrasts the basicity of amine with other organic compounds.
Periods		:	05

Learning outcomes

- Compares the basicity of aliphatic amines with that of aniline.
- Compares the basicity of amides with that of amines.

Guidance for teacher elaboration :

• Dilute mineral acids convert amines into their salts. These salts react with aqueous hydroxides to regenerate the amine.

Hence it is clear that although amines are more basic than water, they are less basic than hydroxide ions.

$$\begin{split} & \mathbb{R} - \mathbb{N}\mathbb{H}_2 + \ \mathbb{H}_3\mathbb{O}^+ \ \rightarrow \mathbb{R}\mathbb{N}\mathbb{H}_3^+ + \mathbb{H}_2\mathbb{O} \\ & \mathbb{R} - \mathbb{N}\mathbb{H}_3^+ + \ \mathbb{O}\mathbb{H}^- \ \rightarrow \mathbb{R}\text{-}\mathbb{N}\mathbb{H}_2 + \mathbb{H}_2\mathbb{O} \end{split}$$

• Amines are more basic than alcohols

:

 $R - OH + H^+ \square$ ROH_2^+ Alkyl oxonium ion $R - NH_2 + H^+ \square$ RNH_3^+ Alkyl ammonium ion

As nitrogen is less electronegative than oxygen it has a higher tendency to donate lone pair of electrons. Hence the stability of the alkyl ammonium ion relative to the amine is stronger than the stability of the alkyl oxonium ion relative to the alcohol. The reason for this is that an atom with low electronegativity can bear a positive charge more easily.

• Aliphatic primary amines are more basic than aniline. The reason for the low basicity of aniline is because the lone pair of electrons on the nitrogen of aniline is not easily available to a proton due to it being delocalized on to the aromatic ring by resonance.



Amides are less basic than amines. It is because the pair of electrons on the nitrogen of the amide group is delocalized on to the carbonyl group by resonance.



Suggested learning – teaching activities :

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• On the basis of the ability to donate the lone pair of electrons on the oxygen and nitrogen atoms of alcohols, amines, aniline and amides explain the basicity of these compounds comparatively.

Competency 11		Investigates the relationship between structure and properties of nitrogen containing organic compounds.		
Competency Level 11.3	:	Investigates the reactions of diazonium salts.		
Periods	:	04		

Learning outcomes

• Describes the preparation of diazoniaum salt.

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- Writes down the reactions of diazonium salts with water, H₃PO₂, CuCl, CuCN, CuBr and KI.
- Writes down examples for the reactions in which the diazonium ion behaves as an electrophile.

Guidence for teacher elaboration :

• Aniline reacts with nitrous acid to give phenol.



Aromatic diazonium salts are more stable than aliphatic diazonium salts. Therefore, when this reaction is carried out at low temperatures, the conversion of the aromatic diazonium salt to the phenol can be slowed down, and the diazonium salt can be isolated.



- · Reactions of diazonium salts in which the diazonium group undergoes replacement.
 - With water



- With CuCl



- With CuBr



- With hypophosphorus acid

.

$$\bigcirc \xrightarrow{H_3PO_2} \bigcirc + N_2 + H_3PO_3 + H^4$$

- Diazonium salts can react as electrophiles in electrophilic substitution reactions. $N_2^+ Cl^{\text{-}}$

Examples:

Benzene diazonuim chloride reacts with phenol to give an orange coloured compound, and with β -naphthol to give a red coloured compound.



Suggested learning – teaching activities :

- Advice the students to draw simple structures for amines, alcohols, aniline and amides.
- Explain comparatively the basicity of these compounds in terms of the ability to donate the lone pairs of electron on their atoms.

Competency 12.0		Uses the principles of chemical kinetics in determining
		the rate of a chemical reaction and in controlling the rate
		of reaction.
Compotency low	.1121.	Determine the factors effecting the rate of a chemical re-

Competency level 12.1: Determine the factors affecting the rate of a chemical reactions.

Periods

Learning outcomes

• States that for any type of change, rate is the change per unit time.

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- Illustrates using various examples that time is the basis in expressing rate.
- Provides examples for chemical reactions taking place at various rates.
- States that the change in the amount of a substance is the fundamental factor in measuring the rate of a reaction.
- Expresses that other properties (refractive index, etc.) which depend on the amount of a substance or concentration can also be used to compare rates.
- States that the study of the rates of instantaneous reactions is difficult because the time for them cannot be measured.
- Provides examples for the fact that for slow reactions where time can be measured, the rates can be studied.
- Demonstrates the effect of temperature on the rate of chemical reactions.
- Provides examples for the fact that concentration affects the rate of chemical reactions.
- Demonstrates the effect of the physical nature of reactants (or surface area) on the rate of chemical reactions.
- Demonstrates the effect of homogeneous catalysts on the rate of chemical reactions.
- Demonstrates the effect of heterogeneous catalysts on the rate of chemical reactions.

Guidance for teacher elaboration :

- Rate of a reaction can be defined as the change of concentration (either decrease of concentration of reactants or increase of concentration in products) within a unit time.
- Factors affecting rate of reactions
 - Temperature
 - Concentration (Pressure)
 - Physical nature (Surface area of reactants)
 - Catalysts (Heterogeneous/Homogeneous)

Suggested learning - teaching activities:

- Classify processes as instant, short-term and long-term. Give as many examples as possible.
- Put copper and zinc metals separately into approximately 50% HNO₃ and show the difference in the reaction rate.
- Put a piece of zinc to a $CuSO_4$ solution and show the change in colour. Since colour is a measure of the concentration of a solution, discuss that the change in colour can be taken as an indicator to compare the reaction rates.

Experiment I : *Effect of concentration on the rate of a reaction.*

• Equal volumes of water (10.0 cm³) are added to test tubes along with two pieces of magnesium ribbon of 2 cm long. Apparatus are arranged as in the diagram keeping all the factors identical except the concentration of an acid by adding 2 drops of a hydrochloric acid solution to one test tube and 4 drops of the same solution to the other.



- Gas bubbles evolve faster in the test tube containing acid in higher concentration.
- It can be concluded that concentration affects the rate of a reaction.

Experiment II : Effect of temperature on the rate of a reaction.

• Apparatus are set as shown in the diagram keeping all the factors identical except temperature.



- It can be seen that the solution kept at higher temperature decolourizes faster.
- Therefore, temperature affects the rate of a reaction.

Experiment III: Effect of the physical nature (surface area) of reactants on the rate of a reaction.

- To two test tubes separately add a lump of CaCO₃ and CaCO₃ powder of equal mass.
- To each test tube, add equal volumes of a HCl solution of the same concentration (e.g. 0.01 mol dm⁻³)
- Keep both tubes in a water bath.
- Observe the difference in the rates of evolution of gas.
- Emphasize the need to immerse in a water bath.
- It can be observed that the tube containing CaCO₃ powder effervesces faster.
- Thus, it can be concluded that the physical nature of reactants affects the rate of a reaction.

Experiment IV : *Effect of catalysts on the rate of a reaction*

- Add 10.0 cm³ samples of '20 volume' H_2O_2 to two boiling tubes. ('20 volume' means that unit volume of H_2O_2 solution gives twenty volumes of O_2 at STP)
- Add 5.0 cm³ of water to one tube and 5.0 cm³ of 0.1 mol dm⁻³ NaOH to the other.
- It is seen that gas bubbles evolve faster in the tube with NaOH.
- This leads to the conclusion that NaOH increases the rate of decomposition of H₂O₂.
- (a) Homogeneous catalysts : If the catalyst and the reactants are in the same phase, they are called homogeneous catalysts.

e.g. (i)
$$2H_2O_2(aq) \xrightarrow{NaOH(aq)} O_2(g) + 2H_2O(1)$$

(ii) $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$

(b) Heterogeneous catalysts : If the catalyst and the reactants are in different phases, they are heterogeneous catalysts.

e.g. (i)
$$2H_2O_2(aq) \xrightarrow{MnO_2(s)} O_2(g) + 2H_2O(l)$$

(ii)
$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_1(g)} 2SO_3(g)$$

12.0	:	Uses the principles of chemical kinetics in determining		
		the rate of a chemical reaction and in controlling the rate		
		of reaction.		
vel 12.2	:	Controls the rate of a reaction by appropriately manipulat- ing the concentration of reactants.		
	12.0 vel 12.2	12.0 : vel 12.2:		

Periods : 14

Learning outcomes

- Generalizes a chemical reaction as $aA + bB \rightarrow cC + dD$.
- Defines rate of reaction as rate with respect to the change of concentration of the

reactant A $\left(-\Delta c_{A} \right)$ or rate with respect to the change of concentration of

the product $D \left(\begin{array}{c} \Delta c_{\mathbf{p}} \\ \Delta t \end{array} \right)$.

- Expresses that in a given reaction, the rates of removal of each reactant and rates of formation of each products are not equal.
- States that the rate of removal of a reactant or formation of a product depends on the stoichiometric coefficients of the respective substances.
- States accordingly that rate of reaction = $-\frac{1}{a} \frac{\Delta c_{A}}{\Delta t} = \frac{1}{d} \frac{\Delta c_{D}}{\Delta t}$.
- Affirms that a specific reactant or a product should be selected to compare reaction rates.
- States that the order of the reaction with respect to a given reactant shows how the concentration of that reactant affects the rate of the reaction.
- Defines the rate law for reactions as, rate = $k [A]^{x} [B]^{y}$.
- Defines the terms in the rate law.
- Writes the rate law (equation) for first and second order reactions.
- Derives the units of the rate constant (coherent SI units and non-coherent SI units) for first and second order reactions.
- Writes the rate law (equation) for zero order reactions.
- Interprets the overall order of a reaction.
- Demonstrates graphically how the rate changes with concentration for a zeroth order, first order and second order reaction.
- Interprets half-life of a reaction.
- Explains that half life of first order reactions does not depend on concentration.
- Provides practical examples for reactions of different orders.
- Displays initial rate, instantaneous rate and average rate of a reaction using suitable graphs.

- Conducts experiments to illustrate zeroth order, first order and second order reactions.
- Determines order of reactions with respect to various reactants by handling appropriately the information obtained from experiments.
- Solves problems related to rate law and order of reactions.

Guidance for teacher elaboration :

 $aA + bB \rightarrow cC + dD$

- Rate of reaction with respect to $A = \frac{-\Delta c_A}{\Delta t}$
- Rate of reaction with respect to $D = \frac{\Delta c_{D}}{\Delta t}$
- Rate law for the above generalized equation $= k [A]^x [B]^y$, where x and y are order of reaction with respect to reactants A and B respectively.
- (x + y) of the above expression is referred as the overall order of the reaction.

Suggested learning teaching activities:

Experiment I : Determination of the effect of concentration of the acid on the reaction between magnesium and acids.

Requirements: $250 \text{ cm}^3 \text{ of } 0.1 \text{ mol } \text{dm}^{-3} \text{ H}_2 \text{SO}_4$

Six pieces of 2.0 cm cleaned magnesium ribbon.

Method :



- Into a boiling tube, 10.0 cm³ of water is added and marked with a rubber band.
- Into the same boiling tube, $40.0 \text{ cm}^3 \text{ of } 0.1 \text{ mol } \text{dm}^{-3} \text{ H}_2 \text{SO}_4$ is added and filled with water brimfully.
- The cleaned magnesium ribbon is fixed as shown in the diagram to the bung, the tube is closed with the bung and turned upside down while switching on the stop watch simultaneously.
- Time taken by the gas to fill up to the level of the rubber band is measured.

• Measurement of time is repeated for different solutions tabulated below, every time fixing a fresh Mg ribbon.

Volume of 0.1 mol dm ⁻³	Time taken for the gas to fill
H_2SO_4/cm^3	up to the graduated level/s
40.0	
35.0	
30.0	
25.0	
20.0	
15.00	

• $R \alpha \left[H^{\dagger}(aq) \right]^{n}$

Initial rate = Average rate for a small change from the starting point.

$$= \frac{\text{Volume of the gas produced}}{\text{Time taken}} = \frac{\text{Constant}}{\text{Time taken}} = \frac{k}{t}$$

• Calculate the concentration of each acid solution and plot a graph between [H⁺] and 1/*t*. Discuss the results.

Experiment II : Determination of the effect of concentration on the rate of the reaction between $Na_{2}S_{2}O_{3}$ and HCl.

Requirements : $0.10 \text{ mol dm}^{-3} \text{Na}_2 \text{S}_2 \text{O}_3$ solution. 2.0 mol dm⁻³ HCl solution, stop watch, boiling tubes, measuring cylinders, 50 cm³ beaker.

Theory :
$$S_2O_3^{2-}(aq)+2H^+(aq) \rightarrow S(s)+SO_2(g)+H_2O(l)$$

Method

:

- Given volume of $Na_2S_2O_3$ solution as shown in the table is added to a 50 cm³ beaker.
- The beaker containing the $Na_2S_2O_3$ solution is kept on a white paper marked with a cross. Relevant volume of the HCl solution is added and the time to disappear the cross is measured keeping the eye at a constant height from the beaker.
- The beaker is cleaned and the experiment is repeated mixing the solutions given in the table below.
 - (i) Determining the relationship between the reaction rate and the thiosulphate ion concentration.

The experiment is done using thiosulphate solutions of different concentrations as given in the table.

Volume of $Na_2S_2O_3$	Volume of	Volume of HCl	Time/s
solution/cm ³	water/cm ³	solution/cm ³	
25.0	-	5.0	
20.0	5.0	5.0	
15.0	10.0	5.0	
10.0	15.0	5.0	
5.0	20.0	5.0	

 $R \alpha \left[S_2 O_3^2 (aq) \right]^{h}$

 (ii) Determining the relationship between the reaction rate and the concentration of hydrogen ions.

The experiment is done using acid solutions of different concentrations as given in the table.

Volume of $Na_2S_2O_3$	Volume of	Volume of HCl	Time/s
solution/cm ³	water/cm ³	solution/cm ³	
25.0	-	5.0	
25.0	1.0	4.0	
25.0	2.0	3.0	
25.0	3.0	2.0	
25.0	4.0	1.0	

$$R \alpha \left[\mathrm{H}^{+}(aq) \right]^{\mathrm{m}}$$

In both the above instances, assume that the rate is constant during the period of

measurement of time taken to disappear cross and it is equal to the initial rate. Then,

Rate = constant / t

In both instances examine how concentration varies with 1/t.

Experiment III: Determination of the effect of concentration on the rate of the reaction between Fe(III) ions and KI.

Theory:
$$2Fe^{3+}(aq) + 2I(aq) \xrightarrow{\text{Slowby}} I_2(aq) + 2Fe^{2+}(aq)$$

The amount of I_2 produced can be used to determine the rate of this reaction. The minimum iodine concentration required to turn starch blue is 1.0×10^{-5} mol dm⁻³. Since this is very small, measuring time is difficult. Therefore, time taken to appear blue colour should be delayed to measure the time. This can be affected through a faster reaction which converts I_2 to I^- . For this Na₂S₂O₃ can be used.

$$2\mathrm{S}_2\mathrm{O}_3^{2\text{\cdot}}(\mathrm{aq}) + \mathrm{I}_2(\mathrm{aq}) \xrightarrow{\mathrm{Fast}} \mathrm{S}_4\mathrm{O}_6^{2\text{\cdot}}(\mathrm{aq}) + 2\mathrm{I}^{\text{\cdot}}(\mathrm{aq})$$

A known amount of $Na_2S_2O_3$ is added to the medium. The moment in which $Na_2S_2O_3$ is over, the solution turns blue. The amount of I_2 formed depends on the amount of $Na_2S_2O_3$ added.

Requirements :

0.10 mol dm⁻³ KI solution, 0.10 mol dm⁻³ FeCl₃ or Fe(NH₄)(SO₄)₂ solution, 0.10 mol dm⁻³ Na₂S₂O₃ solution, 0.10 mol dm⁻³ H₂SO₄ solution, stopwatch

Method:

Step I

(1)	(2)	(3)	(4)	(5)	
Volume of	Volume of	Volume of	Volume of	Volume of	Time taken
0.1 mol dm^{-3}	0.1 mol dm ⁻³	0.1 mol dm ⁻³	0.1 mol dm ⁻³	water/cm ³	to turn
Na ₂ S ₂ O ₃	H_2SO_4	KI	FeCl ₃		starch
solution with	solution/cm ³	solution/cm ³	solution/cm ³		blue/cm ³
starch/cm ³					
10.0	10.0	25.0	10.0	-	
10.0	10.0	20.0	10.0	5.0	
10.0	10.0	15.0	10.0	10.0	
10.0	10.0	10.0	10.0	15.0	
10.0	10.0	5.0	10.0	20.0	

Mix the solutions given in the above table as shown here. Measure the time taken to turn the solution blue. (2) + (4)

(2) + (4)	
(1) + (3) + (5)	

Step II					
(1)	(2)	(3)	(4)	(5)	
Volume of	Volume of	Volume of	Volume of	Volume of	Time taken
0.1 mol dm^{-3}	0.1 mol dm ⁻³	0.1 mol dm ⁻³	0.1 mol dm ⁻³	water/cm ³	to turn
Na ₂ S ₂ O ₃	H ₂ SO ₄	KI	FeCl ₃		starch
solution with	solution/cm ³	solution/cm ³	solution/cm ³		blue/s
starch/cm ³					
10.0	10.0	10.0	25.0	-	
10.0	10.0	10.0	20.0	5.0	
10.0	10.0	10.0	15.0	10.0	
10.0	10.0	10.0	10.0	15.0	
10.0	10.0	10.0	5.0	20.0	

In both instances examine how rate (1/t) varies with concentration.



According to the shape of the graph, order of the reaction (n) can be determined.

Initial rate, instantaneous rate and average rate



 R_1 , R_2 and R_3 are the instantaneous rates of the reaction at time t_1 , t_2 and t_3 respectively.

Half-life of a reaction ($t_{1/2}$)

- Half-life of a reaction is the time required for initial concentration of a reactant to be reduced to half.
- Given below is the graph showing the variation of concentration of a first order reaction with time. The half-life of a first order reaction is independent of the initial concentration.



Competency 12.0	:	Uses the principles of chemical kinetics in determining the rate of a chemical reaction and in controlling the rate of reaction.		
Competency level 12.3:		Uses molecular kinetic theory to explain the effect of factors affecting the rate of chemical reactions.		
Periods	:	04		
Learning outcomes	:	 Lists the factors essential for a reaction to occur. Defines the term activation energy. States that when temperature increases kinetic energy of molecules is also increased. Draws the Boltzmann distribution curve for gaseous molecules at two different temperature and compares the kinetic energy of molecules at different temperatures. Explains the increase of rate of a reaction in terms of the increases of kinetic energy of molecules. Explains the increase of number of collisions per unit volume per unit time using the concept of concentration. States that collisions having appropriate orientation is proportionate to the total number of collisions. States that when the temperature increases the number of molecules with energy exceeding activation energy also increases. States that when surface area of a solid reactant increases rate of reaction also increases due to the increase of number of collisions. Describes the effect of catalyst in terms of the activation energy for the reaction. 		
Guidance for teacher	ela	boration :		

- For a reaction to take place;
 - the reacting molecules should collide.
 - the colliding molecules should have a proper orientation.
 - the reacting molecules should have kinetic energy greater than or equal to certain minimum value. This minimum value of energy is called activation energy.

• Proper orientation

(A)

Consider the following reaction.

 $NO(g) + Cl_2(g) \longrightarrow NOCl(g) + Cl(g)$ Consider two orientations leading to collisions.



Nitrogen atom of NO molecule collides with Cl atom of Cl_2 molecule forming N-Cl bond.



Oxygen atom of NO molecule approaches Cl_2 molecule, so N-Cl bond is not formed. Two molecules bounce away from each other.

• Activation energy

The minimum energy required for colliding molecules to react is called activation energy (E_a) . The value of E_a is different from reaction to reaction. The activation energy is an energy barrier.



- The collisions may also occur between two molecules which have less energy than activation energy. But in this case the reactant molecules fly apart after the collision.
- The rate of reaction depends on the activation energy (E_a) . When E_a decreases, the number of molecules which have higher energy than E_a , increases. So, the number of effective collisions increases and the rate is increased.

Factors affecting the rate of reactions

Temperature

When temperature increases, the kinetic energy and the number of collisions per unit time and per unit volume also increase. Hence, the number of effective collisions per unit time also increases. Thus the rate of reaction increases.

The fraction of molecules having energy greater than the activation energy increases rapidly in most reactions even with a small increase in temperature. This can be explained by the Maxwell-Boltzmann energy distribution graphs.



• Concentration

When the concentration of the reactants increases the number of molecules per unit volume increases. Hence, the number of effective collisions per unit volume and per unit time also increases. So, the rate of reaction increases.

N.B. In gaseous reactions, when the pressure increases at a constant temperature, the volume decreases. So the concentration increases. In gaseous reactions, the rate of reaction increases with the increasing pressure.

Catalysts

A catalyst changes the mechanism of the reaction and provides a new path with low kinetic energy. So the number of molecules with energy greater than the activation energy increases. Therefore, the effective number collisions per unit time also increases leading to an increase in the reaction rate.



 $\mathrm{E_{a}}\,$ - Activation energy without the catalyst.

 $\mathrm{E}_{\mathrm{a/c}}$ - Activation energy with the catalyst.



• Physical nature of the reactants

The smaller the size of solid reactant particles, the greater the surface area with which the reacting molecules can collide. This increases the reaction rate.

e.g. Powdered CaCO₃ reacts faster than lumps of CaCO₃ with a solution of HCl.

Suggested learning-teaching activities :

- Discuss the requirements of a reaction to produce products.
- Discuss how concentration, temperature, surface area and catalyst affect rate of reaction in relation to collision theory.

Competency 12.0	•	ses the principles of chemical kinetics in determining ne rate of a chemical reaction and in controlling the rate f reaction.		
Competency level 12.4:		Uses reaction mechanisms to describe the rate of chemical reactions.		
Periods	:	04		
Learning outcomes	:	 Distinguishes elementary reactions from complex reactions. Explains the relationship between the mechanism of a reaction and the order of a reaction. Constructs energy profiles for reactions to explain the events that follow collisions using basic principles of energetics. States that use of isotopes and study of kinetics can be used 		

 States that use of isotopes and study of kinetics can be used to propose reaction mechanisms.

Guidance for teacher elaboration :

- Some reactions take place in one step. They are called **elementary reactions**. Elementary reactions are not very common.
 - e.g.

(i) NO (g) + O₃(g)
$$\longrightarrow$$
 NO₂(g) + O₂(g)
(ii) CH₂ $\xrightarrow{CH_2}$ CH₂(g) $\xrightarrow{CH_2}$ CH₂(g)

• Most chemical reactions, even apparently simple ones, take place in stages and are really multistep reactions. The following is an example.

$$\begin{array}{l} 2\mathrm{N}_2\mathrm{O}_5(\mathrm{g}) \rightarrow 4\mathrm{NO}_2(\mathrm{g}) + \mathrm{O}_2(\mathrm{g}) & \text{Overall reaction} \\ 2(\mathrm{N}_2\mathrm{O}_5 \ \square & \mathrm{NO}_2 + \mathrm{NO}_3) \\ \mathrm{NO}_2 + \mathrm{NO}_3 & \rightarrow \mathrm{NO}_2 + \mathrm{NO} + \mathrm{O}_2 \\ \hline \mathrm{NO} + \mathrm{NO}_3 & \rightarrow 2\mathrm{NO}_2 \\ \hline 2\mathrm{N}_2\mathrm{O}_5(\mathrm{g}) & \rightarrow 4\mathrm{NO}_2(\mathrm{g}) + \mathrm{O}_2(\mathrm{g}) \end{array}$$

• The fact that reactions proceed through several steps can be shown by adding hydro gen peroxide to an acidified solution of potassium dichromate.

$$Cr_{2}O_{7}^{2-} + 2H^{+} + 4H_{2}O_{2} \longrightarrow 2CrO_{5} + 5H_{2}O$$
(Blue)
$$2CrO_{5} + 6H^{+} \longrightarrow 2Cr^{3+} + 2H_{2}O + H_{2}O_{2} + 3O_{2}$$
(Green)

- The sequence of elementary steps leading to the net change represented by a balanced chemical equation is called the **mechanism** of the reaction.
- Sometimes, isotopes are effectively used to propose mechanisms of reactions.

e.g.
$$R-C$$
 $+$ HO-R' $R-C$ $O-R'$ $+$ $H_2^{18}O$

¹⁸O isotope shows that ¹⁸OH group of the acid is used to produce water during esterification.

$$^{18}\text{OH}^- + \text{R} - \zeta_{O-R} \xrightarrow{H_2O} \text{R} - C_{18O} \xrightarrow{O} + \text{ROH}$$

Absence of ¹⁸O in the alcohol shows that acyl-oxygen fission occurs during the alkaline hydrolysis of esters.

• The number of molecules that appears ina balanced chemical equation is known as **molecularity**. In elementary reactions, molecularity is equal to the **order** of the reaction.

Molecularity	Reaction	Rate expression	Reaction order
Unimolecular	A \longrightarrow Products	R = k [A]	First order
Bimolecular	2A> Products	$R = k[A]^2$	Second order
Trimolecular	3A→ Products	$R = k[A]^3$	Third order

• In complex (multi-step) reactions, the rate is determined by the slowest step. Therefore, it is called the **rate determining step (RDS)**. Hence, RDS is the decisive factor that determines the rate law of a multi-step reaction.

e.g. $A + 2B \longrightarrow AB_2$ (Overall reaction)

 $A + B \xrightarrow{\text{Slow}} AB \text{ (RDS)}$ $AB + B \xrightarrow{\text{Fast}} AB_2$ R = k [A][B]

- When a reaction is zero order with respect to one reactant, it means that the mechanism consists of two or more steps, the step in which this reactant involved being relatively fast.
- For the reasons described above, we cannot predict the influence of concentration of reactants on the reaction rate, just by looking at the overall chemical equation. The order is an empirical entity determined by experiment.
- It is known that if a reaction is to occur, the reacting molecules should collide in proper orientation. Consider the following reaction which is endothermic and believed to occur in a single step.

 $NO + Cl_2 \longrightarrow NOCl + Cl$

When the two molecules approach each other in a collision, the electron clouds experience a gradual increase in their mutual repulsions, and the molecules begin to slow down. While this is happening the **kinetic energy** of the molecules is converted to **potential energy**.

- As the reactant molecules move along the reaction coordinate or progress of the reaction is towards the products, the potential energy passes through a peak. The arrangement of atomic nuclei and bonding electrons at the potential energy maximum is called the **acti vated complex (AC)**. It can be represented as : O=N·····Cl·····Cl. The AC is highly unstable, cannot be isolated and transitory in nature. Therefore, it is also called the **transition state (TS)**.
- If the reacting molecules have sufficient kinetic energy to interpenetrate the electron clouds and break the old bonds, the AC may separate into the products forming new bonds, i.e. NOCl and Cl. In the event that they do not have sufficient energy to attain the summit, they rebound and fly apart.

 $O = N + Cl_2 \implies (O = N \cdots Cl \cdots Cl) \longrightarrow O = N - Cl + Cl^{\bullet}$ (Activated complex or transition state)

This can be represented by the following energy profile.



• The activation energy of the forward reaction $(E_{a(f)})$ is the difference between the

potential energy of the AC and the potential energy of the reactants in the ground state. It is the minimum extra energy that has to be provided to reactants to produce the AC through collision in proper orientation.

The activation energy of the reverse reaction $(E_{a(r)})$ is the difference between the potential energy of the AC and the potential energy of the products in the ground state. It is the minimum energy required to form the AC from the products. The difference between $E_{a(r)}$ and $E_{a(r)}$ is equal to the enthalpy change of the reaction (Δ H).

$$\Delta H = E_{a(f)} - E_{a(r)}$$

(For exothermic reactions it should be noted that the products lie below the level of reactants energetically).

e.g. $NO_2Cl + Cl' \longrightarrow NO_2 + Cl_2$



• Multi-step reactions proceed through more than one potential energy peak or transition state. In these reactions, relatively more stable **reactive intermediate (I)** lies at a dip in the energy profile. The 'I' may be isolated or spotted by virtue of its spectrum. It may change into another AC (TS) before finally being converted into products. The 'I' often provides a great deal of information on the nature of the TS.



- E = Activation energy of the overall reaction $E_{a_1} = Activation energy of the first step$ $E_{a_2}^{a_2} = Activation energy of the second step$ $E_{a_3}^{a_2} = Activation energy of the reverse reaction, I \longrightarrow A+B$ $E_{a_4}^{a_3} = Activation energy of the reverse reaction, D \longrightarrow A+B$
- Substitution of an electrophile (E⁺) to benzene (ArH) can be taken as an example for this type of a reaction.



Suggested learning-teaching activities:

- Collect information about real reactions and ask the students to suggest their rate laws given the RDS.
- Lead a discussion on what would happen when two molecules approach each other in proper orientation and construct the potential energy profile.
- Direct the students to explore how kinetics is useful in determining the mechanisms of reactions.
- Guide students to conduct the proposed experiments.

Competency 13.0	: Uses the concept of equilibrium and its principles to
	determine the macroscopic properties of closed systems in
	dynamic equilibrium.

Competency level 13.1 : Quantitatively determines the macroscopic properties of systems with the help of the concept of equilibrium.

Periods : 14

Learning outcomes :

- Describes closed, open and isolated systems with examples.
- Explains the steady state and systems in the steady state by giving examples.
- Explains the dynamic nature and reversibility of a system.
- Uses physical and chemical processes such as changes of state, equilibria in solutions, chemical systems, ionic systems and electrodes as examples to describe the systems in equilibrium.
- States the equilibrium law.
- Writes the equilibrium constants for the systems given.
- Explains the equilibrium point.
- Applies Le Chatelier's principle to a disturbed system.
- Describes how concentration, pressure, temperature and catalysts affect the equilibrium.
- Solves problems based on $K_{\rm p}$, $K_{\rm c}$ and $K_{\rm D}$.

Guidance for teacher elaboration :

- Refer 'guidance for teacher elaboration' of competency level 5.1.
- Systems in the steady state

When the rate of formation of a component in a system becomes equal to the rate of loss of it from the system, it is said to be in a steady state. This process can take place in open or closed systems. In a steady state, macroscopic properties do not change. Examples :

- (i) When the rate of inflow of water into a tank is equal to the rate of outflow, the volume of water in the tank remains the same.
- (ii) When the ozone layer is considered, the concentration of ozone remains constant due to the following reactions, so it is at the steady state.

$$\bigcirc_{3}(g) \xrightarrow{UV \text{ radiation}} \bigcirc(g) + \bigcirc_{2}(g) \rightarrow \bigcirc_{3}(g)$$

(iii) The concentration of O_2 in the atmosphere remains constant due to various processes that release and consume oxygen.

- (iv) Think of a candle burning uniformly. Apparently the flame does not change because the rates of entry and exit of materials to and from it are equal. The above systems are not in equilibrium.
- Macroscopic properties

The properties experimentally determined or calculated taking a system as a whole are macroscopic properties. Here no attention is paid to the particles constituting the system.

• Dynamic processes and reversibility

Consider the following reversible change taking place in a closed system with only A introduced into it at a constant temperature.

Initially, the rate of turning A into B is high and the rate of the reverse change is zero. With the formation of B, the rate of turning B into A increases and the rate of A becoming B decreases. At a certain moment, the rates of forward and backward reactions become equal. At this point, the system is in dynamic equilibrium. This can be shown by the graph given below.



- This kind of equilibria are established only if the change is reversible.
- The equilibrium is attained only in closed systems at constant temperature.
- The equilibrium can be approached starting from either end.
- The equilibrium is dynamic, i.e. both forward and reverse processes occur even at equilibrium at the same rate.
- The macroscopic properties of the system do not change at equilibrium.
- Dynamic equilibria are prevalent both in physical and chemical systems.

• Liquid - gas equilibria

The following dynamic equilibrium is established between liquid water enclosed in a closed container and water vapour in the space above it.

$$H_2O(1)$$
 \Box $H_2O(g)$

• Solid- gas equilibria

Iodine is a solid which sublimes. The following dynamic equilibrium sets in between iodine crystals and iodine vapour above them when some iodine is kept in a closed bottle.

 $I_2(s) \quad \Box \quad I_2(g)$

The existence of an equilibrium between CO gas adsorbed on to charcoal and CO in the gas phase inside a closed vessel is another example for this type of an equilibrium.

• Equilibrium between a dissolved gas and a gas phase.

Consider a dilute solution formed by the dissolution of a gas like O_2 in water. When this solution is in contact with a gaseous phase containing O_2 such as the atmosphere, following equilibrium is established.

 $O_2(solution) \square O_2(g)$

Immiscible liquids - solute equilibria

These occur when a solute is distributed in two immiscible liquids in contact with each other. For instance, I_2 dissolves both in water and CCl_4 . If some water is added to a solution of I_2 in CCl_4 , iodine starts moving into the aqueous layer.

With the increase of iodine concentration in the aqueous layer, iodine passes into the CCl_4 layer and at a certain stage an equilibrium is established.

 $\mathrm{I_2(H_2O)} \quad \Box \quad \mathrm{I_2(CCl_4)}$

• Chemical equilibria

These are equilibria encountered in relation to reversible chemical reactions.

$$\begin{split} & \mathrm{N_2}(g) + 3\mathrm{H_2}(g) \ \square \ 2\mathrm{NH_3}(g) \\ & \mathrm{NH_4Cl}(s) \ \square \ \mathrm{NH_3}(g) + \mathrm{HCl}(g) \\ & \mathrm{CH_3COOH}(l) + \mathrm{CH_3CH_2OH}(l) \ \square \ \mathrm{CH_3COOC_2H_5}(l) + \mathrm{H_2O}(l) \end{split}$$

• Ionic systems

An ionic system should be a chemical system. Such systems contain ions. An equilibrium establishes between chemicals and ions in such systems.

 $\begin{array}{rcl} H_2O(1) & \Box & H^*(aq) + OH^*(aq) \\ & & AgCl(s) & \Box & Ag^*(aq) + Cl^*(aq) \\ & & CH_3COOH(aq) & \Box & CH_3COO^*(aq) + H^*(aq) \\ & & NH_3(aq) + H_2O(1) & \Box & NH_4^*(aq) + OH^*(aq) \\ & & HIn(aq) & \Box & H^*(aq) + In^*(aq) \end{array}$

• Electrode equlibria

When a metal rod is immersed in a solution of its ions initially the metal atoms lose electrons and enter the solution as ions. The electrons reside in the metal. Consequently the metal becomes negatively charged. As the concentration of the metal ions in the solution increases, they capture electrons from the metal surface and become metal atoms. At a certain instant, the rate of ionization of metal atoms becomes equal to the rate of deposition of ions on the metal. At this equilibrium, the potential difference between the negatively charged metal surface and the positively charged metal ions in solution is called the electrode potential of the metal. *eg.* Consider a zinc rod sunk in a Zn^{2+} ion solution.

Zn²⁺(aq) + 2e 🛛 Zn(s)

Equilibrium law

• Consider the following generalised reaction taking place in a closed system at a constant temperature.

aA+bB □ cC+dD

where A and B are reactants, C and D are products and a, b, c and d are the respective stoichiometric coefficients. According to equilibrium law:

$$K = \frac{\left[C \right]^{\circ} \left[D \right]^{4}}{\left[A \right]^{*} \left[B \right]^{6}}$$

Where *K* is a constant called equilibrium constant. The symbol [] represents the concentrations of respective species at equilibrium.

- *K* depends only on temperature and is independent of initial and final concentrations of reactants and products. When expressing the equilibrium constant, the following requirements should be fulfilled.
- The relevant balanced equation for the equilibrium reaction should be given (Generally this is written so that the stoichiometric coefficient assume lowest whole numbers).
- The relevant temperature should be given.
- The physical states of the reactants and products should be given. Attention should be paid to the following also.
- The equilibrium constant does not give any information with regard to the rate of the reaction.
- The value of *K* does not depend on initial concentrations.
- The value of *K* depends on temperature.
- By convention, the products are placed in the numerator of the expression.
- Since concentration of a solid or a pure substance is constant, they are incorporated into the equilibrium constant.
- The units of K depends on the expression for K (However, according to thermodynamic treatment, the equilibrium constant is dimensionless).

Equilibrium constant related to molar concentration (K_c)

• The equilibrium constant expressed in terms of concentrations is known as K_c ('c' denotes concentration). The units of K_c depends on the stoichiometric equation for which the expression is written.

$$eg. \quad CH_{3}COOH(1) + C_{2}H_{5}OH(1) \square \quad CH_{3}COOC_{2}H_{5}(1) + H_{2}O(1)$$
$$K_{c} = \frac{[CH_{3}COOC_{2}H_{5}(1)][H_{2}O(1)]}{[CH_{3}COOH(1)][C_{2}H_{5}OH(1)]}$$
Units of $K_{c} = \frac{(m \text{ ol } dm^{-3})(m \text{ ol } dm^{-3})}{(m \text{ ol } dm^{-3})(m \text{ ol } dm^{-3})} = 1$

For the reaction,

$$2SO_{2}(g) + O_{2}(g) \square 2SO_{3}(g)$$
$$K_{e} = \frac{\left[SO_{3}(g)\right]^{2}}{\left[SO_{2}(g)\right]^{2}\left[O_{2}(g)\right]}$$
Units of $K_{e} = \frac{\left(\operatorname{mol} \operatorname{dm}^{3}\right)^{2}}{\left(\operatorname{mol} \operatorname{dm}^{3}\right)^{2}\left(\operatorname{mol} \operatorname{dm}^{3}\right)} = \left(\operatorname{mol}^{-1} \operatorname{dm}^{3}\right)$

The equilibrium constant in terms of partial pressures (K_p)

• If the gases in an equilibrium mixture behave ideally,

$$PV = nRT$$
$$\therefore \frac{n}{V} = \frac{P}{RT}$$
$$\therefore c = \frac{P}{RT}$$

 \therefore At constant temperature, the concentration of a gas is proportional to its pressure. Partial pressure of a gas = mole fraction x total pressure

$$P_{\rm G} = P_{\rm T} \times x_{\rm C}$$

Partial pressures are therefore proportional to the amount of gases and are used as a measure of concentration of a gas in a gaseous mixture.

• Consider the reaction between nitrogen gas and hydrogen gas, used to produce ammonia as an example.

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

If the partial pressures of the individual gases in the equilibrium mixture are P_{N_2} , P_{H_2} and P_{NH_3} respectively then the equilibrium constant in terms of partial pressures K_p is given by expression,

$$K_p = \frac{P_{NH_3}^2}{P_{N_2} \times P_{H_2}^3}$$

The units of K_p are (pressure)⁻². Pa (SI Units) or bar (1bar = 10⁵ Pa) can be used as the units of pressure.

- The partial pressures are treated as exact concentrations so they are raised to the power of the respective stoichiometric coefficient in the equation for the reaction.
- The value K_p describes the position of equilibrium and the concentrations of gases that can co-exist in an equilibrium.
- Reversible thermal dissociation in a closed system gives rise to an equilibrium mixture. In a closed system dissociation of dinitrogen tetraoxide into nitrogen dioxide gives the following **homogeneous** equilibrium.

$$N_{2}O_{4}(g) \square 2NO_{2}(g)$$

$$K_{c} = \frac{\left[NO_{2}(g)\right]^{2}}{\left[N_{2}O_{4}(g)\right]} \qquad K_{p} = \frac{P_{NO_{2}}^{2}}{P_{N_{2}O_{4}}}$$

Heterogeneous equilibria

• If ammonium chloride is heated to a sufficient temperature, it decomposes to ammonia gas and hydrogen chloride gas. In a closed vessel the reaction reaches the equilibrium.

 $NH_4Cl(s)$ D $NH_3(g) + HCl(g)$

- The concentration of a pure solid is the amount of moles divided by its volume. Since pure solid has a constant density, it also has a constant concentration.
- Therefore, the equation for equilibrium constant does not need the concentrations of any solids to be included.

$$\begin{split} K_{\rm c} &= \big[\mathrm{NH}_3(\mathrm{g}) \big] \big[\mathrm{HCl}(\mathrm{g}) \big] \\ K_{\rm p} &= P_{N\!H_1} \times P_{\mathrm{HCl}} \end{split}$$

Relationship between K_{c} and K_{p}

• Taking a generalised reaction such as the above and assuming gases A, B, C and D behave ideally, the following equation can be derived.

$$K_{\mathbf{p}} = K_{\mathbf{C}} \left(RT \right)^{\mathbf{A}:}$$

 $\Delta n =$ (Number of gaseous molecules as products - Number of gaseous molecules as reactants) in the stoichiometric equation

Liquid - gas equilibria

• In a closed vessel at constant temperature, the following equilibrium exits between water and water vapour.

$$H_2O(1) \square H_2O(g)$$

• Applying equilibrium law,

$$K' = \frac{\left[H_2O(g)\right]}{\left[H_2O(1)\right]}$$

Since $[H_2O(1)]$ is a constant,

$$K'' = \left[\mathsf{H}_2 \mathsf{O}(\mathsf{g}) \right]$$

Since the concentration of a gas is proportional to its pressure at constant temperature,

$$K = P_{H_2O}^{o}$$

Where $P_{H_2O(g)}^0$ is the saturated vapour pressure of water at the temperature concerned. Hence, the equilibrium constant of this system can be taken as the saturated vapour pressure of water at the temperature concerned.

Partition Coefficient $(K_{\rm p})$

- It is the equilibrium constant describing the distribution of a solute species between two immiscible solvents.
- Immiscible liquids, if shaken together, mix temporarily but eventually separate into distinct phases with the most dense at the bottom and the least dense at the top. A visible boundary, the meniscus, separates two phases.
- The ratio of the concentration of a solute species that is distributed between two immiscible solvents at a given temperature is a constant.

 $X(A) \square X(B)$

$$K_{\rm D} = \frac{\text{Concentration of solute X in solvent B}}{\text{Concentration of solute X in solvent A}}$$
$$K_{\rm D} = \frac{\left[X_{(B)}\right]}{\left[X_{(A)}\right]}$$

 $(K_{\rm D} =$ The partition coefficient or distribution coefficient.)

- The above law holds when,
 - temperature is constant
 - the solvents are immiscible and do not react with each other; and
 - the solute does not react with the solvent
 - the solute exist in the same molecular form in both solvents
- For $K_{\rm sp}$ refer 13.4.
Position of equilibrium

• The extent of a chemical reaction when equilibrium is established is called the position of equilibrium. This varies from one reaction to another and depends upon the temperatue at which the reaction is performed. The equilibrium constant is a measure of the position of an equilibrium. If equilibrium constant is more than one, then the position of equilibrium is said to lie towards the right.

Le Chatelier's principle

- The position of equilibrium is not fixed for a reaction but changes as you change the reaction conditions. When a system which is in dynamic equilibrium is disturbed, it tends to respond in such a way as to minimize the disturbance and to restore equilibrium. This is known as Le Chatelier's principle.
- The following factors change the equilibrium point.
 - Concentration
 - Pressure
 - Temperature

Le Chatelier's principle can be used to deduce the effect of change of those factors on equilibrium.

- Le Chatelier's principle is a qualitative treatment of the equilibrium law. Whenever possible attempt must be made to explain facts quantitatively using equilibrium law. Attention should be paid to the following.
 - 1. Change in concentration of each substance.
 - 2. Increasing the pressure of the system (Decrease in volume here can be considered as an increase in concentration).
 - 3. Introduction of an inert gas or gas that does not affect the reaction, into the system.
 - 4. The influence of temperature on the equilibrium constant is not discussed. Therefore, use Le Chaterlier's principle to predict the results of changes in temperature taking exothermic/endothermic nature of the reaction.
 - 5. A catalyst does not change the position of the equilibrium.

Proposed learning and teaching activities :

- Name physical systems in equilibrium.
- Name chemical systems in equilibrium.
- Assign the students to write the equilibrium constants for systems given.
- Allow the students to plan an experiment to find out whether a system under observation is in equilibrium.
- Give instructions to calculate the equilibrium constant of a system when the concentrations of the components in the system are given.
- Allow the students to apply Le Chatelier's principle when a given system is disturbed.
- Give activities to find concentrations in a system which is in equilibrium giving the relevant data.
- Conduct the experiments given in the syllabus under competency level 13.1.

Competency 13.0	:	Uses the concept of equilibrium and its principles to
		determine the macroscopic properties of closed systems
		in dynamic equilibrium.
Competency level 13.2	:	Investigates how liquid-gas equilibrium varies in single component systems.

Periods :

Learning outcomes

• Identifies pure liquid systems.

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- Explains liquid-gas equilibrium on the basis of molecular motion.
- Explains the variation of vapour pressure of liquids with temperature.
- Identifies the relationship between the vapour pressure and the boiling point.
- Describes critical points.
- Describes triple point.

Guidance for teacher elaboration :

Equilibrium between liquid and vapour

- Consider the molecules of a liquid A and its vapour are in random motion. If the liquid is in an open container, the molecules in the vapour phase spread. Consequently, more and more molecules enter the vapour phase from the liquid phase till the whole liquid evaporates.
- When the evaporation occurs in a closed space, molecules enter the vapour phase from the liquid phase and vice versa and a dynamic equilibrium is established between the two phases at the temperature concerned. At this equilibrium, the rate of evaporation is equal to the rate of condensation.



$A(l) \longrightarrow A(g)$

However, the microscopic changes are not observable. If the temperature remains unchanged the pressure exerted by the vapour at equilibrium remains constant and it is the saturated vapour pressure at the particular temperature. This itself is an equilibrium constant.

- The kinetic energy of molecules depends on the temperature. When the temperature rises, the kinetic energy increases and the molecules with high kinetic energy overcome the intermolecular forces and move into the vapour phase. The higher the intermolecular attractions, the lesser the tendency of the molecules to pass into the vapour phase.
- As more and more molecules move into the vapour phase, the vapour pressure increases. Hence with increasing temperature, the vapour pressure also increases. When the temperature is decreased, the kinetic energy of the molecules in the vapour phase decreases with the result that more molecules return to the liquid phase and the vapour pressure drops.



Vapour pressure and boiling point

- When the liquid is heated, the temperature rises and at a certain temperature the saturated vapour pressure becomes equal to the (external) atmospheric pressure. At this temperature, the liquid boils and therefore, it is the **normal boiling point** of the liquid.
- The increase in vapour pressure of liquids with temperature is not linear (see figure). Moreover, different liquids have different intermolecular attractive forces and hence different volatilities. Therefore, the temperatures at which their s.v.p. becomes equal to the atmospheric pressure are different, so they boil at different temperatures (see Figure and Table).



Critical Point of a liquid

- Consider the liquid-vapour equilibrium established in a closed system. With rise in temperature the equilibrium is disturbed and more molecules pass into the vapour phase from the liquid phase establishing new equilibria increasing the amount in the gas phase. Finally a stage is reached where only the vapour exists.
- This vapour can be liquefied by compression. However, the tendency of the vapour to liquefy decreases with increasing temperature. Hence, a gas has a characteristic minimum temperature, called the **critical temperature**, above which the gas cannot be liquefied by increasing pressure, no matter how high the pressure would be.

Gas/Vapour	Critical temperature/K
H ₂ O	647.4
NH ₃	405.0
CO ₂	304.5

The minimum pressure required to bring about liquefaction at the critical temperature is known as the **critical pressure** and the volume of one mole of the substance at the critical temperature and critical pressure is known as the **critical volume**.

The following phase diagram of water shows the variation of vapour pressure of water with temperature (curve TC) and vapour pressure of ice with temperature (curve AT).Line BT shows the temperatures and pressures at which ice and liquid water are in equilibrium.

At the point T ice, water and vapour exist together in equilibrium, and this point is known as the **triple point**.

•

The curve TC ends at the critical temperature (647.4 K) of water. Above this temperature only the vapour phase can exist.



Proposed learning and teaching activities :

- Discuss liquid gas equilibrium on the basis of molecular motion.
- Explain the variation of vapour pressure of liquids with temperature using the given graph.
- Describe the relationship between the vapour pressure and the boiling point.
- Describe the triple point and the critical point of water using the given graph.

Competency 13.0	: Uses the concept of equilibrium and its principles to
	in dynamic equilibrium.
Competency level 13.3	: Investigates the variation of liquid-vapour equilibrium in
Periods	: 10

Learning outcomes

- Applies the principles of equilibrium and kinetics to a binary liquid system to derive Raoult's law.
- Defines an ideal solution.
- Explains how and why non-ideal solutions deviate from Raoult's law.
- Applies Raoult's law to find liquid and vapour phase compositions at equilibrium.
- Describes ideal and non-ideal behaviour of binary solutions.
- States that simple distillation can be used to separate components of a solution of a non volatile substance in a volatile liquid.
- Gives examples for a simple distillation.

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- States equipment used for simple distillation.
- Explains the utility of those equipments.
- Describes how the necessary equipments are arranged for a simple distillation.
- States that fractional distillation is used to separate components of a mixture composed of volatile liquids.
- Presents examples for fractional distillation.
- States the properties of a binary mixture that can be separated by fractional distillation.
- States the relationship between Raoult's law and fractional distillation.

Guidance for teacher elaboration :

- Liquid-liquid systems can be classified as
 - Totally miscible liquid-liquid systems
 - e.g. water and ethanol, hexane and heptane, benzene and toluene.
 - Partially miscible liquid-liquid systems
 - e.g. water and butanol, water and ether
 - Totally immiscible liquid-liquid systems
 - e.g. water and tetrachloromethane

• Ideal liquid systems

In the case of a binary solution composed of totally miscible liquid components A and B, it may be possible that $f_{(A-B)} = f_{(B-B)} = f_{(B-B)}$ where f denotes inter-molecular attractive forces or interactions. Such a solution is called an **ideal solution**. When the components of an ideal solution are mixed (a) the volume does not change and (b) the enthalpy does not change (and hence there is no observable change in temperature).

When an ideal solution of A and B evaporates into a vacuum in a closed space, the molecules of both A and B with sufficient kinetic energy to surmount the liquid phase interactions



escape from the surface into space above. At the same time, the molecules of A and B in motion in the vapour phase return to the liquid phase. When the rates of these two processes are equal, a dynamic equilibrium sets in. This is testified by the consistency of (a) the total vapour pressure (to which partial pressures of A and B contribute) and (b) the composition of the vapour phase at a constant temperature.

- The composition of the vapour depends on (a) the relative volatilities of A and B (and hence their boiling points) and (b) the relative concentrations of A and B in the solution.
- The higher the volatility and the higher the concentration of a certain component the greater is its tendency to be in the vapour phase and to exert a higher partial pressure.

Roults' law

• In order to find the composition of the vapour of an ideal binary solution quantitatively, let us consider the equilibria existing in a liquid-vapour system.

A(1) **E (g**) ------ (1) B(1) **D** B(g) ------ (2)

If R₁ is the rate of moving A from liquid phase to gas phase

 $R_1 = k' [A(1)]$

Since [A(l)] is proportional to its mole fraction x_A in the liquid phase,

 $\mathbf{R}_{1} = k_{I} \times \mathbf{x}_{A} \quad -----(3)$

If R₂ is the rate of moving A from gas phase to liquid phase

 $R_2 = k'' [A(g)]$

Since [A(g)], is proportional to its partial pressure P_A

 $\mathbf{R}_2 = k_2 \times P_{\mathbf{A}} - \dots - (4)$

At equilibrium $R_1 = R_2$

According to (3) and (4)

$$k_2 \cdot P_A = k_1 \cdot x_A$$

$$\therefore P_A = \frac{k_1}{k_2} \cdot x_A$$

$$\therefore P_A = k \cdot x_A$$

When $x_A = 1$, $P_A = P_A^0$ $k = P_A^0$ $P_A = P_A^0 \cdot x_A$

Similarly $P_{\rm B} = P_{\rm B}^0 \cdot x_{\rm B}$

Thus, in an ideal solution, the partial pressure of a given component A is equal to the product of the vapour pressure of pure A and the mole fraction of A in the liquid phase at constant temperature. This relationship is called **Raoult's law**.

It is understood that $P_A < P_A^0$ and $P_B < P_B^0$ Hence lowering in the vapour pressure of $A = P_A^0 - P_A$ $= P_A^0 - P_A^0 x_A$ $= P_A^0 (1 - x_A)$ $= P_A^0 x_B$ $\therefore \frac{P_A^0 - P_A}{P_A^0} = x_B$ Similarly $\frac{P_B^0 - P_B}{P_B^0} = x_A$

This is an alternate form of Raoults' law.

• Combining Raoults' law with Dalton's law of partial pressures, makes it possible to determine the composition of the vapour phase. If P_{AB} is the total vapour pressure and y_A and y_B are the mole fractions of A and B in the vapour phase respectively :

$$P_{A} = P_{.} y_{A}$$

$$\therefore P_{A} = (P_{A} + P_{B})y_{A}$$

$$\therefore P_{A}^{0} x_{A} = (P_{A}^{0} x_{A} + P_{B}^{0} x_{B}) y_{A}$$

$$\therefore y_{A} = \frac{P_{A}^{0} x_{A}}{P_{A}^{0} x_{A} + P_{B}^{0} x_{B}}$$

$$\therefore y_{B} = \frac{P_{B}^{0} x_{B}}{P_{A}^{0} x_{A} + P_{B}^{0} x_{B}}$$

- According to Raoult's law $P_A = P_A^0 x_A$. Since P_A^0 is a constant at constant temperature, the graph of the partial vapour pressure of a component against its mole fraction in an ideal solution is Vapour
- a straight line. • Assuming A is more volatile than B (i.e. $P_A^0 > P_B^0$ and $\therefore T_{b(A)} < T_{b(B)}$) the plot of vapour pressures versus mole fractions of an ideal solution will be as follows. Here P_{AB} is total pressure and P_A and P_B are vapour pressure of A and B respectively.



Composition

Examples:

Hexane and heptane, benzene and toluene, bromoethane and iodoethane, CCl_4 and $CHCl_3$, C_6H_6 and C_6D_6 (Note : P_{AB} at a given composition is equal to $P_A + P_B$).



The boiling boint-composition graph, however, is not a straight line.

Non ideal systems

- Ideal solutions obey Raoults law. There are solutions which deviate from Raoult's law. In these $f_{(A-B)} \neq f_{(A-A)} \neq f_{(B-B)}$. These are non ideal solutions.
- In some $f_{(A-B)} > f_{(A-A)}$ and $f_{(A-B)} > f_{(B-B)}$ and the freedom for molecules to escape into the vapour phase is lesser than in the case of an ideal solution.

$$\begin{array}{ll} & P_{\rm A} < P_{\rm A}^0 x_{\rm A} & & \\ & P_{\rm B} < P_{\rm B}^0 x_{\rm B} & & \\ & P_{\rm AB} < (P_{\rm A}^0 x_{\rm A} + P_{\rm B}^0 x_{\rm B}) & & \end{array}$$

Therefore, the curves in the vapour pressure - composition diagram dips downwards whereas the boiling point - composition curve rises up.

e.g. Propanone and methanol, trichloromethane and propanone, ethanoic acid and water.

These solutions are said to exhibit a negative deviation. When components of such solutions are mixed, temperature increases and volume decreases.



$$\therefore P_{A} > P_{A}^{0} \cdot x_{A}$$

$$P_{B} > P_{B}^{0} \cdot x_{B}$$

$$P_{AB} > (P_{A}^{0} \cdot x_{A} + P_{B}^{0} \cdot x_{B})$$

Thus the curves in the vapour pressure - composition diagram loops upwards. The boiling point curve dips downwards.

e.g. Propanone and carbon disulphide, ethanol and benzene.



These solutions show positive deviations from Raoult's law. When solvents of such solutions are mixed, temperature decreases and volume increases.

- Simple distillation can be used to get pure water from a solution of salt in water.
- In addition to a distillation flask, for distillation a condenser is also needed (Explain the difference between the air condenser and the water condenser.)
- In simple distillation only one component enters the vapour phase.
- Fractional distillation is used to separate the two volatile components from an ideal or nearly ideal solution of them.
- In addition to simple distillation equipment, a fractionating column is used here.
- In order to separate two liquids by fractional distillation, they should have substantially different boiling points. That is, their volatilities should be considerably different.
- A boiling point-composition phase diagram can be used to find the composition of the distillate at different temperatures.



- $T^{\theta}_{A} > T^{\theta}_{B}$.
- An equimolar mixture of A and B boils at T_1 . The composition of vapour in equilibrium with liquid at T_1 is x_1 . (The vapour is rich with more volatile component.)
- If the vapour of a solution boiling at T_1 is condensed a liquid of composition x_1 is obtained. This condensate contains a higher percentage of B.
- Since the boiling point (T_2) of the solution of composition x_1 is lower than T_1 , it rises further up in the column.
- This kind of separate distillations, successively and continuously occur in the distillation column.
- Finally component B is obtained as the distillate. The mole fraction of A in the solution left in the flask gradually increases, so its boiling point too increases. Finally the residue left in the flask is almost A.
- Arrows show how the solution of composition x_1 changes up the column during the distillation.



Suggested learning-teaching activities :

- Ask children to mix different volumes of the following pairs of solvents and measure the temperature changes.
 - Hexane and heptane
 - Water and ethanol
 - Water and ethanoic acid
- Discuss the observations.
- Get students to work on simple numerical problems based on Raoult's law.
- In instances where possible, discuss reasons as to why some interactions among the solvent molecules are relatively stronger/weaker than in others. For example, attractions between CHCl₃ and CH₃COCH₃ are stronger than the attractions between CHCl₃ and C₆H₁₄.
- Discuss production of alcohol, separation of N_2 and O_2 from air and refining of petroleum as applications of fractional distillation.

Competency 13.0	:	Uses the concept of equilibrium and its principles to determine the macroscopic properties of closed systems in dynamic equilibrium.
Competency level 13.4	:	Quantifies properties of equilibrium systems related to
		weakly soluble ionic compounds.
Periods	:	06
Learning outcomes	:	 States that some ionic compounds are very soluble in water but some are less soluble. Applies K_{sp} for sparingly soluble electrolytes. Applies common ion effect. Identifies the cations by precipitation methods and subsequent solubility of the precipitate in different reagents. Explains the solubility of the precipitate based on solubility product principle. Divides the cations listed into five groups, based on the solubility products of the ionic compounds of the cations.

Guidance for teacher elaboration :

- The solubility of NaCl in water is approximately 5 mol dm⁻³. In the solution there are interactions between Na⁺ and Cl⁻ ions. Though simple, they are not independent of one another.
- In the case of a sparingly soluble electrolyte such as AgCl, the ions exist independently in the solution and the following dynamic equilibrium exists between the solid and the ions in a saturated solution.

Applying the law of equilibrium,

$$K_{\rm c} = \frac{\left[\mathrm{Ag}^+(\mathrm{aq})\right]\left[\mathrm{CI}^+(\mathrm{aq})\right]}{\left[\mathrm{Ag}\mathrm{CI}(\mathrm{s})\right]}$$

[AgCl(s)] is a constant. Therefore, $K_{sp} = [Ag^+(aq)][Cl^-(aq)]$

- K_{sp} is a constant at constant temperature and is called 'solubility product'. If the solubility of AgCl is x mol dm⁻³, $K_{sp} = x^2 \text{ mol}^2 \text{ dm}^{-6}$.
- In general, solubility product is not applied for salts having high solubility.
- If the ionic product is greater than the solubility product of a salt, it will precipitate.

eg. If $\left[Ag^{+}(aq) \right] \left[Cl^{+}(aq) \right] \rangle K_{p}$ AgCl will precipitate.

Cations identified by precipitation

• The precipitates of the cations having d⁷, d⁸, d⁹ and d¹⁰ electronic configurations are soluble in excess ammonia and form the respective stable complex ions.

 $M^{2+}(aq) + X^{2-}(aq) \Longrightarrow MX(s)$

(d ⁷)	$[Co(NH_3)_6]^{2+}$ -	yellow brown	(d^{10})	$[Zn(NH_3)_4]^{2+}$ - colourless
(d^8)	[Ni(NH ₃) ₆] ²⁺	- dark blue	(d^{10})	$[Ag(NH_3)_2]^+$ - colourless
(d ⁹)	$[Cu(NH_3)_4]^{2+}$	- deep blue	(d^{10})	$[Cd(NH_3)_4]^{2+}$ - colourless

Separation procedure of a mixture of cations

• Qualitative analysis of a mixture of cations involves the separation of them to five groups. The scheme of qualitative analysis is based on the principle of selective precipitation. The precipitation of cations from a solution one at a time is called selective precipitation.

Group I

 Cold, excess dilute HCl is added to a solution containing a mixture of cations. Only Ag⁺, Pb²⁺ and Hg₂²⁺ will be precipitated as insoluble chlorides.

$$Ag^{+}(aq) \xrightarrow{\text{Excess c cold}} AgCl(s) \qquad K_{sp} = 1 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$$

$$Pb^{2+}(aq) \xrightarrow{\text{Excess cold}} PbCl_2(s) \quad K_{sp} = 1 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}$$

$$Hg_2^{2+}(aq) \xrightarrow{\text{Excess c cold}} Hg_2Cl_2(s) K_{sp} = 1 \times 10^{-18} \text{ mol}^3 \text{ dm}^{-9}$$

- The K_{sp} values of these chlorides are very low and ionic products can easily exceed them. The K_{sp} values of the other partially soluble chlorides are high and they remain in solutions.
- Cold and dilute HCl is added to prevent the dissolution of PbCl₂(s), due to the formation of complex ions such as [PbCl₄]²(aq) or [PbCl₃]⁻(aq) in conc. HCl.

$$Pb^{2+}(aq) \xrightarrow{Excess c hot} [PbCl_4]^{2-}(aq)$$

Group II

• After the separation of the insoluble chlorides in Group I, the filtrate is still acidic. When H_2S is passed through the solution, only insoluble sulphides having very low K_{sp} values will be precipitated.

K_{sp} values of Group II precipitates

$Bi_2S_3 = 1x10^{-97} mol^5 dm^{-15}$	$CuS = 4x10^{-36} mol^2 dm^{-6}$
$CdS = 8 \times 10^{-27} \text{ mol}^2 \text{ dm}^{-6}$	$Sb_2S_3 = 1x10^{-93} mol^5 dm^{-15}$
PbS = $7 \times 10^{-28} \text{ mol}^2 \text{ dm}^{-6}$	$As_2S_3 = 1x10^{-22} \text{ mol}^5 \text{ dm}^{-15}$
HgS = $1 \times 10^{-52} \text{ mol}^2 \text{ dm}^{-6}$	
$SnS = 1 \times 10^{-26} \text{ mol}^2 \text{ dm}^{-6}$	

For H_2S

$$H_{2}S(aq) \stackrel{K_{a_{1}}}{\underbrace{ }} H^{+}(aq) + HS^{-}(aq) = \frac{[H^{+}(aq)] [HS^{-}(aq)]}{[H_{2}S(aq)]} = 9.1 \times 10^{-8} \text{ mol dm}^{-3}$$

$$HS^{-}(aq) \stackrel{K_{a_{2}}}{\underbrace{ }} H^{+}(aq) + S^{2-}(aq) = \frac{[H^{+}(aq)] [S^{2-}(aq)]}{[HS^{-}(aq)]} = 1.2 \times 10^{-15} \text{ mol dm}^{-3}$$

• The concentration of sulphide ion is relatively low because of the higher concentration of H⁺ ions. Other cations such as Mn^{2+} , Zn^{2+} , Ni^{2+} and Co^{2+} with higher K_{sp} values of their respective sulphides will remain in the solution.

Group III

• The filtrate from Group II is boiled for a few minutes to expel all the dissolved H_2S . Then boil the filtrate for a few minutes with conc. HNO_3 to oxidise Fe^{2+} to Fe^{3+} . The solution is treated with NH_4Cl and NH_4OH .

\rightarrow	$Fe(OH)_3(s)$	$K_{\rm sp} = 1 \times 10^{-28} {\rm mol}^4 {\rm dm}^{-12}$
	(reddish brown)	1
\rightarrow	$Al(OH)_3(s)$	$K_{\rm sp} = 1 \times 10^{-33} {\rm mol}^4 {\rm dm}^{-12}$
	(white gelatinous)	- 1
\rightarrow	Cr(OH) ₃ (s)	$K_{\rm sp} = 1 \times 10^{-31} {\rm mol}^4 {\rm dm}^{-12}$
	(Green)	۰F
$_{\rm l}) \rightarrow$	$NH_{4}^{+}(aq) + Cl^{-}(aq)$	(aq)
aq) 🛛	$NH_4^+(aq) + OH$	[⁻ (aq)
	$ \begin{array}{c} \rightarrow \\ \rightarrow \\ \rightarrow \\ q \end{pmatrix} \rightarrow \\ aq \end{pmatrix} \square $	$ \rightarrow Fe(OH)_{3}(s) $ (reddish brown) $ \rightarrow Al(OH)_{3}(s) $ (white gelatinous) $ \rightarrow Cr(OH)_{3}(s) $ (Green) $ q) \rightarrow NH_{4}^{+}(aq) + Charcer$ $ aq) \square NH_{4}^{+}(aq) + OH$

- NH_4OH is a weak base and the concentration of OH^- ions in the solution is very low. In the presence of NH_4Cl , NH_4^+ concentration is high. As a result, the above equilibrium shift to the left. Therefore the concentration of OH^- ion becomes extremely low. Even at the very low concentration of OH^- , the ionic product is greater than the K_{sp} values of the hydroxides of Al^{3+} , Fe^{3+} and Cr^{3+} which precipitate.
- But on the other hand, the following hydroxides with higher K_{sp} values will remain in the solution. Their K_{sp} values are given below.

$Zn(OH)_2$	- $1 \times 10^{-17} \text{ mol}^3 \text{ dm}^{-9}$
Mn(OH) ₂	- 1x10 ⁻¹⁴ mol ³ dm ⁻⁹
Co(OH) ₂	- 1x10 ⁻¹⁶ mol ³ dm ⁻⁹
Ni(OH) ₂	- 1x10 ⁻¹⁶ mol ³ dm ⁻⁹

 $Ca(OH)_2$ - 1x10⁻⁵ mol³ dm⁻⁹ Mg(OH)_2 - 1x10⁻¹¹ mol³ dm⁻⁹

- The K_{sp} of Fe(OH)₂ is 1x10⁻¹⁴ mol³ dm⁻⁹. When NH₄Cl is present these Fe(OH)₂ cannot be precipitated completely. Hence before adding the reagents Fe²⁺ ion should be converted to Fe³⁺.
- The formation of stable ammine complex with $Co^{2+}(d^7)$, $Ni^{2+}(d^8)$, $Cu^{2+}(d^9)$ and $Zn^{2+}(d^{10})$ also contributes to the dissolution of their respective hydroxides.

Group IV

• The filtrate from Group III contains OH⁻ ions and is basic. H_2S is passed through this solution in the presence of OH⁻ ions. Then H⁺ ions produced from H_2S are neutralised.

H₂S(aq)
$$2H^+(aq) + S^{2-}(aq)$$

 $\downarrow OH^-(aq)$
H₂O(1)

• The above equilibrium shifts to the right and the concentration of S²⁻ ions increases. As a result the ionic products of the metal sulphides, which possess higher K_{sp} values namely the Mn²⁺, Zn²⁺, Ni²⁺ and Co²⁺ get precipitated.

 $\begin{array}{ccc} \text{Co}^{2+}(aq) & \underline{\quad \text{OH /HS}} & \text{CoS}(s) & & & \text{Zn}^{2+}(aq) & \underline{\quad \text{OH /HS}} & \text{ZnS}(s) \\ & & & (black) & & (white) \end{array}$

 $\begin{array}{ccc} \text{Ni}^{2+}(aq) & \underline{\quad \text{OH /HS}} & \text{NiS}((s) & Mn^{2+}(aq) & \underline{\quad \text{OH /HS}} & MnS(s) \\ & (black) & (pink) \end{array}$

• K_{sp} values of the above precipitates are given below. CoS - $1x10^{-23}$ mol²dm⁻⁶ NiS - $1x10^{-28}$ mol²dm⁻⁶ MnS - $1x10^{-25}$ mol²dm⁻⁶

Group V

• Boil off H_2S from Group IV filtrate and add a little amount of NH_4Cl and NH_4OH in excess. Heat the solution, then add $(NH_4)_2CO_3$ solution. Here Ca^{2+} , Sr^{2+} and Ba^{2+} ions are precipitated as carbonates.

 $\begin{array}{ccc} \operatorname{Ca}^{2+}(\operatorname{aq}) & \xrightarrow{(\mathbb{NH}_{4})_{2} \mathbb{C} \operatorname{O}_{3}(\operatorname{aq})} & \operatorname{Ca}\operatorname{CO}_{3}(\operatorname{s}) & K_{sp} = 3 \times 10^{-9} \, \operatorname{mol}^{2} \, \operatorname{dm}^{-6} \\ & (\operatorname{white}) \\ \operatorname{Sr}^{2+}(\operatorname{aq}) & \xrightarrow{(\mathbb{NH}_{4})_{2} \mathbb{C} \operatorname{O}_{3}(\operatorname{aq})} & \operatorname{Sr}\operatorname{CO}_{3}(\operatorname{s}) & K_{sp} = 1 \times 10^{-10} \, \operatorname{mol}^{2} \, \operatorname{dm}^{-6} \\ & (\operatorname{white}) \\ \operatorname{Ba}^{2+}(\operatorname{aq}) & \xrightarrow{(\mathbb{NH}_{4})_{2} \mathbb{C} \operatorname{O}_{3}(\operatorname{aq})} & \operatorname{Ba}\operatorname{CO}_{3}(\operatorname{s}) & K_{sp} = 5 \times 10^{-9} \, \operatorname{mol}^{2} \, \operatorname{dm}^{-6} \\ & (\operatorname{white}) \end{array}$

Common ion effect

• On addition of NaCl solution to a saturated solution of AgCl, concentration of Cl⁻ ions increases. Since K_{sp} is a constant at constant temperature Ag⁺ concentration in the medium should decrease. Therefore, AgCl is precipitated. In other words, the solubility of AgCl in a solution of Cl⁻ ions is less compared to its solubility in pure water. This is called common ion effect. This principle is applicable for the Ag⁺ ion as well.

Proposed learning teaching activities :

- Get students to solve appropriate problems based on solubility product principle and common ion effect.
- Allow the students to identify the cations in the sample given to them.
- Ask them to compare the K_{sp} values of relevant chlorides, sulphides, hydroxides and carbonates.

Competency 13.0	:	Uses the concept of equilibrium and its principles to
		determine the macroscopic properties of closed systems
		in dynamic equilibrium.
Competency level 13.5	:	Quantifies properties of equilibrium systems related to weak acids, weak bases and acidic salts and basic salts.
Periods	:	22

Learning outcomes

- Introduces conjugate acids and bases and polybasic (polyprotic) acids.
- Gives expressions for K_{w} , K_{a} and K_{b} .

:

- Derives the relationship between K_{a} and K_{b} of conjugate acid-base pairs.
- Solves problems using K_{w} , K_{a} and K_{b} .
- Defines pH.
- Derives equations to calculate pH of acidic solutions and basic solutions.
- Applies theory of indicators to choose the correct indicator for a particular titration.
- Calculates the pH value of acid/ base reactions at the equivalence point.
- Sketches the titration curves for different types of titrations.
- Identifies that near the equivalence point an abrupt pH change occurs for a small volume of the solution added.
- States that acid-base (neutralization) indicators are either weak acids or weak bases.
- Expresses that indicators exhibit different colours for their unionized and ionized forms.
- Understands that pH range (colour change interval) of an indicator depends on the value of dissociation constant of the indicator (K_{ln}) .
- Points out that the selection of an indicator depends on its pK_{In} value which corresponds to the equivalence point pH of the titration or pH range in which abrupt pH change occurs.

Guidance for teacher elaboration :

Ionisation of water and Ionic Product of Water (K_w)

• Water, no matter how pure it is, always ionises to a very small extent.

 $H_2O(1) + H_2O(1) \square H_3O^+(aq) + OH^-(aq)$

• This itself is an acid-base equilibrium. Water produces its own conjugate acid and its own conjugate base at the same time.

Applying the equilibrium law,

$$K_{\rm C} = \frac{\left[\mathrm{H}_3 \mathrm{O}^+(\mathrm{aq})\right] \left[\mathrm{OH}^+(\mathrm{aq})\right]}{\left[\mathrm{H}_2 \mathrm{O}(\mathrm{l})\right]^2}$$

 $[H_2O(l)]^2$ is constant since water is in large excess.

 \therefore [H₃O⁺(aq)][OH⁻(aq)] = constant = K_w

 $K_{\rm w}$ is called the ionic product of water or ionisation/dissociation constant of water. In pure water, the concentration of H₃O⁺(aq) ion is the same as that of OH⁻(aq). • At 25 °C, $K_w = 1.0 \ge 10^{-14} \mod^2 dm^{-6} \mod [H_3O^+(aq)] = [OH^-(aq)] = 1. \ge 10^{-7} \mod dm^{-3}$.

Dissociation/Ionisation constant of a weak acid (K)

• An acid HA takes part in the following proton transfer equilibrium in water.

$$\mathrm{HA}(\mathrm{aq}) + \mathrm{H_2O}(\mathrm{l}) \ \Box \quad \mathrm{H_3O^+}(\mathrm{aq}) + \mathrm{A^{\cdot}}(\mathrm{aq})$$

In this expression, A⁻ is the conjugate base of the acid.

$$K_{c} = \frac{\left[\mathbf{H}_{3}^{\bigcirc}(aq)\right]\left[\mathbf{A}^{\cdot}(aq)\right]}{\left[\mathbf{H}\mathbf{A}(aq)\right]\left[\mathbf{H}_{2}^{\bigcirc}(l)\right]}$$

In dilute solution, the concentration of water is constant and the equilibrium can be expressed in terms of the equilibrium constant, K_a .

$$K_{\mathbf{a}} = \frac{\left[\mathbf{H}_{3} \mathbf{O}^{+}(\mathbf{aq})\right] \left[\mathbf{A}^{+}(\mathbf{aq})\right]}{\left[\mathbf{H}\mathbf{A}(\mathbf{aq})\right]}$$

 $K_{\rm a}$ is the ionisation constant or dissociation constant of the acid. For acetic acid

$$CH_{3}COOH(aq) + H_{2}O(l) \square H_{3}O^{+}(aq) + CH_{3}COO^{-}(aq)$$
$$K_{a} = \frac{\left[H_{3}O^{+}(aq)\right]\left[CH_{3}COO^{-}(aq)\right]}{\left[CH_{3}COOH(aq)\right]}$$

 K_a is a measure of the acidic strength of the acid.

Dissociation/Ionisation constant of a weak base $(K_{\rm b})$

• For a base B in water, the characteristic proton transfer equilibrium is

$$B(aq) + H_2O(l) \square BH^*(aq) + OH^{-}(aq)$$
$$K_c = \frac{\left[BH^*(aq)\right]\left[OH^{-}(aq)\right]}{\left[B(aq)\right]\left[H_2O(l)\right]}$$

Here, BH⁺ is the conjugate acid. In dilute solutions concentration of H₂O is constant.

$$K_{b} = \frac{\left[BH^{+}(aq)\right]\left[OH^{-}(aq)\right]}{\left[B(aq)\right]}$$

 $K_{\rm b}$ is the ionisation or dissociation constant of the base. It is a measure of the strength of the base.

eg. For ammonia

$$NH_{3}(aq) + H_{2}O(1) \square NH_{4}^{+}(aq) + OH^{-}(aq)$$
$$K_{b} = \frac{\left[NH_{4}^{+}(aq)\right]\left[OH^{-}(aq)\right]}{\left[NH_{3}(aq)\right]}$$

 $K_{\rm b}$ is a measure of the strength of the base.

Relationship between K_a and K_b

• The proton exchange equilibrium of a base can be given in terms of the interaction of its conjugate acid with water.

$$BH^{+}(aq) + H_{2}O(l) \square B(aq) + H_{3}O^{+}(aq)$$
$$K_{a} = \frac{[B(aq)][H_{3}O^{+}(aq)]}{[BH^{+}(aq)]}$$

Multiplying the expression for acidity constant (K_a) of the conjugate acid BH⁺ and that for the basicity constant,

$$K_{a} \times K_{b} = \frac{\begin{bmatrix} B & (aq) \end{bmatrix} \begin{bmatrix} H_{3}O^{+}(aq) \end{bmatrix}}{\begin{bmatrix} BH^{+}(aq) \end{bmatrix}} \times \frac{\begin{bmatrix} BH^{+}(aq) \end{bmatrix} \begin{bmatrix} OH^{-}(aq) \end{bmatrix}}{\begin{bmatrix} B & (aq) \end{bmatrix}} = K_{w}$$

 $K_{\rm w}$ is the ionization constant of water.

• Weak acids and weak bases partially dissociate in water leading to equilibria.



Applying equilibrium law;

$$K_{a} = \frac{\left[CHCOO^{\cdot}(aq)\right]\left[H_{3}O^{+}(aq)\right]}{\left[CH_{3}COOH(aq)\right]}$$
$$K_{b} = \frac{\left[NH_{4}^{+}(aq)\right]\left[OH^{\cdot}(aq)\right]}{\left[NH_{3}(aq)\right]}$$

• Strong acids like HCl, HNO, and strong bases like NaOH completely ionise in water.

$$\begin{array}{ll} HCl(l) + H_2O(l) \rightarrow H_3O^+(aq) + Cl(aq) \\ 1mol & 1mol \end{array}$$

$$\begin{array}{ll} \mathrm{HNO}_{3}(\mathrm{l}) + \mathrm{H}_{2}\mathrm{O}(\mathrm{l}) & \rightarrow \mathrm{H}_{3}\mathrm{O}^{+}(\mathrm{aq}) + \mathrm{NO}_{3}^{-}(\mathrm{aq}) \\ 1\mathrm{mol} & 1\mathrm{mol} \\ \mathrm{NaOH}(\mathrm{aq}) & \rightarrow \mathrm{Na}^{+}(\mathrm{aq}) + \mathrm{OH}^{-}(\mathrm{aq}) \\ 1\mathrm{mol} & 1\mathrm{mol} \end{array}$$

Therefore, the H⁺ and OH⁻ concentration can be directly computed considering the dissociation.

Ostwald's law of dilution

• Since weak acids and weak bases are incompletely dissociated, the concentrations of H⁺ or OH⁻ cannot be calculated so simply. Given K_a or K_b , they can be calculated using Ostwald's dilution law.

Consider a solution of volume V containing 1 mol of a weak monoprotic acid HX whose degree of dissociation is α .

Initial amounts/mol	=	HX(aq) 1	H ⁺ (aq) 0	$+ X^{-}(aq)$ 0
equilibrium amounts/mol	=	(1-α)	α	α
Equilibrium concentrations/mol dm ⁻³	=	$\left[\frac{1-\alpha}{v}\right]$	$\left[\frac{\alpha}{v}\right]$	$\left[\frac{\alpha}{v}\right]$

Because the acid does not dissociate further at the existing temperature it is considered as a system in equilibrium.

By applying equilibrium law,

$$K_{a} = \frac{\left[H^{+}(aq)\right]\left[X^{-}(aq)\right]}{\left[HX(aq)\right]}$$
$$K_{a} = \frac{\left[\frac{\alpha}{V}\right]\left[\frac{\alpha}{V}\right]}{\left[\frac{1-\alpha}{V}\right]} = \frac{\alpha^{2}}{(1-\alpha)V}$$

 $K_{\rm a}$ is the dissociation constant of weak acid. By substituting the value 1/V equals initial concentration c,

$$K_a = \frac{c \alpha^2}{(1 - \alpha)}$$

This relationship is called Ostwald's dilution law.

When $\alpha << 1$, $1-\alpha$ approximately equals one.

 $\therefore K_{a} = c\alpha^{2}$ (for a weak acid) and $K_{b} = c\alpha^{2}$ (for a weak base)

Using these equations, the $[H^+(aq)]$ and $[OH^-(aq)]$ of solutions of weak acids and weak bases can be found.

pH Value

- The concentration of hydronium ions $[H_3O^+]$ in aqueous solutions is sometimes very small. Hydronium ion concentration of a medium is very important in industrial processes, pollution, acid rain, blood and body chemistry. In many cases its concentration ranges from 10^{-14} to 10 mol dm^{-3} in aqueous solutions.
- Therefore it is convenient to express the [H₃O⁺] of solutions on logarithmic scale. The negative logarithm of hydronium ions or hydrogen ions concentration is called pH. The 'p' in the term pH means power and 'H⁺' stands for hydronium ions or hydrogen ions. The pH is defined mathematically as,

$$pH = -\log \frac{[H_3 \bigcirc^+ (aq)]}{1 \text{ mol } dm^3} = -\log \frac{[H^+(aq)]}{1 \text{ mol } dm^{-3}}$$

• The negative sign in the definition means that the pH decreases as the hydrogen ion (hydronium ion) concentration increases. A change of one unit in the pH scale corresponds to tenfold change in the hydrogen ion concentration.

Calculating the pH of solutions of strong acids

• It is assumed that all strong acids are completely ionised in aqueous solution. The hydronium ion concentration is obtained directly from the concentration of the acid. For monoprotic strong acids $[H_3O^+]$ is equal to its molar concentration.

Eg. If the concentration of hydrochloric acid solution is 0.1 mol dm⁻³.

$$\begin{array}{rl} HCl(aq) + H_2O(l) & \longrightarrow & H_3O^+(aq) + Cl^-(aq) \\ \therefore & [H_3O^+(aq)] = 0.1 \text{ mol } dm^{-3} \\ & -log_{10} 0.1 = 1 \\ & \therefore & pH = 1 \end{array}$$

 Molecules of diprotic strong acids such as sulphuric acid dissociates completely in dilute solutions.

$$H_2SO_4(aq) + 2H_2O(l) \longrightarrow 2H_3O^+(aq) + SO_4^2(aq)$$

In 0.1 mol dm⁻³ sulphuric acid solution, $[H_3O^+(aq)] = 0.2 \text{ mol dm}^{-3}$ (assuming complete dissociation)

$$\log_{10} 0.2 = -0.7$$

 $\therefore -\log_{10} 0.2 = 0.7$
 $\therefore \text{ pH} = 0.7$

Calculating the pH of solutions of strong bases

- Strong bases are also assumed to be completely ionised. The hydroxide ion concentration is therefore easily obtained from the concentration of the base.
 - *eg*. Consider 0.3 mol dm⁻³ solution of sodium hydroxide.

NaOH (aq) \longrightarrow Na⁺(aq) + OH⁻(aq) [OH⁻(aq)] = 0.3 mol dm⁻³

• The hydrogen ion concentration of the solution is determined by the ionic product of water. At 298 K the ionic product is 1x10⁻¹⁴ mol² dm⁻⁶. Hydrogen ion concentration at this temperature is given by

$$\begin{bmatrix} H_{3}O^{+}(aq) \end{bmatrix} = \frac{K_{W}}{\begin{bmatrix} OH^{-}(aq) \end{bmatrix}}$$
$$\begin{bmatrix} H_{3}O^{+}(aq) \end{bmatrix} = \frac{1.0 \times 10^{-14} \text{ m} \circ l^{2} \text{ dm}^{-6}}{0.3 \text{ m} \circ l \text{ dm}^{-3}}$$
$$= 3.33 \times 10^{-14} \text{ mol dm}^{-3}$$
$$pH = -\log_{10}(3.33 \times 10^{-14})$$
$$= 13.5$$

Calculating the pH of solutions of weak acids

• A weak acid does not ionise fully in aqueous solution. An equilibrium is set up as shown below.

$$HA(aq) + H_2O(l) \square H_3O^{+}(aq) + A^{-}(aq)$$

By applying equilibrium law,

$$K_{a} = \frac{[\mathrm{H}_{3}\mathrm{O}^{+}(\mathrm{aq})][\mathrm{A}^{-}(\mathrm{aq})]}{[\mathrm{H}\mathrm{A}(\mathrm{aq})]}$$

Let the degree of dissociation is α and the initial concentration of HA is C. Then,

$$K_{\mathbf{a}} = \frac{\mathbf{C}\boldsymbol{\alpha} \cdot \mathbf{C}\boldsymbol{\alpha}}{\mathbf{C}(1-\boldsymbol{\alpha})}$$

Since the degree of dissociation of a weak acid is small ($\alpha << 1$), (1- α) is approximately equals 1. Then,

$$K_{\alpha} = C\alpha^{2}$$

$$\therefore \alpha = \sqrt{\frac{K_{\alpha}}{C}}$$

$$\left[H_{3}O^{+}(aq)\right] = C\alpha = \sqrt{\frac{K_{\alpha}}{C}} \times C$$

$$= \sqrt{K_{\alpha} \cdot C}$$

$$\therefore pH = -\log_{10} \sqrt{K_{\alpha}C}$$

Similarly; $p OH = -1 \circ g_{10} \sqrt{K_b C}$

Calculating the pH of a solution of a salt formed from a weak acid and a strong base

e.g. CH₃COONa

 $CH_3COONa(s) + H_2O(l) \longrightarrow CH_3COO^{-}(aq) + Na^{+}(aq)$

Consider the involvement of these ions in hydrolysis.

 $\begin{array}{ll} Na^{+}(aq) + H_{2}O(l) \longrightarrow & Negligible \\ CH_{3}COO^{-}(aq) + H_{2}O(l) & CH_{3}COOH(aq) + OH^{-}(aq) \end{array}$

Applying law of equilibrium

$$K_{\mathbf{b}(\mathbf{CH}_{1}\mathbf{COO})} = \frac{\left[CH_{3} COOH(aq)\right]\left[OH'(aq)\right]}{\left[CH_{3}COO'(aq)\right]\left[H_{2}O(l)\right]}$$

 $[H_2O(l)]$ is a constant.

$$\begin{split} K_{b(CH_{3}COO^{-})} &= \frac{\left[CH_{3}COOH(aq)\right]\left[OH^{-}(aq)\right]}{\left[CH_{3}COO^{-}(aq)\right]} \\ K_{w} &= \left[H^{+}(aq)\right]\left[OH^{-}(aq)\right] \\ &\therefore \left[OH^{-}(aq)\right] &= \frac{K_{w}}{\left[H^{+}(aq)\right]} \\ &\therefore \left[OH^{-}(aq)\right] &= \frac{\left[CH_{3}COOH(aq)\right]K_{w}}{\left[CH_{3}COO^{-}(aq)\right]\left[H^{+}(aq)\right]} &= \frac{K_{w}}{K_{a}} \end{split}$$

 Calculate the hydroxide ion concentration, the percentage of the reaction and pH of a 0.050 mol dm⁻³ solution of sodium ethanoate. If x is the concentration of OH⁻,

 $[CH_{3}COO^{-}(aq)] = (0.050 \text{ mol } dm^{-3} - x)$ $[OH^{-}(aq)] = x$ $[CH_{3}COOH(aq)] = x$

$$\therefore K_{\rm b(CH_3C00^{-})} = \frac{K_{\rm w}}{K_{\rm a}} = \frac{1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{1.8 \times 10^{-5} \text{ mol dm}^{-3}} = 5.6 \times 10^{-10} \text{ mol dm}^{-3}$$

$$\therefore 5.6 \times 10^{-10} \text{ mol } dm^{-3} = \frac{x^2}{(0.050 \text{ mol } dm^{-3} - x)}$$
$$\Box \quad \frac{x^2}{0.05 \text{ m } \circ 1 \text{ d } m^{--3}} \quad (x << 0.050)$$
$$x = [OH^{-}(aq)] = 5.3 \times 10^{-6} \text{ mol } dm^{-3}$$

The percentage reacted is =
$$\frac{5.3 \times 10^{-6}}{0.05} \times 100 = 0.011\%$$

$$[H^{+}(aq)] = \frac{1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{5.3 \times 10^{-6} \text{ mol dm}^{-3}} = 1.9 \times 10^{-9} \text{ mol dm}^{-3}$$

$$\mathrm{pH} = -\log_{10} \ 1.9 \ \times \ 10^{19} \ = 8.72$$

Calculating the pH of a solution of a salt formed from a strong acid and a weak base e.g. NH₄Cl

$$NH_4Cl(s) + H_2O(l) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$
 (Completely ionized)

Consider the involvement of these ions in hydrolysis.

$$\begin{split} \mathrm{NH}_{4}^{+}(\mathrm{aq}) + 2\mathrm{H}_{2}\mathrm{O}(\mathrm{l}) & \square & \mathrm{NH}_{4}\mathrm{OH}(\mathrm{aq}) + \mathrm{H}_{3}\mathrm{O}^{+}(\mathrm{aq}) \\ \mathrm{Cl}^{-}(\mathrm{aq}) + \mathrm{H}_{2}\mathrm{O}(\mathrm{l}) & \longrightarrow & \mathrm{Negligible} \\ & \mathcal{K} = \frac{\left[\mathrm{NH}_{4}\mathrm{OH}(\mathrm{aq}) \right] \left[\mathrm{H}_{3}\mathrm{O}^{+}(\mathrm{aq}) \right]}{\left[\mathrm{NH}_{4}^{+}(\mathrm{aq}) \right] \left[\mathrm{H}_{2}\mathrm{O}(\mathrm{l}) \right]^{2}} \end{split}$$

Since $[H_2O(l)]$ is a constant,

$$K_{\mathbf{a}(\mathbf{NH}_{4})} = \frac{\left[\mathbf{NH}_{3}(\mathbf{aq})\right]\left[\mathbf{H}_{3}\mathbf{O}^{+}(\mathbf{aq})\right]}{\left[\mathbf{NH}_{4}^{+}(\mathbf{aq})\right]}$$

Since

$$\begin{bmatrix} \mathbf{H}_{3} \mathbf{O}^{+}(\mathbf{aq}) \end{bmatrix} = \frac{\mathbf{K}_{W}}{\begin{bmatrix} \mathbf{OH}^{+}(\mathbf{aq}) \end{bmatrix}}$$
$$K_{\mathfrak{a}(\mathbf{NH}_{4}^{+})} = \frac{\begin{bmatrix} \mathbf{NH}_{3}(\mathbf{aq}) \end{bmatrix} K_{W}}{\begin{bmatrix} \mathbf{NH}_{4}^{+}(\mathbf{aq}) \end{bmatrix} \begin{bmatrix} \mathbf{OH}^{+}(\mathbf{aq}) \end{bmatrix}}$$
$$\therefore K_{\mathfrak{a}(\mathbf{NH}_{4}^{+})} = \frac{K_{W}}{K_{\mathfrak{b}(\mathbf{NH}_{3})}} = \frac{\begin{bmatrix} \mathbf{NH}_{4} \mathbf{OH}(aq) \end{bmatrix} \begin{bmatrix} \mathbf{H}_{3} \mathbf{O}^{+}(aq) \end{bmatrix}}{\begin{bmatrix} \mathbf{NH}_{4}^{+}(aq) \end{bmatrix}}$$
$$= \frac{\begin{bmatrix} \mathbf{H}_{3} \mathbf{O}^{+}(aq) \end{bmatrix}^{2}}{\begin{bmatrix} \mathbf{NH}_{4}^{+}(aq) \end{bmatrix}}$$

As K_w, K_b and $[NH_4^+(aq)]$ are known $[H_3O^+(aq)]$ and pH can be calculated.

pH Determination

The pH value of a solution can be determined using

- indicators
- indicator papers
- pH meter

Theory of indicators

- Any acid base indicator is a weak acid or a weak base. They show one colour below a certain pH value and another colour above a certain pH value.
- Consider acid-base indicator as weak acid which can be represented as HIn which takes part in the following equilibrium.

 $HIn(aq) + H_2O(1) \square H_3O^+(aq) + In^-(aq)$ Colour I Colour II

Instead of K_{a} the equilibrium is described by the constant K_{In} to show that indicator is used.

$$\begin{split} & \mathcal{K}_{\mathbf{h}} = \frac{\left[\mathbf{H}_{3}\mathbf{O}^{+}(\mathbf{aq})\right] \left[\mathbf{In}^{+}(\mathbf{aq})\right]}{\left[\mathbf{HIn}(\mathbf{aq})\right]} \\ & -\log_{10} \mathcal{K}_{\mathbf{h}} = -\log_{10}[\mathbf{H}_{3}\mathbf{O}^{+}(\mathbf{aq})] - \log_{10}[\mathbf{In}^{+}(\mathbf{aq})] - (4\log_{10}[\mathbf{HIn}(\mathbf{aq})]) \\ & \mathbf{p}\mathcal{K}_{\mathbf{h}} = \mathbf{p}\mathbf{H} + \log\frac{\left[\mathbf{HIn}(\mathbf{aq})\right]}{\left[\mathbf{In}^{+}(\mathbf{aq})\right]} \\ & \mathbf{p}\mathbf{H} = \mathbf{p}\mathcal{K}_{\mathbf{h}} + \log_{10}\frac{\left[\mathbf{In}^{+}(\mathbf{aq})\right]}{\left[\mathbf{HIn}(\mathbf{aq})\right]} \end{split}$$

- The HIn and In are of two different colours.
- The addition of acid to this solution will push the equilibrium to the left and the colour of HIn will become prominent.
- Addition of alkali will result in the equilibrium moving to the right since the OH⁻ will remove the H_3O^+ ion from the equilibrium and the colour of In- will become prominent.
- Colour I displayed at a lower pH may be called 'lower colour' and the colour II shown at higher pH can be called the' higher colour'.
- When the pH of the solution becomes equal to pK_{In} , an intermediate colour of an equimolar mixture of HIn and In⁻ is shown.
- When the pH range of a particular indicator is equal to $pK_{In} + 1$ and $pK_{In} 1$ the colour change occurs over a pH range of about 2 units.

Indicator	pH range	Colour below the lower pH limit	Colour above the uper pH limit	р <i>К</i> _{In}
Methyl orange	2.9 - 4.6	red	yellow	3.7
Methyl red	4.2 - 6.3	red	yellow	5.0
Bromothymol blue	6.0 - 7.6	yellow	blue	7.1
Phenolphthalein	8.3 - 10.0	colourless	red	9.6

- To select the suitable indicator for a particular titration, pH range of the colour change of the indicator should be in the abrupt pH range (vertical portion) that embraces equivalence point of the titration.
- If pH at equilibrium of a titration is equal to the pK_{In} of an indicator, that indicator fits well for that titration.

Calculation of pH value of acid-base reactions at different points and drawing pH curves

- The point at which the reaction completed is called the equivalence point. At the equivalence point of a strong acid- strong base titration,
 [H⁺(aq)] = [OH⁻(aq)]
- In strong acid –strong base titration neither cation (eg. Na⁺, K⁺) nor the anion (eg. Cl⁻, NO₃⁻) undergoes hydrolysis at the equivalence point. Therefore, pH at equivalence point is

7.0. Here pH at the equivalence point is determined only by the dissociation of H_2O .

• But in other titrations cations of weak base and anions of weak acid undergo hydrolysis and determine the pH of the resulting solution. Example 1:

$$\mathrm{NH}_4^+(\mathrm{aq}) + \mathrm{H}_2\mathrm{O}(\mathrm{l}) \square \mathrm{NH}_4\mathrm{OH}(\mathrm{aq}) + \mathrm{H}^+(\mathrm{aq})$$

Here $[H^+] > [OH^-]$ Resulting solution will be acidic. Therefore, pH at the equivalence point is lower than 7.0. Example 2:

$$CH_3COO^{-}(aq) + H_2O(l) \square CH_3COOH(aq) + OH^{-}(aq)$$

Here, $[OH^{-}] > [H^{+}]$

Resulting solution will be basic. Therefore, pH at the equivalence point is higher than 7.0.

• Consider the following titration



Initial pH = 1

pH after adding 5 cm³ of the base

$$= -\log\left(\frac{0.1}{1000} \times \frac{20}{30} \times 1000\right)$$
$$= 1.1761$$
$$\Box 1.2$$

pH after adding 24 cm³ of the base

$$= -\log\left(\frac{0.1}{1000} \times \frac{1}{49} \times 1000\right)$$
$$= 2.6778$$
$$\Box 2.7$$

At the equivalence point pH = 7.

pH after adding 26 cm³

$$= 14 - \left\{-\log\left(\frac{0.1}{1000} \times \frac{1}{51} \times 1000\right)\right\}$$
$$= 11.2924$$
$$\Box 11.3$$

Titration curves





Fig 13.5.1: Titration curve for strong acid strong base titration.

- Titration (a) shows a rapid change in pH from 3 11 around its equivalence point. Hence any indicator having pK_{In} in this range can be used to detect the end point of the titration. eg. Methyl orange ($pK_{In} = 3.7$), Bromothymol blue ($pK_{In} = 7$),
 - Phenolpthalene (p $K_{In} = 9.6$)
- When concentrations of reactants are low the range in which a rapid change is shown becomes narrow. See titration (b). Hence, only bromothymol blue out of the above three indicators can be used for the titration (b).
- 2) Strong base / weak acid titration



 $\begin{aligned} \mathrm{HA}\,(\mathrm{aq}) & \square & \mathrm{H}^{+}\,(\mathrm{aq}) + \mathrm{A}^{-}\,(\mathrm{aq}) & (K_{\mathrm{a}} = 1 \ \mathrm{x} \ 10^{-5} \ \mathrm{mol} \ \mathrm{dm}^{-3}) \\ \mathrm{A}^{-}(\mathrm{aq}) + \mathrm{H}_{2}\mathrm{O}\,(\mathrm{l}) & \square & \mathrm{HA}\,(\mathrm{aq}) \ + \mathrm{OH}^{-}(\mathrm{aq}) \end{aligned}$

• Calculation of approximate initial pH

HA (aq)
$$\square$$
 H⁺ (aq) + A⁻ (aq) \square H⁺ (aq) - \square H⁺ (aq) \square A⁻ (aq)

$$K_{a} = \frac{\left[\text{II} \left(aq \right) \right] \left[\text{II} \left(aq \right) \right]}{\left[\text{HA}(aq) \right]}$$

$$1 \times 10^{-5} \text{ mol } dm^{-3} = \frac{\left[H^{+}(aq)\right]^{2}}{0.1 \text{ mol } dm^{-3}}$$
$$\left[H^{+}(aq)\right]^{2} = 1 \times 10^{-6} \text{ mol}^{2} dm^{-6}$$
$$\left[H^{+}(aq)\right] = 1 \times 10^{-3} \text{ mol } dm^{-3}$$
$$pH = 3.0$$

• Calculation of approximate pH at the equivalance point

Consider the hydrolysis of the conjugate base of the weak acid.

$$A^{-}(aq) + H_{2}O(l) \qquad HA(aq) + OH^{-}(aq)$$
$$K = \frac{\left[HA(aq)\right]\left[OH^{-}(aq)\right]}{\left[A^{-}(aq)\right]} = \frac{\left[HA(aq)\right]\left[OH^{-}(aq)\right]\left[H^{+}(aq)\right]}{\left[A^{-}(aq)\right]\left[H^{+}(aq)\right]} = \frac{K_{w}}{K_{a}}$$

At the equivalence point $[HA(aq)] = [OH^{-}(aq)]$ Assuming $[A^{-}(aq)]$ is 0.05 mol dm⁻³

$$\frac{K_{w}}{K_{a}} = \frac{\left[OH^{-}(aq)\right]^{2}}{0.05 \text{ mol dm}^{-3}}$$
$$\frac{K_{w}}{K_{a}} = \frac{10^{-14} \text{ mol}^{2} \text{ dm}^{-6}}{10^{-5} \text{ mol dm}^{-3}} = 10^{-9} \text{ mol dm}^{-3}$$
$$[OH^{-}(aq)]^{2} = 0.05 \text{ x } 10^{-9} \text{ mol}^{2} \text{ dm}^{-6}$$
$$pOH = 5.15$$
$$pH = 14.0 - 5.15 = 8.85$$

• Graph shows the variation in pH as 0.10 mol dm⁻³ NaOH solution is added in the titration of 0.1 mol dm⁻³ solution of a weak acid HA ($pK_a = 5.0$).





• For the above titration a rapid change in pH shows around 7.5 to 10. Therefore, the suitable indicator is phenolpthalene. $(pK_{In} = 9.6)$

3. Strong acid/ weak base titration



Let's take pK_{h} of MOH as 5.0

• Approximate initial pH

 $MOH(aq) \Box M^{+}(aq) + OH^{-}(aq)$



- For the above titration a rapid change in pH shows around 3 to 6. Therefore, one of the suitable indicators is methyl orange.
- (4) For weak acid weak base titrations there is no rapid change in pH around the equivalence point. Therefore, it is very difficult to accurately detect the end point by using an indicator.
- (5) Titration of 25.00 cm³, 0.05 mol dm⁻³ Na₂A aqueous solution and 0.10 mol dm⁻³ HCl solution. (A = conjugate base of a weak acid, eg. CO_3^{2-})

For H_2A , let $pK_{a_1} = 6$ and $pK_{a_2} = 10$.

$$A^{2} (aq) + H_{2}O(1) \blacksquare \blacksquare \blacksquare HA' (aq) + OH (aq)$$

$$HA' (aq) + H_{2}O(1) \blacksquare \blacksquare \blacksquare H_{2}A(aq) + OH (aq)$$

$$K_{1} = \frac{K_{w}}{K_{a_{2}}} \text{ here } K_{a_{2}} \text{ for HA' (aq) } \blacksquare \blacksquare \blacksquare H^{+}(aq) + A^{2} (aq)$$

an	$\mathfrak{t} K_2 = \frac{K_{\mathbf{w}}}{K_{\mathbf{a}_1}}$ here $K_{\mathbf{a}_1}$	for	H ₂ A(aq)	8600] H ⁺ (aq) + HA ⁻ (aq)
		Vol	ume of HC	l/cm ³	

	Volume of HCl/cm ³
First end point	12.50
Second end point	25.00





- First end point can be detected with phenolphalin and second end point can be detected with methyl orange.
- If we use phenolphthalein as the indicator 12.5 cm³ will be the titre value. If we use methyl orange as the indicator 25.0 cm³ will be the titre value.

Na₂CO₃/HCl titration

• The explanation is similar to the above.

CO3² (aq)+H2O(1) 目節軸 HCO3(aq) + OH (aq) HCO3(aq)+H2O(1) 目節軸 H2CO3(aq) + OH (aq)

For carbonic acid $pK_{\mathbf{a}_1} = 6.37$ and $pK_{\mathbf{a}_2} = 10.33$

 $= 4.27 \text{ x } 10^{-7} \text{ mol dm}^{-3} \text{ and } = 4.68 \text{ x } 10^{-11} \text{ mol dm}^{-3}.$

$$K_{1} = \frac{10^{-14} \text{ m ol}^{2} \text{ dm}^{-6}}{4.68 \times 10^{-11} \text{ m ol} \text{ dm}^{-3}} \text{ where } K_{1} = \frac{K_{w}}{K_{a_{2}}}$$
$$= 2.14 \times 10^{-4} \text{ m ol} \text{ dm}^{-3}$$
$$K_{2} = \frac{10^{-14} \text{ m ol}^{2} \text{ dm}^{-6}}{4.27 \times 10^{-7} \text{ m ol} \text{ dm}^{-3}} \text{ where } K_{2} = \frac{K_{w}}{K_{a_{1}}}$$
$$= 2.34 \times 10^{-8} \text{ m ol} \text{ dm}^{-3}$$

Using K_2 and K_{a_1} values, pH at two equivalence points of the above titration can be calculated.

curculated	L.		
Let's conside	er titraion of 25.00 cr	m^3 of 0.05 mol dm ⁻³ Na ₂	CO_3 with 0.1 mol dm ⁻³ HCl.
		Volume of HCl/cm ³	
	First end point	12.50	
	Second end point	25.00	

The first end point is shown at the completion of the following reaction.

 $\mathrm{CO}_3^{2\cdot}(aq) + \mathrm{H}^+(aq) \rightarrow \mathrm{HCO}_3^{\cdot}(aq)$ At the first end point the following equilibrium takes place. HCO3(aq)+H2O(1) 目 🛉 🖽 H2CO3(aq) + OH (aq)

Hrere,
$$K_2 = \frac{\left[H_2CO_3(aq)\right]\left[OH^*(aq)\right]}{\left[HCO_3(aq)\right]} = \frac{\left[OH^*(aq)\right]^2}{\left[HCO_3(aq)\right]}$$

 $\left[HCO_3(aq)\right] = \frac{\frac{0.1 \times 12.5}{1000}}{37.5} \times 1000 = 0.033 \text{ mol dm}^{-3}$
 $\left[OH^*(aq)\right]^2 = K_2 \times \left[HCO_3(aq)\right] = 2.34 \times 10^{-8} \text{ mol dm}^{-3} \times 0.033 \text{ mol dm}^{-3}$
 $= 7.72 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$
 $\left[OH^*(aq)\right] = 2.79 \times 10^{-5} \text{ mol dm}^{-3}$
Therefore, pH at the first end point = 9.55.

The second end point is shown at the completion of the following reaction.

$$\mathrm{HCO}_{3}^{\cdot}(\mathrm{aq}) + \mathrm{H}^{+}(\mathrm{aq}) \rightarrow \mathrm{H}_{2}\mathrm{CO}_{3}(\mathrm{aq})$$

At the second end point the following equilibrium takes place.

$$\begin{split} H_{2}CO_{3}(aq) & \blacksquare \stackrel{\bullet}{\blacksquare} \quad HCO_{3}^{:}(aq) + H^{+}(aq) \\ K_{a_{1}} &= \frac{\left[HCO_{3}^{:}(aq)\right] \left[H^{+}(aq)\right]}{\left[H_{2}CO_{3}(aq)\right]} = \frac{\left[H^{+}(aq)\right]^{2}}{\left[H_{2}CO_{3}(aq)\right]} \\ \left[H_{2}CO_{3}(aq)\right] &= \frac{\frac{0.1 \times 12.5}{1000}}{50.0} \times 1000 = 0.025 \text{ mol dm}^{-3} \\ \left[H^{+}(aq)\right]^{2} &= K_{a_{1}} \times \left[H_{2}CO_{3}(aq)\right] = 4.27 \times 10^{-7} \text{ mol dm}^{-3} \times 0.025 \text{ mol dm}^{-3} \\ &= 1.07 \times 10^{-8} \text{ mol}^{2} \text{ dm}^{-6} \\ \left[H^{+}(aq)\right] &= 1.03 \times 10^{-4} \text{ mol dm}^{-3} \end{split}$$

Therefore, pH at the second end point = 3.99.

Suggested learning – teaching activities :

- Ask students to prepare indicators using flowers.
- Let students to determine the pH of indicator solutions using indicators and pH papers.
- Let them to determine acidic, basic or neutral nature of aqueous solutions of salts by testing pH.
- Guide the students to calculate pH at different situations/stages when titrating a strong acid with a strong base.
- Allow the students to sketch the titration curves for different titrations such as
 - Strong base strong acid.
 - Strong base weak acid.
 - Weak base strong acid
- Engage the students to determine suitable indicators for the titrations and allow them to calculate titre value when using different indicators for a particular titration.
- Give instructions to sketch titration curves which have more than one step (two steps). eg. Na₂CO₃(aq) and HCl(aq)

Competency 13.0	:	Uses the concept of equilibrium and its principles determine the macroscopic properties of closed systems in dynamic equilibrium.
Competency level 13.6	:	Prepares buffer solutions according to the requirements.
Periods	:	05
Learning outcomes	:	
•	In	vestigates buffer solutions qualitatively and quantitatively.
•	D	erives Henderson equation for monobasic buffer systems

- Uses Henderson equation for simple calculations.
- Explains pH of a buffer system qualitatively and quantitatively.

Guidance for teacher elaboration :

- It can be shown either by calculation or using pH papers that pH of chemically pure water can be changed by 3 units by adding 1 cm³ of 0.1 mol dm⁻³ HCl or NaOH to 1.0 dm³ of water. This shows that a small amount of an acid or an alkali can cause a drastic change in pH. But there are solutions/systems that can resist such changes.
- A **buffer solution** is a one which resists the change in pH on addition of a small amount of H⁺ or OH⁻ or water.
- The following table shows how pH changes when the given volumes of a 0.1 mol dm⁻³ NaOH solution are added to 50.00 cm³ of a 0.1 mol dm⁻³ CH₃COOH solution.

Volume of the 0.1 mol dm ⁻³	pН
NaOH solution added/cm ³	
0.00	2.88
5.00	3.88
10.00	4.15
15.00	4.39
20.00	4.60
25.00	4.75
35.00	5.12
45.00	5.71
50.00	8.75

• According to the above table, the change in pH in between the addition of 10.00 cm³ and 25.00 cm³ of NaOH solution is very small showing that in this range, the system is resistant to the change in pH brought about by the addition of NaOH. This action is called **buffer action**.

Buffer systems

- Solutions containing a weak acid and its conjugate base act as buffers. *eg.* CH₃COOH and CH₃COONa.
- Solutions containing a weak base and its conjugate acid also act as buffers.
 eg. NH₄OH and NH₄Cl.

• The buffer action can be explained using the CH₃COOH and CH₃COONa system.

 $CH_{3}COONa(aq) \longrightarrow CH_{3}COO^{-}(aq) + Na^{+}(aq) \quad (Complete dissociation)$ $CH_{3}COOH(aq) + H_{2}O(l) \Longrightarrow CH_{3}COO^{-}(aq) + H_{3}O^{+}(aq) \quad (Incomplete dissociation)$

When H_3O^+ ions are added to the system, they are removed by the CH_3COO^- ion forming weakly dissociated CH_3COOH .

 $CH_3COO^{-}(aq) + H_3O^{+}(aq) \implies CH_3COOH(aq) + H_2O(l)$

Therefore, pH almost remains constant

When a small amount of OH⁻ ions are added to the system, they are immediately removed forming almost unionised water.

 $OH^{-}(aq) + H_{3}O^{+}(aq) \implies 2H_{2}O(1)$

More CH₃COOH ionises to replenish the lost H₃O⁺, so pH remains almost constant.

• The buffer action can also be explained using the $NH_4OH(aq)$ and $NH_4Cl(aq)$ system.

$$NH_4OH(aq) \implies NH_4^+(aq) + OH^-(aq)$$
$$NH_4Cl(aq) \implies NH_4^+(aq) + Cl^-(aq)$$

When a small amount of an acid is added, H^+ ions are removed by the OH⁻ forming water and more NH_4OH ionises restoring the OH⁻ ions. Hence, pH does not change widely. When an alkali is added, OH⁻ ions combine with NH_4^+ to form NH_4OH bringing down the OH⁻ concentration. Hence, pH approximately remains constant.

Henderson equation

• Henderson equation can be derived to determine the pH of a buffer system such as CH₃COOH and CH₃COONa.

$$CH_{3}COONa(aq) \longrightarrow CH_{3}COO^{\cdot}(aq) + Na^{+}(aq)$$

$$CH_{3}COOH(aq) + H_{2}O(1) \rightleftharpoons CH_{3}COO^{-}(aq) + H_{3}O^{+}(aq)$$

$$K_{a} = \frac{[CH_{3}COO^{\cdot}(aq)][H_{3}O^{+}(aq)]}{[CH_{3}COOH(aq)]}$$

$$\therefore \log K_{a} = \log[CH_{3}COO^{\cdot}(aq)] + \log[H_{3}O^{+}(aq)] - \log[CH_{3}COOH(aq)]$$

$$-\log[H^{+}(aq)] = -\log K_{a} + \log[CH_{3}COO^{\cdot}(aq)] - \log[CH_{3}COOH(aq)]$$

$$\therefore pH = pK_{a} + \log \frac{[CH_{3}COO^{\cdot}(aq)]}{[CH_{3}COOH(aq)]}$$

- Since CH_3COOH is weakly ionised, $[CH_3COOH(aq)]$ is approximately equal to the initial concentration of the acid and $[CH_3COO^{-}(aq)]$ can be considered to be provided by the salt.
- It is important to keep the pH constant in certain instances.
 e.g. in blood, in industries and in biological experiments.
 The pH of blood is 7.4 and change in this by about 0.5 units is fatal. Therefore, in giving injections, this has to be taken into consideration.

Proposed learning - teaching activities:

- Let students to predict the buffer action of different systems.
- Show that weak acid-strong base and weak base-strong acid systems behave as buffer systems before the equivalance point.
| Competency | 14.0 : | Investigates practical importance of electrochemical sys- |
|------------------------|--------|---|
| | | tems. |
| Competency level 14.1: | | Uses conductivity to understand the nature of solutes and |
| | | their concentration in an aqueous solution. |
| Periods | : | 04 |

Learning outcomes

- Explains the terms strong electrolyte, weak electrolyte, and non electrolyte.
- States examples for electrolyte, non electrolyte, strong electrolyte and weak electrolyte in an aqueous medium.
- Compares electronic conductors and ionic conductors in terms of current carrying entities.
- Expresses that the electrode reactions at both the electrodes are necessary to pass a current through an electrolyte.
- Defines the terms resistance and resistivity.

:

- Defines the terms conductance and conductivity.
- States the factors that affect the conductivity of an electrolyte solution.
- Derives the coherent and non coherent SI units for the conductivity
- Measures and compares the approximate conductivities of different water samples.

Guidance for teacher elaboration :

• Strong electrolytes

Strong electrolytes are substances that are virtually fully ionized in solution, and include ionic solids and strong acids. As a result of their complete ionization, the concentration of ions in solution is proportional to the concentration of strong electrolyte added. eg. NaCl, KNO₃, HCl in aqueous solutions

- Weak electrolytes
 Weak electrolytes are not fully ionized in solution. They include weak Bronsted acids and bases. *eg.* CH₃COOH, NH₃, H₂O
- Non-electrolytes

Liquids/solutions that do not contain ions are referred as non electrolytes. They do not conduct electricity. eg. C_6H_6 , Kerosene



A metal cuboid is shown on the left hand side above. A cuboid shape portion of a solution with the similar dimensions of the metal cube which is in between two electrodes is shown on the right hand side.

Here l = Length of the metal cube or the selected cuboid shape portion of the solution (m) A =Area of cross section (m²) $R = \text{Resistance}(\Omega)$ $\rho = \text{Resistivity}(\Omega_m)$ $\frac{1}{R}$ = Conductance (Ω^{-1} or S where S stands

Regarding the above cuboids,

$$R \alpha l \quad \text{and} \quad R \alpha \frac{1}{A}$$

$$\therefore R \alpha \frac{l}{A}$$

$$R = \rho \frac{l}{A}$$

$$\rho = \frac{RA}{l}$$

$$k = \frac{1}{\rho} = \frac{l}{AR}$$

- Coherent SI unit of conductivity is Ω^{-1} m⁻¹ and the most practical unit is μ S cm⁻¹. •
- Conductivity and resistivity are constants for the particular substance (metal or solution with a given concentration) and it changes with temperature (about 2% per one degree Celsius in solution).
- Factors affecting conductivity of a solution •
 - Nature of the solute (aqueous solutions of strong, weak and non electrolytes, molten • electrolytes)
 - Concentration of the solute
 - Temperature •

	Sample	Conductivity/ μ S cm $^{-1}$
	Distilled water	1-2
	0.01 mol dm ⁻³ KCl solution	1,480
	0.10 mol dm ⁻³ KCl solution	12,400
Table 14.1.1 Conductivities of various water sample	1.0 mol dm ⁻³ KCl solution	110,000
	Well water	100-200
	Pipe borne water	50-150
and solutions at 298 K	Sea Water	40,000

• For dilute solutions decrease in conductivity is approximately proportional to the concentration and this is very correct for very dilute solutions. The reason is the decrease of interactions among ions in dilution.

	Cond	uctivity/(µS cm ⁻¹	¹)
Concentration / (mol dm ⁻³)	0 °C	13 °C	25 °C
1.0	6.543 x 10 ⁴	$9.820 \ge 10^4$	1.117 x 10 ⁵
0.1	7.154×10^3	$1.119 \text{ x } 10^4$	1.289 x 10 ⁴
0.01	7.751×10^2	1.223×10^3	1.411 x 10 ³

Table 14.1.2 : Conductivities of KCl solutions of different concentrations at different temperatures

• Current = Charge / Time.

Current carried by an ion at a given temperature in a given electric field depends on the concentration of ions and their speed. Speed of an ion depends on its charge, size and potential gradient of the applied electric field.

Table14.1.3 : Speeds of ions in an aqueous	
solution under the potential gradien	t
1 V cm ⁻¹ at 298 K	

Ion	Speed/mm min ⁻¹
H^{+}	2.05
OH-	1.12
Na^+	0.29
K^+	0.42
NO_3^-	0.40
Cl	0.42
SO ₄ ²⁻	0.88
Ca ²⁺	0.67

 H⁺ and OH⁻ ions have the highest speeds. So those ions contributes a lot for the conductance. For example, H⁺ ions contribute about 80% for the conductance of dilute HCl solution.

Proposed learning teaching actitivities :

- Describe the terms strong electrolyte, weak electrolyte and non electrolyte in aqueous solutions.
- Make students understand that an electrolyte conducts electricity by ions in liquid state or solution. Explain that a metallic conductor conducts electricity by way of electrons.
- Make them aware that there are interactions among the ions in an ionic solution or in an ionic liquid. State that, under the influence of a potential difference, ions tend to move in opposite directions, their speeds of movements are very small and they depend on the potential gradient, charge and size of ion.
- Using the table 14.1.1 emphasize that conductivity gives important information on the concentrations of ions in a solution.
- Discuss the applications of conductivity measurements.
 - Measurement of concentrations of solutions
 - Determination of purity of water (measurement of salinity)
 - Determination of equivalence point in titrations.

Competency	14.0 :	Investigates practical importance of electrochemical sys-
		tems.
Competency lev	vel 14.2:	Investigates electrodes in equilibrium and electrode reactions related to them.
Periods	:	02

Learning outcomes

- Sketches metal- metal ions electrode.
- Giving examples, writes the reversible electrode reactions for common metal-metal ion electrodes.
- Describe the existence of a potential difference between an electrode and its solution at the electrode/electrolyte interface.
- Diagrammatically represents different types of electrodes.(Gas electrodes, metalmetal ion electrodes, redox electrodes)
- Writes the reversible electrode reactions for different types of electrodes.
- Defines the standard electrode.
- Denotes cells using standard notation.

Guidance for teacher elaboration :

Table 14.2.1: Types of electrodes

Type of electrode	Symbol	Equilibrium electrode reaction
Metal-metal ion	$Cu(s) Cu^{2+}(aq) $	$Cu^{2+}(aq) + 2e \square Cu(s)$
	Ag(s) Ag ⁺ (aq)	$Ag^{+}(aq) + e \square Ag(s)$
Metal-insoluble salt	Ag(s),AgCl(s) Cl ⁻ (aq)	$AgCl(s) + e \square Ag(s) + Cl(aq)$
	$Hg(l), Hg_2Cl_2(s) Cl^-(aq)$	$\frac{1}{2}$ Hg ₂ Cl ₂ (s) +e \square Hg(l) + Cl ⁻ (aq)
Gas	$Pt(s),H_2(g) H^+(aq)$	$2H^+(aq) + 2e \square H_2(g)$
	Pt(s),O ₂ (g) OH ⁻ (aq)	$2O_2(g) + 2H_2O(l) + 4e \square 4OH(aq)$
Redox	$Pt(s) Fe^{3+}(aq),Fe^{2+}(aq)$	$Fe^{3+}(aq) + e \square Fe^{2+}(aq)$
	$Pt(s) Sn^{4+}(aq),Sn^{2+}(aq)$	$\operatorname{Sn}^{4+}(\operatorname{aq}) + 2e \square \operatorname{Sn}^{2+}(\operatorname{aq})$

- It is necessary to indicate concentration for solutions (e.g. $Fe^{2+}(aq, 1.0 \text{ mol dm}^{-3})$ and pressure in case of gases (e.g. $H_2(g, 1.0 \text{ atm})$.
- Metal-metal ion electrodes

When a piece of active metal such as magnesium is dipped in a beaker of water, there will be some tendency for the metal atoms to leave electrons and go into solution as metal ions. The electrons will be left behind on the metal. In a very short time, there will be a build -up of electrons on the metal, and it will be surrounded in the solution by a layer of positive ions. These will tend to stay close because they are attracted to the negative charge on the piece of metal. This is called double layer as shown in figure (a).



- Some of them will be attracted enough so that they will reclaim their electrons and stick back on to the piece of metal. A dynamic equilibrium will be established when the rate at which ions are leaving the surface is exactly equal to the rate at which they are joining it again. Here, the double layer reach to its equilibrium. At this point there will be a constant negative charge on the metal and a constant number of metal ions present in the solution around it. However, at the dynamic equilibrium, ions are continually leaving and rejoining the surface with equal rates. The potential that is created between the metal and adjecent layers of solution is known as the electrode potential.
- If a less active metal such as copper is considered, it forms its ions less readily. Any ions which do break away are more likely to reclaim their electrons and stick back on to the metal again. It will still reach an equilibrium position, but there will be a lesser charge on the metal, and fewer ions in the solution.
- If both equilibria are considered together it is clear that the position of the magnesium equilibrium $Mg^{2+}(aq) + 2e \square Mg(s)$ lies further to the left than that of the copper equilibrium $Cu^{2+}(aq) + 2e \square Cu(s)$.
- By IUPAC convention, all these equilibria are written with the electrons on the left-hand side of the equation. It is recommenned to stick on to this convention.
- Metal insoluble salts electrodes *eg.* Calomel electrode



eg. Silver-Silver chloride electrode

$$AgCl(s) + e \Box Ag(s) + Cl'(aq)$$

Gas electrodes

Redox electrodes

eg. Fe³⁺/Fe²⁺ electrode

eg. Hydrogen electrode

$$\mathrm{H}^{+}(\mathrm{aq}) + \mathrm{e} \Box = \frac{1}{2}\mathrm{H}_{2}(\mathrm{g})$$



Cell notation

- The anode, or oxidation half-cell is always written on the left; the cathode, or reduction halfcell, is written on the right. The two electrodes are electrically connected by means of a salt bridge, denoted by two vertical bars.
- The cell terminals are at the extreme ends in the cell notation. Electrode and electrolyte interface of each half cell is separated by a single vertical bar. Other constituents are separated by commas.

 $Pt(s)|Fe^{2+}(aq, 1 \text{ mol } dm^{-3}), Fe^{3+}(aq, 1 \text{ mol } dm^{-3})$ Examples:

 $Hg(l), Hg_2Cl_2(s)|Cl^{-}(aq, 1 mol dm^{-3})$

- When the half-reaction involves a gas, an inert material such as platinum serves as a terminal and as an electrode surface on which half-reaction occurs. The notation for the hydrogen electrode, written as a cathode and as an anode are given below respectively. $H^{+}(aq, 1 \text{ mol } dm^{-3})|H_{2}(g)|Pt(s)|$ $Pt(s)|H_{2}(g)|H^{+}(aq, 1 \text{ mol } dm^{-3})$
- Cell notations of several cells are given below.

 $Zn(s)|Zn^{2+}(aq, 1 \mod dm^{-3})||Cu^{2+}(aq, 1 \mod dm^{-3})|Cu(s)|$

 $Cd(s)|Cd^{2+}(aq, 1 \text{ mol } dm^{-3})||H^{+}(aq, 1 \text{ mol } dm^{-3})|H_{2}(g)|Pt(s)|$

Proposed learning-teaching activities :

- Draw sketches of the electrodes given in Table 14.2.1. •
- State that there is a potential difference between the metal and the solution at ٠ equilibrium.
- Write relevant reactions in the standard form (reduction reaction, reversible sign and • physical states are important).

Competency 14.0 : Investigates practical importance of electrochemical systems. Competency level 14.3 : Determines the properties of electrochemical cells. Periods : 06

Learning outcomes

- Defines the term electrode potential of an electrode.
- Introduces the standard hydrogen electrode as a reference electrode.
- Diagrammatically represents the standard hydrogen electrode.
- Defines the term standard electrode.

:

- Explains how to measure the standard electrode potential of an electrode.
- States the factors affecting the electrode potential.
- Defines the term standard electrode potential of an electrode.
- Defines the term electromotive force.
- Solves simple problems related to electromotive force.
- Describes the factors affecting electromotive force.
- Determines the electromotive force of a cell experimentally.
- Constructs the electrochemical series using the standard electrode potentials.
- Describes relationships between the position of metals in the electrochemical series and their existence, method of extraction and chemical properties.
- States the calomel electrode and silver-silver chloride electrode as practical reference electrodes.
- Gives examples for electrochemical cells in equilibrium.
- Explains what is cell with a liquid junction and a cell without a liquid junction.
- Writes the electrode reactions and the cell reactions for equilibrium electrochemical cells involving simple electrodes.

Guidance for teacher elaboration :

- The potential difference in the double layer of a given electrode is considered its electrode potential. This absolute difference cannot be measured. It can only be measured relative to another electrode.
- An electrode with a known or a defined potential used to measure the potential of a given electrode is called a reference electrode. Standard electrode potentials are measured with reference to the standard hydrogen electrode. The potential of the standard hydrogen electrode is defined as $0.00 \text{ V} \{[\text{H}^+(\text{aq})] \text{ is } 1.0 \text{ mol dm}^{-3} \text{ and pressure of H}_2(g) \text{ is } 1 \text{ atm and temperature is } 298 \text{ K}\}$. Calomel electrode and AgCl(s)|Ag(s) electrode are used as practical reference cells. Standard electrode potentials of Calomel electrode and AgCl(s)|Ag(s) electrode are 40.22 V and 40.2415 V respectively.

- The value of the potential of a given electrode under standard conditions measured relative to the standard hydrogen electrode (SHE) is its standard electrode potential.
- The following diagram illustrates a set up that can be used for measuring the standard electrode potential of the Zn²⁺(aq)|Zn(s) electrode.



- When the standard electrode potentials (reduction potential) of different electrodes are arranged in the ascending order, the **electrochemical series** is obtained.
 - Factors affecting the electrode potential
 - Temperature
 - Concentration of the electrolyte
 - Nature of electrolyte
 - Pressure (of a gas)
 - Type of electrode
- Electromotive force (e.m.f.) is defined as the potential difference between the two electrodes when no current flows through the cell.
- Temperature, concentration of the electrolyte, electrode type and the nature of the electrolyte are the factors that affect the electromotive force. It is independent of the distance between the electrodes and the surface area of the electrodes.
- Electrolytes in the two electrodes of an electrochemical cell are connected to complete the internal circuit through a salt bridge or a permeable membrane/diaphragm/porous partition. A tube filled with a solution of a salt such as KCl or NH₄NO₃ which is gelified with agar is used as a salt bridge. Such an electrochemical cell is known as a cell with a liquid junction.
- In a cell, when both electrodes are not separated by a salt bridge or a permeable membrane/ diaphragm/porous partition is referred as a cell without a liquid junction.

Proposed learning teaching activities :

- Introduce the standard hydrogen electrode and other standard electrodes. Introduce the e.m.f. of a cell. Record the potentials of the other electrodes by connecting them with the silver-silver chloride electrode.
- Direct students to measure the emf of different cells.
- According to the international convention, electrode potentials are measured relative to the standard hydrogen electrode. On this standard, the electrode potential of the standard silver-silver chloride electrode is 0.22 V. Similarly, the electrode potentials of other standard electrodes can also be calculated. Show that in arranging these in the ascending order, electrochemical series is obtained.
- Calculate the electrode potentials of Cu^{2+}/Cu electrode and Zn^{2+}/Zn electrode using the data given below.

Positive terminal	Negative terminal	e.m.f./V
(Cathode)	(Anode)	Potential of the other electrode
		relative to Ag(s), AgCl(s) Cl ⁻ (aq)
		<i>ie</i> . $E_{cell} = E_{cathode} - E_{anode}$
$Cu^{2+}(aq) Cu(s)$	Ag(s),AgCl(s) Cl ⁻ (aq)	+ 0.12
Ag(s),AgCl(s) Cl ⁻ (aq)	$Zn^{2+}(aq) Zn(s)$	+ 0.98

- Explain how cell reaction is obtained using electrode reactions and how the corresponding e.m.f. of the cell is obtained using $E_{cell} = E_R E_L$ or $E_{cell} = E_C E_A$.
- Explain effect of concentration of electrolyte and temperature on electromotive force qualitatively.
- Discuss the relationship between the position of an element in the electrochemical series and its chemical properties (oxidation and reduction properties), occurrence and method of extraction.

Competency	4.0 : Investigates practical importance of electrochemical systems.
Competency le	14.4 : Investigates the different types of cells.
Periods	: 04
Learning outco	s • • Identifies different types of practical cells (primary cells

- Learning outcomes : Identifies different types of practical cells (primary cells, secondary cells, fuel cells).
 - Gives examples for primary practical cells (Daniel cells, Leclanche cell).
 - Writes the electrode reactions and the cell reactions for practical primary cells.
 - Identifies lead accumulator as a secondary cell.
 - Write reactions involving in charge-discharge process of the lead accumulator.
 - Differentiates a fuel cell from other types of cells.

Guidance for teacher elaboration :

• The cell in which the cell reaction cannot be reversed by providing electrical energy is called a "primary cell".

Normal Leclanche cell







• A cell in which the reactants can be regenerated from the products by charging after its discharge is referred to as a 'secondary cell'.

eg. Lead accumulator



Cell	Electrolyte	ctrolyte (+) Pole (-) Pole (C		Reaction at (+) Pole (Cathode reaction)	Reaction at (-) Pole (Anode reaction)	Cell reaction
Normal Leclanche cell	NH ₄ Cl/ZnCl ₂	C/MnO ₂	Zn	$2NH_4^+(aq)+2MnO_2(s)+2e$ $Mn_2O_2(s) + H_2O(l)+2NH_3(aq)$	$Zn(s)$ — $Zn^{2+}(aq) + 2e$	$2MnO_2(s)+Zn(s)+H_2O(l)$
Daniel cell	ZnSO ₄ /CuSO ₄	Cu	Zn	$Cu^{2+}(aq) + 2e - Cu(s)$	$Zn(s) Zn^{2+}(aq) + 2e$	Zn(s) + Cu2+(aq) $Zn2+(aq) + Cu(s)$

Cell	Electrolyte	Anode	Cathode	Anode reaction during discharge*	Cathode reaction during discharge*
Lead accumulator	dil. H ₂ SO ₄	Pb	PbO ₂	$\frac{Pb(s) + SO_4^{2-}(aq)}{PbSO_4(s) + 2e}$	$\frac{PbO_{2}(s) + 4H^{+}(aq) + SO_{4}^{2-}(aq) + 2e}{PbSO_{4}(s) + 2H_{2}O(l)}$

* In charging cells, opposite (reverse) reactions take place.

• Fuel cells

Electrochemcal cells in which reactants are continuously supplied from outside are referred as fuel cells. Dihydrogen and dioxygen, methane and dioxygen are commonly used for this purpose. One of the electrolyte used is concentrated KOH solution, maintained at 200 °C. Porous C-Ni electrodes are commonly used.

Relevent reactions for the dihydrogen-dioxygen fuel cell are given below.

Oxydation; $2H_2(g) + 4OH(aq) \longrightarrow 4H_2O(l) + 4e$

Reduction; $O_2(g) + 2H_2O(aq) + 4e \longrightarrow 4OH^{-}(aq)$

Cell reaction $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$



Proposed learning teaching activities :

- Discuss reaction related to the above mentioned primary and secondary cells.
- Explain reasons for the fact that the study of various types of cells in practical use is a very important section in electrochemistry.
- Present electrode reactions and cell reactions taking place when all the primary and secondary cells in the syllabus are put into action practically.
- Describe the construction and the chemistry of fuel cell.

Competency	14.0	:	Investigates practical importance of electrochemical sys-
			tems.
Competency le	vel 14.5	:	Identifies the requirements to be fulfilled in the process of
			electrolysis and carries out related calculations using
			Faraday constant.
Periods		:	06
Learning outco	mes	:	• Explains the meaning of electrolysis.

- Describes principals of electrolysis.
- Predicts the electrolytic products of simple electrolytic systems.
- States Faraday's laws.
- Solves simple problems based on Faraday's laws.
- Explains and demonstrates the process of electroplating.

Guidance for teacher elaboration :

• Electrolysis is the passage of a direct current through a substance that is either molten or dissolved in a suitable solvent, resulting in chemical reactions at the electrodes and separation of mixtures.

Principles of electrolysis

- An ion-electron half reaction occurs at each electrode.
- The overall reaction is a redox reaction.
- The terminal at which oxidation occurs is the anode whereas the terminal at which reduction occurs is the cathode .
- The electrode connected to the positive terminal of the external source of electricity is the positive electrode. The electrode connected to the negative terminal is the negative electrode.
- The positive ions in the solution are attracted by the negative electrode. The negative ions are attracted by the positive electrode.
- Under certain conditions, a different species in the medium/set up may be oxidized or reduced in preference to the relevant ions.
- Electrolysis of water (acidic or basic) using inert (carbon or platinum) electrodes At anode; $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e$ At cathode; $2H_2O(l) + 2e \longrightarrow H_2(g) + 2OH^-(aq)$
- Electrolysis of aqueous $CuSO_4$ solution using copper electrodes At anode; $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e$ At cathode; $Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$
- Electrolysis of aqueous $CuSO_4$ solution using inert electrodes At anode; $2H_2O(1) \longrightarrow O_2(g) + 4H^+(aq) + 4e$ At cathode; $Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$
- Electrolysis of aqueous NaCl solution using inert electrodes At anode; $2Cl^{-}(aq) \longrightarrow Cl_{2}(g) + 2e$ At cathode; $2H_{2}O(l) + 2e \longrightarrow H_{2}(g) + 2OH^{-}(aq)$

- Electrolysis of molten NaCl using inert electrodes At anode: 2Cl-(1) \longrightarrow Cl₂(g) + 2e At cathode; $Na^{+}(l) + e \longrightarrow Na(l)$
- **Faraday's Laws**
 - (1) The quantity of a substance liberated at an electrode is directly proportional to the quantity of electric charge that has flowed in the circuit.
 - (2) For a given quantity of electric charge, the amount of any metal deposited is proportional to its equivalent weight (atomic weight devided by the charge on the metal ion)

Faraday's constant (F) = Molar charge of a proton = $1.602 \times 10^{-19} \text{ C} \times 6.022 \times 10^{23} \text{ mol}^{-1}$ $= 96484 \text{ C mol}^{-1}$ ⊔ 96 500 C mol⁻¹

Electroplating

- Electroplating means coating a metal with another metal using electricity. This is different • from the deposition of a less reactive metal on a more reactive metal.
- In order to have a quality coating during electrolysis, the coating should strongly bind with the metal. In addition, it should have the following qualities.
 - Strength • Lustre
- Chemical inertness
- Good mechanical properties
- Uniformity in thickness and appearance •
- To get a quality metal coating the following factors should be appropriately controlled.

•

- The nature and purity of the electrolyte
- Temperature
- pH value
- Potential difference

• Concentration of ions

Absence of cracks and holes

- Current density
- Nature of the other ions presents •
- Purity of the anode •
- Relative positioning of the anode and the cathode •
- Cleanliness of the object and the nature of its surface
- Two or more reactions may also occur simultaneously on the electrodes. They can be controlled by changing the temperature, concentration, voltage and the nature of electrodes.

Proposed learning teaching activities :

- Electrolyse water and collect dihydrogen and dioxygen gases. Measure the approximate volumes of the gases and qualitatively evaluate the relationship between the quantities of the gases and the current passed.
- Apply Cu or Ag practically on an aluminium wire by using electroplating.
- ٠ Direct students to solve problems based on Faraday's laws.

Competency 14.0	:	Inv	vestigates practical importance of electrochemical sys-
		ten	18.
Competency level 14.6	:	Inv	estigates ways to control corrosion.
Periods	:	04	
Learning outcomes	:	•	Identifies corrosion as an electrochemical process.
		•	Controls corrosion by electrochemical manner.
		•	Describes bimetal corrosion.
		•	Gives examples for cathodic protection.

• Describes the process of passivation.

Guidance for teacher elaboration :

Bimetallic Corrosion

In bimetallic corrosion, the more reactive metal corrodes faster in case where a pair of metals with electrical and physical contact is dipped in a corrosive electrolyte. The less corrosion resistant or the "active" member of the couple experiences accelerated corrosion while the more corrosion resistant or the "noble" member of the couple experiences reduced corrosion due to the "cathodic protection" effect. The most severe attack occurs at the joint between the two dissimilar metals. Further away from the bi-metallic joint, the degree of accelerated attack is reduced.

Cathodic protection

It is a technique to control the corrosion of a metal surface by making it work as a cathode of an electrochemical cell. This is achieved by placing in contact with the metal to be protected another more easily corroded metal to act as the anode of the electrochemical cell. Cathodic protection systems are most commonly used to protect steel, water or fuel pipelines and storage tanks, steel pier piles, ships, offshore oil platforms and onshore oil well casings. Galvanizing of iron is an another example.

Passivation

Protection of a metal by rendering its surface inactive by chemical methods is called passivation. In the context of corrosion, passivation is the spontaneous formation of a hard non-reactive surface film that inhibits further corrosion. This layer is usually an oxide or nitride that is a few molecules thick. Stainless Steels can be passivated using a solution of nitric acid, to remove foreign particles from the surface and promote the growth of a protective oxide layer. Nickel can be used for handling elemental fluorine, due to a passivation layer of nickel fluoride.

Proposed learning-teaching process :

- Introduce wet corrosion as an electrochemical process. Describe the corrosion taking place when metals of different reactivity are kept in contact in a wet medium. Show that corrosion may occur in the same metal due to differences in structure in different places or changes in the environment (e.g. oxygen concentration). Conduct experiments on bimetallic corrosion using magnesium (or zinc) and iron.
- Show practical instances where cathodic protection is used. Show the difference of protection of iron using zinc and tin.
- Conduct experiments to study factors affecting and methods of controlling of corrosion.

Competency 15.0	:	Investigates the occurrence, industrial extraction/
		production and uses of some elements and compounds.
Competency level 15.1	:	Investigates occurrence, industrial extraction/
		production and uses of s-block elements and their
		compounds.
Periods	:	08

Learning outcomes

- Lists out basic requirements for establishing a chemical industry. •
- Describes characteristics of a natural resource that can be used as a raw material • for an industry.
- Describes the occurrence of *s*-block elements and compounds.
- Describes the extraction of Na (Down's cell method) and its uses. •
- Describes the production of salt, NaOH (Membrane cell method), soap and Na₂CO₃ (Solvay process).
- Describes the production of quicklime bleaching powder and CaC_2 using CaCO₃ as the raw material.

Guidance for teacher elaboration :

Basic requirements for stabilising a chemical industry

:

• Capital

Labour

•

•

- Technology
- Availability of raw materials
- Power (electricity, fuel, etc.)
- Transport facilities and the market •
- •
- Government rules and regulations
- Characteristics of natural resources that can be used as raw materials for an industry
 - Occurring as large ores appropriate for long term usage •
 - High purity Easy access
- Occurrence of s-block elements and compounds
 - s-block elements do not occur freely in the nature because they are very reactive and they exist as compounds

	NaCl
	NaCl, MgCl ₂ , CaCl ₂ , CaSO ₄ , Ca(HCO ₃) ₂ , MgSO ₄
	KCI
	$Na_{2}B_{4}O_{7}\cdot 10H_{2}O$
	3BeO·Al ₂ O ₃ ·6SiO ₂
	MgCO ₃
	CaCO ₃ ·.MgCO ₃
ר	
}	CaCO ₃
J	
	CaSO ₄ ·2H ₂ O
	CaF ₂
	$Ca_{3}(PO_{4})_{3}X$ or $3Ca_{3}(PO_{4})_{2}$ · CaX_{2} (X = F, Cl,OH)
	}

- Controlling the environmental pollution
- Waste management

.• Extraction of Sodium (Down's cell method)

- Sodium is extracted using electrolysis of molten NaCl. CaCl₂ is added to reduce the melting point of NaCl to 600 °C.
 - At the cathode,
 - $Na^{+}(l) + e \longrightarrow Na(l)$
 - At the anode, $2Cl^{-}(l) \longrightarrow Cl_{2}(g) + 2e$
- Anode and cathode are separated by a circular disc (steel gauze diaphragm) to prevent the reaction between chlorine gas and sodium.
- A large current is passed through the cell, but at a low voltage.



• Uses of sodium

- Sodium vapour lamps
- Molten sodium is used as a coolant in nuclear reactors.
- Solid sodium is used to dry organic solvents like ether and benzene.
- Used in organic synthesis
- Used to synthesise sodamide (NaNH₂) which is a strong reducing agent.

• Production of *s*-block compounds

• Production of salt

The places where salt produced are referred to as saltterns. In Sri Lanka two main saltterns are placed in Puttalam and Hambantota.

- Characteristic features of the places where saltterns are established
 - Plane land by the sea or lagoon Less rainfall
 - Dry air, more sunlight
 Water impervious clay sand



- Sea water is pumped into the first tank of the salttern. The sea water is evaporated by sunlight. When the concentration of sea water increases CaCO₃ gets precipitated in the first tank of the salttern. CaCO₃ precipitate is allowed to settle down.
- Remaining solution is transferred into the second tank of the salttern and evaporated by sunlight. When the concentration further increases CaSO₄ gets precipitated.
- Remaining solution is transferred into the third tank of the salttern and evaporated. When the concentration further increases NaCl gets precipitated. NaCl is removed from the third tank of the salttern. This NaCl contains Ca²⁺, Mg²⁺ and SO₄²⁻ as impurities.
- Pure NaCl is not hygroscopic. But NaCl having the impurities is hygroscopic. Sodium chloride collected from the third tank is stored outside for nearly six months. During this storage period NaCl is almost purified as Ca²⁺ and Mg²⁺ salts absorb water from air and become solution while NaCl remains as a solid.
- Iodized salt is produced by mixing with KIO₃.
- Uses of NaCl
 - Cooking
 - Food preservative (Maldivian fish, Pickle)
 - Manufacture of Na metal, Na₂CO₃, NaHCO₃ and NaOH
 - Saline
 - To reduce the melting point of ice
- As Mg²⁺ and Br- concentrations are high in bittern soultion it can be used to produce Mg and Br₂.
- Manufacture of Sodium Hydroxide
- Sodium hydroxide is commercially produced by the electrolysis of aqueous sodium chloride in chloro-alkali cells.
- There are three types of chloro alkali cells
 - Mercury cell
 Diaphragm cell
 Membrane cell
- The membrane cell is very similar to the diaphragm cell and the same reactions occur. The main difference is that two electrodes of membrane cell are separated by an ion selective membrane rather than by a diaphragm.



- The advantage of using membrane cell is that the NaOH that is produced is very pure and also uses less electricity, lowest environmental impact.
- The half reactions are

$$2\text{Cl}^{-}(\text{aq}) \rightarrow \text{Cl}_{2}(\text{g}) + 2\text{e}$$
 (at anode)

- $2H_2O(l) + 2e \rightarrow 2OH^-(aq) + H_2(g)$ (at cathode)
- The overal reaction is $2NaCl(aq) + 2H_2O(l) \rightarrow 2NaOH(aq) + Cl_2(g) + H_2(g)$
- The anode is made of titanium and cathode is made of nickel.
- The anodic and cathodic compartments are separated by a polymer cation-exchange membrane.
- The membrane can exchange cations and hence permits Na⁺ ions to migrate from anodic compartment to cathodic compartment.
- The flow of cations maintain electro-neutrality in the two compartments because, during electrolysis, charge is removed at the anode and supplied at the cathode.
- OH⁻ would react with Cl₂, and spoil the process. But migration of OH⁻ is suppressed because the membrane does not exchange anions.
- NaOH solution is partially evaporated and allowed to cool.
- Chlorine is produced as a by-product.
- Uses of sodium hydroxide
 - Use in the laboratory as a convenient strong base
 - Absorb carbon dioxide and other acidic gases
 - Manufacture of soap, paper, atificial silk and dye stuffs
 - Treatment of effluents for removal of heavy metals (as hydroxides) and of acidity
- Uses of chlorine
 - Used directly or in combination form as a bleach for textiles, wood, and paper pulps.
 - Disinfection of drinking water
 - One quarter of the hydrochloric acid produced in U.K. is synthesized from chlorine and hydrogen.
 - Used in recovery of tin, titanium and magnesium from scrap.
 - Used to produce chlorinated rubbers, insecticides, dyes and drugs.
 - Used in the manufacture of polymeric materials such as polyvinyl chloride.

• Manufacture of Soap

Oils, fats or their fatty acids and inorganic water soluble bases (NaOH, KOH) are used as raw materials.

- The industrial soap making involves four basic steps.
 - Step 1 Saponification

The saponification process involves the mixing of tallow (animal fat), coconut oil or vegetable oil with sodium hydroxide and the application of heat. The process results in formation of soap, which is a salt of long chain carboxylic acid.

$$\begin{array}{c} O \\ R - C - O - CH_{2} \\ O \\ R - C - O - CH \\ O \\ R - C - O - CH_{2} \end{array} \xrightarrow{} 3RCOO^{-}Na^{+} + \begin{array}{c} CH_{2} - OH \\ | \\ CH_{2} - OH \\ Soap \end{array} \xrightarrow{} 3RCOO^{-}Na^{+} + \begin{array}{c} CH_{2} - OH \\ | \\ CH_{2} - OH \\ CH_{2} - OH \\ Glycerol \\ R = C_{17}H_{35} / C_{15}H_{31} / C_{11}H_{23} \end{array} \xrightarrow{} \left(\begin{array}{c} CH_{2} - OH \\ CH_{2} - OH \\ Glycerol \\ (By-product) \end{array} \right)$$

• Step 2 - Removal of glycerin

Glycerin is more valuable than soap, and hence most of it is removed for its uses in more expensive cosmetic products. Some of the glycerin is left in soap to make it soft and smooth.

• Step 3 - Soap purification

In the soap purification stage any remaining sodium hydroxide is neutralized with a weak acid like citric acid and two thirds of the remaining water is removed to obtain pure soap.

- Step 4 Finishing The final stage of industrial soap manufacturing process, finishing stage involves mixing of additives such as colours, preservatives and perfume into soap, which is then shaped into bars for sale.
- Instead of NaOH, KOH could be used. The soap manufactured using KOH is softer on skin. Therefore KOH is used mainly in the manufacture of baby soap.
- The percentage of RCOO⁻Na⁺ in the soap is referred as total fatty matter(TFM) value.

• Manufacture of sodium carbonate (Solvay Process)

- Brine (concentrated NaCl solution), limestone and ammonia (manufactured by Haber process) are used as raw materials.
- NH₃ gas is dissolved in brine. This reaction is exothermic. Therefore low temperatures are favoured.
- Counter current principle is used to achieve higher efficiency of dissolving.



- Brine saturated with NH_3 is allowed to react with $CO_2(g)$ which is obtained by heating limestone. The reaction is exothermic. Therefore, low temperatures are favoured.
- Again the counter current principle is used for achieving higher efficiency.



• Here, following reversible reactions take place. $NH_3(aq) + H_2O(l) \implies NH_4^+(aq) + OH^-(aq)$

 $OH^{-}(aq) + CO_{2}(aq) \Longrightarrow HCO_{3}^{-}(aq)$

- As OH⁻ is removed by the second reaction more and more OH⁻ ions are formed by the first reaction.
- When HCO₃⁻ concentration increases NaHCO₃ crystallizes. Na⁺(aq) + HCO₃⁻(aq) → NaHCO₃(s)
- Low temperature is maintained to facilitate the separation of solid NaHCO₃
- NaHCO₃(s) is isolated and heated. CO₂ formed is used again. 2NaHCO₃(s) $\xrightarrow{\Delta}$ $\xrightarrow{\Delta}$ Na₂CO₃(s) + CO₂(g) + H₂O(g)
- Net reaction for the formation of NaHCO₃ is
 NaCl (aq) + NH₃(aq) + CO₂(aq) + H₂O(l) >> NaHCO₃(s) + NH₄Cl(aq)
- The NH₄Cl and lime are used to regenerate NH₃. This NH₃ is used again. CaO(s) + 2NH₄Cl(aq) \longrightarrow CaCl₂(aq) + 2NH₃(aq) + H₂O(*l*) or Ca(OH)₂(s) + NH₄Cl(aq) \longrightarrow CaCl₂(aq) + NH₃(aq) + H₂O(*l*)



• Uses of sodium carbonate

- Washing soda
- Manufacture of glass
- Softening of hard water
- Manufacture of detergents
- Manufacture of soap
- Manufacture of paper
- The solubility of KHCO₃ is greater than that of NaHCO₃ and cannot be precipitated by the above method. Therefore, K_2CO_3 could not be manufactured using Solvay process.

• Manufacture of Quicklime (CaO)

- In this process alternate layers of crushed CaCO₃ and fuel (firewood) are fed into the kiln from top. A fire is started at the bottom and gradually spreads upward.
- The high temperature causes CO_2 to be expelled from the kiln leaving CaO. After the kiln is cooled the quicklime is withdrawn from the bottom.

• Disadvantages of this method

- $CaCO_3(s) \stackrel{900 \ ^{\circ}C}{\Longrightarrow} CaO(s) + CO_2(g)$ Dissociation temperature of $CaCO_3(900 \ ^{\circ}C)$ is relatively high, if the fuel (firewood) does not supply this temperature $CaCO_3$ may not fully dissociate.
- If CO₂ is not expelled fully from the kiln, it can combine with CaO again and form CaCO₃ (as the reaction is reversible).
- CaO gets mixed with ash of the burnt fuel.
- Pollution due to the heat released to the environment.
- Air pollution caused by CO₂ released and fine particles emitted.

• Uses of CaO (Quicklime)

- Production of slaked lime and milk of lime
- Manufacture of calcium carbide
- Reducing acidity of the soil
- Manufacture of bleaching powder
- Construction of building
- Absorbing acidic gases

• Manufacture of bleaching powder

- Heating limestone to obtain quicklime (CaO)
- Sprinkling water on CaO to obtain slaked lime $[Ca(OH)_2(s)]$ and allow to cool
- Passing $Cl_2(g)$ over wet solid $Ca(OH)_2$ at room temperature for about 12-15 hours in rotating kilns with intermittent raking
- Counter current principle is used for higher efficiency of the reaction.

$$CaCO_3(s) \implies CaO(s) + CO_2(g)$$

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

 $3Ca(OH)_2(s) + 2Cl_2(g) \longrightarrow Ca(OCl)_2 \cdot Ca(OH)_2 \cdot CaCl_2 \cdot 2H_2O(s)$

• Uses of bleaching powder

- Bleaching agent
- Disinfectant (especially for water)

- Manufacture of calcium carbide (CaC₂)
 - Quicklime (CaO) and coke (C) are heated in an electric arc at a temperature of about 2000 °C.

 $CaO(s) + 3C(s) \longrightarrow CaC_2(s) + CO(g)$

 $2CaO(s) + 5C(s) \longrightarrow 2CaC_2(s) + CO_2(g)$

- CaC_2 reacts with H_2O and produces C_2H_2 . $CaC_2(s) + H_2O(l) \longrightarrow Ca(OH)_2(s) + C_2H_2(g)$
- Uses of CaC₂
 - In the production of oxyacetylene flame
 - Used to induce flowering
 - Used to induce ripening of fruits

Suggested learning and teaching activities :

- Discuss the difference between a laboratory preparation and industrial manufacture of a chemical substance.
- Discuss the requirements to start and carry out a chemical industry successfully.
- Recall the characteristics of a natural resource that can be used as a raw material for an industry.
- Recall the s block elements in the periodic table.
- Tabulate the occurrence of the *s* block elements in nature.
- Outline steps of the process in the extraction of sodium and physicochemical principles applied.
- Outline steps of the process and physicochemical principles applied in the production of salt, NaOH, soap, sodium carbonate, quicklime, bleaching powder and calcium carbide.
- Discuss the uses of by-products of each industry.

Competency 15.0	: Investigates the occurrence, industrial extraction/
	production and uses of some elements and compounds.
Competency level 15.2	: Investigates industrial extraction / production and uses of
	<i>p</i> -block elements and their compounds.

Periods

Learning outcomes

• Describes the production and identifies the physicochemical principles underlying in the production of ammonia, urea, nitric acid, phosphate fertilizers and sulphuric acid and their uses.

Guidance for teacher elaboration

Production of ammonia (Haber process)

• Nitrogen and hydrogen gases are used as raw materials.

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• Nitrogen is obtained by the fractional distillation of liquid air.

• Hydrogen is obtained from naptha or natural gas as follows. $C_{6}H_{14}(g) + 6H_{2}O(g) \rightarrow 6CO(g) + 13H_{2}(g)$ in naptha $CH_{4}(g) + H_{2}O(g) \rightarrow CO(g) + 3H_{2}(g)$ in natural gas or partial oxidation with oxygen: $C_{6}H_{14}(g) + 3O_{2}(g) \rightarrow 6CO(g) + 7H_{2}(g)$ in naptha $2CH_{4}(g) + O_{2}(g) \rightarrow 2CO(g) + 4H_{2}(g)$ in natural gas

• Nitrogen and hydrogen form an equilibrium mixture containing ammonia.

 $N_{2}(g) + 3H_{2}(g) = 2NH_{3}(g)$ $\Delta H = -92 \text{ kJ mol}^{-1}$

- Le Chatelier's principle suggests that increase in pressure and decrease in temperature will increase the proportion of ammonia at equilibrium.
- High pressure obviously gives a high yield of ammonia, but the higher the pressure greater the cost and maintenance of equipment. The favoured pressure nowadays is 250 atm.
- The temperature must be low to give a higher yield of ammonia. But at low temperature the rate of reaction is so low that it makes the process uneconomical. In practice, the optimum temperature is usually about 450 °C. As the reaction is exothermic the system must be cooled.
- In addition to pressure and temperature, the catalyst is a vitally important variable. Here iron is used as a catalyst and small amounts of potassium oxide and aluminium oxide are used as promoters.
- Low concentrations of NH_3 is favourable for the forward reaction. So NH_3 is cooled under pressure and the liquid ammonia is removed.



Process of production of ammonia

• Uses of ammonia

- Production of nitric acid, fertilizers and nylon
- Petroleum industry utilizes ammonia in neutralizing the acid constituents of crude oil.
- Used in water and waste water treatment, such as pH control, in solution form to regenerate weak anion exchange resins.
- Used in stack emission control systems to neutralize sulphur oxides from combustion of sulphur-containing fuels.
- Used as a refrigerant in industrial refrigeration systems found in the food, beverage, petrochemical and cold storage industries.
- Used in the rubber industry for the stabilization of natural and synthetic latex to prevent premature coagulation.
- Production of urea
 - Ammonia and carbon dioxide are used as raw materials.
 - Production of urea is a two step process.



(i) $2NH_3(g) + CO_2(g)$ $NH_2COONH_4(s)$

(ii) $NH_2COONH_4(s)$ $CO(NH_2)_2(aq) + H_2O(l)$

- Reaction of the step 1 is fast and exothermic and essentially goes to completion under reaction conditions used industrially. Unreacted NH₃ and CO₂ are fed into the first step.
- Reaction of step 2 is slower and endothermic and does not go to completion. The conversion is in the order of 50-80%.
- Uses of urea
 - Urea is a popular solid nitrogen fertilizer because of its high nitrogen content (46%).
 - Urea is used in the manufacture of urea-formaldehyde polymer.

• Manufacture of nitric acid (Ostwald process)

• Ammonia, air and water are used as raw materials.



- The oxidation of ammonia by air to give nitric oxide is an exothermic reaction. The temperature is adjusted to and maintained at about 900 °C by controlling the flow rate of the gases.
- The process is operated under increased pressure because this packs more reactants into the same capacity plant and increases the rate slightly by increasing the number of molecular collisions per second at the catalyst surface.
- An excess air is used to ensure complete oxidation of NH₃.
- Cold air is added to the mixture as it leaves the catalyst because the next stage is an exothermic equilibrium and is therefore favoured by low temperature.
- Extensive cooling of the gases is necessary before nitrogen dioxide is absorbed in water in the presence of air to give nitric acid.

- Thus the actual conditions used leading to about 96% conversion are
 - Pressure: 1 9 atm
 - Temperature : 850 -1225 °C
 - Catalyst : platinum containing 10% rhodium
- Uses of nitric acid
 - Used in the synthesis of ammonium nitrate for use as a fertilizer and in explosives.
 - Used to prepare nitrates which are of great importance in industry.
 - NaNO₃ is used as a preservative for meat.
 - KNO₃ is used in fertilizers and for making gun powder.
 - AgNO₃ is used to prepare photographic film and paper.
 - For the preparation of aquaregia.
 - Used to clean soldering surfaces

Production of phosphate fertilizers

- Phosphorus is an essential nutrient for all living organisms.
- An important phosphorus containing fertilizer for plants is superphosphate which is a mixture of calcium dihydrogenphosphate $Ca(H_2PO_4)_2$ and hydrated calcium sulphate (gypsum) $CaSO_4 \cdot 2H_2O$.
- Eppawela apatite $[3Ca_3(PO_4)_2.CaX_2 \text{ or } Ca_5(PO_4)_3X \text{ where } X = F/Cl/OH]$ is a good raw material for the production of phosphate fertilzers.
- Apatite is insoluble and made soluble for short term crops by complete and partial acidulation.
- Sulphuric acid, nitric acid, hydrochloric acid and phosphoric acid can be used for acidulation.

$$3Ca_{3}(PO_{4})_{2} \cdot CaX_{2}(s) + 7H_{2}SO_{4}(aq) = 3Ca(H_{2}PO_{4})_{2}(s) + 7CaSO_{4}(s) + 2HX(aq) ---(1)$$

 $3Ca_{3}(PO_{4})_{2} \cdot CaX_{2}(s) + 14HCl(aq)$ $3Ca(H_{2}PO_{4})_{2}(s) + 7CaCl_{2}(s) + 2HX(aq) -----(2)$

- Apatite is finely ground and mixed with acid and left for 4-6 weeks. Then the product single superphosphate (SSP) is obtained.
- Addition of ammonium sulphate to products of reaction (2) produces a non hygroscopic fertilizer.

 $CaCl_{2}(s) + (NH_{4})_{2}SO_{4}(aq) \rightarrow CaSO_{4}(s) + 2NH_{4}Cl(aq)$

Manufacture of sulphuric acid (Contact process)

• Sulphur or sulphur containing minerals, air and water are used as raw materials. Sulphur dioxide produced during the extraction of metals such as lead and zinc from their sulphide ores can also be used.



- The reaction between sulphur dioxide and oxygen is reversible. Sulphur trioxide continuously breaks down again to sulphur dioxide and oxygen. So the mixture is passed over several beds of catalyst to let the gases react again.
- The sulphur trioxide is removed between the last two beds of catalyst in order to increase the yield.
- As the reaction of formation of sulphur trioxide is exothermic and three moles of reactants form two moles of products, Le Chatelier's principle predicts that the maximum yield of SO₂ at equilibrium will be obtained at high pressure and at low temperature.
- In practice, a compromise temperature of 450 °C is chosen. This is the lowest that can be used without reducing the reaction rate to an unacceptable level. There are other reasons for keeping the temperature as low as possible. Fuel cost and corrosion of reaction chambers increase rapidly with rising temperature.
- At $450 \,^{\circ}$ C conversion to SO₃ is 97% and this high conversion even at atmospheric pressure, makes it unnecessary to carry out the process at increased pressure.
- As the reaction proceeds, the heat evolved in the exothermic reaction moves the system to higher temperature. At this higher temperature the percentage conversion to SO₃ is much reduced. Thus, it is necessary to cool gases between successive beds of catalyst. This is done using cold water pipes. The water is converted to steam and used to generate power(electricity).
- The sulphur trioxide is dissolved in concentrated acid rather than water. If it is dissolved in water, a thick mist of acid forms. This would be a pollution hazard.
- Oleum is mixed carefully with water to produce concentrated sulphuric acid.

• Uses of sulphuric acid

- Manufacture of phosphate fertilizers
- Manufacture of ammonium sulphate fertilizers
- Manufacture of synthetic fibres rayon and plastics
- In the production of detergents mostly alkyl and aryl sulphonates
- In the production of dyes, explosives and drugs
- In the production of battery acid
- Drying gases (Cl_2)

Suggested learning teaching activities:

- Outline steps of the process and physicochemical principles applied in the production of ammonia, urea, nitric acid, phosphate fertilizers and sulphuric acid.
- Recall the reactions of concentrated HNO₃ as an oxidizing agent.
- Recall the reactions of concentrated H_2SO_4 as an oxidizing agent and dehydrating agent.

Competency 15.0	:	Investigates the occurrence, industrial extraction/
		production and uses of some elements and compounds.
Competency level 15.3	:	Investigates occurrence, extraction and uses of <i>d</i> -block
		elements and their compounds.
Periods	:	02

Learning outcomes

• Describes the extraction of iron by blast furnace method.

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- Writes equations for the reactions that occur in the blast furance.
- Diagrammatically illustrates the extraction of iron by blast furnance method.

Guidance for teacher elaboration

• Occurrence of d block elements

Ti	Ilmenite	FeTiO ₃
	Rutile	TiO ₂
Fe	Hematite	Fe_2O_3
	Magnetite	Fe ₃ O ₄
	Iron pyrites	FeS ₂
	Siderite	FeCO ₃
Cu	Chalcopyrite	CuFeS ₂

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• Extraction of iron (Blast furnace method)

• Iron ore, coke (as a reducing agent) and limestone (as a slag forming substance) are used as raw materials. The amount of CaCO₃ used is dependent on the amount of silicate materials in the ore.



Iron ore, coke, and limestone

• Hot air is blown in at the bottom. Coke burns producing heat and CO.

 $C(s) + O_2(g) \rightarrow CO_2(g)$ $CO_2(g) + C(s) \rightarrow 2CO(g)$

- The temperature at the point where air enters is at about 2000 K and at the top is about 700 K.
- The iron(III) oxide is reduced to iron mainly by CO and some by carbon.
- The molten iron containing 3-4% dissolved carbon forms pig iron. Melting point of the pure iron is 1535 °C but the melting point of pig iron is at about 1015 °C, due to the presence of impurities.
- CaCO₃ decomposes to CaO and CO₂ gas. CaO reacts with silicate impurities and forms slag (CaSiO₃). Slag is also molten and floats on molten iron into the bottom. Slag protects iron from oxidizing by the air which is blown in the bottom.
- Pig iron contains 3-4 % of carbon and possibly other impurities such as Si, P, S and Mn.
- Following reactions are taken place in the temperature range of 700 K 2000 K. At low temperature (Below 1000 °C)

 $3Fe_2O_3(s) + CO(g) \rightarrow 2Fe_3O_4(s) + CO_2(g)$ $Fe_3O_4(s) + CO(g) \rightarrow 3FeO(s) + CO_2(g)$ $FeO(s) + CO(g) \rightarrow Fe(1) + CO_2(g)$ $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

At high temperature (Above 1000 °C)

 $\begin{array}{l} 2 FeO(s) + C(s) \rightarrow 2 Fe(l) + CO_2(g) \\ CO_2(g) + C(s) \rightarrow 2 CO(g) \\ CaO(s) + SiO_2(s) \rightarrow CaSiO_3(slag) \\ CaO(s) + Al_2O_3(s) \rightarrow Ca(AlO_2)_2(slag) \end{array}$

Suggested learning teaching activities :

- Discuss the occurrence of the *d* block elements.
- Describe steps of the extraction of iron highlight the physicochemical principles applied.
- Discuss the constituent elements and uses of steel, stainless steel, cast iron and wrought iron.

Competency 15.0	:	Investigates the occurrence, industrial extraction/
		production and uses of some elements and compounds.
Competency level 15.4	:	Uses polymeric substances in day to day life effectively.
Periods	:	10
Learning outcomes		

- Introduces polymers.
- Classifies polymers as natural and synthetic.
- Classifies polymers according to the method of synthesis and thermal properties.
- Identifies the structures, properties and uses of polymers.
- Describes structure, properties and uses of natural rubber.
- Describes vulcanisation of rubber.
- Explains the process of rubber compounding.

Guidance for teacher elaboration

- Polymers are large molecules formed by the union of a large number of repeating units.
 eg. n(C₂H₄) → Polymer
- Polymers can be classified as natural and synthetic.
 - Natural polymers are naturally synthesised in living/bio systems. *eg*. Natural rubber, proteins enzymes.
 - Synthetic polymers are synthesised by man (man made polymers). *eg.* Polythene, polyvinyl chloride, polyesters, Teflon, Bakelite, nylon, urea-formaldehyde.
- Polymers can be classified in accordance with the method of synthesis.
 - Addition polymers
 - Condensation polymers
- Polymers can be classified based on their thermal properties.
 - Thermoplastic polymers :
 - Can be softened by heating, allow to cool and harden and then re-softened many times. The forces of attraction between chains are weak.
 - eg. Polythene, PVC, Polystyrene
 - Thermosetting polymers:

During the first stage of manufacture, once moulded they set and then cannot be re-softened by heating. Polymer chains are cross linked to form a three dimensional structure.

eg. Bakelite, Urea-formaldehyde

Addition Polymers

Unsaturated monomers undergo additional polymerization to form addition polymers.





• Polythene is a tasteless, odourless, light, non-poisonous, relatively cheap, thermoplastic polymer. It is used to produce packing materials, trash bags, seat covers, bottles, various containers, toys etc.

Polyvinyl chloride (PVC)



• Although PVC is a thermoplastic, due to the presence of chlorine, PVC does not catch fire easily. Its attractive forces among the chains are stronger than those in polyethylene and therefore is more harder. A special feature of PVC is that it can be processed with stablisers and fillers making it versatile. PVC is used to make water pipes, gutters, wire insulations, films, floor covers, seat covers, raicoat covers, umbrella materials, etc.

Polystyrene

• The monomer is styrene.



• Polystyrene is a transparent substance and a thermoplastic. Made into foam and solidified, it can be used as a insulation and packing material popularly known as 'Rigifoam'.

Teflon



 Although it is a thermoplastic due to the presence of halogen it can withstand high temperatures. Therefore, it is used in making fire proof clothing. In addition Teflon is not wettable and therefore, it is used as coatings in non-stick cooking vessels. Being chemically inert, teflon can resist almost all corrosive chemicals, so it is used in valves, seals, gaskets etc. in plants used in chemical industry.



- Rubber is used to make tyres, tubes, mattresses and gloves used in the medical field.
- Natural rubber vulcanization
 - Presence of cis-polyisoprene chains is the reason for elasticity of rubber. In order to change the elastic nature of rubber as required and to make it stronger, it is heated with 1% 3% sulphur by weight. This is called vulcanisation. Vulcanisation makes cross links among polyisoprene chains through sulphur bridges and more resilient and tougher. By heating with 25% 35% sulphur, ebonite is obtained. The vulcanized rubber is not sticky and has superior mechanical properties such as higher elesticity.

• Rubber compounding

Natural rubber or other rubber itself may not be a useful material for a particular purpose. But, based on the material mixed, rubber compounding makes it a useful material with desired properties. Material used in rubber compounding can be classified by the function they serve. Main functional cases are given below.

- Elastomers
- Vulcanizing or cross linking agents
- Accelerators
- Activators / retarders
- Process aids
- Softeners and plasticizers
- Reinforces / Fillers
- Age resistors
- For example, cover of a conveyor belt is made of the following compounds. Natural rubber (Elastomer) Carbon black (Filler) ZnO (Accelerator)
 Steerie acid

Stearic acid Rubber process oil Resin N-Cyclohexylbenzothiozole-2-sulfonamide (CBS) Sulphur (Vulcanizing agent)

• Condensation polymers

The polymers formed by the joining of monomers with elimination of small molecules such as H_2O , NH_3 or HCl are called condensation polymers.

- Polyamides
- Polymers formed by joining of monomers by CONH group are known as polyamides. Nylons are polyamides. One of the commonest is nylon 6,6 which is made by condensation polymerisation between 1, 6 - diaminohexane and hexanedioic acid. The reaction is more effective when acid chloride is used instead of the dicarboxylic acid.

Nylon-6,6
• Nylon is a thermoplastic polymer and it is used to produce fibres which have structural similarities to silk and wool. Despite its structural similarity to wool, nylon lacks the softness and the moisture - absorbing properties of the natural fibre. It is, however, harder wearing and has good 'wash and wear' characteristics. Nylon is mainly used to make soft and light clothing. Other uses include tufted carpets, tyre cords, machine gear wheels and bearings, fishing nets and non wetable tent covers. The elasticity and strength of nylon make it ideal for making stockings and tights.

• Polyesters

- Polymers with monomers linked by the -COO- (ester) groups are commonly called polyesters.
- Terelene

Terelene formed by the condensation polymerisation between ethane -1,2-diol (ethylene glycol) and benzene - 1,4 - dicarboxylic acid (Terephthalic acid) is an example for a polyester.



Polymerisation



- Terelene is a thermoplastic. It is used as a substitute for natural fibres such as cotton and wool. Being strong, the fibres are used in the manufacture of fibre glass. It is also used in the production of textiles, photographic films and audio tapes.
- Bakelite

In the presence conc. H_2SO_4 phenol and formaldehyde (methanal) react to form a thermosetting polymer know as Bakelite.



• Bakelite is a cross linked three dimensional polymer. These cross links lead to a very rigid structure because the various groups are not free to twist round and move their positions. Bakelite is used to make heat resistant parts of electric utensils.

• Urea-formaldehyde

In the presence conc. H_2SO_4 urea and formal dehyde react to form a thermosetting polymer know as urea-formal dehyde.



• Urea-formaldehyde is a cross linked three dimensional polymer. Ther are used as thermosetting plastic or adhesives.

Suggested learning teaching process:

- Inquire the prior knowledge of students about polymers.
- Classify polymers as natural/artificial, addition/condensation and thermoplastic/thermoset.
- Discuss the monomer, repeating unit, properties and uses of commonly used polymers.
- Introduce the process of rubber vulcanization and its uses.
- Point out the importance of rubber compounding.

Competency 15.0	:	Investigates the occurrence industrial extraction /
		production and uses of some elements and compounds.
Competency level 15.5	:	Investigates some chemical industries based on plant
		materials.
Periods	:	10

Learning outcomes :

- Describes plants as a source of carbon compounds.
- Describes production of paper as an example for the use of cellulose.
- Describes basic steps of the paper industry.
- Describes essential oils as complex mixtures of volatile constituents of plants.
- Explains the principles of steam distillation used to extract essential oils.
- Recognizes the use of plants as medicines.
- Describes the process of solvent extraction used to extract medicinal compounds.
- Describes production of ethanol as an example of the use of starch and sugar.
- Explains the basic principles of adsorption and partition chromatography.
- Explains the uses of gas chromatography in essential oils.
- Separates a mixture of leaf pigments using paper chromatography.

Guidance for teacher elaboration :

Paper industry

- Woody materials are the main raw materials for the paper industry.
- Paper is made from cellulose which is a major component of the plant cell wall.
- Cellulose is a linear polymer of glucose. The molecular weight of cellulose molecules are in range 250,000-1,000,000.
- Each cellulose molecule has many hundreds of OH groups.
- Because of the possibility of H bonding between OH groups, cellulose molecules stack closely alongside each other to form cellulose fibres.
- Paper is an aggregation of these fibres spread out as a thin layer.
- The plant cell wall also contains lignin which is a complex phenolic material with molecular weight in the range 1,000 10,000. Lignin plays an important role providing strength to the cell wall.
- In producing cellulose from woody materials lignin is removed by heating the material with aqueous NaOH.
- The dark coloured liquid obtained from this process is known as 'black liquor'. This is the major waste product in the paper industry.
- The paper pulp obtained after removal of lignin is bleached by bleaching agents.
- CaO or china clay is added to the pulp as the filler. Pigments and other chemicals that make the paper durable are also added at this stage.

- The pulp is compressed by rollers to remove water. The thinning of the paper to the required thickness is also done at this stage.
- Following the removal of water, the paper is dried.

Essential oils industry

- Essential oils are the volatile constituents of certain plants that confer a characteristic odour to the plant containing them.
- Essential oils are complex mixtures of compounds and may contain amongst other types of compounds hydrocarbons, alcohols, ketones, aldehydes, ethers and esters. Most components of essential oils have a limited solubility in water.
- Some essential oils containing plant parts are used as spices.
 - *e.g.* cinnamon (Bark of *cinnamon zeylanicum*), tumeric (Rizhome of *curcuma longa*) and pepper (fruit of *piper nigrum*).
- Essential oils isolated from plants are used mainly in the food industry, pharmaceutical industry and perfumery industry.
 - *e.g.* Food Nutmeg oil (from the kernel of ripped seeds of *myristica fragrans*) Perfumery – Vetiver oil (from roots of *vetiveria zizanioides*) Pharmaceutical – Mint oil (leaves of Mentha species)
- Most essential oils are extracted from plant by steam distillation because it enables to distill out below 100 °C. (Discuss the physical principles involved. That is; Total vapour pressure = vapour pressure of the oil + vapour pressure of water)

Manufacture of Soap (Refer 15.1)

Pharmaceutical industry

- Plants were the main source of medicinal compounds before the development of synthetic drugs (Last hundred years).
- In traditional medical systems such as 'Ayurveda' extracts of plants are used as medicine.
- Modern pharmaceutical industry extracts pharmacologically active compounds from plants and markets them as drugs. Some examples are given below.

Compound	Plant source	Usage
Vincristine	Catharanthus roseus	Anti-cancer
Morphine	Papaver somniferum	Narcotic Analgesic
Digitoxin	Digitalis lanata	Cardio tonic in congestive heart failures
Artemisinin	Artemisia annua	Antimalarial

- These active compounds which are generally solids are extracted from plants by solvent extraction.
- Different compounds will dissolve to different extents in different solvents.
- If the compounds to be extracted are stable, the extraction process can be accelerated by heating.
- The solvent extract will contain a mixture of compounds from which the active compound has to be separated using various techniques, one of which is chromatography.

Chromatography

- There are many different types of chromatography but in each case, there are two phases a mobile phase that moves and a stationary phase that stays still.
- Different compounds that are dissolved in the mobile phase travel with it at different speeds over the stationary phase and thereby get separated from each other.
- When the stationary phase is a solid such as silica, and the mobile phase is an organic solvent such as hexane or ethanol, then it is the forces of interaction amongst the molecules of the dissolved compounds and the solvent molecules and the surface of the silica particles that control the speed of movements of the dissolved compound. Because the surface of the silica particles is involved, this type of chromatography is called adsorption chromatography.
- When the stationary phase is a 'liquid' such as the water molecules trapped on a sheet of paper, and the mobile phase is an organic solvent which is not miscible with water (such as n-butanol), then the partitioning of the dissolved compound between the organic solvent (mobile phase) and water (stationary phase) will control the speed of movement of compound. This type of chromatography is called 'partition chromatography'.
- Chromatography can be used on a small scale to analyze mixtures as well as on a larger scale to isolate/purify compounds.
- Mixtures of volatile compounds such as essential oils are analyzed by gas chromatography. Here, the mobile phase is a gas $(e.g. N_2)$ and the stationary phase is a solid or a liquid contained in a narrow tube. In gas chromatography the speed of movement of compounds along the tube is dependent on their boiling point as well as their interactions with the stationary phase.

Ethanol Industry

- Ethanol is used widely as a solvent for perfumes and flavourings. It is used as a medium for chemical reactions. It is also being increasingly used as an environmental friendly renewable fuel.
- Ethanol is produced industrially by hydration of ethylene or by fermentation of sugar or starch by yeast.
- Ethanol found in alcoholic beverages arises from fermentation of different plant sources.
 e.g. Grapes (wine), barley (beer)
 Industrial alcohol is produced by fermentation of molasses and grains.

- The highest concentration of ethanol in fermented product is around 12%, as the yeast cannot survive in a higher concentration of alcohol.
- Distillation of the aqueous liquid obtained by fermentation gives products containing higher levels of ethanol.
 - *e.g.* Brandy (around 40%) from the distillation of wine
 - Arrack (around 40%) from the distillation of coconut toddy
- The higher concentration of ethanol that can be obtained from the fractional distillation of aqueous ethanol is 95.6% (rectified spirit).

Proposed learning-teaching activities:

- Direct the students to collect information about the plant materials which provide essential oils and their constituents.
- Discuss the principles of steam distillation and how it is used to extract essential oils.
- Discuss the principles of solvent extraction and how it is used to extract medicinal compounds.
- Using a suitable set up of apparatus present how steam distillation is used to extract cinnamon oil.
- Recall the knowledge of partition coefficient that students have studied.
- Discuss applications of partition coefficient in chromatography.
- Explain the term stationary phase and mobile phase.
- Do the simple chromatographic technique given below.
 - Grind some leaves with water and ethanol.
 - Filter the solution and obtain the extract.
 - Using blotting paper as chromatographic paper, try to separate the different pigments which are present in the extract.
- Discuss use of gas chromatography in essential oils.

Competency 15.0	:	Investigates the occurrence, industrial extraction/
		production and uses of some elements and compounds.
Competency level 15.6	:	Investigates some chemical industries based on mineral
		resources.
Periods	:	05

Learning outcomes

- Recalls the raw materials essential for the production of Portland cement.
- Describes the major chemical changes taking place during the manufacturing process of Portland cement.
- Describes the hardening process of Portland cement.
- Describes the extraction process of Ti and TiO₂ from rutile or ilmenite.
- Describes the process of production/cracking of petroleum.

Guidance for teacher elaboration :

Portland Cement

- A cement is an adhesive substance capable of uniting fragments into a solid mass. The most common type of cement used in the building industry is Portland cement.
- Three types of raw materials are used for the production of Portland cement.
 - a. Lime stone CaCO₃ (calcareous component)

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- b. Clay Al₂O₃·2SiO₂·2H₂O (argillaceous component)
- c. Gypsum CaSO₄·2H₂O (component controls the setting properties of cement)
- The calcareous component contributes CaO to the composition of cement and this is added in the form of limestone which mainly contains $CaCO_3$. Marble or coral may also be used in place of limestone. The argillaceous component contributes SiO_2 , Al_2O_3 and Fe_2O_3 to the composition of cement. Examples include clay, shale and slate.
- Two distinct processes the wet process and the dry process are used in the manufacture of Portland cement.
- The dry process, which is used in Sri Lanka, uses dry raw materials. Limestone and clay are crushed, dried and mixed (in the proportion of 1 : 5) and fed into a rotary kiln. The kiln is a refractory lined steel cylinder which rotates about an axis inclined 10 degrees from the horizontal. The kiln feed is roasted in the kiln at temperatures ranging from 600 °C 1500 °C. When cooked at these temperatures, the two ingredients fuse together chemically without melting. This process is called sintering and it produces small sized lumps called clinkers. Natural gas, furnace oil or coal is used to heat the mixture.
- The rotary kiln is composed of four parts. They are;
 - a. Preheating zone
 - b. Calcining zone
 - c. Clinkering zone
 - d. Cooling zone
- The loss of free water takes place in the preheating zone. Decomposition of $CaCO_3$, clay and oxidation of organic matter occur up to 1000 °C in the calcining zone. Free oxides react to form calcium silicates and calcium aluminates in the clinkering zone at 1300-1500 °C.



- The clinker obtained from the lower end of the kiln is cooled and ground with the correct percentage of gypsum (4% 5%) in a ball mill to produce cement.
- The binding property and hardening of cement is due to the formation of hydrated products when cement is treated with water.

e.g. $2Ca_3SiO_5 + 6H_2O \implies Ca_3Si_2O_7 \cdot 3H_2O + 3Ca(OH)_2$ ($Ca_3SiO_5 = 3CaO \cdot SiO_2$)

• Gypsum (CaSO₄·2H₂O) controls the setting properties of cement. In its absence cement hardens too quickly.

Extraction of Titanium and TiO, from rutite/ilmenite

- Titanium is found in abundance in the southern coast and Pulmuddai of Sri Lanka as rutile (TiO₂) and ilmenite (FeO·TiO₂).
- Because of the high melting point and the high stability of TiO₂, titanium metal cannot be extracted easily.

Extraction of Titanium

• The mineral is heated with carbon and chlorine to 900 °C. Reaction with rutile;

 $TiO_2(s) + 2C(s) + 2Cl_2(g) \longrightarrow TiCl_4(l) + 2CO(g)$

Reaction with ilmenite;

 $2(\text{FeO} \cdot \text{TiO}_2)(s) + 6C(s) + 7Cl_2(g) \longrightarrow 2TiCl_4(l) + 2FeCl_3(s) + 6CO(g)$

- FeCl₃ and other waste products are removed and pure TiCl₄ liquid is separated.
- By reducuing TiCl₄ liquid with a powerful reducing metal such as sodium or magnesium under a cover of argon gas, titanium metal is extracted.
- Excess magnesium metal is reacted with dilute HCl acid. With the removal of all the MgCl₂, formed titanium metal separates out as a block.

 $TiCl_{4}(l) + 2Mg(s)^{1000 - 1500}$ $Ti(s) + 2MgCl_{2}(s)$

Uses of Titanium

• Due to lightness, high tensile strength, high melting point and resistance to corrosion titanium is used to make parts of aircrafts, space crafts and aircrafts carrying nuclear weapons.

Extraction of TiO₂

- Though TiO₂ is white in colour it appears coloured mineral due to the presence of impurities.
- To obtain TiO₂, the following method can be used.
 - Rutile is heated with coke and chlorine gas to 900 °C.
 - $TiO_2(s) + 2C(s) + 2Cl_2(g) \longrightarrow TiCl_4(l) + 2CO(g)$
 - Liquid TiCl₄ obtained after the removal of impurities is heated to $1200 \,^{\circ}$ C in air. TiCl₄(l) + O₂(g) \longrightarrow TiO₂(s) + 2Cl₂(g)

Uses of TiO,

• Because of the stability of TiO_2 it is used as a coating for medicinal tablets. It is also used as white pigment in paint industry and also as a photocatalyst.

Crude oil and cracking of petroleum

- The mineral oil extracted from oil wells is a complex mixture of various hydrocarbons and cyclic organic compounds with N, P and S. This is called crude oil and its hydrocarbons can be divided into three major categories.
 - a. Open chain alkanes
 - b. Alicyclic hydrocarbons
 - c. Aromatic hydrocarbons
- Fractional distillation of crude oil results in a series of fractions, each consisting of a mixture of hydrocarbons boiling within a given temperature range. The substances within a fraction may be separated by further distillation.
- Hydrocarbons with large molecules cannot be used directly in automobiles. One of the most important industrial processes at a refinery is cracking which breaks down large molecules into smaller ones. When the original molecule is an alkane, the product molecules are an alkane and an alkene.

e.g.
$$C_8 H_{18}(l) \longrightarrow C_6 H_{14}(l) + C_2 H_4(g)$$

or $C_8 H_{18}(l) \longrightarrow C_5 H_{12}(g) + C_3 H_6(g)$

- There are three main cracking processes.
 - Thermal cracking: The alkane is heated to a high temperature above its boiling point for about half a second sometimes in the presence of superheated steam.

Catalytic cracking : The hydrocarbon is heated to a relatively low temperature in the presence of a catalyst such as silica or alumina.

Hydro cracking : Hydrocarbon is heated in hydrogen gas kept under high pressure.

Suggested learning teaching activities :

- Give the students to mark the regions where the raw materials for the production of cement occur in abundance in a map of Sri Lanka.
- Mark in a map of Sri Lanka, the areas where minerals ilmenite and rutile are found in abundance.
- Take the children on educational tours to cement factories at Puttlam and Galle, petroleum refinery at Sapugaskanda and to see mineral sand sifting at Pulmmddai.

Competency	16.0	:	Applies the knowledge of chemistry to understand the earth's environment.
Competency leve	1 16.1	:	Investigates the composition of the ecosphere and its relation to maintain life on earth.
Number of period	s	:	06

Learning outcomes

• Identifies the composition of the atmosphere.

:

- Identifies the composition of the hydrosphere.
- Expresses the composition of the earth's crust.
- Describes carbon cycle, oxygen cycle, nitrogen cycle and hydrological cycle.
- Recognizes the importance of optimum compositions of atmosphere, hydrosphere and earth's surface on environmental equilibrium.

Guidance for teacher elaboration :

Atmospheric Composition

Table 16.1.1 Composition of major components in clean dry air at the sea level

Component	% by volume
N ₂	78.08
O ₂	20.99
Ar	0.94
CO ₂	0.03

- Also present are smaller amounts of Ne, He, CH₄, Kr, H₂ and in addition variable trace quantities of other pollutants such as NH₃, SO₂, CO, NO₂, O₃ and H₂S. Water vapour present to about 4% in the atmosphere may not be uniformly distributed (may vary from time to time) but concentrated close to the oceans and large water bodies.
- The amount of N_2 in the atmosphere is high because of its inertness due to the presence of strong $N \equiv N$ bond. Reactivity of O_2 is greater than N_2 and the amount of O_2 is smaller than N_2 in the atmosphere. Presence of O_2 makes the atmosphere to be active and sustains life on theearth.
- CO₂ and H₂O are the main ingredients for photosynthesis.

Variation of atmospheric temperature, molar mass and pressure according to the altitude

• With the altitude mass is gradually decreasing and accordingly pressure is also coming down. But the temperature undergoes several inversions. Based on these thermal inversions atmosphere is divided into different regions. The region closer to the ground is the troposphere and the region above the troposphere is stratosphere. Ozone layer is located in the stratosphere.

Composition of hydrosphere

Water covers 70% of the earth's surface. Very little of the world's water is fresh water (2.6%).
 Most of the water (97.4%) is in the oceans. Most of the fresh water (76%) is frozen in glaciers and in the polar ice caps. Only a tiny fraction (0.01%) is available for human use.



Figure 16.1.1 : Composition of water on earth and distribution of freshwater

Element	% Composition	% Composition			
	of earth's crust	of whole earth			
Oxygen (O)	46.71	29.3			
Silicon (Si)	27.60	14.9			
Aluminium(Al)	8.07	2.4			
Iron (Fe)	5.05	36.9			
Calcium (Ca)	3.65	3.0			
Sodium (Na)	2.75	0.6			
Potassium (K)	2.58	-			
Magnesium (Mg)	2.08	7.4			
Others	1.14	1.0			

Tabl	e 16.	1.2 (Compo	osition	of	earth	's su	rface	and	who	le e	art	h
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Major cycles

• Knowledge of chemical cycles is very important to understand the fate of the chemicals, their abundance in different spheres, their possible environmental impacts and controlling the pollution problems.

• Carbon cycle



Figure 16.1.2 Carbon cycle

- The only way that carbon gets into ecosystem is through photosynthesis.
- Animal gain carbon through their food.
- Decomposers get their carbon by digesting dead organisms.
- All living organisms return carbon to the air in the form of carbon dioxide through respiration.
- If plants or animals die in situations where there are no decomposers (E.g. : deep oceans) the carbon in them can get turned into fossil fuels over millions of years.
- The carbon in fossil fuels is released during the combustion.
- Microorganisms are important in the carbon cycle because they can quickly get the carbon in dead material back into the atmosphere.

Oxygen cycle



Figure 16.1.3 Oxygen cycle

- Atmospheric oxygen is removed through combustion (chemical/biological) and respiration and replenished through photosynthesis.
- Most oxygen is stored in the oxide minerals of the earth crust and mantle but is bound to rocks and unavailable for use.
- Most available oxygen comes from photosynthesis and some is made in the atmosphere when sunlight breaks down (photolysis) water.



Fig 16.1.4 Nitrogen cycle

- Atmospheric nitrogen is fixed by bacteria. Some live free in the soil (Eg:-*Azotobacter*). Others like *Rhizobium* are found inside root nodules of leguminous plants (hat's peas, beans and cloves). Atmospheric nitrogen is changed into ammonia, nitrites and then nitrates which all plants can absorb and use to make protein.
- Nitrogen in the plant proteins is passed onto animals through food chains.
- When living organisms die their nitrogen is returned to the soil in the form of ammonium compounds by micro organisms. Animals get rid of excess aminoacids via deamination in their liver. The nitrogen gets back into the soil via their urine.
- Ammonium compounds are changed into nitrates by nitrifying bacteria. Firstly *nitrosomonas* changes ammonium compounds into nitrites, then *Nitrobacter* changes the compounds into nitrates.
- Nitrates are converted back into atmospheric nitrogen by denitrifying bacteria like *Pseudomonas* and *Thiobacillus*.

Hydrological cycle



Fig 16.1.5 Hydrological cycle

- Optimum compositions of atmosphere, hydrosphere and earth's surface are important on environmental equilibrium for sustainability of earth. If this equilibrium is disturbed the following problems could occur.
 - Damaging effects on human health
 - Damage on plants and hindrance of their growth
 - Damage on marble buildings and metallic structures
 - Increase in salinity / alkalinity
 - Weathering of rocks
 - Climatic changes (may cause drought / flood)

Suggested learning-teaching activities :

- Ask the students to tabulate the composition of air and to calculate the mole fraction of the each component of air.
- Divide the class into few groups and assign each group of students to collect more information on one of the natural cycle.
- Let group of students to discuss the importance of the cycle assigned to them.
- Ask each group to present their findings to the whole class.

Competency	16.0	:	Applies the knowledge of chemistry to understand the earth's environment.
Competency level 16.2		:	Investigates the changes in atmosphere due to human activities.
Number of periods	i	:	06
Learning outcome	S	:	• Identifies the gases, which change the atmospheric composition.
			• Investigates the ways in which the gases are added to the atmosphere.
			• Explains the effects of these added gases to the environment.
			• Describes the changes of the composition of earth due to acid rain.
			• Describes precautionary measures that can be taken to minimize air pollution.
			• Describes health problems arising due to air pollution.

Guidance for teacher elaboration

- CO(g), H₂S(g), SO₂(g), SO₃(g), NO(g), NO₂(g) and CO₂(g) are the inorganic compounds which change the atmospheric composition. Organic compounds including hydrocarbons, halo hydrocarbons and particles such as dust and carbon also contribute to change the composition of the atmosphere.
- Some CO(g) in atmosphere is formed by the oxidation of methane, which is formed naturally by the anaerobic degradation of organic matter. CO (g) is emitted from all the incomplete combustion processes including the internal combustion engines of motor vehicles.
- SO₂(g) enters the atmosphere from the combustion of sulphur containing fossil fuels, volcanic eruption, biological decay of S containing organic matter, reduction of sulphates and recovery of metals from their sulphides. SO₂(g) reacts with oxygen and forms SO₃(g). NO(g) increases the rate of oxidation of atmospheric SO₂(g) in to SO₃(g).
- NO_x(g) [NO(g) and NO₂(g)] enters the atmosphere from natural processes such as lightening discharges, and from pollutant sources. The combustion of fossil fuels gives most of the NO_x(g). Much of the NO_x(g) entering the atmosphere is from the internal combustion engines.
- Microbial decay of S containing organic matter and reduction of sulphate ion are the most common natural sources of H₂S.

• Hydrocarbons are widely used as fuels and enter the atmosphere directly or as byproducts in the partial combustion of other hydrocarbons. Uncontrolled vehicle exhausts contain alkanes, alkenes and aromatic hydrocarbons. Methane is produced in large quantities from the anaerobic decomposition of organic matter submerged in water.

Greenhouse effect

- The temperature of the earth is fixed by a steady state balance between the energy received from the sun and the energy radiated back by the earth. One mechanism for regulating the earth's temperature is the greenhouse effect.
- The loss of energy from the earth is achieved by means of conduction, convection and radiation. A fraction of the earth's heat is transmitted to clouds by conduction and convection before being lost by radiation.
- Convection carries heat in the form of the enthalpy of vaporization of water. The water vapour releases heat as it condenses.
- The radiation that carries energy away from the earth is of longer wavelength, in the infrared region.
- If all the outgoing radiation were able to escape, the surface of the earth would be at -16 °C (Same temperature as in the moon).
- Most heteroatomic molecules and some homoatomic molecules (O₃) are known as greenhouse gases and these are the ones which contribute to the greenhouse effect.
- Accordingly $CO_2(g)$, water vapour, methane, dinitrogen oxide, ozone, SO_2 and CFCs absorb radiation given out from the earth and some of it re-radiate back to the earth's surface. This re-radiation helps to warm the earth and maintain a climate that will support life. This is called greenhouse effect and these gases are called greenhouse gases.

Understanding the problems due to air pollution

1. Global warming

- When the greenhouse gases exceed their permissible level. Hence, the temperature of the atmosphere increases. This is called "Global Warming".
- $CO_2(g)$ plays the key role in this global warming. Gases such as NO_x and CFCs are the other examples. Though the CFC levels are low they have a longer residence time and they have a high efficiency of absorbing IR radiations. Therefore, their contribution is high.
- The results of global warming include melting of polar ice caps, sinking of low lying countries due to the thermal expansion of sea water, desertification due to loss of soil moisture, drying of fresh water reserviors, changes in biodiversity and weather patterns.
- A significant amount of atmospheric carbon dioxide dissolves in water. Thus, it reduces the contribution of CO₂ to global warming. However, with the increase of temperature dissolution of carbon dioxide is reduced and dissolved carbon dioxide returns to the atmosphere.

- Increasing CO₂ level in the atmosphere increases the photosynthesis. This is a positive effect of global warming.
- As far as Sri Lanka is concerned global warming can have a higher effect because we are an island situated closer to the equator.

2. Acid rain

Acidic gases in the atmosphere dissolves in water to contribute to the acidity. Two important factors are

- (i) Dissolution of acidic gases in water
- (ii) Strength of the resulting acid

In this context even though CO_2 levels are high, their contribution to the acidity is very low (pH 5.1 - 5.8) and it is not considered as acid rain. But the SO_x and NO_x even though they are present in smaller quantities have a higher contribution resulting in a pH of 4 - 5.

• Reactions of atmospheric SO₂(g)

(i)
$$SO_2(g) + H_2O(1) = H_2SO_3(aq)$$

 $H_2SO_3(aq) + H_2O(1)$ $H_3O^+(aq) + HSO_3^-(aq)$

 $HSO_{3}(aq) + H_{2}O(1)$ $H_{3}O^{+}(aq) + SO_{3}^{2}(aq)$

(ii) Oxidants in the atmosphere can oxidize SO_2 to SO_3 .

 $\operatorname{SO}_2(g) \xrightarrow{\operatorname{Oxidant}} \operatorname{SO}_3(g)$

 $O_2(g)$, O(g), OH(g) and peroxides can serve as oxidants. Some salts can catalyse the oxidation. Then $SO_3(g)$ dissolves in H_2O to form H_2SO_4 .

(iii) Both SO_2 and the oxidant (normally O_2) can dissolve in a rain drop. Rain drop facilitates the oxidation process by bringing two chemicals together.

$$2SO_{2}(aq) + 2H_{2}O(l) + O_{2}(aq) \longrightarrow 2H_{2}SO_{4}(aq)$$
$$H_{2}SO_{4}(aq) + 2H_{2}O(l) \longrightarrow 2H_{3}O^{+}(aq) + SO_{4}^{-2}(aq)$$

• Similarly NO_x reacts in the atmosphere.

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

 $4NO_2(aq) + 2H_2O(l) + O_2(aq) \longrightarrow 4HNO_3(aq)$

 $HNO_3(aq) \longrightarrow H^+(aq) + NO_3(aq)$

- Acid rain damages plants and causes the death of fish in the lakes. Acids such as sulphuric
 acid and nitric acid dissolve aluminium from aluminosilicate materials of soil giving free Al³⁺ to
 water. It interferes with the operation of fish gills.
- Acid rain water, draining through soils washes out nutrients and liberates aluminum ions. The roots of the trees may take up the aluminum ions instead of essential nutrients.

eg. Ca^{2+} and Mg^{2+} .

• Limestone, metallic structures, bridges, ships, motor vehicles, etc. are also affected.

Change of the composition of earth's surface due to acid rain

- Dolomite, limestone or marble are soluble in acidic water.
- Under mild acidic conditions;

$$\begin{aligned} &\text{CaCO}_{3}(s) + \text{H}^{+}(aq) \longrightarrow \text{Ca}^{2+}(aq) + \text{HCO}_{3}^{-}(aq) \\ &\text{MgCO}_{3}(s) + \text{H}^{+}(aq) \longrightarrow \text{Mg}^{2+}(aq) + \text{HCO}_{3}^{-}(aq) \\ &\text{CaCO}_{3} \cdot \text{MgCO}_{3}(s) + 2\text{H}^{+}(aq) \longrightarrow \text{Ca}^{2+}(aq) + \text{Mg}^{2+}(aq) + 2\text{HCO}_{3}^{-}(aq) \end{aligned}$$

Here, insoluble substances become soluble.

• Under strong acidic conditions;

$$\begin{array}{rcl} CaCO_{3}(s) &+& 2H^{+}(aq) &\longrightarrow & Ca^{2+}(aq) &+& H_{2}O(l) &+& CO_{2}(g) \\ MgCO_{3}(s) &+& 2H^{+}(aq) &\longrightarrow Mg^{2+}(aq) &+& H_{2}O(l) &+& CO_{2}(g) \\ CaCO_{3} \cdot MgCO_{3}(s) &+& 4H^{+}(aq) &\longrightarrow & Ca^{2+}(aq) &+& Mg^{2+}(aq) &+& 2H_{2}O(l) &+& 2CO_{2}(g) \end{array}$$

• Many other salts in the rocks and sand also dissolve in the acid rain. Soil becomes gradually more acidic in the natural course of events. Cations are removed from the soil solution by plants and replaced by H⁺ ions. Minerals such as sulphides are oxidized to form acids. At low pH, hydrogen ions displace other cations from soil. Not only Al³⁺, Mg²⁺, Ca²⁺ but heavy metal ions are also displaced by H⁺ ions. The leaving of these ions deprives plants of the nutrients required for healthy growth. The acidic water passing through the soil, causes to leaching Al³⁺ and other minerals and also weathering of rocks. The Ca²⁺ and Mg²⁺ concentration increase in water, and hardness of water also increases. The acidity, salinity and nitrogen concentration also increase insurface water. Concentration of the heavy metal ions also increases in the surface water.

3. Photochemical smog

 Motor vehicle emissions contain NO_x and unburnt hydrocarbons (C_xH_y). They are converted to ozone, aldehydes, peroxyacetyl nitrate (PAN), peroxy benzoyl nitrate (PBN), etc. in the presence of sunlight and temperatures above 15 °C.

- This is known as photochemical smog as those chemicals are formed in the presence of sunlight
- Smog is a yellowish haze which reduces visibility and causes eye irritation.
- The word smog is used to describe the combination of smoke and fog.
- The starting reaction of photochemical smog is dissociation of NO₂ to NO and 'O'.
- The steps in the formation of a photochemical smog are given below.
 - (i) NO₂ absorbs sunlight and undergoes photolysis.

 $NO_2 \xrightarrow{h} NO + O$

- (ii) The resulting atomic oxygen combines with O₂ molecules
 - a) to form ozone.

$$O + O_2 + M \rightarrow O_3 + M$$

(M is known as third body which absorbs excess energy. M can be an airborne particle or a gas.)

b) to form OH radicals.

$$O + H_2 O \rightarrow 2\dot{O} H$$

- (iii) The resulting H O converts other airborne chemicals into radicals and they start a set of reactions to produce aldehydes, PAN, PBN, etc.
- Effects of photochemical smog are given below.
 - Effects on human health and comfort : Photochemical smog affects the respiratory system. It causes coughing, wheezing, etc.
 - Damage to materials : Ozone causes rubber to deteriorate through fission of the double bond and also reduces the quality of fabrics and bleaches dyes.
 - Effects on the atmosphere : Aerosol particles scatter light and reduce the visibility.
 - Toxicity to plants : Most of the photochemical smog products are toxic to plants. Plant growth is inhibited by the prodets from photochemical smog. This can effect the food production.

4. Depletion of ozone layer

- There is a layer of ozone in the stratosphere. The ozone layer prevents high energy UV light from reaching the troposphere.
- Some reactions involving O₂(g) and O₃(g) are;
 - a) The $O_{2}(g)$ is dissociated by solar UV radiations.

$$O_2(g) \xrightarrow{\hbar\nu} O(g) + O(g) \quad \Delta H > 0$$

b) Some of the atomic oxygen (O) combines with dioxygen molecules to form trioxygen molecules (O_2) .

$$O(g) + O_2(g) + M \longrightarrow O_3(g) + M; \quad \Delta H \langle 0 \rangle$$

c) $O_3(g)$ absorbs UV light with different frequencies and dissociates.

$$O_3(g) \xrightarrow{\quad \text{tw} \quad} O_2(g) + O(g) \quad \ ; \quad \ \Delta H \ \rangle 0$$

d) O_3 molecule reacts with O atom and forms O_2 molecule.

 $O_3(g) + O(g) \longrightarrow 2O_2(g)$

There is a natural balance which keeps the ozone layer at a constant thickness.

• Ozone is destroyed by reactions with H, NO, OH and other free radicals. These radicals act as catalysts and destroy thousands of O₃ molecules. The catalysed destruction of ozone in the stratosphere is known as ozone layer depletion.

$$O_2(g) \rightarrow 2O(g) ----- (2)$$

$$\mathbb{XO}(g) + \mathbb{O}(g) \to \mathbb{X}(g) + \mathbb{O}_2(g) - \dots - (3)$$

(1) x 2 + (2) + (3) x 2;

 $2O_3(g) \square 3O_2(g)$ Where X = H, NO, OH, Cl

• Chlorine radicals from the chlorofluorocarbon have been recognized as a major contribution to ozone layer depletion. This chloroflurocarbons are stable in the atmosphere but produce radicals in stratosphere with UV radiation.



• There is a strong connection between UV radiation and the cataract formation as well as incidence of both non-fatal and fatal skin cancer in humans. The ozone layer protects us.

Minimization of CO, emissions

To minimize the environmental and health effect of the above mentioned global issues, emission of pollutant gases has to be minimized. Such several remedial actions are given below.

• Minimization of fuel combustion

Motor vehicles, industries and routine household activities (such as cooking) releases large amount of carbon dioxide to the environment. Some of the releases can be controlled. For example, we can reduce drastically the number of vehicles on our roads. The development of an efficient public transport system involving electric trains and electric cars is an alternative. Using fuels of lower carbon to hydrogen ratio will minimize the CO_2 in combustion. Use of the other energy sources such as nuclear and solar energy instead of fossil fuel is another option. Proper vehicle inspection and burning fuel only (without impurities) when necessary will help in this issue.

• Absorption of CO₂ by trees

Carbon dioxide produced by the respiration of living organisms and the normal activities of man is fixed by the green plants during the photosynthesis. Photosynthetic organisms utilize solar radiation to convert carbon dioxide and water to carbohydrates using a chlorophyll catalyst.

 $6 \operatorname{CO}_2(g) + 6 \operatorname{H}_2O(l) \xrightarrow[\text{Solar energy}]{} C_6\operatorname{H}_{12}O_6(s) + 6 \operatorname{O}_2(g)$

- Here green plants in a way purify our air since oxygen is produced as a byproduct of photosynthesis.
- Tropical rain forests are warm and humid. These conditions are ideal for photosynthesis. Their destruction is one of the factors that is causing an increase in atmospheric carbon dioxide level. Therefore, preservation of forest areas and planting are the best ways of controlling CO₂ increase.

Minimization of CO emissions

- Complete combustion
 - Carbon monoxide is a major air pollutant which is formed due to incomplete combustion of fuels. The largest amount of CO comes from motor vehicle exhaust.

• The combustion of butane, for example requires 6.5 moles of oxygen per mole of hydrocarbon. If only six moles of oxygen are present one mole of CO will result.

 $2C_4H_{10}(g) + 13 O_2(g) \rightarrow 8 CO_2(g) + 10 H_2O(g)$ $C_4H_{10}(g) + 6 O_2(g) \rightarrow 3 CO_2(g) + CO(g) + 5 H_2O(g)$

• Maintaining the air / fuel ratio(by mass) leads to a complete combustion. The equation for the complete combustion of octane is;

 $2 C_8 H_{18}(l) + 25 O_2(g) \rightarrow 16 CO_2(g) + 18 H_2O(g)$

From the stoichiometry of the equation it follows that;

(mass of air)/(mass of octane) = 14:7. This is called the air/fuel ratio.

- A rich mixture [which is having more hydrocarbons (fuels) or having oxygen less than the stoichiometric proportion] gives an exhaust gas which is high in CO and partially combusted organic products. A lean mixture (with an excess of air or less fuel) gives an exhaust gas with less CO but has more oxides of nitrogen (NO_x). The best way to control the emissions is "tuning up" (adjusting the air to fuel ratio for the optimum condition) and the use of a catalytic converter to convert the pollutants to harmless products.
- The control of emission from the internal combustion engine is the best hope of reducing CO level.
- Several soil microorganisms have enzymes which catalyze the oxidation and remove CO from the atmosphere.

Minimization of emission of acidic gases

- Remind the students that both N and S will form different oxides and they are acidic in nature. Hence the burning of any material containing N or S in air can produce SO₂ and NO_x. Atmospheric N₂ is not reactive due to a strong triple bond between two nitrogen atoms. But, if the temperature is greater than 900 °C this bond can be cleaved forming NO_x's (NO and NO₂). The burning temperature exceeds 900 °C in most of the combustions including internal combustion engines, burning cigarettes and in the cooking stoves. Also it happens naturally, with thundering and lightening. The best way to minimize the emissions of SO₂ and NO_x is lowering the temperature of the combustion process and reducing the burning of S and N containing material. Following methods can also be used to reduce the release of acidic gases to the atmosphere.
- Absorption methods

Acidic gases can be neutralized by reacting with a base. We have enough natural bases such as limestone $(CaCO_3)$ and magnesium oxide (MgO) that can be used to remove (scrub) the acidic gases. The products that are formed can be converted to the valuable industrial chemical, sulphuric acid.

(i) Slurry of limestone and lime is used to "scrub" the fuel gases.

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

$$CaO(s) + SO_{2}(g) \rightarrow CaSO_{3}(s)$$

$$2 CaSO_{3}(s) + O_{2}(g) + 2 H_{2}O(l) \rightarrow 2 CaSO_{4} \cdot 2H_{2}O(s)$$

(ii) Slurry of magnesium oxide is used as a scrubber.

$$MgO(s) + SO_2(g) \rightarrow MgSO_3(s) \xrightarrow{a} MgO(s) + SO_2(g)$$

The MgSO₃ is heated to give MgO which is recycled and SO₂ at a concentration high enough is used in the manufacture of sulphuric acid.

(iii) A solution of sodium sulphite can be used for scrubbing.

$$Na_2SO_3(s) + H_2O(l) + SO_2(g) \rightarrow 2NaHSO_3(aq)$$

The NaHSO₃ produced can be heated to give Na_2SO_3 for recycling and SO_2 can be sold to sulphuric acid manufacturers.

Minimization of emission of hydrocarbons and partially combusted products

Minimization of pollutant gases from car exhaust

The most significant pollutant gases in vehicle exhausts are CO, NO_x and un-burnt or partially burned hydrocarbons. The partial combustion is due to lack of oxygen. This can be reduced by adjusting the air to fuel ratio as discussed above and this is known as "tuning up" of a vehicle. Toxic gases in automobile exhaust fumes could be controlled by installing catalytic converters along the exhaust pipes of the vehicles. An efficient catalytic converter should oxidize carbon monoxide and unburnt hydrocarbons to carbon dioxide and water and also reduce nitric oxide and nitrogen dioxide to nitrogen and oxygen. These oxidations and reductions are done at two stages on the catalytic surfaces of the catalytic converter which is fixed to the silencer (muffler) of a vehicle. Hot exhaust gases are fed through catalytic converter such as platinum and transition metal oxides such as copper and chromium oxides.

$$2 \operatorname{NO}(g) + 2 \operatorname{CO}(g) \rightarrow \operatorname{N}_{2}(g) + 2 \operatorname{CO}_{2}(g)$$
$$2 \operatorname{CO}(g) + \operatorname{O}_{2}(g) \rightarrow 2 \operatorname{CO}_{2}(g)$$
$$\operatorname{C}_{7}\operatorname{H}_{16}(g) + 11 \operatorname{O}_{2}(g) \rightarrow 7 \operatorname{CO}_{2}(g) + 8 \operatorname{H}_{2}\operatorname{O}(l)$$

Three way catalytic converters (**oxygen** monitor fitted) transform harmful exhausts of CO, NO_x and C_xH_y to relatively harmless N₂, CO₂ and H₂O. The catalytic converters do not start working until the catalyst has reached a temperature about 200 °C. So they are not effective until the engine has warmed up.

Suggested learning teaching activities :

- Ask the students to indentify the ways in which the gases are added to the atmosphere in their area.
- Student can list the mobile sources and stationary sources separately and assist the students to recognize their input to the environment.
- Discuss their contribution to the atmospheric pollution.
- Discuss how to minimise the pollutant gases in the atmosphere.
- Ask the students to collect more information on chlorofluorocarbons and their uses.

Competency 16.0	:	Applies knowledge of chemistry to understand the
		earth's environment.
Competency level 16.3	:	Investigates the contamination of hydrosphere and
		drinking water.
Periods	:	08

Learning outcomes

- Identifies the sources of water pollution.
- Identifies the water quality parameters and methods of monitoring them.
- Describes method of water purification.
- Describes different disinfection processes.

Guidance for teacher elaboration :

Water pollution sources

• Domestic and animal waste

:

- Pathogens bacteria and viruses
- Artificial chemicals (pesticides, surfactants, fertilizers, etc.)
- Suspended solid particles
- Heavy metals
- Hot water from industries

Water quality

Physical Parameters

(i) Temperature

Temperature should less than 40 $^{\circ}$ C. Hot water accelerates the biological processes. It reduces the dissolved O₂ and affects the aquatic organisms.

(ii) pH Value

- A pH range of 6.0 9.0 appears to provide protection for the life of fresh water fish and bottom dwelling invertebrates.
- pH of water may also be changed due to dissolved gas from air such as CO₂, SO₂ and the mixing with industrial effluents.
- Normal pH range of ground water which is useful is 6.0 8.5.
 If pH < 6.5 it is acidic water which is corrosive. Usually soda ash is used to neutralise the acidity.
- Dolomite can also be used in agriculture. Dolomite slowly neutralises acidity of water.

 $2H^+(aq) + CaCO_3 \cdot MgCO_3(s) \rightarrow Ca^{2+}(aq) + Mg^{2+}(aq) + 2 HCO_3^-(aq)$ Dolomite

(iii) Conductivity

- Conductivity is a measure of the ability of an aqueous solution to conduct an electric current.
- Conductivity depends on the following factors.
 - Concentration of ions
- Mobility of ions
- Oxidation state • Temperature of water
- The unit used to measure the conductance is ohm⁻¹ = Ω^{-1} or Siemens (S). Conductance = 1/Resistance

This measures the ionic strength but does not identify the ions present.

(iv) Turbidity

Sediments in the water prevents the penetration of light to the bottom of water bodies. This will reduce the photosynthesis activity and also creates anaerobic environment introducing a bad smell to the water.

(v) Dissolved amount of oxygen and water quality

- O₂ is required for the metabolism of aerobic organisms and also influences some chemical reactions.
- O₂ in air dissolves in water. Photosynthesis is the process of producing O₂.
- Concentration of dissolved O₂ decreases as temperature increases.
- Submerged green plants and algae increase the dissolved O₂ content in a water body in the day time.
- Decaying organic matter consumes dissolved O₂ in a water body.

Chemical oxygen demand (COD)

- $(CHO)_n(aq) + O_2(g) \longrightarrow x CO_2(g) + y H_2O(l)$ Amount of oxygen required in mg dm⁻³ for this oxidation of organic matter wastes to be carried out chemically is called chemical oxygen demand (COD).
- Since the amount of O₂ consumed cannot be easily quantified, dichromate is used for ٠ laboratory determination. In this determination the sample is heated with an acid solution of potassium dichromate. All oxidizable organic matter will react with dichromate at this stage. Silver sulphate is generally added as a catalyst.
- Chloride present in water can be oxidized to chlorine under these conditions by dichromate. ٠ This is prevented by converting chloride to undissociated mercuric chloride. The excess of unreacted dichromate is determined by titrating with iron(II) ammonium sulphate.

 $\operatorname{Cr}_{2}O_{7}^{2-}(\operatorname{aq}) + 14\operatorname{H}^{+}(\operatorname{aq}) + 6e \longrightarrow 2\operatorname{Cr}^{3+}(\operatorname{aq}) + 7\operatorname{H}_{2}O(\operatorname{l})$

• In acidic medium;

 $O_2(g) + 4H^+(aq) + 4e \longrightarrow 2H_2O(l)$ (CHO)_n(aq) + O₂(g) $\longrightarrow xCO_2(g) + yH_2O(l)$

• If the organic matter is oxidized by acid dichromate, then

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \longrightarrow 2Cr^{3+}(aq) + 7H_2O(1)$$

 $1 \mod O_2(aq) \equiv 2/3 \mod of Cr_2O_7^{2-}(aq)$

Biochemical oxygen demand / Biological oxygen demand (BOD)

 $(CHO)_n(aq) + O_2(g) \longrightarrow x CO_2(g) + y H_2O(l)$

- Amount of O₂ required to be carried out for the above oxidation by microorganisms is called biochemical oxygen demand.
- The consumed dissolved oxygen can be used to determine the BOD value.
- Substances which use up dissolved oxygen will contribute to the value of BOD. Pollutants such as human and animal wastes, food canneries, meat etc. controls the BOD.
- When a water sample is saturated with oxygen, the initial concentration of dissolved oxygen can be determined. If it is incubated at 20 °C for a known period, usually 5 days, the microorganisms in the water oxidize the organic matter. The oxygen that remains in the water can be measured. The oxygen used up or the BOD value can be calculated, for the particular water body.

Dissolved ionic compounds

Hardness

Hardness isdue to dissolved metal ions, namely Ca²⁺ and Mg²⁺. Here the contribution of Ca and Mg are the most considered and other metals are negligible because they are less soluble in water. Therefore, we discuss Ca and Mg only here. Hard water has no adverse health effects. Hard water is less desirable because it requires more soap for cleaning. It forms scum and curd and it toughens vegetables during cooking and forms scales in boilers, hot water heaters and pipes. The composition of ground water naturally reflects the underlying geology, the residence time in the rock, the previous composition of the ground water and in some instances, the flow path. Due to the slower movement of ground water in the aquifers as compared to that of surface water, the composition of the former shows a negligible variation with time for a given aquifer.

 $Ca^{2+}(aq)/Mg^{2+}(aq) + 2HCO_3(aq) \rightarrow CaCO_3(s) + MgCO_3(s) + CO_2(g) + H_2O(l)$

• Aquifer - A porous permeable rock layer containing water (Groundwater).

Iron (Fe)

• The primary source of iron in water is rock layers containing iron ore. Iron is typically dissolved in water and when brought to the surface, can form 'rust' which may settle out. Another source of iron is iron-reducing bacteria, which depends upon iron to live. The commonest iron containing water is red, laundry spotting, metallic in taste and staining of plumbing fixtures. These are usually due to the presence of iron above 0.3 mg dm⁻³. Iron affects the taste of drinking water.

Fluoride (F⁻)

 Varying amounts of fluoride are found in groundwater of different areas of Sri Lanka. For example, due to the apatite ore in Eppawala fluoride, concentration of ground water in the surrounding areas is high. Fluoride can affect teeth during the period when permanent teeth are being formed. For tropical countries the fluoride content should not exceed 0.6 mg dm⁻³

Nitrates

• Nitrate is a common contaminant found mainly in ground water. High nitrate concentrations can be particularly dangerous to babies under six months, since nitrates interfere with the ability of blood to carry oxygen. Nitrate also causes cancer. Fertilizers, human and animal sewage are usually enriched with of nitrogenous compounds which may enter into a ground water body as a result of leaching. The conversion of ammonia to nitrate is brought about by highly specialized soil bacteria.

Phosphates

• Phosphate ions are added to water by chemical fertilizers and artificial detergents. Due to nitrates ions and phosphate ions, an eutrophication condition arises in water and enhances the growth of algae. As a result, amount of dissolved oxygen in water decreases.

Methods of water purifications

Sedimentation

- The separation of a suspension of solid particles into a concentrated slurry. The supernatant liquid, after sedimentation is clear.
- If the effluent is suitable it will be discharged into waterways. Otherwise it is passed to a secondary treatment.

Coagulation

- Muddy river water in large water supply schemes can be coagulated using aluminium salt (alum).
- Water is stored in large tanks and can be coagulated with A1(III) or Fe(III).
- A gelatinous precipitate of aluminum hydroxide or iron(III) hydroxide is formed. As it settles and sinks to the bottom, the precipitate carries suspended material with it as sludge.

Flocculation and Filtration

- During the flocculation smaller particles are agglomerated to form bigger particles and these particles are filtered.
- After that water is passed slowly through sand filters. Different types of sand filters are used for water flow.
 - Fine sand
 - Course sand
 - Gravel
 - Stones
- Filtration removes microbes and other suspended particles from water. Many filters will also remove some harmful chemicals found in water.

Disinfection process

• Use of chlorine

 $Cl_2 ClO_2$, chloroamines are used as disinfectants. They kill bacteria by oxidising. The residual Cl_2 prevents the formation of further bacteria. But excess Cl_2 reacts with organic substances and forms harmful substances including trihalomethanes and chlorinated phenols.

• Use of ozone

Ozone also destroys bacteria by oxidation. But it dissociates quickly. Ozone does not give further protection from bacteria. Therefore the water disinfected by ozone has to be used quickly. Since ozone doesn't give any side effects it is preferably used by human. Unlike Cl_2 , ozone needs no storage and it can be generated easily.

• Use of UV radiation It kills both the bacteria and viruses. As ozone it cannot have a further protection from bacteria.

Suggested learning- teaching activities :

- Direct students to identify sources of water pollution.
- Divide the class into three groups and assign each group to investigate two variables that determines the quality of water.
- Allow them to discuss and analyse how these factors determine the quality of water.

Competency 16.0	:	Applies knowledge of chemistry to understand the earth's
		environment
Competency level 16.4	:	Investigates the contamination of soil and the solid waste

Periods : 04

Learning outcomes

• Describes natural inputs and soil fertility.

:

- Identifies the sources of soil pollution.
- Identifies the agrochemicals and e-waste inputs.
- Describes methods of waste management.

Guidance for teacher elaboration:

Natural inputs and soil fertility

- Earth is a crucial source of natural capital including essential metals, fuels, and plant nutrients.
- These earth resources are used in various natural and human processes.
- Earth is also an important repository of wastes enriching soil fertility.
- Unfortunately, recycling process is not uniform around the globe.
- In some locations, waste is accumulated creating hazardous environment. Whereas, some essential nutrients are deprived requiring the addition of synthetic chemicals such as agrochemicals.
- Leaching of hazardous substances from the accumulated wastes contributed to degrade the soil fertility and threatens the existence of different forms of life

Sources of soil pollution

Household wastes

• Includes the food waste, human excretes, waste water, garden debris, plastics

Agrochemicals

- Pesticides
- Pesticide is a substance used for controlling, preventing, destroying, repelling or mitigating any pests. There are two main classes of pesticides used.
 - Natural pesticides
 - Neem (Kohomba) extract is an example for a natural pesticide.
 - Synthetic pesticides.
- The main types of pesticides used are weedicides and insecticides.
- Weedicides (weed killers) kill plants that would otherwise compete with crop for light and nutrients.

- Insecticides kill insects that would damage the crop.
- Insect pests can reduce the yield in two main ways. They might eat the part of the plants that the farmer wants to harvest. By damaging leaves they reduce photosynthesis which affects the food production.
- Insecticides used against insect pest are of three types (Based on their action).
- Three main groups of synthetic insecticides are known.
 - Chlorinated hydrocarbons eg. DDT (Dichlorodiphenyltrichloroethane).
 - Organophosphorus eg. Melathion.
 - Heavy metal salts eg. Copper dithiocarbomates.
- An ideal pesticide should have the following properties
 - Should kill only the target pest.
 - Should biodegrade easily in the environment or soil water system.
 - The pest should not develop any tolerance to the pesticide.
 - Should be cheap, abundant and non-toxic to humans.
- Problems of using pesticides
 - Pesticides can be deposited on our food. They can harm people as well. If the dose is large enough it could poison us.
 - Bio accumulation of persistent pesticides leads to concentration at each level of the food chains. The concentration at the end of the food chain may reach very high levels.
 - They damage the environment. Pesticides often kill harmless or even beneficial species as well as pests.
 - Pests can become resistant to pesticides over a period of time. Repeated use of same pesticide increases the resistance to it through natural selection. Then the pesticide becomes less effective. Natural predators are killed by the pesticide. This may cause a worse outbreak than before.
- L.D. value Lethal dose value LD₅₀. The chemical dose needed to kill 50% of the population of one species under test is called LD₅₀.

Fertilizers

- Fertilizers make plant grow faster because they give the plant essential minerals and nutrients. *eg.* NPK
- The most important mineral ions are nitrate, phosphate and potassium. But there are some trace elements needed in small amounts. NPK content of a fertilizer is expressed as N%, P₂O₅ %, K₂O%.
- There are two main types of fertilizers. Each has its own advantages.
- Natural fertilizers are organic matter. They include manure, sewage and sludge.

- Natural fertilizers supply a wide range of nutrients and release them slowly with long lasting effects. They are less harmful to the environment and are suitable for "organic" farming.
- Natural fertilizers are cheap.
- Natural fertilizers can improve the soil structure (texture).
- Natural fertilizers are expensive to transport and to apply and might not have ideal balance of nutrients.
- Artificial fertilizers are inorganic. They contain pure chemicals (eg. NH₄NO₃) as powders or pellets.
- Artificial fertilizers are fast acting and easy to transport and supply.
- Artificial fertilizers can be used to target particular mineral ions needed and the amount of each mineral supplied can be accurately controlled.
- Artificial fertilizerscan affect the balance of the soil and are more easily washed out of the soil leading to eutrophication of surface water bodies.
- Artificial fertilizers can affect the quality of ground water. *eg.* Nitrate content.

Heavy metals

- Used and scrapped metals, used equipments, vehicles
- Heavy metals are leached in to drinking water and contaminate soil
- Uptake of heavy metals through drinking or food can cause numerous health problems
- Heavy metals such as lead can accumulate in body lowering the intelligence

e-waste

- The term "e-waste" is used to identify all the waste originated from electronic and electrical equipments and related accessories including used or outdated computers, electronic equipments, mobile phones, televisions, sound systems, CFL bulbs, electric and electronic accessories.
- The impact of e-waste has already witnessed by the developed countries and they are attempting to mitigate the problem by dumping them to poor countries.
- Rapid technology change, low initial cost, high obsolescence rate have resulted the ewaste to be the fastest growing problem making yesterday's electronic dream machines to become today's environmental nightmare.
- The average obsolescence rate for a computer is estimated to be 7 years, and it is 15 years for a television or a refrigerator or a washing machine while a mobile phone has a life span of 1.5 years only.
- Common list hazardous chemicals from e-waste include metallic lead (in batteries, circuit boards, cathode ray tubes in TV), mercury (in thermometers, thermostats, discharge lamps, sensors, relay and switches), cadmium (in batteries, mobile phones), beryllium (in computer, telecommunication equipments, and automotive electronics), arsenic (in light emitting diodes), polyvinyl chlorides (in computer casings and cables), polychlorinated biphenyls (in transformers)
- Also form hazardous fumes upon burning the PVC containing e-waste.

Waste Management 3R Systems (Reduce, Reuse and Recycle)

• Reduce, Reuse

Most effetive way to reduce waste is to not create it in the first place. Making a new product requires a lot of materials and energy: raw materials must be extracted from the earth, and the product must be fabricated and then transported to wherever it will be sold. As a result, reduction and reuse are the most effective ways you can save natural resources, protect the environment and save money.

Using as raw materials for the other productions

- Solid wastes can be used to produce various materials.
- Chromium wastes in a tannery effluent can be precipitated as Cr(OH)₃ using MgO and is reused in all leather tannery processes.

Using as raw materials for energy generation

• Dry garbage is a fuel. In Sri Lanka about 80% of the garbage is organic material. They can be converted to obtain energy.

 $\begin{array}{rrrr} (CHO)_n + & O_2(g) & \to & CO_2(g) & + & H_2O(g) & + & heat \\ Heat can be used in industries . \end{array}$

• Recycling

Recycling is the process of collecting and processing materials that would otherwise be thrown away as trash and turning them into new products. Recycling can benefit your community and the environment.

- Many countries have established the recycling of domestic and industrial waste water. Since a large quantity of ground water is used by some industries in Sri Lanka, it is important to encourage them to reuse the water in the same industry. Since the composition of garbage in Sri Lanka is over 80% organic matter, the solid waste can easily be used as a fuel to generate electricity.
- Metals are valuable resources. Instead of burying metal waste it makes sense to collect it and recycle the metals. There are two savings, for instance when scrap iron is collected, melted and re-used, it saves earths reserves of iron ore. In addition the energy required to mine ore, transport it and smelt it is several times greater than the energy required to recycle scrap iron.
- Glass, paper and plastic also can be recycled.
- These materials can be recycled if they are collected and separated at the sources.

Benefits of the recycling process

- Saving in energy
- Saving in natural resources
- Saving in refuse disposal costs
- A source of income for local authorities

• Composting

Fresh plant biomass has a C:N ratio of 100:1. Organic matter is decomposed in solid by bacteria and fungi (microorganisms) to form humus with a C:N ratio of 10:1. If the C:N ratio of the organic matter in the soil is too high, nitrogen may be the limiting factor in the growth of organisms which decompose organic matter and recycle nutrients. If straw (C:N=80:1) is ploughed in to the soil, a nitrogenous fertilizer is usually applied to lower the C:N ratio. Composting can be used to reduce the C:N ratio. Storing organic matter in a compost pile with moisture and air allows carbon dioxide and water to escape, while nitrogen is retained as amino acids and proteins of microorganisms. Adding fertilizer to compost increases the population of microorganisms and speeds composting.

Biogas production

Biogas typically refers to a gas produced by breakdown of organic matters in the absence of oxygen. Organic waste such as dead plants and animal materials, animal feces, and kitchen waste can be converted into a gaseous fuel called biogas. Biogas originates from biogenic material and is a type of bio fuel.

Biogas is produced by the anaerobic digestion or fermentation of biodegradable materials such as biomass, manure, sewage, municipal waste, green wastes, plant material and crops. Biogas comprises primarily methane, and carbon dioxide and may have small amounts of hydrogen sulphide, moisture, etc.

• Incineration

The incineration of waste needs a temperature at which complete combustion of oxidisable material will occur and ash, glass, metal and other materials remain. A temperature of 770-970 °C is used. In many incinerators the heat of combustion of the waste is used to help to maintain the temperature. It is always recommended that the solid wastes from hospitals should be subjected to incineration.

Suggested learning-teaching activities:

- Direct students to identify the sources of soil pollution in the area.
- Ask the students to set a up a collection centre for glass, plastics and paper and encourage the students to bring the segregated solid waste.
- Ask the students to develop a suitable solid waste management system for the school.
- Ask the students collect the information about the usage of agrochemicals and the local industries that make a significant impact to the soil and water bodies.
- Ask the students to compile the data for lifetime of electrical and electronic equipments and accessories to estimate the e-waste inputs.
SCHOOL BASED ASSESSMENT

Introduction- School Based Assessment

Learning –Teaching and Evaluation are three major components of the process of education. It is a fact that teachers should know that evaluation is used to assess the progress of learning – teaching process. Moreover, teachers should know that these components influence mutually and develop each other .According to formative assessment (continuous assessment) fundamentals, it should be done while teaching or it is an ongoing process. Formative assessment can be done at the beginning, in the middle, at the end and at any instance of the learning teaching process.

Teachers who expect to assess the progress of learning of the students should use an organized plan. School based assessment (SBA) process is not a mere examination method or a testing method. This programme is known as the method of intervening to develop learning in students and teaching of teachers. Furthermore, this process can be used to maximize the student's capacities by identifying their strengths and weaknesses closely.

When implementing SBA programmes, students are directed to exploratory process through learning teaching activities and it is expected that teachers should be with the students facilitating, directing and observing the task they are engaged in.

At this juncture students should be assessed continuously and the teacher should confirm whether the skills of the students get developed up to the expected level by assessing continuously. Learning teaching process should not only provide proper experiences to the students but also check whether the students have acquired them properly. For this to happen, proper guiding should be given.

Teachers who are engaged in evaluation (assessment) would be able to supply guidance in two ways. They are commonly known as feed-back and feed- forward. Teacher's role should be providing feedback to avoid learning difficulties when the students' weaknesses and inabilities are revealed and provide feed-forward when the abilities and the strengths are identified, to develop such strong skills of the students.

Student should be able to identify what objectives have been achieved to which level, leading to success of the learning teaching process. Teachers are expected to judge the competency levels of students have reached through evaluation and they should communicate information about student progress to parents and other relevant sectors. The best method that can be used to assess is the SBA that provides the opportunity to assess students continuously.

Teachers who have got the above objective in mind will use effective learning, teaching, evaluation methods to make the teaching process and learning process effective. Following are the types of evaluation tools student and, teachers can use. These types were introduced to teachers by the Department of Examination and National Institute of Education with the new reforms. Therefore, we expect that the teachers in the system know about them well

Types of assessment tools:

1.	Assignments	2.	Projects
3.	Survey	4.	Exploration
5.	Observation	6.	Exhibitions
7.	Field trips	8.	Short written tests
9.	Structured essays	10.	Open book test
11.	Creative activities	12.	Listening tests
13.	Practical work	14.	Speech
15.	Self -creations	16.	Group work
17.	Concept maps	18.	Double entry journal
19.	Wall papers	20.	Quizzes
21.	Question and answer book	22.	Debates
23.	Panel discussions	24.	Seminars
25.	Impromptu speeches	26.	Role-plays

Teachers are not expected to use above mentioned activities for all the units and for all the subjects. Teachers should be able to pick and choose the suitable type for the relevant units for the relevant subjects to assess the progress of the students appropriately. The types of assessment tools are mentioned in Teacher's Instructional Manuals.

If the teachers try to avoid administering the relevant assessment tools in their classes there will be lapses in exhibiting the growth of academic abilities, affective factors and psycho- motor skills in the students.

Extended learning - teaching and assessment tools -Grade -12

 1.0 Evaluation State 2.0 Competency which covered 3.0 Content covered 4.0 Nature of the tool 5.0 Objectives of the tool 	 1st Term, Tool 01 From 1.1 to 1.5 Investigation of sub atomic particles or history of classification of elements. Literature survey Give the practice for learning - teaching process using various communication media. Direct to appreciate role of scientist
 1.0 Evaluation state 2.0 Competency level covered 3.0 Content covered 4.0 Nature of the tool 5.0 Objectives of the tool 	 1st Term, Tool 02 1.4 Content relevant to syllabus Problem and answer book Give the practice for learning teaching process using various communication media. Upgrade knowledge, comprehension and application of the content relevant to the competency level.
 Evaluation state Competency level covered Content covered Nature of the tool Objectives of the tool 	 1st Term, Tool 03 2.1 Content relevant to the syllabus Concept map Enhance the knowledge and comprehension about the classification of primary attractive forces.
 Evaluation State Competency level covered Content covered Nature of the tool Objectives of the tool 	 1st Term, Tool 04 2.2 Content relevant to the syllabus Students' exhibition Using Lewis structure and valence shell electron pair repulsion theory to predict the shape of molecules and construct their models using suitable materials.
 1.0 Evaluation State 2.0 Competency levels covered 3.0 Content Covered 4.0 Nature of the tool 5.0 Objectives of the tool 	 1st Term, Tool 05 From 3.1 and 3.2 Content relevant to the syllabus Chemical calculations Build up chemical formulae using physical quantities relevant to atoms and molecules. Express the composition of mixtures of various types Do the chemical calculations using relevant constants Do the calculations associated with balanced chemical equations

 1.0 Evaluation State 2.0 Competency levels covered 3.0 Content Covered 4.0 Nature of the tool 5.0 Objectives of the tool 	 2nd Term, Tool 01 From 4.1 to 4.5 Content relevant to the syllabus Quiz programme Enhance the knowledge and comprehension about the states of matter and specially gases Provide the skills to make challengeable questions Develop the ability to conduct quiz programme
 Evaluation State Competency levels covered Content Covered Nature of the tool Objectives of the tool 	 2nd Term, Tool 02 4.2 and 5.3 Content relevant to the syllabus Problem and answer book Enhance the calculation skills related to gases using ideal gas equation
 1.0 Evaluation State 2.0 Competency levels covered 3.0 Content Covered 4.0 Nature of the tool 5.0 Objectives of the tool 	 2nd Term, Tool 03 5.2 Content relevant to the syllabus Calculations Using the enthalpy diagrams and thermo chemical cycle develop the calculation skills associated with the enthalpy changes Using Born - Haber cycle to develop the skills to determine the standard formation of enthalpy.
 1.0 Evaluation state 2.0 Competency levels covered 3.0 Content Covered 4.0 Nature of the tool 5.0 Objectives of the tool 	 2nd Term, Tool 04 6.2 Content relevant to syllabus Practical work Give ability to test reactions of s and p block elements, thermal stability and solubility in water of compounds. Development of skills in using chemicals and laboratory equipments.
 1.0 Evaluation state 2.0 Competency levels covered 3.0 Content covered 4.0 Nature of the tool 5.0 Objectives of the tool 	 2nd Term, Tool 05 6.6 and 6.7 Content relevant to the syllabus Practical work Test the oxidation ability of CrO₄²⁻, Cr₂O₇²⁻ and MnO₄⁻ ions. Determine the factors affect the colour of the complex compounds.

 Evaluation state Competency level covered Content covered Nature of the tool Objectives of the tool 	 3rd Term, Tool 01 7.1 Content relevant to the syllabus Panel discussions Surfacing the importance of organic chemistry in day to day life citing examples from different fields Develop the skills of expression when participate in a discussion.
 Evaluation state Competency level covered Content covered Nature of the tool Objectives of the tool 	 2nd Term, Tool 02 7.4 Content relevant to the syllabus Concept map Enhance the understanding of the isomerism relevant to organic chemistry syllabus Identify the diversity of isomers
 1.0 Evaluation state 2.0 Competency levels covered 3.0 Content covered 4.0 Nature of the tool 5.0 Objectives of the tool 	 3rd Term, Tool 03 8.3, 8.4, 9.1, 9.2, 10.1 and 10.4 Content relevant to the syllabus Concept map Identify the types of reactions in organic chemistry Understands about the types of reactions and investigates comparatively
 1.0 Evaluation state 2.0 Competency levels covered 3.0 Content covered 4.0 Nature of the tool 5.0 Objectives of the tool 	 3 rd Term, Tool 04 10.1, 10.2, 10.4 and 10.6 Content relevant to the syllabus Exhibition Present the diversity of organic compounds in an exhibition Give the knowledge to others using various techniques.
 1.0 Evaluation state 2.0 Competency levels covered 3.0 Content covered 4.0 Nature of the tool 5.0 Objectives of the tool 	 3rd Term, Tool 05 11.1, 11.2 and 11.3 Content relevant to the syllabus Quiz programme Using the knowledge about the reactions, develop the knowledge and understanding to distinguish the compounds. Develop the conducting and participating ability in quiz programme.

Extended learning - teaching and assessment tools - Grade 13

1.0	Evaluation State	- 1st Term, Tool 01
2.0	Competency which covered	- From 12.1
3.0	Content covered	- Content relevant to syllabus
4.0	Nature of the tool	- Panel discussion
5.0	Objectives of the tool	 Comparing the rates of processes experienced in day to day life Develop the skills of expressions when participate in a discussion
1.0	Evaluation state	- 1st Term, Tool 02
2.0	Competency level covered	- 12.2, 13.1, 13.5, and 13.6
3.0	Content covered	- Content relevant to syllabus
4.0	Nature of the tool	- Calculations
5.0	Objectives of the tool	 Does calculations using rate laws. Applires equilibrium law for given systems and does calculations Calculates the pH values of acid, base and salt solutions Does calculation using Henderson's equation.
1.0	Evaluation state	- 1st Term, Tool 03
2.0	Competency level covered	- 13.1
3.0	Content covered	- Content relevant to the syllabus
4.0	Nature of the tool	- Practical work
5.0	Objectives of the tool	 Give the ability to do practical related to the different systems. Development of skills in using chemical and

laboratory equipments.

1.0 Evaluation State	- 2nd Term, Tool 01
2.0 Competency level coverved	- 14.4
3.0 Content covered	- Content relevant to the syllabus
4.0 Nature of the tool	- Quizzes
5.0 Objectives of the tool	- • Exploring about primary and secondary cells.
	• Comparing the efficiency of the above cells.
1.0 Evaluation State	- 2nd Term, Tool 02
2.0 Competency levels covered	- 13.8 and 14.5
3.0 Content Covered	- Content relevant to the syllabus
4.0 Nature of the tool	- Panel discussion
5.0 Objectives of the tool	- • Identifying the relationship between the position of the metals in the electro chemical series an extraction of metals.
	• Identifying the usage of electroplating in day to day life.
1.0 Evaluation State	- 2nd Term, Tool 03
2.0 Competency levels covered	1 - 15.5
3.0 Content Covered	- Content relevant to the syllabus
4.0 Nature of the tool	- Practical work
5.0 Objectives of the tool	- • Separating the pigments in the leaf extract
	using paper chromatography.
	• Identifying the metal ions by flame test.
1.0 Evaluation State	- 3rd Term, Tool 01
2.0 Competency levels covered	- From 15.1 to 15.6
3.0 Content Covered	- Content relevant to the syllabus
4.0 Nature of the tool	- Quizzes
5.0 Objectives of the tool	- Enhance the knowledge and comprehension about the industries of Sri Lanka.
	• Provide the skills to make challengeable questions.

1.0 Evaluation State	-	3rd Term, Tool 02
2.0 Competency levels covered	-	From 16.1 to 16.4
3.0 Content Covered	-	Content relevant to the syllabus
4.0 Nature of the tool	-	Panel discussion
5.0 Objectives of the tool	-	 Surfacing the importance of maintaining the equilibrium of the environment. Develop the skills of expressions when partici pate in a discussion.
1.0 Evaluation state	_	3rd Term, Tool 03
2.0 Competency levels covered	-	16.3
3.0 Content Covered	-	Content relevant to syllabus
4.0 Nature of the tool	-	Practical work
5.0 Objectives of the tool	-	 Determine the quality of water by doing practical. Realize the importance of water in the environment. Development of skills in using chemicals and
		laboratory equipments.