



GOVERNMENT OF TAMIL NADU

HIGHER SECONDARY FIRST YEAR
CHEMISTRY
VOLUME - I

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Department of School Education

Untouchability is Inhuman and a Crime

Government of Tamil Nadu

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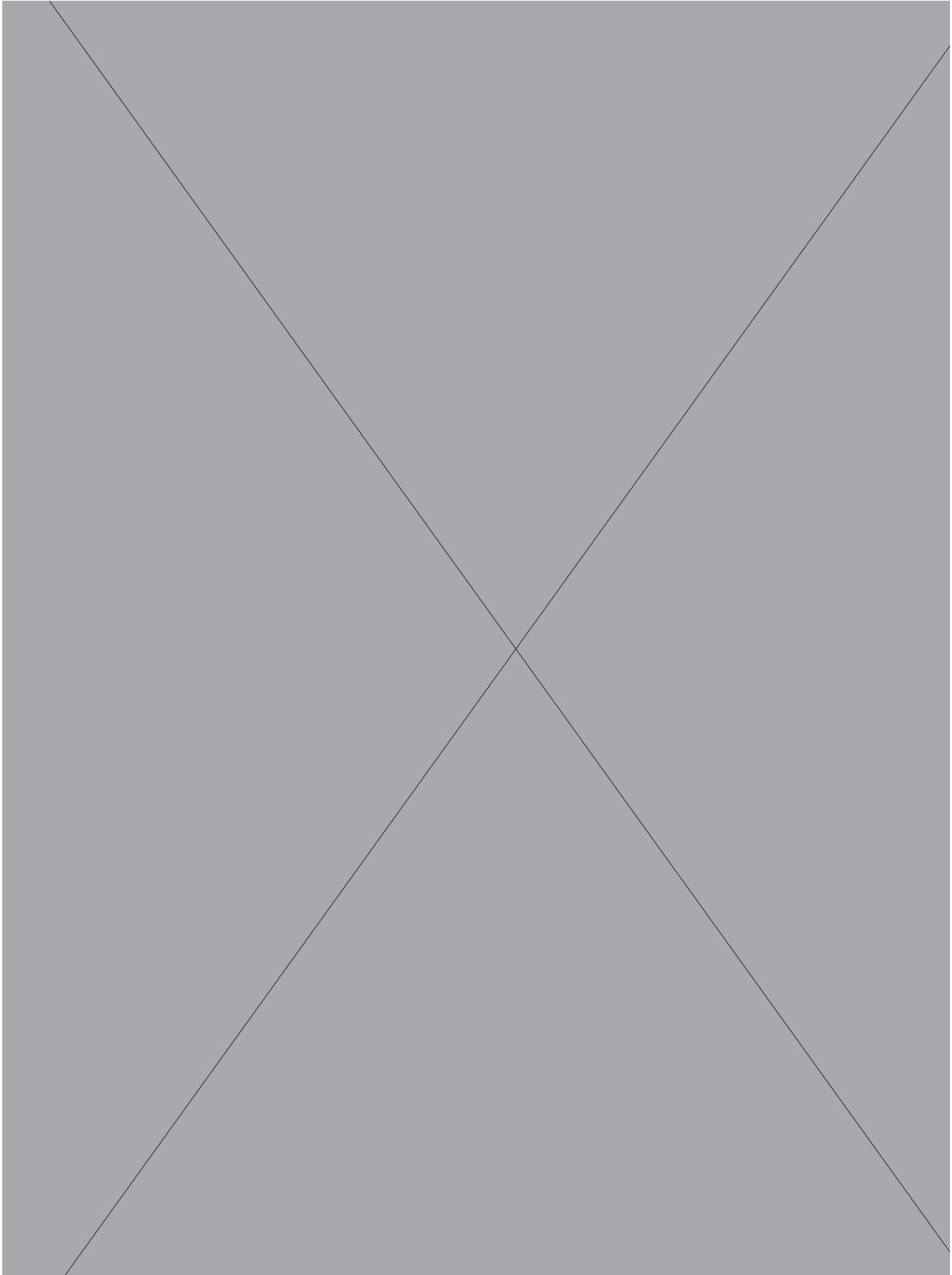


Tamil Nadu Textbook and Educational
Services Corporation

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Key features

	Scope of Chemistry	Awareness about higher education avenues in the field of Chemistry	
	Learning objectives	Describe the specific competency / performance capability acquired by the learner	
	Do you know	Additional information provided to relate the content to day-to-day life / development in the field	
	Example Problems	Model problems worked out for clear-cut comprehension by the learners	
	Evaluate yourself	To help the students to assess their own conceptual understanding	
	Q.R code	Quick access to concepts, videos, animations and tutorials	
	ICT	Opens up resources for learning; enables the learners to access, extend transform ideas / informations	
	Summary	A glance on the substance of the unit	
	Concept map	Inter relating the concepts for enabling learners to visualize the essence of the unit	
	Evaluation	To assess the level of understanding through multiple choice question, numerical problems etc.	
	Books for Reference	List of relevant books for further reading	
	Key answers	To help the learners confirm the accuracy of the answers arrived and remedy the gaps in learning	
	Glossary	Important terms are enlisted with equivalent Tamil words	
	Appendix	Comprises fundamental constants and Data tables	



IV



Courses Bachelor Degree	Institution	Selection Mode	Careers in Chemistry
<ul style="list-style-type: none"> • M.Sc. (Integrated Chemistry) 	<ul style="list-style-type: none"> • Pondicherry University • Indian Institute of Technology (IIT Roorkee) • Indian Institute of Technology (IIT Khagarpur) • Indian Institute of Technology (IIT Bombay) • Central University of Tamil Nadu : School of Basic and Applied Science, Thiruvarur • NISER School of Chemical Sciences, Cuttack • Birla Institute of Technology and Science • Annamalai University • Arts and Science Colleges in India 	<ul style="list-style-type: none"> #Pondicherry University Entrance exam #Joint Admission Test for M.Sc. (JAM) #CUCET entrance #NEST entrance #BITSAT entrance #Annamalai University Entrance exam Based on percentage scored in degree and Separate Entrance exams will be conducted by the concern institute 	<ul style="list-style-type: none"> • Analytical Chemist • Higher Secondary Teacher • Production Chemist • Research & Development Manager • Biomedical Chemist • Industrial Research Scientist • Materials Technologist • Quality Controller • Safety Health and Environment Specialist • Pharmaceutical Companies • Environmental Law • Space Exploration Agencies • Forensic Science Department • Ceramics Industry and Paper Industry • Military Systems Department • Patent Attorney • Nuclear engineer
<ul style="list-style-type: none"> • M.Sc.-General Chemistry, Analytical Chemistry, Inorganic Chemistry Organic Chemistry, Physical Chemistry, Polymer Chemistry Environmental Science NanoScience and Nanotechnology 	<ul style="list-style-type: none"> • Government Universities like University of Madras, Alagappa University, Anna University, Annamalai University, Bharathiar University, Bharathidasan University, Madurai Kamaraj University and IISc, Bangalore, University of Delhi, etc. Arts and Sciences colleges in India 	<ul style="list-style-type: none"> Separate Entrance exams will be conducted by the concern institute 	<ul style="list-style-type: none"> • Industry related jobs • Quality Control Chemist • Production Chemist • Petrochemical industry • Food processing • Paint industry
<ul style="list-style-type: none"> • M.Sc. Applied Chemistry Chemistry (Hons) Applied Chemistry(Hons) Industrial Chemistry Medicinal Chemistry Pharmaceutical Chemistry Drug Chemistry 	<ul style="list-style-type: none"> • Anna University • Andhra University • Birla Institute of Technology Cochin • University of Science and technology • PSG College, Coimbatore • Sri Venkateshwara University, Tirupati. 	<ul style="list-style-type: none"> Separate Entrance exams will be conducted by the concern institute 	<ul style="list-style-type: none"> • Industry related jobs • Quality Control Chemist • Production Chemist • Petrochemical industry • Food processing • Paint industry

Courses Bachelor Degree	Institution	Selection Mode	Careers in Chemistry
<ul style="list-style-type: none"> M.Tech. -Polymer Science And Technology Industrial Safety And Hazards Management 	<ul style="list-style-type: none"> Anna University and Alagappa College of Technology 	# Tamil Nadu Common Entrance Test (TANCET)	<ul style="list-style-type: none"> Industrial Safety and Hazards Management jobs in various industry
M.Phil.			
M.Phil.-Chemistry Analytical Chemistry Applied Chemistry Industrial Chemistry Crystal Science	<ul style="list-style-type: none"> Universities in India Arts and Science Colleges in India 	Entrance/direct interview depending upon the College/ University	<ul style="list-style-type: none"> Teaching related jobs All industries related jobs Technicians in imaging labs Patent Law
Research			
<ul style="list-style-type: none"> Ph.D. (Chemistry) Area: Organic Synthesis, Inorganic complexes, Computational Chemistry, Nanotechnology Electrochemistry, Material Science & Polymer Composites, Bio-sensors, Molecular modelling, chemoinformatics, Green Chemistry, Catalysts for Green Oxidation Chemistry etc. 	<ul style="list-style-type: none"> Indian Institute of Science, Indian Institute of Technology, Kharagpur University of Delhi, Delhi Indian Institute of Technology, Bombay Tata Institute of Fundamental Research, Mumbai Anna University, Chennai Indian Institute of Technology, Madras Jawaharlal Nehru Centre for Advanced Scientific Research, University of Madras, Bharathiar University, Jawaharlal Nehru University, National Institute of Technology, Annamalai University, etc. 	Separate Entrance exams will be conducted by the concern institute	<ul style="list-style-type: none"> Professor for Govt. colleges and Universities Chemical scientists Scientist posts in many central government industry Post Doctoral Fellow Quality control in Toxicology Formulation Chemistry Chemical Information Management Specialist

Entrance Exams and Pattern

<p>JEE-Main Paper I -3 hrs Paper II-3 hrs www.jeemain.nic.in</p>	<ul style="list-style-type: none"> Indian Institutes of Information Technology (IITs) Indian Institute of Engineering Science and Technology (IIEST) National Institutes of Technology (NITs) Indian Institute of Technology (IITs) Government Funded Technical Institutes (GFTIs) 	<p>OMR based and Online based (choice of candidate)</p>	<p>Notification: 1st week of Dec Exam Date: April Negative marking: 4/-1 Total Marks:360</p>	<p>Physics Chemistry Mathematics Total Questions</p>	<p>30 30 30 90</p>
<p>JEE-Advanced Paper I -3 hrs Paper II-3 hrs Should qualify JEE main (paper-I) www.jeeadv.ac.in</p>	<ul style="list-style-type: none"> Indian Institutes of Information Technology (IITs) Indian Institute of Engineering Science and Technology (IIEST) National Institutes of Technology (NITs) Indian Institute of Technology (IITs) Government Funded Technical Institutes (GFTIs) 	<p>Online</p>	<p>Notification: last week of April Exam Date: May second week Negative marking: 4/-1 Total Marks: 306 (Variable each year)</p>	<p>Physics Chemistry Mathematics Total Questions</p>	<p>18 18 18 54</p>
<p>BITSAT http://www.bitsadmission.com Time: 3 hrs</p>	<ul style="list-style-type: none"> Birla Institute of Technology and Science 	<p>Online</p>	<p>Notification: 2nd week of Dec Exam Date: 2nd week of May Negative marking: 3/-1 Total Marks: 450</p>	<p>Physics Chemistry Mathematics English Proficiency Logical Reasoning Total Questions</p>	<p>40 40 45 15 10 150</p>
<p>CUCET https://cucetexam.in Time: 2 hrs</p>	<ul style="list-style-type: none"> All Central Universities 	<p>Online</p>	<p>Notification: 2nd week of Feb Exam Date: April Negative marking: 1/0.25 Total Marks:175</p>	<p>English General Awareness Mathematical Aptitude Analytical Skill Science Total Questions</p>	<p>25 25 25 25 75 175</p>
<p>JAM http://jam.iitb.ac.in/ Time: 3 hrs</p>	<ul style="list-style-type: none"> All IITs 	<p>Online</p>	<p>Notification: September Exam Date: February Negative marking: 1/0.33 2/0.66 Total Marks:100</p>	<p>Chemistry Total Questions</p>	<p>60 60</p>

CSIR-UGC Net http://csirhrdg.res.in Time: 3 hrs	<ul style="list-style-type: none"> Ph.D. admission in all Universities and Colleges 	OMR	Sessions: June From out : March Exam Date: June Session: December From out : September Exam Date: December	General Science, Quantitative Reasoning & Analysis and Research Aptitude Chemistry Total Questions	60 15 75
GATE http://gate.iitg.ac.in/ Time: 3 hrs	<ul style="list-style-type: none"> Ph.D. admission in all IITs 	OMR	From out : September Exam Date: February Negative marking: 1/0.33 2/0.66 Total Marks:100	General Aptitude Chemistry Total Questions	10 55 65
TANCET https://www.annauniv.edu Time: 2 hrs	<ul style="list-style-type: none"> Anna University Entrance exam for technology courses 	Pen and Paper based exam	From out : January Exam Date: March Negative marking: 1/0.33 Total Marks:100	Engineering Mathematics Basic Engineering and Sciences Chemistry Total Questions	20 20 60 100
University of Madras http://www.unom.ac.in Time: 3 hrs	<ul style="list-style-type: none"> M.Sc. Entrance exam 	Pen and Paper based exam	From out : 2 nd week of Feb Exam Date: April Negative marking: Nil Total Marks:100	Analytical Chemistry Inorganic Chemistry Organic Chemistry Physical Chemistry Total Questions	25 25 25 25 100
Anna University https://www.annauniv.edu Time: 1 hr	<ul style="list-style-type: none"> M.Sc. Entrance exam 	Online	From out : April Exam Date : May Negative marking : 1/0.25 Total Marks : 100	Chemistry Total Questions	100 100
Annamalai University http://www.annamalaiuniversity.ac.in	<ul style="list-style-type: none"> M.Sc. Admission B.Sc. Admission 	Based on percentage scored in degree and Personal Interview. Counseling based on 12 th Marks in Science Subjects			
Bharathiar University www.b-u.ac.in Time: 1.30 hrs	<ul style="list-style-type: none"> M.Sc. Entrance exam 	Pen and Paper based exam	From out : May Exam Date : Roughly July Total Marks : 60	Chemistry Total Questions	60 60
Bharathidasan University http://www.bdu.ac.in/	<ul style="list-style-type: none"> M.Sc. Entrance exam 	Pen and Paper based exam	From out : last week of May Exam Date : second week of June		
Madurai Kamaraj University mkuuniversity.ac.in	<ul style="list-style-type: none"> M.Sc. Entrance exam 	Online	From out : March Exam Date : May/June		

(Note: All these dates are tentative and they are subjected to change every year)

CONTENTS

CHEMISTRY

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E-book



Assessment



DIGI links



Lets use the QR code in the text books ! How ?

- Download the QR code scanner from the Google PlayStore/ Apple App Store into your smartphone
- Open the QR code scanner application
- Once the scanner button in the application is clicked, camera opens and then bring it closer to the QR code in the text book.
- Once the camera detects the QR code, a url appears in the screen.Click the url and goto the content page.



X



Basic Concepts of Chemistry and Chemical Calculations



We think there is colour, we think there is sweet, we think there is bitter, but in reality there are atoms and a void.

– Democritus



Natural Fibre
(Cotton)

Synthetic Fibre
(Nylon)



Pesticide
(Malathion)

Pharmaceutical
(Tablets)



Refinery
(Oil)

Learning Objectives

After studying this unit, students will be able to

- explain the importance of chemistry in different spheres of life.
- classify different substances into elements, compounds and mixtures.
- define atomic mass and molecular mass.
- define the amount of substance using SI unit 'mole'.
- describe Avogadro number.
- explain the relationship among mass, moles and number of atoms (or) molecules and perform calculations relating to the conversions.
- define equivalent mass and calculate equivalent mass of acid, base and oxidising/reducing agents.
- deduce empirical and molecular formula of a compound from experimental data.
- solve numerical problems based on stoichiometric calculations.
- identify the limiting reagent and calculate the amount of reactants and products in a reaction.
- define the terms oxidation, reduction, oxidant and reductant.
- predict the oxidation states of elements in various compounds.
- explain the process involved in a redox reaction and describe the electron transfer process.
- classify redox reactions into different types.
- formulate a balanced redox reaction from two half-reactions.

1.1 Chemistry - the Centre of Life

'Unna unavu, udukka udai, irukka idam' - in Tamil classical language means food to eat, cloth to wear and place to live. These are the three basic needs of human life. Chemistry plays a major role in providing these needs and also helps us to improve the quality of life. Chemistry has produced many compounds such as fertilizers, insecticides etc. that could enhance the agricultural production. We build better and stronger buildings that sustain different weather conditions with modern cements, concrete mixtures and better quality steel. We also have better quality fabrics.

Chemistry is everywhere in the world around us. Even our body is made up of chemicals. Continuous biochemical reactions occurring in our body are responsible for human activities. Chemistry touches almost every aspect of our lives, culture and environment. The world in which we are living is constantly changing, and the science of chemistry continues to expand and evolve to meet the challenges of our modern world. Chemical industries manufacture a broad range of new and useful materials that are used in every day life.

Examples : polymers, dyes, alloys, life saving drugs etc.

When HIV/AIDS epidemic began in early 1980s, patients rarely lived longer than a few years. But now many effective medicines are available to fight the

infection, and people with HIV infection have longer and better life.

The understanding of chemical principles enabled us to replace the non eco friendly compounds such as CFCs in refrigerators with appropriate equivalents and increasing number of green processes. There are many researchers working in different fields of chemistry to develop new drugs, environment friendly materials, synthetic polymers etc. for the betterment of the society.

As chemistry plays an important role in our day-to-day life, it becomes essential to understand the basic principles of chemistry in order to address the mounting challenges in our developing country.

1.2 Classification of Matter:

Look around your classroom. What do you see? You might see your bench, table, blackboard, window etc. What are these things made of? They are all made of matter. Matter is defined as anything that has mass and occupies space. All matter is composed of atoms. This knowledge of matter is useful to explain the experiences that we have with our surroundings. In order to understand the properties of matter better, we need to classify them. There are different ways to classify matter. The two most commonly used methods are classification by their physical state and by chemical composition as described in the chart.

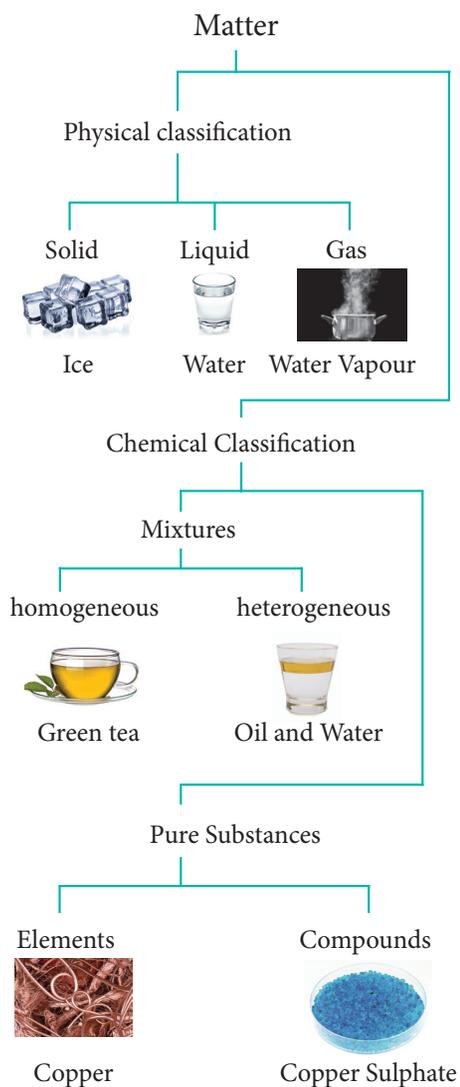


Fig. 1.1 Classification of Matter

1.2.1 Physical Classification of Matter :

Matter can be classified as solids, liquids and gases based on their physical state. The physical state of matter can be converted into one another by modifying the temperature and pressure suitably.

1.2.2 Chemical Classification :

Matter can be classified into mixtures and pure substances based on chemical compositions. Mixtures consist of more than one chemical entity present without any chemical interactions. They can be further classified as homogeneous

or heterogeneous mixtures based on their physical appearance.

Pure substances are composed of simple atoms or molecules. They are further classified as elements and compounds.

Element :

An element consists of only one type of atom. We know that an atom is the smallest electrically neutral particle, being made up of fundamental particles, namely electrons, protons and neutrons.

Element can exist as monatomic or polyatomic units.

Example : **Monatomic unit** - Gold (Au), Copper (Cu); **Polyatomic unit** - Hydrogen (H_2), Phosphorous (P_4) and Sulphur (S_8)

Compound:

Compounds are made up of molecules which contain two or more atoms of different elements.

Example : Carbon dioxide (CO_2), Glucose ($C_6H_{12}O_6$), Hydrogen Sulphide (H_2S), Sodium Chloride (NaCl)

Properties of compounds are different from those of their constituent elements. For example, sodium is a shiny metal, and chlorine is an irritating gas. But the compound formed from these two elements, sodium chloride, shows different characteristics as it is a crystalline solid, vital for biological functions.

Evaluate Yourself

- 1) By applying the knowledge of chemical classification, classify each of the following into elements, compounds or mixtures.
- Sugar
 - Sea water
 - Distilled water
 - Carbon dioxide
 - Copper wire
 - Table salt
 - Silver plate
 - Naphthalene balls

1.3 Atomic and Molecular Masses

1.3.1 Atomic Masses

How much does an individual atom weigh? As atoms are too small with diameter of 10^{-10} m and weigh approximately 10^{-27} kg, it is not possible to measure their mass directly. Hence it is proposed to have relative scale based on a standard atom.

The C-12 atom is considered as standard by the IUPAC (International Union of Pure and Applied Chemistry), and its mass is fixed as 12 amu (or) u. The amu (or) unified atomic mass unit is defined as one twelfth of the mass of a Carbon-12 atom in its ground state.

i.e. 1 amu (or) 1u $\approx 1.6605 \times 10^{-27}$ kg.

In this scale, the relative atomic mass is defined as the ratio of the average atomic mass to the unified atomic mass unit.

$$\begin{aligned} \text{Relative atomic mass } (A_r) &= \frac{\text{Average mass of the atom}}{\text{Unified atomic mass}} \end{aligned}$$

For example,

$$\begin{aligned} \text{Relative atomic mass of hydrogen } (A_r)_H &= \frac{\text{Average mass of H-atom (in kg)}}{1.6605 \times 10^{-27} \text{ kg}} \\ &= \frac{1.6736 \times 10^{-27} \text{ kg}}{1.6605 \times 10^{-27} \text{ kg}} \\ &= 1.0078 \approx 1.008 \text{ u.} \end{aligned}$$

Since most of the elements consist of isotopes that differ in mass, we use average atomic mass. Average atomic mass is defined as the average of the atomic masses of all atoms in their naturally occurring isotopes. For example, chlorine consists of two naturally occurring isotopes ${}_{17}\text{Cl}^{35}$ and ${}_{17}\text{Cl}^{37}$ in the ratio 77 : 23, the average relative atomic mass of chlorine is

$$\begin{aligned} &= \frac{(35 \times 77) + (37 \times 23)}{100} \\ &= 35.46 \text{ u} \end{aligned}$$

1.3.2 Molecular Mass

Similar to relative atomic mass, relative molecular mass is defined as the ratio of the mass of a molecule to the unified atomic mass unit. The relative molecular mass of any compound can be calculated by adding the relative atomic masses of its constituent atoms.

For example,

- Relative molecular mass of hydrogen molecule (H_2)

$$= 2 \times (\text{relative atomic mass of hydrogen atom})$$

$$= 2 \times 1.008 \text{ u}$$

$$= 2.016 \text{ u.}$$

ii) Relative molecular mass of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$)

$$= (6 \times 12) + (12 \times 1.008) + (6 \times 16)$$

$$= 72 + 12.096 + 96$$

$$= 180.096 \text{ u}$$

Table 1.1 Relative atomic masses of some elements

Element	Relative atomic mass	Element	Relative atomic mass
H	1.008	Cl	35.45
C	12	K	39.10
N	14	Ca	40.08
O	16	Cr	51.99
Na	23	Mn	54.94
Mg	24.3	Fe	55.85
S	32.07	Cu	63.55

Evaluate Yourself

2) Calculate the relative molecular mass of the following.

- (i) Ethanol ($\text{C}_2\text{H}_5\text{OH}$)
- (ii) Potassium permanganate (KMnO_4)
- (iii) Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$)
- (iv) Sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$)

1.4 Mole Concept

Often we use special names to express the quantity of individual items for our convenience. For example, a dozen

roses means 12 roses and one quire paper means 24 single sheets. We can extend this analogy to understand the concept of mole that is used for quantifying atoms and molecules in chemistry. Mole is the SI unit to represent a specific amount of a substance.

To understand the mole concept, let us calculate the total number of atoms present in 12 g of carbon -12 isotope or molecules in 158.03 g of potassium permanganate, 294.18 g of potassium dichromate and 180 g of glucose.

12 Numbers = 1 Dozen



12 Roses



12 Balls



12 Apples

1 Mole $\equiv 6.023 \times 10^{23}$ entities



158.03g of KMnO_4



294.18g of $\text{K}_2\text{Cr}_2\text{O}_7$

Fig. 1.2 Mole Concept

Table 1.2 Calculation of number of entities in one mole of substance.

S. No.	Name of substance	Mass of the substance taken (gram)	Mass of single atom or molecule (gram) = Atomic mass or Molar mass / Avogadro Number	No. of atoms or molecules = Mass of substance ÷ Mass of single atom or molecule
	(1)	(2)	(3)	(2)÷(3)
1.	Elemental Carbon (C-12)	12	1.9926×10^{-23}	$\frac{12}{1.9926 \times 10^{-23}} = 6.022 \times 10^{23}$
2.	Glucose (C ₆ H ₁₂ O ₆)	180	29.89×10^{-23}	$\frac{180}{29.89 \times 10^{-23}} = 6.022 \times 10^{23}$
3.	Potassium dichromate (K ₂ Cr ₂ O ₇)	294.18	48.851×10^{-23}	$\frac{294.18}{48.851 \times 10^{-23}} = 6.022 \times 10^{23}$
4.	Potassium permanganate (KMnO ₄)	158.03	26.242×10^{-23}	$\frac{158.03}{26.242 \times 10^{-23}} = 6.022 \times 10^{23}$

From the calculations we come to know that 12 g of carbon-12 contains 6.022×10^{23} carbon atoms and same numbers of molecules are present in 158.03 g of potassium permanganate and 294.18 g of potassium dichromate. Similar to the way we use the term 'dozen' to represent 12 entities, we can use the term 'mole' to represent 6.022×10^{23} entities (atoms or molecules or ions)

One mole is the amount of substance of a system, which contains as many elementary particles as there are atoms in 12 g of carbon-12 isotope. The elementary particles can be molecules, atoms, ions, electrons or any other specified particles.

DO YOU KNOW?

Gastric acid and antacids:

Antacids are commonly used medicines for treating heartburn and acidity. Do you know the chemistry behind it?

Gastric acid is a digestive fluid formed in the stomach and it contains hydrochloric acid. The typical concentration of the acid in gastric acid is 0.082 M. When the concentration exceeds 0.1 M it causes the heartburn and acidity.

Antacids used to treat acidity contain mostly magnesium hydroxide or aluminium hydroxide that neutralises the excess acid. The chemical reactions are as follows.

$$3 \text{HCl} + \text{Al(OH)}_3 \rightarrow \text{AlCl}_3 + 3 \text{H}_2\text{O}$$

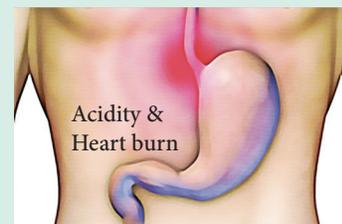
$$2 \text{HCl} + \text{Mg(OH)}_2 \rightarrow \text{MgCl}_2 + 2 \text{H}_2\text{O}$$

From the above reactions we know that 1 mole of aluminium hydroxide neutralises 3 moles of HCl while 1 mole of magnesium hydroxide neutralises 2 moles of HCl.

Let us calculate the amount of acid neutralised by an antacid that contains 250 mg of aluminium hydroxide and 250 mg of magnesium hydroxide.

Active Compound	Mass in (mg)	Molecular mass (g mol^{-1})	No. of moles of active compound	No. of moles OH^-
$\text{Al}(\text{OH})_3$	250	78	0.0032	0.0096
$\text{Mg}(\text{OH})_2$	250	58	0.0043	0.0086
Total no. of moles of OH^- ion from one tablet				0.0182

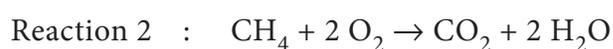
One tablet of above composition will neutralise 0.0182 mole of HCl for a person with gastric acid content of 0.1 mole. One tablet can be used to neutralize the excess acid which will bring the concentration back to normal level. ($0.1 - 0.018 = 0.082 \text{ M}$)



1.4.1 Avogadro Number:

The total number of entities present in one mole of any substance is equal to 6.022×10^{23} . This number is called Avogadro number which is named after the Italian physicist Amedeo Avogadro who proposed that equal volume of all gases under the same conditions of temperature and pressure contain equal number of molecules. Avogadro number does not have any unit.

In a chemical reaction, atoms or molecules react in a specific ratio. Let us consider the following examples



In the first reaction, one carbon atom reacts with one oxygen molecule to give one carbon dioxide molecule. In the second reaction, one molecule of methane burns with two molecules of oxygen to give one molecule of carbon dioxide and two molecules of water. It is clear that the ratio of reactants is based on the number of molecules. Even though the ratio is based on the number of molecules it is practically difficult to count the number of



**Lorenzo Romano
Amedeo Carlo
Avogadro (1776-1856)**

He is known for the Avogadro's hypothesis. In honour of his contributions, the number of fundamental particles in a mole of substance was named as Avogadro number. Though Avogadro didn't predict the number of particles in equal volumes of gas, his hypothesis did lead to the eventual determination of the number as 6.022×10^{23} Rudolf Clausius, with his kinetic theory of gases, provided evidence for Avogadro's law.

molecules. Because of this reason it is beneficial to use '**mole**' concept rather than the actual number of molecules to quantify the reactants and the products. We can explain the first reaction as one mole of carbon reacts with one mole of oxygen to give one mole of carbon dioxide and the second reaction as one mole of methane burns with two moles of oxygen to give one mole of carbon dioxide and two moles of water. When only atoms are involved, scientists also use the term one gram atom instead of one mole.

1.4.2 Molar Mass:

Molar mass is defined as the mass of one mole of a substance. The molar mass of a compound is equal to the sum of the relative atomic masses of its constituents expressed in g mol^{-1} .

Examples:

- relative atomic mass of one hydrogen atom = 1.008 u
- molar mass of hydrogen atom = 1.008 g mol^{-1}
- relative molecular mass of glucose = 180 u
- molar mass of glucose = 180 g mol^{-1}

1.4.3 Molar Volume:

The volume occupied by one mole of any substance in the gaseous state at a given temperature and pressure is called molar volume.

Conditions	Volume occupied by one mole of any gaseous substances (in litre)
273 K and 1 bar pressure (STP)	22.71
273 K and 1 atm pressure	22.4
298 K and 1 atm pressure (Room Temperature & pressure (SATP))	24.47

Evaluate Yourself



- 3a) Calculate the number of moles present in 9 g of ethane.
- 3b) Calculate the number of molecules of oxygen gas that occupies a volume of 224 ml at 273 K and 3 atm pressure.

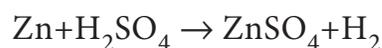
1.5 Gram Equivalent Concept:

Similar to mole concept gram equivalent concept is also widely used in chemistry especially in analytical chemistry. In the previous section, we have understood that mole concept is based on molecular mass. Similarly gram equivalent concept is based on equivalent mass.

Definition:

Gram equivalent mass is defined as the mass of an element (compound or ion) that combines or displaces 1.008 g hydrogen or 8 g oxygen or 35.5 g chlorine.

Consider the following reaction:



In this reaction 1 mole of zinc (i.e. 65.38 g) displaces one mole of hydrogen molecule (2.016 g).

Mass of zinc required to displace 1.008 g hydrogen is

$$\begin{aligned} &= \frac{65.38}{2.016} \times 1.008 \\ &= \frac{65.38}{2} \end{aligned}$$

The equivalent mass of zinc = 32.69

The gram equivalent mass of zinc
= 32.69 g eq^{-1}

Equivalent mass has no unit but gram equivalent mass has the unit g eq^{-1}

It is not always possible to apply the above mentioned definition which is

based on three references namely hydrogen, oxygen and chlorine, because we can not conceive of reactions involving only with those three references. Therefore, a more useful expression used to calculate gram equivalent mass is given below.

$$\text{Gram equivalent mass} = \frac{\text{Molar mass (g mol}^{-1}\text{)}}{\text{Equivalence factor (eq mol}^{-1}\text{)}}$$

On the basis of the above expression, let us classify chemical entities and find out the formula for calculating equivalent mass in the table below.

1.5.1 Equivalent Mass of Acids, Bases, Salts, Oxidising Agents and Reducing Agents

Chemical entity	Equivalent Factor(n)	Formula for calculating equivalent mass (E)	Example
Acids	basicity (no. of moles of ionisable H ⁺ ions present in 1 mole of the acid)	$E = \frac{\text{Molar mass of the acid}}{\text{Basicity of the acid}}$	$\begin{aligned} \text{H}_2\text{SO}_4 \text{ basicity} &= 2 \text{ eq mol}^{-1} \\ \text{Molar mass of H}_2\text{SO}_4 &= (2 \times 1) + (1 \times 32) + (4 \times 16) \\ &= 98 \text{ g mol}^{-1} \\ \text{Gram equivalent mass of H}_2\text{SO}_4 &= \frac{98}{2} \\ &= 49 \text{ g eq}^{-1} \end{aligned}$
Bases	Acidity (no. of moles of ionisable OH ⁻ ion present in 1 mole of the base)	$E = \frac{\text{Molar mass of the base}}{\text{Acidity of the base}}$	$\begin{aligned} \text{KOH acidity} &= 1 \text{ eq mol}^{-1} \\ \text{Molar mass of KOH} &= (1 \times 39) + (1 \times 16) + (1 \times 1) \\ &= 56 \text{ g mol}^{-1} \\ \text{Gram equivalent mass of KOH} &= \frac{56}{1} = 56 \text{ g eq}^{-1} \end{aligned}$
Oxidising agent (or) reducing agent	No. of moles of electrons gained (or) lost by one mole of the reagent during redox reaction	$E = \frac{\text{Molar mass of the oxidising (or) reducing agent}}{\text{No. of moles of electrons gained or lost by one mole of the oxidising (or) reducing agent}}$	<p>KMnO₄ is an oxidising agent, Molar mass of KMnO₄</p> $\begin{aligned} &= (1 \times 39) + (1 \times 55) + (4 \times 16) \\ &= 158 \text{ g mol}^{-1} \end{aligned}$ <p>In acid medium permanganate is reduced during oxidation and is given by the following equation, MnO₄⁻ + 8H⁺ + 5e⁻ → Mn²⁺ + 4H₂O ∴ n = 5 eq mol⁻¹.</p> <p>Gram equivalent mass of KMnO₄ = $\frac{158}{5}$ = 31.6 g eq⁻¹.</p>

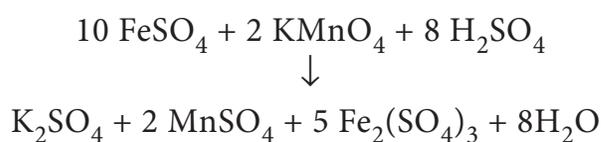
Mole concept requires a balanced chemical reaction to find out the amount of reactants involved in the chemical reaction while gram equivalent concept does not

require the same. We prefer to use mole concept for non-redox reactions and gram equivalent concept for redox reactions.

For example,

If we know the equivalent mass of KMnO_4 and anhydrous ferrous sulphate, without writing balanced chemical reaction we can straightaway say that 31.6 g of KMnO_4 reacts with 152 g of FeSO_4 using gram equivalent concept.

The same can also be explained on the basis of mole concept. The balanced chemical equation for the above mentioned reaction is



i.e. 2 moles ($2 \times 158 = 316$ g) of potassium permanganate reacts with 10 moles ($10 \times 152 = 1520$ g) of anhydrous ferrous sulphate.

\therefore 31.6 g KMnO_4 reacts with

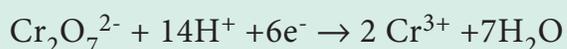
$$\frac{1520}{316} \times 31.6 = 152 \text{ g of FeSO}_4$$

Evaluate Yourself



4a) 0.456 g of a metal gives 0.606 g of its chloride. Calculate the equivalent mass of the metal.

4b) Calculate the equivalent mass of potassium dichromate. The reduction half-reaction in acid medium is,



1.6 Empirical Formula and Molecular Formula

Elemental analysis of a compound gives the mass percentage of atoms present in the compound. Using the mass percentage, we can determine the empirical formula of the compound. Molecular formula of the compound can be arrived at from the empirical formula using the molar mass of the compound.

Empirical formula of a compound is the formula written with the simplest ratio of the number of different atoms present in one molecule of the compound as subscript to the atomic symbol. Molecular formula of a compound is the formula written with the actual number of different atoms present in one molecule as a subscript to the atomic symbol.

Let us understand the empirical formula by considering acetic acid as an example.

The molecular formula of acetic acid is $\text{C}_2\text{H}_4\text{O}_2$

The ratio of C : H : O is 1 : 2 : 1 and hence the empirical formula is CH_2O .

1.6.1 Determination of Empirical Formula from Elemental Analysis Data :

Step 1: Since the composition is expressed in percentage, we can consider the total mass of the compound as 100 g and the percentage values of individual elements as mass in grams.

Step 2: Divide the mass of each element by its atomic mass. This gives the relative number of moles of various elements in the compound.

Step 3: Divide the value of relative number of moles obtained in the step 2 by the smallest number of them to get the simplest ratio.

Step 4: (only if necessary) in case the simplest ratios obtained in the step 3 are not whole numbers then they may be converted into whole number by multiplying by a suitable smallest number.

Example:

1. An acid found in Tamarind on analysis shows the following percentage composition: 32 % Carbon; 4 % Hydrogen; 64 % Oxygen. Find the empirical formula of the compound.

Element	Percentage	molar mass	Relative no. of moles	Simplest ratio	Simplest ratio (in whole nos)
C	32	12	$\frac{32}{12} = 2.66$	$\frac{2.66}{2.66} = 1$	2
H	4	1	$\frac{4}{1} = 4$	$\frac{4}{2.66} = 1.5$	3
O	64	16	$\frac{64}{16} = 4$	$\frac{4}{2.66} = 1.5$	3

The empirical formula is $C_2H_3O_3$

2. An organic compound present in vinegar has 40 % carbon, 6.6 % hydrogen and 53.4 % oxygen. Find the empirical formula of the compound.

Element	Percentage	Atomic Mass	Relative no. of moles	Simplest ratio	Simplest ratio (in whole no)
C	40	12	$\frac{40}{12} = 3.3$	$\frac{3.3}{3.3} = 1$	1
H	6.6	1	$\frac{6.6}{1} = 6.6$	$\frac{6.6}{3.3} = 2$	2
O	53.4	16	$\frac{53.4}{16} = 3.3$	$\frac{3.3}{3.3} = 1$	1

The empirical formula is CH_2O

Evaluate Yourself



- 5) A Compound on analysis gave the following percentage composition C=54.55%, H=9.09%, O=36.36%. Determine the empirical formula of the compound.

Molecular formula of a compound is a whole number multiple of the empirical formula. The whole number can be calculated from the molar mass of the compound using the following expression

$$\text{Whole number (n)} = \frac{\text{Molar mass of the compound}}{\text{Calculated empirical formula mass}}$$

1.6.2 Calculation of Molecular Formula from Empirical Formula:

Compound	Empirical Formula	Molar mass	Empirical Formula mass	Whole number (n)	Molecular formula
Acetic acid	CH ₂ O	60	30	$\frac{60}{30} = 2$	(CH ₂ O) × 2 C ₂ H ₄ O ₂
Hydrogen Peroxide	HO	34	17	$\frac{34}{17} = 2$	(HO) × 2 H ₂ O ₂
Lactic acid	CH ₂ O	90	30	$\frac{90}{30} = 3$	(CH ₂ O) × 3 C ₃ H ₆ O ₃
Tartaric acid	C ₂ H ₃ O ₃	150	75	$\frac{150}{75} = 2$	(C ₂ H ₃ O ₃) × 2 C ₄ H ₆ O ₆
Benzene	CH	78	13	$\frac{78}{13} = 6$	(CH) × 6 C ₆ H ₆

Let us understand the calculations of molecular formula from the following example.

Two organic compounds, one present in vinegar (molar mass: 60 g mol⁻¹), another one present in sour milk (molar mass : 90 g mol⁻¹) have the following mass percentage composition. C-40%, H-6.6% ; O-53.4%. Find their molecular formula.

Since both compounds have same mass percentage composition, their empirical formula are the same as worked out in the example **problem no 2** . Empirical formula is CH₂O. Calculated empirical formula mass (CH₂O) = 12 + (2×1) + 16 = 30 g mol⁻¹.

Formula for the compound present in vinegar

$$n = \frac{\text{Molar mass}}{\text{calculated empirical formula mass}} = \frac{60}{30} = 2$$

$$\begin{aligned} \therefore \text{Molecular formula} &= (\text{CH}_2\text{O})_2 \\ &= \text{C}_2\text{H}_4\text{O}_2 \\ &\text{(acetic acid)} \end{aligned}$$

Calculation of molecular formula for the compound present in sour milk.

$$n = \frac{\text{Molar mass}}{30} = \frac{90}{30} = 3$$

$$\begin{aligned} \text{Molecular formula} &= (\text{CH}_2\text{O})_3 \\ &= \text{C}_3\text{H}_6\text{O}_3 \\ &\text{(lactic acid)} \end{aligned}$$

Evaluate Yourself

6) Experimental analysis of a compound containing the elements x,y,z on analysis gave the following data. x = 32 %, y = 24 %, z = 44 %. The relative number of atoms of x, y and z are 2, 1 and 0.5, respectively. (Molecular mass of the compound is 400 g) Find out.

- The atomic masses of the element x,y,z.
- Empirical formula of the compound and
- Molecular formula of the compound.

1.7 Stoichiometry

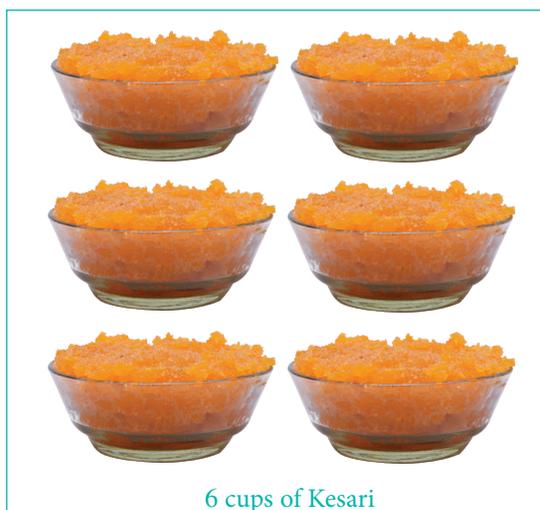
Have you ever noticed the preparation of *kesari* at your home? In one of the popular methods for the preparation of *kesari*, the required ingredients to prepare six cups of *kesari* are as follows.

- 1) Rava - 1 cup
- 2) Sugar - 2 cups
- 3) Ghee - $\frac{1}{2}$ cup
- 4) Nuts and Dry fruits - $\frac{1}{4}$ cup

Otherwise,

$$1 \text{ cup rava} + 2 \text{ cups sugar} + \frac{1}{2} \text{ cup ghee} + \frac{1}{4} \text{ cup nuts and dry fruits} \rightarrow 6 \text{ cups kesari.}$$

From the above information, we will be able to calculate the amount of



ingredients that are required for the preparation of 3 cups of kesari as follows

$$\frac{1 \text{ cup rava}}{6 \text{ cups kesari}} \times 3 \text{ cups kesari} = \frac{1}{2} \text{ cup rava}$$

Alternatively, we can calculate the amount of kesari obtained from 3 cups rava as below.

$$\frac{6 \text{ cups kesari}}{1 \text{ cup rava}} \times 3 \text{ cups rava} = 18 \text{ cups kesari}$$

Similarly, we can calculate the required quantity of other ingredients too.

We can extend this concept to perform stoichiometric calculations for a chemical reaction. In Greek, *stoicheion* means element and *metron* means measure that is, **stoichiometry gives the numerical relationship between chemical quantities in a balanced chemical equation.** By applying the concept of stoichiometry, we can calculate the amount of reactants required to prepare a specific amount of a product and vice versa using balanced chemical equation.

Let us consider the following chemical reaction.



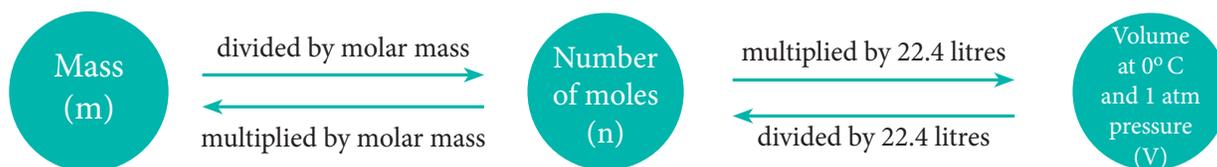
From this equation, we learnt that 1 mole of carbon reacts with 1 mole of oxygen molecule to form 1 mole of carbon dioxide.

$$1 \text{ mole of C} \equiv 1 \text{ mole of O}_2 \equiv 1 \text{ mole of CO}_2$$

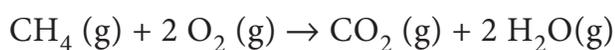
The symbol ' \equiv ' means '**stoichiometrically equal to**'

1.7.1 Stoichiometric Calculations:

Stoichiometry is the quantitative relationship between reactants and products in a balanced chemical equation in moles. The quantity of reactants and products can be expressed in moles or in terms of mass unit or as volume. These three units are inter convertible.



Let us explain these conversions by considering the combustion reaction of methane as an example. The balanced chemical equation is,



CH ₄ (g) + 2 O ₂ (g) → CO ₂ (g) + 2 H ₂ O(g)				
Content	Reactants		Products	
	CH ₄ (g)	O ₂ (g)	CO ₂ (g)	H ₂ O(g)
Stoichiometric coefficients	1	2	1	2
Mole-mole relationship	1 mole	2 moles	1 mole	2 moles
Mass-mass relationship = no. of mole × molar mass	1 mol × 16 g mol ⁻¹ 16 g	2 mol × 32 g mol ⁻¹ 64 g	1 mol × 44 g mol ⁻¹ 44 g	2 mol × 18 g mol ⁻¹ 36 g
mass - volume relationship mass of reactants = No. of moles × molar mass of reactants Volume of product (1 mole of any gas occupy a volume of 22.4 litre at 273 K and 1 atm pressure)	16 g	64 g	22.4 L	44.8 L
Volume - volume relationship	1 × 22.4 L 22.4 L	2 × 22.4 L 44.8 L	1 × 22.4 L 22.4 L	2 × 22.4 L 44.8 L

Calculations based on Stoichiometry

1. How many moles of hydrogen is required to produce 10 moles of ammonia?

The balanced stoichiometric equation for the formation of ammonia is



As per the stoichiometric equation,

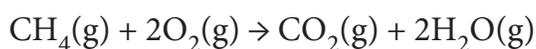
to produce 2 moles of ammonia, 3 moles of hydrogen are required

∴ to produce 10 moles of ammonia,

$$\frac{3 \text{ moles of H}_2}{2 \text{ moles of NH}_3} \times 10 \text{ moles of NH}_3$$

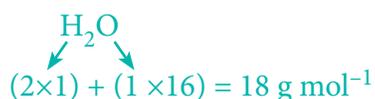
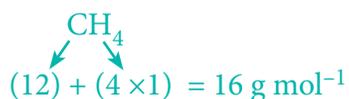
= 15 moles of hydrogen are required.

2. Calculate the amount of water produced by the combustion of 32 g of methane.



As per the stoichiometric equation,

Combustion of 1 mole (16 g) CH_4 produces 2 moles ($2 \times 18 = 36$ g) of water.

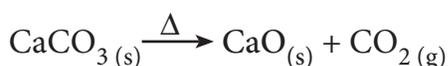


Combustion of 32 g CH_4 produces

$$\frac{36 \text{ g H}_2\text{O}}{16 \text{ g CH}_4} \times 32 \text{ g CH}_4 = 72 \text{ g of water}$$

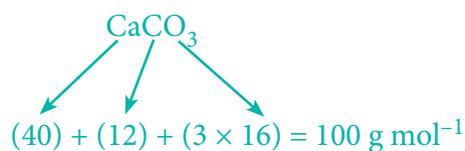
3. How much volume of carbon dioxide is produced when 50 g of calcium carbonate is heated completely under standard conditions?

The balanced chemical equation is,



As per the stoichiometric equation,

1 mole (100g) CaCO_3 on heating produces 1 mole CO_2



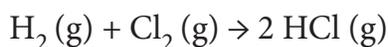
At STP, 1 mole of CO_2 occupies a volume of 22.7 litres

∴ At STP, 50 g of CaCO_3 on heating produces,

$$\frac{22.7 \text{ litres of CO}_2}{100 \text{ g CaCO}_3} \times 50 \text{ g CaCO}_3 = 11.35 \text{ litres of CO}_2$$

4. How much volume of chlorine is required to form 11.2 L of HCl at 273 K and 1 atm pressure?

The balanced equation for the formation of HCl is



As per the stoichiometric equation, under given conditions,

To produce 2 moles of HCl, 1 mole of chlorine gas is required

To produce 44.8 litres of HCl, 22.4 litres of chlorine gas are required.

∴ To produce 11.2 litres of HCl,

$$\frac{22.4 \text{ L Cl}_2}{44.8 \text{ L of HCl}} \times 11.2 \text{ L of HCl}$$

= 5.6 litres of chlorine are required.

5. Calculate the percentage composition of the elements present in magnesium carbonate. How many kilogram of CO₂ can be obtained by heating 1 kg of 90 % pure magnesium carbonate.

The balanced chemical equation is



Molar mass of MgCO₃ is 84 g mol⁻¹.

84 g MgCO₃ contain 24 g of Magnesium.

∴ 100 g of MgCO₃ contain

$$\frac{24 \text{ g Mg}}{84 \text{ g MgCO}_3} \times 100 \text{ g MgCO}_3$$

= 28.57 g Mg.

i.e. percentage of magnesium

= 28.57 %.

84 g MgCO₃ contain 12 g of carbon



∴ 100 g MgCO₃ contain

$$\frac{12 \text{ g C}}{84 \text{ g MgCO}_3} \times 100 \text{ g MgCO}_3$$

= 14.29 g of carbon.

∴ Percentage of carbon

= 14.29 %.

84 g MgCO₃ contain 48 g of oxygen

∴ 100 g MgCO₃ contains

$$\frac{48 \text{ g O}}{84 \text{ g MgCO}_3} \times 100 \text{ g MgCO}_3$$

= 57.14 g of oxygen.

∴ Percentage of oxygen

= 57.14 %.

As per the stoichiometric equation,

84 g of 100 % pure MgCO₃ on heating gives 44 g of CO₂.

∴ 1000 g of 90 % pure MgCO₃ gives

$$= \frac{44 \text{ g}}{84 \text{ g} \times 100 \%} \times 90 \% \times 1000 \text{ g}$$

= 471.43 g of CO₂

= 0.471 kg of CO₂

1.7.2 Limiting Reagents:

Earlier, we learnt that the stoichiometry concept is useful in predicting the amount of product formed in a given chemical reaction. If the reaction is carried out with stoichiometric quantities of reactants, then all the reactants will be converted into products. On the other hand, when a reaction is carried out using non-stoichiometric quantities of the reactants, the product yield will be determined by the reactant that is completely consumed. It limits the further reaction from taking place and is called as the limiting reagent. The other reagents which are in excess are called the excess reagents.

Recall the analogy that we used in stoichiometry concept i.e. kesari preparation,

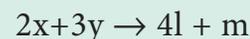
As per the recipe requirement, 2 cups of sugar are needed for every cup of rava. Consider a situation where 8 cups of sugar and 3 cups of rava are available (all other ingredients are in excess), as per the cooking recipe, we require 3 cups of rava and 6 cups of sugar to prepare 18 cups of kesari. Even though we have 2 more cups of sugar left, we cannot make any more quantity of Kesari as there is no rava available and hence rava limits the quantity of Kesari in this case. Extending this analogy for the chemical reaction in which three moles of sulphur are allowed to react with twelve moles of fluorine to give sulfur hexafluoride.

The balanced equation for this reaction is, $S + 3F_2 \rightarrow SF_6$

Evaluate Yourself



7) The balanced equation for a reaction is given below



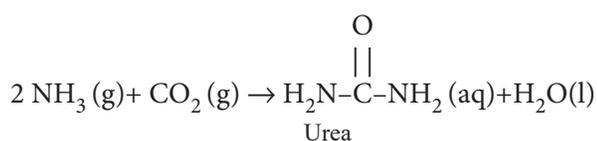
When 8 moles of x react with 15 moles of y, then

- Which is the limiting reagent?
- Calculate the amount of products formed.
- Calculate the amount of excess reactant left at the end of the reaction.

As per the stoichiometry,

1 mole of sulphur reacts with 3 moles of fluorine to form 1 mole of sulphur hexafluoride and therefore 3 moles of sulphur reacts with 9 moles of fluorine to form 3 moles of sulphur hexafluoride. In this case, all available sulphur gets consumed and therefore it limits the further reaction. Hence sulphur is the limiting reagent and fluorine is the excess reagent. The remaining three moles of fluorine are in excess and do not react.

Urea, a commonly used nitrogen based fertilizer, is prepared by the reaction between ammonia and carbon dioxide as follows.



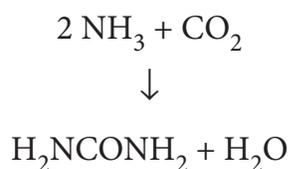
In a process, 646 g of ammonia is allowed to react with 1.144 kg of CO_2 to form urea.

- 1) If the entire quantity of all the reactants is not consumed in the reaction

which is the limiting reagent ?

- 2) Calculate the quantity of urea formed and unreacted quantity of the excess reagent.

The balanced equation is



Answer :

1. The entire quantity of ammonia is consumed in the reaction. So

ammonia is the limiting reagent. Some quantity of CO_2 remains unreacted, so CO_2 is the excess reagent.

- 2) Quantity of urea formed

$$= \text{number of moles of urea formed} \times \text{molar mass of urea}$$

$$= 19 \text{ moles} \times 60 \text{ g mol}^{-1}$$

$$= 1140 \text{ g} = 1.14 \text{ kg}$$

Excess reagent leftover at the end of the reaction is carbon dioxide.

Amount of carbon dioxide leftover

$$= \text{number of moles of } \text{CO}_2 \text{ left over} \times \text{molar mass of } \text{CO}_2$$

$$= 7 \text{ moles} \times 44 \text{ g mol}^{-1}$$

$$= 308 \text{ g.}$$

	Reactants		Products	
	NH_3	CO_2	Urea	H_2O
Stoichiometric coefficients	2	1	1	1
Number of moles of reactants allowed to react $n = \frac{\text{Mass}}{\text{Molar mass}}$	$\frac{646}{17} = 38 \text{ moles}$	$\frac{1144}{44} = 26 \text{ moles}$	-	-
Actual number of moles consumed during reaction Ratio (2 : 1)	38 moles	19 moles	-	-
No. of moles of product thus formed	-	-	19 moles	19 moles
No. of moles of reactant left at the end of the reaction	-	7 moles	-	-

1.8 Redox Reactions

When an apple is cut, it turns brown after sometime. Do you know the reason behind this colour change? It is because of a chemical reaction called oxidation. We come across oxidation reactions in our daily life. For example 1) burning of LPG gas 2) rusting of iron



Fig. 1.4 Oxidation reactions in daily life

- 3) Oxidation of carbohydrates, lipids, etc. into CO_2 and H_2O to produce energy in the living organisms.

All oxidation reactions are accompanied by reduction reactions and vice versa. Such reactions are called redox reactions. As per the classical concept, addition of oxygen (or) removal of hydrogen is called oxidation and the reverse is called reduction.

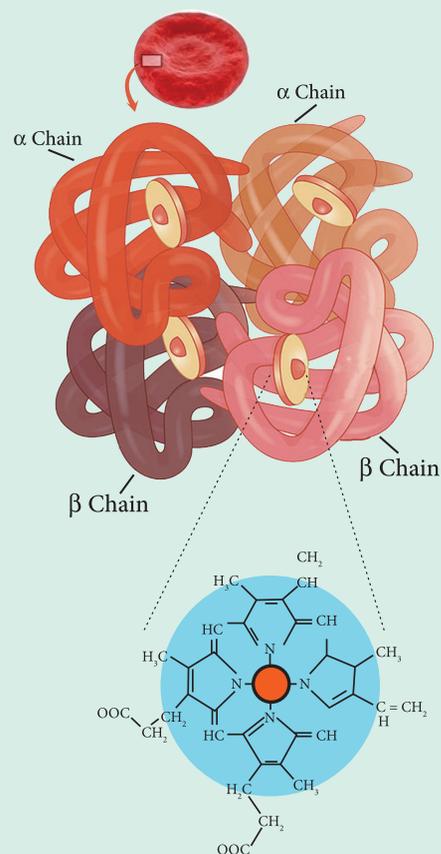


Haemoglobin and oxygen transport

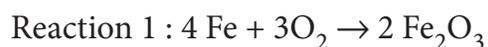
Even a small amount of oxygen present in air leads to the rusting of iron, i.e. iron is oxidised to Fe^{3+} . But the Fe^{2+} present in haemoglobin which binds oxygen during transport of oxygen from lungs to tissues never gets oxidised. Do you know why?

The answer lies in the structural features of haemoglobin. Haemoglobin contains four sub units each with a porphyrin ring (heme) attached to the protein (globin) molecule. In this structure, the iron (Fe^{2+}) forms a co-ordination complex with an octahedral geometry. The four positions of the octahedron are occupied by porphyrin rings, fifth position is filled by imidazole ring of a histidine residue and the sixth position is utilized for binding the oxygen molecule. Generally the Fe^{2+} in heme is susceptible to oxidation. Since the Fe^{2+} ion in haemoglobin is surrounded by the globin protein chain that provides a hydrophobic environment, the oxidation of Fe^{2+} becomes difficult. However, 3% of haemoglobin is oxidised to methemoglobin (haemoglobin where the iron is present in Fe^{3+} state and oxygen does not bind to this) daily. The enzyme methemoglobin reductase reduces it back to haemoglobin.

Cyanide poisoning: While oxygen binds reversibly to haemoglobin, cyanide binds irreversibly to haemoglobin and blocks oxygen binding. As a result the transport of oxygen from the lungs to tissues is stopped. It leads to the quick death of the person.



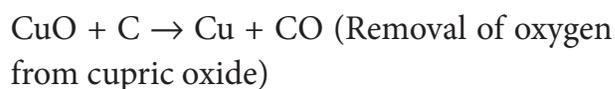
Consider the following two reactions.



Both these reactions are oxidation reactions as per the classical concept.

In the first reaction which is responsible for the rusting of iron, the oxygen adds on to the metal, iron. In the second reaction, hydrogen is removed from Hydrogen sulphide (H_2S). Identity which species gets reduced.

Consider the following two reactions in which the removal of oxygen and addition of hydrogen take place respectively. These reactions are called reduction reactions as per the classical concept.



Oxidation-reduction reactions i.e. redox reactions are not always associated with oxygen or hydrogen. In such cases, the process can be explained on the basis of electrons. The reaction involving loss of electron is termed oxidation and gain of electron is termed reduction.

For example,



Redox reactions can be better explained using oxidation numbers.

1.8.1 Oxidation Number:

It is defined as the imaginary charge left on the atom when all other atoms of the compound have been removed in their usual oxidation states that are assigned according to set of rules. A term that is often used interchangeably with oxidation number is oxidation state

- 1) The oxidation state of a free element (i.e. in its uncombined state) is zero.

Example : each atom in H_2 , Cl_2 , Na , S_8 have the oxidation number of zero.

- 2) For a monatomic ion, the oxidation state is equal to the net charge on the ion.

Example : The oxidation number of sodium in Na^+ is +1.

The oxidation number of chlorine in Cl^- is -1.

- 3) The algebraic sum of oxidation states of all atoms in a molecule is equal to zero, while in ions, it is equal to the net charge on the ion.

Example:

In H_2SO_4 ; $2 \times$ (oxidation number of hydrogen) + (oxidation number of S) + 4 (oxidation number of oxygen) = 0.

In SO_4^{2-} ; (oxidation number of S) + 4 (oxidation number of oxygen) = -2.

- 4) Hydrogen has an oxidation number of +1 in all its compounds except in metal hydrides where it has -1 value.

Example:

Oxidation number of hydrogen in hydrogen chloride (HCl) is + 1.

Oxidation number of hydrogen in sodium hydride (NaH) is -1.

- 5) Fluorine has an oxidation state of - 1 in all its compounds.
- 6) The oxidation state of oxygen in most compounds is -2. Exceptions are peroxides, super oxides and compounds with fluorine.

Example : Oxidation number of oxygen,

i) in water (H₂O) is -2.

ii) in hydrogen peroxide (H₂O₂) is -1.

$$2(+1) + 2x = 0; \quad \Rightarrow 2x = -2; \quad \Rightarrow x = -1$$

iii) in super oxides such as KO₂ is $-\frac{1}{2}$

$$+1 + 2x = 0; \quad 2x = -1; \quad x = -\frac{1}{2}$$

iv) in oxygen difluoride (OF₂) is + 2.

$$x + 2(-1) = 0; \quad x = +2$$

- 7) Alkali metals have an oxidation state of + 1 and alkaline earth metals have an oxidation state of + 2 in all their compounds.

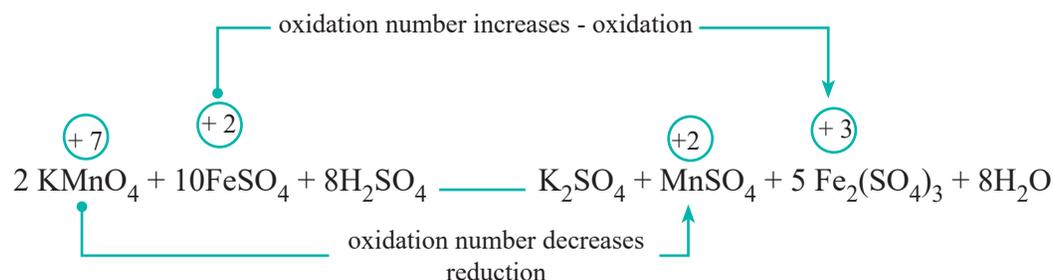
Calculation of oxidation number using the above rules.

Sl.No	Oxidation number of the element	In the compound	Calculation
1	C	CO ₂	$x + 2(-2) = 0$ $x = +4$
2	S	H ₂ SO ₄	$2(+1) + x + 4(-2) = 0$ $2 + x - 8 = 0$ $x = +6$
3	Cr	Cr ₂ O ₇ ²⁻	$2x + 7(-2) = -2$ $2x - 14 = -2$ $x = +6$
4	C	CH ₂ F ₂	$x + 2(+1) + 2(-1) = 0$ $x = 0$
5	S	SO ₂	$x + 2(-2) = 0$ $x = +4$

Redox reactions in terms of oxidation numbers

During redox reactions, the oxidation number of elements changes. A reaction in which oxidation number of the element increases is called oxidation. A reaction in which it decreases is called reduction.

Consider the following reaction



In this reaction, manganese in potassium permanganate (KMnO_4) favours the oxidation of ferrous sulphate (FeSO_4) into ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$) by gaining electrons and thereby gets reduced. Such reagents are called oxidising agents or oxidants. Similarly, the reagents which facilitate reduction by releasing electrons and get oxidised are called reducing agents.

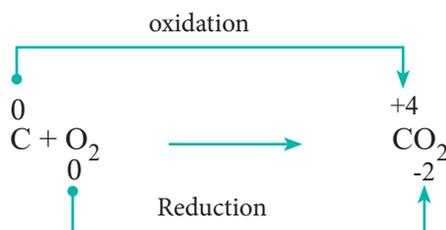
1.8.2 Types of Redox Reactions

Redox reactions are classified into the following types.

1. Combination reactions:

Redox reactions in which two substances combine to form a single compound are called combination reaction.

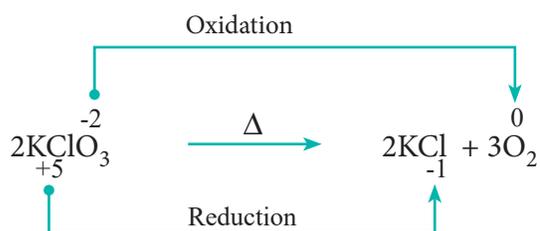
Example:



2. Decomposition reactions:

Redox reactions in which a compound breaks down into two or more components are called decomposition reactions. These reactions are opposite to combination reactions. In these reactions, the oxidation number of the different elements in the same substance is changed.

Example:



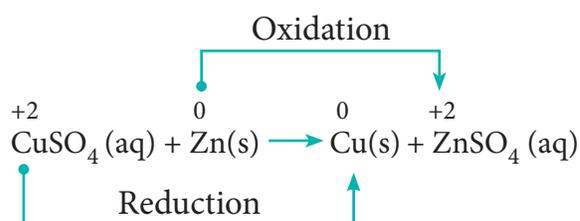
3. Displacement reactions:

Redox reactions in which an ion (or an atom) in a compound is replaced by an ion (or atom) of another element are called displacement reactions. They are further classified into (i) metal displacement reactions (ii) non-metal displacement reactions.

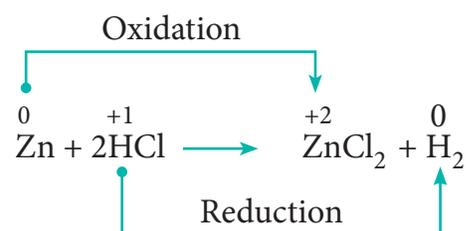
(i) Metal displacement reactions:

Place a zinc metal strip in an aqueous copper sulphate solution taken in a beaker. Observe the solution, the intensity of blue colour of the solution slowly reduced and finally disappeared.

The zinc metal strip became coated with brownish metallic copper. This is due to the following metal displacement reaction.



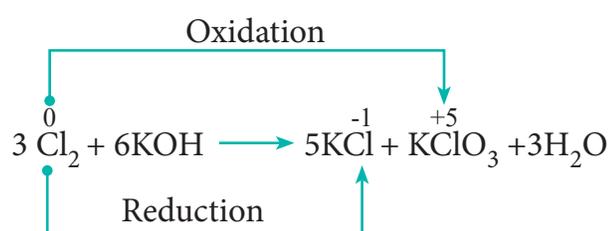
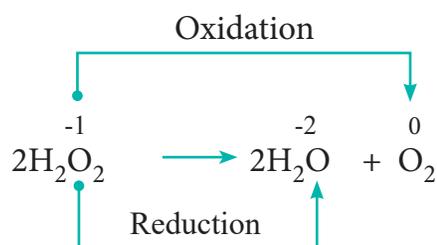
ii) Non-metal displacement



4. Disproportionation reaction (Auto redox reactions)

In some redox reactions, the same compound can undergo both oxidation and reduction. In such reactions, the oxidation state of one and the same element is both increased and decreased. These reactions are called disproportionation reactions.

Examples:

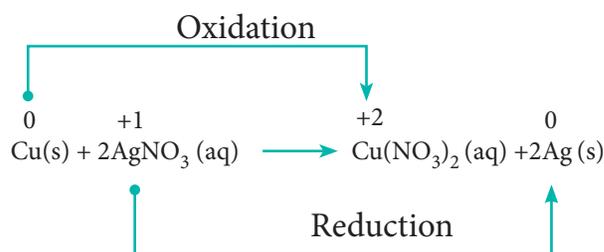


5. Competitive electron transfer reaction

In metal displacement reactions, we learnt that zinc replaces copper from copper sulphate solution. Let us examine whether the reverse reaction takes place or not. As discussed earlier, place a metallic copper strip in zinc sulphate solution. If copper replaces zinc from zinc sulphate solution, Cu^{2+} ions would be released into the solution and the colour of the solution

would change to blue. But no such change is observed. Therefore, we conclude that among zinc and copper, zinc has more tendency to release electrons and copper to accept the electrons.

Let us extend the reaction to copper metal and silver nitrate solution. Place a strip of metallic copper in silver nitrate solution taken in a beaker. After some time, the solution slowly turns blue. This is due to the formation of Cu^{2+} ions, i.e. copper replaces silver from silver nitrate. The reaction is,



It indicates that between copper and silver, copper has the tendency to release electrons and silver to accept electrons.

From the above experimental observations, we can conclude that among the three metals, namely, zinc, copper and silver, the electron releasing tendency is in the following order.

Zinc > Copper > Silver

This kind of competition for electrons among various metals helps us to design (galvanic) cells. In XII standard we will study the galvanic cell in detail.

1.8.3. Balancing (the Equation) of Redox Reactions

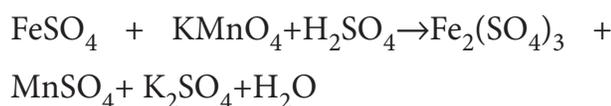
The two methods for balancing the equation of redox reactions are as follows.

- i) The oxidation number method
- ii) Ion-electron method / half reaction method.

Both are based on the same principle: In oxidation - reduction reactions the total number of electrons donated by the reducing agent is equal to the total number of electrons gained by the oxidising agent.

Oxidation number method

In this method, the number of electrons lost or gained in the reaction is calculated from the oxidation numbers of elements before and after the reaction. Let us consider the oxidation of ferrous sulphate by potassium permanganate in acid medium. The unbalanced chemical equation is,



Step 1

Using oxidation number concept, identify the reactants (atom) which undergo oxidation and reduction.

Ion - Electron method

This method is used for ionic redox reactions.

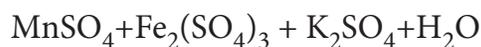
Step 1

Using oxidation number concept, find out the reactants which undergo oxidation and reduction.

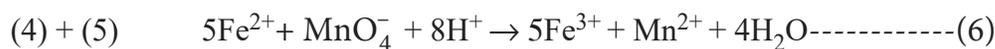
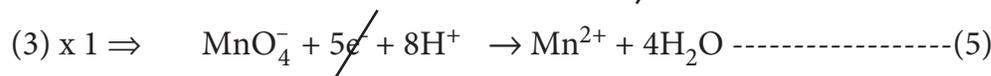
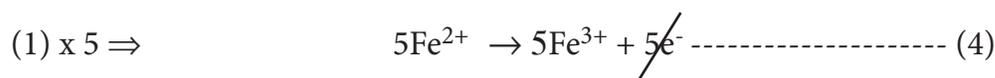
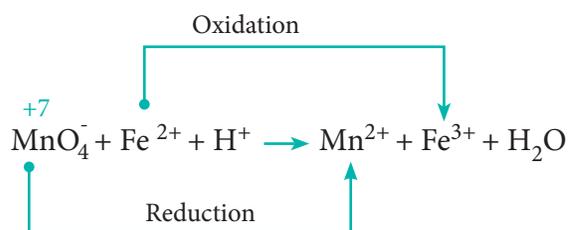
Step 2

Write two separate half equations for oxidation and reduction reaction,

Let us consider the same example which we have already discussed in oxidation number method.



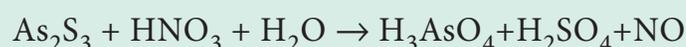
The ionic form of this reaction is,



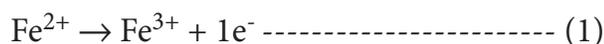
Evaluate Yourself



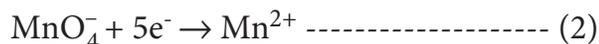
8) Balance the following equation using oxidation number method



The two half reactions are,



and

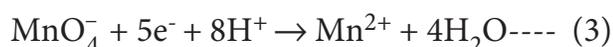


Balance the atoms and charges on both sides of the half reactions.

Equation (1) \Rightarrow No changes i.e.,



Equation (2) \Rightarrow 4'O' on the reactant side, therefore add 4H₂O on the product side, to balance 'H' - add, 8H⁺ in the reactant side



Step 3

Equate both half reactions such that the number of electrons lost is equal to number of electrons gained.

Addition of two half reactions gives the balanced equation represented by equation (6).

SUMMARY

Chemistry plays a major role in providing needs of human life in our day-to-day life. All things that we come across in life are made of matter. Anything that has mass and occupies space is called matter. Matter is classified based on the physical state and by chemical composition. An element consists of only one type of atom. Compounds contain two or more atoms of same or different elements and their properties are different from those of its constituent elements.

Atoms are too small to measure their masses directly. The IUPAC introduced relative scale of mass based on a standard atom C-12. One twelfth of the mass of a Carbon-12 atom in its ground state is called as Unified atomic mass. 1 amu (or) $1\text{u} \approx 1.6605 \times 10^{-27}$ kg. Relative atomic mass is defined as the ratio of the average atomic mass to the unified atomic mass unit. Average atomic mass of an element is the average of the atomic masses of all its naturally occurring isotopes. Molecular mass is the ratio of the mass of a molecule to the unified atomic mass unit. Relative molecular mass is obtained by adding the relative atomic masses of its constituent atoms.

Amounts of substances are usually expressed in moles. A mole is the amount of substance which contains as many elementary entities as there are in 12 gram of Carbon-12 isotope. Avogadro number is the total number of entities present in one mole of any substance and is equal to 6.022×10^{23} . Molar mass is the mass of one mole of that substance expressed in

g mol^{-1} . One mole of an ideal gas occupies a volume of 22.4 litre at 273 K and 1 atm pressure. Similar to the mole concept, the concept of equivalent mass is also used in analytical chemistry. Gram equivalent mass is the mass of an element (compound/ion) that combines or displaces 1.008 g hydrogen, 8 g oxygen or 35.5 g chlorine. Elemental analysis of a compound gives the mass percentage of atoms from which empirical and molecular formula are calculated. Empirical formula is the simplest ratio of the number of different atoms present in one molecule of the compound. Molecular formula is the formula written with the actual number of different atoms present in one molecule. A quantitative relationship between reactants and products can be understood from stoichiometry. Stoichiometry gives the numerical relationship between chemical quantities in a balanced equation. When a reaction is carried out using non-stoichiometric quantities of the reactants, the product yield will be determined by the reactant that is completely consumed and is called the limiting reagent. It limits the further reaction to take place. The other reagent which is in excess is called the excess reagent.

The reaction involving loss of electron is oxidation and gain of electron is reduction. Usually both these reactions take place simultaneously and are called as redox reactions. These redox reactions can be explained using oxidation number concept. Oxidation number is the imaginary charge left on the atom when all other atoms of the compound have



been removed in their usual oxidation states. A reaction in which oxidation number of the element increases is called oxidation and decreases is called reduction.

Redox reactions in which

- two substances combine to form compound are called combination reaction.
- a compound breaks down into two (or) more components is called decomposition reaction
- an ion (or atom) in a compound is replaced by an atom (or ion) of another element are called displacement reactions
- the same compound can undergo both oxidation and reduction and the oxidation state of one and the same element is both increased and decreased called disproportionate reactions.
- competition for electrons occurs between various metals is called competitive electron transfer reactions.

The equation of redox reaction is balanced either by oxidation number method or by ion-electron method.

EVALUATION



I. Choose the best answer.

- 40 ml of methane is completely burnt using 80 ml of oxygen at room temperature. The volume of gas left after cooling to room temperature is
(a) 40 ml CO₂ gas (b) 40 ml CO₂ gas and 80 ml H₂O gas
(c) 60 ml CO₂ gas and 60 ml H₂O gas (d) 120 ml CO₂ gas
- An element X has the following isotopic composition ²⁰⁰X = 90 %, ¹⁹⁹X = 8 % and ²⁰²X = 2 %. The weighted average atomic mass of the element X is closest to
(a) 201 u (b) 202 u
(c) 199 u (d) 200 u
- Assertion : Two mole of glucose contains 12.044×10^{23} molecules of glucose
Reason : Total number of entities present in one mole of any substance is equal to 6.02×10^{22}
(a) both assertion and reason are true and the reason is the correct explanation of assertion
(b) both assertion and reason are true but reason is not the correct explanation of assertion
(c) assertion is true but reason is false
(d) both assertion and reason are false
- Carbon forms two oxides, namely carbon monoxide and carbon dioxide. The equivalent mass of which element remains constant?
(a) Carbon (b) oxygen
(c) both carbon and oxygen (d) neither carbon nor oxygen
- The equivalent mass of a trivalent metal element is 9 g eq⁻¹ the molar mass of its anhydrous oxide is
(a) 102 g (b) 27 g (c) 270 g (d) 78 g



6. The number of water molecules in a drop of water weighing 0.018 g is
(a) 6.022×10^{26} (b) 6.022×10^{23}
(c) 6.022×10^{20} (d) 9.9×10^{22}
7. 1 g of an impure sample of magnesium carbonate (containing no thermally decomposable impurities) on complete thermal decomposition gave 0.44 g of carbon dioxide gas. The percentage of impurity in the sample is
(a) 0 % (b) 4.4 % (c) 16 % (d) 8.4 %
8. When 6.3 g of sodium bicarbonate is added to 30 g of acetic acid solution, the residual solution is found to weigh 33 g. The number of moles of carbon dioxide released in the reaction is
(a) 3 (b) 0.75 (c) 0.075 (d) 0.3
9. When 22.4 litres of H_2 (g) is mixed with 11.2 litres of Cl_2 (g), each at 273 K at 1 atm the moles of HCl (g), formed is equal to
(a) 2 moles of HCl (g) (b) 0.5 moles of HCl (g)
(c) 1.5 moles of HCl (g) (d) 1 moles of HCl (g)
10. Hot concentrated sulphuric acid is a moderately strong oxidising agent. Which of the following reactions does not show oxidising behaviour?
(a) $\text{Cu} + 2\text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$
(b) $\text{C} + 2\text{H}_2\text{SO}_4 \rightarrow \text{CO}_2 + 2\text{SO}_2 + 2\text{H}_2\text{O}$
(c) $\text{BaCl}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + 2\text{HCl}$
(d) none of the above
11. Choose the disproportionation reaction among the following redox reactions.
(a) $3\text{Mg} (\text{s}) + \text{N}_2 (\text{g}) \rightarrow \text{Mg}_3\text{N}_2 (\text{s})$
(b) $\text{P}_4 (\text{s}) + 3 \text{NaOH} + 3\text{H}_2\text{O} \rightarrow \text{PH}_3 (\text{g}) + 3\text{NaH}_2\text{PO}_2 (\text{aq})$
(c) $\text{Cl}_2 (\text{g}) + 2\text{KI} (\text{aq}) \rightarrow 2\text{KCl} (\text{aq}) + \text{I}_2$
(d) $\text{Cr}_2\text{O}_3 (\text{s}) + 2\text{Al} (\text{s}) \rightarrow \text{Al}_2\text{O}_3 (\text{s}) + 2\text{Cr} (\text{s})$



19. Two 22.4 litre containers A and B contains 8 g of O_2 and 8 g of SO_2 respectively at 273 K and 1 atm pressure, then
- (a) Number of molecules in A and B are same
 - (b) Number of molecules in B is more than that in A.
 - (c) The ratio between the number of molecules in A to number of molecules in B is 2:1
 - (d) Number of molecules in B is three times greater than the number of molecules in A.
20. What is the mass of precipitate formed when 50 ml of 8.5 % solution of $AgNO_3$ is mixed with 100 ml of 1.865 % potassium chloride solution?
- (a) 3.59 g (b) 7 g (c) 14 g (d) 28 g
21. The mass of a gas that occupies a volume of 612.5 ml at room temperature and pressure ($25^0 C$ and 1 atm pressure) is 1.1g. The molar mass of the gas is
- (a) $66.25 g mol^{-1}$ (b) $44 g mol^{-1}$
(c) $24.5 g mol^{-1}$ (d) $662.5 g mol^{-1}$
22. Which of the following contain same number of carbon atoms as in 6 g of carbon-12.
- (a) 7.5 g ethane (b) 8 g methane
(c) both (a) and (b) (d) none of these
23. Which of the following compound(s) has /have percentage of carbon same as that in ethylene (C_2H_4)
- (a) propene (b) ethyne
(c) benzene (d) ethane
24. Which of the following is/are true with respect to carbon -12.
- (a) relative atomic mass is 12 u
(b) oxidation number of carbon is +4 in all its compounds.
(c) 1 mole of carbon-12 contain 6.022×10^{22} carbon atoms.
(d) all of these



25. Which one of the following is used as a standard for atomic mass.

- (a) ${}_6\text{C}^{12}$ (b) ${}_7\text{C}^{12}$ (c) ${}_6\text{C}^{13}$ (d) ${}_6\text{C}^{14}$

II. Write brief answer to the following questions.

26) Define relative atomic mass.

27) What do you understand by the term mole.

28) Define equivalent mass.

29) What do you understand by the term oxidation number.

30) Distinguish between oxidation and reduction.

31) Calculate the molar mass of the following compounds.

- i) Urea [$\text{CO}(\text{NH}_2)_2$]
- ii) Acetone [CH_3COCH_3]
- iii) Boric acid [H_3BO_3]
- iv) Sulphuric acid [H_2SO_4]

32) The density of carbon dioxide is equal to 1.965 kgm^{-3} at 273 K and 1 atm pressure. Calculate the molar mass of CO_2 .

33) Which contains the greatest number of moles of oxygen atoms

- i) 1 mol of ethanol
- ii) 1 mol of formic acid
- iii) 1 mol of H_2O

34) Calculate the average atomic mass of naturally occurring magnesium using the following data

Isotope	Isotopic atomic mass	Abundance (%)
Mg^{24}	23.99	78.99
Mg^{25}	24.99	10.00
Mg^{26}	25.98	11.01

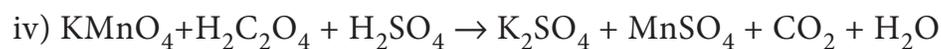
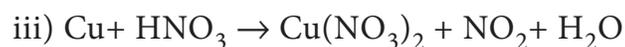
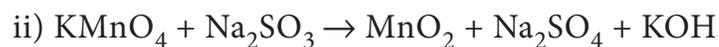
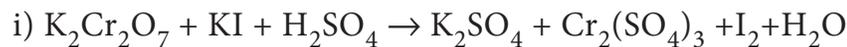


- 35) In a reaction $x + y + z_2 \rightarrow xyz_2$ identify the Limiting reagent if any, in the following reaction mixtures.
- (a) 200 atoms of x + 200 atoms of y + 50 molecules of z_2
 - (b) 1 mol of x + 1 mol of y + 3 mol of z_2
 - (c) 50 atoms of x + 25 atoms of y + 50 molecules of z_2
 - d) 2.5 mol of x + 5 mol of y + 5 mol of z_2
- 36) Mass of one atom of an element is 6.645×10^{-23} g. How many moles of element are there in 0.320 kg.
- 37) What is the difference between molecular mass and molar mass? Calculate the molecular mass and molar mass for carbon monoxide.
- 38) What is the empirical formula of the following ?
- i) Fructose ($C_6H_{12}O_6$) found in honey
 - ii) Caffeine ($C_8H_{10}N_4O_2$) a substance found in tea and coffee.
- 39) The reaction between aluminium and ferric oxide can generate temperatures up to 3273 K and is used in welding metals. (Atomic mass of Al = 27 u Atomic mass of O = 16 u)
- $2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$; If, in this process, 324 g of aluminium is allowed to react with 1.12 kg of ferric oxide.
- i) Calculate the mass of Al_2O_3 formed.
 - ii) How much of the excess reagent is left at the end of the reaction?
- 40) How many moles of ethane is required to produce 44 g of CO_2 (g) after combustion.
- 41) Hydrogen peroxide is an oxidising agent. It oxidises ferrous ion to ferric ion and reduced itself to water. Write a balanced equation.
- 42) Calculate the empirical and molecular formula of a compound containing 76.6% carbon, 6.38 % hydrogen and rest oxygen its vapour density is 47.

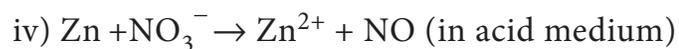
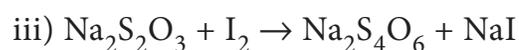
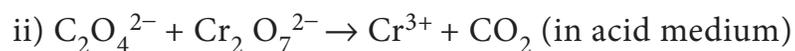
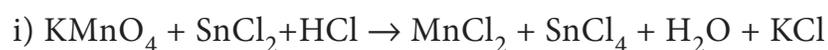


43) A Compound on analysis gave Na = 14.31% S = 9.97% H= 6.22% and O= 69.5% calculate the molecular formula of the compound, if all the hydrogen in the compound is present in combination with oxygen as water of crystallization. (molecular mass of the compound is 322).

44) Balance the following equations by oxidation number method

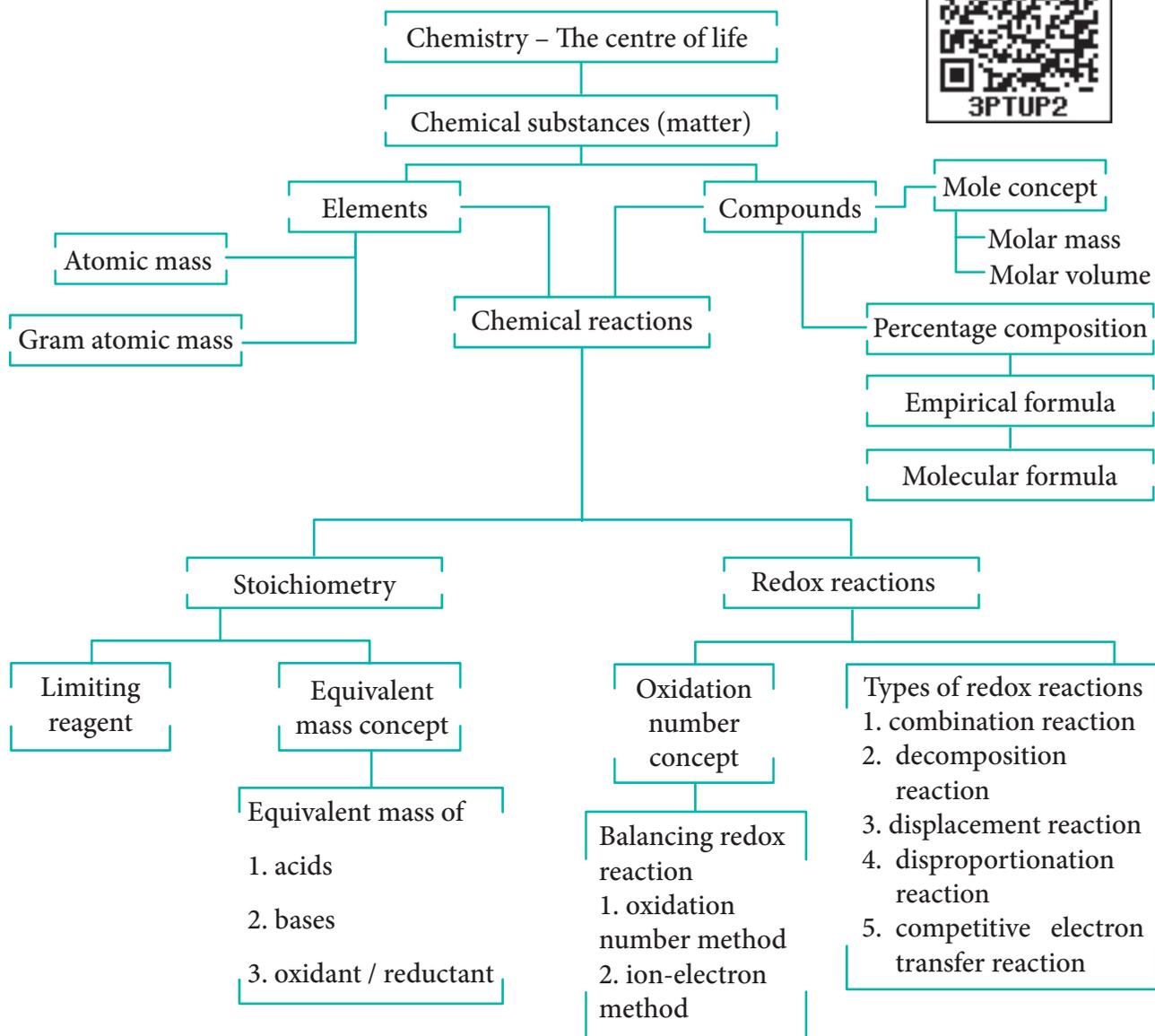


45) Balance the following equations by ion electron method.





CONCEPT MAP





ICT Corner

Calculation of Empirical and Molecular Formula

By using this tool you will be able to calculate the empirical and **molecular formula from the percentage composition of elements**

Please go to the URL <https://ggbm.at/FbUwkmUw> (or) Scan the QR code on the right side



TN_QR_ENG

Step – 1

Open the Browser and type the URL given (or) Scan the QR Code. You can see a GeoGebra Work book named “11th Standard Chemistry”. Open the worksheet named “Empirical Formula”. You will see a webpage as shown in the figure.

Step – 2

Find the serial number of the elements of the compound under examination from the table present on the right side of the page and enter it in the space provided (1). And enter their percentage of composition in the corresponding space (2)

Step – 3

Now you can see the molar mass, relative no. of moles and the simplest ratio all automatically calculated and filled in the corresponding boxes. If the simplest ratio contains fractions then use the slider (3) to choose a smallest number to bring the simplest ratio to whole number.

You can now see the calculated empirical formula (4)

Step – 4

In order to calculate the Molecular formula, enter the molar mass in the corresponding box (5). Now the ‘n’ will be displayed (6) and Molecular formula is displayed at the bottom (7)

DETERMINATION OF EMPIRICAL FORMULA FROM ELEMENTAL ANALYSIS DATA

Element	Percentage	Molar Mass	Relative No. of Moles	Simplest Ratio	Move the slider and fix Simplest ratio in whole no.
1st Element Serial No. 3 C	32	12.01	2.66	1	2
2nd Element Serial No. 1 H	4	1.01	3.96	1.5	3
3rd Element Serial No. 2 O	64	16	4	1.5	3

Choose the serial number of the given elements from the table and enter here

The Empirical formula = $C_2H_3O_3$

Calculated Empirical formula mass = $2 \times 12 + 3 \times 1 + 3 \times 16 = 75$

Enter the respective Percentage composition

Enter Molar Mass = 171

$n = \frac{\text{Molar mass (171)}}{\text{Calculated Empirical formula mass (75)}} = 2$

Molecular formula = $(C_2H_3O_3)_2$

Serial No.	Element
1	H
2	O
3	C
4	N
5	S
6	F
7	Cl
8	Br
9	I
10	Li
11	Na
12	K
13	Be
14	Mg
15	Ca
16	Cr
17	Mn
18	Fe
19	Co
20	Ni
21	Cu
22	Zn
23	Al
24	P
25	Ba
26	Si

Quantum Mechanical Model of Atom



Erwin Schrödinger
(1887 - 1961)

Erwin Schrödinger was awarded the Nobel Prize in physics in 1933 for “the discovery of new productive forms of atomic theory”. Schrödinger had wide interests starting from chemistry, physics, maths and botany. He was not satisfied with the quantum condition in Bohr's orbit theory and believed that atomic spectra should really be determined by some kind of eigenvalue problem and proposed the wave equation, now named after him.

Learning Objectives:



After studying this unit, students will be able to

- Recognise various atomic models
- Explain the dual behaviour of matter
- Derive de Broglie equation and solve numerical problems
- Explain Heisenberg's uncertainty principle and solve related problems
- Appreciate the significance of quantum numbers
- Summarise important features of quantum mechanical model of atom
- Draw the shapes of various atomic orbitals
- Explain the Aufbau principle
- Describe Hund's rule and Pauli's exclusion principle
- Apply the relevant rules for filling electrons in atoms and write the electronic configuration of various atoms



2.1 Introduction to atom models:

Let us recall the history of the development of atomic models from the previous classes. We know that all things are made of matter. The basic unit that makes up all matter is atom. The word 'atom' has been derived from the Greek word '*a-tomio*' meaning non-divisible. Atom was considered as non-divisible until the discovery of sub-atomic particles such as electron, proton and neutron. J. J. Thomson's cathode ray experiment revealed that atoms consist of negatively charged particles called electrons. He proposed that atom is a positively charged sphere in which the electrons are embedded like the seeds in the watermelon. Later, Rutherford's α -ray scattering experiment results proved that Thomson's model was wrong. Rutherford bombarded a thin gold foil with a stream of fast moving α -particles. It was observed that

- (i) most of the α -particles passed through the foil
- (ii) some of them were deflected through a small angle and
- (iii) very few α -particles were reflected back by 180°

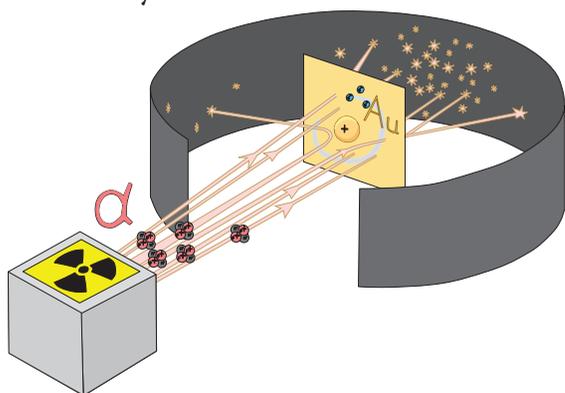


Figure. 2.1 Rutherford's α -ray scattering experiment

Based on these observations, he proposed that in an atom there is a tiny positively charged nucleus and the electrons are moving around the nucleus with high speed. The theory of electromagnetic radiation states that a moving charged particle should continuously lose its energy in the form of radiation. Therefore, the moving electron in an atom should continuously lose its energy and finally collide with nucleus resulting in the collapse of the atom. However, this doesn't happen and the atoms are stable. Moreover, this model does not explain the distribution of electrons around the nucleus and their energies.

2.1.1 Bohr atom model:

The work of Planck and Einstein showed that the energy of electromagnetic radiation is quantised in units of $h\nu$ (where ν is the frequency of radiation and h is Planck's constant 6.626×10^{-34} Js). Extending Planck's quantum hypothesis to the energies of atoms, Niels Bohr proposed a new atomic model for the hydrogen atom. This model is based on the following assumptions:

1. The energies of electrons in an atom are quantised.
2. The electron is revolving around the nucleus in a certain circular path of fixed energy called stationary orbit.
3. Electron can revolve only in those orbits in which the angular momentum (mvr) of the electron must be equal to an integral multiple of $h/2\pi$.

$$\text{i.e. } mvr = nh/2\pi \text{ ----- (2.1)}$$

where $n = 1, 2, 3, \dots$ etc.,

4. As long as an electron revolves in the fixed stationary orbit, it doesn't lose its energy. However, when an electron jumps from higher energy state (E_2) to a lower energy state (E_1), the excess energy is emitted as radiation. The frequency of the emitted radiation is

$$E_2 - E_1 = h\nu$$

and

$$\nu = \frac{(E_2 - E_1)}{h} \text{ ----- (2.2)}$$

Conversely, when suitable energy is supplied to an electron, it will jump from lower energy orbit to a higher energy orbit.

Applying Bohr's postulates to a hydrogen like atom (one electron species such as H, He⁺ and Li²⁺ etc..) the radius of the nth orbit and the energy of the electron revolving in the nth orbit were derived. The results are as follows:

$$r_n = \frac{(0.529)n^2}{Z} \text{ \AA} \text{ ----- (2.3)}$$

$$E_n = \frac{(-13.6)Z^2}{n^2} \text{ eV atom}^{-1} \text{ ----- (2.4)}$$

(or)

$$E_n = \frac{(-1312.8)Z^2}{n^2} \text{ kJ mol}^{-1} \text{ ----- (2.5)}$$

The detailed derivation of r_n and E_n will be discussed in 12th standard atomic physics unit.

2.1.2 Limitation of Bohr's atom model:

The Bohr's atom model is applicable only to species having one electron such as hydrogen, Li²⁺ etc... and not applicable to multi electron atoms. It was unable to explain the splitting of spectral lines in the presence of magnetic field (Zeeman effect) or an electric field (Stark effect). Bohr's theory was unable to explain why the electron is restricted to revolve around the nucleus in a fixed orbit in which the angular momentum of the electron is equal to $nh/2\pi$ and a logical answer for this, was provided by Louis de Broglie.

2.2 Wave particle duality of matter

Albert Einstein proposed that light has dual nature. i.e. light photons behave both like a particle and as a wave. Louis de Broglie extended this concept and proposed that all forms of matter showed dual character. To quantify this relation, he derived an equation for the wavelength of a matter wave. He combined the following two equations of energy of which one represents wave character ($h\nu$) and the other represents the particle nature (mc^2).

- (i) Planck's quantum hypothesis:

$$E = h\nu \text{ ----- (2.6)}$$

- (ii) Einstein's mass-energy relationship

$$E = mc^2 \text{ ----- (2.7)}$$

From (2.6) and (2.7)

$$h\nu = mc^2$$

$$hc/\lambda = mc^2$$

$$\lambda = h / mc \text{ -----(2.8)}$$

The equation 2.8 represents the wavelength of photons whose momentum is given by mc (Photons have zero rest mass)

For a particle of matter with mass m and moving with a velocity v , the equation 2.8 can be written as

$$\lambda = h / mv \text{ ----- (2.9)}$$

This is valid only when the particle travels at speeds much less than the speed of Light.

This equation implies that a moving particle can be considered as a wave and a wave can exhibit the properties (i.e momentum) of a particle. For a particle with high linear momentum (mv) the wavelength will be so small and cannot be observed. For a microscopic particle such as an electron, the mass is of the order of 10^{-31} kg, hence the wavelength is much larger than the size of atom and it becomes significant.

Let us understand this by calculating de Broglie wavelength in the following two cases:

(i) A 6.626 kg iron ball moving at 10 ms^{-1}

(ii) An electron moving at 72.73 ms^{-1}

$$\lambda_{\text{iron ball}} = h/mv$$

$$= \frac{6.626 \times 10^{-34} \text{ kgm}^2\text{s}^{-1}}{6.626 \text{ kg} \times 10 \text{ ms}^{-1}} = 1 \times 10^{-35} \text{ m}$$

$$\lambda_{\text{electron}} = h/mv$$

$$\begin{aligned} &= \frac{6.626 \times 10^{-34} \text{ kgm}^2\text{s}^{-1}}{9.11 \times 10^{-31} \text{ kg} \times 72.73 \text{ ms}^{-1}} \\ &= \frac{6.626}{662.6} \times 10^{-3} \text{ m} = 1 \times 10^{-5} \text{ m} \end{aligned}$$

For the electron, the de Broglie wavelength is significant and measurable while for the iron ball it is too small to measure, hence it becomes insignificant.

Evaluate Yourself



1. Calculate the de-Broglie wavelength of an electron that has been accelerated from rest through a potential difference of 1 keV.

2.2.1 Quantisation of angular momentum and de Broglie concept:

According to the de Broglie concept, the electron that revolves around the nucleus exhibits both particle and wave character. In order for the electron wave to exist in phase, the circumference of the orbit should be an integral multiple of the wavelength of the electron wave. Otherwise, the electron wave is out of phase.

$$\text{Circumference of the orbit} = n\lambda$$

$$2\pi r = n\lambda \text{ -----(2.10)}$$

$$2\pi r = nh/mv$$

Rearranging,

$$mvr = nh/2\pi \text{ -----(2.11)}$$

$$\text{Angular momentum} = nh/2\pi$$

The above equation was already predicted by Bohr. Hence, De Broglie and Bohr's concepts are in agreement with each other.

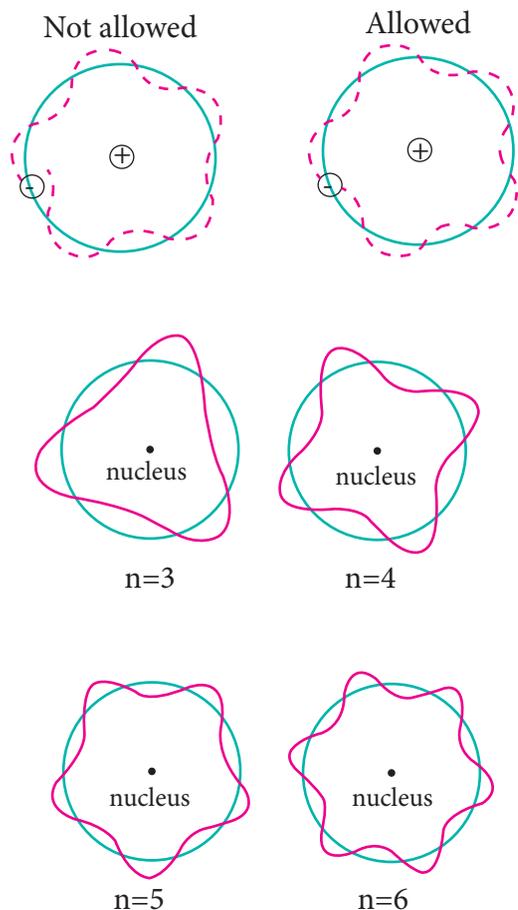


Figure. 2.2 Wave nature of electrons in allowed Bohr orbits

Davison and Germer experiment :

The wave nature of electron was experimentally confirmed by Davison and Germer. They allowed the accelerated beam of electrons to fall on a nickel crystal and recorded the diffraction pattern. The resultant diffraction pattern is similar to the x-ray diffraction pattern. The finding of wave nature of electron leads to the development of various experimental techniques such as electron microscope, low energy electron diffraction etc...

2.3 Heisenberg's uncertainty principle

The dual nature of matter imposes a limitation on the simultaneous

determination of position and momentum of a microscopic particle. Based on this, Heisenberg arrived at his uncertainty principle, which states that 'It is impossible to **accurately** determine both the position and the momentum of a microscopic particle **simultaneously**'. The product of uncertainty (error) in the measurement is expressed as follows.

$$\Delta x \cdot \Delta p \geq h/4\pi \text{ ----- (2.11)}$$

where, Δx and Δp are uncertainties in determining the position and momentum, respectively.

The uncertainty principle has negligible effect for macroscopic objects and becomes significant only for microscopic particles such as electrons. Let us understand this by calculating the uncertainty in the velocity of the electron in hydrogen atom. (Bohr radius of 1st orbit is 0.529 Å) Assuming that the position of the electron in this orbit is determined with the accuracy of 0.5 % of the radius.

Uncertainty in position = Δx

$$\begin{aligned} &= \frac{0.5\%}{100\%} \times 0.529 \text{ \AA} \\ &= \frac{0.5}{100} \times 0.529 \times 10^{-10} \text{ m} \\ \Delta x &= 2.645 \times 10^{-13} \text{ m} \end{aligned}$$

From the Heisenberg's uncertainty principle,

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x \cdot (m \cdot \Delta v) \geq \frac{h}{4\pi}$$

$$\Delta v \geq \frac{h}{4\pi \cdot m \cdot \Delta x}$$

$$\Delta v \geq \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.14 \times 9.11 \times 10^{-31} \text{ kg} \times 2.645 \times 10^{-13} \text{ m}}$$

$$\Delta v \geq 2.189 \times 10^8 \text{ ms}^{-1}$$

Therefore, the uncertainty in the velocity of the electron is comparable with the velocity of light. At this high level of uncertainty it is very difficult to find out the exact velocity.

Evaluate Yourself



2. Calculate the uncertainty in the position of an electron, if the uncertainty in its velocity is $5.7 \times 10^5 \text{ ms}^{-1}$.

2.4 Quantum mechanical model of atom – Schrödinger Equation:

The motion of objects that we come across in our daily life can be well described using classical mechanics which is based on the Newton's laws of motion. In classical mechanics the physical state of the particle is defined by its position and momentum. If we know both these properties, we can predict the future state of the system based on the force acting on it using classical mechanics. However, according to Heisenberg's uncertainty principle both these properties cannot be measured simultaneously with absolute accuracy for a microscopic particle such as an electron. The classical mechanics does not consider the dual nature of the matter which is significant for microscopic particles. As a consequence, it fails to explain the motion of microscopic particles. Based on

the Heisenberg's principle and the dual nature of the microscopic particles, a new mechanics called quantum mechanics was developed.

Erwin Schrödinger expressed the wave nature of electron in terms of a differential equation. This equation determines the change of wave function in space depending on the field of force in which the electron moves. The time independent Schrödinger equation can be expressed as,

$$\hat{H}\Psi = E\Psi \text{ ----- (2.12)}$$

Where \hat{H} is called Hamiltonian operator, Ψ is the wave function and is a function of position co-ordinates of the particle and is denoted as $\Psi(x, y, z)$ E is the energy of the system

$$\hat{H} = \left[\frac{-\hbar^2}{8\pi^2 m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V \right]$$

(2.12) can be written as,

$$\left[\frac{-\hbar^2}{8\pi^2 m} \left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + V\Psi \right] = E\Psi$$

Multiply by $-\frac{8\pi^2 m}{\hbar^2}$ and rearranging

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{8\pi^2 m}{\hbar^2} (E - V)\Psi = 0 \text{ ----- (2.13)}$$

The above Schrödinger wave equation does not contain time as a variable and is referred to as time independent Schrödinger wave equation. This equation can be solved only for certain values of E , the total energy. i.e. the energy of the system is quantised. The permitted total energy values are called eigen values and corresponding wave functions represent the atomic orbitals.

2.4.1 Main features of the quantum mechanical model of atom

1. The energy of electrons in atoms is quantised
2. The existence of quantized electronic energy levels is a direct result of the wave like properties of electrons. The solutions of Schrödinger wave equation gives the allowed energy levels (orbits).
3. According to Heisenberg uncertainty principle, the exact position and momentum of an electron can not be determined with absolute accuracy. As a consequence, quantum mechanics introduced the concept of orbital. Orbital is a three dimensional space in which the probability of finding the electron is maximum.
4. The solution of Schrödinger wave equation for the allowed energies of an atom gives the wave function ψ , which represents an atomic orbital. The wave nature of electron present in an orbital can be well defined by the wave function ψ .
5. The wave function ψ itself has no physical meaning. However, the probability of finding the electron in a small volume $dx dy dz$ around a point (x,y,z) is proportional to $|\psi(x,y,z)|^2 dx dy dz$. $|\psi(x,y,z)|^2$ is known as probability density and is always positive.

2.5 Quantum numbers

The electron in an atom can be characterised by a set of four quantum numbers, namely principal quantum number (n), azimuthal quantum number (l), magnetic quantum number (m)

and spin quantum number (s). When Schrödinger equation is solved for a wave function Ψ , the solution contains the first three quantum numbers n , l and m . The fourth quantum number arises due to the spinning of the electron about its own axis. However, classical pictures of species spinning around themselves are incorrect.

Principal quantum number (n):

This quantum number represents the energy level in which electron revolves around the nucleus and is denoted by the symbol 'n'.

1. The 'n' can have the values 1, 2, 3, ...
 $n=1$ represents K shell; $n=2$ represents L shell and $n = 3, 4, 5$ represent the M, N, O shells, respectively.
2. The maximum number of electrons that can be accommodated in a given shell is $2n^2$.
3. 'n' gives the energy of the electron,
$$E_n = \frac{(-1312.8) Z^2}{n^2} \text{ kJ mol}^{-1}$$
 and the distance of the electron from the nucleus is given by $r_n = \frac{(0.529)n^2}{Z} \text{ \AA}$

Azimuthal Quantum number (l) or subsidiary quantum number :

1. It is represented by the letter 'l', and can take integral values from zero to $n-1$, where n is the principal quantum number
2. Each l value represents a subshell (orbital). $l = 0, 1, 2, 3$ and 4 represents the s, p, d, f and g orbitals respectively.
3. The maximum number of electrons that can be accommodated in a given subshell (orbital) is $2(2l+1)$.

4. It is used to calculate the orbital angular momentum using the expression

$$\text{Angular momentum} = \sqrt{l(l+1)} \frac{h}{2\pi} \text{---(2.14)}$$

Magnetic quantum number (m_l):

1. It is denoted by the letter ' m_l '. It takes integral values ranging from $-l$ to $+l$ through 0. i.e. if $l=1$; $m = -1, 0$ and $+1$
2. Different values of m for a given l value, represent different orientation of orbitals in space.
3. The Zeeman Effect (the splitting of spectral lines in a magnetic field) provides the experimental justification for this quantum number.
4. The magnitude of the angular momentum is determined by the quantum number l while its direction is given by magnetic quantum number.

Spin quantum number (m_s):

1. The spin quantum number represents the spin of the electron and is denoted by the letter ' m_s '
2. The electron in an atom revolves not only around the nucleus but also spins. It is usual to write this as electron spins about its own axis either in a clockwise direction or in anti-clockwise direction. The visualisation is not true. However spin is to be understood as representing a property that revealed itself in magnetic fields.
3. Corresponding to the clockwise and anti-clockwise spinning of the electron, maximum two values are possible for this quantum number.
4. The values of ' m_s ' is equal to $-\frac{1}{2}$ and $+\frac{1}{2}$

Table 2.1 Quantum numbers and its significance

Shell	Principal quantum number (n)	maximum number of electron in a shell (orbital) $2n^2$	Azimuthal quantum number ($l = 0, 1, \dots, (n-1)$)	Maximum no. of electron in a orbital $2(2l+1)$	Magnetic quantum number (m) different possible orientation of orbital	Designation of orbitals in a given shell
K	1	$2(1)^2 = 2$	0	$2[2(0)+1] = 2$	0	1s
L	2	$2(2)^2 = 8$	0	2	0	2s
			1	$2[2(1)+1] = 6$	-1, 0, +1	$2p_y, 2p_z, 2p_x$

Shell	Principal quantum number (n)	maximum number of electron in a shell (orbital) $2n^2$	Azimuthal quantum number (l) = 0,1.... (n-1)	Maximum no. of electron in a orbital $2(2l+1)$	Magnetic quantum number (m) different possible orientation of orbital	Designation of orbitals in a given shell
M	3	$2(3)^2 = 18$	0	2	0	3s
			1	6	-1, 0, +1	$3p_y, 3p_z, 3p_x$
			2	$2[2(2)+1] = 10$	-2, -1, 0, +1, +2	$3d_{x^2-y^2}, 3d_{yz}, 3d_{z^2}, 3d_{zx}, 3d_{xy}$
N	4	$2(4)^2 = 32$	0	2	0	4s
			1	6	-1, 0, +1	$4p_y, 4p_z, 4p_x$
			2	10	-2, -1, 0, +1, +2	$4d_{x^2-y^2}, 4d_{xy}, 4d_{z^2}, 4d_{yz}, 4d_{zx}$
			3	$2[2(3)+1] = 14$	-3, -2, -1, 0, +1, +2, +3	$f_{y(3x^2-y^2)}, f_{z(x^2-y^2)}, f_{yz^2}, f_{z^3}, f_{xz^2}, f_{xyz}, f_{x(x^2-3y^2)}$

The labels on the orbitals, such as p_x, d_{z^2}, f_{xyz} etc. are not associated with specific 'm' values

Evaluate Yourself



3. How many orbitals are possible in the 4th energy level? (n=4)

2.5.1 Shapes of atomic orbitals:

The solution to Schrödinger equation gives the permitted energy values called eigen values and the wave functions corresponding to the eigen values are called atomic orbitals. The solution (Ψ) of the Schrödinger wave equation for one electron system like hydrogen can be represented in the following form in spherical polar coordinates r, θ, φ as,

$$\Psi(r, \theta, \varphi) = R(r).f(\theta).g(\varphi) \text{ ----- (2.15)}$$

(where $R(r)$ is called radial wave function, other two functions are called angular wave functions)

As we know, the Ψ itself has no physical meaning and the square of the wave function $|\Psi|^2$ is related to the probability of finding the electrons within a given volume of space. Let us analyse how $|\Psi|^2$ varies with the distance from nucleus (radial distribution of the probability) and the direction from the nucleus (angular distribution of the probability).

Radial distribution function:

Consider a single electron of hydrogen atom in the ground state for which the quantum numbers are $n=1$ and

$l=0$. i.e. it occupies 1s orbital. The plot of $R(r)^2$ versus r for 1s orbital is given in Figure 2.3

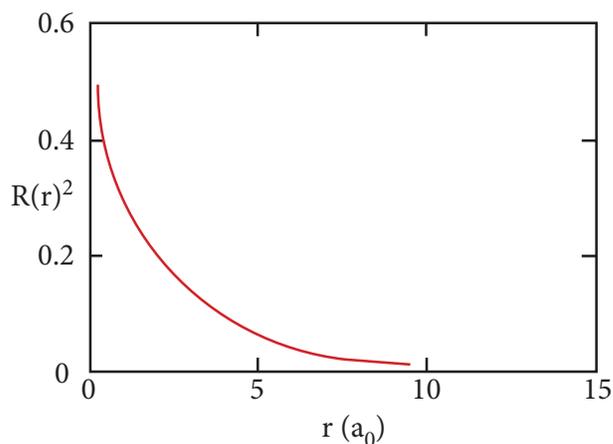


Figure. 2.3 Plot of $R(r)^2$ versus r for 1s orbital of hydrogen

The graph shows that as the distance between the electron and the nucleus decreases, the probability of finding the electron increases. At $r=0$, the quantity $R(r)^2$ is maximum i.e. The maximum value for $|\Psi|^2$ is at the nucleus. However, probability of finding the electron in a given spherical shell around the nucleus is important. Let us consider the volume (dV) bounded by two spheres of radii r and $r+dr$.

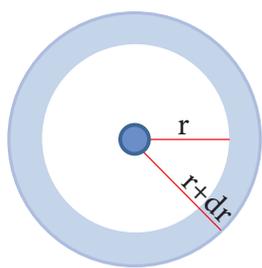


Figure 2.4

Volume of the sphere, $V = \frac{4}{3} \pi r^3$

$$\frac{dV}{dr} = \frac{4}{3} \pi (3r^2)$$

$$dV = 4\pi r^2 dr$$

$$\Psi^2 dV = 4\pi r^2 \Psi^2 dr \text{ ----- (2.16)}$$

The plot of $4\pi r^2 \cdot R(r)^2$ versus r is given below.

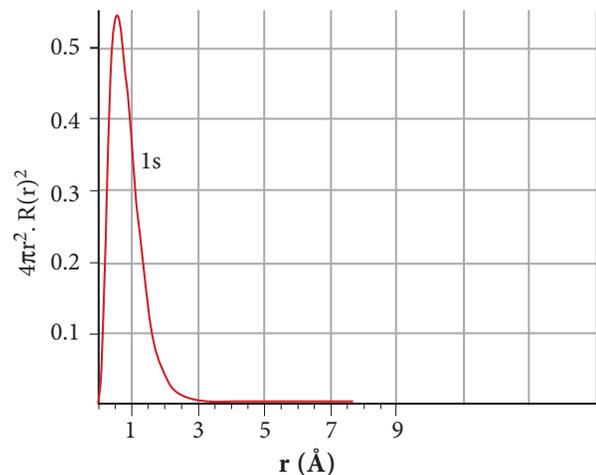


Figure 2.5 Plot of $4\pi r^2 \cdot R(r)^2$ versus r for 1s orbital of hydrogen

The above plot shows that the maximum probability occurs at distance of 0.52 \AA from the nucleus. This is equal to the Bohr radius. It indicates that the maximum probability of finding the electron around the nucleus is at this distance. However, there is a probability to find the electron at other distances also. The radial distribution function of 2s, 3s, 3p and 3d orbitals of the hydrogen atom are represented as follows.

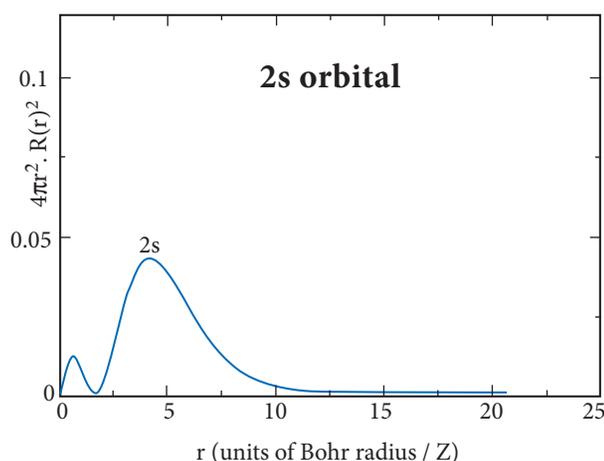


Figure 2.6 (a) - Plot of $4\pi r^2 \cdot R(r)^2$ versus r for 2s orbitals of hydrogen

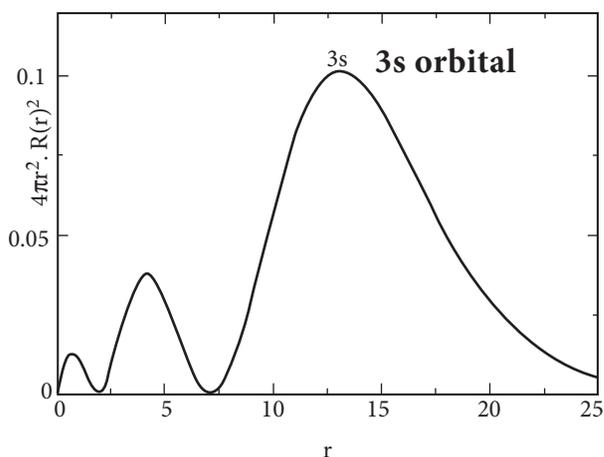


Figure 2.6 (b) - Plot of $4\pi r^2 \cdot R(r)^2$ versus r for 3s orbitals of hydrogen

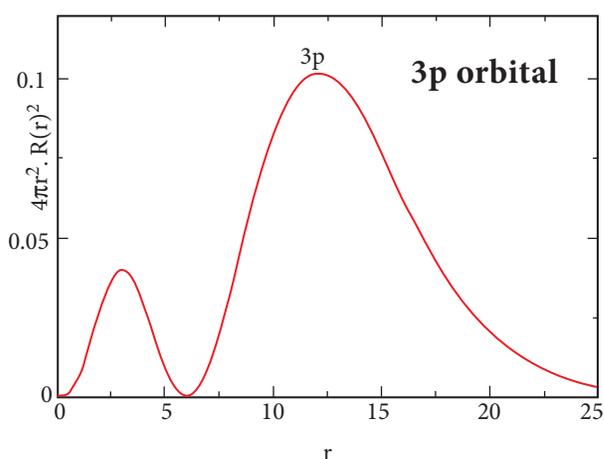


Figure 2.6 (c) - Plot of $4\pi r^2 \cdot R(r)^2$ versus r for 3p orbitals of hydrogen

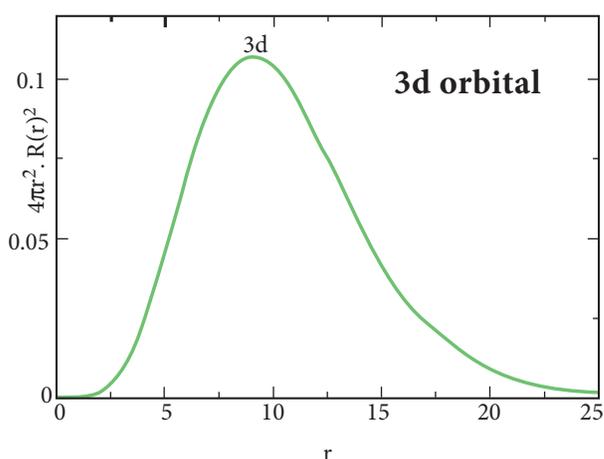


Figure 2.6 (d) - Plot of $4\pi r^2 \cdot R(r)^2$ versus r for 3d orbitals of hydrogen

For 2s orbital, as the distance from nucleus r increases, the probability density first increases, reaches a small maximum followed by a sharp decrease to zero and then increases to another maximum, after that decreases to zero. The region where this probability density function reduces to zero is called nodal surface or a radial node. In general, it has been found that ns -orbital has $(n-1)$ nodes. In other words, number of radial nodes for 2s orbital is one, for 3s orbital it is two and so on. The plot of $4\pi r^2 \cdot R(r)^2$ versus r for 3p and 3d orbitals shows similar pattern but the number of radial nodes are equal to $(n-l-1)$ (where n is principal quantum number and l is azimuthal quantum number of the orbital).

Angular distribution function:

The variation of the probability of locating the electron on a sphere with nucleus at its centre depends on the azimuthal quantum number of the orbital in which the electron is present. For 1s orbital, $l=0$ and $m=0$. $f(\theta) = 1/\sqrt{2}$ and $g(\phi) = 1/\sqrt{2}\pi$. Therefore, the angular distribution function is equal to $1/2\sqrt{\pi}$. i.e. it is independent of the angle θ and ϕ . Hence, the probability of finding the electron is independent of the direction from the nucleus. The shape of the s orbital is spherical as shown in the figure 2.7

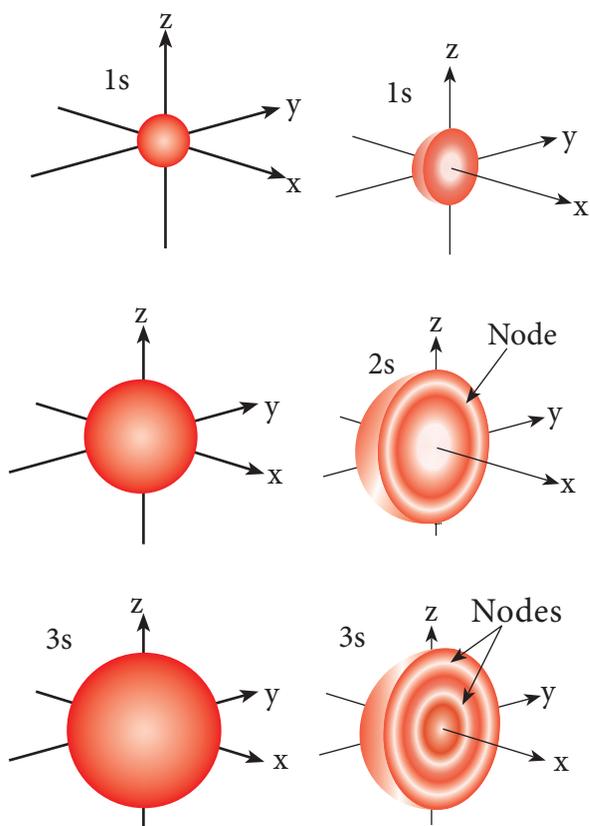
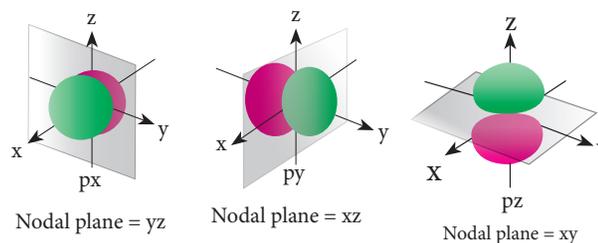


Figure 2.7 Shapes of 1s, 2s and 3s orbitals

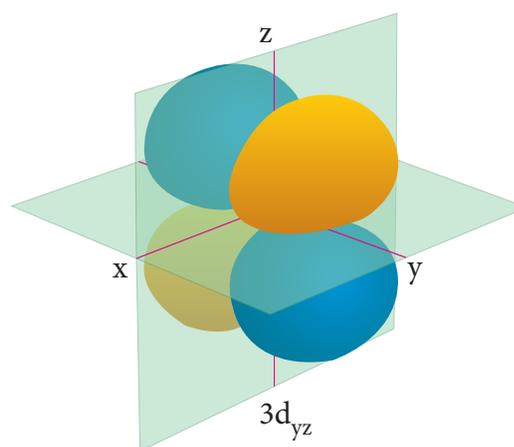
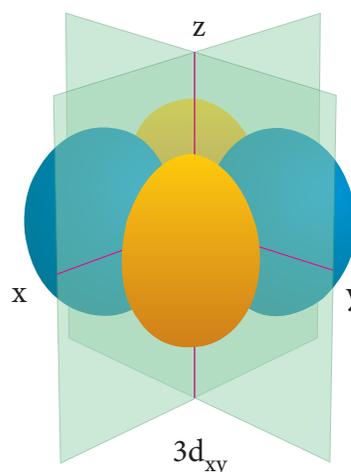
For p orbitals $l=1$ and the corresponding m values are -1, 0 and +1. The angular distribution functions are quite complex and are not discussed here. The shape of the p orbital is shown in Figure 2.8. The three different m values indicates that there are three different orientations possible for p orbitals. These orbitals are designated as p_x , p_y and p_z and the angular distribution for these orbitals shows that the lobes are along the x, y and z axis respectively. As seen in the Figure 2.8 the 2p orbitals have one nodal plane.



(b) Cartoon representations of 2p orbitals

Figure 2.8 Shapes of 2p orbitals

For 'd' orbital $l = 2$ and the corresponding m values are -2, -1, 0 +1,+2. The shape of the d orbital looks like a 'clover leaf'. The five m values give rise to five d orbitals namely d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$ and d_{z^2} . The 3d orbitals contain two nodal planes as shown in Figure 2.9.



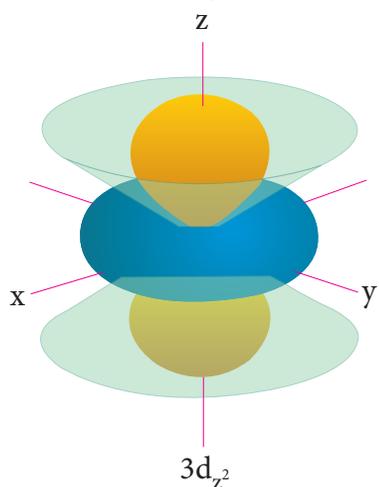
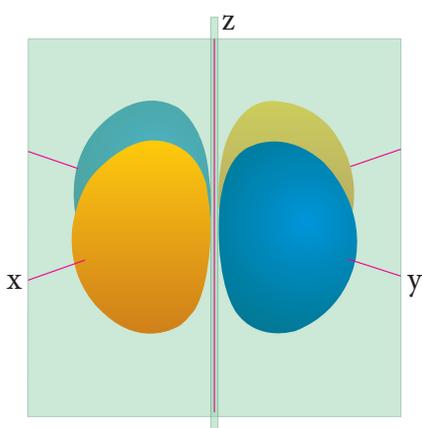
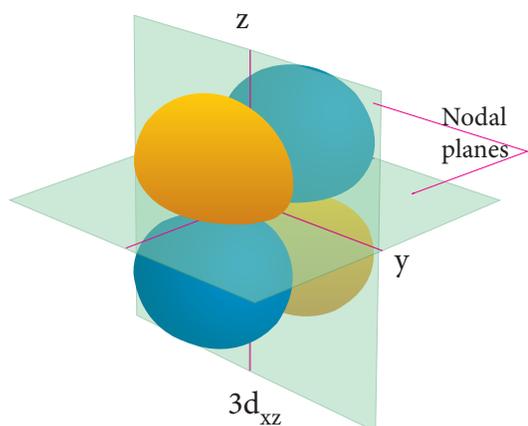


Figure 2.9 shapes of d orbitals

For 'f' orbital, $l = 3$ and the m values are $-3, -2, -1, 0, +1, +2, +3$ corresponding to seven f orbitals $f_{z^3}, f_{xz^2}, f_{yz^2}, f_{xyz}, f_{z(x^2-y^2)}, f_{x(x^2-3y^2)}, f_{y(3x^2-y^2)}$, which are shown in Figure 2.10. There are 3 nodal planes in the f-orbitals.

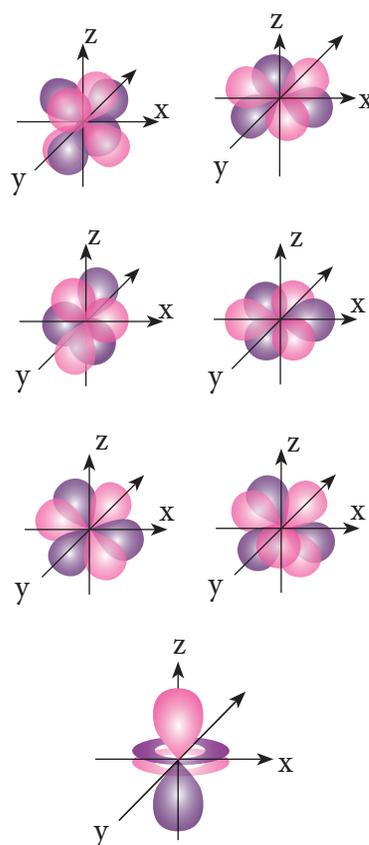


Figure 2.10 shapes of f-orbitals

Evaluate Yourself



- Calculate the total number of angular nodes and radial nodes present in 3d and 4f orbitals.

2.5.2 Energies of orbitals

In hydrogen atom, only one electron is present. For such one electron system, the energy of the electron in the n^{th} orbit is given by the expression

$$E_n = \frac{(-1312.8) Z^2}{n^2} \text{ kJ mol}^{-1}$$

From this equation, we know that the energy depends only on the value of principal quantum number. As the n value increases the energy of the orbital also increases. The energies of various orbitals

will be in the following order:

$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < 5s = 5p = 5d = 5f < 6s = 6p = 6d = 6f < 7s$$

The electron in the hydrogen atom occupies the 1s orbital that has the lowest energy. This state is called ground state. When this electron gains some energy, it moves to the higher energy orbitals such as 2s, 2p etc... These states are called excited states.

However, the above order is not true for atoms other than hydrogen (multi-electron systems). For such systems the Schrödinger equation is quite complex. For these systems the relative order of energies of various orbitals is given approximately by the (n+l) rule. It states that, the lower the value of (n + l) for an orbital, the lower is its energy. If two orbitals have the same value of (n + l), the orbital with lower value of n will have the lower energy. Using this rule the order of energies of various orbitals can be expressed as follows.

Table 2.2 n+l values of different orbitals

Orbital	n	l	n+l
1s	1	0	1
2s	2	0	2
2p	2	1	3
3s	3	0	3
3p	3	1	4
3d	3	2	5
4s	4	0	4
4p	4	1	5
4d	4	2	6
4f	4	3	7
5s	5	0	5

5p	5	1	6
5d	5	2	7
5f	5	3	8
6s	6	0	6
6p	6	1	7
6d	6	2	8
7s	7	0	7

Based on the (n+l) rule, the increasing order of energies of orbitals is as follows:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d$$

As we know there are three different orientations in space that are possible for a p orbital. All the three p orbitals, namely, p_x , p_y and p_z have same energies and are called degenerate orbitals. However, in the presence of magnetic or electric field the degeneracy is lost.

In a multi-electron atom, in addition to the electrostatic attractive force between the electron and nucleus, there exists a repulsive force among the electrons. These two forces are operating in the opposite direction. This results in the decrease in the nuclear force of attraction on electron. The net charge experienced by the electron is called effective nuclear charge. The effective nuclear charge depends on the shape of the orbitals and it decreases with increase in azimuthal quantum number l . The order of the effective nuclear charge felt by a electron in an orbital within the given shell is $s > p > d > f$. Greater the effective nuclear charge, greater is the stability of the orbital. Hence, within a given energy level, the energy of the orbitals are in the following order. $s < p < d < f$.

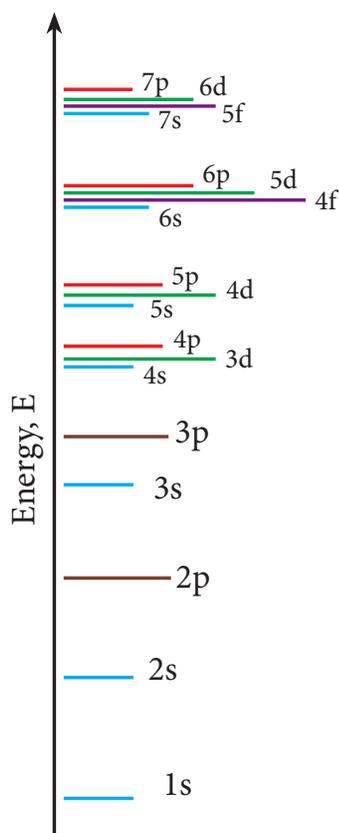


Figure. 2.11 Energy levels of atomic orbitals

The energies of same orbital decrease with an increase in the atomic number. For example, the energy of the 2s orbital of hydrogen atom is greater than that of 2s orbital of lithium and that of lithium is greater than that of sodium and so on, that is, $E_{2s}(\text{H}) > E_{2s}(\text{Li}) > E_{2s}(\text{Na}) > E_{2s}(\text{K})$.

Evaluate Yourself



5. Energy of an electron in hydrogen atom in ground state is -13.6 eV. What is the energy of the electron in the second excited state?

2.6 Filling of orbitals:

In an atom, the electrons are filled in various orbitals according to aufbau principle, Pauli exclusion principle and

Hund's rule. These rules are described below.

2.6.1 Aufbau principle:

The word Aufbau in German means 'building up'. In the ground state of the atoms, the orbitals are filled in the order of their increasing energies. That is the electrons first occupy the lowest energy orbital available to them.

Once the lower energy orbitals are completely filled, then the electrons enter the next higher energy orbitals. The order of filling of various orbitals as per the Aufbau principle is given in the figure 2.12 which is in accordance with $(n+l)$ rule.

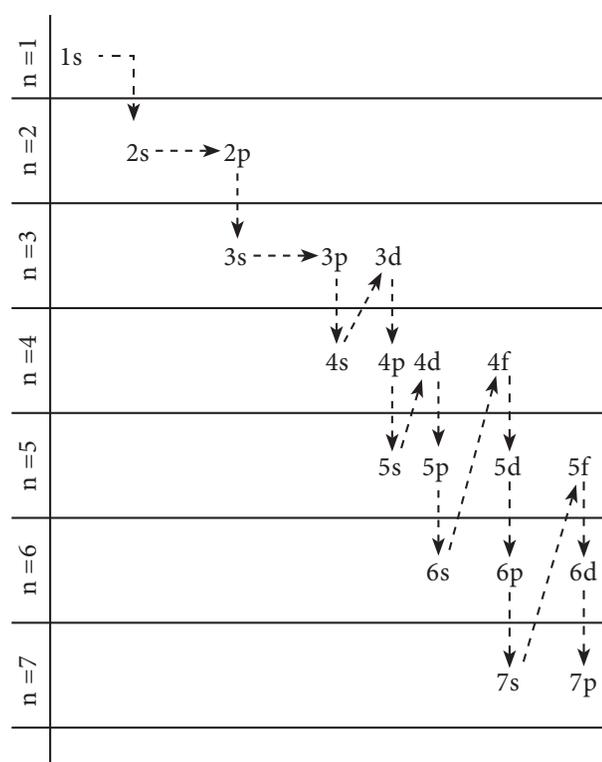


Figure. 2.12 Aufbau principle

2.6.2 Pauli Exclusion Principle :

Pauli formulated the exclusion principle which states that "No two electrons in an atom can have the same set

of values of all four quantum numbers." It means that, each electron must have unique values for the four quantum numbers (n , l , m and s).

For the lone electron present in hydrogen atom, the four quantum numbers are: $n = 1$; $l = 0$; $m = 0$ and $s = +\frac{1}{2}$. For the two electrons present in helium, one electron has the quantum numbers same as the electron of hydrogen atom, $n = 1$, $l = 0$, $m = 0$ and $s = +\frac{1}{2}$. For other electron, the fourth quantum number is different i.e., $n = 1$, $l = 0$, $m = 0$ and $s = -\frac{1}{2}$.

As we know that the spin quantum number can have only two values $+\frac{1}{2}$ and $-\frac{1}{2}$, only two electrons can be accommodated in a given orbital in accordance with Pauli exclusion principle. Let us understand this by writing all the four quantum numbers for the eight electron in L shell.

Table 2.3 Quantum numbers of electrons in L shell

Electron	n	l	m	s
1 st	2	0	0	$+\frac{1}{2}$
2 nd	2	0	0	$-\frac{1}{2}$
3 rd	2	1	-1	$+\frac{1}{2}$
4 th	2	1	0	$+\frac{1}{2}$
5 th	2	1	+1	$+\frac{1}{2}$
6 th	2	1	-1	$-\frac{1}{2}$
7 th	2	1	0	$-\frac{1}{2}$
8 th	2	1	+1	$-\frac{1}{2}$

2.6.3 Hund's rule of maximum multiplicity

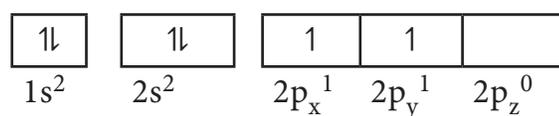
The Aufbau principle describes how

the electrons are filled in various orbitals. But the rule does not deal with the filling of electrons in the degenerate orbitals (i.e. orbitals having same energy) such as p_x , p_y and p_z . In what order these orbitals to be filled? The answer is provided by the Hund's rule of maximum multiplicity. It states that electron pairing in the degenerate orbitals does not take place until all the available orbitals contains one electron each.

We know that there are three p orbitals, five d orbitals and seven f orbitals. According to this rule, pairing of electrons in these orbitals starts only when the 4th, 6th and 8th electron enters the p, d and f orbitals respectively.

For example, consider the carbon atom which has six electrons. According to Aufbau principle, the electronic configuration is $1s^2, 2s^2, 2p^2$

It can be represented as below,



In this case, in order to minimise the electron-electron repulsion, the sixth electron enters the unoccupied $2p_y$ orbital as per Hund's rule. i.e. it does not get paired with the fifth electron already present in the $2p_x$ orbital.

Evaluate Yourself



6. How many unpaired electrons are present in the ground state of Fe^{3+} ($z=26$), Mn^{2+} ($z=25$) and argon ($z=18$)?

2.6.4 Electronic configuration of atoms

The distribution of electrons into various orbitals of an atom is called its electronic configuration. It can be written by applying the aufbau principle, Pauli exclusion principle and Hund's rule. The electronic configuration is written as $n l^x$, where n represents the principle of quantum number, ' l ' represents the letter designation of the orbital [$s(l=0)$, $p(l=1)$, $d(l=2)$ and $f(l=3)$] and ' x ' represents the number of electron present in that orbital.

Let us consider the hydrogen atom which has only one electron and it occupies the lowest energy orbital i.e. $1s$ according to aufbau principle. In this case $n=1$; $l=s$; $x=1$.

Hence the electronic configuration is $1s^1$. (read as one-ess-one).

The orbital diagram for this configuration is,



The electronic configuration and orbital diagram for the elements upto atomic number 10 are given below :

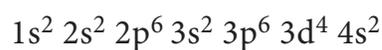
Table 2. 4 Electronic configuration and orbital diagrams for first 10 elements

Element	Electronic Configuration	Orbital diagram
H ¹	$1s^1$	$\begin{array}{ c } \hline 1 \\ \hline 1s^1 \end{array}$
He ²	$1s^2$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline 1s^2 \end{array}$
Li ³	$1s^2 2s^1$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline 1s^2 \end{array} \quad \begin{array}{ c } \hline 1 \\ \hline 2s^1 \end{array}$
Be ⁴	$1s^2 2s^2$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline 1s^2 \end{array} \quad \begin{array}{ c } \hline \uparrow\downarrow \\ \hline 2s^2 \end{array}$
B ⁵	$1s^2 2s^2 2p^1$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline 1s^2 \end{array} \quad \begin{array}{ c } \hline \uparrow\downarrow \\ \hline 2s^2 \end{array} \quad \begin{array}{ c } \hline 1 \\ \hline 2p_x^1 \end{array} \quad \begin{array}{ c } \hline \\ \hline 2p_y \end{array} \quad \begin{array}{ c } \hline \\ \hline 2p_z \end{array}$
C ⁶	$1s^2 2s^2 2p^2$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline 1s^2 \end{array} \quad \begin{array}{ c } \hline \uparrow\downarrow \\ \hline 2s^2 \end{array} \quad \begin{array}{ c } \hline 1 \\ \hline 2p_x^1 \end{array} \quad \begin{array}{ c } \hline 1 \\ \hline 2p_y^1 \end{array} \quad \begin{array}{ c } \hline \\ \hline 2p_z \end{array}$
N ⁷	$1s^2 2s^2 2p^3$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline 1s^2 \end{array} \quad \begin{array}{ c } \hline \uparrow\downarrow \\ \hline 2s^2 \end{array} \quad \begin{array}{ c } \hline 1 \\ \hline 2p_x^1 \end{array} \quad \begin{array}{ c } \hline 1 \\ \hline 2p_y^1 \end{array} \quad \begin{array}{ c } \hline 1 \\ \hline 2p_z^1 \end{array}$
O ⁸	$1s^2 2s^2 2p^4$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline 1s^2 \end{array} \quad \begin{array}{ c } \hline \uparrow\downarrow \\ \hline 2s^2 \end{array} \quad \begin{array}{ c } \hline \uparrow\downarrow \\ \hline 2p_x^2 \end{array} \quad \begin{array}{ c } \hline 1 \\ \hline 2p_y^1 \end{array} \quad \begin{array}{ c } \hline 1 \\ \hline 2p_z^1 \end{array}$
F ⁹	$1s^2 2s^2 2p^5$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline 1s^2 \end{array} \quad \begin{array}{ c } \hline \uparrow\downarrow \\ \hline 2s^2 \end{array} \quad \begin{array}{ c } \hline \uparrow\downarrow \\ \hline 2p_x^2 \end{array} \quad \begin{array}{ c } \hline \uparrow\downarrow \\ \hline 2p_y^2 \end{array} \quad \begin{array}{ c } \hline 1 \\ \hline 2p_z^1 \end{array}$
Ne ¹⁰	$1s^2 2s^2 2p^6$	$\begin{array}{ c } \hline \uparrow\downarrow \\ \hline 1s^2 \end{array} \quad \begin{array}{ c } \hline \uparrow\downarrow \\ \hline 2s^2 \end{array} \quad \begin{array}{ c } \hline \uparrow\downarrow \\ \hline 2p_x^2 \end{array} \quad \begin{array}{ c } \hline \uparrow\downarrow \\ \hline 2p_y^2 \end{array} \quad \begin{array}{ c } \hline \uparrow\downarrow \\ \hline 2p_z^2 \end{array}$

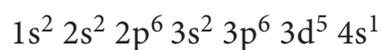
The actual electronic configuration of some elements such as chromium and copper slightly differ from the expected electronic configuration in accordance with the Aufbau principle.

For chromium - 24

Expected configuration :

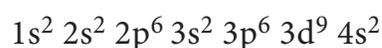


Actual configuration :

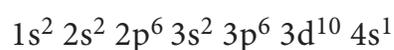


For copper - 29

Expected configuration :



Actual configuration :



The reason for above observed configuration is that fully filled orbitals and half filled orbitals have been found to have extra stability. In other words, p^3 , p^6 , d^5 , d^{10} , f^7 and f^{14} configurations are more stable than p^2 , p^5 , d^4 , d^9 , f^6 and f^{13} . Due to this stability, one of the 4s electrons occupies the 3d orbital in chromium and copper to attain the half filled and the completely filled configurations respectively.

Evaluate Yourself



7. Explain the meaning of the symbol $4f^2$. Write all the four quantum numbers for these electrons.

2.6.5 Stability of half filled and completely filled orbitals:

The exactly half filled and completely filled orbitals have greater stability than other partially filled configurations in

degenerate orbitals. This can be explained on the basis of symmetry and exchange energy. For example chromium has the electronic configuration of $[\text{Ar}]3d^5 4s^1$ and not $[\text{Ar}]3d^4 4s^2$ due to the symmetrical distribution and exchange energies of d electrons.

Symmetrical distribution of electron:

Symmetry leads to stability. The half filled and fully filled configurations have symmetrical distribution of electrons (Figure 2.13) and hence they are more stable than the unsymmetrical configurations.

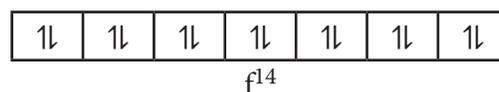
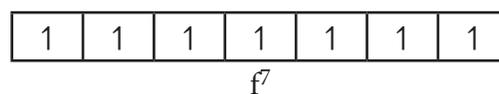
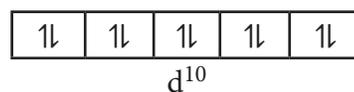
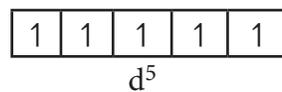
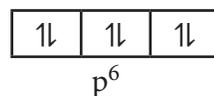
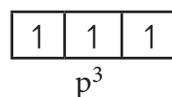


Figure 2.13 Half filled and fully filled p, d and f orbitals

The degenerate orbitals such as p_x , p_y and p_z have equal energies and their orientation in space are different as shown

in Figure 2.14. Due to this symmetrical distribution, the shielding of one electron on the other is relatively small and hence the electrons are attracted more strongly by the nucleus and it increases the stability.

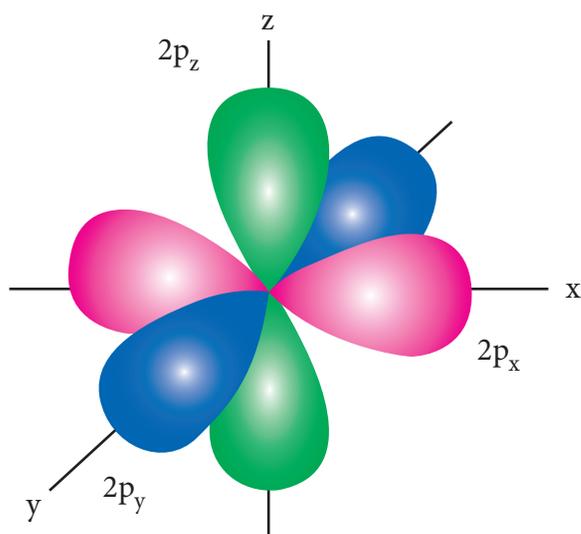


Figure 2.14 Shape of the degenerate p orbitals.

Exchange energy:

If two or more electrons with the same spin are present in degenerate orbitals, there is a possibility for exchanging their positions. During exchange process the energy is released and the released energy is called exchange energy. If more number of exchanges are possible, more exchange energy is released. More number of exchanges are possible only in case of half filled and fully filled configurations.

For example, in chromium the electronic configuration is $[\text{Ar}]3d^5 4s^1$. The 3d orbital is half filled and there are ten possible exchanges as shown in Figure 2.15. On the other hand only six exchanges are possible for $[\text{Ar}]3d^4 4s^2$ configuration. Hence, exchange energy for the half filled configuration is more. This increases the stability of half filled 3d orbitals.

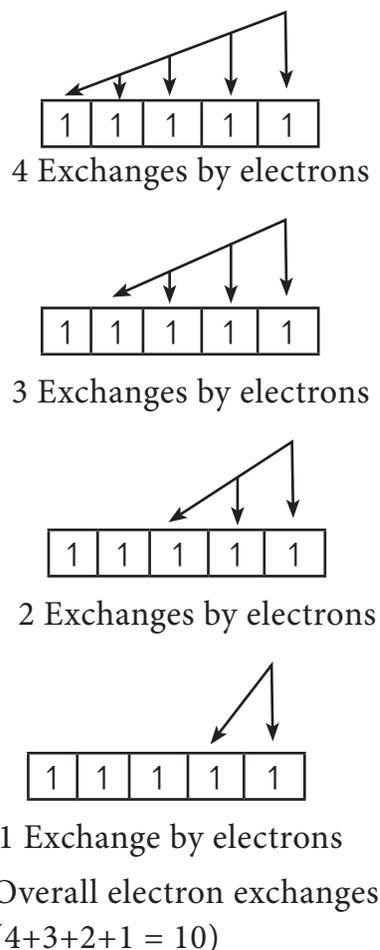


Figure 2.15 (a)

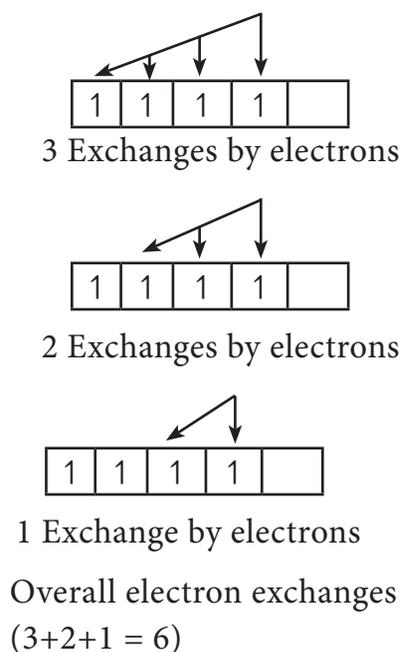


Figure 2.15 (b)

Figure 2.15 Possible exchanges in chromium d orbitals: a) for d^5 configuration b) for d^4 configuration



The exchange energy is the basis for Hund's rule, which allows maximum multiplicity, that is electron pairing is possible only when all the degenerate orbitals contain one electron each.

Evaluate Yourself



8. Which ion has the stable electronic configuration? Ni^{2+} or Fe^{3+} .

SUMMARY

The atoms were believed to be non-divisible until the discovery of subatomic particles. J. J. Thomson proposed that the atom is a positively charged sphere in which the electrons are embedded. However, it fails to explain the stability of atoms. Rutherford, based on his α -rays scattering experiment, introduced the term nucleus which is a positively charged one and the negatively charged electrons are revolving around it, at high speeds. Bohr modified the Rutherford theory and introduced stationary orbits by taking into account the quantisation of energy. Louis de Broglie proposed that all matter possess dual nature. i.e. they behave both as a wave and a particle. De Broglie wavelength $\lambda = h/mv = h/\sqrt{2mev}$ is significant for a microscopic particle such as an electron. The wave nature of electron is also proved by Davisson and Germer through electron diffraction. For a microscopic particle such as an electron, the simultaneous measurement of the conjugate variables such as position and momentum involves uncertainty which is known as Heisenberg's uncertainty principle and it is expressed as $\Delta x \cdot \Delta p \geq h/4\pi$.

De Broglie's concept and Heisenberg's uncertainty principle lead to the development of quantum mechanical model of atom. Erwin Schrodinger, developed an equation for an electron wave which is expressed as $\hat{H}\psi = E\psi$. This second order differential equation is exactly solvable for one electron system such as H, He^+ etc... but it is quite

complex for multi-electron systems. The Schrödinger wave equation is solvable for certain energy values called eigen values. The wave functions corresponding to these eigen values are called atomic orbitals. The wave function ψ itself has no physical meaning. However, $|\psi|^2$ is related to the probability of finding electron around the nucleus. Thus the quantum mechanical model introduced us the term orbital which is the three dimensional space in which the probability of finding the electron is maximum. The electron in an orbital can be described by a set of four quantum numbers namely, principal quantum number (n) representing the principal energy level, azimuthal quantum number (l) representing the sub shell (orbital), magnetic quantum number (m) representing the different orientation of orbitals in space and spin quantum number (s) representing the spinning of electron about its own axis.

The general solution of Schrodinger for a one electron system can be expressed in spherical polar coordinates (r, θ, φ)

$$\Psi(r, \theta, \varphi) = R(r) \cdot f(\theta) \cdot g(\varphi)$$

(where $R(r)$ is called radial wave function, other two functions are called angular wave functions).

The plot of $4\pi r^2 \cdot R(r)^2$ versus r gives the radial distribution curves. The number of radial nodes is given by $(n-l-1)$ whereas the angular nodes is equal to l . The angular distribution curve gives the boundary space diagram of orbital.



s orbital is spherical in nature and the d orbital has clover leaf shape.

Electrons are filled in various orbitals in the increasing order of their energies which is known as Aufbau principle. The relative energies of various orbitals are given by $(n+l)$ rule which states that, the lower the value of $(n + l)$ for an orbital, the lower is its energy. If two orbitals have the same value of $(n + l)$, the orbital with lower value of n will have the lower energy. As per Pauli's exclusion principle, the maximum number of

electrons that can be accommodated in an orbital is two. In the case of degenerate orbitals electron pairing does not take place until all the available degenerate orbitals contain one electron each. This is known as Hund's rule. Based on these principles, electronic configurations of atoms can be written. In degenerate orbitals, the completely filled and half filled configurations are more stable than the partially filled configurations. This is due to the symmetry and exchange energies.

EVALUATION :



Choose the best answer

- Electronic configuration of species M^{2+} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ and its atomic weight is 56. The number of neutrons in the nucleus of species M is
 - 26
 - 22
 - 30
 - 24
- The energy of light of wavelength 45 nm is
 - $6.67 \times 10^{15} \text{J}$
 - $6.67 \times 10^{11} \text{J}$
 - $4.42 \times 10^{-18} \text{J}$
 - $4.42 \times 10^{-15} \text{J}$
- The energies E_1 and E_2 of two radiations are 25 eV and 50 eV respectively. The relation between their wavelengths ie λ_1 and λ_2 will be
 - $\frac{\lambda_1}{\lambda_2} = 1$
 - $\lambda_1 = 2\lambda_2$
 - $\lambda_1 = \sqrt{25 \times 50} \lambda_2$
 - $2\lambda_1 = \lambda_2$
- Splitting of spectral lines in an electric field is called
 - Zeeman effect
 - Shielding effect
 - Compton effect
 - Stark effect
- Based on equation $E = -2.178 \times 10^{-18} \text{J} \left(\frac{z^2}{n^2} \right)$, certain conclusions are written. Which of them is not correct ? (NEET)
 - Equation can be used to calculate the change in energy when the electron changes orbit
 - For $n = 1$, the electron has a more negative energy than it does for $n = 6$ which means that the electron is more loosely bound in the smallest allowed orbit
 - The negative sign in equation simply means that the energy of electron bound to the nucleus is lower than it would be if the electrons were at the infinite distance from the nucleus.
 - Larger the value of n , the larger is the orbit radius.
- According to the Bohr Theory, which of the following transitions in the hydrogen atom will give rise to the least energetic photon ?
 - $n = 6$ to $n = 1$
 - $n = 5$ to $n = 4$
 - $n = 5$ to $n = 3$
 - $n = 6$ to $n = 5$

7. Assertion : The spectrum of He^+ is expected to be similar to that of hydrogen
Reason : He^+ is also one electron system.
- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false
(d) If both assertion and reason are false
8. Which of the following pairs of d-orbitals will have electron density along the axes ?
(NEET Phase - II)
- a) d_{z^2}, d_{xz} b) d_{xz}, d_{yz} c) $d_{z^2}, d_{x^2-y^2}$ d) $d_{xy}, d_{x^2-y^2}$
9. Two electrons occupying the same orbital are distinguished by
- a) azimuthal quantum number b) spin quantum number
c) magnetic quantum number d) orbital quantum number
10. The electronic configuration of Eu (Atomic no. 63) Gd (Atomic no. 64) and Tb (Atomic no. 65) are (NEET - Phase II)
- a) $[\text{Xe}] 4f^6 5d^1 6s^2$, $[\text{Xe}] 4f^7 5d^1 6s^2$ and $[\text{Xe}] 4f^8 5d^1 6s^2$
b) $[\text{Xe}] 4f^7, 6s^2$, $[\text{Xe}] 4f^7 5d^1 6s^2$ and $[\text{Xe}] 4f^9 6s^2$
c) $[\text{Xe}] 4f^7, 6s^2$, $[\text{Xe}] 4f^8 6s^2$ and $[\text{Xe}] 4f^8 5d^1 6s^2$
d) $[\text{Xe}] 4f^6 5d^1 6s^2$, $[\text{Xe}] 4f^7 5d^1 6s^2$ and $[\text{Xe}] 4f^9 6s^2$
11. The maximum number of electrons in a sub shell is given by the expression
- a) $2n^2$ b) $2l + 1$ c) $4l + 2$ d) none of these
12. For d-electron, the orbital angular momentum is
- a) $\frac{\sqrt{2}h}{2\pi}$ b) $\frac{\sqrt{2}h}{2\pi}$ c) $\frac{\sqrt{2 \times 4} h}{2\pi}$ d) $\frac{\sqrt{6} h}{2\pi}$



13. What is the maximum numbers of electrons that can be associated with the following set of quantum numbers ? $n = 3, l = 1$ and $m = -1$

- a) 4 b) 6 c) 2 d) = 10

14. Assertion : Number of radial and angular nodes for 3p orbital are 1, 1 respectively.

Reason : Number of radial and angular nodes depends only on principal quantum number.

- (a) both assertion and reason are true and reason is the correct explanation of assertion.
(b) both assertion and reason are true but reason is not the correct explanation of assertion.
(c) assertion is true but reason is false
(d) both assertion and reason are false

15. The total number of orbitals associated with the principal quantum number $n = 3$ is

- a) 9 b) 8 c) 5 d) 7

16. If $n = 6$, the correct sequence for filling of electrons will be,

- a) $ns \rightarrow (n - 2) f \rightarrow (n - 1)d \rightarrow np$ b) $ns \rightarrow (n - 1) d \rightarrow (n - 2) f \rightarrow np$
c) $ns \rightarrow (n - 2) f \rightarrow np \rightarrow (n - 1) d$ d) none of these are correct

17. Consider the following sets of quantum numbers :

	n	l	m	s
(i)	3	0	0	$+\frac{1}{2}$
(ii)	2	2	1	$-\frac{1}{2}$
(iii)	4	3	-2	$+\frac{1}{2}$
(iv)	1	0	-1	$+\frac{1}{2}$
(v)	3	4	3	$-\frac{1}{2}$

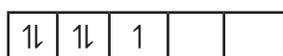


Which of the following sets of quantum number is not possible ?

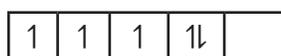
- a) (i), (ii), (iii) and (iv) b) (ii), (iv) and (v)
c) (i) and (iii) d) (ii), (iii) and (iv)
18. How many electrons in an atom with atomic number 105 can have $(n + l) = 8$?
a) 30 b) 17 c) 15 d) unpredictable
19. Electron density in the yz plane of $3d_{xy}$ orbital is
a) zero b) 0.50 c) 0.75 d) 0.90
20. If uncertainty in position and momentum are equal, then minimum uncertainty in velocity is
a) $\frac{1}{m} \sqrt{\frac{h}{\pi}}$ d) $\sqrt{\frac{h}{\pi}}$ c) $\frac{1}{2m} \sqrt{\frac{h}{\pi}}$ d) $\frac{h}{4\pi}$
21. A macroscopic particle of mass 100 g and moving at a velocity of 100 cm s^{-1} will have a de Broglie wavelength of
a) $6.6 \times 10^{-29} \text{ cm}$ b) $6.6 \times 10^{-30} \text{ cm}$ c) $6.6 \times 10^{-31} \text{ cm}$ d) $6.6 \times 10^{-32} \text{ cm}$
22. The ratio of de Broglie wavelengths of a deuterium atom to that of an α - particle, when the velocity of the former is five times greater than that of later, is
a) 4 b) 0.2 c) 2.5 d) 0.4
23. The energy of an electron in the 3rd orbit of hydrogen atom is $-E$. The energy of an electron in the first orbit will be
a) $-3E$ b) $-\frac{E}{3}$ c) $-\frac{E}{9}$ d) $-9E$
24. Time independent Schrodinger wave equation is
a) $\hat{H}\psi = E\psi$ b) $\nabla^2\psi + \frac{8\pi^2m}{h^2}(E+V)\psi = 0$
c) $\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{h^2}(E-V)\psi = 0$ d) all of these
25. Which of the following does not represent the mathematical expression for the Heisenberg uncertainty principle ?
a) $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$ b) $\Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$
c) $\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$ d) $\Delta E \cdot \Delta x \geq \frac{h}{4\pi}$

Write brief answer to the following questions

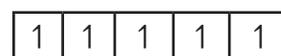
26. Which quantum number reveal information about the shape, energy, orientation and size of orbitals?
27. How many orbitals are possible for $n = 4$?
28. How many radial nodes for 2s, 4p, 5d and 4f orbitals exhibit? How many angular nodes?
29. The stabilisation of a half filled d - orbital is more pronounced than that of the p-orbital why?
30. Consider the following electronic arrangements for the d^5 configuration.



(a)



(b)



(c)

- (i) which of these represents the ground state
- (ii) which configuration has the maximum exchange energy.
31. State and explain pauli exclusion principle.
32. Define orbital? what are the n and l values for $3p_x$ and $4d_{x^2-y^2}$ electron?
33. Explain briefly the time independent schrodinger wave equation?
34. Calculate the uncertainty in position of an electron, if $\Delta v = 0.1\%$ and $v = 2.2 \times 10^6 \text{ ms}^{-1}$
35. Determine the values of all the four quantum numbers of the 8th electron in O- atom and 15th electron in Cl atom.
36. The quantum mechanical treatment of the hydrogen atom gives the energy value:

$$E_n = \frac{-13.6}{n^2} \text{ ev atom}^{-1}$$

- i) use this expression to find ΔE between $n = 3$ and $n=4$
- ii) Calculate the wavelength corresponding to the above transition.



37. How fast must a 54g tennis ball travel in order to have a de Broglie wavelength that is equal to that of a photon of green light 5400\AA ?
38. For each of the following, give the sub level designation, the allowable m values and the number of orbitals
- i) $n = 4, l = 2$, ii) $n = 5, l = 3$ iii) $n = 7, l = 0$
39. Give the electronic configuration of Mn^{2+} and Cr^{3+}
40. Describe the Aufbau principle
41. An atom of an element contains 35 electrons and 45 neutrons. Deduce
- i) the number of protons
- ii) the electronic configuration for the element
- iii) All the four quantum numbers for the last electron
42. Show that the circumference of the Bohr orbit for the hydrogen atom is an integral multiple of the de Broglie wave length associated with the electron revolving around the nucleus.
43. Calculate the energy required for the process.



The ionisation energy for the H atom in its ground state is $-13.6 \text{ eV atom}^{-1}$.

44. An ion with mass number 37 possesses unit negative charge. If the ion contains 11.1% more neutrons than electrons. Find the symbol of the ion.
45. The Li^{2+} ion is a hydrogen like ion that can be described by the Bohr model. Calculate the Bohr radius of the third orbit and calculate the energy of an electron in 4th orbit.
46. Protons can be accelerated in particle accelerators. Calculate the wavelength (in \AA) of such accelerated proton moving at $2.85 \times 10^8 \text{ ms}^{-1}$ (the mass of proton is $1.673 \times 10^{-27} \text{ Kg}$).
47. What is the de Broglie wavelength (in cm) of a 160g cricket ball travelling at 140 Km hr^{-1} .

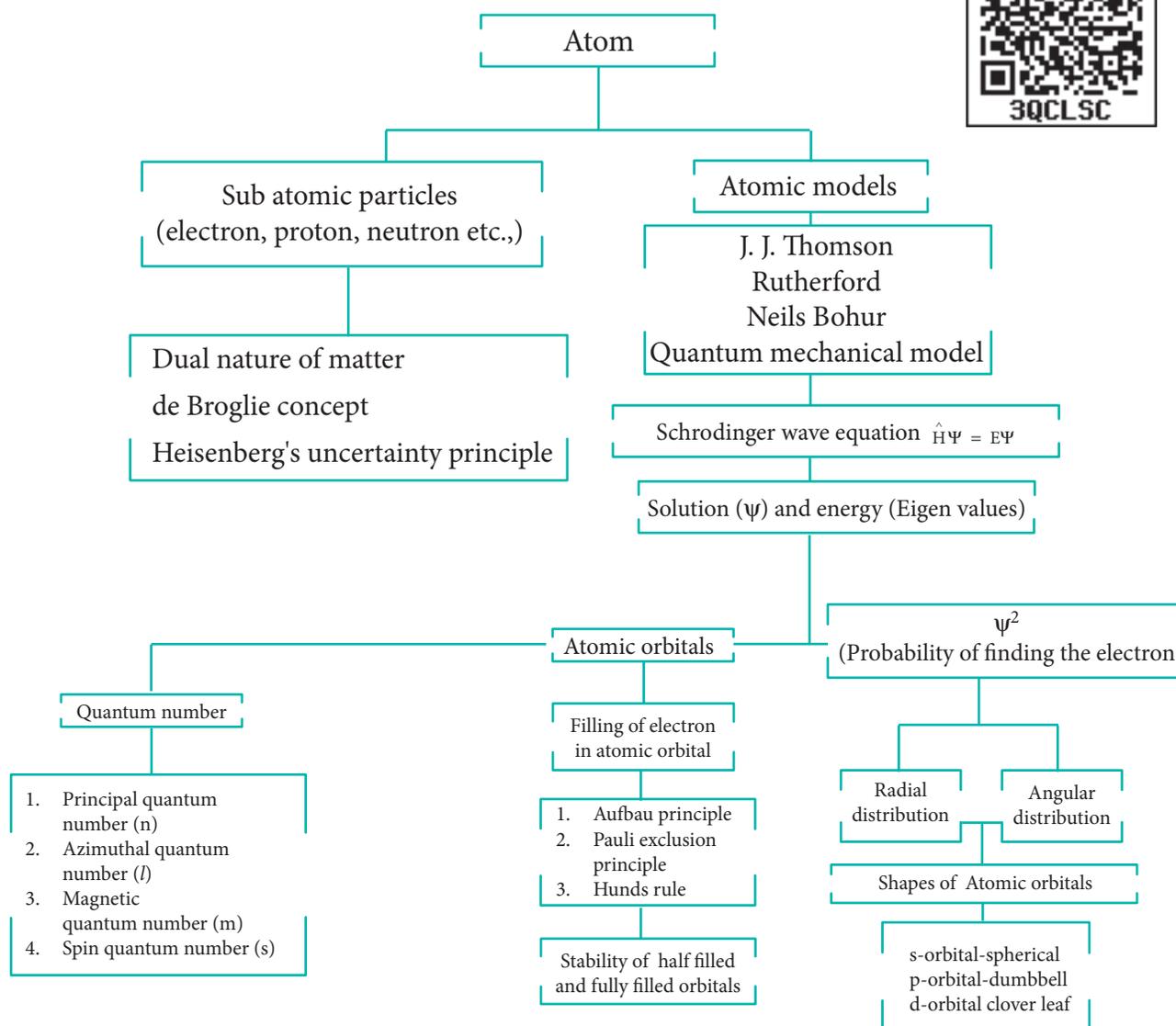


48. Suppose that the uncertainty in determining the position of an electron in an orbit is 0.6 \AA . What is the uncertainty in its momentum?
49. Show that if the measurement of the uncertainty in the location of the particle is equal to its de Broglie wavelength, the minimum uncertainty in its velocity (ΔV) is equal to $1/4\pi$ of its velocity (V)
50. What is the de Broglie wave length of an electron, which is accelerated from the rest, through a potential difference of $100V$?
51. Identify the missing quantum numbers and the sub energy level

n	l	m	Sub energy level
?	?	0	4d
3	1	0	?
?	?	?	5p
?	?	-2	3d



CONCEPT MAP

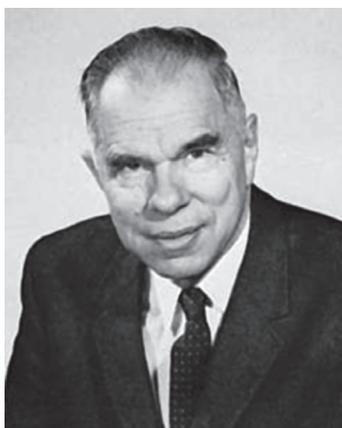




PERIODIC CLASSIFICATION OF ELEMENTS

"An awareness of the periodic table is essential to anyone who wishes to disentangle the world and see how it is built up from the fundamental building blocks of the chemistry, the chemical elements "

- Glenn T. Seaborg



Glenn T. Seaborg

Glenn Theodore Seaborg received Nobel Prize in 1951 in chemistry for the discoveries of trans-uranium elements. He was the co-discoverer of plutonium and other trans-uranium elements. He along with his colleagues has discovered over a hundred isotopes of other elements. He demonstrated that actinide elements are analogues to rare earth series of lanthanide elements.

Learning Objectives

After studying this unit, students will be able to



- recognise the development of the periodic table
- explain the work of Mosley's and modern periodic law
- outline the concept of grouping elements
- name the elements with atomic number greater than 100 using IUPAC nomenclature
- classify the elements into s, p, d and f blocks
- recognise the periodic trends and describe qualitatively the variation in periodic properties such as atomic radius, ionisation energy etc.
- explain the anomalies in the expected trend in the periodic properties
- calculate the effective nuclear charge using Slater's rule
- calculate the ionic radius using Pauling's method
- predict the probable position for a given element in the periodic table
- explain the anomalous properties of second period elements and the diagonal relationship

Introduction

There are millions of chemical compounds existing in nature with different compositions and properties, formed from less than 100 naturally occurring elements.

The discovery of elements is linked with human civilization. In stone age, man has used some metals to suit his needs without knowing that they are elements. Soon he learnt to extract elements from ores and fashion them into his daily life. Over the years, more and more elements were discovered. In 1789, Lavoisier from France, published the first list of chemical elements containing 23 elements after several experimental investigations.

Antoine Lavoisier classified the substances into four groups of elements namely acid-making elements, gas-like elements, metallic elements and earthy elements

Table 3.1 Lavoisier table

acid-making elements	gas-like elements
sulphur	light
phosphorus	caloric (heat)
charcoal (carbon)	oxygen
	azote (nitrogen)
	hydrogen

metallic elements	earthy elements
cobalt, mercury, tin	lime (calcium oxide)
copper, nickel, iron	magnesia (magnesium oxide)
gold, lead, silver, zinc	barytes (barium sulphate)
manganese, tungsten	argilla (aluminium oxide)
platina (platinum)	silex (silicon dioxide)

3.1 Classification of Elements

During the 19th century, scientists have isolated several elements and the list of known elements increased. Currently, we have 118 known elements. Out of 118 elements, 92 elements with atomic numbers 1 to 92 are found in nature. Scientists have found out there are some similarities in properties among certain elements. This observation has led to the idea of classification of elements based on their properties. In fact, classification will be beneficial for the effective utilization of these elements. Several attempts were made to classify the elements. However, classification based on the atomic weights led to the construction of a proper form of periodic table.

In 1817, J. W. Döbereiner classified some elements such as chlorine, bromine and iodine with similar chemical properties into the group of three elements called as triads. In triads, the atomic weight of the middle element nearly equal to the arithmetic mean of the atomic weights of the remaining two elements. However, only a limited number of elements can be grouped as triads.

Table 3.2 Döbereiner Triads

S. No.	Elements in the Triad	Atomic weight of middle element	Average atomic weight of the remaining elements
1	Li, Na, K	23	$\frac{7+39}{2} = 23$
2	Cl, Br, I	80	$\frac{35.5+127}{2} = 81.25$
3	Ca, Sr, Ba	88	$\frac{40+137}{2} = 88.5$

This concept can not be extended to some triads which have nearly same atomic masses such as [Fe, Co, Ni], [Ru, Rh, Pd] and [Os, Ir, Pt].

In 1862, A. E. B. de Chancourtois reported a correlation between the properties of the elements and their atomic weights. He said ‘the properties of bodies are the properties of numbers’. He intended the term numbers to mean the value of atomic weights. He designed a helix by tracing at an angle 45° to the vertical axis of a cylinder with circumference of 16 units. He arranged the elements in the increasing atomic weights along the helix on the surface of this cylinder. One complete turn of a helix corresponds to an atomic weight increase of 16. Elements which lie on the 16 equidistant vertical lines drawn on the surface of cylinder shows similar properties. This was the first reasonable attempt towards the creation of periodic table. However, it did not attract much attention.

In 1864, J. Newland made an attempt to classify the elements and proposed the law of octaves. On arranging the elements in the increasing order of atomic weights, he observed that the properties of every

eight element are similar to the properties of the first element. This law holds good for lighter elements up to calcium.

Table 3.3 Newlands’ Octaves

${}^7\text{Li}$	${}^9\text{Be}$	${}^{11}\text{B}$	${}^{12}\text{C}$	${}^{14}\text{N}$	${}^{16}\text{O}$	${}^{19}\text{F}$
${}^{23}\text{Na}$	${}^{24}\text{Mg}$	${}^{27}\text{Al}$	${}^{29}\text{Si}$	${}^{31}\text{P}$	${}^{32}\text{S}$	${}^{35.5}\text{Cl}$
${}^{39}\text{K}$	${}^{40}\text{Ca}$					

3.1.1 Mendeleev's Classification

In 1868, Lothar Meyer had developed a table of the elements that closely resembles the modern periodic table. He plotted the physical properties such as atomic volume, melting point and boiling point against atomic weight and observed a periodical pattern.

During same period Dmitri Mendeleev independently proposed that “the properties of the elements are the periodic functions of their atomic weights” and this is called periodic law. Mendeleev listed 70 elements, which were known till his time in several vertical columns in order of increasing atomic weights. Thus, Mendeleev constructed the first periodic table based on the periodic law.

Table 3.4 Mendeleev's periodic table

Group of Elements											
Series	0	1	II	III	IV	V	VI	VII	VIII		
1		Hydrogen H 1.0008	-	-	-	-	-	-	-	-	-
2	Helium He 4.0	Lithium Li 7.03	Beryllium Be 9.1	Boron B 11.0	Carbon C 12.0	Nitrogen N 14.04	Oxygen O 16.00	Fluorine F 19.0			
3	Neon Ne 19.9	Sodium Na 23.5	Magnesium Mg 24.3	Aluminium Al 27.0	Silicon Si 28.04	Phosphorus P 31.0	Sulphur S 32.06	Chlorine Cl 35.45			
4	Argon Ar 38	Potassium K 39.1	Calcium Ca 40.1	Scandium Sc 44.1	Titanium Ti 48.1	Vanadium V 51.4	Chromium Cr 52.1	Manganese Mn 55.0	Iron Fe 55.9	Cobalt Co 59	Nickel (Ni) (Cu) 59
5		Copper Cu 63.6	Zinc Zn 65.4	Gallium Ga 70.0	Germanium Ge 72.3	Arsenic As 75	Selenium Se 79	Bromine Br 79.95			
6	Krypton Kr 81.8	Rubidium Rb 85.4	Strontium Sr 87.6	Yttrium Y 89.0	Zirconium Zr 90.6	Niobium Nb 94.0	Molybdenum Mo 96.0		Ruthenium Ru 101.7	Rhodium Rh 103	Palladium (Pd) (Ag) 106.5
7		Silver Ag 107.9	Cadmium Cd 112.4	Indium In 114.0	Tin Sn 119.0	Antimony Sb 120.0	Tellurium Te 127.6	Iodine I 126.9			
8	Xenon Xe 128	Caesium Cs 132.9	Barium Ba 137.4	Lanthanum La 139	Cerium Ce 140	-	-	-	-	-	-
9											
10				Ytterbium Yb 173	-	Tantalum Ta 183	Tungsten W 184		Osmium Os 191	Iridium Ir 193	Platinum (Pt) (Au) 194.9
11		Gold Au 197.2	Mercury Hg 200.0	Thallium Tl 204.1	Lead Pb 206.9	Bismuth Bi 208					
12			Radium Ra 224	-	Thorium Th 232	Uranium U 239					

As shown in the periodic table, he left some blank spaces since there were no known elements with the appropriate properties at that time. He and others predicted the physical and chemical properties of the missing elements. Eventually these missing elements were discovered and found to have the predicted properties. For example, Gallium (Ga) of group III and germanium (Ge) of group IV were unknown at that time. But Mendeleev predicted their existence and properties. He referred the predicted elements as eka-aluminium and eka-silicon. After discovery of the actual elements, their properties were found to match closely to those predicted by Mendeleev (Table 3.4).

Table 3.5 Properties predicted for Eka-aluminium and Eka-silicon

S.No.	Property	Eka-aluminium (Predicted)	Gallium (Observed)	Eka-silicon (Predicted)	Germanium (Observed)
1.	Atomic weight	68	70	72	72.59
2.	Density (g/cm ³)	5.9	5.94	5.5	5.36
3.	Melting point	low	29.78°C	High	947°C
4.	Formula of oxide	E ₂ O ₃	Ga ₂ O ₃	EO ₂	GeO ₂
5.	Formula of chloride	ECl ₃	GaCl ₃	ECl ₄	GeCl ₄

3.1.2 Anomalies of Mendeleev's Periodic Table

Some elements with similar properties were placed in different groups and those with dissimilar properties were placed in same group. Similarly elements with higher atomic weights were placed before lower atomic weights based on their properties in contradiction to his periodic law. Example ⁵⁹Co₂₇ was placed before ^{58.7}Ni₂₈; Tellurium (127.6) was placed in VI group but Iodine (127.0) was placed in VII group.

3.2 Moseley's Work and Modern Periodic Law

In 1913, Henry Moseley studied the characteristic X-rays spectra of several elements by bombarding them with high energy electrons and observed a linear correlation between atomic number and the frequency of X-rays emitted which is given by the following expression.

$$\sqrt{\nu} = a(Z - b)$$

Where, ν is the frequency of the X-rays emitted by the element with atomic number 'Z'; a and b are constants and have same values for all the elements.

The plot of $\sqrt{\nu}$ against Z gives a straight line. Using this relationship, we can determine the atomic number of an unknown (new) element from the frequency of X-ray emitted.

Based on his work, the modern periodic law was developed which states that, "the physical and chemical properties of the elements are periodic functions of their atomic numbers." Based on this law, the elements were arranged in order of their increasing atomic numbers. This mode of arrangement reveals an important truth that the elements with similar properties recur after regular intervals. The repetition of physical and chemical properties at regular intervals is called periodicity.

3.2.1 Modern Periodic Table

The physical and chemical properties of the elements are correlated to the arrangement of electrons in their outermost shell (valence shell). Different elements having similar outer shell electronic configuration possess similar properties. For example, elements having one electron in their valence shell s-orbital possess similar physical and chemical properties. These elements are grouped together in the modern periodic table as first group elements.

Evaluate Yourself

1. What is the basic difference in approach between Mendeleev's periodic table and modern periodic table ?

Table 3.6 Electronic configuration of alkali metals (ns^1)

Elements in Group 1	Atomic number	Number of electrons in various shells in the order K, L, M, N, P	Valence shell configuration
Li	3	2, 1	$2s^1$
Na	11	2, 8, 1	$3s^1$
K	19	2, 8, 8, 1	$4s^1$
Rb	37	2,8,18,8,1	$5s^1$
Cs	55	2, 8, 18, 18, 8, 1	$6s^1$
Fr	87	2, 8, 18, 32, 18, 8, 1	$7s^1$

Similarly, all the elements are arranged in the modern periodic table which contains 18 vertical columns and 7 horizontal rows. The vertical columns are called groups and the horizontal rows are called periods. Groups are numbered 1 to 18 in accordance with the IUPAC recommendation which replaces the old numbering scheme IA to VIIA, IB to VIIB and VIII.

Each period starts with the element having general outer electronic configuration ns^1 and ends with $ns^2 np^6$. Here 'n' corresponds to the period number (principal quantum number). The aufbau principle and the electronic configuration of atoms provide a theoretical foundation for the modern periodic table.



Table 3.7 Modern periodic table

PERIOD NUMBER	Representative elements		d-Transition elements										Representative elements					Noble gases																					
	GROUP NUMBER	GROUP NUMBER	GROUP NUMBER										GROUP NUMBER																										
1	1	H $1s^1$											13	14	15	16	17	18																					
2	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																						
3		Li $2s^1$	Be $2s^2$	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36										
4		Na $3s^1$	Mg $3s^2$	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
5		K $4s^1$	Ca $4s^2$	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
6		Rb $5s^1$	Sr $5s^2$	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	
7		Fr $7s^1$	Ra $7s^2$	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120		

f - Inner transition elements

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce $4f^1 5d^1 6s^2$	Pr $4f^3 5d^0 6s^2$	Nd $4f^4 5d^0 6s^2$	Pm	Sm $4f^6 5d^0 6s^2$	Eu $4f^7 5d^0 6s^2$	Gd $4f^7 5d^1 6s^2$	Tb $4f^9 5d^0 6s^2$	Dy $4f^{10} 5d^0 6s^2$	Ho $4f^{11} 5d^0 6s^2$	Er $4f^{12} 5d^0 6s^2$	Tm $4f^{13} 5d^0 6s^2$	Yb $4f^{14} 6s^2$	Lu $4f^{14} 5d^1 6s^2$
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th $5f^6 6d^2 7s^2$	Pa $5f^6 6d^1 7s^2$	U $5f^6 6d^1 7s^2$	Np $5f^6 6d^1 7s^2$	Pu $5f^6 6d^1 7s^2$	Am $5f^7 6d^0 7s^2$	Cm $5f^7 6d^1 7s^2$	Bk $5f^7 6d^1 7s^2$	Cf $5f^{10} 6d^1 7s^2$	Es $5f^{11} 6d^1 7s^2$	Fm $5f^{12} 6d^0 7s^2$	Md $5f^{13} 6d^1 7s^2$	No $5f^{14} 6d^1 7s^2$	Lr $5f^{14} 6d^1 7s^2$

Lanthanoids
 $4f^m 5d^{0-1} 6s^2$

** Actinoids
 $5f^n 6d^{0-2} 7s^2$

3.3 Nomenclature of Elements with Atomic Number Greater than 100

Usually, when a new element is discovered, the discoverer suggests a name following IUPAC guidelines which will be approved after a public opinion. In the meantime, the new element will be called by a temporary name coined using the following IUPAC rules, until the IUPAC recognises the new name.

1. The name was derived directly from the atomic number of the new element using the following numerical roots.

Table 3.8 Notation for IUPAC Nomenclature of elements

Digit	0	1	2	3	4	5	6	7	8	9
Root	nil	un	bi	tri	quad	pent	hex	sept	oct	enn
Abbreviation	n	u	b	t	q	p	h	s	o	e

2. The numerical roots corresponding to the atomic number are put together and 'ium' is added as suffix
3. The final 'n' of 'enn' is omitted when it is written before 'nil' (enn + nil = enil) similarly the final 'i' of 'bi' and 'tri' is omitted when it is written before 'ium' (bi + ium = bium; tri + ium = trium)
4. The symbol of the new element is derived from the first letter of the numerical roots.

The following table illustrates these facts.

Table 3.9 Name of elements with atomic number above 100

Atomic number	Temporary Name	Temporary Symbol	Name of the element	Symbol
101	Unnilunium	Unu	Mendelevium	Md
102	Unnilbium	Unb	Nobelium	No
103	Unniltrium	Unt	Lawrencium	Lr
104	Unnilquadium	Unq	Rutherfordium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassium	Hs

Atomic number	Temp. Name	Temp. Symbol	Name of the element	Symbol
109	Unnilennium	Une	Meitnerium	Mt
110	Ununnilium	Uun	Darmstadtium	Ds
111	Unununium	Uuu	Roentgenium	Rg
112	Ununbium	Uub	Copernicium	Cn
113	Ununtrium	Uut	Nihonium	Nh
114	Ununquadium	Uuq	Flerovium	Fl
115	Ununpentium	Uup	Moscovium	Mc
116	Ununhexium	Uuh	Livermorium	Lv
117	Ununseptium	Uus	Tennessine	Ts
118	Ununoctium	Uuo	Oganesson	Og

Evaluate Yourself



- The element with atomic number 120 has not been discovered so far. What would be the IUPAC name and the symbol for this element? Predict the possible electronic configuration of this element.

3.4 Grouping of Elements based on Electronic Configurations

In the modern periodic table, the elements are organised in 7 periods and 18 groups based on the modern periodic law. The placement of element in the periodic table is closely related to its outer shell electronic configuration. Let us analyse the change in the electronic configuration of elements along the periods and down the groups.

3.4.1 Variation of Electronic Configuration along the periods

We have already learnt that each period starts with the element having general outer electronic configuration ns^1 and ends with ns^2, np^6 where n is the period number. The first period starts with the filling of valence electrons in $1s$ orbital, which can accommodate only two electrons. Hence, the first period has two elements, namely hydrogen and helium. The second period starts with the filling of valence electrons in $2s$ orbital followed by three $2p$ orbitals with eight elements from lithium to neon. The third period starts with filling of valence electrons in the $3s$ orbital followed by $3p$ orbitals. The fourth period starts with filling of valence electrons from $4s$ orbital followed by $3d$ and $4p$ orbitals in accordance with Aufbau principle. Similarly, we can explain the electronic configuration of elements in the subsequent periods (Table 3.10).

Table 3.10 Electronic configuration of elements in a period

Period number (n)	Filling of electrons in orbitals		Number of elements	Outer shell Electronic configuration	
	Starts from	Ends with		First element	Last element
1	1s	1s	2	H - 1s ¹	He - 1s ²
2	2s	2p	8	Li - 2s ¹	Ne - 2s ² 2p ⁶
3	3s	3p	8	Na - 3s ¹	Ar - 3s ² 3p ⁶
4	4s	4p	18	K - 4s ¹	Kr - 4s ² 4p ⁶
5	5s	5p	18	Rb - 5s ¹	Xe - 5s ² 5p ⁶
6	6s	6p	32	Cs - 6s ¹	Rn - 6s ² 6p ⁶
7	7s	7p	32	Fr - 7s ¹	Og - 7s ² 7p ⁶

In the fourth period the filling of 3d orbitals starts with scandium and ends with zinc. These 10 elements are called first transition series. Similarly 4d, 5d and 6d orbitals are filled in successive periods and the corresponding series of elements are called second, third and fourth transition series respectively.

In the sixth period the filling of valence electrons starts with 6s orbital followed by 4f, 5d and 6p orbitals. The filling up of 4f orbitals begins with Cerium (Z=58) and ends at Lutetium (Z=71). These 14 elements constitute the first inner-transition series called Lanthanides. Similarly, in the seventh period 5f orbitals are filled, and it's -14 elements constitute the second inner-transition series called Actinides. These two series are placed separately at the bottom of the modern periodic table.

3.4.2 Variation of Electronic Configuration in the Groups:

Elements of a group have similar electronic configuration in the outer shell. The general outer electronic configurations for the 18 groups are listed in the Table 3.11. The groups can be combined as s, p, d and f block elements on the basis of the orbital in which the last valence electron enters.

The elements of group 1 and group 2 are called s-block elements, since the last valence electron enters the ns orbital. The group 1 elements are called alkali metals while the group 2 elements are called alkaline earth metals. These are soft metals and possess low melting and boiling points with low ionisation enthalpies. They are highly reactive and form ionic compounds. They are highly electropositive in nature and most of the elements imparts colour to the flame. We will study the properties of these group elements in detail in subsequent chapters.

The elements of groups 13 to 18 are called p-block elements or representative elements and have a general electronic configuration ns^2, np^{1-6} . The elements of the group 16 and 17 are called chalcogens and halogens respectively. The elements of 18th group contain completely filled valence shell electronic configuration (ns^2, np^6) and are called inert gases or nobles gases. The elements of p-block have high negative electron gain enthalpies. The ionisation energies are higher than that of s-block elements. They form mostly covalent compounds and shows more than one oxidation states in their compounds.

The elements of the groups 3 to 12 are called d-block elements or transition elements with general valence shell electronic configuration $ns^{1-2}, (n-1)d^{1-10}$. These elements also show more than one oxidation state and form ionic, covalent and co-ordination compounds. They can form interstitial compounds and alloys which can also act as catalysts. These elements have high melting points and are good conductors of heat and electricity.

The lanthanides ($4f^{1-14}, 5d^{0-1}, 6s^2$) and the actinides ($5f^{0-14}, 6d^{0-2}, 7s^2$) are called f-block elements. These elements are metallic in nature and have high melting points. Their compounds are mostly coloured. These elements also show variable oxidation states.

Table 3.11 General outer electronic configuration of elements in groups:

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
ns^1	ns^2	$ns^2(n-1)d^1$	$ns^2(n-1)d^2$	$ns^2(n-1)d^3$	$ns^1(n-1)d^5$	$ns^2(n-1)d^5$	$ns^2(n-1)d^6$	$ns^2(n-1)d^7$	$ns^2(n-1)d^8$	$ns^1(n-1)d^{10}$	$ns^2(n-1)d^{10}$	$ns^2 np^1$	$ns^2 np^2$	$ns^2 np^3$	$ns^2 np^4$	$ns^2 np^5$	$ns^2 np^6$
s-block elements	d-block elements										p-block elements						
f-block elements	Lanthanides $4f^{1-14} 5d^{0-1} 6s^2$ Actinides $5f^{0-14} 6d^{0-2} 7s^2$																

Evaluate Yourself



3. Predict the position of the element in periodic table satisfying the electronic configuration $(n-1)d^2, ns^2$ where $n=5$

3.5 Periodic Trends in Properties

As discussed earlier, the electronic configuration of the elements shows a periodic variation with increase in atomic numbers. Similarly a periodic trend is observed in physical and chemical behaviour of elements. In this section, we will study the periodic trends in the following properties of elements.

1. Atomic radius
2. Ionic radius
3. Ionisation enthalpy (energy)
4. Electron gain enthalpy (electron affinity)
5. Electronegativity

3.5.1 Atomic radius

Atomic radius of an atom is defined as the distance between the centre of its nucleus and the outermost shell containing the valence electron.

It is not possible to measure the radius of an isolated atom directly. Except for noble gases, usually atomic radius is referred to as covalent radius or metallic radius depending upon the nature of bonding between the concerned atoms.

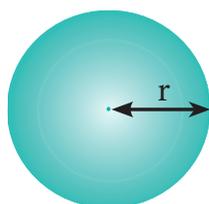


Figure 3.1 (a) Atomic radius

Covalent radius

It is one-half of the internuclear distance between two identical atoms linked together by a single covalent bond. Inter nuclear distance can be determined using x-ray diffraction studies.

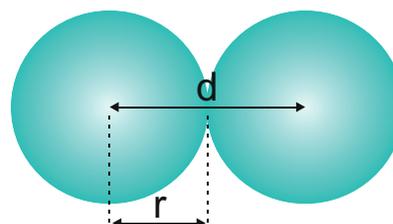


Figure 3.1 (b) Atomic and covalent radius

Example:

The experimental internuclear distance in Cl_2 molecule is 1.98 \AA . The covalent radius of chlorine is calculated as below.

$$\begin{aligned}d_{\text{Cl-Cl}} &= r_{\text{Cl}} + r_{\text{Cl}} \\ \Rightarrow d_{\text{Cl-Cl}} &= 2r_{\text{Cl}} \\ \Rightarrow r_{\text{Cl}} &= \frac{d_{\text{Cl-Cl}}}{2} \\ \Rightarrow r_{\text{Cl}} &= \frac{1.98}{2} = 0.99 \text{ \AA}\end{aligned}$$

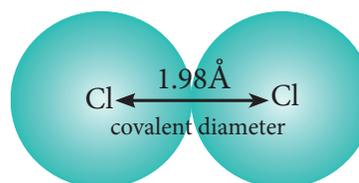


Figure 3.1 (c) Covalent radius of Cl

The formation of covalent bond involves the overlapping of atomic orbitals and it reduces the expected internuclear distance. Therefore covalent radius is always shorter than the actual atomic radius.

In case of hetero nuclear diatomic molecules, the covalent radius of individual atom can also be calculated using the internuclear distance (d_{A-B}) between two different atoms A and B. The simplest method proposed by Schomaker and Stevenson is as follows.

$$d_{A-B} = r_A + r_B - 0.09 (\chi_A - \chi_B)$$

where χ_A and χ_B are the electronegativities of A and B respectively in Pauling units. Here $\chi_A > \chi_B$ and radius is in Å.

Let us calculate the covalent radius of hydrogen using the experimental d_{H-Cl} value is 1.28 Å and the covalent radius of chlorine is 0.99 Å. In Pauling scale the electronegativity of chlorine and hydrogen are 3 and 2.1 respectively.

$$\begin{aligned} d_{H-Cl} &= r_H + r_{Cl} - 0.09 (\chi_{Cl} - \chi_H) \\ 1.28 &= r_H + 0.99 - 0.09 (3 - 2.1) \\ 1.28 &= r_H + 0.99 - 0.09 (0.9) \\ 1.28 &= r_H + 0.99 - 0.081 \\ 1.28 &= r_H + 0.909 \\ \therefore r_H &= 1.28 - 0.909 = 0.371 \text{ Å} \end{aligned}$$

Metallic radius

It is defined as one-half of the distance between two adjacent metal atoms in the closely packed metallic crystal lattice.

For example, the distance between the adjacent copper atoms in solid copper is 2.56 Å and therefore the metallic radius of copper is

$$\frac{2.56}{2} = 1.28 \text{ Å}$$

The metallic radius can be calculated using the unit cell length of the metallic crystal. You will study the detailed calculation procedure in XII standard solid state unit.

Periodic Trends in Atomic Radius

Variation in Periods

Atomic radius tends to decrease in a period. As we move from left to right along a period, the valence electrons are added to the same shell. The simultaneous addition of protons to the nucleus, increases the nuclear charge, as well as the electrostatic attractive force between the valence electrons and the nucleus. Therefore atomic radius decreases along a period.

Effective nuclear charge

In addition to the electrostatic forces of attraction between the nucleus and the electrons, there exists repulsive forces among the electrons. The repulsive force between the inner shell electrons and the valence electrons leads to a decrease in the electrostatic attractive forces acting on the valence electrons by the nucleus. Thus, the inner shell electrons act as a shield between the nucleus and the valence electrons. This effect is called shielding effect.

The net nuclear charge experienced by valence electrons in the outermost shell is called the effective nuclear charge. It is approximated by the below mentioned equation.

$$Z_{\text{eff}} = Z - S$$

Where Z is the atomic number and 'S' is the screening constant which can be calculated using Slater's rules as described below.

Step 1 :

Write the electronic configuration of the atom and rearrange it by grouping ns and np orbitals together and others separately in the following form.

(1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p)...

Step 2 :

Identify the group in which the electron of interest is present. The electron present right to this group does not contribute to the shielding effect.

Each of the electrons within the identified group (denoted by 'n') shields to an extent of 0.35 unit of nuclear charge. However, it is 0.30 unit for 1s electron.

Step 3 :

Shielding of inner shell electrons.

If the electron of interest belongs to either s or p orbital,

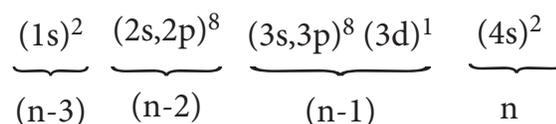
- each electron within the (n-1) group shields to an extent of 0.85 unit of nuclear charge, and
- each electron within the (n-2) group (or) even lesser group (n-3), (n-4) etc... completely shields i.e. to an extent of 1.00 unit of nuclear charge.

If the electron of interest belongs to d or f orbital, then each of electron left of the group of electron of interest shields to an extent of 1.00 unit of nuclear charge.

Step 4 :

Summation of the shielding effect of all the electrons gives the shielding constant 'S'

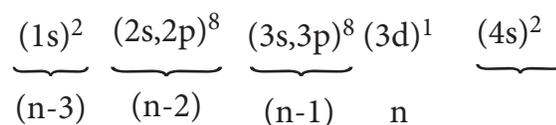
Example: Let us explain the calculation of effective nuclear charge on 4s electron and 3d electron in scandium. The electronic configuration of scandium is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^1$. we can rearrange as below.



Group	number of electron in the group	contribution of each electron to 'S' value	contribution of a particular group to electrons to 'S' value
(n)	1	0.35	0.35
(n-1)	9	0.85	7.65
(n-2) & others	10	1	10.00
S value			18.00

$$Z_{\text{eff}} = Z - S \quad \text{i.e.} = 21 - 18 \quad \therefore Z_{\text{eff}} = 3$$

Calculation of effective nuclear charge on 3d electron



Group	number of electron in the group	contribution of each electron to 'S' value	contribution of a particular group to electrons to 'S' value
n	0	0.35	0
(n-1) & others	18	1	18
S Value			18

$$\therefore Z_{\text{eff}} = Z - S \quad \text{i.e.} = 21 - 18 \quad \therefore Z_{\text{eff}} = 3$$

Table 3.12 Shielding effect from inner shell electrons (Slater's rules)

Electron Group	Electron of interest either S or P	Electron of interest either d or f
n	0.35 (0.30 for S electron)	0.35
(n-1)	0.85	1.00
(n-2) and others	1.00	1.00

Table 3.13 Atomic radius (covalent radius) of second period elements.

Elements	Effective nuclear charge	Covalent radius (pm)
${}^3\text{Li}$	1.30	152
${}^4\text{Be}$	1.95	111
${}^5\text{B}$	2.60	89
${}^6\text{C}$	3.25	77
${}^7\text{N}$	3.90	74
${}^8\text{O}$	4.55	66
${}^9\text{F}$	5.20	64
${}^{10}\text{Ne}$	5.85	

* Van der waals radius

Evaluate Yourself

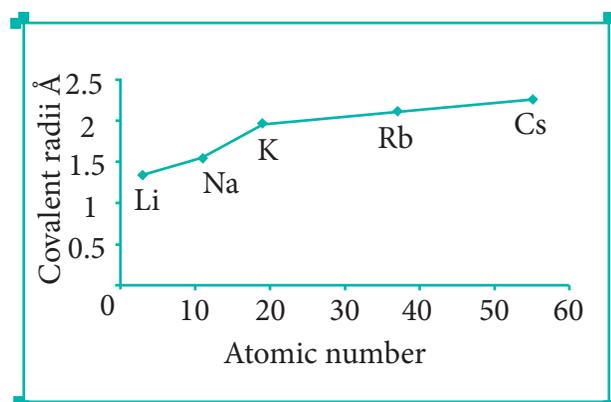


4. Using Slater's rule calculate the effective nuclear charge on a 3p electron in aluminium and chlorine. Explain how these results relate to the atomic radii of the two atoms.

Variation in Group

In the periodic table, the atomic radius of elements increases down the group. As we move down a group, new shells are opened to accommodate the newly added valence electrons. As a result, the distance between the centre of the nucleus and the outermost shell containing the valence electron increases. Hence, the atomic radius increases. The trend in the variation of the atomic radius of the alkali metals down the group is shown below.

Table 3.14 Variation of covalent radius of group 1 elements



Element	Outermost shell containing valence electron	Covalent radius (Å)
Li	L (n=2)	1.34
Na	M (n=3)	1.54
K	N (n=4)	1.96
Rb	O (n=5)	2.11
Cs	P (n=6)	2.25

Activity 3.1

Covalent radii (in Å) for some elements of different groups and periods are listed below. Plot these values against atomic number. From the plot, explain the variation along a period and a group.

2nd group elements : Be (0.89), Mg (1.36), Ca (1.74), Sr (1.91) Ba(1.98)

17th group elements : F (0.72), Cl (0.99), Br (1.14), I (1.33)

3rd Period elements : Na(1.57), Mg(1.36), Al (1.25), Si(1.17), P(1.10), S(1.04), Cl(0.99)

4th period elements: K(2.03), Ca(1.74), Sc(1.44), Ti(1.32), V(1.22), Cr(1.17), Mn(1.17), Fe(1.17), Co(1.16), Ni(1.15), Cu(1.17), Zn(1.25), Ga(1.25), Ge(1.22), As(1.21), Se(1.14), Br(1.14)

3.5.2 Ionic radius

It is defined as the distance from the centre of the nucleus of the ion up to which it exerts its influence on the electron cloud of the ion. Ionic radius of uni-univalent crystal can be calculated using Pauling's method from the inter ionic distance between the nuclei of the cation and anion. Pauling assumed

that ions present in a crystal lattice are perfect spheres, and they are in contact with each other. Therefore,

$$d = r_{C^+} + r_{A^-} \text{ ----- (1)}$$

Where d is the distance between the centre of the nucleus of cation C⁺ and anion A⁻ and r_{C⁺}, r_{A⁻} are the radius of the cation and anion respectively.

Pauling also assumed that the radius of the ion having noble gas electronic configuration (Na⁺ and Cl⁻ having 1s² 2s², 2p⁶ configuration) is inversely proportional to the effective nuclear charge felt at the periphery of the ion.

$$\text{i.e. } r_{C^+} \propto \frac{1}{(Z_{\text{eff}})_{C^+}} \text{ ----- (2)}$$

$$r_{A^-} \propto \frac{1}{(Z_{\text{eff}})_{A^-}} \text{ ----- (3)}$$

Where Z_{eff} is the effective nuclear charge and Z_{eff} = Z - S

Dividing the equation 2 by 3

$$\frac{r_{C^+}}{r_{A^-}} = \frac{(Z_{\text{eff}})_{A^-}}{(Z_{\text{eff}})_{C^+}} \text{ ----- (4)}$$

On solving equation (1) and (4) the values of r_{C⁺} and r_{A⁻} can be obtained

Let us explain this method by calculating the ionic radii of Na⁺ and F⁻ in NaF crystal whose interionic distance is equal to 231 pm .

$$d = r_{\text{Na}^+} + r_{\text{F}^-} \text{ --- (5)}$$

$$\text{i.e. } r_{\text{Na}^+} + r_{\text{F}^-} = 231 \text{ pm --- (6)}$$

We know that

$$\frac{r_{\text{Na}^+}}{r_{\text{F}^-}} = \frac{(Z_{\text{eff}})_{\text{F}^-}}{(Z_{\text{eff}})_{\text{Na}^+}}$$

$$(Z_{\text{eff}})_{\text{F}^-} = Z - S$$

$$= 9 - 4.15$$

$$= 4.85$$

$$(Z_{\text{eff}})_{\text{Na}^+} = 11 - 4.15$$

$$= 6.85$$

$$\therefore \frac{r_{\text{Na}^+}}{r_{\text{F}^-}} = \frac{4.85}{6.85}$$

$$= 0.71$$

$$\Rightarrow r_{\text{Na}^+} = 0.71 \times r_{\text{F}^-}$$

Substituting r_{Na^+} in (5)

$$(5) \Rightarrow 0.71 r_{\text{F}^-} + r_{\text{F}^-} = 231 \text{ pm}$$

$$1.71 r_{\text{F}^-} = 231 \text{ pm}$$

$$r_{\text{F}^-} = \frac{231}{1.71} = 135.1 \text{ pm}$$

Substituting the value of r_{F^-} in equation (6)

$$r_{\text{Na}^+} + 135.1 = 231$$

$$r_{\text{Na}^+} = 95.9 \text{ pm}$$

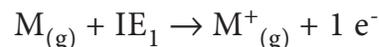
Evaluate Yourself



5. A student reported the ionic radii of isoelectronic species X^{3+} , Y^{2+} and Z^- as 136 pm, 64 pm and 49 pm respectively. Is that order correct? Comment.

3.5.3 Ionisation energy

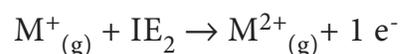
It is defined as the minimum amount of energy required to remove the most loosely bound electron from the valence shell of the isolated neutral gaseous atom in its ground state. It is expressed in kJ mol^{-1} or in electron volts (eV).



Where IE_1 represents the first ionisation energy.

Successive Ionisation energies

The minimum amount of energy required to remove an electron from a unipositive cation is called second ionisation energy. It is represented by the following equation.



In this way we can define the successive ionisation energies such as third, fourth etc.

The total number of electrons are less in the cation than the neutral atom while the nuclear charge remains the same. Therefore the effective nuclear charge of the cation is higher than the corresponding neutral atom. Thus the successive ionisation energies, always increase in the following order

$$IE_1 < IE_2 < IE_3 < \dots$$

Periodic Trends in Ionisation Energy

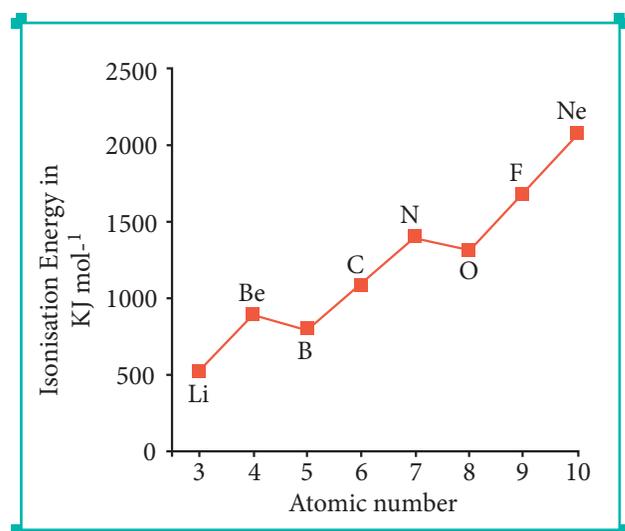
The ionisation energy usually increases along a period with few exceptions. As discussed earlier, when we move from left to right along a period, the valence electrons are added to the same shell, at the same time protons are added to the nucleus. This successive increase of nuclear charge increases the electrostatic attractive force on the valence electron and more energy is required to remove the valence electron resulting in high ionisation energy.

Let us consider the variation in ionisation energy of second period

elements. The plot of atomic number vs ionisation energy is given below.

In the following graph, there are two deviation in the trends of ionisation energy. It is expected that boron has higher ionisation energy than beryllium since it has higher nuclear charge. However, the actual ionisation energies of beryllium and boron are 899 and 800 kJ mol⁻¹ respectively contrary to the expectation. It is due to the fact that beryllium with completely filled 2s orbital, is more stable than partially filled valence shell electronic configuration of boron. (2s²2p¹)

Figure 3.2 Variation of Ionisation energy along the II period



The electronic configuration of beryllium (Z=4) in its ground state is 1s², 2s² and that of boron is (Z = 5) 1s² 2s² 2p¹

Similarly, nitrogen with 1s², 2s², 2p³ electronic configuration has higher ionisation energy (1402 kJ mol⁻¹) than oxygen (1314 kJ mol⁻¹). Since the half filled electronic configuration is more stable, it requires higher energy to remove an electron from 2p orbital of nitrogen. Whereas the removal one 2p electron from oxygen leads to a stable half filled

configuration. This makes comparatively easier to remove 2p electron from oxygen.

Periodic variation in group

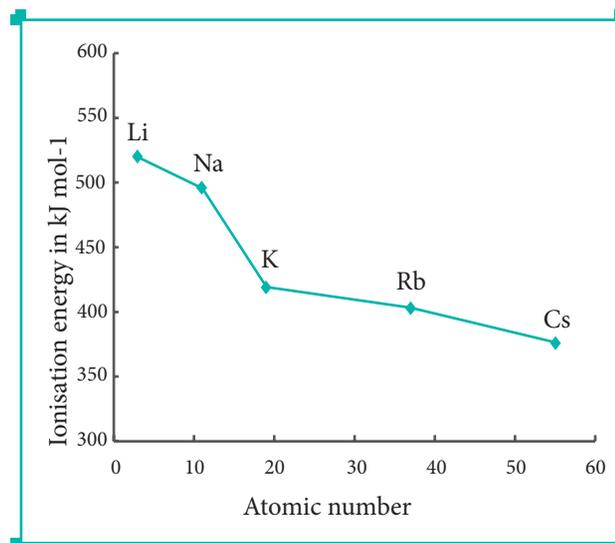
The ionisation energy decreases down a group. As we move down a group, the valence electron occupies new shells, the distance between the nucleus and the valence electron increases. So, the nuclear forces of attraction on valence electron decreases and hence ionisation energy also decreases down a group.

Ionisation energy and shielding effect

As we move down a group, the number of inner shell electron increases which in turn increases the repulsive force exerted by them on the valence electrons, i.e. the increased shielding effect caused by the inner electrons decreases the attractive force acting on the valence electron by the nucleus. Therefore the ionisation energy decreases.

Let us understand this trend by considering the ionisation energy of alkali metals.

Figure 3.3 Variation of Ionisation energy down the I Group.



Evaluate Yourself



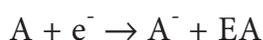
6. The first ionisation energy (IE_1) and second ionisation energy (IE_2) of elements X, Y and Z are given below.

Element	IE_1 (kJ mol^{-1})	IE_2 (kJ mol^{-1})
X	2370	5250
Y	522	7298
Z	1680	3381

Which one of the above elements is the most reactive metal, the least reactive metal and a noble gas?

3.5.4 Electron Affinity

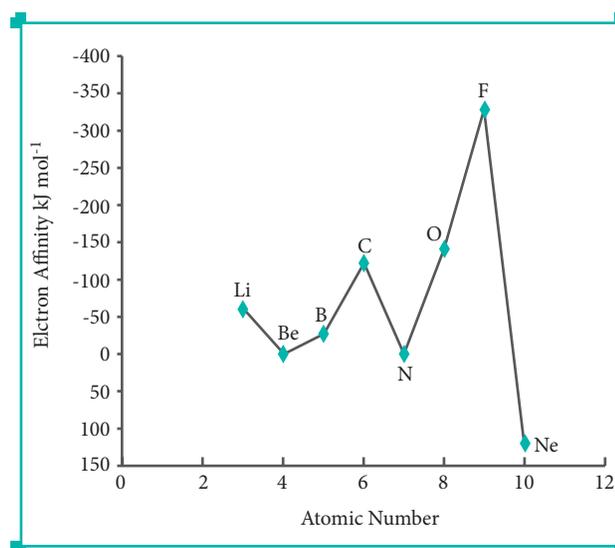
It is defined as the amount of energy released (required in the case noble gases) when an electron is added to the valence shell of an isolated neutral gaseous atom in its ground state to form its anion. It is expressed in kJ mol^{-1}



Variation of Electron Affinity in a period:

The variation of electron affinity is not as systematic as in the case of ionisation energy. As we move from alkali metals to halogens in a period, generally electron affinity increases, i.e. the amount of energy released will be more. This is due to an increase in the nuclear charge and decrease in size of the atoms. However, in case of elements such as beryllium ($1s^2, 2s^2$), nitrogen ($1s^2, 2s^2, 2p^3$) the addition of extra electron will disturb their stable electronic configuration and they have almost zero electron affinity.

Figure 3.4 Variation of electron affinity (electron gain energy) along II period



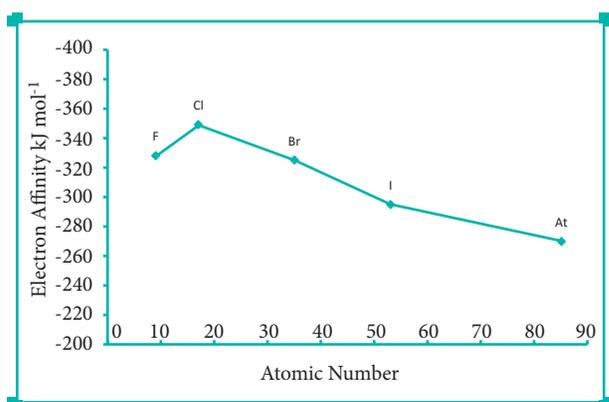
Noble gases have stable ns^2, np^6 configuration, and the addition of further electron is unfavourable and requires energy. Halogens having the general electronic configuration of ns^2, np^5 readily accept an electron to get the stable noble gas electronic configuration (ns^2, np^6), and therefore in each period the halogen has high electron affinity. (high negative values)

Variation of Electron affinity in a group:

As we move down a group, generally the electron affinity decreases. It is due to increase in atomic size and the shielding effect of inner shell electrons. However, oxygen and fluorine have lower affinity than sulphur and chlorine respectively. The sizes of oxygen and fluorine atoms are comparatively small and they have high electron density. Moreover, the extra electron added to oxygen and fluorine has to be accommodated in the $2p$ orbital which is relatively compact compared to the $3p$ orbital of sulphur

and chlorine so, oxygen and fluorine have lower electron affinity than their respective group elements sulphur and chlorine.

Figure 3.5 Variation of Electron Affinity (electron gain energy) along 17th group



Evaluate Yourself



7. The electron gain enthalpy of chlorine is 348 kJ mol^{-1} . How much energy in kJ is released when 17.5 g of chlorine is completely converted into Cl^- ions in the gaseous state?

3.5.5 Electronegativity:

It is defined as the relative tendency of an element present in a covalently bonded molecule, to attract the shared pair of electrons towards itself.

Electronegativity is not a measurable quantity. However, a number of scales are available to calculate its value. One such method was developed by Pauling, he assigned arbitrary value of electronegativities for hydrogen and fluorine as 2.1 and 4.0 respectively. Based on this the electronegativity values for other elements can be calculated using the following expression

$$(\chi_A - \chi_B) = 0.182 \sqrt{E_{AB} - (E_{AA} \times E_{BB})^{1/2}}$$

Where E_{AB} , E_{AA} and E_{BB} are the bond dissociation energies (K cal) of AB, A_2 and B_2 molecules respectively.

The electronegativity of any given element is not a constant and its value depends on the element to which it is covalently bound. The electronegativity values play an important role in predicting the nature of the bond.

Variation of Electronegativity in a period:

The electronegativity generally increases across a period from left to right. As discussed earlier, the atomic radius decreases in a period, as the attraction between the valence electron and the nucleus increases. Hence the tendency to attract shared pair of electrons increases. Therefore, electronegativity also increases in a period

Figure 3.6 Variation of Electronegativity along II period

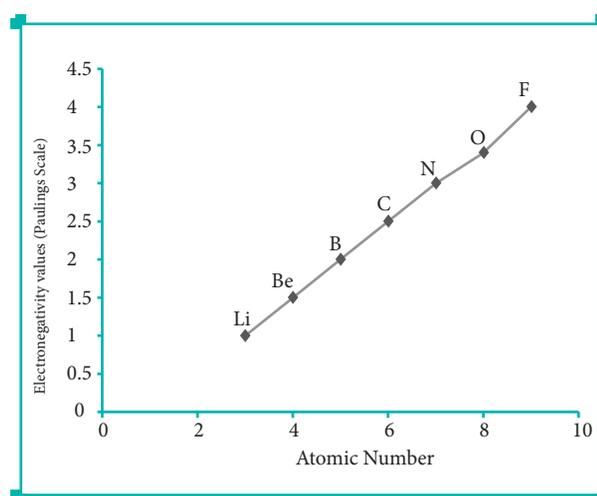


Table 3.15 Electronegativities of various elements (Paulings scale)

H																	B	C	N	O	F											
2.1																	2.0	2.5	3.0	3.5	4.0											
Li	Be															Al	Si	P	S	Cl												
1.0	1.6															1.5	1.8	2.1	2.5	3.0												
Na	Mg															K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
0.9	1.2															0.8	1.0	1.3	1.5	1.6	1.6	1.5	1.8	1.9	1.9	1.9	1.6	1.6	1.8	2.0	2.4	2.8
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br																
0.8	1.0	1.3	1.5	1.6	1.6	1.5	1.8	1.9	1.9	1.9	1.6	1.6	1.8	2.0	2.4	2.8																
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I																
0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.2	2.2	1.9	1.7	1.7	1.8	1.9	2.1	2.5																
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At																
0.7	0.9	1.0	1.3	1.5	1.7	1.9	2.2	2.2	2.2	2.4	1.9	1.8	1.9	1.9	2.0	2.1																

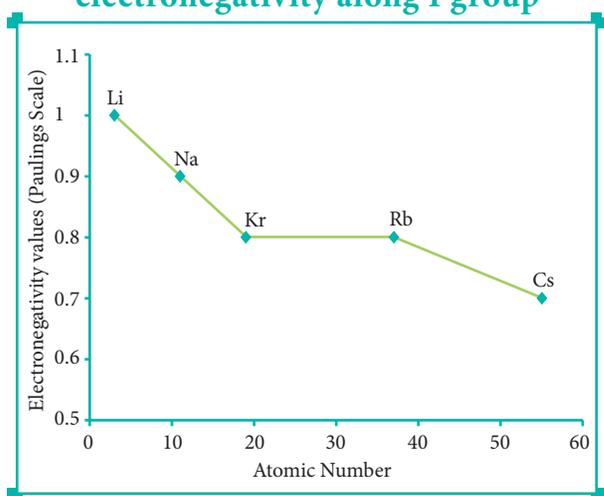
low
medium
high

Variation of Electronegativity in a group:

The electronegativity generally decreases down a group. As we move down a group the atomic radius increases and the nuclear attractive force on the valence electron decreases. Hence, the electronegativity decreases.

Noble gases are assigned zero electronegativity. The electronegativity values of the elements of s-block show the expected decreasing order in a group. Except 13th and 14th group all other p-block elements follow the expected decreasing trend in electronegativity.

Figure 3.7 Variation of electronegativity along I group



3.6 Periodic Trends in Chemical Properties:

Sofar, we have studied the periodicity of the physical properties such as atomic radius, ionisation enthalpy, electron gain enthalpy and electronegativity. In addition, the chemical properties such as reactivity, valence, oxidation state etc... also show periodicity to certain extent.

In this section, we will discuss briefly about the periodicity in valence (oxidation state) and anomalous behaviour of second period elements (diagonal relationship).

Valence or Oxidation States

The valence of an atom is the combining capacity relative to hydrogen atom. It is usually equal to the total number of electrons in the valence shell or equal to eight minus the number of valence electrons. It is more convenient to use oxidation state in the place of valence.

Periodicity of Valence or Oxidation States

The valence of an atom primarily depends on the number of electrons in the

valence shell. As the number of valence electrons remains same for the elements in same group, the maximum valence also remains the same. However, in a period the number of valence electrons increases, hence the valence also increases.

Table 3.16 Variation of valence in groups

Alkali Metals (Group 1)			Group 15		
Element	No. of electrons in valence shell	Valence	Element	No. of electrons in valence shell	Valence
Li	1	1	N	5	3, 5
Na	1	1	P	5	3, 5
K	1	1	As	5	3, 5
Rb	1	1	Sb	5	3, 5
Cs	1	1	Bi	5	3, 5
Fr	1	1			

Table 3.17 Variation of valence in period (1st period)

Element	Li	Be	B	C	N	O	F	Ne
No. of electrons in valence shell	1	2	3	4	5	6	7	8
Valence (Combining capacity)	1	2	3	4	5, 3	6, 2	7, 1	8, 0

In addition to that some elements have variable valence. For example, most of the elements of group 15 which have 5 valence electrons show two valences 3 and 5. Similarly transition metals and inner transition metals also show variable oxidation states.

3.6.1 Anomalous properties of second period elements:

As we know, the elements of the same group show similar physical and chemical properties. However, the first element of each group differs from other members of the group in certain properties. For example, lithium and beryllium form more covalent compounds, unlike the alkali and alkaline earth metals which predominantly form ionic compounds. The elements of the second period have only four orbitals (2s & 2p) in the valence shell and have a maximum co-valence of 4, whereas the other members of the subsequent periods have more orbitals in their valence shell and shows higher valences. For example, boron forms BF_4^- and aluminium forms AlF_6^{3-} .

Diagonal Relationship

On moving diagonally across the periodic table, the second and third period elements show certain similarities. Even though the similarity is not same as we see in a group, it is quite pronounced in the following pair of elements.



The similarity in properties existing between the diagonally placed elements is called 'diagonal relationship'.

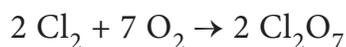
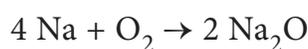
3.6.2 Periodic Trends and Chemical Reactivity:

The physical and chemical properties of elements depend on the valence shell electronic configuration as discussed earlier. The elements on the left side of the periodic table have less ionisation energy and readily lose their valence electrons. On the other hand, the elements on right side of the periodic table have high electron affinity and readily accept electrons. As a consequence of this, elements of these extreme ends show high reactivity when compared to the elements present in the middle. The noble gases having completely filled electronic configuration neither accept nor lose their electron readily and hence they are chemically inert in nature.

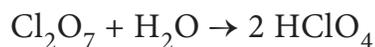
The ionisation energy is directly related to the metallic character and the elements located in the lower left portion of the periodic table have less ionisation energy and therefore show metallic

character. On the other hand the elements located in the top right portion have very high ionisation energy and are non-metallic in nature.

Let us analyse the nature of the compounds formed by elements from both sides of the periodic table. Consider the reaction of alkali metals and halogens with oxygen to give the corresponding oxides.



Since sodium oxide reacts with water to give strong base sodium hydroxide, it is a basic oxide. Conversely Cl_2O_7 gives strong acid called perchloric acid upon reaction with water So, it is an acidic oxide.

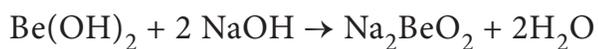
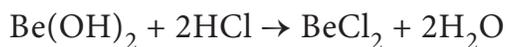


Thus, the elements from the two extreme ends of the periodic table behave differently as expected.

As we move down the group, the ionisation energy decreases and the electropositive character of elements increases. Hence, the hydroxides of these elements become more basic. For example, let us consider the nature of the second group hydroxides:

$\text{Be}(\text{OH})_2$ amphoteric; $\text{Mg}(\text{OH})_2$ weakly basic; $\text{Ba}(\text{OH})_2$ strongly basic

Beryllium hydroxide reacts with both acid and base as it is amphoteric in nature.



Activity 3.2

The electronegativity for some elements on Pauling scale of different groups and periods are listed below. Plot these values against atomic number. From the pattern, explain the variation along a period and a group.

2nd group elements : Be (1.6), Mg (1.2), Ca (1.0), Sr (1.0) Ba(0.9)

17th group elements : F (4.0), Cl (3.0), Br (2.8), I (2.5)

3rd Period elements : Na(0.9), Mg(1.2), Al (1.5), Si(1.8), P(2.1), S(2.5), Cl(3.0)

4th period elements: K(0.8), Ca(1.0), Sc(1.3), Ti(1.5), V(1.6), Cr(1.6), Mn(1.5), Fe(1.8), Co(1.9), Ni(1.9), Cu(1.9), Zn(1.6), Ga(1.6), Ge(1.8), As(2.0), Se(2.4), Br(2.8)

SUMMARY

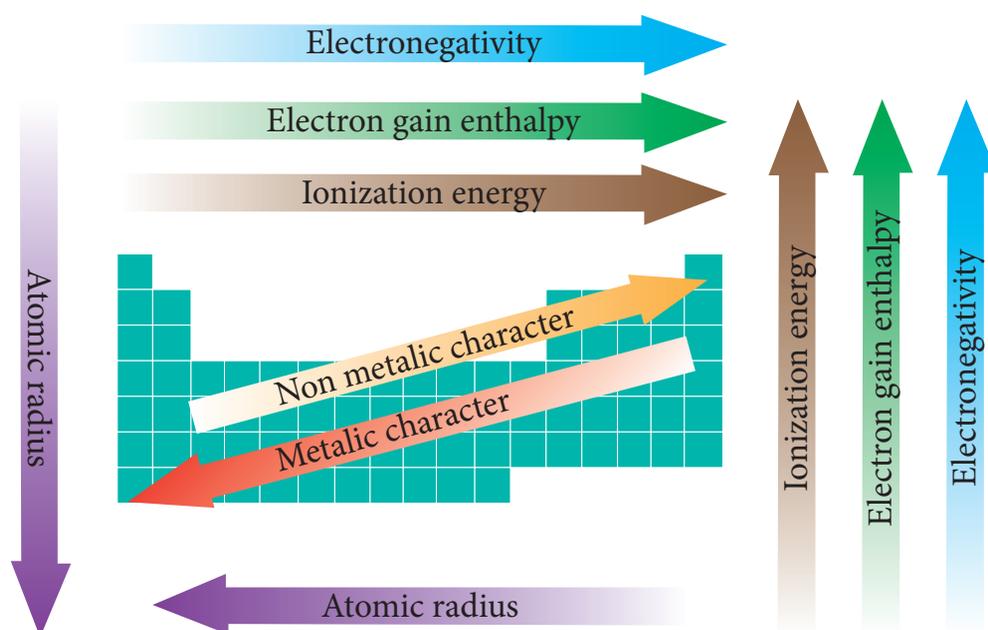
The periodic table was developed to systematically arrange the different elements. Lavoisier made the first attempt to arrange the known elements in a particular order based on properties. This followed by Johann Dobereiner, A. E. B. de Chancourtois and Newlands. First meaningful periodic table was constructed by Mendeleev based on atomic mass. This was later modified based on the modern periodic law which states that the properties of elements are the periodic functions of their atomic numbers. The modern periodic table is made up of 18 groups and 7 periods.

The elements in the same groups have similar properties because their valence shell electronic configurations are similar. The properties of the elements of the same period differ because they have different valence shell electronic configurations. On the basis of electronic configuration the elements are also classified as s-block, p-block, d-block and f-block elements. The elements belonging to “s, p, d and f” blocks have unique characteristic

properties. In this table, more than 78% of all known elements are metals. They appear on the left side of the periodic table. Non-metals are located at the top right hand side of the periodic table. Some elements show properties that are characteristic of both metals and non-metals and are called semi-metals or metalloids.

The periodic properties such as atomic radius, ionic radius, ionization enthalpy, electron gain enthalpy, electronegativity are possessing periodic trends. The variations of these properties are described in the following scheme.

The elements at the extreme left exhibit strong reducing property whereas the elements at extreme right strong oxidizing property. The reactivity of elements at the centre of the periodic table is low compared to elements at the extreme right and left. The similarity in chemical properties observed between the elements of second and third period which are diagonally related.



EVALUATION :



I. Choose the best Answer:

- What would be the IUPAC name for an element with atomic number 222?
a) bibibium b) bididium c) didibium d) bibibium
- The electronic configuration of the elements A and B are $1s^2, 2s^2, 2p^6, 3s^2$ and $1s^2, 2s^2, 2p^5$ respectively. The formula of the ionic compound that can be formed between these elements is
a) AB b) AB_2 c) A_2B d) none of the above.
- The group of elements in which the differentiating electron enters the anti penultimate shell of atoms are called
a) p-block elements b) d-block elements
c) s-block elements d) f-block elements
- In which of the following options the order of arrangement does not agree with the variation of property indicated against it? (NEET 2016 Phase 1)
a) $I < Br < Cl < F$ (increasing electron gain enthalpy)
b) $Li < Na < K < Rb$ (increasing metallic radius)
c) $Al^{3+} < Mg^{2+} < Na^+ < F^-$ (increasing ionic size)
d) $B < C < O < N$ (increasing first ionisation enthalpy)
- Which of the following elements will have the highest electronegativity?
a) Chlorine b) Nitrogen c) Cesium d) Fluorine
- Various successive ionisation enthalpies (in kJ mol^{-1}) of an element are given below.

IE_1	IE_2	IE_3	IE_4	IE_5
577.5	1,810	2,750	11,580	14,820

The element is

- a) phosphorus b) Sodium c) Aluminium d) Silicon



7. In the third period the first ionization potential is of the order.
- a) $\text{Na} > \text{Al} > \text{Mg} > \text{Si} > \text{P}$ b) $\text{Na} < \text{Al} < \text{Mg} < \text{Si} < \text{P}$
c) $\text{Mg} > \text{Na} > \text{Si} > \text{P} > \text{Al}$ d) $\text{Na} < \text{Al} < \text{Mg} < \text{P} < \text{Si}$
8. Identify the wrong statement.
- a) Amongst the isoelectronic species, smaller the positive charge on cation, smaller is the ionic radius
b) Amongst isoelectronic species greater the negative charge on the anion, larger is the ionic radius
c) Atomic radius of the elements increases as one moves down the first group of the periodic table
d) Atomic radius of the elements decreases as one moves across from left to right in the 2nd period of the periodic table.
9. Which one of the following arrangements represent the correct order of least negative to most negative electron gain enthalpy
- a) $\text{Al} < \text{O} < \text{C} < \text{Ca} < \text{F}$ b) $\text{Al} < \text{Ca} < \text{O} < \text{C} < \text{F}$
c) $\text{C} < \text{F} < \text{O} < \text{Al} < \text{Ca}$ d) $\text{Ca} < \text{Al} < \text{C} < \text{O} < \text{F}$
10. The correct order of electron gain enthalpy with negative sign of F, Cl, Br and I having atomic number 9, 17, 35 and 53 respectively is
- a) $\text{I} > \text{Br} > \text{Cl} > \text{F}$ b) $\text{F} > \text{Cl} > \text{Br} > \text{I}$
c) $\text{Cl} > \text{F} > \text{Br} > \text{I}$ d) $\text{Br} > \text{I} > \text{Cl} > \text{F}$
11. Which one of the following is the least electronegative element?
- a) Bromine b) Chlorine c) Iodine d) Hydrogen
12. The element with positive electron gain enthalpy is
- a) Hydrogen b) Sodium c) Argon d) Fluorine
13. The correct order of decreasing electronegativity values among the elements X, Y, Z and A with atomic numbers 4, 8, 7 and 12 respectively
- a) $\text{Y} > \text{Z} > \text{X} > \text{A}$ b) $\text{Z} > \text{A} > \text{Y} > \text{X}$
c) $\text{X} > \text{Y} > \text{Z} > \text{A}$ d) $\text{X} > \text{Y} > \text{A} > \text{Z}$



21. Which one of the following is true about metallic character when we move from left to right in a period and top to bottom in a group?
- Decreases in a period and increases along the group
 - Increases in a period and decreases in a group
 - Increases both in the period and the group
 - Decreases both in the period and in the group
22. How does electron affinity change when we move from left to right in a period in the periodic table?
- Generally increases
 - Generally decreases
 - Remains unchanged
 - First increases and then decreases
23. Which of the following pairs of elements exhibit diagonal relationship?
- Be and Mg
 - Li and Be
 - Be and B
 - Be and Al

II. Write brief answer to the following questions

24. Define modern periodic law.
25. What are isoelectronic ions? Give examples.
26. What is effective nuclear charge ?
27. Is the definition given below for ionisation enthalpy is correct?
"Ionisation enthalpy is defined as the energy required to remove the most loosely bound electron from the valence shell of an atom"
28. Magnesium loses electrons successively to form Mg^+ , Mg^{2+} and Mg^{3+} ions. Which step will have the highest ionisation energy and why?
29. Define electronegativity.
30. How would you explain the fact that the second ionisation potential is always higher than first ionisation potential?
31. Energy of an electron in the ground state of the hydrogen atom is -2.18×10^{-18} J. Calculate the ionisation enthalpy of atomic hydrogen in terms of kJ mol^{-1} .
32. The electronic configuration of atom is one of the important factor which affects the value of ionisation potential and electron gain enthalpy. Explain
33. In what period and group will an element with $Z = 118$ will be present?





34. Justify that the fifth period of the periodic table should have 18 elements on the basis of quantum numbers.
35. Elements a, b, c and d have the following electronic configurations:
- a: $1s^2, 2s^2, 2p^6$ b: $1s^2, 2s^2, 2p^6, 3s^2, 3p^1$
- c: $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$ d: $1s^2, 2s^2, 2p^1$

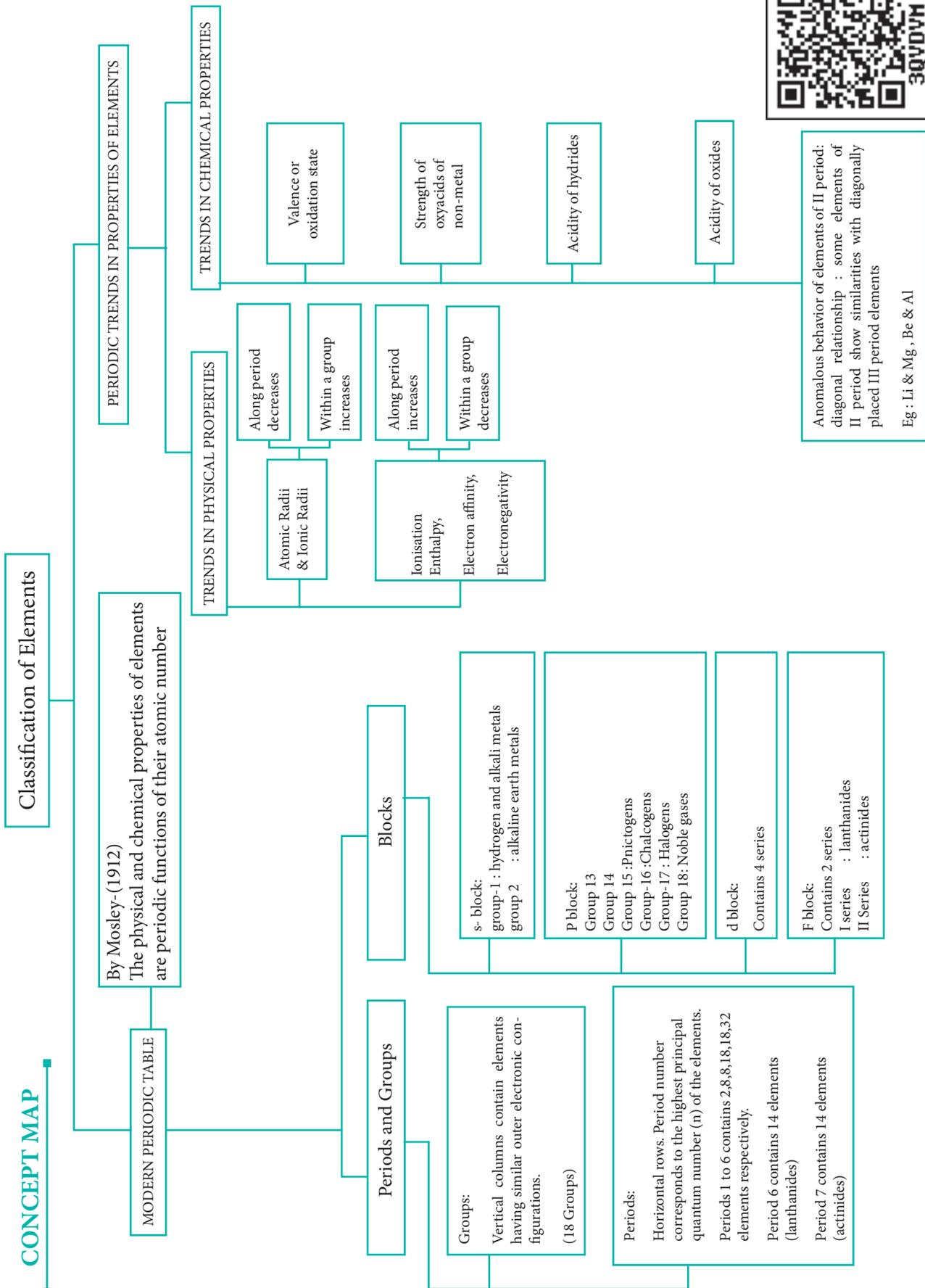
Which elements among these will belong to the same group of periodic table

36. Give the general electronic configuration of lanthanides and actinides?
37. Why halogens act as oxidising agents?
38. Mention any two anomalous properties of second period elements.
39. Explain the pauling method for the determination of ionic radius.
40. Explain the periodic trend of ionisation potential.
41. Explain the diagonal relationship.
42. Why the first ionisation enthalpy of sodium is lower than that of magnesium while its second ionisation enthalpy is higher than that of magnesium?
43. By using pauling's method calculate the ionic radii of K^+ and Cl^- ions in the potassium chloride crystal. Given that $d_{K^+ - Cl^-} = 3.14 \text{ \AA}$
44. Explain the following, give appropriate reasons.
- Ionisation potential of N is greater than that of O
 - First ionisation potential of C-atom is greater than that of B atom, where as the reverse is true is for second ionisation potential.
 - The electron affinity values of Be and Mg are almost zero and those of N (0.02 eV) and P (0.80 eV) are very low
 - The formation of $F^-(g)$ from $F(g)$ is exothermic while that of $O^{2-}(g)$ from $O(g)$ is endothermic.
45. What is screening effect?
46. Briefly give the basis for pauling's scale of electronegativity.
47. State the trends in the variation of electronegativity in group and periods.





CONCEPT MAP





Properties of Elements

By using this modern periodic table you will be able to visualise the elements belonging to a specific group, period and block and other properties of the elements.

Please go to the URL
<http://www.rsc.org/periodic-table/>
(or)
Scan the QR code on the right side



Open the Browser and type the URL given (or) Scan the QR Code. You can see an interactive modern periodic table of elements from atomic number 1 to 118.

Options:

1. You can hover over any element in the periodic table to get the basic information such as electronic configuration, ionisation energy, density etc. in the panel (3).
2. If you click on any elements it shows the complete list of properties of the elements.
3. Click the Visual Elements Image (1) to view the Images for each element. If you hover over any element additional information regarding the element will be displayed in the panel (3)
4. You can view metals and non-metals present in the periodic table by choosing the appropriate choice (8)
5. You can view the physical state of the elements at a given temperature by using the slider (7)
6. You can view s, p, d or f block elements by selecting a specific block (6)
7. You can view the elements of a specific group (2) or a period (5) by selecting the group or period
8. You can clear the selections you have made by clicking the clear filters (4)

The screenshot shows the Royal Society of Chemistry's interactive periodic table. At the top, there are controls for 'Visual Elements images', a temperature slider (0 K to 6000 K), classification filters (Metal, Non-metal), and a 'Clear filters' button. Below these are dropdown menus for 'Groups' (1-18), 'Blocks' (s, p, d, f), and 'Periods' (1-7, Lanthanides, Actinides). The periodic table itself is color-coded by groups and periods. A tooltip for element Lithium (Li) is visible, showing its atomic number (3), symbol (Li), and name (Lithium). Red arrows point to numbered callouts: 1 points to the 'Visual Elements images' button; 2 points to the 'Groups' dropdown menu; 3 points to the tooltip for Lithium; 4 points to the 'Clear filters' button; 5 points to the 'Periods' dropdown menu; 6 points to the 'Blocks' dropdown menu; 7 points to the temperature slider; 8 points to the 'Classification' filters.



Hydrogen



Hydrogen, third most abundant on the surface of the Universe, is being visualised as the major feature source of energy



Antoine - Laurent de Lavoisier
(1743-1794)

He recognised and named hydrogen and oxygen. He introduced a new system for chemical nomenclature in 1787

Learning Objectives

After studying this unit, the students will be able to

- Justify the position of hydrogen in the periodic table
- Recognise the different isotopes of hydrogen
- Explain the methods of preparation of hydrogen.
- Explain the properties of hydrogen
- Appraise the uses of hydrogen
- Differentiate various types of hydrides
- Translate the knowledge of structure of water for explaining its physical and chemical properties
- Differentiate hard and soft water and select the suitable method for water softening.
- Recognise heavy water and explain its properties.
- Explain the preparation and properties of hydrogen peroxide
- List the uses of hydrogen peroxide



4.1 Introduction

Hydrogen is the simplest atom which contains one electron and one proton. In contrast to other elements (except helium) its valence electron is directly in the sphere of action of the nucleus. It is invariably present in most of the compounds we come across in our daily life such as water, carbohydrate, proteins etc. As it has an unpaired electron, it is reactive and exists as a diatomic molecule (H_2). However, the abundance of hydrogen gas in the earth's atmosphere is very small.

4.1.1 Position in Periodic Table

The hydrogen has the electronic configuration of $1s^1$ which resembles with ns^1 general valence shell configuration of alkali metals and shows similarity with them as follows:

1. It forms unipositive ion (H^+) like alkali metals (Na^+ , K^+ , Cs^+)
2. It forms halides (HX), oxides (H_2O), peroxides (H_2O_2) and sulphides (H_2S) like alkali metals (NaX , Na_2O , Na_2O_2 , Na_2S)
3. It also acts as a reducing agent.

However, unlike alkali metals which have ionization energy ranging from 377 to 520 kJ mol^{-1} , the hydrogen has $1,314 \text{ kJ mol}^{-1}$ which is much higher than alkali metals.

Like the formation of halides (X^-) from halogens, hydrogen also has a tendency to gain one electron to form hydride ion (H^-) whose electronic configuration is similar to the noble gas, helium. However, the electron affinity of hydrogen is much less than that of halogen atoms. Hence, the tendency of hydrogen to form hydride ion

is low compared to that of halogens to form the halide ions as evident from the following reactions:



Since, hydrogen has similarities with alkali metals as well as the halogens; it is difficult to find the right position in the periodic table. However, in most of its compounds hydrogen exists in +1 oxidation state. Therefore, it is reasonable to place the hydrogen in group 1 along with alkali metals as shown in the latest periodic table published by IUPAC.

4.1.2 Isotopes of Hydrogen

Hydrogen has three naturally occurring isotopes, viz., protium (${}_1H^1$ or H), deuterium (${}_1H^2$ or D) and tritium (${}_1H^3$ or T). Protium (${}_1H^1$) is the predominant form (99.985 %) and it is the only isotope that does not contain a neutron.

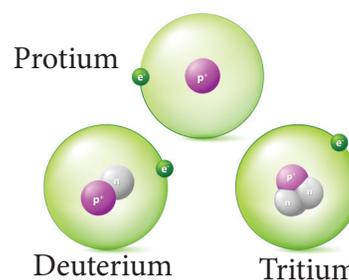


Figure 4.1 Isotopes of hydrogen

Deuterium, also known as heavy hydrogen, constitutes about 0.015 %. The third isotope, tritium is a radioactive isotope of hydrogen which occurs only in traces (~ 1 atom per 10^{18} hydrogen atoms). Due to the existence of these isotopes naturally occurring hydrogen exists as H_2 , HD , D_2 , HT , T_2 and DT . The properties of these isotopes are shown in Table 4.1.

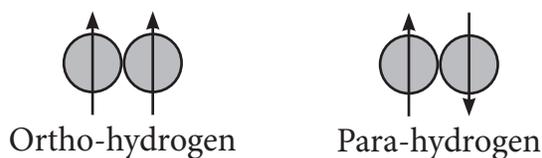
Table 4.1 Properties of Hydrogen, Deuterium and Tritium molecules.

Property	Protium	Deuterium	Tritium
Atomic Hydrogen			
Symbol	H	D	T
Atomic mass (<i>amu</i>)	1.008	2.014	3.016
No of electron / protons / neutrons	1 / 1 / 0	1 / 1 / 1	1 / 1 / 2
Nuclear stability	Stable	Stable	Radioactive ($t_{1/2}=12.3$ yrs)
Molecular Hydrogen	H ₂	D ₂	T ₂
Abundance (%)	99.985	0.0156	$\sim 10^{-15}$
Molecular mass (<i>amu</i>)	2.016	4.028	6.032
Melting point (K)	13.96	18.73	20.62
Boiling point (K)	20.39	23.67	25.04
Internuclear distance (<i>pm</i>)	74.14	74.14	74.14
Critical Temperature (K)	33.19	38.35	40.60
Enthalpy of dissociation (<i>kJ/mol</i>) [†]	435.9	443.4	446.9

[†] Bond dissociation energy

4.1.3 Ortho and Para-Hydrogen:

In the hydrogen atom, the nucleus has a spin. When molecular hydrogen is formed, the spins of two hydrogen nuclei can be in the same direction or in the opposite direction as shown in the figure. These two forms of hydrogen molecules are called *ortho* and *para* hydrogens respectively.



At room temperature, normal hydrogen consists of about 75% ortho-form and 25% para-form. As the ortho-form is more stable than para-form, the conversion of one isomer into the other is a slow process. However, the equilibrium shifts in favour of para hydrogen when the temperature is lowered. The para-form can be catalytically transformed into ortho-form using platinum or iron. Alternatively, it can also be converted by passing an electric discharge, heating above 800°C and mixing with paramagnetic molecules such as O₂, NO, NO₂ or with nascent/atomic hydrogen.

Ortho and para hydrogen are similar in chemical properties but differ in some of the physical properties. For example, the melting point of para hydrogen is 13.83 K while that of ortho hydrogen 13.95 K; boiling point of para hydrogen is 20.26 K while that of ortho hydrogen 20.39 K. Since the nuclear spins are in opposite directions the magnetic moment of para hydrogen is zero and ortho hydrogen has magnetic moment twice that of a proton.

4.2 Preparation of Hydrogen

High purity hydrogen (>99.9 %) is obtained by the electrolysis of water containing traces of acid or alkali or the electrolysis of aqueous solution of sodium hydroxide or potassium hydroxide using a nickel anode and iron cathode. However, this process is not economical for large-scale production.

At anode : $2 \text{OH}^- \rightarrow \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 + 2\text{e}^-$

At cathode : $2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow 2 \text{OH}^- + \text{H}_2$

Overall reaction : $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$

4.2.1 Laboratory Preparation

Hydrogen is conveniently prepared in laboratory by the reaction of metals, such as zinc, iron, tin with dilute acid.

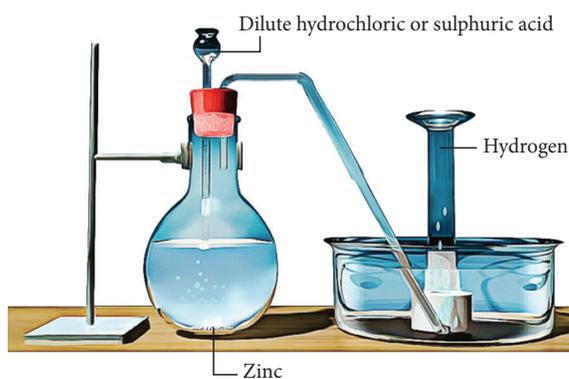
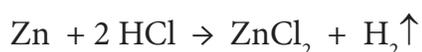
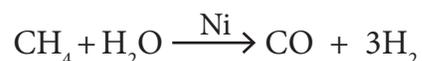


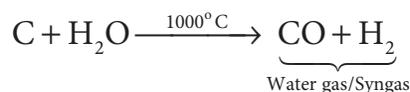
Figure 4.2 Laboratory preparation of hydrogen

4.2.2 Industrial Production

In the large-scale, hydrogen is produced by steam-reforming of hydrocarbons. In this method hydrocarbon such as methane is mixed with steam and passed over nickel catalyst in the range 800-900 °C and 35 atm pressures.

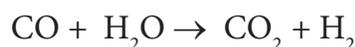


In an another process, steam is passed over a red-hot coke to produce carbon monoxide and hydrogen. The mixture of gases produced in this way is known as *water gas* ($\text{CO} + \text{H}_2$). This is also called *syngas* (Synthetic gas) as it is used in the synthesis of organic compounds such as methanol and simple hydrocarbons.



Conversion of Carbon monoxide in water gas to Carbon dioxide:

The carbon monoxide of the water gas can be converted to carbon dioxide by mixing the gas mixture with more steam at 400°C and passed over a shift converter containing iron/copper catalyst. This reaction is called as *water-gas shift reaction*.



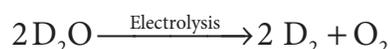
The CO_2 formed in the above process is absorbed in a solution of potassium carbonate.



4.2.3 Preparation of Deuterium:

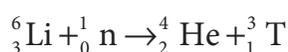
Electrolysis of heavy water:

Normal water contains 1.6×10^{-4} percentage of heavy water. The dissociation of protium water (H_2O) is more than heavy water (D_2O). Therefore, when water is electrolysed, hydrogen is liberated much faster than D_2 . The electrolysis is continued until the resulting solution becomes enriched in heavy water. Further electrolysis of the heavy water gives deuterium.



4.2.4 Preparation of Tritium:

As explained earlier the tritium is present only in trace amounts. So it can be artificially prepared by bombarding lithium with slow neutrons in a nuclear fission reactor. The nuclear transmutation reaction for this process is as follows.



4.3 Properties of Hydrogen

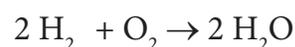
4.3.1 Physical Properties:

Hydrogen is a colorless, odorless, tasteless, lightest and highly flammable gas. It is a non-polar diatomic molecule. It can be liquefied under low temperature and high pressure. Hydrogen is a good reducing agent. Various physical constants of hydrogen molecule are listed in Table 4.1.

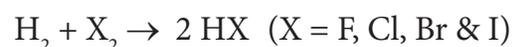
4.3.2 Chemical Properties:

Hydrogen reacts with oxygen to give water. This is an explosive reaction and

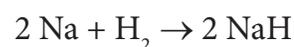
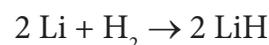
releases lot of energy. This is used in fuel cells to generate electricity.



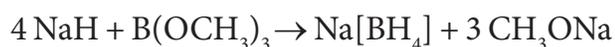
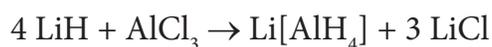
Similarly, hydrogen also reacts with halogens to give corresponding halides. Reaction with fluorine takes place even in dark with explosive violence while with chlorine at room temperature under light. It combines with bromine on heating and reaction with iodine is a photochemical reaction.



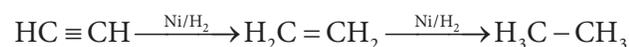
In the above reactions the hydrogen has an oxidation state of +1. It also has a tendency to react with reactive metals such as lithium, sodium and calcium to give corresponding hydrides in which the oxidation state of hydrogen is -1.



These hydrides are used as reducing agents in synthetic organic chemistry. It is used to prepare other important hydrides such as lithium aluminium hydride and sodium boro hydride.

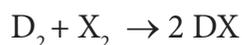
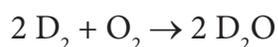


Hydrogen itself acts as a reducing agent. In the presence of finely divided nickel, it adds to the unsaturated organic compounds to form saturated compounds.



4.3.3 Chemical properties of Deuterium

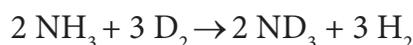
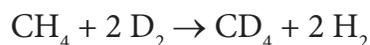
Like hydrogen, deuterium also reacts with oxygen to form deuterium oxide called heavy water. It also reacts with halogen to give corresponding halides.



(X = F, Cl, Br & I)

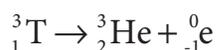
Deuterium exchange reactions:

Deuterium can replace reversibly hydrogen in compounds either partially or completely depending upon the reaction conditions. These reactions occur in the presence of deuterium or heavy water.



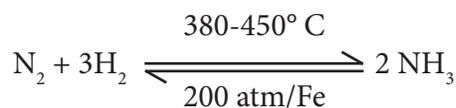
4.3.4 Properties of Tritium

It is a β -emitter with a half-life period of 12.3 years .



4.4 Uses of Hydrogen

1. Over 90 % hydrogen produced in industry is used for synthetic applications. One such process is Haber process which is used to synthesis ammonia in large scales. Ammonia is used for the manufacture of chemicals such as nitric acid, fertilizers and explosives.

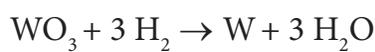
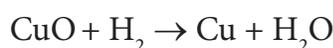


2. It can be used to manufacture the industrial solvent, methanol from carbon monoxide using copper as catalyst.



3. Unsaturated fatty oils can be converted into saturated fats called Vanaspati (margarine) by the reduction reaction with Pt/H₂.

4. In metallurgy, hydrogen can be used to reduce many metal oxides to metals at high temperatures.



5. Atomic hydrogen and oxy-hydrogen torches are used for cutting and welding.

6. Liquid hydrogen is used as a rocket fuel.

7. Hydrogen is also used in fuel cells for generating electrical energy. The reversible uptake of hydrogen in metals is also attractive for rechargeable metal hydride battery.

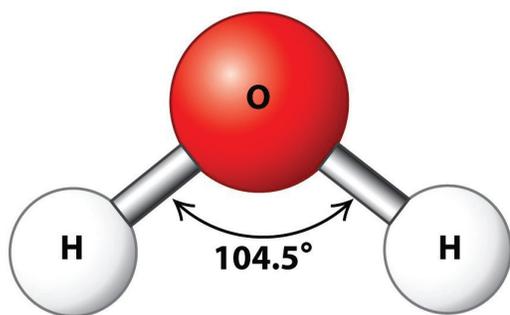


Figure 4.3: Application of rocket fuel

4.5 Compounds of Hydrogen

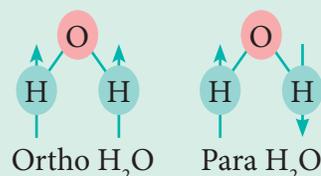
4.5.1 Water

Water is one of the most abundant compounds of hydrogen and our earth's surface contains approximately 70 % of ocean which is the major source of water. However, sea water contains many dissolved salts hence it can not be used directly. Water is essential for all living things and our body contains about 65% water.



Ortho-H₂O and Para-H₂O

Water exists in the interstellar clouds and icy satellites of the solar system. In particular, the ortho-to-para ratio (OPR) of water in space has recently received attention. Like hydrogen, water can also be classified into ortho-H₂O, in which the spin directions of the nuclei of the hydrogen atoms are parallel, and para-H₂O, in which the directions are antiparallel. OPR of H₂(300K) on earth should be 3:1. OPR of H₂O(50K) in interstellar clouds and comets should be 2:5:1.



4.5.2 Physical Properties:

Water is a colourless and volatile liquid. The peculiar properties of water in the condensed phases are due to the presence of inter molecular hydrogen bonding between water molecules. Hydrogen bonding is responsible for the high melting and boiling points of water. Some of the physical parameters of water are listed in Table 4.2.

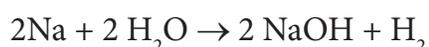
Table 4.2 Properties of water, heavy water and super heavy water[†].

Property	H ₂ O	D ₂ O	T ₂ O
Molecular weight	18.015	20.0276	22.031
Melting point (K)	273.0	276.8	277.5
Boiling point (K)	373.0	374.4	374.5
Temperature of maximum density (K)	277.0	284.2	286.4
Maximum density (g/cm ³)	1.000	1.106	1.215
Density (g/cm ³)	0.997	1.104	1.214
Vapour pressure (mm Hg)	23.75	20.51	19.80
Viscosity (cP)	0.890	1.107	---
Dielectric constant	78.39	78.06	---
Enthalpy of formation (kJ/mol)	- 285.9	- 294.6	---
Enthalpy of vaporization (kJ/mol)	40.66	41.61	---

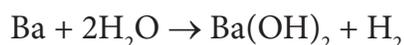
[†]Unless otherwise stated, all data are at 298 K.

4.5.3 Chemical Properties:

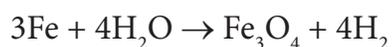
Water reacts with metals, non-metals and other compounds differently. The most reactive metals are the alkali metals. They decompose water even in cold with the evolution of hydrogen leaving an alkali solution.



The group 2 metals (except beryllium) react in a similar way but less violently. The hydroxides are less soluble than those of Group 1.

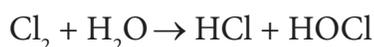


Some transition metals react with hot water or steam to form the corresponding oxides. For example, steam passed over red hot iron results in the formation of iron oxide with the release of hydrogen.

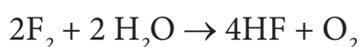


Lead and copper decompose water only at a white heat. Silver, gold, mercury and platinum do not have any effect on water. In the elemental form, the non-metals such as carbon, sulphur and phosphorus normally do not react with water. However, as we have seen earlier, carbon will react with steam when it is red (or white) hot to give *water gas*.

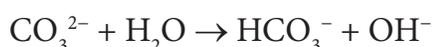
On the other hand, the halogens react with water to give an acidic solution. For example, chlorine forms hydrochloric acid and hypo chlorous acid. It is responsible for the antibacterial action of chlorine water, and for its use as bleach.



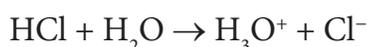
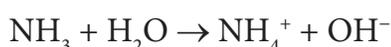
Fluorine reacts differently to liberate oxygen from water.



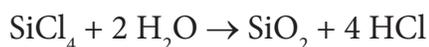
In a similar way, compounds of non-metals react with water to give acidic or alkaline solutions. For example, solutions of carbonates are slightly alkaline.



Water is an amphoteric oxide. It has the ability to accept as well as donate protons and hence it can act as an acid or a base. For example, in the reaction with HCl it accepts proton whereas in the reaction with weak base ammonia it donates proton.



Water dissolves ionic compounds. In addition, it also hydrolyses some covalent compounds.



Many salts crystallized from aqueous solutions form hydrated crystals. The water in the hydrated salts may form co-ordinate bond or just present in interstitial positions of crystals.

Examples: $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ – All six water molecules form co-ordinate bond

$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ – Both the water molecules are present in interstitial positions.

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ – In this compound four water molecules form co-ordinate bonds while the fifth water molecule, present outside the co-ordination, can form intermolecular hydrogen bond with another molecule. $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$

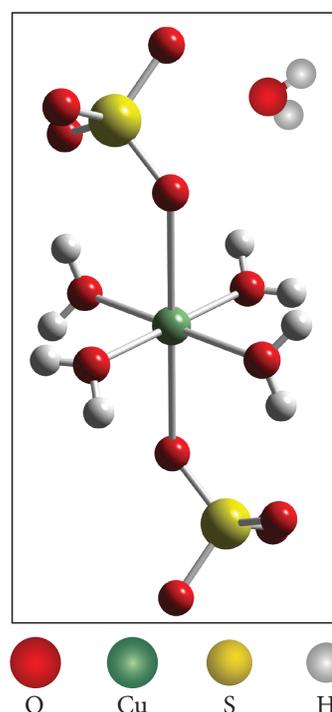


Figure 4.4 structure of copper sulphate pentahydrate

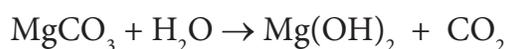
4.5.4 Hard and Soft Water:

Hard water contains high amounts of mineral ions. The most common ions found in hard water are the soluble metal cations such as magnesium & calcium, though iron, aluminium, and manganese may also be found in certain areas. Presence of these metal salts in the form of bicarbonate,

chloride and sulphate in water makes water 'hard'. When hard water is boiled carbonates of magnesium and calcium present in it gets precipitated. On the other hand, water free from soluble salts of calcium and magnesium is called soft water. The hardness of water is of two types, viz., temporary hardness and permanent hardness.

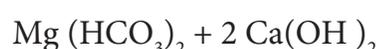
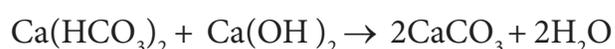
Temporary Hardness and its removal:

Temporary hardness is primarily due to the presence of soluble bicarbonates of magnesium and calcium. This can be removed by boiling the hard water followed by filtration. Upon boiling, these salts decompose into insoluble carbonate which leads to their precipitation. The magnesium carbonate thus formed further hydrolysed to give insoluble magnesium hydroxide.

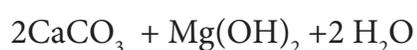


The resulting precipitates can be removed by filtration.

Alternatively, we can use Clark's method in which, calculated amount of lime is added to hard water containing the magnesium and calcium, and the resulting carbonates and hydroxides can be filtered-off.

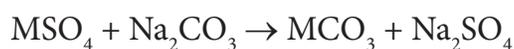
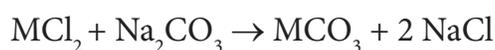


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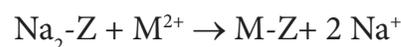


Permanent Hardness:

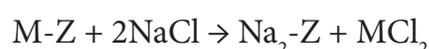
Permanent hardness of water is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates in it. It can be removed by adding washing soda, which reacts with these metal (M = Ca or Mg) chlorides and sulphates in hard water to form insoluble carbonates.



In another way to soften the hard water is by using a process called ion-exchange. That is, hardness can be removed by passing through an ion-exchange bed like zeolites or column containing ion-exchange resin. Zeolites are hydrated sodium aluminosilicates with a general formula, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ ($x = 2$ to 10 , $y = 2$ to 6). Zeolites have porous structure in which the monovalent sodium ions are loosely held and can be exchanged with hardness producing metal ions (M = Ca^{2+} or Mg^{2+}) in water. The complex structure can conveniently be represented as $\text{Na}_2\text{-Z}$ with sodium as exchangeable cations.



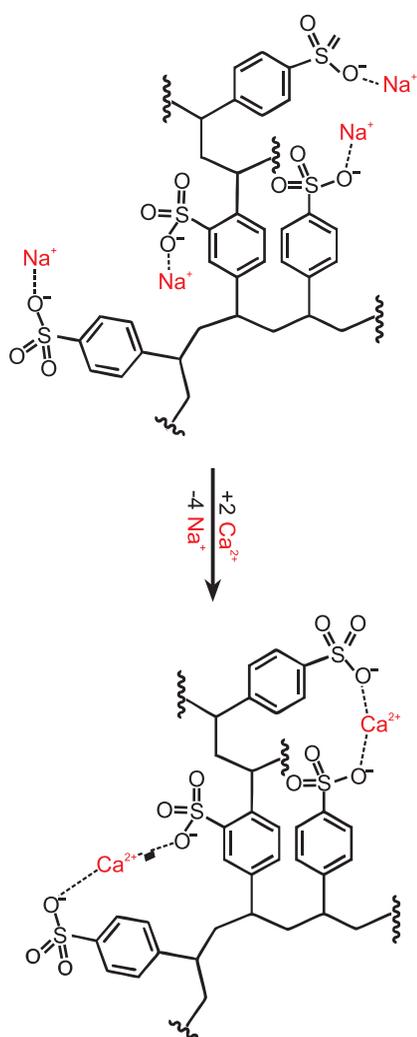
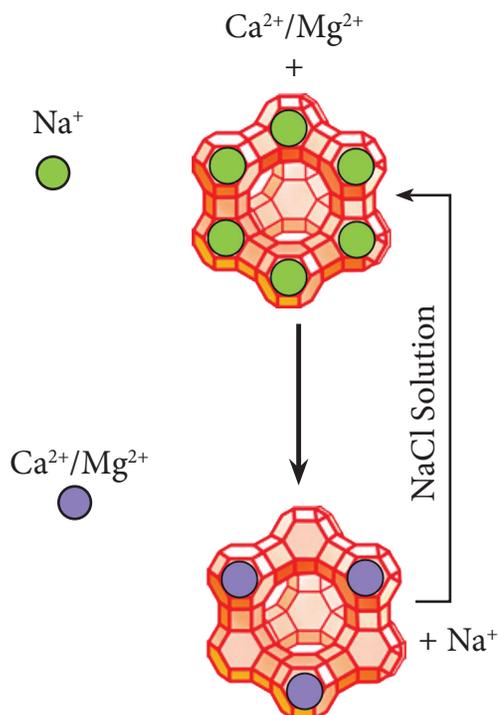
When exhausted, the materials can be regenerated by treating with aqueous sodium chloride. The metal ions (Ca^{2+} and Mg^{2+}) caught in the zeolite (or resin) are released and they get replenished with sodium ions.



4.6 Heavy Water:

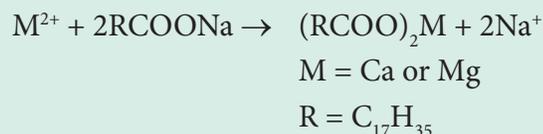
Heavy water (D_2O) is the oxide of heavy hydrogen. One part of heavy water is present in 5000 parts of ordinary water. It is mainly obtained as the product of electrolysis of water, as D_2O does not undergo electrolysis as easily as H_2O .

D_2O is a colorless, odorless and tasteless liquid. However, there is a marked difference between physical properties of water and heavy water as shown in Table 4.2.



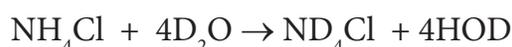
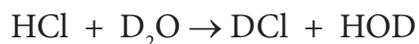
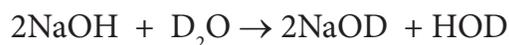
Hard water produces less foam with detergents. Do you know why?

The cleaning capacity of soap is reduced when used in hard water. Soaps are sodium or potassium salts of long chain fatty acids (e.g., coconut oil). When soap is added to hard water, the divalent magnesium and calcium ions present in hard water react with soap. The sodium salts present in soaps are converted to their corresponding magnesium and calcium salts which are precipitated as scum/precipitate.



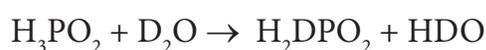
4.6.1 Chemical properties of heavy water:

When compounds containing hydrogen are treated with D_2O , hydrogen undergoes an exchange for deuterium

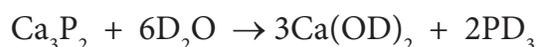
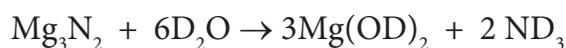
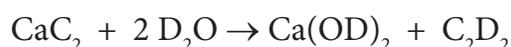
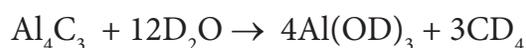


These exchange reactions are useful in determining the number of ionic hydrogens present in a given compound.

For example, when D_2O is treated with hypo-phosphorus acid only one hydrogen atom is exchanged with deuterium. It indicates that, it is a monobasic acid.



It is also used to prepare some deuterium compounds:

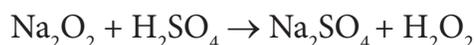
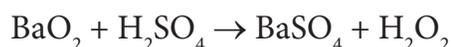


4.6.2 Uses of heavy water:

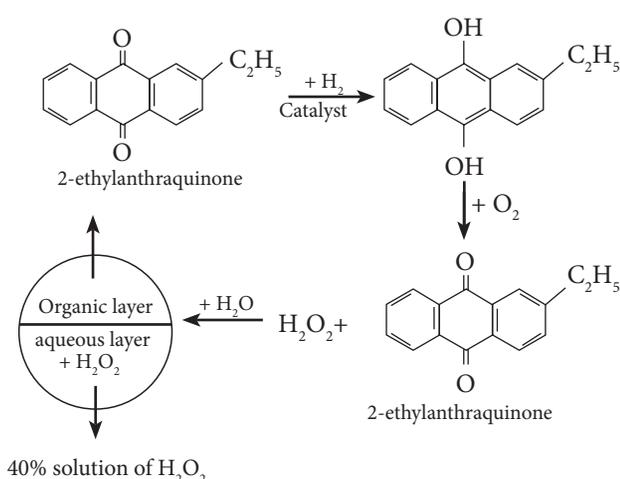
1. Heavy water is widely used as moderator in nuclear reactors as it can lower the energies of fast neutrons
2. It is commonly used as a tracer to study organic reaction mechanisms and mechanism of metabolic reactions
3. It is also used as a coolant in nuclear reactors as it absorbs the heat generated.

4.7 Hydrogen Peroxide:

Hydrogen peroxide (H_2O_2) is one of the most important peroxides. It can be prepared by treating metal peroxide with dilute acid.



On an industrial scale, hydrogen peroxide is now prepared exclusively by autoxidation of 2-alkyl anthraquinol.



4.7.1 Physical properties:

Pure hydrogen peroxide is almost a colorless liquid (pale blue), less volatile and more viscous than water.

A 30 % solution of hydrogen peroxide is marketed as '100-volume' hydrogen peroxide indicating that at S.T.P., 100 ml of oxygen is liberated by 1 ml of this solution on heating.

4.7.2 Chemical properties:

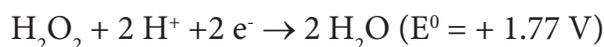
Hydrogen peroxide is highly unstable and the aqueous solution spontaneously

disproportionates to give oxygen and water. The reaction is, however, slow but is explosive when catalyzed by metal. If it is stored in glass container, it dissolves the alkali metals from the glass, which catalyzes the disproportionation reaction. For this reason, H_2O_2 solutions are stored in plastic bottles.

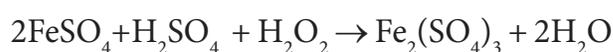


Hydrogen peroxide can act both as an oxidizing agent and a reducing agent. Oxidation is usually performed in acidic medium while the reduction reactions are performed in basic medium

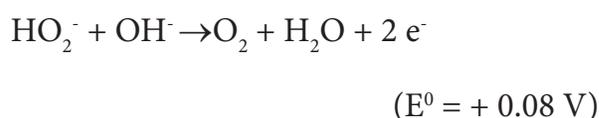
In acidic conditions:



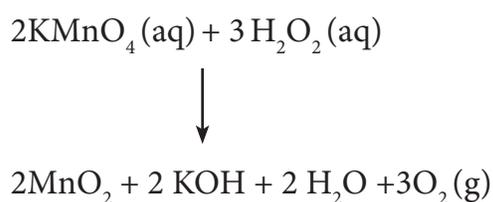
For example



In basic conditions:



For Example,

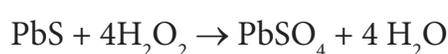


4.7.3 Uses of hydrogen peroxide:

The oxidizing ability of hydrogen peroxide and the harmless nature of its products, i.e., water and oxygen, lead to its many applications. It is used in water treatment to oxidize pollutants, as a mild

antiseptic, and as bleach in textile, paper and hair-care industry.

Hydrogen peroxide is used to restore the white colour of the old paintings which was lost due to the reaction of hydrogen sulphide in air with the white pigment $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ to form black colored lead sulphide. Hydrogen peroxide oxidises black coloured lead sulphide to white coloured lead sulphate, thereby restoring the colour.



4.7.4 Structure of hydrogen peroxide:

Both in gas-phase and solid-phase, the molecule adopts a skew conformation due to repulsive interaction of the OH bonds with lone-pairs of electrons on each oxygen atom. Indeed, it is the smallest molecule known to show hindered rotation about a single bond.

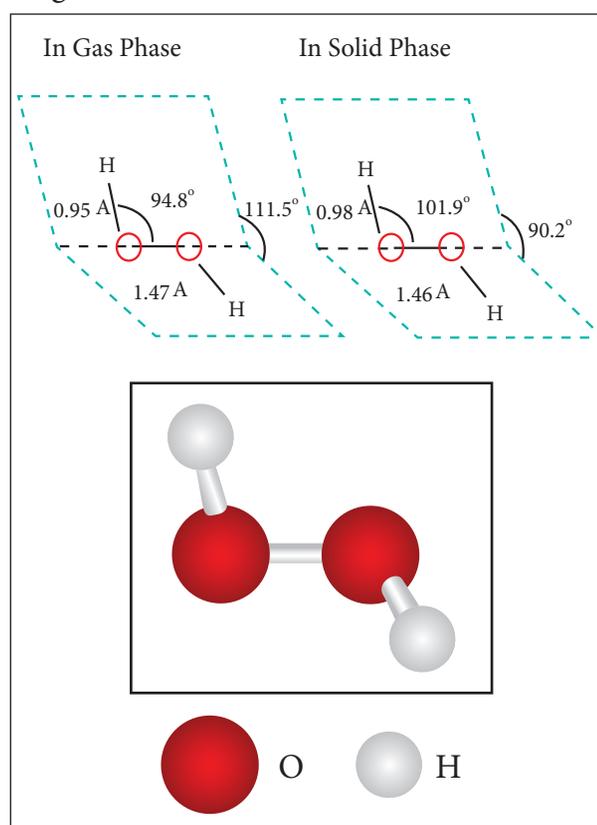


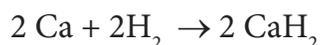
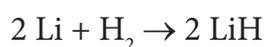
Figure 4.5 structure of H_2O_2

H_2O_2 has a non-planar structure. The molecular dimensions in the gas phase and solid phase differ as shown in figure 4.5. Structurally, H_2O_2 is represented by the dihydroxyl formula in which the two OH groups do not lie in the same plane. One way of explaining the shape of hydrogen peroxide is that the hydrogen atoms would lie on the pages of a partly opened book, and the oxygen atoms along the spine. In the solid phase of molecule, the dihedral angle reduces to 90.2° due to hydrogen bonding and the O-O-H angle expands from 94.8° to 101.9° .

4.8 Hydrides

Hydrogen forms binary hydrides with many electropositive elements including metals and non-metals. It also forms ternary hydrides with two metals. E.g., LiBH_4 and LiAlH_4 . The hydrides are classified as ionic, covalent and metallic hydrides according to the nature of bonding. Hydrides formed with elements having lower electronegativity than hydrogen are often ionic, whereas with elements having higher electronegativity than hydrogen form covalent hydrides.

Ionic (Saline) hydrides: These are hydrides composed of an electropositive metal, generally, an alkali or alkaline-earth metal, except beryllium and magnesium, formed by transfer of electrons from metal to hydrogen atoms. They can be prepared by the reaction of elements at about 400°C . These are salt-like, high-melting, white crystalline solids having hydride ions (H^-) and metal cations (M^{n+}).



Covalent (Molecular) hydrides: They are compounds in which hydrogen is attached to another element by sharing of electrons. The most common examples of covalent hydrides of non-metals are methane, ammonia, water and hydrogen chloride. Covalent hydrides are further divided into three categories, viz., electron precise (CH_4 , C_2H_6 , SiH_4 , GeH_4), electron-deficient (B_2H_6) and electron-rich hydrides (NH_3 , H_2O). Since most of the covalent hydrides consist of discrete, small molecules that have relatively weak intermolecular forces, they are generally gases or volatile liquids.

Metallic (Interstitial) hydrides: Metallic hydrides are usually obtained by hydrogenation of metals and alloys in which hydrogen occupies the interstitial sites (voids). Hence, they are called interstitial hydrides; the hydrides show properties similar to parent metals and hence they are also known as metallic hydrides. Most of the hydrides are non-stoichiometric with variable composition ($\text{TiH}_{1.5-1.8}$ and $\text{PdH}_{0.6-0.8}$), some are relatively light, inexpensive and thermally unstable which make them useful for hydrogen storage applications. Electropositive metals and some other metals form hydrides with the stoichiometry MH or sometimes MH_2 ($\text{M} = \text{Ti, Zr, Hf, V, Zn}$).

4.9 Hydrogen Bonding

Hydrogen bonding is one of the most important natural phenomena occurring in chemical and biological sciences. These interactions play a major role in the

structure of proteins and DNA. When a hydrogen atom (H) is covalently bonded to a highly electronegative atom such as fluorine (F) or oxygen (O) or nitrogen (N), the bond is polarized. Due to this effect, the polarized hydrogen atom is able to form a weak electrostatic interaction with another electronegative atom present in the vicinity. This interaction is called as a hydrogen bond ($20\text{-}50\text{ kJ mol}^{-1}$) and is denoted by dotted lines (...).

It is weaker than covalent bond ($> 100\text{ kJ mol}^{-1}$) but stronger than the van der Waals interaction ($< 20\text{ kJ mol}^{-1}$). Hydrogen bond has profound effect on various physical properties including vapour pressure (H_2O and H_2S), boiling point, miscibility of liquids (H_2O and $\text{C}_2\text{H}_5\text{OH}$), surface tension, densities, viscosity, heat of vaporization and fusion, etc. Hydrogen bonds can occur within a molecule (*intramolecular hydrogen bonding*) and between two molecules of the same type or different type (*intermolecular hydrogen bonding*).

Intramolecular Hydrogen Bond

Intramolecular hydrogen bonds are those which occur within a single molecule.

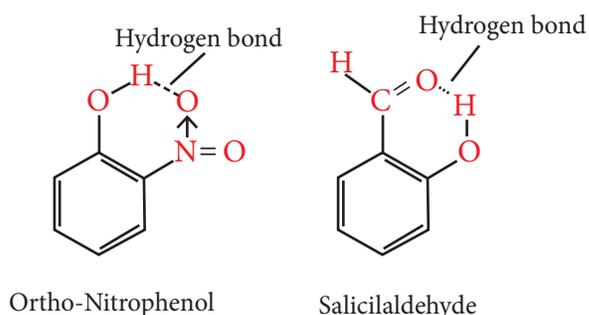


Figure 4.6 Intramolecular hydrogen bonding

Intermolecular hydrogen bond

Intermolecular hydrogen bonds occur between two separate molecules. They can occur between any numbers of like or unlike molecules as long as hydrogen donors and acceptors are present in positions which enable the hydrogen bonding interactions. For example, intermolecular hydrogen bonds can occur between ammonia molecule themselves or between water molecules themselves or between ammonia and water.

Water molecules form strong hydrogen bonds with one another. For example, each water molecule is linked to four others through hydrogen bonds. The shorter distances (100 pm) correspond to covalent bonds (solid lines), and the longer distances (180 pm) correspond to hydrogen bonds (dotted lines).

In ice, each atom is surrounded tetrahedrally by four water molecules through hydrogen bonds. That is, the presence of two hydrogen atoms and two lone pairs of electron on oxygen atoms in each water molecule allows formation of a three-dimensional structure. This arrangement creates an open structure, which accounts for the lower density of ice compared with water at 0°C . While in liquid water, unlike ice where hydrogen bonding occurs over a long-range, the strong hydrogen bonding prevails only in a short range and therefore the denser packing.

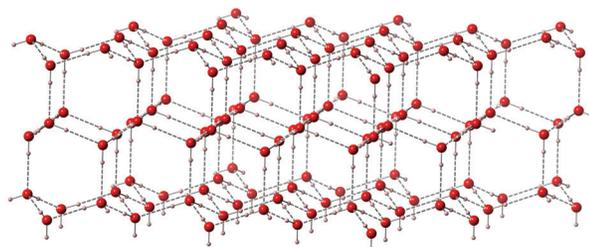


Figure 4.7 (a) Structure of Ice

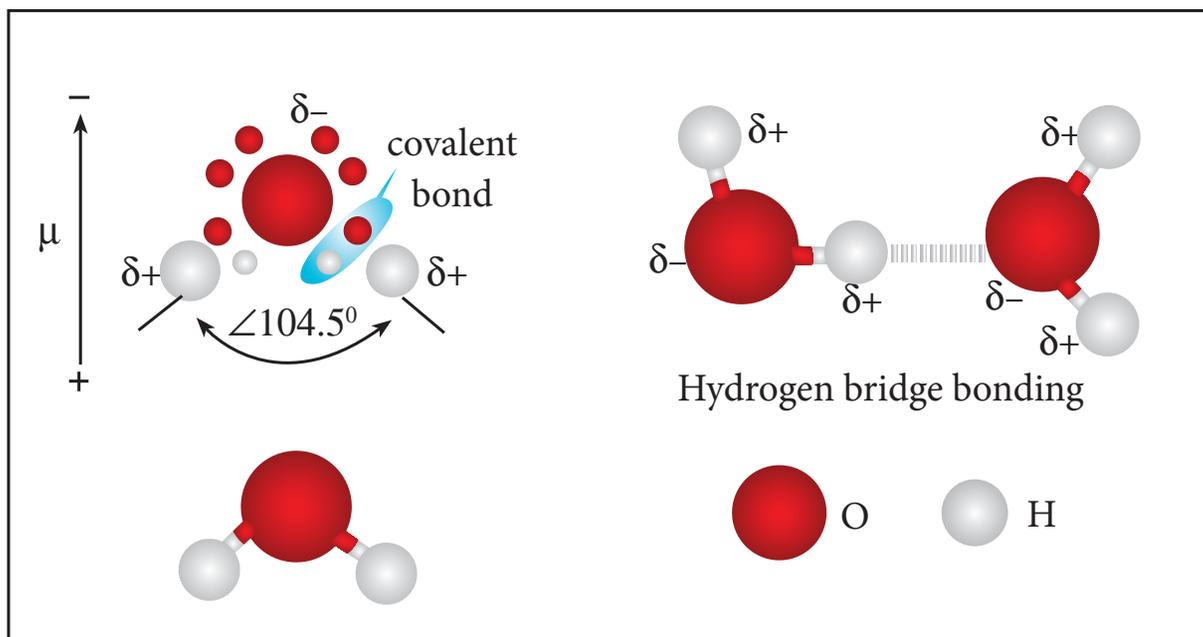


Figure 4.7 (b) Hydrogen bonding in water

Hydrogen bond occurs not only in simple molecules but also in complex biomolecules such as proteins, and they are crucial for biological processes. For example, hydrogen bonds play an important role in the structure of deoxyribonucleic acid (DNA), since they hold together the two helical nucleic acid chains (strands).

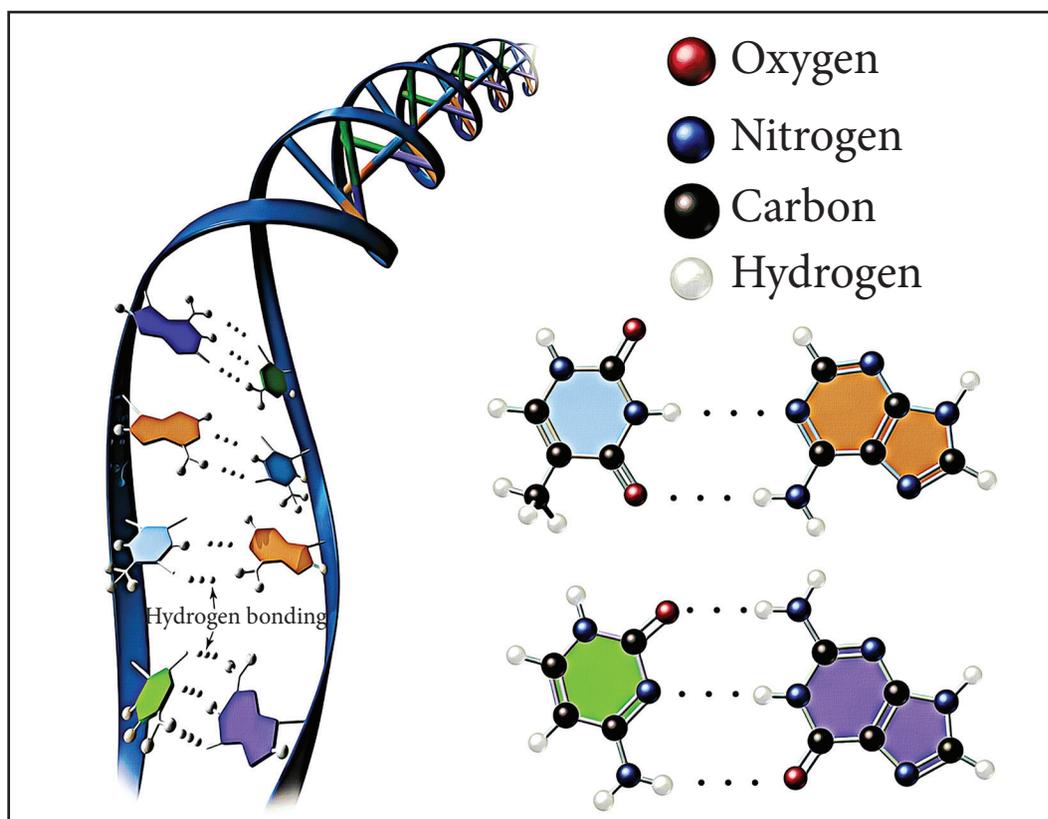


Figure 4.8 Hydrogen bonding in DNA molecules



Significant developments related to hydrogen

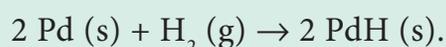
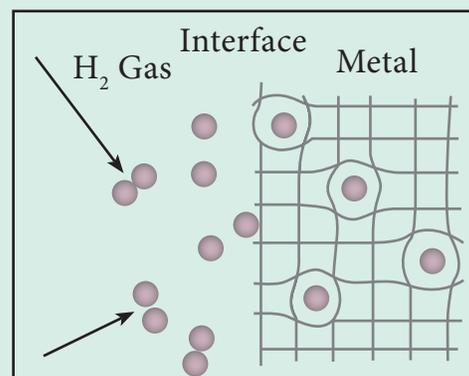
1670	Robert Boyle produced flammable gas by reacting metals with acid.
1700	Nicolas Lemery showed that the gas produced in the sulphuric acid/iron reaction was explosive in air.
1766	Henry Cavendish, discovered of hydrogen by reacting zinc metal with hydrochloric acid and isolated a gas.
1780	Felice Fontana discovered the water-gas shift reaction
1783	Antoine Lavoisier named the element hydrogen (Greek meaning – water former).
1800	William Nicholson and Anthony Carlisle decomposed water into hydrogen and oxygen by electrolysis.
1801	Humphrey Davy discovered the concept of the Fuel Cell.
1806	François I. de Rivaz built the first internal combustion engine powered by a mixture of hydrogen and oxygen.
1811	Humphrey Davy discovered gas hydrates ($\text{Cl}_2 \cdot 7\text{H}_2\text{O}$).
1818	J.L. Thenard recognized and prepared hydrogen peroxide from BaO_2 .
1834	Michael Faraday published Faraday's laws of electrolysis
1866	T. Graham discovered solubility/absorption of hydrogen on palladium.
1897	Paul Sabatier facilitated the use of hydrogenation with the discovery of the Sabatier reaction.
1898	James Dewar liquefied hydrogen.
1909	S.P.L. Sorensen introduced the pH scale for hydrogen ion concentration.

1910	Fritz Haber patented the Haber process.
1913	Niels Bohr explained the Rydberg formula for the spectrum of hydrogen by imposing a quantization condition on classical orbits of the electron in hydrogen
1924	R. Mecke discovered ortho- and para-hydrogen.
1931	Harold C. Urey discovered deuterium.
1932	Harold C. Urey discovered heavy water
1932	L.P. Hammett proposed acidity function (H_0) for very strong acids.
1934	Ernest Rutherford, Mark Oliphant, and Paul Harteck discovered tritium.
1935	Eugene Wigner and H.B. Huntington predicted metallic hydrogen.
1947	A.E. Finholt, A.C. Bond and H.I. Schlesinger discovered LiAlH_4 and subsequently shown to be a versatile reducing agent.
1950	V. Faltings and P. Harteck detected first tritium in atmosphere.
1967	Akira Fujishima discovered the phenomenon of photocatalytic water decomposition.
1971	Alexandar I. Kloss and Boris I. Tsenter patented the Nickel-Hydrogen battery.
1990	Solar-Wasserstoff-Bayern, The first solar-powered hydrogen production plant became operational.
2000	Peter Toennies demonstrated superfluidity of hydrogen at 0.15 K.

METAL HYDRIDE (HYDROGEN SPONGE)



The best studied binary hydrides are the palladium-hydrogen system. Hydrogen interacts with palladium in a unique way, and forms a limiting monohydride, PdH. Upon heating, H atoms diffuse through the metal to the surface and recombine to form molecular hydrogen. Since no other gas behaves this way with palladium, this process has been used to separate hydrogen gas from other gases:



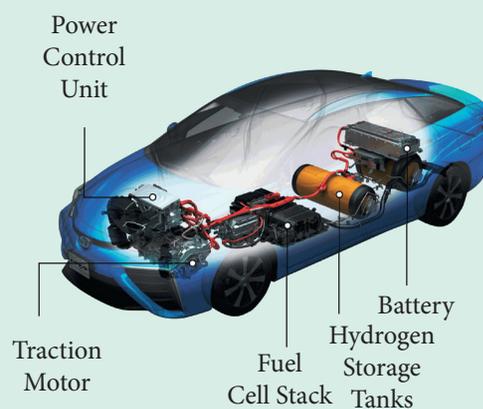
The hydrogen molecule readily adsorb on the palladium surface, where it dissociates into atomic hydrogen. The dissociated atoms dissolve into the interstices or voids (octahedral/tetrahedral) of the crystal lattice.

Technically, the formation of metal hydride is by chemical reaction but it behaves like a physical storage method, i.e., it is absorbed and released like a water sponge. Such a reversible uptake of hydrogen in metals and alloys is also attractive for hydrogen storage and for rechargeable metal hydride battery applications.

The Hydrogen – Future Fuel



The depletion of fossil fuel reserves and the threat of global warming make the world to shift toward alternative fuels. In this regard, hydrogen is often considered as a potential candidate for this purpose as it is a clean burning fuel as it does not produce any pollutants upon burning. Hence, hydrogen can directly be used as a fuel and can replace existing gasoline (petrol)/diesel/kerosene powered engines, and/or indirectly be used with oxygen in fuel cells to generate electricity. However, there are some difficulties needs to be overcome. The production cost is high and also uses more fossil fuels. Due to its volatile and flammable nature in its native form, it is difficult to store and transport. Being the smallest molecule it is prone to leakage.



SUMMARY

Hydrogen is the simplest atom which contains one electron and one proton. It has three isotopes namely protium, deuterium and tritium. The hydrogen exists as diatomic gaseous molecule. The molecule has two nuclear spin isomers namely ortho and para-hydrogen. Elemental hydrogen having an electronic configuration of $1s^1$, has properties similar to alkali metals as well as halogens. Based on its electronic configuration and existence of the +1 oxidation state in most of the compounds it is placed in group 1 along with alkali metals.

Hydrogen is prepared by the action of metal with mineral acids in laboratory. In industrial scale, hydrogen is produced by the steam-reforming of hydrocarbons. Deuterium can be synthesized by the electrolysis of heavy water, while the radioactive tritium is prepared by the nuclear transmutation reaction of lithium with slow neutrons.

Hydrogen reacts with nonmetals like oxygen and halogens to form water and hydrogen halides respectively. It reacts with metals to form metal hydrides. It acts as good reducing agent. Deuterium undergoes

exchange reactions with hydrogen. Tritium with a half-life period of 12.3 years and emits β -particles spontaneously. Hydrogen has many uses including in the preparation of ammonia, methanol, and hydrogenation of oils and reduction of metal oxides. It can also be used as fuel.

Water is an important amphoteric oxide of hydrogen and used a universal solvent. It hydrolyses oxides and forms metal hydroxides with metals such as sodium and barium. Due to the presence of soluble salts of calcium and magnesium in water, the water shows hardness. Clark's method can be used to remove temporary hardness. Like water, another important oxide is hydrogen peroxide. It is used as a mild antiseptic and as a bleaching agent in textile and paper industries. Hydrogen bound to strong electronegative atoms such as fluorine, nitrogen or oxygen atoms, forms a peculiar type of electrostatic interactions with another strong electronegative atom. This is called hydrogen bond. This is one of important interactions observed in many biological molecules such as proteins, DNA etc...

EVALUATION



I. Choose the best answer

- Which of the following statements about hydrogen is incorrect ? (NEET - 2016)
 - Hydrogen ion, H_3O^+ exists freely in solution.
 - Dihydrogen acts as a reducing agent.
 - Hydrogen has three isotopes of which tritium is the most common.
 - Hydrogen never acts as cation in ionic salts.
- Water gas is
 - $\text{H}_2\text{O}(\text{g})$
 - $\text{CO} + \text{H}_2\text{O}$
 - $\text{CO} + \text{H}_2$
 - $\text{CO} + \text{N}_2$
- Which one of the following statements is incorrect with regard to ortho and para dihydrogen ?
 - They are nuclear spin isomers
 - Ortho isomer has zero nuclear spin whereas the para isomer has one nuclear spin
 - The para isomer is favoured at low temperatures
 - The thermal conductivity of the para isomer is 50% greater than that of the ortho isomer.
- Ionic hydrides are formed by
 - halogens
 - chalcogens
 - inert gases
 - group one elements
- Tritium nucleus contains
 - $1\text{p} + 0\text{n}$
 - $2\text{p} + 1\text{n}$
 - $1\text{p} + 2\text{n}$
 - none of these
- Non-stoichiometric hydrides are formed by
 - palladium, vanadium
 - carbon, nickel
 - manganese, lithium
 - nitrogen, chlorine



7. Assertion : Permanent hardness of water is removed by treatment with washing soda.
Reason : Washing soda reacts with soluble calcium and magnesium chlorides and sulphates in hard water to form insoluble carbonates
- a) Both assertion and reason are true and reason is the correct explanation of assertion.
b) Both assertion and reason are true but reason is not the correct explanation of assertion.
c) Assertion is true but reason is false
d) Both assertion and reason are false
8. If a body of a fish contains 1.2 g hydrogen in its total body mass, if all the hydrogen is replaced with deuterium then the increase in body weight of the fish will be
- a) 1.2 g b) 2.4 g c) 3.6 g d) $\sqrt{4.8}$ g
9. The hardness of water can be determined by volumetrically using the reagent
- a) sodium thio sulphate b) potassium permanganate
c) hydrogen peroxide d) EDTA
10. The cause of permanent hardness of water is due to
- a) $\text{Ca}(\text{HCO}_3)_2$ b) $\text{Mg}(\text{HCO}_3)_2$ c) CaCl_2 d) MgCO_3
11. Zeolite used to soften hardness of water is, hydrated
- a) Sodium aluminium silicate b) Calcium aluminium silicate
c) Zinc aluminium borate d) Lithium aluminium hydride
12. A commercial sample of hydrogen peroxide marked as 100 volume H_2O_2 , it means that
- a) 1 ml of H_2O_2 will give 100 ml O_2 at STP
b) 1 L of H_2O_2 will give 100 ml O_2 at STP
c) 1 L of H_2O_2 will give 22.4 L O_2
d) 1 ml of H_2O_2 will give 1 mole of O_2 at STP





13. When hydrogen peroxide is shaken with an acidified solution of potassium dichromate in presence of ether, the ethereal layer turns blue due to the formation of
- a) Cr_2O_3 b) CrO_4^{2-} c) $\text{CrO}(\text{O}_2)_2$ d) none of these
14. For decolourisation of 1 mole of acidified KMnO_4 , the moles of H_2O_2 required is
- a) $\frac{1}{2}$ b) $\frac{3}{2}$ c) $\frac{5}{2}$ d) $\frac{7}{2}$
15. Volume strength of 1.5 N H_2O_2 is
- a) 1.5 b) 4.5 c) 16.8 d) 8.4
16. The hybridisation of oxygen atom in H_2O and H_2O_2 are, respectively
- a) sp and sp^3 b) sp and sp c) sp and sp^2 d) sp^3 and sp^3
17. The reaction $\text{H}_3\text{PO}_2 + \text{D}_2\text{O} \rightarrow \text{H}_2\text{DPO}_2 + \text{HDO}$ indicates that hypo-phosphorus acid is
- a) tribasic acid b) dibasic acid c) mono basic acid d) none of these
18. In solid ice, oxygen atom is surrounded
- a) tetrahedrally by 4 hydrogen atoms
- b) octahedrally by 2 oxygen and 4 hydrogen atoms
- c) tetrahedrally by 2 hydrogen and 2 oxygen atoms
- d) octahedrally by 6 hydrogen atoms
19. The type of H-bonding present in ortho nitro phenol and p-nitro phenol are respectively
- a) inter molecular H-bonding and intra molecular H-bonding
- b) intra molecular H-bonding and inter molecular H-bonding
- c) intra molecular H - bonding and no H - bonding
- d) intra molecular H - bonding and intra molecular H - bonding



20. Heavy water is used as
- a) moderator in nuclear reactions b) coolant in nuclear reactions
- c) both (a) and (b) d) none of these
21. Water is a
- a) basic oxide b) acidic oxide
- c) amphoteric oxide d) none of these

II. Write brief answer to the following questions:

22. Explain why hydrogen is not placed with the halogen in the periodic table.
23. Discuss the three types of Covalent hydrides.
24. Predict which of the following hydrides is a gas on a solid (a) HCl (b) NaH. Give your reason.
25. Write the expected formulas for the hydrides of 4th period elements. What is the trend in the formulas? In what way the first two members of the series different from the others ?
26. Write chemical equation for the following reactions.
- i) reaction of hydrogen with tungsten (VI) oxide on heating.
- ii) hydrogen gas and chlorine gas.
27. Complete the following chemical reactions and classify them in to (a) hydrolysis (b) redox (c) hydration reactions.
- i) $\text{KMnO}_4 + \text{H}_2\text{O}_2 \rightarrow$
- ii) $\text{CrCl}_3 + \text{H}_2\text{O} \rightarrow$
- iii) $\text{CaO} + \text{H}_2\text{O} \rightarrow$
28. Hydrogen peroxide can function as an oxidising agent as well as reducing agent. substantiate this statement with suitable examples.



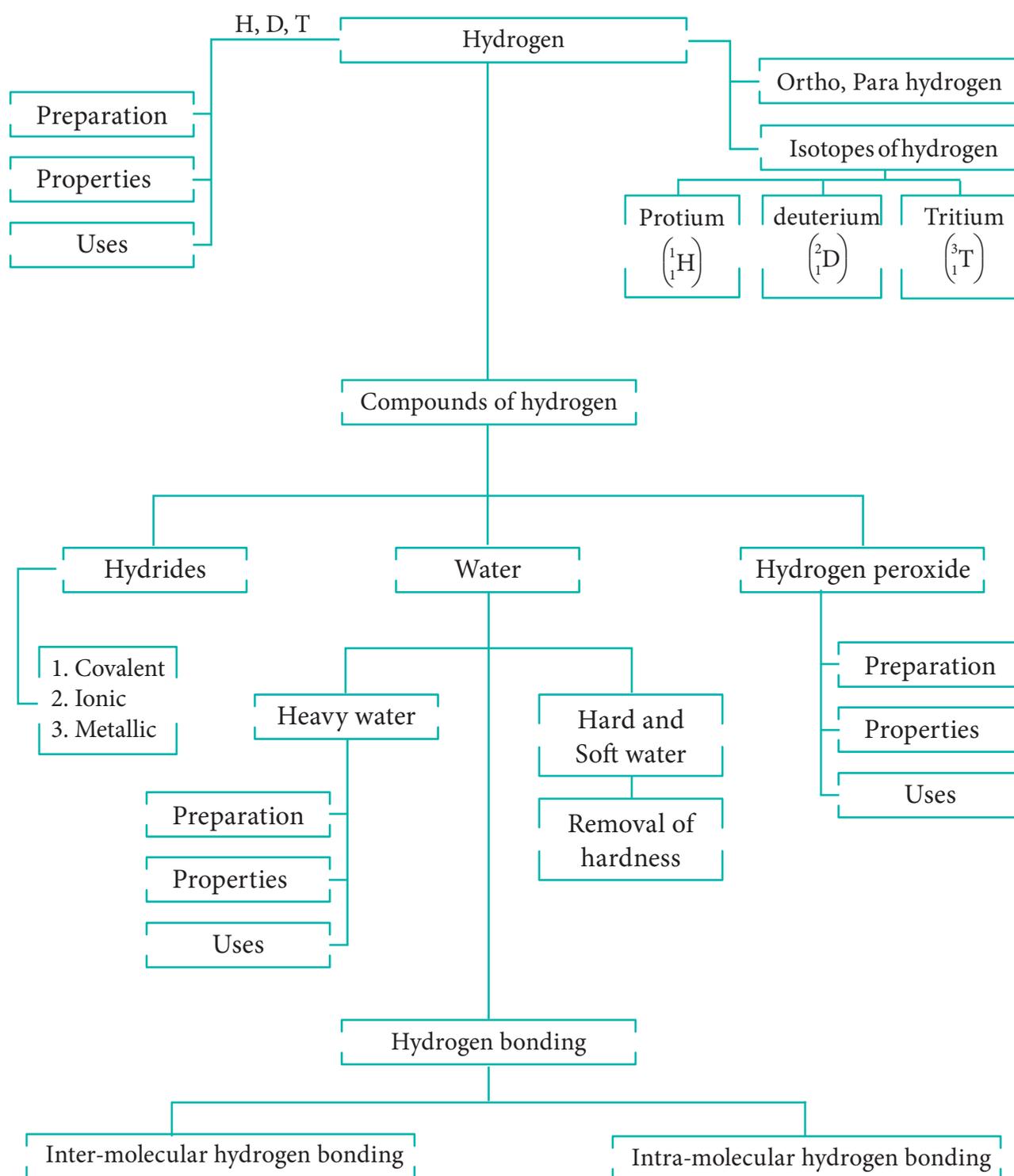


29. Do you think that heavy water can be used for drinking purposes ?
30. What is water-gas shift reaction ?
31. Justify the position of hydrogen in the periodic table ?
32. What are isotopes? Write the names of isotopes of hydrogen.
33. Give the uses of heavy water.
34. Explain the exchange reactions of deuterium.
35. How do you convert para hydrogen into ortho hydrogen ?
36. Mention the uses of deuterium.
37. Explain preparation of hydrogen using electrolysis.
38. A group-1 metal (A) which is present in common salt reacts with (B) to give compound (C) in which hydrogen is present in -1 oxidation state. (B) on reaction with a gas (C) to give universal solvent (D). The compound (D) on reacts with (A) to give (E), a strong base. Identify A, B, C, D and E. Explain the reactions.
39. An isotope of hydrogen (A) reacts with diatomic molecule of element which occupies group number 16 and period number 2 to give compound (B) is used as a moderator in nuclear reaction. (A) adds on to a compound (C), which has the molecular formula C_3H_6 to give (D). Identify A, B, C and D.
40. NH_3 has exceptionally high melting point and boiling point as compared to those of the hydrides of the remaining element of group 15 - Explain.
41. Why interstitial hydrides have a lower density than the parent metal.
42. How do you expect the metallic hydrides to be useful for hydrogen storage ?
43. Arrange NH_3 , H_2O and HF in the order of increasing magnitude of hydrogen bonding and explain the basis for your arrangement.
44. Compare the structures of H_2O and H_2O_2 .





CONCEPT MAP





Alkali and Alkaline Earth Metals



Learning Objectives

After studying this unit, students will be able to

- ◆ Explain the properties of alkali metals and alkaline earth metals
- ◆ Recognise the anomalous properties of Li and Be
- ◆ List the uses of alkali metals and alkaline earth metals
- ◆ Describe the general characteristics of compounds of alkali metals and alkaline earth metals
- ◆ Appreciate the biological importance of sodium and potassium, Magnesium and Calcium
- ◆ Explain the preparation, properties and uses of calcium oxide, calcium hydroxide, gypsum and plaster of paris.



Rock salt



Sylvite



Spodumene

5.1 s-Block Elements:

The elements belonging to the group 1 and 2 in the modern periodic table are called s-block elements. The elements belonging to these two groups are commonly known as alkali and alkaline earth metals respectively. In this unit, we study their properties, uses, important compounds and biological importance.

5.2 Alkali metals:

The word “alkali” is derived from the word al-qaliy meaning the plant ashes, referring to the original source of alkaline substances. A water-extract of burnt plant ashes, called potash contain mainly potassium carbonate. Alkali metal group consists of the elements: lithium, sodium, potassium, rubidium, caesium and francium. They are all metals, generally soft and highly reactive. They form oxides and hydroxides and these compounds are basic in nature.

5.2.1 General characteristics of alkali metals:

Alkali metals are highly reactive and are found in nature only as compounds. Rubidium and caesium are found associated in minute quantities with minerals of other alkali metals. Francium is radioactive and does not occur appreciably in nature. Francium is highly radioactive; its longest-lived isotope has a half-life of only 21 minutes.

Table 5.1 Abundance of important alkali metals and their sources

Elements	Abundance in earth crust (%)	Relative Abundance	Mineral source
Lithium	0.0018	35	Spodumene [$\text{LiAl}(\text{SiO}_3)_2$]
Sodium	2.27	7	Rock Salt [NaCl]
Potassium	1.84	8	Sylvite [KCl]
Rubidium	0.0078	23	No convenient Source (obtained as by product of lithium processing)
Cesium	0.00026	46	



Figure 5.1 Alkali metals Li, Na and K stored under oil

Electronic configuration

The general valence shell electronic configuration of alkali metals is ns^1 , where 'n' represents the period number.

Table 5.2 Electronic configuration of alkali metals

Element	Symbol	Atomic No.	Electronic configuration
Lithium	Li	3	[He]2s ¹
Sodium	Na	11	[Ne]3s ¹
Potassium	K	19	[Ar]4s ¹
Rubidium	Rb	37	[Kr]5s ¹
Caesium	Cs	55	[Xe]6s ¹
Francium	Fr	87	[Rn]7s ¹

Common oxidation state

All these elements are highly electropositive in nature. They readily lose their valence electron to give monovalent cations (M^+). Alkali metals have only one oxidation state which is +1.

Atomic and ionic radii

Being the first element of each period, alkali metals have the largest atomic and ionic radii in their respective periods. On moving down the group, there is an increase in the number of shells and, therefore, atomic and ionic radii increase. The monovalent ions (M^+) are smaller than the respective parent atoms as expected.

Table 5.3 Physical properties of alkali metals

Physical property	Li	Na	K	Rb	Cs
Atomic radius / Metallic radius (Å)	1.52	1.86	2.27	2.48	2.65
Ionic radius (Å)	0.76	1.02	1.38	1.52	1.67
Melting point (°C)	181	98	63	39	28.5
Boiling point (°C)	1347	881	766	688	705
First ionization enthalpy (kJ mol ⁻¹)	520.2	495.8	418.8	403.0	375.7
Electronegativity (Paulings scale)	1.0	0.9	0.8	0.8	0.7
Density (g cm ⁻³)	0.54	0.97	0.86	1.53	1.90
Standard potential E^0 for M^+/M (V)	-3.04	-2.71	-2.92	-2.93	-2.93
Hydration enthalpy (kJ mol ⁻¹)	-506	-406	-330	-310	-276

Ionisation enthalpy

Alkali metals have the lowest ionisation enthalpy compared to other elements present in the respective period. As we go down the group, the ionisation enthalpy decreases due to the increase in atomic size. In addition, the number of inner shells also increases, which in turn increases the magnitude of screening effect and consequently, the ionisation enthalpy decreases down the group.

The second ionisation enthalpies of alkali metals are very high. The removal of an electron from the alkali metals gives monovalent cations having stable electronic configurations similar to the noble gas. Therefore, it becomes very difficult to remove the second electron from the stable configurations already attained.

Hydration enthalpy

Lithium salts are more soluble than the salts of other metals of group 1. eg. LiClO_4 is upto 12 times more soluble than NaClO_4 . Other salts KClO_4 , RbClO_4 and CsClO_4 have solubilities only 10^{-3} times of that of LiClO_4 . The high solubility of Li salts is due to strong solvation of small size Li^+ ion.

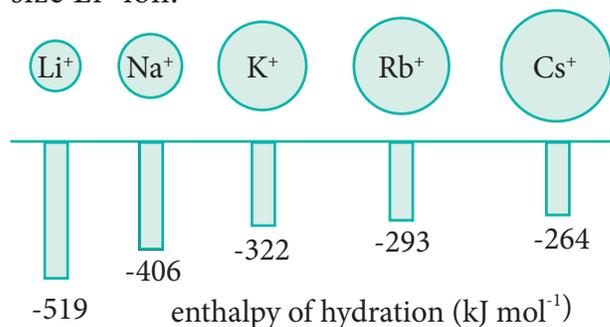


Figure 5.2 Hydration enthalpy of alkali metals

Electronegativity:

Alkali metals have comparatively smaller value of electronegativity than the other elements in the respective period. When they react with other elements, they usually produce ionic compounds. For example, they react with halogens to form ionic halides.

Flame colour and the spectra:

When the alkali metal salts moistened with concentrated hydrochloric acid are heated on a platinum wire in a flame, they show characteristic coloured flame as shown below.

Table 5.4 Flame colour and wavelength

Element	Colour	Wavelength (nm)
Lithium	Crimson red	670.8
Sodium	Yellow	589.2
Potassium	Lilac (violet)	766.5
Rubidium	Reddish violet	780.0
Caesium	Blue	455.5

The heat in the flame excites the valence electron to a higher energy level. When it drops back to its actual energy level, the excess energy is emitted as light, whose wavelength is in the visible region as shown in the above table.

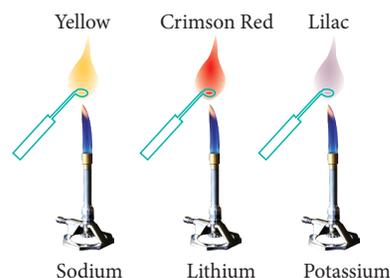


Figure 5.3 Flame colours of alkali metal salts

5.2.2 Distinctive behavior of lithium

The distinctive behaviour of Li^+ ion is due to its exceptionally small size, high polarising power, high hydration energy and non availability of d-orbitals.

Table 5.5 Comparison of properties of lithium with other elements of the group:

Lithium	Other elements of the family
Hard, high melting and boiling point	Soft and Lower melting and boiling point
Least reactive (For example it reacts with oxygen to form normal oxide, forms peroxides with great difficulty and its higher oxides are unstable)	More reactive
Reacts with nitrogen to give Li_3N $6\text{Li} + \text{N}_2 \rightarrow 2\text{Li}_3\text{N}$	No reaction
Reacts with bromine slowly	React violently
Reacts directly with carbon to form ionic carbides. For example $2\text{Li} + 2\text{C} \rightarrow \text{Li}_2\text{C}_2$	Do not react with carbon directly, but can react with carbon compounds. $2\text{Na} + \text{C}_2\text{H}_2 \rightarrow \text{Na}_2\text{C}_2 + \text{H}_2$
Lithium nitrate decomposes to give an oxide	Decompose to give nitrites

Table 5.6 Similarities between lithium and Magnesium

S.No.	Properties
1	Both lithium and magnesium are harder than other elements in the respective groups
2	Lithium and magnesium react slowly with water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating.
3	Both form a nitride, Li_3N and Mg_3N_2 , by direct combination with nitrogen
4	They do not give any superoxides and form only oxides, Li_2O and MgO
5	The carbonates of lithium and magnesium decompose upon heating to form their respective oxides and CO_2 .
6	Lithium and magnesium do not form bicarbonates.
7	Both LiCl and MgCl_2 are soluble in ethanol and are deliquescent. They crystallise from aqueous solution as hydrates, $\text{LiCl} \cdot 2\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$

Diagonal Relationship:

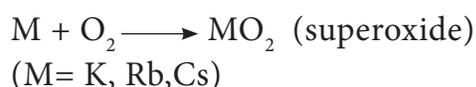
Similarity between the first member of group 1 (Li) and the diagonally placed second element of group 2 (Mg) is called diagonal relationship. It is due to similar size ($r_{\text{Li}^+} = 0.766 \text{ \AA}$ and $r_{\text{Mg}^{2+}} = 0.72 \text{ \AA}$) and comparable electronegativity values ($\text{Li} = 1.0$; $\text{Mg} = 1.2$).

5.2.3 Chemical properties of alkali metals

Alkali metals exhibit high chemical reactivity. The reactivity of alkali metals increases from Li to Cs, since the ionisation energy decreases down the group. All alkali metals are highly reactive towards the more electronegative elements such as oxygen and halogens. Some characteristic chemical properties of alkali metals are described below.

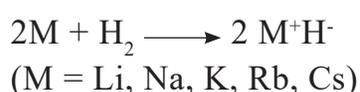
Reaction with oxygen

All the alkali metals on exposure to air or oxygen burn vigorously, forming oxides on their surface. Lithium forms only monoxide, sodium forms the monoxide and peroxide and the other elements form monoxide, peroxide, and superoxides. These oxides are basic in nature.



Reaction with hydrogen

All alkali metals react with hydrogen at about 673 K (lithium at 1073 K) to form the corresponding ionic hydrides. Reactivity of alkali metals with hydrogen decreases from Li to Cs.

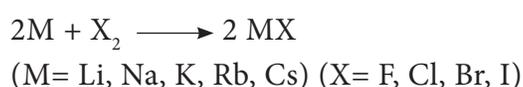


The ionic character of the hydrides increases from Li to Cs and their stability decreases. The hydrides behave as strong

reducing agents and their reducing nature increases down the group.

Reaction with halogen

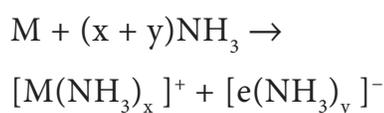
Alkali metals combine readily with halogens to form ionic halides MX. Reactivity of alkali metals with halogens increases down the group because of corresponding decrease in ionisation enthalpy.



All metal halides are ionic crystals. However Lithium iodide shows covalent character, as it is the smallest cation that exerts high polarising power on the iodide anion. Additionally, the iodide ion being the largest can be polarised to a greater extent by Li^+ ion.

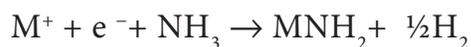
Reaction with liquid ammonia:

Alkali metals dissolve in liquid ammonia to give deep blue solutions that are conducting in nature. The conductivity is similar to that of pure metals (The specific conductivity of Hg is $10^4 \Omega^{-1}$ and for sodium in liquid ammonia is $0.5 \times 10^4 \Omega^{-1}$). This happens because the alkali metal atom readily loses its valence electron in ammonia solution. Both the cation and the electron are ammoniated to give ammoniated cation and ammoniated electron.



The blue colour of the solution is due to the ammoniated electron which

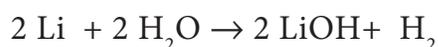
absorbs energy in the visible region of light and thus imparts blue colour to the solution. The solutions are paramagnetic and on standing slowly liberate hydrogen resulting in the formation of an amide.



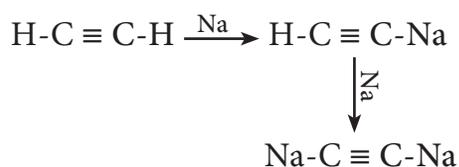
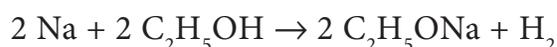
In concentrated solution, the blue colour changes to bronze colour and become diamagnetic.

Reaction with water:

Alkali metals react with water to give corresponding hydroxides with the liberation of hydrogen.



They also react with alcohol, and alkynes which contain active hydrogens.



Reducing activity:

Alkali metals can lose their valence electron readily hence they act as good reducing agents.



Reaction with carbon:

Lithium directly reacts with carbon to form the ionic compound, lithium carbide. Other metals do not react with carbon directly. However, when they are treated with compounds like acetylene they form acetylides.



5.2.4 Uses of alkali metals:

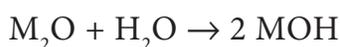
- Lithium metal is used to make useful alloys. For example with lead it is used to make 'white metal' bearings for motor engines, with aluminium to make aircraft parts, and with magnesium to make armour plates. It is used in thermonuclear reactions.
- Lithium is also used to make electrochemical cells.
- Sodium is used to make Na/Pb alloy needed to make $Pb(Et)_4$ and $Pb(Me)_4$. These organolead compounds were earlier used as anti-knock additives to petrol, but nowadays lead-free petrol in use.
- Liquid sodium metal is used as a coolant in fast breeder nuclear reactors.
- Potassium has a vital role in biological systems. Potassium chloride is used as a fertilizer.
- Potassium hydroxide is used in the manufacture of soft soap. It is also used as an excellent absorbent of carbon dioxide.
- Caesium is used in devising photoelectric cells.

5.3 General characteristics of the compounds of alkali metals

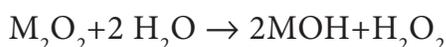
All the common compounds of the alkali metals are generally ionic in nature. General characteristics of some of their compounds are discussed here.

Oxides and Hydroxides

On combustion in excess of air, alkali metals form normal oxides with formula M_2O . They react with water to form corresponding hydroxides which are basic in nature.

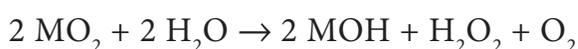


Alkali metals apart from lithium form peroxides in addition to normal oxides upon combustion with excess air. These peroxides produce hydroxides and H_2O_2 upon reacting with water.



(M = Na, K, Rb, Cs)

Except lithium and sodium, all the other alkali metals form superoxides also. These superoxides also give basic hydroxides upon treatment with water.



(M = K, Rb, Cs)

Under appropriate conditions pure compounds M_2O , M_2O_2 or MO_2 may be prepared.

Properties of oxides and hydroxides:

The oxides and the peroxides are colourless when pure, but the superoxides are yellow or orange in colour. The peroxides are diamagnetic while the superoxides are paramagnetic. Sodium peroxide is widely used as an oxidising agent. The hydroxides which are obtained by the reaction of the oxides with water are all white crystalline solids. The alkali metal hydroxides are strong bases. They

dissolve in water with evolution of heat on account of intense hydration.

Halides:

The alkali metal halides, MX , (X=F, Cl, Br, I) are colourless crystalline solids with high melting points. They can be prepared by the reaction of the appropriate oxide, hydroxide or carbonate with aqueous hydrohalic acid (HX). As the electropositive character of alkali metal increases from Li to Cs, the ease with which the metals form halides increases from Li to Cs. All halides are ionic in nature except LiBr and LiI. Except LiF, all other halides are soluble in water. The low solubility of LiF in water is due to its high lattice enthalpy (small size of Li^+ and F^-). Due to the presence of covalent nature both LiBr and LiI are soluble in organic solvents.

Salts of oxo-acids

Alkali metals form salts with all the oxo-acids. Most of these salts are soluble in water and are thermally stable. As the electropositive character increases down the group, the stability of the carbonates and bicarbonates increases. This is due to the decrease in polarising power of alkali metal cations. The carbonates (M_2CO_3) of alkali metals are remarkably stable up to 1273 K, above which they first melt and then eventually decompose to form oxides. However, Li_2CO_3 is considerably less stable and decomposes readily.



This is presumably due to large size difference between Li^+ and CO_3^{2-} which

makes the crystal lattice unstable. Being strongly basic, alkali metals except lithium form solid bicarbonates. No other metal forms solid bicarbonates.



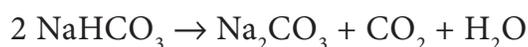
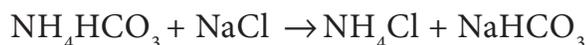
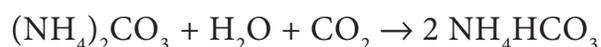
(M = Na, K, Rb, Cs)

All the carbonates and bicarbonates are soluble in water and their solubilities increase rapidly on descending the group. This is due to the reason that lattice energies decrease more rapidly than their hydration energies on moving down the group.

5.3.1 Important compounds of alkali metals:

Sodium Carbonate $Na_2CO_3 \cdot 10H_2O$ (Washing soda):

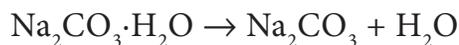
Sodium carbonate is one of the important inorganic compounds used in industries. It is prepared by Solvay process. In this process, ammonia is converted into ammonium carbonate which then converted to ammonium bicarbonate by passing excess carbon dioxide in a sodium chloride solution saturated with ammonia. The ammonium bicarbonate thus formed reacts with the sodium chloride to give sodium bicarbonate and ammonium chloride. As sodium bicarbonate has poor solubility, it gets precipitated. The sodium bicarbonate is isolated and is heated to give sodium carbonate. The equations involved in this process are,



The ammonia used in this process can be recovered by treating the resultant ammonium chloride solution with calcium hydroxide. Calcium chloride is formed as a by-product.

Properties:

Sodium carbonate, commonly known as washing soda, crystallises as decahydrate which is white in colour. It is soluble in water and forms an alkaline solution. Upon heating, it loses the water of crystallisation to form monohydrate. Above 373 K, the monohydrate becomes completely anhydrous and changes to a white powder called soda ash.



Uses:

- Sodium carbonate known as washing soda and is used mainly for laundering.
- It is also used in water treatment to convert the hard water to soft water.
- It is used in the manufacturing of glass, paper, paint etc...

Sodium chloride NaCl (Cooking salt or Table salt):

Sodium chloride is isolated by evaporation from sea water which contains

2.7 to 2.9% by mass. Approximately 50 lakh tons of salt are produced annually in India by solar evaporation. Crude sodium chloride can be obtained by crystallisation of brine solution which contains sodium sulphate, calcium sulphate, calcium chloride and magnesium chloride as impurities. Pure sodium chloride can be obtained from crude salt as follows. Firstly removal of insoluble impurities by filtration from the crude salt solution with minimum amount of water. Sodium chloride can be crystallised by passing HCl gas into this solution. Calcium and magnesium chloride, being more soluble than sodium chloride, remain in solution.

Sodium chloride melts at 1081K. It has a solubility of 36.0 g in 100 g of water at 273 K. The solubility does not increase appreciably with increase in temperature.

Uses :

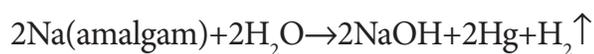
- (i) It is used as a common salt or table salt for domestic purpose.
- (ii) It is used for the preparation of many inorganic compounds such as NaOH and Na_2CO_3

Sodium hydroxide:

Sodium hydroxide is prepared commercially by the electrolysis of brine solution in Castner-Kellner cell using a mercury cathode and a carbon anode. Sodium metal is discharged at the cathode and combines with mercury to form sodium amalgam. Chlorine gas is evolved at the anode. The sodium amalgam thus obtained is treated with water to give sodium hydroxide.

At cathode : $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}(\text{amalgam})$

At anode : $\text{Cl}^- \rightarrow \frac{1}{2} \text{Cl}_2 \uparrow + \text{e}^-$



Sodium hydroxide is a white, translucent and deliquescent solid, that dissolves in water to give a strong alkaline solution. It melts at 591 K. The sodium hydroxide solution at the surface reacts with the CO_2 in the atmosphere to form Na_2CO_3

Uses:

- Sodium hydroxide is used in the purification of bauxite (ore of Aluminium) and petroleum refining
- It is used in the textile industries for mercerising cotton fabrics
- It is used in the manufacture of soap, paper and artificial silks.

Sodium bicarbonate NaHCO_3 (Baking soda):

Sodium hydrogen carbonate or sodium bicarbonate is used in baking cakes pastries etc. It is called so because it decomposes on heating to generate bubbles of carbon dioxide, leaving holes in cakes or pastries and making them light and fluffy. This compound is prepared by saturating a solution of sodium carbonate with carbon dioxide. The white crystalline powder of sodium bicarbonate, being less soluble, precipitated out.

Uses:

- Primarily used as an ingredient in baking.
- Sodium hydrogen carbonate is a mild antiseptic for skin infections.
- It is also used in fire extinguishers.

5.4 Biological importance of sodium and potassium

Monovalent sodium and potassium ions are found in large proportions in biological fluids. These ions perform important biological functions such as maintenance of ion balance and nerve impulse conduction. A typical 70 kg man contains about 90 g of sodium and 170 g of potassium compared with only 5 g of iron and 0.06 g of copper.

Sodium ions are found primarily on the outside of cells, being located in blood plasma and in the interstitial fluid which surrounds the cells. These ions participate in the transmission of nerve signals, in regulating the flow of water across cell membranes and in the transport of sugars and amino acids into cells. Sodium and potassium, although so similar chemically, differ quantitatively in their ability to penetrate cell membranes, in their transport mechanisms and in their efficiency to activate enzymes. Thus, potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in the oxidation of glucose to produce ATP and, with sodium, are responsible for the transmission of nerve signals.

Sodium-potassium pump play an important role in transmitting nerve signals.

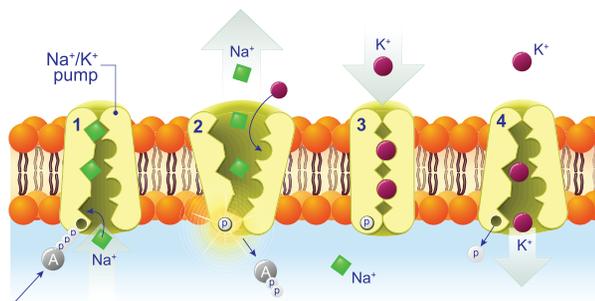


Figure 5.4 Sodium-potassium pump

5.5 Alkaline earth metals

Group 2 in the modern periodic table contains the elements beryllium, magnesium, calcium, strontium, barium and radium. These elements with the exception of beryllium are commonly known as the alkaline earth metals because their oxides and hydroxides are alkaline in nature and these metal oxides are found in the earth's crust.



Figure 5.5 Alkaline earth metals

Table 5.7 Abundance of important alkaline earth metals and their sources

Element	Abundance in Earth crust by weight (ppm)	Mineral source
Be	2.0	beryl $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$
Mg	27640	Carnallite ($\text{KCl}\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$) Dolomite MgCO_3 CaCO_3
Ca	1.84	Fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$
Sr	384	Celestite SrSO_4
Ba	390	barytes BaSO_4

5.5.1 General characteristics of alkaline earth metals

Physical state

Beryllium is rare and radium is the rarest of all comprising only 10 % of igneous rocks. Magnesium and calcium are very common in the earth's crust, with calcium the fifth-most-abundant element, and magnesium the eighth. Magnesium and calcium are found in many rocks and minerals: magnesium in carnallite, magnesite, dolomite and calcium in chalk, limestone, gypsum. Most strontium is found in the minerals celestite and strontianite. Barium is slightly less common, much of it in the mineral barite. Radium, being a decay product of uranium, is found in all uranium-bearing ores.

FIREWORK



Many alkaline and alkaline earth metals are used in creating colours, such as strontium and barium, are the colourful stars of a fireworks show. Combined with the element chlorine, barium sends up a green spark, calcium gives orange and lithium gives medium red. Strontium carbonate gives a bright red colour Nitrates of sodium gives orange, potassium and rubidium gives violet colour and caesium gives indigo colour. The burning "excites" the electrons, pushing them into higher than normal energy level; they release their extra energy as a colourful burst of light



The blue fireworks are the hardest to make, since the compound copper chloride breaks down in a hot flame. In recent years, fireworks experts have used magnalium- a mixture of the alkaline earth metal magnesium and aluminium - to boost all firework colours. Magnalium has made the blues brighter, but pyro technicians are still searching for a blue as brilliant as the red, green and yellow colours.

Electronic configuration

These elements have two electrons in the valence shell of their atoms, preceded by the noble gas configuration. Their general electronic configuration is written

as [Noble gas] ns^2 where 'n' represents the valence shell.

Table 5.8 Electronic configuration of alkaline earth metals

Element	Atomic No.	Electronic configuration
Be	4	[He] $2s^2$
Mg	12	[Ne] $3s^2$
Ca	20	[Ar] $4s^2$
Sr	38	[Kr] $5s^2$
Ba	56	[Xe] $6s^2$
Ra	88	[Rn] $7s^2$

Atomic and ionic radii

The atomic and ionic radii of alkaline earth metals are smaller than the corresponding members of the alkali metals. This is due to the fact the Group 2 elements having a higher nuclear charge that allows electrons to be attracted more strongly towards the nucleus. On moving down the group, the radii increases due to gradual increase in the number of the shells and the screening effect.

Common oxidation state

The group 2 elements have two electrons in their valence shell and by losing these electrons, they acquire the stable noble gas configuration. So these elements exhibit +2 oxidation state in their compounds.

Ionisation enthalpy

Due to a fairly large size of the atoms, alkaline earth metals have low ionisation enthalpies when compared to 'p' block elements. Down the group the ionisation enthalpy decreases as atomic size increases. This is due to the addition of new shells as well as increase in the magnitude of the screening effect of inner shell electrons. Members of group 2 have higher ionization enthalpy values than group 1 because of their smaller size, with electrons being more attracted towards the nucleus of the atoms. Correspondingly they are less electropositive than alkali metals.

Table 5.9 Physical properties of alkaline earth metals

Physical property	Be	Mg	Ca	Sr	Ba
Atomic radius - non bonded (Å)	1.12	1.60	1.97	2.15	2.22
Ionic radius (Å)	0.27(0.31)	0.72	1.00	1.18	1.35
First ionization energy (kJ mol ⁻¹)	899.5	737.8	589.8	549.5	502.9
Second ionization energy (kJ mol ⁻¹)	1757.1	1450.7	1145.5	1064.2	965.2
Hydration enthalpy (kJ mol ⁻¹)	-2494	-1921	-1577	-1443	-1305
Melting Point (°C)	1287	651	851	789	729
Boiling Point (°C)	2472	1090	1494	1382	1805
Density (g cm ⁻³)	1.84	1.74	1.55	2.63	3.59
Standard Potential E ⁰ for M ⁺ /M (V)	-1.97	-2.36	-2.84	-2.89	-2.92
Electronegativity (Paulings scale)	1.6	1.2	1.0	1.0	0.9

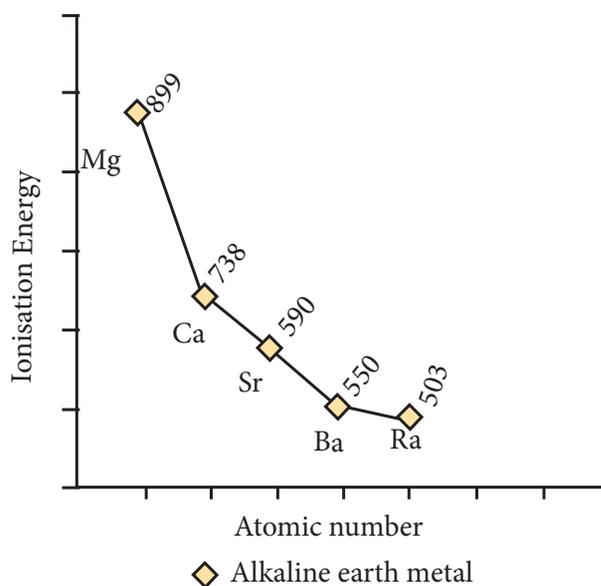


Figure 5.6 Variation of ionisation energy - Alkaline earth metals.

Although IE_1 values of alkaline earth metals are higher than that of alkali metals, the IE_2 values of alkaline earth metals are much smaller than those of alkali metals. This occurs because in alkali metals the second electron is to be removed from a cation, which has already acquired a noble gas configuration. In the case of alkaline earth metals, the second electron is to be removed from a monovalent cation, which still has one electron in the outermost shell. Thus, the second electron can be removed more easily in the case of group 2 elements than in group 1 elements.

Hydration Enthalpies

Compounds of alkaline earth metals are more extensively hydrated than those of alkali metals, because the hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions.

Like alkali metal ions, the hydration enthalpies of alkaline earth metal ions also decrease with increase in ionic size down the group.



e.g., Magnesium chloride and calcium chloride exist as their hydrated crystals $MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 6H_2O$ respectively, whereas NaCl and KCl do not form such hydrates.

Electronegativity

In alkaline earth metals the electronegativity values decrease as we go down the group as seen in the alkali metals.

Flame colour and the spectra:

When the alkaline earth metal salts moistened with concentrated hydrochloric acid are heated on a platinum wire in a flame, they show characteristic coloured flame as shown below.

Table 5.10 Flame Colour and wavelength

Element	Colour	Wavelength (nm)
Calcium	Brick - Red	622
Strontium	Crimson- Red	689
Barium	Apple Green	554

The heat in the flame excites the valence electron to a higher energy level. when it drops back to its actual energy level, the excess energy is emitted as light, whose wavelength is in the visible region as shown in the above table.

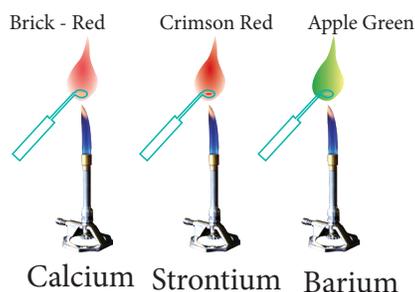


Figure 5.7: Flame colours of alkaline earth metal salts

5.5.2 Distinctive behavior of beryllium

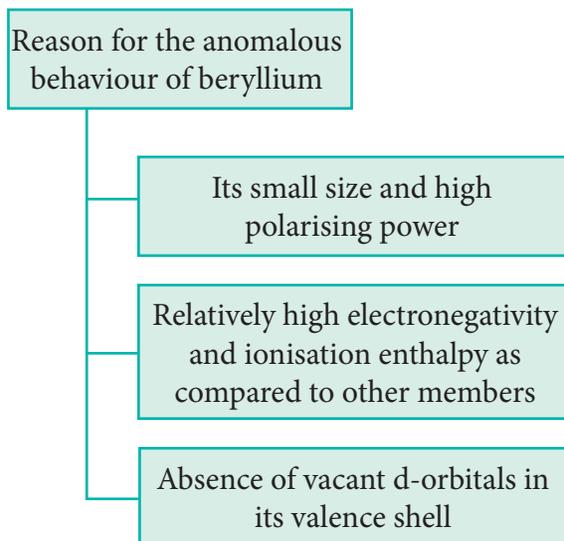


Figure 5.8 Distinctive behaviour of beryllium

The anomalous properties of beryllium is mainly due to its small size, high electronegativity, high ionisation energy and high polarising power compared to the other elements in the block. The anomalous properties of beryllium compared to other elements of the group are mentioned in Table 5.11

Table 5.11 Comparison of Properties of Beryllium with other elements of the group

Beryllium	Other elements of the family
Forms covalent compounds	form ionic compounds
High melting and boiling point	Low melting and boiling point
Does not react with water even at elevated temperature	React with water
Does not combine directly with hydrogen	Combine directly with hydrogen
Does not combine directly with halogens. Halides are covalent.	Combine directly with halogens Halides are electrovalent.

Hydroxide and oxides of beryllium are amphoteric in nature	Basic in nature.
It is not readily attacked by acids because of the presence of an oxide film	Readily attacked by acids
Beryllium carbide evolves methane with water.	evolve acetylene with water.
Salts of Be are extensively hydrolysed	Hydrolysed

Diagonal Relationship:

As observed in alkali metals, beryllium (the first member of group 2) shows a diagonal relationship with aluminium. In this case, the size of these ions ($r_{\text{Be}^{2+}} = 0.45 \text{ \AA}$ and $r_{\text{Al}^{3+}} = 0.54 \text{ \AA}$) is not as close. However, their charge per unit area is closer ($\text{Be}^{2+} = 2.36$ and $\text{Al}^{3+} = 2.50$). They also have same electronegativity values ($\text{Be} = 1.5$; $\text{Al} = 1.5$).

Table 5.12 Similarities between Beryllium and Aluminium

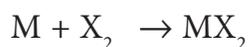
S.No.	Properties
1	Beryllium chloride forms a dimeric structure like aluminium chloride with chloride bridges. Beryllium chloride also forms polymeric chain structure in addition to dimer. Both are soluble in organic solvents and are strong Lewis acids.
2	Beryllium hydroxide dissolves in excess of alkali and gives beryllate ion and $[\text{Be}(\text{OH})_4]^{2-}$ and hydrogen as aluminium hydroxide which gives aluminate ion, $[\text{Al}(\text{OH})_4]^-$.
3	Beryllium and aluminium ions have strong tendency to form complexes, BeF_4^{2-} , AlF_6^{3-} .
4	Both beryllium and aluminium hydroxides are amphoteric in nature.
5	Carbides of beryllium (Be_2C) like aluminium carbide (Al_4C_3) give methane on hydrolysis.
6	Both beryllium and aluminium are rendered passive by nitric acid.

5.5.3 Chemical properties of alkaline earth metals

The alkaline earth metals are less reactive than the alkali metals. The reactivity of these elements increases on going down the group.

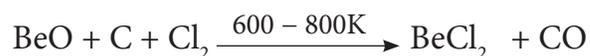
Reactivity towards the halogens:

All the alkaline earth metals combine with halogen at elevated temperatures to form their halides.



(M= Be, Mg, Ca, Sr, Ba, Ra ,
X = F, Cl, Br, I)

Thermal decomposition of $(\text{NH}_4)_2\text{BeF}_4$ is the best route for the preparation of BeF_2 . BeCl_2 is conveniently made from the oxide.



Reactivity towards hydrogen:

All the elements except beryllium, combine with hydrogen on heating to form their hydrides with general formula MH_2 . BeH_2 can be prepared by the reaction of BeCl_2 with LiAlH_4 .



5.5.4 Uses of alkaline earth metals

Uses of beryllium

1. Because of its low atomic number and very low absorption for X-rays, it is used as radiation windows for X-ray tubes and X-ray detectors.
2. The sample holder in X-ray emission studies usually made of beryllium
3. Since beryllium is transparent to energetic particles, it is used to build the 'beam pipe' in accelerators.
4. Because of its low density and diamagnetic nature, it is used in various detectors.

Uses of magnesium

1. Removal of sulphur from iron and steel.

2. Used as photoengrave plates in printing industry.
3. Magnesium alloys are used in aeroplane and missile construction.
4. Mg ribbon is used in synthesis of Grignard reagent in organic synthesis.
5. It alloys with aluminium to improve its mechanical, fabrication and welding property.
6. As a desiccant .
7. As sacrificial anode in controlling galvanic corrosion.

Uses of calcium

1. As a reducing agent in the metallurgy of uranium, zirconium and thorium.
2. As a deoxidiser, desulphuriser or decarboniser for various ferrous and non-ferrous alloys.
3. In making cement and mortar to be used in construction.
4. As a getter in vacuum tubes.
5. In dehydrating oils
6. In fertilisers, concrete and plaster of paris.

Uses of strontium

1. ^{90}Sr is used in cancer therapy.
2. $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios are commonly used

in marine investigations as well as in teeth, tracking animal migrations or in criminal forensics.

3. Dating of rocks.
4. As a radioactive tracer in determining the source of ancient archaeological materials such as timbers and coins.

Uses of Barium

1. Used in metallurgy, its compounds are used in pyrotechnics, petroleum mining and radiology.
2. Deoxidiser in copper refining.
3. Its alloys with nickel readily emits electrons hence used in electron tubes and in spark plug electrodes.
4. As a scavenger to remove last traces of oxygen and other gases in television and other electronic tubes.
5. An isotope of barium ^{133}Ba , used as a source in the calibration of gamma ray detectors in nuclear chemistry.

Uses of Radium

Used in self-luminous paints for watches, nuclear panels, aircraft switches, clocks and instrument dials.

5.6. General characteristics of the compounds of the alkaline earth metals

The dipositive oxidation state (M^{2+}) is the predominant valence of group 2 elements. The alkaline earth metals form compounds which are predominantly ionic. However, they are less ionic than

the corresponding compounds of alkali metals. This is due to increased nuclear charge and smaller size. The general characteristics of some of the compounds of alkaline earth metals are described below.

(a) Oxides

Generally alkaline earth metals form monoxides and peroxides.

Monoxides

Monoxides are obtained by heating the metals in oxygen. BeO and MgO are almost insoluble in water. On the other hand, oxides of other elements form hydroxides. BeO is amphoteric; MgO is weakly basic while CaO , SrO and BaO are strongly basic.

BeO oxide is covalent due to the small size of Be^{2+} ion, while other oxides are ionic in nature.

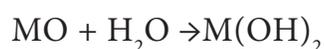
Peroxides

Except beryllium, all the remaining metals form peroxides. It is prepared by heating monoxides with oxygen at high temperature.



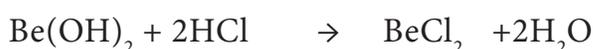
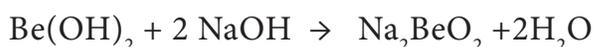
b) Hydroxides:

All the oxides except BeO are basic in nature and react with water to form sparingly soluble hydroxides.



The solubility, thermal stability

and the basic character of the hydroxides increase down the group. The alkaline earth metal hydroxides are, however, less basic and less stable than alkali metal hydroxides. Beryllium hydroxide is amphoteric in nature as it reacts with both acid and alkali.



c) Halides:

Alkaline earth metals form halides with general formula MX_2 . They can be prepared by heating metals with halogens on heating.



Beryllium halides are covalent on account of smaller size of Be^{+2} . Beryllium halides are hygroscopic, fume in moist air and soluble in organic solvents. Beryllium chloride has a chain structure in the solid state as shown in figure 5.9 (structure-a). In the vapour phase BeCl_2 tends to form a chloro-bridged dimer (structure-c) which dissociates into the linear monomer at high temperatures of the order of 1200 K. (structure-b).

Except beryllium halides, all the other halides of alkaline earth metals are ionic in nature. Chloride and fluorides of the other metals are ionic solids. These are good conductors of electricity in fused state and in aqueous solutions. The tendency to form halide hydrates gradually decreases (for example, $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) down the group.

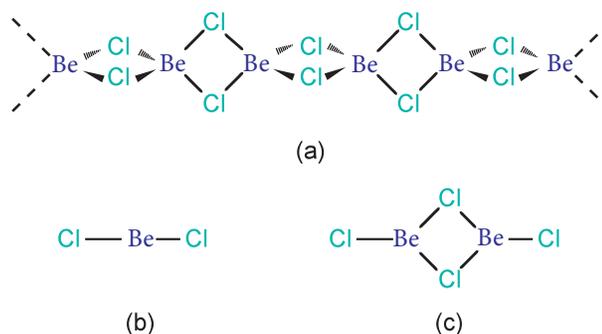


Figure 5.9 Structure of beryllium chloride

Salts of oxo acids

The alkaline earth metals form salts of oxo acids. Some of these are given below:

Carbonates:

All the carbonates decompose on heating to give carbon dioxide and the oxide.



- The solubility of carbonates in water decreases down the group.
- The thermal stability increases down the group with increasing cationic size.

Table 5.13 Decomposition temperature of alkaline metal carbonates and sulphates

Element	Decomposition temp for carbonates (in °C)	Decomposition temp for sulphates (in °C)
Be	25	500
Mg	540	895
Ca	900	1149
Sr	1290	1374
Ba	1360	-

Sulphates:

The sulphates of the alkaline earth metals are all white solids and stable to heat. BeSO_4 , and MgSO_4 are readily soluble in water; the solubility decreases from CaSO_4 to BaSO_4 . The greater hydration enthalpies of Be^{2+} and Mg^{2+} ions overcome the lattice enthalpy factor and therefore their sulphates are soluble in water.

Nitrates:

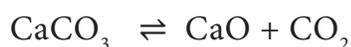
The nitrates are made by dissolution of the carbonates in dilute nitric acid. Magnesium nitrate crystallises with six molecules of water, whereas barium nitrate crystallises as the anhydrous salt. This again shows a decreasing tendency to form hydrates with increasing size. All of them decompose on heating to give the oxide.

5.6.1 Important compounds of calcium

Quick lime, CaO

Preparation

It is produced on a commercial scale by heating limestone in a lime kiln in the temperature range 1070-1270K.



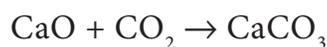
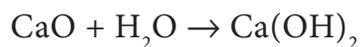
The reaction being reversible, carbon dioxide is removed as soon as it is produced to enable the reaction to proceed to completion.

Properties

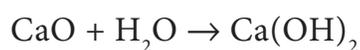
Calcium oxide is a white amorphous solid.

It has a melting point of 2870 K.

(i) It absorbs moisture and carbon dioxide on exposure to atmosphere.



(ii) The addition of limited amount of water breaks the lump of lime. This process is called slaking of lime and the product is slaked lime.



(iii) The mixture of Quick lime (CaO) and sodium hydroxide is called soda lime.

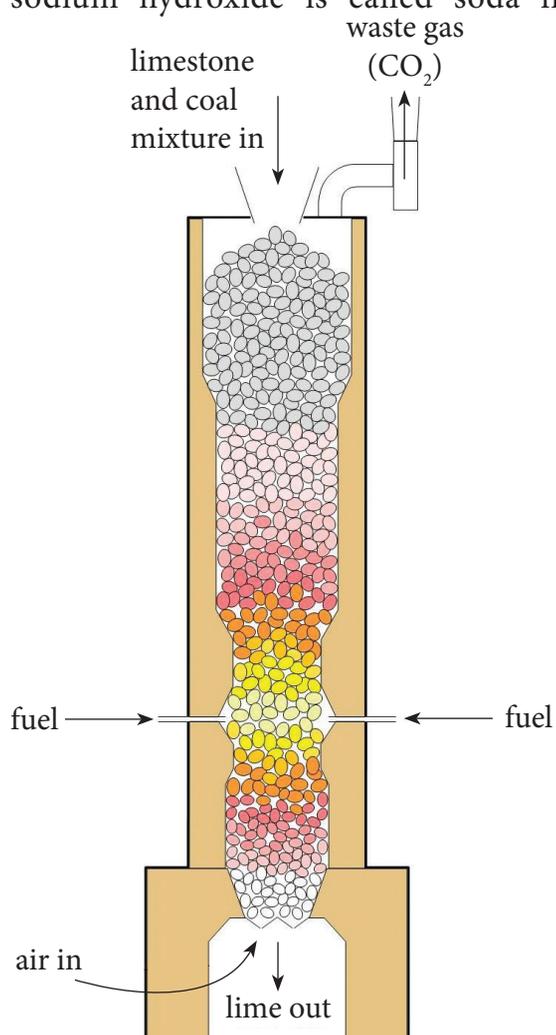
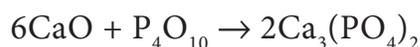
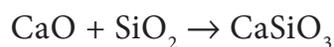


Figure 5.10 Preparation of Quick Lime

(iv) It combines with acidic oxides such as SiO_2 and P_4O_{10} to form CaSiO_3 and $\text{Ca}_3(\text{PO}_4)_2$, respectively.



Uses

Calcium oxide is used

- (i) to manufacture cement, mortar and glass.
- (ii) in the manufacture of sodium carbonate and slaked lime.
- (iii) in the purification of sugar.
- (iv) as a drying agent.

5.6.2 Calcium hydroxide

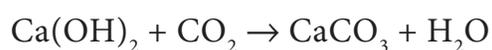
Preparation

Calcium hydroxide is prepared by adding water to quick lime, CaO .

Properties

It is a white powder. It is sparingly soluble in water. The aqueous solution is known as lime water and a suspension of slaked lime in water is known as milk of lime.

When carbon dioxide is passed through lime water, it turns milky due to the formation of calcium carbonate.

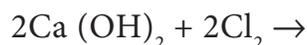


On passing excess of carbon dioxide, the precipitate dissolves to form calcium hydrogen carbonate.



Milk of lime reacts with chlorine

to form hypochlorite, a constituent of bleaching powder.



Uses:

Calcium hydroxide is used

- (i) in the preparation of mortar, a building material.
- ii) in white wash due to its disinfectant nature.
- (iii) in glass making, in tanning industry, in the preparation of bleaching powder and for the purification of sugar.

5.6.3 Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)

Gypsum beds were formed due to the evaporation of water from the massive prehistoric sea basins. When water evaporates, the minerals present in it become concentrated, and crystallise.



Figure 5.11 A Gypsum Quarry

Properties of Gypsum

- Gypsum is a soft mineral, which is moderately soluble in water. The solubility of this mineral in water is

affected by temperature. Unlike other salts, gypsum becomes less soluble in water as the temperature increases. This is known as retrograde solubility, which is a distinguishing characteristic of gypsum.

- Gypsum is usually white, colorless, or gray in color. But sometimes, it can also be found in the shades of pink, yellow, brown, and light green, mainly due to the presence of impurities.
- Gypsum crystals are sometimes found to occur in a form that resembles the petals of a flower. This type of formation is referred to as 'desert rose', as they mostly occur in arid areas or desert terrains.
- Gypsum is known to have low thermal conductivity, which is the reason why it is used in making drywalls or wallboards. Gypsum is also known as a natural insulator.

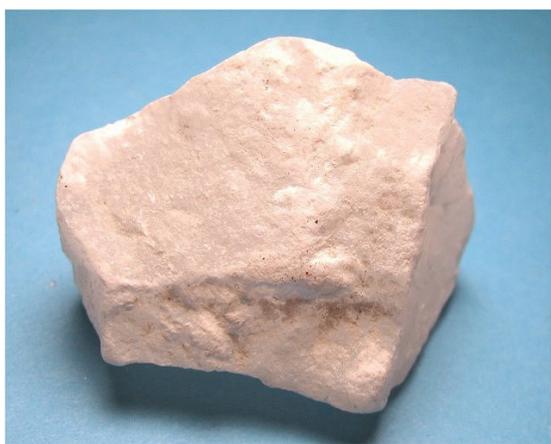


Figure 5.12 -The Alabaster Variety of Gypsum

- Gypsum has hardness between 1.5 to 2 on Moh's Hardness Scale. Its specific gravity is 2.3 to 2.4.
- ### Uses of Gypsum
- The alabaster variety of gypsum was used in ancient Egypt and Mesopotamia by the sculptors. The ancient Egyptians knew how to turn gypsum into plaster of Paris about 5,000 years ago. Today, gypsum has found a wide range of uses and applications in human society, some of which are enlisted below.
 - Gypsum is used in making drywalls or plaster boards. Plaster boards are used as the finish for walls and ceilings, and for partitions.
 - Another important use of gypsum is the production of plaster of Paris. Gypsum is heated to about 300 degree Fahrenheit to produce plaster of Paris, which is also known as gypsum plaster. It is mainly used as a sculpting material.
 - Gypsum is used in making surgical and orthopedic casts, such as surgical splints and casting moulds.
 - Gypsum plays an important role in agriculture as a soil additive, conditioner, and fertilizer. It helps loosen up compact or clay soil, and provides calcium and sulphur, which are essential for the healthy growth of a plant. It can also be used for removing sodium ion from soils having excess salinity.
- Alabaster is a variety of gypsum, that is highly valued as an ornamental stone. It has been used by the sculptors for centuries. Alabaster is granular and opaque.

- Gypsum is used in toothpastes, shampoos, and hair products, mainly due to its binding and thickening properties.
- Gypsum is a component of Portland cement, where it acts as a hardening retarder to control the speed at which concrete sets.
- To sum up, gypsum is one of the most abundant minerals that have endless uses and applications. Mining of gypsum is simple and easy, as the mineral occurs in large thick beds near the Earth's surface. However, large-scale mining of gypsum involves considerable damage to the environment. Gypsum can also be recycled, but not much importance has been given to recycle this mineral due to its abundance.

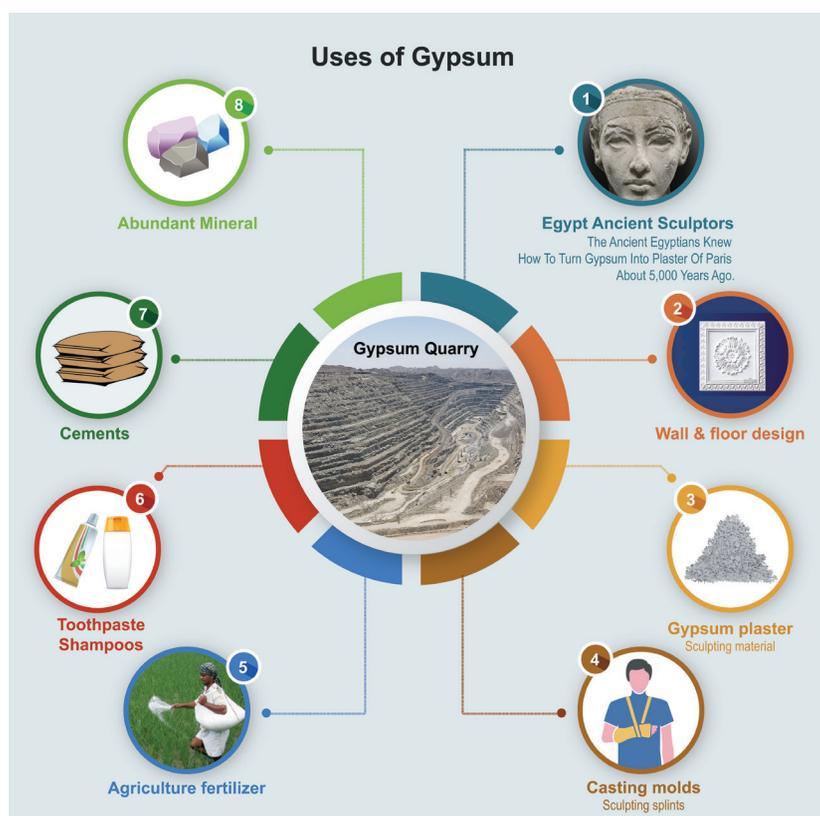


Figure 5.13 -Uses of Gypsum

5.6.4 Plaster of paris

Calcium Sulphate hemihydrate : $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ (Plaster of Paris)

It is a hemihydrate of calcium sulphate. It is obtained when gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is heated to 393 K.



Above 393 K, no water of crystallisation is left and anhydrous calcium sulphate, CaSO_4 is formed. This is known as 'dead burnt plaster'.



It has a remarkable property of setting with water. On mixing with an adequate quantity of water it forms a plastic mass that gets into a hard solid in 5 to 15 minutes.

Uses:

Plaster of Paris is used as/in,

1. The building industry as well as plasters.
2. For immobilising the affected part of organ where there is a bone fracture or sprain.
3. Employed in dentistry, in ornamental work and for making casts of statues and busts.



5.7 Biological importance of magnesium and calcium

Magnesium and calcium also plays a vital role in biological functions. A typical adult human body contains about 25 g of magnesium and 1200 g of calcium. Magnesium plays an important role in many biochemical reactions catalysed by enzymes. It is the co-factor of all enzymes that utilize ATP in phosphate transfer and energy release. It also essential for DNA synthesis and is responsible for the stability and proper functioning of DNA. It is also used for balancing electrolytes in our body. Deficiency of magnesium results into convulsion and neuromuscular irritation.

Calcium is a major component of bones and teeth. It is also present in in blood and its concentration is maintained by hormones (calcitonin and parathyroid hormone). Deficiency of calcium in blood causes it to take longer time to clot. It is also important for muscle contraction.

The main pigment that is responsible for photosynthesis, chlorophyll, contains magnesium which plays an important role in photosynthesis.

SUMMARY

The elements belonging to groups 1 and 2 of the modern periodic table are called s-block elements. They are called so because the valence electron occupies the s orbitals. The group 1 elements have a general outer electronic configuration ns^1 and are called alkali metals. The group 2 elements have a general outer electronic configuration ns^2 and these are called alkaline earth metals as they are found in earth's crust and their oxides and hydroxides are alkaline in nature. Elements belonging to group 1 and 2 are highly reactive and forms M^+ and M^{2+} cations respectively. Their physical and chemical properties of both groups show a regular trend as we move down the group. The atomic and ionic radii increase as we move down the group while their ionisation enthalpies decrease.

The first element in each of these groups, lithium in Group 1 and beryllium in Group 2 shows some difference in behaviour with the elements in rest of their groups and show similarities in properties to the second member of the next group. This behaviour is known as the 'diagonal relationship' in the periodic table.

The alkali metals are soft and silvery white in colour with low melting points. They are highly reactive. The compounds of alkali metals are predominantly ionic. They form metal hydrides and halides with hydrogen and halogens respectively. Their oxides and hydroxides are soluble in water forming

strong alkalies. Important compounds of sodium include sodium carbonate, sodium chloride, sodium hydroxide and sodium hydrogen carbonate. Sodium hydroxide is manufactured by Castner-Kellner process and sodium carbonate by Solvay process.

The chemistry of alkaline earth metals is similar to alkali metals. However, we observe some differences because of their reduced atomic and ionic sizes and increased cationic charges. Their oxides and hydroxides are less basic than the alkali metal oxides and hydroxides. They also form hydrides and halides with hydrogen and halogens respectively. Industrially important compounds of calcium include calcium oxide (lime), calcium hydroxide (slaked lime), calcium sulphate hemihydrate (Plaster of Paris), calcium carbonate (limestone) and cement. Portland cement is an important constructional material. It is manufactured by heating a pulverised mixture of limestone and clay in a rotary kiln. The clinker thus obtained is mixed with some gypsum (2-3%) to give a fine powder of cement. All these substances find variety of uses in different areas.

Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in large proportions in biological fluids. These ions perform important biological functions such as maintenance of ion balance and nerve impulse conduction.

EVALUATION



- For alkali metals, which one of the following trends is incorrect ?
 - Hydration energy : $\text{Li} > \text{Na} > \text{K} > \text{Rb}$
 - Ionisation energy : $\text{Li} > \text{Na} > \text{K} > \text{Rb}$
 - Density : $\text{Li} < \text{Na} < \text{K} < \text{Rb}$
 - Atomic size : $\text{Li} < \text{Na} < \text{K} < \text{Rb}$
- Which of the following statements is incorrect ?
 - Li^+ has minimum degree of hydration among alkali metal cations.
 - The oxidation state of K in KO_2 is +1
 - Sodium is used to make Na / Pb alloy
 - MgSO_4 is readily soluble in water
- Which of the following compounds will not evolve H_2 gas on reaction with alkali metals ?
 - ethanoic acid
 - ethanol
 - phenol
 - none of these
- Which of the following has the highest tendency to give the reaction
$$\text{M}^+(\text{g}) \xrightarrow[\text{Medium}]{\text{Aqueous}} \text{M}^+(\text{aq})$$
 - Na
 - Li
 - Rb
 - K
- sodium is stored in
 - alcohol
 - water
 - kerosene
 - none of these
- RbO_2 is
 - superoxide and paramagnetic
 - peroxide and diamagnetic
 - superoxide and diamagnetic
 - peroxide and paramagnetic

7. Find the wrong statement
- sodium metal is used in organic qualitative analysis
 - sodium carbonate is soluble in water and it is used in inorganic qualitative analysis
 - potassium carbonate can be prepared by solvay process
 - potassium bicarbonate is acidic salt
8. Lithium shows diagonal relationship with
- sodium
 - magnesium
 - calcium
 - aluminium
9. In case of alkali metal halides, the ionic character increases in the order
- $MF < MCl < MBr < MI$
 - $MI < MBr < MCl < MF$
 - $MI < MBr < MF < MCl$
 - none of these
10. In which process, fused sodium hydroxide is electrolysed for extraction of sodium ?
- Castner's process
 - Cyanide process
 - Down process
 - All of these
11. The product obtained as a result of a reaction of nitrogen with CaC_2 is (NEET - Phase I)
- $Ca(CN)_3$
 - CaN_2
 - $Ca(CN)_2$
 - Ca_3N_2
12. Which of the following has highest hydration energy
- $MgCl_2$
 - $CaCl_2$
 - $BaCl_2$
 - $SrCl_2$
13. Match the flame colours of the alkali and alkaline earth metal salts in the bunsen burner
- (p) Sodium (1) Brick red



- (q) Calcium (2) Yellow
(r) Barium (3) Lilac (violet)
(s) Strontium (4) Apple green
(t) Cesium (5) Crimson red
(u) Potassium (6) Blue

- a) p - 2, q - 1, r - 4, s - 5, t - 6, u - 3
b) p - 1, q - 2, r - 4, s - 5, t - 6, u - 3
c) p - 4, q - 1, r - 2, s - 3, t - 5, u - 6
d) p - 6, q - 5, r - 4, s - 3, t - 1, u - 2

14. Assertion : Generally alkali and alkaline earth metals form superoxides

Reason : There is a single bond between O and O in superoxides.

- a) both assertion and reason are true and reason is the correct explanation of assertion
b) both assertion and reason are true but reason is not the correct explanation of assertion
c) assertion is true but reason is false
d) both assertion and reason are false

15. Assertion : BeSO_4 is soluble in water while BaSO_4 is not

Reason : Hydration energy decreases down the group from Be to Ba and lattice energy remains almost constant.

- a) both assertion and reason are true and reason is the correct explanation of assertion
b) both assertion and reason are true but reason is not the correct explanation of assertion
c) assertion is true but reason is false
d) both assertion and reason are false





16. Which is the correct sequence of solubility of carbonates of alkaline earth metals ?
- $\text{BaCO}_3 > \text{SrCO}_3 > \text{CaCO}_3 > \text{MgCO}_3$
 - $\text{MgCO}_3 > \text{CaCO}_3 > \text{SrCO}_3 > \text{BaCO}_3$
 - $\text{CaCO}_3 > \text{BaCO}_3 > \text{SrCO}_3 > \text{MgCO}_3$
 - $\text{BaCO}_3 > \text{CaCO}_3 > \text{SrCO}_3 > \text{MgCO}_3$
17. In context with beryllium, which one of the following statements is incorrect ?
(NEET Phase - 2)
- It is rendered passive by nitric acid
 - It forms Be_2C
 - Its salts are rarely hydrolysed
 - Its hydride is electron deficient and polymeric
18. The suspension of slaked lime in water is known as (NEET Phase - II)
- lime water
 - quick lime
 - milk of lime
 - aqueous solution of slaked lime
19. A colourless solid substance (A) on heating evolved CO_2 and also gave a white residue, soluble in water. Residue also gave CO_2 when treated with dilute HCl.
- Na_2CO_3
 - NaHCO_3
 - CaCO_3
 - $\text{Ca}(\text{HCO}_3)_2$
20. The compound (X) on heating gives a colourless gas and a residue that is dissolved in water to obtain (B). Excess of CO_2 is bubbled through aqueous solution of B, C is formed. Solid (C) on heating gives back X. (B) is
- CaCO_3
 - $\text{Ca}(\text{OH})_2$
 - Na_2CO_3
 - NaHCO_3
21. Which of the following statement is false ? (NEET - Phase - I)
- Ca^{2+} ions are not important in maintaining the regular beating of the heart
 - Mg^{2+} ions are important in the green parts of the plants
 - Mg^{2+} ions form a complex with ATP
 - Ca^{2+} ions are important in blood clotting



22. The name 'Blue John' is given to which of the following compounds ?
- a) CaH_2 b) CaF_2 c) $\text{Ca}_3(\text{PO}_4)_2$ d) CaO
23. Formula of Gypsum is
- a) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ b) $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$
c) $3 \text{CaSO}_4 \cdot \text{H}_2\text{O}$ d) $2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
24. When CaC_2 is heated in atmospheric nitrogen in an electric furnace the compound formed is
- a) $\text{Ca}(\text{CN})_2$ b) CaNCN
c) CaC_2N_2 d) CaNC_2
25. Among the following the least thermally stable is
- (a) K_2CO_3 b) Na_2CO_3
(c) BaCO_3 d) Li_2CO_3

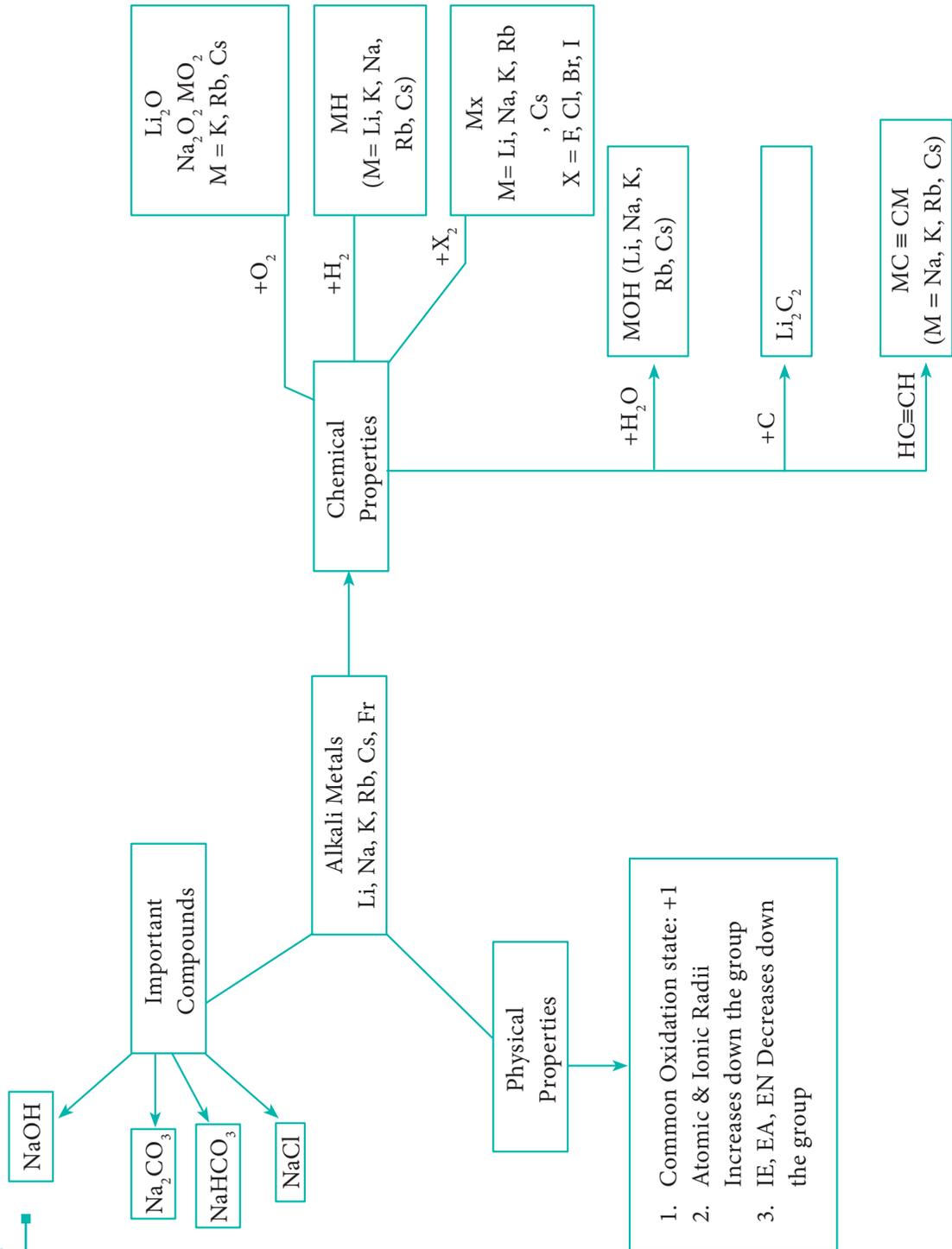
II. Write brief answer to the following questions:

26. Why sodium hydroxide is much more water soluble than sodium chloride?
27. Write the chemical equations for the reactions involved in solvay process of preparation of sodium carbonate.
28. An alkali metal (x) forms a hydrated sulphate, $\text{X}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Is the metal more likely to be sodium (or) potassium.
29. Write balanced chemical equation for each of the following chemical reactions.
- Lithium metal with nitrogen gas
 - heating solid sodium bicarbonate
 - Rubidium with oxygen gas
 - solid potassium hydroxide with CO_2
 - heating calcium carbonate
 - heating calcium with oxygen



30. Discuss briefly the similarities between beryllium and aluminium.
31. Give the systematic names for the following
 - (i) milk of magnesia
 - (ii) lye
 - (iii) lime
 - (iv) Caustic potash
 - (v) washing soda
 - (vi) soda ash
 - (v) trona
32. Substantiate Lithium fluoride has the lowest solubility among group one metal fluorides.
33. Mention the uses of plaster of paris
34. Beryllium halides are covalent whereas magnesium halides are ionic why?
35. Alkaline earth metal (A), belongs to 3rd period reacts with oxygen and nitrogen to form compound (B) and (C) respectively. It undergoes metal displacement reaction with AgNO_3 solution to form compound (D). Identify A,B.C and D.
36. Write balanced chemical equation for the following processes
 - (a) heating calcium in oxygen
 - (b) heating calcium carbonate
 - (c) evaporating a solution of calcium hydrogen carbonate
 - (d) heating calcium oxide with carbon
37. Explain the important common features of Group 2 elements.
38. Discuss the similarities between beryllium and aluminium.
39. Why alkaline earth metals are harder than alkali metals.
40. How is plaster of paris prepared?
41. Give the uses of gypsum.
42. Describe briefly the biological importance of Calcium and magnesium.
43. Which would you expect to have a higher melting point, magnesium oxide or magnesium fluoride? Explain your reasoning.

CONCEPT MAP





ICT Corner

Flame test of alkali and alkaline earth elements (Virtual Lab)

By using this virtual lab you can perform the flame test of different alkali and alkali earth metals and see the colour of the flame produced.

Please go to the URL
https://www.newpathonline.com/free-curriculumresources/virtual_lab/Flame_Test/9/12,13,14/1914
(or)
Scan the QR code on the right side



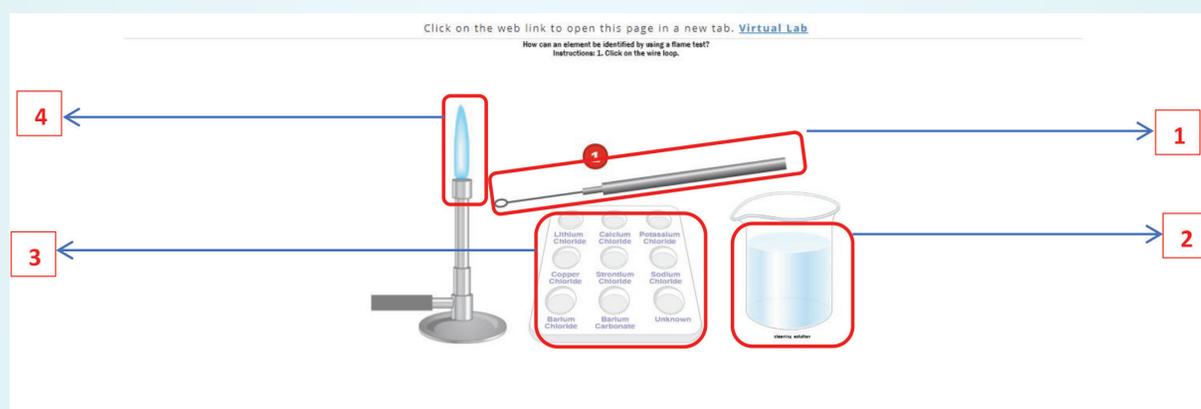
Step - 1

Open the Browser and type the URL given (or) Scan the QR Code. Just click the view button on the Flame test panel. This will open a flame test window as shown in the figure.

Step - 2

Follow the instructions to perform a virtual flame test.

1. Click on the wire loop (1).
2. Move the wire loop to the cleaning solution (2). Click on the cleaning solution. The wire must be cleaned before each test to ensure there is no other salt on the loop.
3. Move the wire loop to the salt solution you want to test (3). Click on the salt solution.
4. Move the wire loop to the flame (4) and click on it.
5. You will see the characteristic colour change in the flame with respect to the metal ion

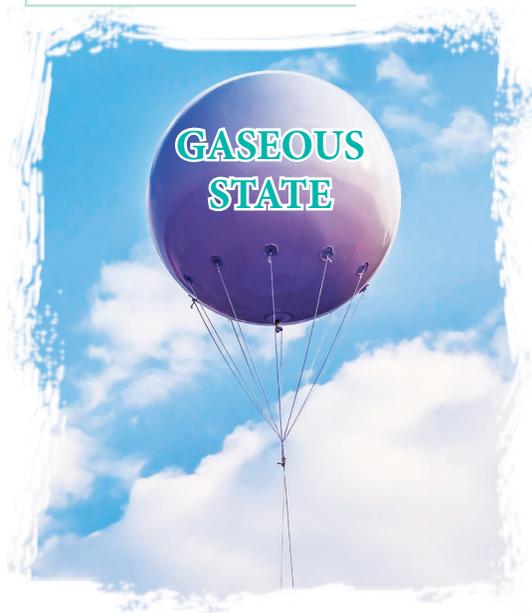




GASEOUS STATE

So many properties of properties of matter, especially when in gaseous form, can be deduced from hypothesis that their minute parts are in rapid motion, the velocity increasing with temperature, that the precise nature of this motion becomes a subject of rational curiosity.

James Clerk Maxwell



Jacques Charles
(1746-1823)

Learning Objectives

After studying this unit, students will be able to

- State the laws governing an ideal gas
- Demonstrate gas laws in various real life situations
- Derive ideal gas equation and perform calculations using it.
- State the deviations from ideal behavior
- Derive van der Waals equation.
- Define Graham's law of diffusion
- Define compressibility factor
- Explain critical phenomena
- Derive critical constants in terms of van der Waal's constants
- Explain Andrew's isotherms of carbon dioxide
- Describe Joule – Thomson effect and liquefaction of gases.



6.1. Introduction

We can survive for weeks without food, days without water, but only minutes without air. Thus, we inhale a lungful of air every few seconds, keep some of the molecules for our own end, and some of the molecules that our body no longer needs, and exhale the mixture back into the surrounding air. The air around us is in the gaseous state, which is the simplest of the states of matter. Although the chemical behaviour of gases depends on their composition, all the gases have remarkably similar physical behaviour.

DO YOU KNOW? Do you know the difference between gas and vapour?

Gas is a substance that is normally in a gaseous state at room temperature and 1 atm pressure, while vapour is the gaseous form of any substance that is a liquid or solid at room temperature and 1 atm pressure.

Earth is surrounded by an atmosphere of air whose composition in volume percentage is roughly 78 % nitrogen, 21 % oxygen and 1 % other gases. Of the known elements, only eleven are gases under normal atmospheric conditions. The elements hydrogen (H_2), nitrogen (N_2), oxygen (O_2), fluorine (F_2) and chlorine (Cl_2) exist as gaseous diatomic molecules. Another form of oxygen, namely, ozone (O_3) is also a gas at room temperature. The noble gases, namely, helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn) of 18th group are monatomic gases. Compounds such as carbon monoxide

(CO), carbon dioxide (CO_2), nitrogen dioxide (NO_2) and nitric oxide (NO) also exist in gaseous state under normal atmospheric conditions. In this unit you will learn the properties of gases and other related phenomena.

6.2. The Gas Laws

The gas laws have played a major role in the development of chemistry. The physical properties of all gases are governed by the gas laws that were formulated based on the studies of the properties like pressure, volume, etc., as a function of temperature. Before studying the gas laws in detail, let us understand an important parameter, namely, the pressure.

Pressure is defined as force divided by the area to which the force is applied. The SI unit of pressure is pascal which is defined as 1 Newton per square meter (Nm^{-2}). There are other units that are commonly used and their relation with the SI unit is as follows.

$$\text{Pressure} = \frac{\text{Force (N or kg m s}^{-2}\text{)}}{\text{Area (m}^2\text{)}}$$

Table 6.1 Units of pressure

Unit	Symbol	Value (Nm^{-2} or $kgm^{-1}s^{-2}$)
pascal	Pa	1 Pa = $1 Nm^{-2}$
atmosphere	atm	1 atm = 101325 Pa
millimeter of mercury	mmHg	1 mmHg = 133.322 Pa
bar	bar	1 bar = 10^5 Pa
torr	Torr	1 Torr = 133.322 Pa
pound per square inch	psi	1 psi = 6894.76 pa

6.2.1 Boyle's Law: Pressure-Volume Relationship

Robert Boyle performed a series of experiments to study the relation between the pressure and volume of gases. The schematic of the apparatus used by him is shown in figure 6.1.

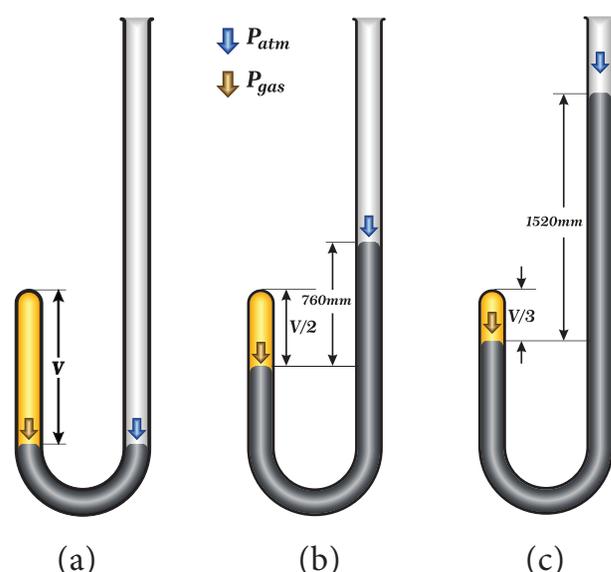


Figure 6.1 Boyle's law experiment

Mercury was added through the open end of the apparatus such that the mercury level on both ends are equal as shown in the figure 6.1(a). Add more amount of mercury until the volume of the trapped air is reduced to half of its original volume as shown in figure 6.1(b). The pressure exerted on the gas by the addition of excess mercury is given by the difference in mercury levels of the tube. Initially the pressure exerted by the gas is equal to 1 atm as the difference in height of the mercury levels is zero. When the volume is reduced to half, the difference in mercury levels increases to 760 mm. Now the pressure exerted by the gas is equal to 2 atm. It led him to conclude that at a given temperature the volume occupied by a fixed mass of a gas is inversely proportional to its pressure.

Mathematically, the Boyle's law can be written as

$$V \propto \frac{1}{P} \text{ ----- (6.1)}$$

(T and n are fixed, T-temperature, n- number of moles)

$$V = k \times \frac{1}{P} \text{ ----- (6.2)}$$

k – proportionality constant

When we rearrange equation 6.2.

$$PV = k \text{ ----- (6.2a)(at constant temperature and mass)}$$

Boyle's law is applicable to all gases regardless of their chemical identity (provided the pressure is low). Therefore, for a given mass of a gas under two different sets of conditions at constant temperature we can write

$$P_1 V_1 = P_2 V_2 = k \text{ ----- (6.3)}$$

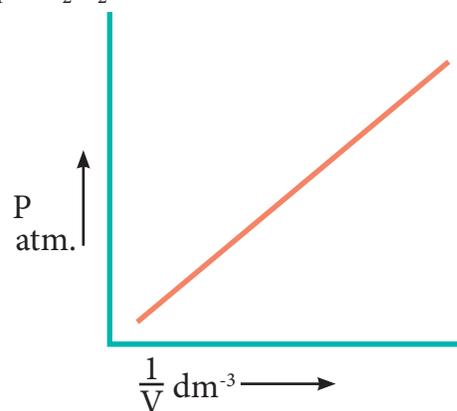


Figure. 6.2 a Graphical representation of Boyle's law (equation 6.2)

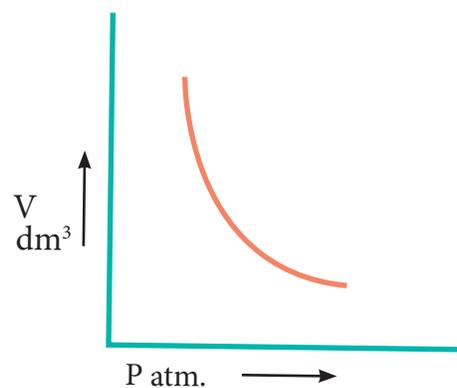


Figure. 6.2 b Graphical representation of Boyle's law (equation 6.2 a)

The PV relationship can be understood as follows. The pressure is due to the force of the gas particles on the walls of the container. If a given amount of gas is compressed to half of its volume, the density is doubled and the number of particles hitting the unit area of the container will be doubled. Hence, the pressure would increase twofold.

Consequence of Boyle's law

The pressure-density relationship can be derived from the Boyle's law as shown below.

$$P_1 V_1 = P_2 V_2 \quad (\text{Boyle's law})$$

$$P_1 \frac{m}{d_1} = P_2 \frac{m}{d_2}$$

where "m" is the mass, d_1 and d_2 are the densities of gases at pressure P_1 and P_2 .

$$\frac{P_1}{d_1} = \frac{P_2}{d_2} \quad \text{----- (6.4)}$$

In other words, the density of a gas is directly proportional to pressure.

All the passenger aeroplane cabins have to be artificially pressurised. do you know why?

Most commercial aeroplanes fly at about 30,000 feet altitude. The pressure decreases with the increase in altitude as there are fewer molecules per unit volume of air. Hence, while at air, the pressure around the aeroplane will be so low that one could pass out for lack

of oxygen. For this reason aeroplanes cabins are artificially pressurized.



Similarly, the effect of drop in pressure is felt as a little pain in the ears by a person while ascending a mountain in a plain. Though the external pressure drops, the internal pressure within the ear cavities remains the same. This creates an imbalance. The greater internal pressure forces the eardrum to bulge outward causing pain. The excess air within the ear cavities escapes after some time and with the help of yawning and thereby equalizing the internal and external pressure to relieve the pain.

Underwater divers are advised not to hold the breath unnecessarily while diving. Do you know why?

In figure (6.3) let us find the missing parameters (volume in 6.3 (b) and pressure in 6.3(c))

Fig. 6.3(a) Fig. 6.3 (b) Fig. 6.3(c)

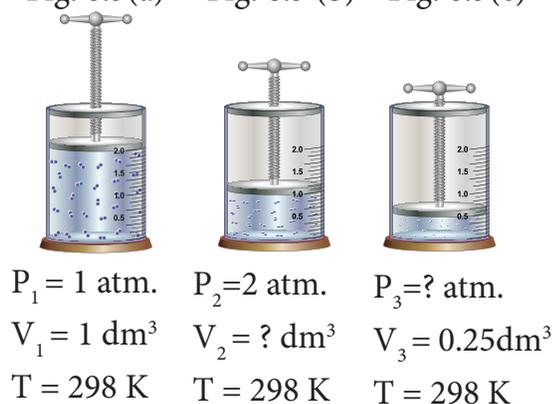


Figure. 6.3 Effect of pressure on volume of the gas to verify Boyle's law

Solution:

According to Boyle's law, at constant temperature for a given mass of gas at constant temperature,

$$P_1 V_1 = P_2 V_2 = P_3 V_3$$

$$1 \text{ atm} \times 1 \text{ dm}^3 = 2 \text{ atm} \times V_2 = P_3 \times 0.25 \text{ dm}^3$$

$$\therefore 2 \text{ atm} \times V_2 = 1 \text{ atm} \times 1 \text{ dm}^3$$

$$V_2 = \frac{1 \text{ atm} \times 1 \text{ dm}^3}{2 \text{ atm}}$$

$$V_2 = 0.5 \text{ dm}^3$$

$$\text{and } P_3 \times 0.25 \text{ dm}^3 = 1 \text{ atm} \times 1 \text{ dm}^3$$

$$P_3 = \frac{1 \text{ atm} \times 1 \text{ dm}^3}{0.25 \text{ dm}^3}$$

$$P_3 = 4 \text{ atm}$$

Evaluate Yourself



1. Freon-12, the compound widely used in the refrigerator system as coolant causes depletion of ozone layer. Now it has been replaced by eco-friendly compounds. Consider 1.5 dm^3 sample of gaseous Freon at a pressure of 0.3 atm . If the pressure is changed to 1.2 atm . at a constant temperature, what will be the volume of the gas increased or decreased?
2. Inside a certain automobile engine, the volume of air in a cylinder is 0.375 dm^3 , when the pressure is 1.05 atm . When the gas is compressed to a volume of 0.125 dm^3 at the same temperature, what is the pressure of the compressed air?

6.2.2 Charles Law (Volume-temperature relationship)

The relationship between volume of a gas and its temperature was examined by J. A. C. Charles. He observed that for a fixed mass of a gas at constant pressure, the volume is directly proportional to its temperature (K). Mathematically it can be represented as (at constant P and n)

$$V = kT \text{ ----- (6.5)}$$

$$\text{or } \frac{V}{T} = \text{Constant}$$

If the temperature of the gas increases, the volume also increases in direct proportion, so that $\frac{V}{T}$ is a constant. For the same system at constant pressure, one can write

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \text{Constant} \text{ ----- (6.6)}$$

For example, if a balloon is moved from an ice cold water bath to a boiling water bath, the temperature of the gas increases. As a result, the gas molecules inside the balloon move faster and gas expands. Hence, the volume increases.

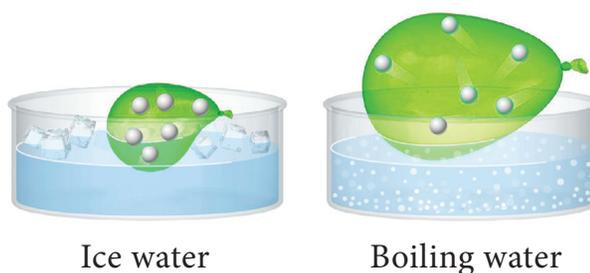


Figure. 6.4 Air filled balloon in ice cold and hot water

Variation of volume with temperature at constant pressure

The plot of the volume of the gas against its temperature at a given pressure

is shown in the figure 6.5. From the graph it is clear that the volume of the gas linearly increases with temperature at a given pressure. Such lines are called isobars. It can be expressed by the following straight line equation.

$V = mT + C$ where T is the temperature in degree Celsius and m & C are constants.

When $T = 0^\circ\text{C}$ the volume becomes V_0 . Hence, $V_0 = C$ and slope of the straight line m is equal to $\Delta V / \Delta T$. Therefore the above equation can be written in the following form.

$$V = \left(\frac{\Delta V}{\Delta T}\right)T + V_0 \quad \text{----- (6.7)}$$

(n, P are constant)

Divide the equation 6.7 by V_0

$$\frac{V}{V_0} = \frac{1}{V_0} \left(\frac{\Delta V}{\Delta T}\right)T + 1 \quad \text{----- (6.8)}$$

Charles and Gay Lussac found that under constant pressure, the relative increase in volume per degree increase in temperature is same for all gases. The relative increase in volume per $^\circ\text{C}$ (α) is equal to $\frac{1}{V_0} \left(\frac{\Delta V}{\Delta T}\right)$.

Therefore

$$\frac{V}{V_0} = \alpha T + 1$$

$$V = V_0(\alpha T + 1) \quad \text{----- (6.9)}$$

Charles found that the coefficient of expansion is approximately equal to $1/273$. It means that at constant pressure for a given mass, for each degree rise in temperature, all gases expand by $1/273$ of their volume at 0°C

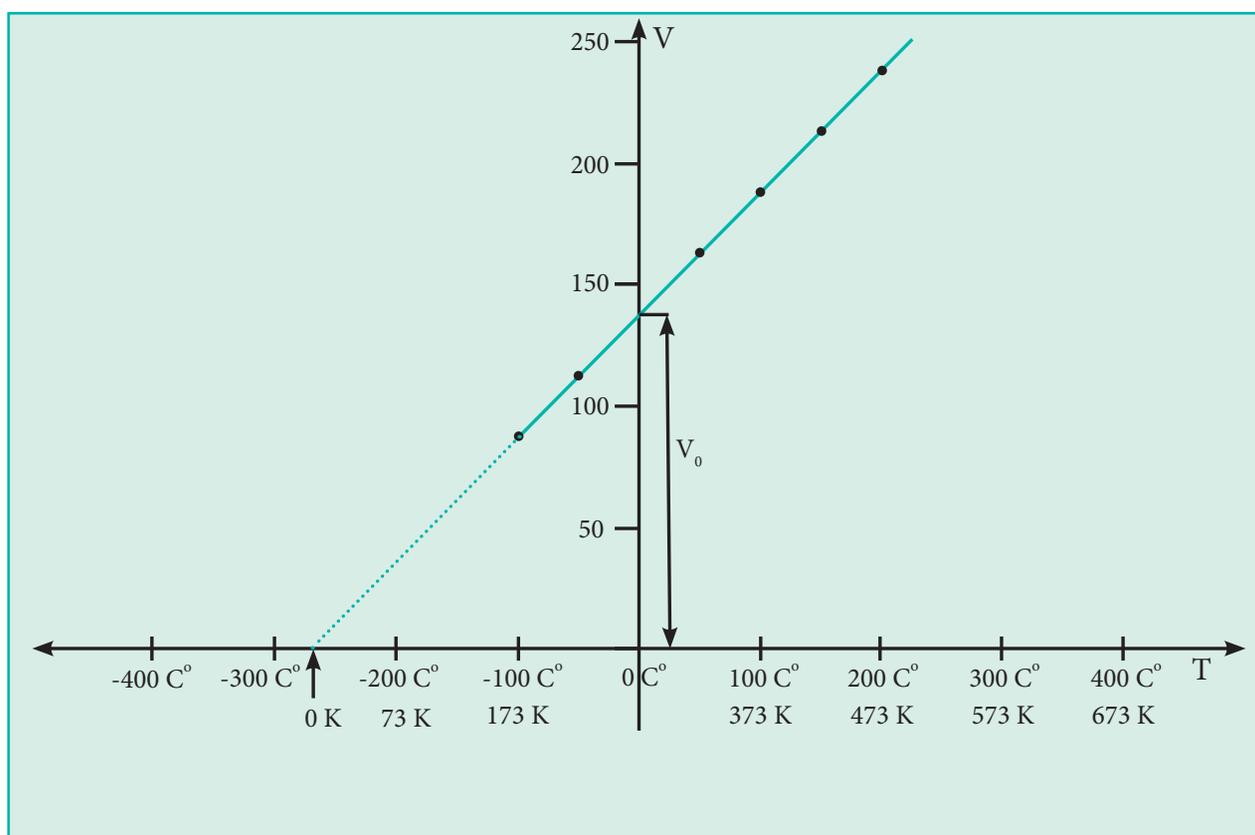


Figure. 6.5 Plot of volume vs temperature for an ideal gas

If we extrapolate the straight line in the figure 6.5 beyond the experimental measurements, the straight line intersects the temperature axis (x-axis) at -273°C . This shows that the volume of the gas becomes zero at -273°C , more precisely this temperature is -273.15°C . Beyond this temperature the gas would have a negative volume which is physically impossible. For this reason, this temperature was defined as absolute zero by Kelvin and he proposed a new temperature scale with absolute zero as starting point which is now called Kelvin scale. The only difference between the Kelvin scale of temperature and Celsius scale of temperature is that the zero position is shifted. The boiling and freezing point of water in both scales are given below.

	Kelvin Scale	Celsius scale
Absolute Zero	0 K	-273.15°C
Freezing point of water	273.15 K	0°C
Boiling point of water	373.15 K	100°C

Example:

In figure 6.6 let us find the missing parameters (volume in 6.6 (b) and temperature in 6.6(c))

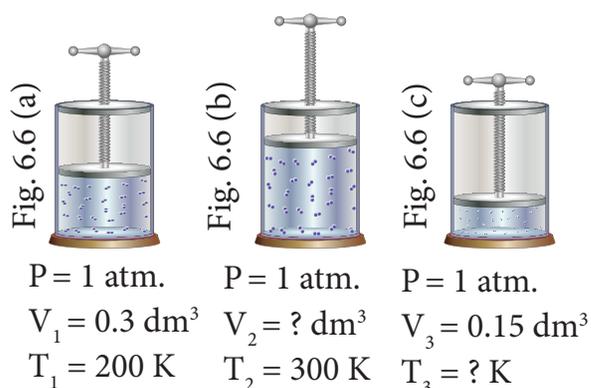


Fig. 6.6. Effect of temperature on volume of the gas to verify Charles law

Solution:

According to Charles law,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3}$$

$$\frac{0.3 \text{ dm}^3}{200 \text{ K}} = \frac{V_2}{300 \text{ K}} = \frac{0.15 \text{ dm}^3}{T_3}$$

$$\frac{V_2}{300 \text{ K}} = \frac{0.3 \text{ dm}^3}{200 \text{ K}}$$

$$V_2 = \frac{1.5}{\cancel{300 \text{ K}}} \times 0.3 \text{ dm}^3$$

$$V_2 = \frac{0.45 \text{ dm}^3}{\cancel{200 \text{ K}}}$$

$$V_2 = 0.45 \text{ dm}^3 \quad \text{and}$$

$$\frac{0.15 \text{ dm}^3}{T_3} = \frac{0.3 \text{ dm}^3}{200 \text{ K}}$$

$$T_3 = \frac{0.5}{\cancel{0.15 \text{ dm}^3}} \times 200 \text{ K}$$

$$T_3 = \frac{100 \text{ K}}{\cancel{0.3 \text{ dm}^3}}$$

$$T_3 = 100 \text{ K}$$

Evaluate Yourself



3. A sample of gas has a volume of 3.8 dm^3 at an unknown temperature. When the sample is submerged in ice water at 0°C , its volume gets reduced to 2.27 dm^3 . What is its initial temperature?

6.2.3 Gay-Lussac's Law (Pressure-temperature relationship)

Joseph Gay-Lussac stated that, at constant volume the pressure of a fixed mass of a gas is directly proportional to temperature.

$$P \propto T$$

$$\text{or } \frac{P}{T} = \text{Constant } k$$

If P_1 and P_2 are the pressures at temperatures T_1 and T_2 , respectively, then from Gay Lussac's law

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Activity -1

The table below contains the values of pressure measured at different temperatures for 1 mole of an ideal gas. Plot the values in a graph and verify the Gay Lussac's law. [Lines in the pressure vs temperature graph are known as isochores (constant volume) of a gas.]

Temperature (in deg celcius)	32	69	94	130	154	191
Pressure in 50 L container (atm)	0.51	0.56	0.6	0.66	0.7	0.76
Pressure in 75 L container (atm)	0.34	0.37	0.40	0.44	0.47	0.51

6.2.4 Avogadro's Hypothesis

Avogadro hypothesised that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules. The mathematical form of Avogadro's hypothesis may be expressed as

$$V \propto n,$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} = \text{constant} \text{ ----- (6.10)}$$

where V_1 & n_1 are the volume and number

of moles of a gas and V_2 & n_2 are a different set of values of volume and number of moles of the same gas at same temperature and pressure.

Evaluate Yourself

- An athlete in a kinesiology research study has his lung volume of 7.05 dm³ during a deep inhalation. At this volume the lungs contain 0.312 mole of air. During exhalation the volume of his lung decreases to 2.35 dm³. How many moles of air does the athlete exhale during exhalation? (assume pressure and temperature remain constant)

6.3. Ideal gas equation

The gaseous state is described completely using the following four variables T , P , V and n and their relationships were governed by the gas laws studied so far.

$$\text{Boyle's law } V \propto \frac{1}{P}$$

$$\text{Charles law } V \propto T$$

$$\text{Avogadro's law } V \propto n$$

We can combine these equations into the following general equation that describes the physical behaviour of all gases.

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

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

where, R is the proportionality

constant called universal gas constant.

The above equation can be rearranged to give the ideal gas equation

$$PV = nRT. \text{ ----- (6.11)}$$

We already know that pressure is expressed in many different units (Table 6.1) hence it is important to know the values of gas constant R in different units as well.

We can calculate R using the equation,

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

For Conditions in which P is 1 atm., volume 22.414 dm³. for 1 mole at 273.15 K.

$$\begin{aligned} R &= \frac{1 \text{ atm.} \times 22.414 \text{ dm}^3}{1 \text{ mol.} \times 273.15 \text{ K}} \\ &= \mathbf{0.0821 \text{ dm}^3 \text{ atm. mol}^{-1} \text{ K}^{-1}} \end{aligned}$$

Under standard conditions (STP) Where P = 1 bar (10⁵ pascal), V= 22.71 × 10⁻³ m³ for 1 mole of a gas at 273.15 K

$$\begin{aligned} R &= \frac{10^5 \text{ Pa} \times 22.71 \times 10^{-3} \text{ m}^3}{1 \text{ mol.} \times 273.15 \text{ K}} \\ &= \mathbf{8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}} \\ &= \mathbf{8.314 \times 10^{-5} \text{ bar m}^3 \text{ K}^{-1} \text{ mol}^{-1}} \\ &= \mathbf{8.314 \times 10^{-2} \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}} \\ &= \mathbf{8.314 \times 10^{-2} \text{ bar L K}^{-1} \text{ mol}^{-1}} \\ &= \mathbf{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

The ideal gas equation is a relationship between four variables (P, V,

T, n). Since it describes the state of any gas, it is referred to as the equation of state of gases.

Let us calculate the pressure exerted by 2 moles of sulphur hexafluoride in a steel vessel of volume 6 dm³ at 70 °C assuming it is an ideal gas.

We will use the ideal gas equation for this calculation as below:

$$\begin{aligned} P &= \frac{nRT}{V} = \frac{2 \text{ mol} \times 0.0821 \text{ L atm. K}^{-1} \cdot \text{mol}^{-1} \times (70 + 273 \text{ K})}{6 \text{ dm}^3} \\ &= 9.39 \text{ atm.} \end{aligned}$$

Evaluate Yourself



5. A small bubble rises from the bottom of a lake where the temperature and pressure are 8° C and 6.4 atm. to the water surface, where the temperature is 25°C and pressure is 1 atm. Calculate the final volume in (mL) of the bubble, if its initial volume is 2.1 mL.

6.4 Mixture of gases - Dalton's law of partial pressures

Studies of non-reacting gaseous mixtures showed that in a gaseous mixture each component behaves independently. For a gaseous mixture, it is important to know, how the pressure of individual component contributes to the total pressure of the mixture.

John Dalton stated that "the total

pressure of a mixture of non-reacting gases is the sum of partial pressures of the gases present in the mixture" where the partial pressure of a component gas is the pressure that it would exert if it were present alone in the same volume and temperature. This is known as *Dalton's law of partial pressures*.

i.e., for a mixture containing three gases 1, 2 and 3 with partial pressures p_1 , p_2 and p_3 in a container with volume V , the total pressure P_{total} will be give by

$$P_{\text{total}} = p_1 + p_2 + p_3 \text{----- (6.12)}$$

Assuming that the gases behave ideally,

$$p_1 = n_1 \frac{RT}{V}; p_2 = n_2 \frac{RT}{V}; p_3 = n_3 \frac{RT}{V}$$

$$P_{\text{Total}} = n_1 \frac{RT}{V} + n_2 \frac{RT}{V} + n_3 \frac{RT}{V}$$

$$= (n_1 + n_2 + n_3) \frac{RT}{V}$$

$$P_{\text{Total}} = n_{\text{Total}} \left(\frac{RT}{V} \right) \text{----- (6.13)}$$

The partial pressure can also be expressed as

$$\left(\frac{RT}{V} \right) \text{ can be expressed as } \frac{p_1}{n_1} \text{ or } \frac{p_2}{n_2} \text{ or } \frac{p_3}{n_3}$$

$$\text{or in general } \frac{p_i}{n_i}$$

Therefore

$$P_{\text{Total}} = n_{\text{Total}} \frac{p_i}{n_i} = \frac{n_{\text{Total}}}{n_i} p_i$$

$$\Rightarrow p_i = \frac{n_i}{n_{\text{Total}}} P_{\text{Total}} = x_i P_{\text{Total}} \text{----- (6.14)}$$

where x_i is the mole fraction of the i^{th} component.

Application of Dalton's law

In a reaction involving the collection of gas by downward displacement of water, the pressure of dry vapor collected can be calculated using Dalton's law.

$$P_{\text{dry gas collected}} = P_{\text{total}} - p_{\text{water vapour}}$$

$p_{\text{water vapour}}$ is generally referred as aqueous tension and its values are available for air at various temperatures.

Let us understand Dalton's law by solving this problem. A mixture of gases contains 4.76 mole of Ne, 0.74 mole of Ar and 2.5 mole of Xe. Calculate the partial pressure of gases, if the total pressure is 2 atm. at a fixed temperature.

Solution:

$$P_{\text{Ne}} = x_{\text{Ne}} P_{\text{Total}}$$

$$x_{\text{Ne}} = \frac{n_{\text{Ne}}}{n_{\text{Ne}} + n_{\text{Ar}} + n_{\text{Xe}}}$$

$$= \frac{4.76}{4.76 + 0.74 + 2.5} = 0.595$$

$$x_{\text{Ar}} = \frac{n_{\text{Ar}}}{n_{\text{Ne}} + n_{\text{Ar}} + n_{\text{Xe}}}$$

$$= \frac{0.74}{4.76 + 0.74 + 2.5} = 0.093$$

$$x_{\text{Xe}} = \frac{n_{\text{Xe}}}{n_{\text{Ne}} + n_{\text{Ar}} + n_{\text{Xe}}}$$

$$= \frac{2.5}{4.76 + 0.74 + 2.5} = 0.312$$

$$P_{\text{Ne}} = x_{\text{Ne}} P_{\text{Total}} = 0.595 \times 2$$

$$= 1.19 \text{ atm.}$$

$$P_{\text{Ar}} = x_{\text{Ar}} P_{\text{Total}} = 0.093 \times 2 = 0.186 \text{ atm.}$$

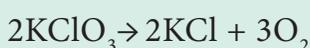
$$P_{\text{Xe}} = x_{\text{Xe}} P_{\text{Total}} = 0.312 \times 2 = 0.624 \text{ atm.}$$

Evaluate Yourself



6. (a) A mixture of He and O₂ were used in the 'air' tanks of underwater divers for deep dives. For a particular dive 12 dm³ of O₂ at 1 atm. and 46 dm³ of He, at 1 atm. were both pumped into a 5 dm³ tank. Calculate the partial pressure of each gas and the total pressure in the tank at 298 K

(b) A sample of solid KClO₃ (potassium chlorate) was heated in a test tube to obtain O₂ according to the reaction



The oxygen gas was collected by downward displacement of water at 295 K. The total pressure of the mixture is 772 mm of Hg. The vapour pressure of water is 26.7 mm of Hg at 300K. What is the partial pressure of the oxygen gas?

6.4.1 Graham's Law of Diffusion

Gases have a tendency to occupy all the available space. When two non-reactive gases are allowed to mix, the gas molecules migrate from region of higher concentration to a region of lower concentration. This property of gas which involves the movement of the gas molecules through another gases is called diffusion. Effusion is another process in which a gas escapes from a container

through a very small hole.

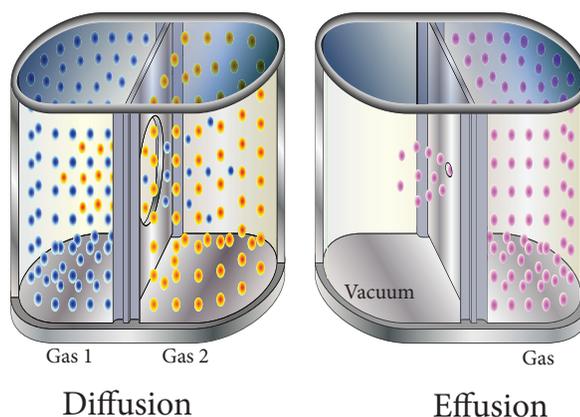


Figure. 6.7 Diffusion and effusion of gases

The rate of diffusion or effusion is inversely proportional to the square root of molar mass. This statement is called Graham's law of diffusion/effusion.

Mathematically, rate of diffusion $\propto \frac{1}{\sqrt{M}}$

Otherwise

$$\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}} \text{ ----- (6.15)}$$

When diffusing gases are at different pressures (P_A, P_B),

$$\frac{r_A}{r_B} = \frac{P_A}{P_B} \sqrt{\frac{M_B}{M_A}} \text{ ----- (6.16)}$$

where r_A and r_B are the rates of diffusion of A and B and the M_A and M_B are their respective molar masses.



Graham's Law forms the basis of the process of enriching the isotopes of U²³⁵ from other isotopes.

Example:

1. An unknown gas diffuses at a rate of 0.5 time that of nitrogen at the same

temperature and pressure. Calculate the molar mass of the unknown gas

Solution:

$$\frac{\text{rate}_{\text{unknown}}}{\text{rate N}_2} = \sqrt{\frac{M_{\text{N}_2}}{M_{\text{unknown}}}}$$

$$0.5 = \sqrt{\frac{28 \text{ g mol}^{-1}}{M_{\text{unknown}}}}$$

Squaring on both sides

$$(0.5)^2 = \frac{28 \text{ g mol}^{-1}}{M_{\text{unknown}}}$$

$$\Rightarrow M_{\text{unknown}} = \frac{28}{0.25} = 112 \text{ g mol}^{-1}$$

Evaluate Yourself



7. A flammable hydrocarbon gas of particular volume is found to diffuse through a small hole in 1.5 minutes. Under the same conditions of temperature and pressure an equal volume of bromine vapour takes 4.73 min to diffuse through the same hole. Calculate the molar mass of the unknown gas and suggest what this gas might be.

(Given that molar mass of bromine = 159.8 g/mole)

6.5 Deviation from ideal gas behaviour

The kinetic theory of gases (postulates of kinetic theory of gases are described in physics text book) which is the basis for the gas equation ($PV=nRT$),

assumes that the individual gas molecules occupy negligible volume when compared to the total volume of the gas and there is no attractive force between the gas molecules. Gases whose behaviour is consistent with these assumptions under all conditions are called ideal gases. But in practice both these assumptions are not valid under all conditions. For example, the fact that gases can be liquefied shows that the attractive force exists among molecules. Hence, there is no gas which behaves ideally under all conditions. The non-ideal gases are called real gases. The real gases tend to approach the ideal behaviour under certain conditions.

6.5.1 Compressibility factor Z

The deviation of real gases from ideal behaviour is measured in terms of a ratio of PV to nRT . This is termed as compressibility factor. Mathematically,

$$Z = \frac{PV}{nRT}$$

For ideal gases $PV = nRT$, hence the compressibility factor, $Z = 1$ at all temperatures and pressures. For these gases the plot of Z vs P should be a straight line parallel to the pressure axis. When a gas deviates from ideal behaviour, its Z value deviates from unity. For all gases, at very low pressures and very high temperature the compressibility factor approaches unity and they tend to behave ideally. The plot of the compressibility factor vs pressure for some common gases are shown in Figure 6.8.

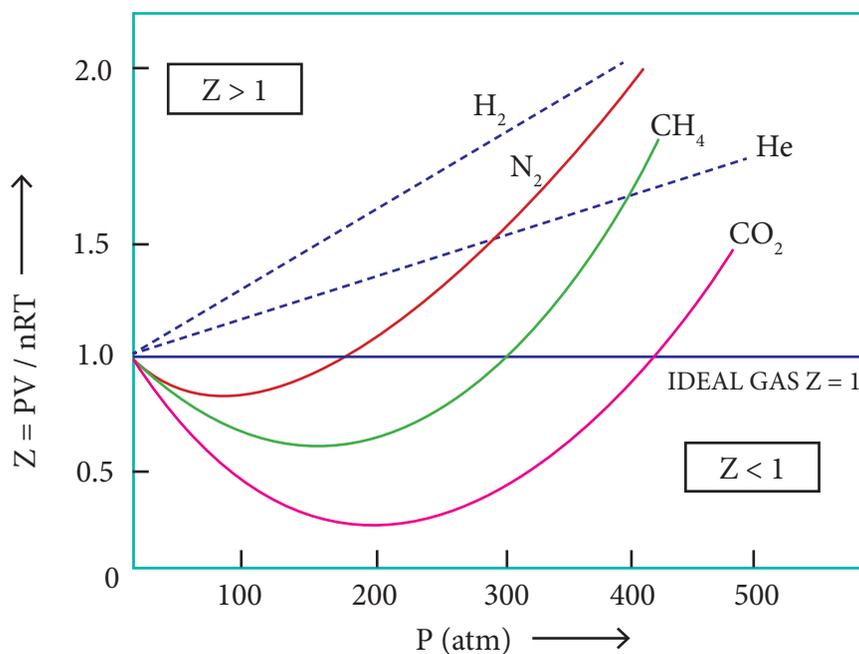


Figure. 6.8 Plot of compressibility factor(Z) vs pressure for some common gases

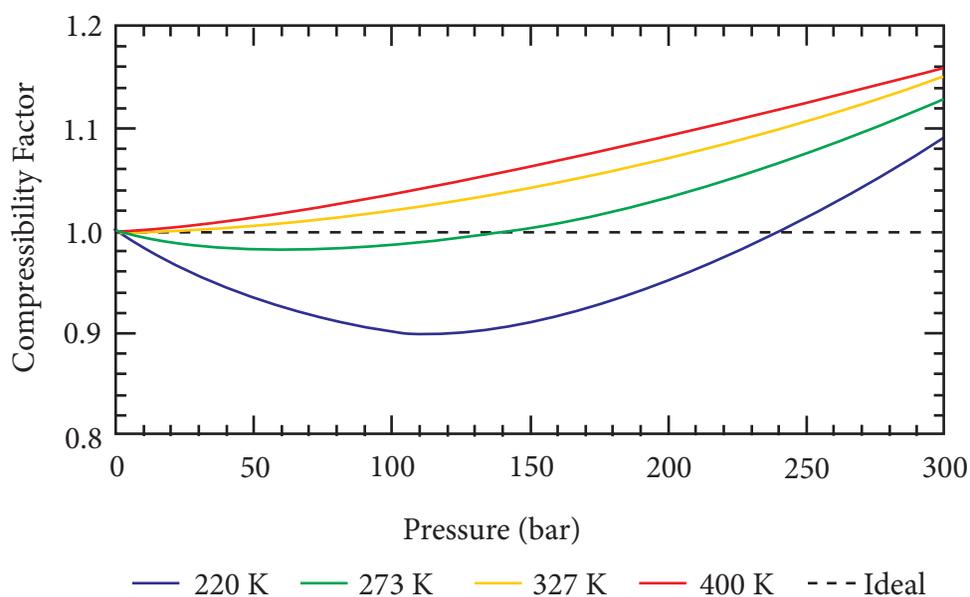


Figure. 6.9 Compressibility factor vs pressure at different temperatures for Nitrogen

When the pressure is low, the volume of the container is very large compared to the volume of the gas molecules so that individual volume of the gas molecules can be neglected. In addition, the molecules in a gas are far apart and attractive forces are negligible. As the pressure increases,

the density of gas also increases and the molecules are much closer to one another. Hence, the intermolecular force becomes significant enough to affect the motion of the molecules and the gas will not behave ideally.

At high temperatures the average kinetic energy of the molecules is very high and hence intermolecular attractions will become insignificant. As the temperature

decreases, the average kinetic energy of molecules also decreases, hence the molecular attraction is enhanced. The temperature at which a real gas obeys ideal gas law over an appreciable range of pressure is called Boyle temperature or Boyle point. The Boyle point varies with the nature of the gas. Above the Boyle point, for real gases, $Z > 1$, i.e., the real gases show positive deviation. Below the Boyle point, the real gases first show a decrease for Z , reaches a minimum and then increases with the increase in pressure. So, it is clear that at low pressure and at high temperature, the real gases behave as ideal gases.

6.5.2 Compressibility factor for real gases

The compressibility factor Z for real gases can be rewritten

$$Z = \frac{PV_{\text{real}}}{nRT} \quad \text{----- (6.17)}$$

$$V_{\text{ideal}} = \frac{nRT}{P} \quad \text{----- (6.18)}$$

Substituting 6.18 in 6.17

$$Z = \frac{V_{\text{real}}}{V_{\text{ideal}}} \quad \text{----- (6.19)}$$

Where V_{real} is the molar volume of the real gas and V_{ideal} is the molar volume of it when it behaves ideally.

6.5.3 Van der Waals Equation

J. D. Van der Waals made the first mathematical analysis of real gases. His

treatment provides us an interpretation of real gas behaviour at the molecular level. He modified the ideal gas equation $PV = nRT$ by introducing two correction factors, namely, pressure correction and volume correction.

Pressure Correction:

The pressure of a gas is directly proportional to the force created by the bombardment of molecules on the walls of the container. The speed of a molecule moving towards the wall of the container is reduced by the attractive forces exerted by its neighbours. Hence, the measured gas pressure is lower than the ideal pressure of the gas. Hence, van der Waals introduced a correction term to this effect.

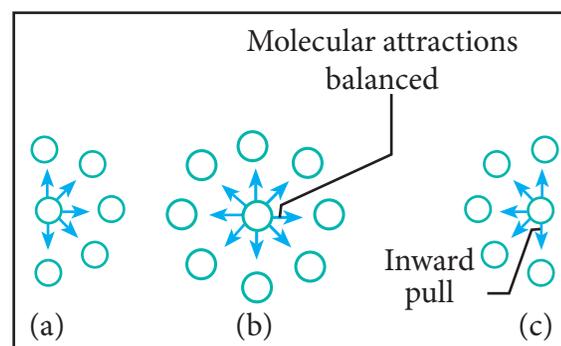


Figure. 6.10 Inter-molecular forces of attraction

Van der Waals found out the forces of attraction experienced by a molecule near the wall are directly proportional to the square of the density of the gas.

$$P' \propto \rho^2$$

$$\rho = \frac{n}{V}$$

where n is the number of moles of gas and V is the volume of the container

$$\Rightarrow P' \propto \frac{n^2}{V^2}$$

$$\Rightarrow P' = a \frac{n^2}{V^2}$$

where a is proportionality constant and depends on the nature of gas

Therefore,

$$P_{\text{ideal}} = P + \frac{an^2}{V^2} \text{ ----- (6.20)}$$

Volume Correction

As every individual molecule of a gas occupies a certain volume, the actual volume is less than the volume of the container, V . Van der Waals introduced a correction factor V' to this effect. Let us calculate the correction term by considering gas molecules as spheres.

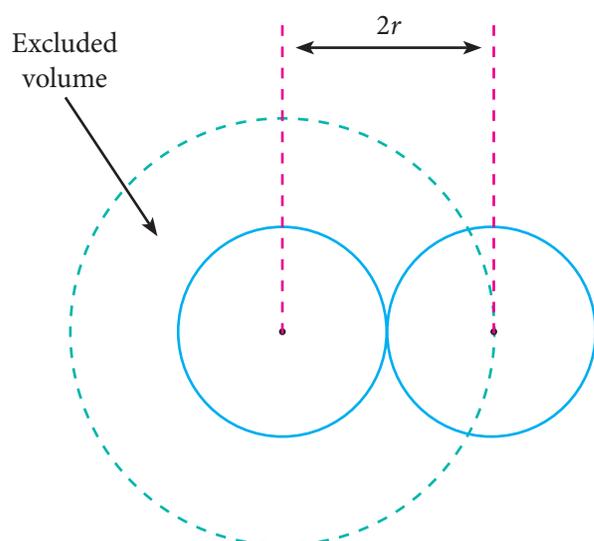


Figure. 6.11 Excluded volume

$V =$ excluded volume

Excluded volume for two molecules

$$= \frac{4}{3} \pi (2r)^3$$

$$= 8 \left(\frac{4}{3} \pi r^3 \right) = 8 V_m$$

where v_m is a volume of a single molecule

Excluded volume for single molecule

$$= \frac{8 V_m}{2} = 4 V_m$$

Excluded volume for n molecule

$$= n (4 V_m) = nb$$

Where b is van der waals constant

which is equal to $4 V_m$

$$\Rightarrow V' = nb$$

$$V_{\text{ideal}} = V - nb \text{ ----- (6.21)}$$

Replacing the corrected pressure and volume in the ideal gas equation $PV=nRT$ we get the van der Waals equation of state for real gases as below,

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT \text{ . ----(6.22)}$$

The constants a and b are van der Waals constants and their values vary with the nature of the gas. It is an approximate formula for the non-ideal gas.

6.6 Pressure-Volume isotherms of Carbon dioxide

Andrew's isotherm

Thomas Andrew gave the first complete data on pressure-volume-temperature of a substance in the gaseous and liquid states. He plotted isotherms of carbon dioxide at different temperatures which is shown in Figure. 6.12. From the plots we can infer the following.

At low temperature isotherms, for example, at 13° C as the pressure increases, the volume decreases along AB and is a gas until the point B is reached. At B, a liquid separates along the line BC, both the liquid and gas co-exist and the pressure remains constant. At C, the gas is completely converted into liquid. If the pressure is higher than at C, only the liquid is compressed so, there is no significant change in the volume. The successive isotherms shows similar trend with the shorter flat region. i.e. The volume range in which the liquid and gas coexist becomes shorter. At the temperature of 31.1 °C the length of the shorter portion is reduced to zero at point P. In other words, the CO₂ gas is liquefied completely at this point. This temperature is known as the liquefaction temperature or critical temperature of CO₂. At this point the pressure is 73 atm. Above this temperature CO₂ remains as a gas at all pressure values. It is then proved that many real gases behave in a similar manner to carbon dioxide.

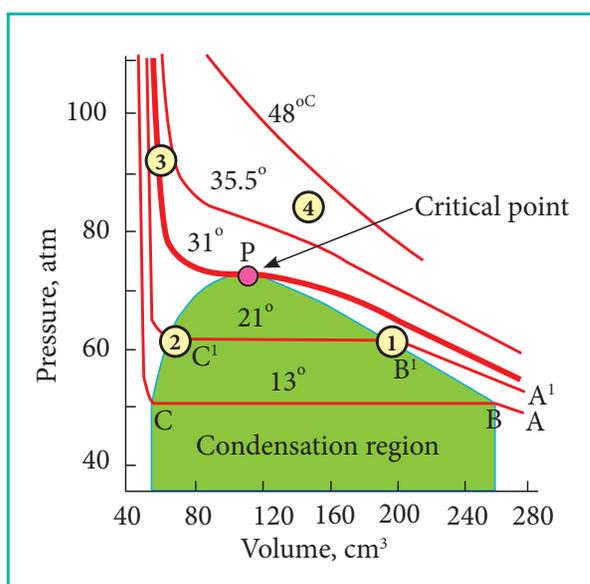


Figure. 6.12 Isotherms of Carbon dioxide at different temperatures

Though the nature of isotherm remains similar, the critical temperature, the corresponding pressure and volume are characteristics of a particular gas.

Now we can define the critical constants as follows. Critical temperature (T_c) of a gas is defined as the temperature above which it cannot be liquefied even at high pressure. Critical pressure (P_c) of a gas is defined as the minimum pressure required to liquefy 1 mole of a gas at its critical temperature. Critical volume (V_c) is defined as the volume occupied by 1 mole of a gas at its critical temperature and critical pressure. The critical constants of some common gases are given in Table 6.2

Table 6.2 Critical constants of some gases

Name of the Gas	Critical Temperature (T_c) in K	Critical Pressure (P_c) in atm	Critical Volume (V_c) cm ³ mol ⁻¹
Helium (He)	5.2	2.26	57.8
Carbon dioxide (CO ₂)	304.2	72.9	94.0
Oxygen (O ₂)	154.8	50.14	78.0
Nitrogen (N ₂)	126.3	33.54	90.1
Hydrogen (H ₂)	33.2	12.80	65
Water (H ₂ O)	647.4	218.3	55.3
Ammonia (NH ₃)	405.5	111.3	72.5
Hydrogen Chloride (HCl)	324.7	81.5	81.0
Methane (CH ₄)	190.6	45.6	98.7
Ethylene (C ₂ H ₄)	283.1	50.50	124

Evaluate Yourself



8. Critical temperature of H_2O , NH_3 , and CO_2 are 647.4, 405.5 and 304.2 K, respectively. When we start cooling from a temperature of 700 K which will liquefy first and which will liquefy finally?

6.6.1 Derivation of critical constants from van der Waals constant:

The van der Waals equation for n moles is

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad \text{----- (6.22)}$$

For 1 mole

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad \text{----- (6.23)}$$

From the equation we can derive the values of critical constants P_c , V_c and T_c in terms of a and b, the van der Waals constants, On expanding the above equation

$$PV + \frac{a}{V} - Pb - \frac{ab}{V^2} - RT = 0 \quad \text{----- (6.24)}$$

Multiply equation (6.24) by V^2 / P

$$\frac{V^2}{P} \left(PV + \frac{a}{V} - Pb - \frac{ab}{V^2} - RT\right) = 0$$
$$V^3 + \frac{aV}{P} - bV^2 - \frac{ab}{P} - \frac{RTV^2}{P} = 0 \quad \text{---- (6.25)}$$

When the above equation is rearranged in powers of V

$$V^3 - \left[\frac{RT}{P} + b\right]V^2 + \left[\frac{a}{P}\right]V - \left[\frac{ab}{P}\right] = 0 \quad \text{--- (6.26)}$$

The equation (6.26) is a cubic equation in V. On solving this equation,

we will get three solutions. At the critical point all these three solutions of V are equal to the critical volume V_c . The pressure and temperature becomes P_c and T_c respectively

$$\text{i.e., } V = V_c$$

$$V - V_c = 0$$

$$(V - V_c)^3 = 0$$

$$V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0 \quad \text{---- (6.27)}$$

As equation (6.26) is identical with equation (6.27), we can equate the coefficients of V^2 , V and constant terms in (6.26) and (6.27).

$$-3V_cV^2 = -\left[\frac{RT_c}{P_c} + b\right]V^2$$

$$3V_c = \frac{RT_c}{P_c} + b \quad \text{---- (6.28)}$$

$$3V_c^2 = \frac{a}{P_c} \quad \text{---- (6.29)}$$

$$V_c^3 = \frac{ab}{P_c} \quad \text{---- (6.30)}$$

Divide equation (6.30) by equation (6.29)

$$\frac{V_c^3}{3V_c^2} = \frac{ab/P_c}{a/P_c}$$

$$\frac{V_c}{3} = b$$

$$\text{i.e., } V_c = 3b \quad \text{----- (6.31)}$$

when equation (6.31) is substituted in (6.29)

$$3V_c^2 = \frac{a}{P_c}$$

$$P_c = \frac{a}{3V_c^2} = \frac{a}{3(3b^2)} = \frac{a}{3 \times 9b^2} = \frac{a}{27b^2}$$

$$P_c = \frac{a}{27b^2} \text{ ----- (6.32)}$$

substituting the values of V_c and P_c in equation (6.28),

$$3V_c = b + \frac{R T_c}{P}$$

$$3(3b) = b + \frac{R T_c}{\left(\frac{a}{27b^2}\right)}$$

$$9b - b = \left(\frac{R T_c}{a}\right) 27b^2$$

$$8b = \frac{T_c R 27b^2}{a}$$

$$\therefore T_c = \frac{8ab}{27Rb^2} = \frac{8a}{27Rb}$$

$$T_c = \frac{8a}{27Rb} \text{ ----- (6.33)}$$

The critical constants can be calculated using the values of van der waals constant of a gas and vice versa.

$$a = 3V_c^2 P_c \text{ and } b = \frac{V_c}{3}$$

6.7 Liquefaction of gases

For important commercial operations such as LPG and rocket fuels, we require gases in their liquid state. The liquefaction methods are based on the Joule-Thomson effect. He observed appreciable cooling when the compressed gas is forced through an orifice plug into

a low-pressure region. This phenomenon of lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure is known as Joule-Thomson effect. This effect is observed only below a certain temperature, which is a characteristic one for each gas. This temperature below which a gas obeys Joule-Thomson effect is called inversion temperature (T_i). This value is given using van der waals constants a and b .

$$T_i = \frac{2a}{Rb} \text{ ----- (6.34)}$$

Gases like O_2 , He, N_2 and H_2 have very low T_c , hence Joule-Thomson effect can be applied for cooling effectively. At the inversion temperature, no rise or fall in temperature of a gas occurs while expanding. But above the inversion temperature, the gas gets heated up when allowed to expand through a hole.

There are different methods used for liquefaction of gases:

- 1) In **Linde's method**, Joule-Thomson effect is used to get liquid air or any other gas.
- 2) In **Claude's process**, the gas is allowed to perform mechanical work in addition to Joule-Thomson effect so that more cooling is produced.
- 3) In **Adiabatic process**, cooling is produced by removing the magnetic property of magnetic material such as gadolinium sulphate. By this method, a temperature of 10^{-4} K i.e. as low as 0 K can be achieved.

SUMMARY

The state of a gas is defined by a relationship between the four independent variables pressure (P), volume (V), temperature (T) and number of moles (n). The relationship between these parameters is governed by different gas laws as summarised below.

LAW	Expression	Conditions	Expression for two different states
Boyle's law	$PV = \text{constant}$	n and T are constant	$P_1 V_1 = P_2 V_2$
Charles's law	$\frac{V}{T} = \text{constant}$	P and n are constant	$\frac{V_1}{T_1} = \frac{V_2}{T_2}$
Gay Lussac's law	$\frac{P}{T} = \text{constant}$	V and n are constant	$\frac{P_1}{T_1} = \frac{P_2}{T_2}$
Combined gas law	$\frac{PV}{T} = \text{constant}$	n is constant	$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$
Avogadro's Hypothesis	$\frac{V}{n} = \text{constant}$	T and P are constant	$\frac{V_1}{n_1} = \frac{V_2}{n_2}$
Dalton's law of partial pressure	$P_{\text{Total}} = p_1 + p_2 + p_3 + \dots$	T and V are constant	
Graham's law of diffusion	$r \propto \frac{1}{\sqrt{M}}$	T and P are constant	$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$

Gases that obey the equation $PV=nRT$ under all conditions are called ideal gases. But in practice there is no ideal gas. Gases tend to behave ideally at high temperatures and at low pressures. For real gases, van der Waals modified the ideal gas equation as

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

Critical temperature (T_c) of a gas is defined as the temperature above which it cannot be liquefied at any pressure. Critical pressure (P_c) of a gas is defined as the minimum pressure required to liquefy 1 mole of a gas at its critical temperature. Critical volume (V_c) is defined as the volume occupied by 1 mole of a gas at its critical temperature and critical pressure.

The critical constants are related to Van der Waals constants as follows

$$T_c = \frac{8a}{27Rb}, \quad P_c = \frac{a}{27b^2} \quad \text{and} \quad V_c = 3b$$

When a gas is made to expand adiabatically from a region of high pressure into a region of low pressure, the temperature of the gas is reduced rapidly and this is known as Joule-Thomson effect. This effect is used in the liquefaction of gases.

EVALUATION



I. Choose the best answer

- Gases deviate from ideal behavior at high pressure. Which of the following statement(s) is correct for non-ideality?
 - at high pressure the collision between the gas molecule become enormous
 - at high pressure the gas molecules move only in one direction
 - at high pressure, the volume of gas become insignificant
 - at high pressure the intermolecular interactions become significant
- Rate of diffusion of a gas is
 - directly proportional to its density
 - directly proportional to its molecular weight
 - directly proportional to its square root of its molecular weight
 - inversely proportional to the square root of its molecular weight
- Which of the following is the correct expression for the equation of state of van der Waals gas?
 - $\left(P + \frac{a}{n^2V^2}\right)(V - nb) = nRT$
 - $\left(P + \frac{na}{n^2V^2}\right)(V - nb) = nRT$
 - $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$
 - $\left(P + \frac{n^2a^2}{V^2}\right)(V - nb) = nRT$
- When an ideal gas undergoes unrestrained expansion, no cooling occurs because the molecules
 - are above inversion temperature
 - exert no attractive forces on each other
 - do work equal to the loss in kinetic energy
 - collide without loss of energy
- Equal weights of methane and oxygen are mixed in an empty container at 298 K. The fraction of total pressure exerted by oxygen is
 - $\frac{1}{3}$
 - $\frac{1}{2}$
 - $\frac{2}{3}$
 - $\frac{1}{3} \times 273 \times 298$

13. Consider the following statements
- Atmospheric pressure is less at the top of a mountain than at sea level
 - Gases are much more compressible than solids or liquids
 - When the atmospheric pressure increases the height of the mercury column rises
- Select the correct statement
- a) I and II b) II and III c) I and III d) I, II and III
14. Compressibility factor for CO_2 at 400 K and 71.0 bar is 0.8697. The molar volume of CO_2 under these conditions is
- a) 22.04 dm^3 b) 2.24 dm^3 c) 0.41 dm^3 d) 19.5 dm^3
15. If temperature and volume of an ideal gas is increased to twice its values, the initial pressure P becomes
- a) 4P b) 2P c) P d) 3P
16. At identical temperature and pressure, the rate of diffusion of hydrogen gas is $3\sqrt{3}$ times that of a hydrocarbon having molecular formula $\text{C}_n\text{H}_{2n-2}$. What is the value of n ?
- a) 8 b) 4 c) 3 d) 1
17. Equal moles of hydrogen and oxygen gases are placed in a container, with a pin-hole through which both can escape what fraction of oxygen escapes in the time required for one-half of the hydrogen to escape. (NEET phase I)
- a) $\frac{3}{8}$ b) $\frac{1}{2}$ c) $\frac{1}{8}$ d) $\frac{1}{4}$
18. The variation of volume V, with temperature T, keeping pressure constant is called the coefficient of thermal expansion ie $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$. For an ideal gas α is equal to
- a) T b) $\frac{1}{T}$ c) P d) none of these
19. Four gases P, Q, R and S have almost same values of 'b' but their 'a' values (a, b are Vander Waals Constants) are in the order $Q < R < S < P$. At a particular temperature, among the four gases the most easily liquefiable one is
- a) P b) Q c) R d) S
20. Maximum deviation from ideal gas is expected from (NEET)
- a) $\text{CH}_4(\text{g})$ b) $\text{NH}_3(\text{g})$ c) $\text{H}_2(\text{g})$ d) $\text{N}_2(\text{g})$
21. The units of Vander Waals constants 'b' and 'a' respectively
- a) mol L^{-1} and $\text{L atm}^2 \text{mol}^{-1}$ b) mol L and L atm mol^2
c) mol^{-1}L and $\text{L}^2 \text{atm mol}^{-2}$ d) none of these



22. Assertion : Critical temperature of CO_2 is 304K, it can be liquefied above 304K.

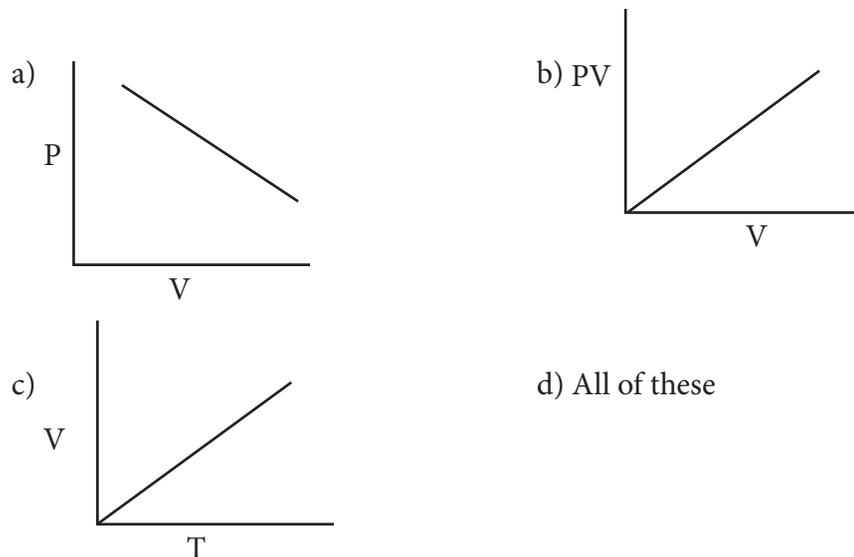
Reason : For a given mass of gas, volume is to directly proportional to pressure at constant temperature

- a) both assertion and reason are true and reason is the correct explanation of assertion
- b) both assertion and reason are true but reason is not the correct explanation of assertion
- c) assertion is true but reason is false
- d) both assertion and reason are false

23. What is the density of N_2 gas at 227°C and 5.00 atm pressure? ($R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$)

- a) 1.40 g/L
- b) 2.81 g/L
- c) 3.41 g/L
- d) 0.29 g/L

24. Which of the following diagrams correctly describes the behaviour of a fixed mass of an ideal gas ? (T is measured in K)



25. 25g of each of the following gases are taken at 27°C and 600 mm Hg pressure. Which of these will have the least volume ?

- a) HBr
- b) HCl
- c) HF
- d) HI



II. Write brief answer to the following questions:

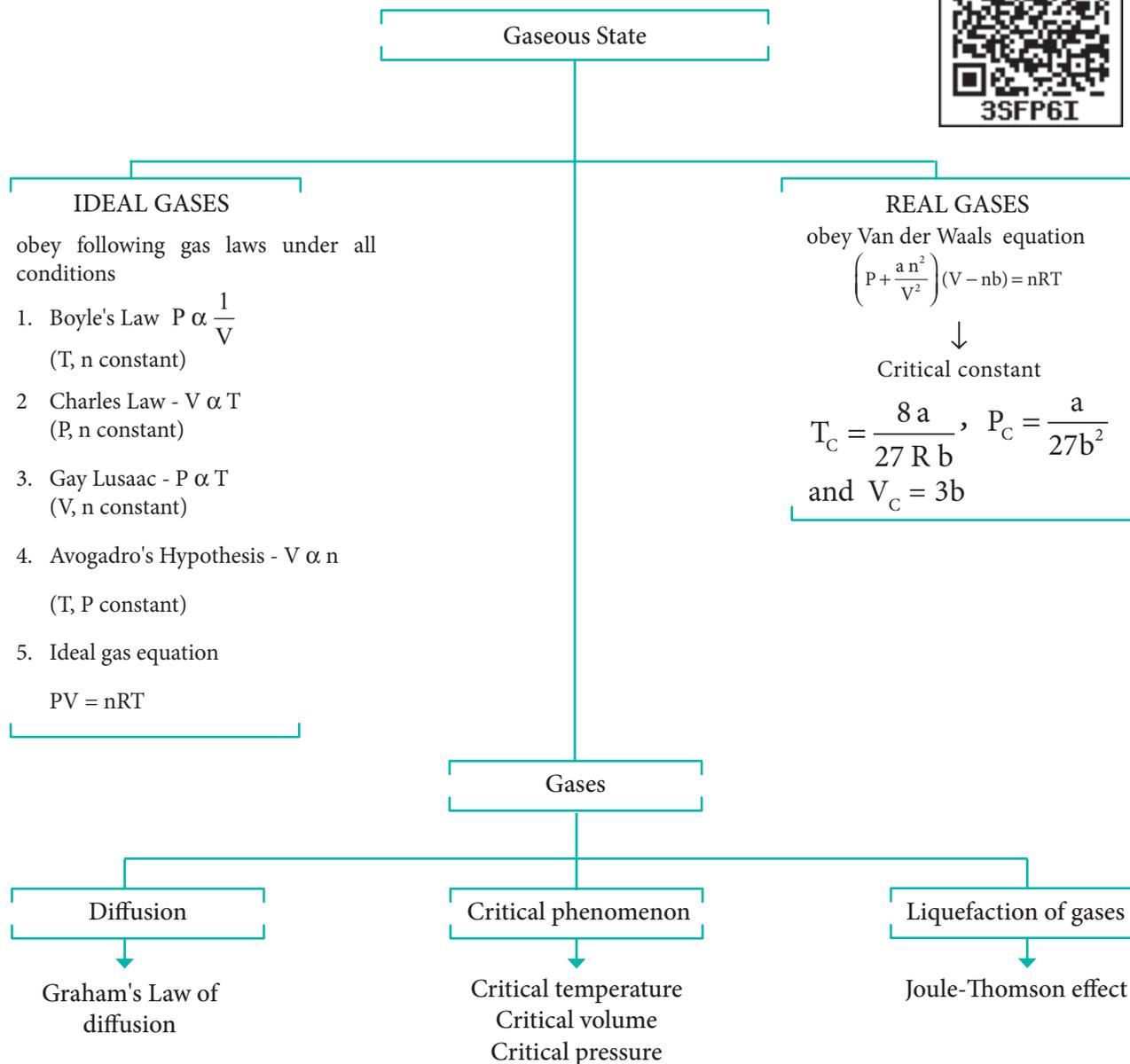
26. State Boyle's law.
27. Name two items that can serve as a model for Gay Lusaac' law and explain.
28. Give the mathematical expression that relates gas volume and moles.
29. What are ideal gases? In what way real gases differ from ideal gases.
30. Can a Van der Waals gas with $a=0$ be liquefied? explain.
31. Suppose there is a tiny sticky area on the wall of a container of gas. Molecules hitting this area stick there permanently. Is the pressure greater or less than on the ordinary area of walls?
32. Explain the following observations
 - a) Aerated water bottles are kept under water during summer
 - b) Liquid ammonia bottle is cooled before opening the seal
 - c) The tyre of an automobile is inflated to slightly lesser pressure in summer than in winter
 - d) The size of a weather balloon becomes larger and larger as it ascends up into larger altitude
33. Give suitable explanation for the following facts about gases.
 - a) Gases don't settle at the bottom of a container
 - b) Gases diffuse through all the space available to them
34. Suggest why there is no hydrogen (H_2) in our atmosphere. Why does the moon have no atmosphere?
35. Explain whether a gas approaches ideal behavior or deviates from ideal behaviour if
 - a) it is compressed to a smaller volume at constant temperature.
 - b) the temperature is raised while keeping the volume constant
 - c) more gas is introduced into the same volume and at the same temperature
36. Which of the following gases would you expect to deviate from ideal behaviour under conditions of low temperature F_2 , Cl_2 or Br_2 ? Explain.
37. Distinguish between diffusion and effusion.
38. Aerosol cans carry clear warning of heating of the can. Why?
39. Would it be easier to drink water with a straw on the top of Mount Everest?
40. Write the Van der Waals equation for a real gas. Explain the correction term for pressure and volume
41. Derive the values of critical constants in terms of van der Waals constants.
42. Why do astronauts have to wear protective suits when they are on the surface of moon?
43. When ammonia combines with HCl, NH_4Cl is formed as white dense fumes. Why do more fumes appear near HCl?



44. A sample of gas at $15\text{ }^{\circ}\text{C}$ at 1 atm . has a volume of 2.58 dm^3 . When the temperature is raised to $38\text{ }^{\circ}\text{C}$ at 1 atm does the volume of the gas increase? If so, calculate the final volume.
45. A sample of gas has a volume of 8.5 dm^3 at an unknown temperature. When the sample is submerged in ice water at $0\text{ }^{\circ}\text{C}$, its volume gets reduced to 6.37 dm^3 . What is its initial temperature?
46. Of two samples of nitrogen gas, sample A contains 1.5 moles of nitrogen in a vessel of volume of 37.6 dm^3 at 298K , and the sample B is in a vessel of volume 16.5 dm^3 at 298K . Calculate the number of moles in sample B.
47. Sulphur hexafluoride is a colourless, odourless gas; calculate the pressure exerted by 1.82 moles of the gas in a steel vessel of volume 5.43 dm^3 at $69.5\text{ }^{\circ}\text{C}$, assuming ideal gas behaviour
48. Argon is an inert gas used in light bulbs to retard the vaporization of the tungsten filament. A certain light bulb containing argon at 1.2 atm and 18°C is heated to 85°C at constant volume. Calculate its final pressure in atm.
49. A small bubble rises from the bottom of a lake where the temperature and pressure are 6°C and 4 atm . to the water surface, where the temperature is 25°C and pressure is 1 atm . Calculate the final volume in (mL) of the bubble, if its initial volume is 1.5 mL .
50. Hydrochloric acid is treated with a metal to produce hydrogen gas. Suppose a student carries out this reaction and collects a volume of $154.4 \times 10^{-3}\text{ dm}^3$ of a gas at a pressure of 742 mm of Hg at a temperature of 298 K . What mass of hydrogen gas (in mg) did the student collect?
51. It takes 192 sec for an unknown gas to diffuse through a porous wall and 84 sec for N_2 gas to effuse at the same temperature and pressure. What is the molar mass of the unknown gas?
52. A tank contains a mixture of 52.5 g of oxygen and 65.1 g of CO_2 at 300 K the total pressure in the tanks is 9.21 atm . Calculate the partial pressure (in atm.) of each gas in the mixture.
53. A combustible gas is stored in a metal tank at a pressure of 2.98 atm at $25\text{ }^{\circ}\text{C}$. The tank can withstand a maximum pressure of 12 atm after which it will explode. The building in which the tank has been stored catches fire. Now predict whether the tank will blow up first or start melting? (Melting point of the metal = 1100 K).



CONCEPT MAP





Properties of Gases

By using this tool you will be able to understand the relationship between T, P of V gases and verify the gas laws.

Please go to the URL
<https://phet.colorado.edu/en/simulation/gas-properties>
(or)
Scan the QR code on the right side



Step - 1

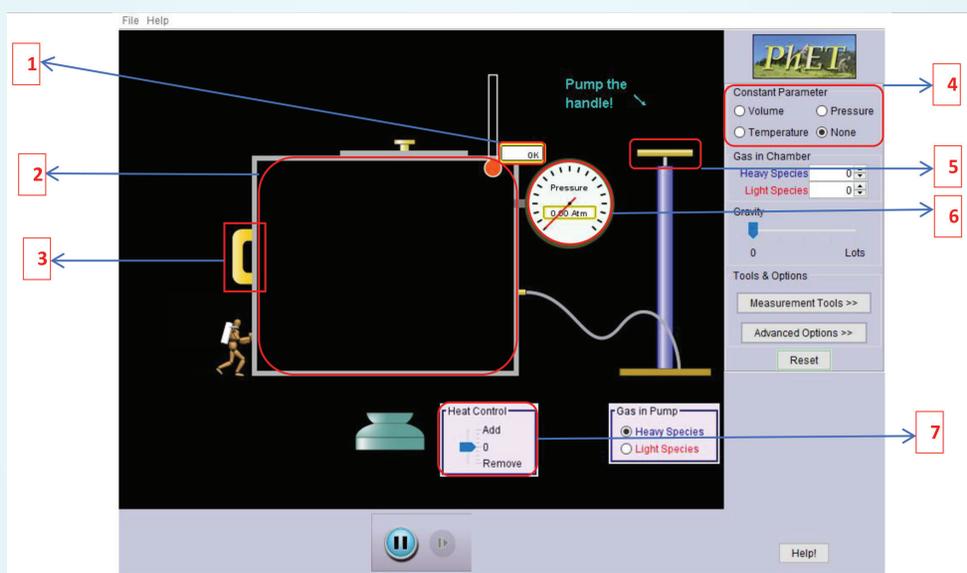
Open the Browser and type the URL given (or) Scan the QR Code. In the website click the gas properties applet, then you will see a Java applet named 'gas properties' opening up as shown in the figure.

Set up instructions:

- In the chamber (2) you can pump some gas molecules by using the pump handle (5).
- The temperature (1) and pressure (6) of the gas molecules in the chamber can be monitored by using the corresponding gauges.
- The volume of the chamber can be altered by moving the left side wall (3).
- The temperature of the chamber can be altered by heating or cooling using the slider (7)
- Any of the three properties can be kept as constant by making appropriate selections in the box (4)

Verifying the gas laws:

By using the above instructions you can understand the gas laws. To understand the Boyle's law, keep the temperature constant (4) and pump few molecules of gas (5) and keep it as constant. Now reduce the volume by pushing the left side wall (3) then you can see that the pressure of the gas increases. Similarly the other two gas laws can also be verified.

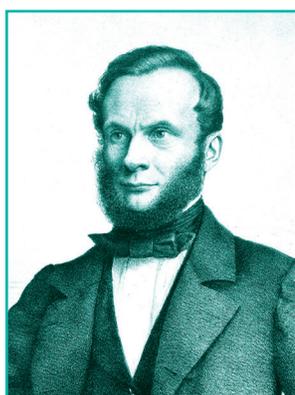


THERMODYNAMICS



Classical thermodynamics... is the only physical theory of universal physical theory of universal content which I am convinced... will never be overthrown.

Albert Einstein



Rudolf Clausius
(1822-1888)

Learning Objectives:

After studying this unit, students will be able to

- distinguish between the system and surroundings
- define closed, open and isolated systems
- distinguish between state and path functions
- describe the relation between internal energy, work and heat
- state four laws of thermodynamics
- correlate internal energy change (ΔU) and enthalpy change (ΔH) and their measurement.
- calculate enthalpy changes for various types of reactions
- apply Hess's law to calculate lattice energy of crystals
- define spontaneous and non spontaneous processes
- establish the relationship between thermodynamic state functions enthalpy (H), entropy (S) and Gibbs free energy (G)
- list the factors that determines spontaneity of the process
- establish the link between ΔG and spontaneity, and the relationship between ΔG^0 and equilibrium constant

7.1 Introduction

The term 'Thermodynamics' means flow of heat and is derived from the Greek 'Thermos' (heat) and 'dynamics' (flow). In our daily life, we come across many useful reactions such as burning of fuel to produce heat energy, flow of electrons through circuit to produce electrical energy, metabolic reactions to produce the necessary energy for biological functions and so on. Thermodynamics, the study of the transformation of energy, explains all such processes quantitatively and allows us to make useful predictions.

In the 19th century, scientists tried to understand the underlying principles of steam engine which were already in operation, in order to improve their efficiency. The basic problem of the investigation was the transformation of heat into mechanical work. However, over time, the laws of thermodynamics were developed and helped to understand the process of steam engine. These laws have been used to deduce powerful mathematical relationships applicable to a broad range of processes.

Thermodynamics evaluates the macroscopic properties (heat, work) and their inter relationships. It deals with properties of systems in equilibrium and is independent of any theories or properties of the individual molecules which constitute the system.

The principles of thermodynamics are based on three laws of thermodynamics. The first two laws (First and second law) summarise the actual experience of inter

conversion of different forms of energy. The third law deals with the calculation of entropy and the unattainability of absolute zero Kelvin. Thermodynamics carries high practical values but bears certain limitations. It is independent of atomic and molecular structure and reaction mechanism. The laws can be used to predict whether a particular reaction is feasible or not under a given set of conditions, but they cannot give the rate at which the reaction takes place. In other words, thermodynamics deals with equilibrium conditions quantitatively, but does not take into account the kinetic approach to the equilibrium state.

7.2 System and Surrounding

Before studying the laws of thermodynamics and their applications, it is important to understand the meaning of a few terms used frequently in thermodynamics.

System:

The universe is divided into two parts, the system and its surroundings. The system is the part of universe which is under thermodynamic consideration. It is separated from the rest of the universe by real or imaginary boundaries.

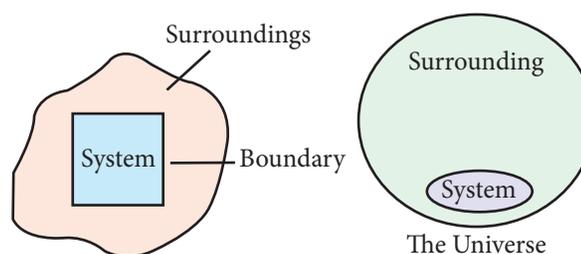


Figure 7.1 System, surrounding & boundary Homogeneous and heterogeneous systems

Example:

The system may be water in a beaker, a balloon filled with air, an aqueous solution of glucose etc.

On the basis of physical and chemical properties, systems can be divided into two types.

A system is called homogeneous if the physical state of all its constituents are the same. Example: a mixture of gases, completely miscible mixture of liquids etc.

A system is called heterogeneous, if physical state of all its constituents is not the same.

Example: mixture of oil and water

Surrounding:

Everything in the universe that is not the part of the system is called surroundings.

Boundary:

Anything which separates the system from its surrounding is called boundary.

7.2.1 Types of systems:

There are three types of thermodynamic systems depending on the nature of the boundary.

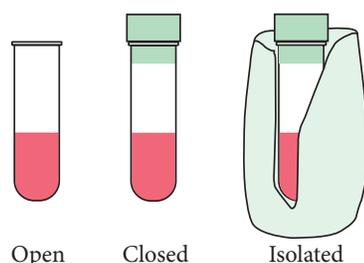


Figure 7.2 Types of Systems

Isolated system:

A system which can exchange neither matter nor energy with its surroundings is called an isolated system. Here boundary is sealed and insulated. Hot water contained in a thermos flask, is an example for an isolated system. In this isolated system both energy (heat) and matter (water vapour) neither enter nor leave the system.

Closed system:

A system which can exchange only energy but not matter with its surroundings is called a closed system. Here the boundary is sealed but not insulated. Hot water contained in a closed beaker is an example for a closed system. In this system energy (heat) is transferred to the surroundings but no matter (water vapour) can escape from this system. A gas contained in a cylinder fitted with a piston constitutes a closed system.

Open system:

A System which can exchange both matter and energy with its surrounding is called an open system. Hot water contained in an open beaker is an example for open system. In this system both matter (water vapour) and energy (heat) is transferred to the surrounding.

All living things and chemical reactions are open systems because they exchange matter and energy with the surroundings.

7.2.2 Properties of the system:

Intensive and extensive properties

Some of the properties of a system depend on its mass or size whereas other properties do not depend on its mass or size. Based on this, the properties of a system are grouped as *extensive* property and *intensive* property.

Extensive properties:

The property that depends on the mass or the size of the system is called an extensive property.

Examples: Volume, Number of moles, Mass, Internal energy, etc.,

Intensive properties:

The property that is independent of the mass or the size of the system is called an intensive property.

Examples : Refractive index, Surface tension, density, temperature, Boiling point, Freezing point, molar volume, etc.,

Table: 7.1 Typical List of Extensive and Intensive properties

Extensive properties	Intensive properties
volume, mass, amount of substance (mole), energy, enthalpy, entropy, free energy, heat capacity	molar volume, density, molar mass, molarity, mole fraction, molality, specific heat capacity

7.2.3 Thermodynamic processes

The method of operation which can bring about a change in the system is called thermodynamic process. Heating, cooling, expansion, compression, fusion, vaporization etc., are some examples of a thermodynamic process.

Types of processes:

A thermodynamic process can be carried out in different ways and under different conditions. The processes can be classified as follows:

Reversible process:

The process in which the system and surrounding can be restored to the initial state from the final state without producing any changes in the thermodynamic properties of the universe is called a reversible process. There are two important conditions for the reversible process to occur. Firstly, the process should occur infinitesimally slowly and secondly throughout the process, the system and surroundings must be in equilibrium with each other.

Irreversible Process:

The process in which the system and surrounding cannot be restored to the initial state from the final state is called an irreversible process. All the processes occurring in nature are irreversible processes. During the irreversible process the system and surroundings are not in equilibrium with each other.

Adiabatic process:

An adiabatic process is defined as one in which there is no exchange of heat (q) between the system and surrounding during the process. Those processes in which no heat can flow into or out of the system are called **adiabatic processes**. This condition is attained by thermally insulating the system. In an adiabatic process if work is done by the system its temperature decreases, if work is done on the system its temperature increases, because, the system cannot exchange heat with its surroundings.

For an adiabatic process $q = 0$

Isothermal process :

An isothermal process is defined as one in which the temperature of the system remains constant, during the change from its initial to final state. The system exchanges heat with its surrounding and the temperature of the system remains constant. For this purpose the experiment is often performed in a thermostat.

For an isothermal process $dT = 0$

Isobaric process

An isobaric process is defined as one in which the pressure of the system remains constant during its change from the initial to final state.

For an isobaric process $dP = 0$.

Isochoric process

An isochoric process is defined as

the one in which the volume of system remains constant during its change from initial to final state. Combustion of a fuel in a bomb calorimeter is an example of an isochoric process.

For an isochoric process, $dV = 0$.

Cyclic process:

When a system returns to its original state after completing a series of changes, then it is said that a cycle is completed. This process is known as a cyclic process.

For a cyclic process $dU = 0$, $dH = 0$, $dP = 0$, $dV = 0$, $dT = 0$

Table: 7.2 Overview of the process and its condition

Process	Condition
Adiabatic	$q = 0$
Isothermal	$dT = 0$
Isobaric	$dP = 0$
Isochoric	$dV = 0$
Cyclic	$dE = 0$, $dH = 0$, $dP = 0$, $dV = 0$, $dT = 0$

State functions, path functions:

State function

A thermodynamic system can be defined by using the variables P , V , T and n . A state function is a thermodynamic property of a system, which has a specific value for a given state and does not depend on the path (or manner) by which the particular state is reached.

Example : Pressure (P), Volume (V), Temperature(T), Internal energy (U), Enthalpy (H), free energy (G) etc.

Path functions:

A path function is a thermodynamic property of the system whose value depends on the path by which the system changes from its initial to final states.

Example: Work (w), Heat (q).

Work (w) will have different values if the process is carried out reversibly or irreversibly.

Internal Energy (U)

The internal energy is a characteristic property of a system which is denoted by the symbol U. The internal energy of a system is equal to the energy possessed by all its constituents namely atoms, ions and molecules. The total energy of all molecules in a system is equal to the sum of their translational energy (U_t), vibrational energy (U_v), rotational energy (U_r), bond energy (U_b), electronic energy (U_e) and energy due to molecular interactions (U_i).

Thus:

$$U = U_t + U_v + U_r + U_b + U_e + U_i$$

The total energy of all the molecules of the system is called internal energy. In thermodynamics one is concerned only with the change in internal energy (ΔU) rather than the absolute value of energy.

Importance of Internal energy

The internal energy possessed by a substance differentiates its physical structure. For example, the allotropes of carbon, namely, graphite (C_{graphite}) and diamond (C_{diamond}), differ from each other because they possess different internal energies and have different structures.

Characteristics of internal energy (U):

- The internal energy of a system is an extensive property. It depends on the amount of the substances present in the system. If the amount is doubled, the internal energy is also doubled.
- The internal energy of a system is a state function. It depends only upon the state variables (T, P, V, n) of the system. The change in internal energy does not depend on the path by which the final state is reached.
- The change in internal energy of a system is expressed as $\Delta U = U_f - U_i$
- In a cyclic process, there is no internal energy change. $\Delta U_{\text{(cyclic)}} = 0$
- If the internal energy of the system in the final state (U_f) is less than the internal energy of the system in its initial state (U_i), then ΔU would be negative.

$$\Delta U = U_f - U_i = -ve \quad (U_f < U_i)$$

- If the internal energy of the system in the final state (U_f) is greater than the internal energy of the system in its initial state (U_i), then ΔU would be positive.

$$\Delta U = U_f - U_i = +ve \quad (U_f > U_i)$$

HEAT(q)

The heat (q) is regarded as an energy in transit across the boundary separating a system from its surrounding. Heat changes lead to temperature differences between system and surrounding. Heat is a path function.

Units of heat:

The SI unit of heat is joule (J). Heat quantities are generally measured in calories (cal). A calorie is defined as the quantity of heat required to raise the temperature of 1 gram of water by 1° C in the vicinity of 15° C.

Sign convention of heat:

The symbol of heat is q .

If heat flows into the system from the surrounding, energy of a system increases. Hence it is taken to be positive (+q).

If heat flows out of the system into the surrounding, energy of the system decreases. Hence, it is taken to be negative (-q).

Work(w)

Work is defined as the force (F) multiplied by the displacement(x).

$$-w = F \cdot x \quad \text{-----(7.1)}$$

The negative sign (-) is introduced to indicate that the work has been done by the system by spending a part of its internal energy.

The work,

- (i) is a path function.
- (ii) appears only at the boundary of the system.
- (iii) appears during the change in the state of the system.
- (iv) In thermodynamics, surroundings is so large that macroscopic changes to surroundings do not happen.

Units of work:

The SI unit of work is joule (J), which is defined as the work done by a force of one Newton through a displacement of one meter ($J = Nm$). We often use kilojoule (kJ) for large quantities of work. $1 \text{ kJ} = 1000 \text{ J}$.

Sign convention of work:

The symbol of work is 'w'.

If work is done by the system, the energy of the system decreases, hence by convention, work is taken to be negative (- w).

If work is done on the system, the energy of the system increases, hence by convention, the work is taken to be positive (+w).

Pressure - volume work

In elementary thermodynamics the only type of work generally considered is the work done in expansion (or compression) of a gas. This is known as pressure-volume work, PV work or expansion work.

Work involved in expansion and compression processes:

In most thermodynamic calculations we are dealing with the evaluation of work involved in the expansion or compression of gases. The essential condition for expansion or compression of a system is that there should be difference between external pressure (P_{ext}) and internal pressure (P_{int}).

For understanding pressure-volume work, let us consider a cylinder which contains 'n' moles of an ideal gas fitted with a frictionless piston of cross sectional area A . The total volume of the gas inside is V_i and pressure of the gas inside is P_{int} .

If the external pressure P_{ext} is greater than P_{int} , the piston moves inward till the pressure inside becomes equal to P_{ext} . Let this change be achieved in a single step and the final volume be V_f .

In this case, the work is done on the system (+w). It can be calculated as follows

$$w = -F \cdot \Delta x \quad \text{----- (7.2)}$$

where dx is the distance moved by the piston during the compression and F is the force acting on the gas.

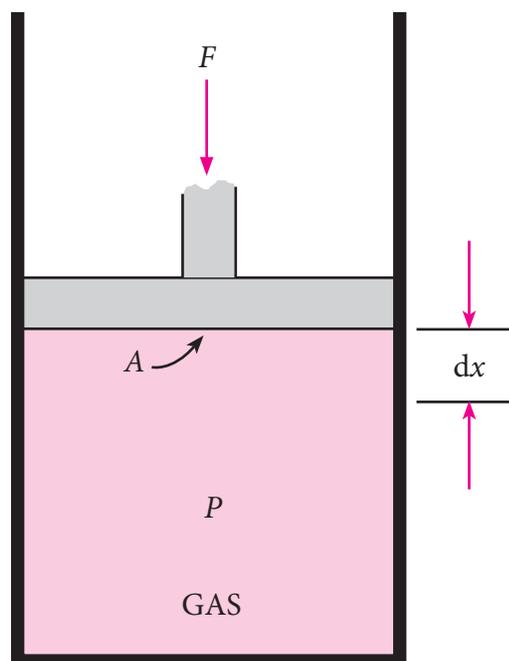


Figure 7.3 showing work involved in compression processes

$$F = P_{\text{ext}} A \quad \text{----- (7.3)}$$

Substituting 7.3 in 7.2

$$w = -P_{\text{ext}} \cdot A \cdot \Delta x$$

$$A \cdot \Delta x = \text{change in volume} = V_f - V_i$$

$$w = -P_{\text{ext}} \cdot (V_f - V_i) \quad \text{----- (7.4)}$$

$$w = -P_{\text{ext}} \cdot (-\Delta V) \quad \text{----- (7.5)}$$

$$= P_{\text{ext}} \cdot \Delta V$$

Since work is done on the system, it is a positive quantity.

If the pressure is not constant, but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV . In such a case we can calculate the work done on the gas by the relation

$$w_{rev} = - \int_{V_i}^{V_f} P_{ext} dV$$

In a compression process, P_{ext} the external pressure is always greater than the pressure of the system.

$$\text{i.e. } P_{ext} = (P_{int} + dP).$$

In an expansion process, the external pressure is always less than the pressure of the system

$$\text{i.e. } P_{ext} = (P_{int} - dP).$$

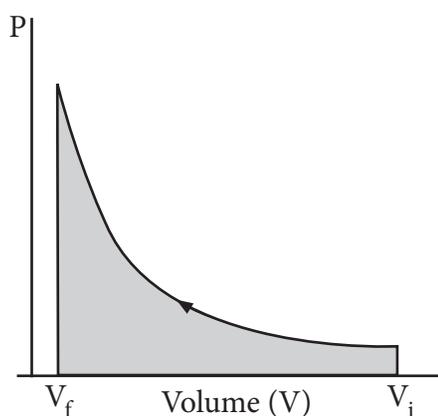


Figure 7.4

When pressure is not constant and changes in infinitesimally small steps (reversible conditions) during compression from V_i to V_f , the P-V plot looks like in fig 7.4 Work done on the gas is represented by the shaded area.

In general case we can write,

$P_{ext} = (P_{int} \pm dP)$. Such processes are called reversible processes. For a compression process work can be related to internal pressure of the system under reversible conditions by writing equation

$$w_{rev} = - \int_{V_i}^{V_f} P_{int} dV$$

For a given system with an ideal gas

$$P_{int} V = nRT$$

$$P_{int} = \frac{nRT}{V}$$

$$w_{rev} = - \int_{V_i}^{V_f} \frac{nRT}{V} dV$$

$$w_{rev} = -nRT \int_{V_i}^{V_f} \left(\frac{dV}{V} \right)$$

$$w_{rev} = -nRT \ln \left(\frac{V_f}{V_i} \right)$$

$$w_{rev} = -2.303 nRT \log \left(\frac{V_f}{V_i} \right) \text{ ----- 7.6}$$

If $V_f > V_i$ (expansion), the sign of work done by the process is negative.

If $V_f < V_i$ (compression) the sign of work done on the process is positive.

Table: 7.3 Summary of sign conventions

1.	If heat is absorbed by the system	:	$+q$
2.	If heat is evolved by the system	:	$-q$
3.	work is done by the system	:	$-w$
4.	work is done on the system	:	$+w$

7.3 Zeroth law of thermodynamics:

The zeroth law of thermodynamics, also known as the law of thermal equilibrium, was put forward much after the establishment of the first and second laws of thermodynamics. It is placed

before the first and second laws as it provides a logical basis for the concept of temperature of the system.

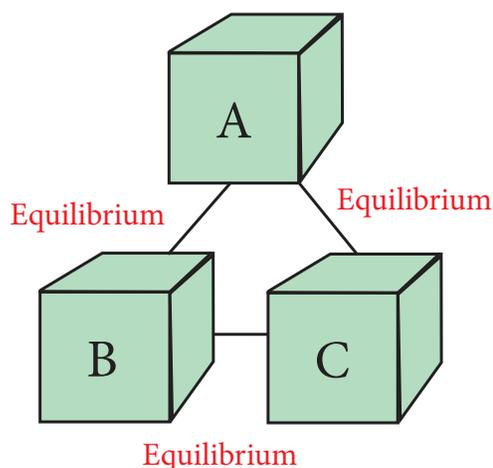


Figure : 7.5 Zeroth law of thermodynamics:

The law states that 'If two systems are separately in thermal equilibrium with a third one, then they tend to be in thermal equilibrium with themselves'.

According to this law, if systems B and C separately are in thermal equilibrium with another system A, then systems B and C will also be in thermal equilibrium with each other. This is also the principle by which thermometers are used.

7.4 First Law of Thermodynamics:

The first law of thermodynamics, known as the law of conservation of energy, states that the total energy of an isolated system remains constant though it may change from one form to another.

When a system moves from state 1 to state 2, its internal energy changes from U_1 to U_2 . Then change in internal energy

$$\Delta U = U_2 - U_1.$$

This internal energy change is brought about by the either absorption or evolution of heat and/or by work being done by/on the system.

Because the total energy of the system must remain constant, we can write the mathematical statement of the First Law as:

$$\Delta U = q + w \text{ -----(7.7)}$$

Where q - the amount of heat supplied to the system; w - work done on the system

Other statements of first law of thermodynamics

- (1) Whenever an energy of a particular type disappears, an equivalent amount of another type must be produced.
- (2) The total energy of a system and surrounding remains constant (or conserved)
- (3) "Energy can neither be created nor destroyed, but may be converted from one form to another".
- (4) "The change in the internal energy of a closed system is equal to the energy that passes through its boundary as heat or work".
- (5) "Heat and work are two ways of changing a system's internal energy".

7.4.1 Mathematical statement of the first law

The mathematical statement of the first law of thermodynamics is

$$\Delta U = q + w \text{ ----- (7.7)}$$

Case 1 : For a cyclic process involving isothermal expansion of an ideal gas,

$$\Delta U = 0.$$

$$\text{eqn (7.7)} \Rightarrow \therefore q = -w$$

In other words, during a cyclic process, the amount of heat absorbed by the system is equal to work done by the system.

Case 2 : For an isochoric process (no change in volume) there is no work of expansion. i.e. $\Delta V = 0$

$$\begin{aligned}\Delta U &= q + w \\ &= q - P\Delta V \\ \Delta V &= 0 \\ \Delta U &= q_v\end{aligned}$$

In other words, during an isochoric process, the amount of heat supplied to the system is converted to its internal energy.

Case 3 : For an adiabatic process there is no change in heat. i.e. $q = 0$. Hence

$$q = 0$$

$$\text{eqn (7.7)} \Rightarrow \Delta U = w$$

In other words, in an adiabatic process, the decrease in internal energy

is exactly equal to the work done by the system on its surroundings.

Case 4 : For an isobaric process. There is no change in the pressure. P remains constant. Hence

$$\begin{aligned}\Delta U &= q + w \\ \Delta U &= q - P\Delta V\end{aligned}$$

In other words, in an isobaric process a part of heat absorbed by the system is used for P - V expansion work and the remaining is added to the internal energy of the system.

Problem: 7.1

A gas contained in a cylinder fitted with a frictionless piston expands against a constant external pressure of 1 atm from a volume of 5 litres to a volume of 10 litres. In doing so it absorbs 400 J of thermal energy from its surroundings. Determine the change in internal energy of system.

Solution:

Given data $q = 400 \text{ J}$ $V_1 = 5 \text{ L}$ $V_2 = 10 \text{ L}$

$\Delta u = q - w$ (heat is given to the system (+q); work is done by the system (-w))

$$\begin{aligned}\Delta u &= q - PdV \\ &= 400 \text{ J} - 1 \text{ atm} (10 - 5) \text{ L} \\ &= 400 \text{ J} - 5 \text{ atm L} \\ &[\therefore 1 \text{ L atm} = 101.33 \text{ J}] \\ &= 400 \text{ J} - 5 \times 101.33 \text{ J} \\ &= 400 \text{ J} - 506.65 \text{ J} \\ &= -106.65 \text{ J}\end{aligned}$$

7.5 Enthalpy (H)

The enthalpy (H), is a thermodynamic property of a system, is defined as the sum of the internal energy (U) of a system and the product of pressure and volume of the system. That is,

$$H = U + PV \text{ -----(7.8)}$$

It reflects the capacity to do mechanical work and the capacity to release heat by the system. When a process occurs at constant pressure, the heat involved (either released or absorbed) is equal to the change in enthalpy.

Enthalpy is a state function which depends entirely on the state functions T, P and U. Enthalpy is usually expressed as the change in enthalpy (ΔH) for a process between initial and final states at constant pressure.

$$\Delta H = \Delta U + P\Delta V \text{ -----(7.9)}$$

The change in enthalpy (ΔH) is equal to the heat supplied at the constant pressure to a system (as long as the system does no additional work).

$$\Delta H = q_p$$

In an endothermic reaction heat is absorbed by the system from the surroundings that is $q > 0$ (positive). Therefore, ΔH is also positive. In an exothermic reaction heat is evolved by the system to the surroundings that is, $q < 0$ (negative). If q is negative, then ΔH will also be negative.

7.5.1 Relation between enthalpy 'H' and internal energy 'U'

When the system at constant pressure undergoes changes from an initial state with H_1 , U_1 and V_1 to a final state with H_2 , U_2 and V_2 the change in enthalpy ΔH , can be calculated as follows:

$$H = U + PV$$

In the initial state

$$H_1 = U_1 + PV_1 \text{ -----(7.10)}$$

In the final state

$$H_2 = U_2 + PV_2 \text{ -----(7.11)}$$

change in enthalpy is (7.11) - (7.10)

$$(H_2 - H_1) = (U_2 - U_1) + P(V_2 - V_1)$$

$$\Delta H = \Delta U + P\Delta V \text{ ----- (7.12)}$$

As per first law of thermodynamics,

$$\Delta U = q + w$$

Equation 7.12 becomes

$$\Delta H = q + w + P\Delta V$$

$$w = -P\Delta V$$

$$\Delta H = q_p - P\Delta V + P\Delta V$$

$$\Delta H = q_p \text{ ----- (7.13)}$$

q_p - is the heat absorbed at constant pressure and is considered as heat content.

Consider a closed system of gases which are chemically reacting to form gaseous products at constant temperature

and pressure with V_i and V_f as the total volumes of the reactant and product gases respectively, and n_i and n_f as the number of moles of gaseous reactants and products, then,

For reactants (initial state) :

$$PV_i = n_i RT \text{ ----- (7.14)}$$

For products (final state) :

$$PV_f = n_f RT \text{ ----- (7.15)}$$

(7.15) - (7.14)

$$P (V_f - V_i) = (n_f - n_i) RT$$

$$P \Delta V = \Delta n_{(g)} RT \text{ ----- (7.16)}$$

Substituting in 7.16 in 7.12

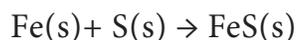
$$\Delta H = \Delta U + \Delta n_{(g)} RT \text{ ----- (7.17)}$$

7.5.2 Enthalpy Changes for Different Types of Reactions and Phase Transitions:

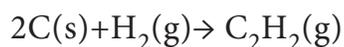
The heat or enthalpy changes accompanying chemical reactions is expressed in different ways depending on the nature of the reaction. These are discussed below.

Standard heat of formation

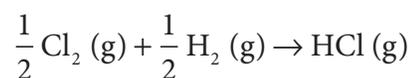
The standard heat of formation of a compound is defined as "the change in enthalpy that takes place when one mole of a compound is formed from its elements, present in their standard states (298 K and 1 bar pressure)". By convention the standard heat of formation of all elements is assigned a value of zero.



$$\Delta H_f^0 = -100.42 \text{ kJ mol}^{-1}$$



$$\Delta H_f^0 = +222.33 \text{ kJ mol}^{-1}$$



$$\Delta H_f^0 = -92.4 \text{ kJ mol}^{-1}$$

The standard heats of formation of some compounds are given in Table 7.4.

Table: 7.4 standard heat of formation of some compounds

Substance	ΔH_f^0 (kJ mol ⁻¹)	Substance	ΔH_f^0 (kJ mol ⁻¹)
H ₂ O(l)	-242	CH ₄ (g)	-74.85
HCl(g)	-92.4	C ₂ H ₆ (g)	-84.6
HBr(g)	-36.4	C ₆ H ₆ (g)	+49.6
NH ₃ (g)	-46.1	C ₂ H ₂ (g)	+222.33
CO ₂ (g)	-393.5	CH ₃ OH(l)	-239.2

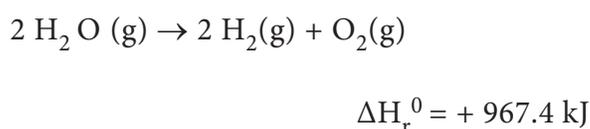
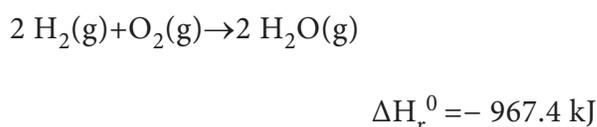
7.6 Thermochemical Equations:

A thermochemical equation is a balanced stoichiometric chemical equation that includes the enthalpy change (ΔH). The following conventions are adopted in thermochemical equations:

- (i) The coefficients in a balanced thermochemical equation refer to number of moles of reactants and products involved in the reaction.

- (ii) The enthalpy change of the reaction ΔH_r has to be specified with appropriate sign and unit.
- (iii) When the chemical reaction is reversed, the value of ΔH is reversed in sign with the same magnitude.
- (iv) The physical states (gas, liquid, aqueous, solid in brackets) of all species are important and must be specified in a thermochemical reaction, since ΔH depends on the physical state of reactants and products.
- (v) If the thermochemical equation is multiplied throughout by a number, the enthalpy change is also multiplied by the same number.
- (vi) The negative sign of ΔH_r indicates that the reaction is exothermic and the positive sign of ΔH_r indicates an endothermic reaction.

For example, consider the following reaction,



Standard enthalpy of reaction (ΔH_r^0) from standard enthalpy of formation (ΔH_f^0)

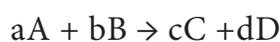
The standard enthalpy of a reaction is the enthalpy change for a reaction

when all the reactants and products are present in their standard states. Standard conditions are denoted by adding the superscript 0 to the symbol (ΔH^0)

We can calculate the enthalpy of a reaction under standard conditions from the values of standard enthalpies of formation of various reactants and products. The standard enthalpy of reaction is equal to the difference between standard enthalpy of formation of products and the standard enthalpies of formation of reactants.

$$\Delta H_r^0 = \sum \Delta H_f^0 (\text{products}) - \sum \Delta H_f^0 (\text{reactants})$$

For a general reaction

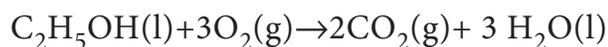


$$\Delta H_r^0 = \sum \Delta H_f^0 (\text{products}) - \sum \Delta H_f^0 (\text{reactants})$$

$$\Delta H_r^0 = \{c \Delta H_f^0 (\text{C}) + d \Delta H_f^0 (\text{D})\} - \{a \Delta H_f^0 (\text{A}) + b \Delta H_f^0 (\text{B})\}$$

Problem : 7.2

The standard enthalpies of formation of $\text{C}_2\text{H}_5\text{OH}(\text{l})$, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are -277, -393.5 and -285.5 kJ mol^{-1} respectively. Calculate the standard enthalpy change for the reaction

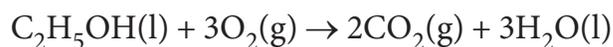


The enthalpy of formation of $\text{O}_2(\text{g})$ in the standard state is Zero, by definition

Solution:

For example, the standard enthalpy change for the combustion of ethanol can be calculated from the standard enthalpies of formation of $\text{C}_2\text{H}_5\text{OH}(\text{l})$, $\text{CO}_2(\text{g})$

and H₂O(l). The enthalpies of formation are -277, -393.5 and -285.5 kJ mol⁻¹ respectively.

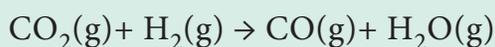


$$\begin{aligned} \Delta H_r^0 &= \left\{ (\Delta H_f^0)_{\text{products}} - (\Delta H_f^0)_{\text{reactants}} \right\} \\ \Delta H_r^0 &= \left[2(\Delta H_f^0)_{\text{CO}_2} + 3(\Delta H_f^0)_{\text{H}_2\text{O}} \right] \\ &\quad - \left[1(\Delta H_f^0)_{\text{C}_2\text{H}_5\text{OH}} + 3(\Delta H_f^0)_{\text{O}_2} \right] \\ \Delta H_r^0 &= \left[2\text{mol}(-393.5)\text{kJ mol}^{-1} \right] \\ &\quad + \left[3\text{mol}(-285.5)\text{kJ mol}^{-1} \right] \\ &\quad - \left[1\text{mol}(-277)\text{kJ mol}^{-1} \right] \\ &\quad - \left[3\text{mol}(0)\text{kJ mol}^{-1} \right] \\ &= [-787 - 856.5] - [-277] \\ &= -1643.5 + 277 \end{aligned}$$

$$\Delta H_r^0 = -1366.5 \text{ KJ}$$

Evaluate Yourself - 1

Calculate ΔH_f^0 for the reaction

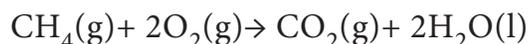


given that ΔH_f^0 for CO₂(g), CO(g) and H₂O(g) are -393.5, -111.31 and -242 kJ mol⁻¹ respectively.

Heat of combustion

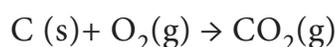
The heat of combustion of a substance is defined as “The change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen”. It is denoted by ΔH_C . For example, the heat of combustion of

methane is -87.78 kJ mol⁻¹



$$\Delta H_C = -87.78 \text{ kJ mol}^{-1}$$

For the combustion of carbon,



$$\Delta H_C = -394.55 \text{ kJ mol}^{-1}$$

Combustion reactions are always exothermic. Hence the enthalpy change is always negative.

Molar heat capacities

When heat (q) is supplied to a system, the molecules in the system absorb the heat and hence their kinetic energy increases, which in turn raises the temperature of the system from T₁ to T₂. This increase (T₂ - T₁) in temperature is directly proportional to the amount of heat absorbed and inversely proportional to mass of the substance. In other words,

$$q \propto m\Delta T$$

$$q = c m \Delta T$$

$$c = q/m \Delta T$$

The constant c is called heat capacity.

$$c = \left(\frac{q}{m(T_2 - T_1)} \right) \text{ ----- (7.18)}$$

when m=1 kg and (T₂ - T₁) = 1 K then the heat capacity is referred as specific heat capacity. The equation 7.18 becomes

$$c = q$$

Thus specific heat capacity of a system is defined as “The heat absorbed by one kilogram of a substance to raise its temperature by one Kelvin at a specified temperature”.

The heat capacity for 1 mole of substance, is called molar heat capacity (c_m). It is defined as “The amount of heat absorbed by one mole of the substance to raise its temperature by 1 kelvin”.

Units of Heat Capacity:

The SI unit of molar heat capacity is $\text{JK}^{-1}\text{mol}^{-1}$

The molar heat capacities can be expressed either at constant volume (C_v) or at constant pressure (C_p).

According to the first law of thermodynamics

$$U = q + w \quad \text{or} \quad U = q - PdV$$

$$q = U + PdV \text{ -----(7.19)}$$

Differentiate (7.19) with respect to temperature at constant volume i.e $dV=0$,

$$\left(\frac{\partial q}{\partial T}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v \text{ -----7.20}$$

Thus the heat capacity at constant volume (C_v) is defined as the rate of change of internal energy with respect to temperature at constant volume.

Similarly the molar heat capacity at constant pressure (C_p) can be defined as

the rate of change of enthalpy with respect to temperature at constant pressure.

$$c_p = \left(\frac{\partial H}{\partial T}\right)_p \text{ ----- (7.21)}$$

Relation between C_p and C_v for an ideal gas.

From the definition of enthalpy

$$H=U+PV \text{ -----(7.8)}$$

for 1 mole of an ideal gas

$$PV = nRT \text{ -----(7.22)}$$

By substituting (7.22) in (7.8)

$$H = U + nRT \text{ ---- (7.23)}$$

Differentiating the above equation with respect to T,

$$\frac{\partial H}{\partial T} = \frac{\partial U}{\partial T} + nR \frac{\partial T}{\partial T}$$

$$C_p = C_v + nR \quad (1) \quad \left[\begin{array}{l} \because \left(\frac{\partial H}{\partial T}\right)_P = C_P \\ \text{and} \left(\frac{\partial U}{\partial T}\right)_V = C_V \end{array} \right]$$

$$C_p - C_v = nR \text{(7.24)}$$

At constant pressure processes, a system has to do work against the surroundings. Hence, the system would require more heat to effect a given temperature rise than at constant volume, so C_p is always greater than C_v

Calculation of ΔU and ΔH

For one mole of an ideal gas, we have

$$C_v = \frac{dU}{dT}$$

$$dU = C_v dT$$

For a finite change, we have

$$\Delta U = C_v \Delta T$$

$$\Delta U = C_v (T_2 - T_1)$$

and for n moles of an ideal gas we get

$$\Delta U = n C_v (T_2 - T_1) \text{ ----- (7.25)}$$

Similarly for n moles of an ideal gas we get

$$\Delta H = n C_p (T_2 - T_1) \text{ ----- (7.26)}$$

Problem 7.3

Calculate the value of ΔU and ΔH on heating 128.0 g of oxygen from 0°C to 100°C . C_v and C_p on an average are 21 and 29 $\text{J mol}^{-1} \text{K}^{-1}$. (The difference is $8 \text{J mol}^{-1} \text{K}^{-1}$ which is approximately equal to R)

Solution.

We know

$$\Delta U = n C_v (T_2 - T_1)$$

$$\Delta H = n C_p (T_2 - T_1)$$

Here $n = \frac{128}{32} = 4 \text{ moles};$

$$T_2 = 100^\circ \text{C} = 373\text{K}; T_1 = 0^\circ \text{C} = 273\text{K}$$

$$\Delta U = n C_v (T_2 - T_1)$$

$$\Delta U = 4 \times 21 \times (373 - 273)$$

$$\Delta U = 8400 \text{ J}$$

$$\Delta U = 8.4 \text{ kJ}$$

$$\Delta H = n C_p (T_2 - T_1)$$

$$\Delta H = 4 \times 29 \times (373 - 273)$$

$$\Delta H = 11600 \text{ J}$$

$$\Delta H = 11.6 \text{ kJ}$$



Evaluate Yourself -2

Calculate the amount of heat necessary to raise 180 g of water from 25°C to 100°C . Molar heat capacity of water is $75.3 \text{ J mol}^{-1} \text{K}^{-1}$

7.7 Measurement of ΔU and ΔH using Calorimetry.

Calorimeter is used for measuring the amount of heat change in a chemical or physical change. In calorimetry, the temperature change in the process is measured which is inversely proportional to the heat change. By using the expression $C = q/m\Delta T$, we can calculate the amount of heat change in the process. Calorimetric measurements are made under two different conditions

i) At constant volume (q_v)

ii) At constant pressure (q_p)

(A) ΔU Measurements

For chemical reactions, heat evolved at constant volume, is measured in a *bomb calorimeter*.

The inner vessel (the bomb) and its cover are made of strong steel. The cover is fitted tightly to the vessel by means of metal lid and screws.

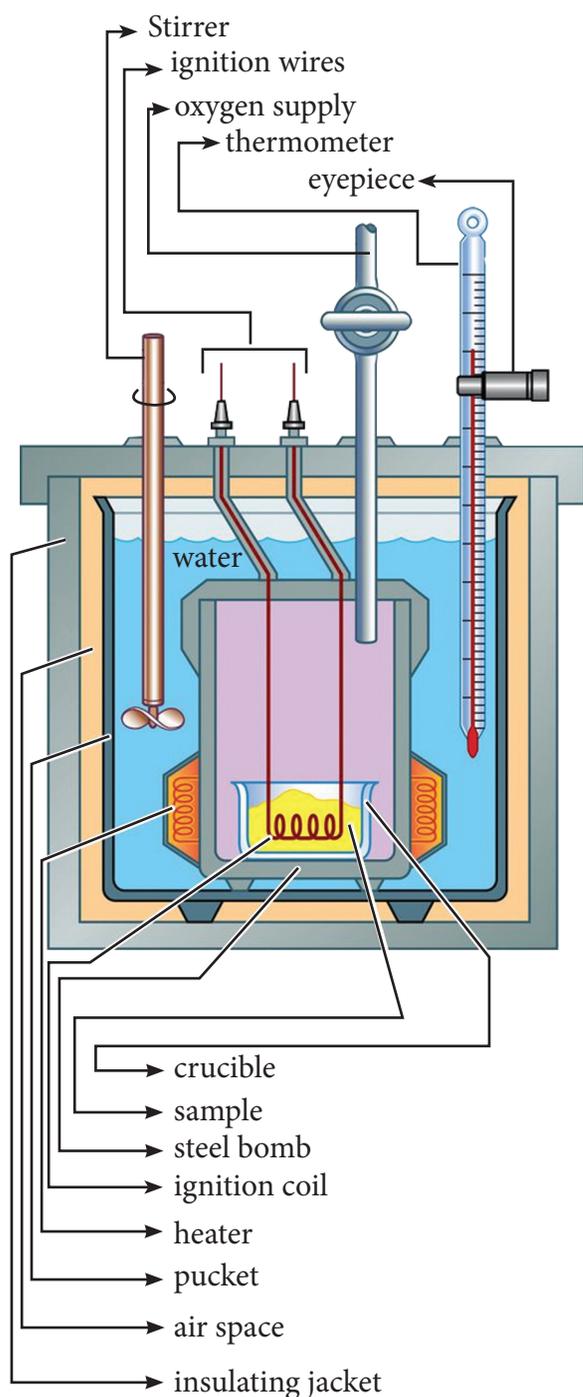


Figure 7.6 Bomb calorimeter

A weighed amount of the substance is taken in a platinum cup connected with

electrical wires for striking an arc instantly to kindle combustion. The bomb is then tightly closed and pressurized with excess oxygen. The bomb is immersed in water, in the inner volume of the calorimeter. A stirrer is placed in the space between the wall of the calorimeter and the bomb, so that water can be stirred, uniformly. The reaction is started by striking the substance through electrical heating.

A known amount of combustible substance is burnt in oxygen in the bomb. Heat evolved during the reaction is absorbed by the calorimeter as well as the water in which the bomb is immersed. The change in temperature is measured using a Beckman thermometer. Since the bomb is sealed its volume does not change and hence the heat measurements is equal to the heat of combustion at a constant volume (ΔU_c^0).

The amount of heat produced in the reaction (ΔU_c^0) is equal to the sum of the heat absorbed by the calorimeter and water.

Heat absorbed by the calorimeter

$$q_1 = k \cdot \Delta T$$

where k is a calorimeter constant equal to $m_c C_c$ (m_c is mass of the calorimeter and C_c is heat capacity of calorimeter)

Heat absorbed by the water

$$q_2 = m_w C_w \Delta T$$

where m_w is molar mass of water

C_w is molar heat capacity of water ($75.29 \text{ J K}^{-1} \text{ mol}^{-1}$)

$$\begin{aligned}\text{Therefore } \Delta U_c &= q_1 + q_2 \\ &= k.\Delta T + m_w C_w \Delta T \\ &= (k+m_w C_w)\Delta T\end{aligned}$$

Calorimeter constant can be determined by burning a known mass of standard sample (benzoic acid) for which the heat of combustion is known (-3227 kJmol^{-1})

The enthalpy of combustion at constant pressure of the substance is calculated from the equation (7.17)

$$\Delta H_{C(\text{pressure})}^0 = \Delta U_{C(\text{Vol})}^0 + \Delta n_g RT$$

Applications of bomb calorimeter:

1. Bomb calorimeter is used to determine the amount of heat released in combustion reaction.
2. It is used to determine the calorific value of food.
3. Bomb calorimeter is used in many industries such as metabolic study, food processing, explosive testing etc.

(b) ΔH Measurements

Heat change at constant pressure (at atmospheric pressure) can be measured using a coffee cup calorimeter. A schematic representation of a coffee cup calorimeter is given in Figure 7.7. Instead of bomb, a styrofoam cup is used in this calorimeter. It acts as good adiabatic wall and doesn't allow transfer of heat produced during the reaction to its surrounding. This entire heat energy is absorbed by the water inside the cup. This method can be used for the reactions where there is no

appreciable change in volume. The change in the temperature of water is measured and used to calculate the amount of heat that has been absorbed or evolved in the reaction using the following expression.

$$q = m_w C_w \Delta T$$

where m_w is the molar mass of water and C_w is the molar heat capacity of water ($75.29 \text{ J K}^{-1} \text{ mol}^{-1}$)

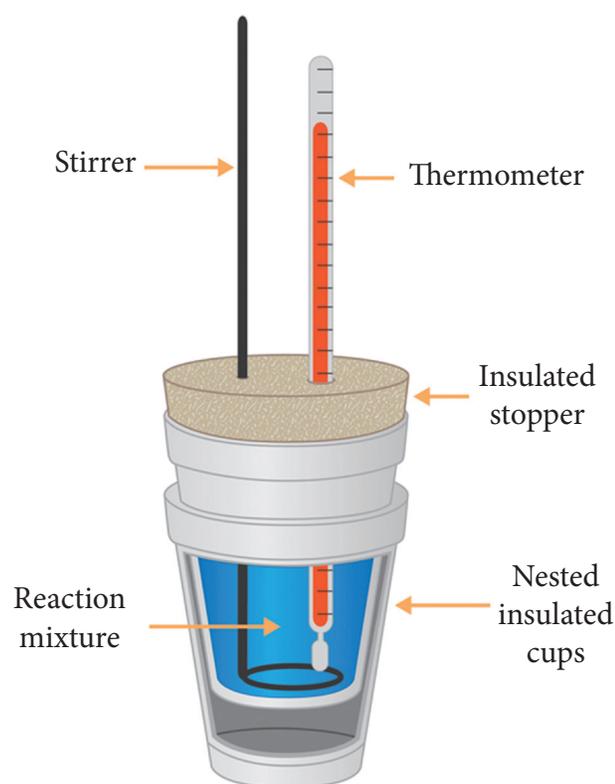
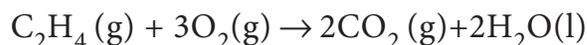


Figure 7.7 Coffee cup Calorimeter

Problem 7.4

Calculate the enthalpy of combustion of ethylene at 300 K at constant pressure, if its heat of combustion at constant volume (ΔU) is -1406 kJ .

The complete ethylene combustion reaction can be written as,



$$\Delta U = -1406 \text{ kJ}$$

$$\Delta n = n_{\text{p}(\text{g})} - n_{\text{r}(\text{g})}$$

$$\Delta n = 2 - 4 = -2$$

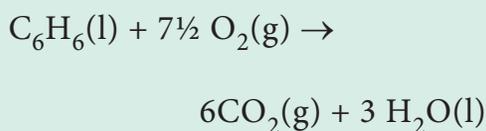
$$\Delta H = \Delta U + RT\Delta n_{\text{g}}$$

$$\Delta H = -1406 + (8.314 \times 10^{-3} \times 300 \times (-2))$$

$$\Delta H = -1410.9 \text{ kJ}$$

Evaluate Yourself - 3

From the following data at constant volume for combustion of benzene, calculate the heat of this reaction at constant pressure condition.



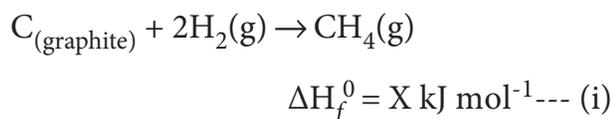
$$\Delta U \text{ at } 25^\circ \text{C} = -3268.12 \text{ kJ}$$

Applications of the heat of combustion:

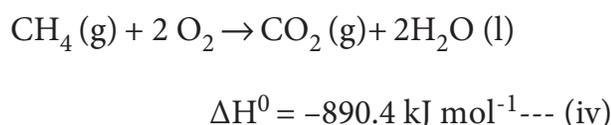
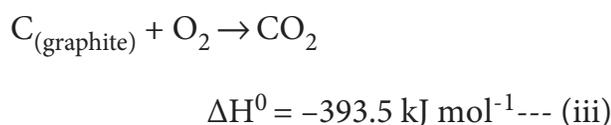
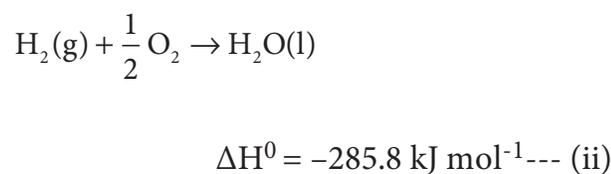
(1) Calculation of heat of formation: Since the heat of combustion of organic compounds can be determined with considerable ease, they are employed to calculate the heat of formation of other compounds.

For example let us calculate the standard enthalpy of formation ΔH_f^0 of CH_4 from the values of enthalpy of combustion for H_2 , $\text{C}(\text{graphite})$ and CH_4 which are -285.8 , -393.5 , and $-890.4 \text{ kJ mol}^{-1}$ respectively.

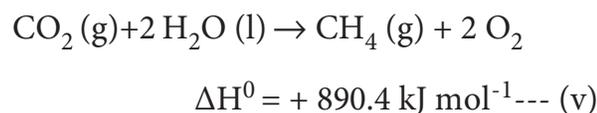
Let us interpret the information about enthalpy of formation by writing out the equations. It is important to note that the standard enthalpy of formation of pure elemental gases and elements is assumed to be zero under standard conditions. Thermochemical equation for the formation of methane from its constituent elements is,



Thermo chemical equations for the combustion of given substances are,



Since methane is in the product side of the required equation (i), we have to reverse the equation (iv)



In order to get equation (i) from the remaining,

$$(i) = [(ii) \times 2] + (iii) + (v)$$

$$X = [(-285.8) \times 2] + [-393.5] + [+890.4]$$

$$= -74.7 \text{ kJ}$$

Hence, the amount of energy required for the formation of 1 mole of methane is -74.7 kJ

The heat of formation methane = -74.7 kJ mol⁻¹

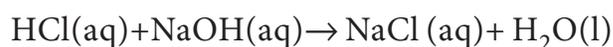
(2) Calculation of calorific value of food and fuels: The calorific value is defined as the amount of heat produced in calories (or joules) when one gram of the substance is completely burnt. The SI unit of calorific value is J kg⁻¹. However, it is usually expressed in cal g⁻¹.

Heat of solution:

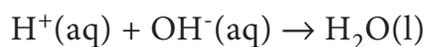
Heat changes are usually observed when a substance is dissolved in a solvent. The heat of solution is defined as the change in enthalpy when one mole of a substance is dissolved in a specified quantity of solvent at a given temperature.

Heat of neutralisation:

The heat of neutralisation is defined as “The change in enthalpy when one gram equivalent of an acid is completely neutralised by one gram equivalent of a base or vice versa in dilute solution”.



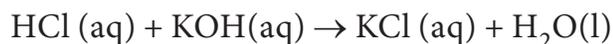
$$\Delta H = - 57.32 \text{ kJ}$$



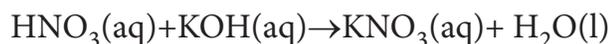
$$\Delta H = - 57.32 \text{ kJ}$$

The heat of neutralisation of a strong acid and strong base is around - 57.32 kJ, irrespective of nature of acid or base used which is evident from the below

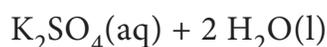
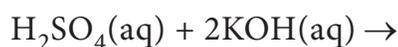
mentioned examples.



$$\Delta H = - 57.32 \text{ kJ}$$

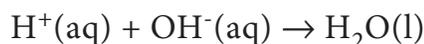


$$\Delta H = - 57.32 \text{ kJ}$$



$$\Delta H = - 57.32 \text{ kJ} \times 2$$

The reason for this can be explained on the basis of Arrhenius theory of acids and bases which states that strong acids and strong bases completely ionise in aqueous solution to produce H⁺ and OH⁻ ions respectively. Therefore in all the above mentioned reactions the neutralisation can be expressed as follows.

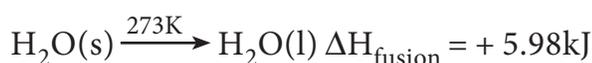


$$\Delta H = - 57.32 \text{ kJ}$$

Molar heat of fusion

The molar heat of fusion is defined as “the change in enthalpy when one mole of a solid substance is converted into the liquid state at its melting point”.

For example, the heat of fusion of ice can be represented as

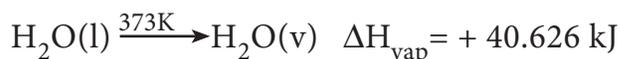


Molar heat of vapourisation

The molar heat of vaporisation is defined as “the change in enthalpy when

one mole of liquid is converted into vapour state at its boiling point”.

For example, heat of vaporisation of water can be represented as



Molar heat of sublimation

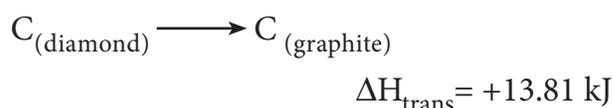
Sublimation is a process when a solid changes directly into its vapour state without changing into liquid state. Molar heat of sublimation is defined as “the change in enthalpy when one mole of a solid is directly converted into the vapour state at its sublimation temperature”. For example, the heat of sublimation of iodine is represented as



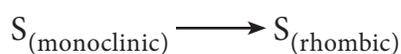
Another example of sublimation process is solid CO_2 to gas at atmospheric pressure at very low temperatures.

Heat of transition

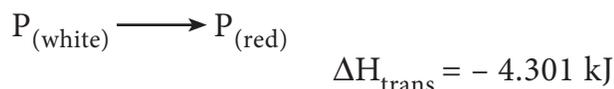
The heat of transition is defined as “The change in enthalpy when one mole of an element changes from one of its allotropic form to another. For example, the transition of diamond into graphite may be represented as



Similarly the allotropic transitions in sulphur and phosphorous can be represented as follows,



$$\Delta H_{\text{trans}} = - 0.067 \text{ kJ}$$

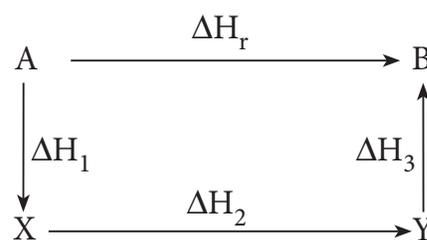


7.8 Hess's law of constant heat summation

We have already seen that the heat changes in chemical reactions are equal to the difference in internal energy (ΔU) or heat content (ΔH) of the products and reactants, depending upon whether the reaction is studied at constant volume or constant pressure. Since ΔU and ΔH are functions of the state of the system, the heat evolved or absorbed in a given reaction depends only on the initial state and final state of the system and not on the path or the steps by which the change takes place.

This generalisation is known as **Hess's law** and stated as:

The enthalpy change of a reaction either at constant volume or constant pressure is the same whether it takes place in a single or multiple steps provided the initial and final states are same.



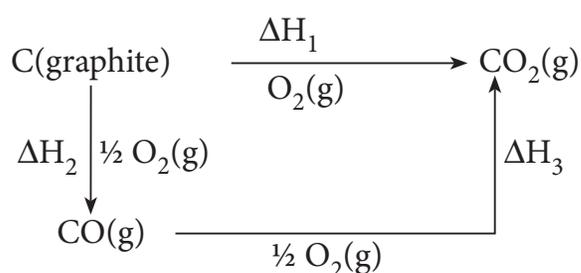
$$\Delta H_r = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Application of Hess's Law: Hess's law can be applied to calculate enthalpies of reactions that are difficult to measure. For example, it is very difficult to measure the heat of combustion of graphite to give pure CO .

However, enthalpy for the oxidation of graphite to CO_2 and CO to CO_2 can easily be measured. For these conversions, the heat of combustion values are -393.5 kJ and -283.5 kJ respectively.

From these data the enthalpy of combustion of graphite to CO can be calculated by applying Hess's law.

The reactions involved in this process can be expressed as follows



According to Hess law,

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

$$-393.5 \text{ kJ} = X - 283.5 \text{ kJ}$$

$$X = -110.5 \text{ kJ}$$

7.9 Lattice energy ($\Delta H_{\text{lattice}}$)

Lattice energy is defined as the amount of energy required to completely remove the constituent ions from its crystal lattice to an infinite distance from one mole of crystal. It is also referred as lattice enthalpy.



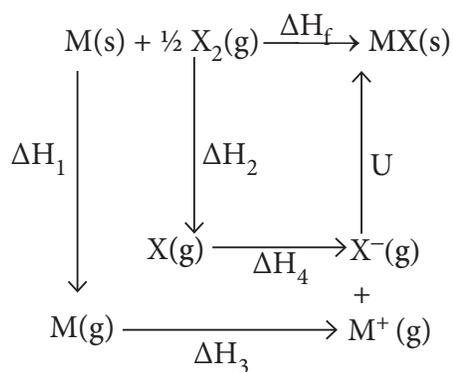
$$\Delta H_{\text{lattice}} = +788 \text{ kJ mol}^{-1}$$

From the above equation it is clear that 788 kJ of energy is required to separate Na^+ and Cl^- ions from 1 mole of NaCl .

Born - Haber cycle

The Born–Haber cycle is an approach to analyse reaction energies. It was named after two German scientists Max Born and Fritz Haber who developed this cycle. The cycle is concerned with the formation of an ionic compound from the reaction of a metal with a halogen or other non-metallic element such as oxygen.

Born–Haber cycle is primarily used in calculating lattice energy, which cannot be measured directly. The Born–Haber cycle applies Hess's law to calculate the lattice enthalpy. For example consider the formation of a simple ionic solid such as an alkali metal halide MX , the following steps are considered.



ΔH_1 - enthalpy change for the sublimation $\text{M}(\text{s})$ to $\text{M}(\text{g})$

ΔH_2 - enthalpy change for the dissociation of $\frac{1}{2} \text{X}_2(\text{g})$ to $\text{X}(\text{g})$

ΔH_3 - Ionisation energy for $\text{M}(\text{g})$ to $\text{M}^+(\text{g})$

ΔH_4 - electron affinity for the conversion of $\text{X}(\text{g})$ to $\text{X}^-(\text{g})$

U - the lattice enthalpy for the formation of solid MX

ΔH_f - enthalpy change for the formation of solid MX directly from elements

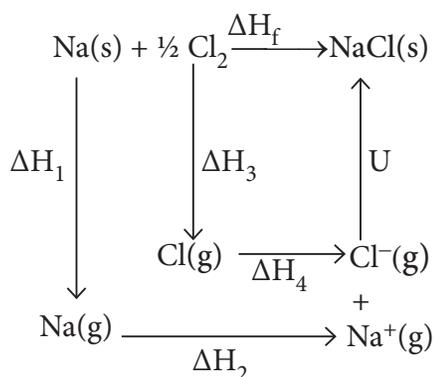
According to Hess's law of heat summation

$$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + U$$

Let us use the Born - Haber cycle for determining the lattice enthalpy of NaCl as follows:

Since the reaction is carried out with reactants in elemental forms and products in their standard states, at 1 bar, the overall enthalpy change of the reaction is also the enthalpy of formation for NaCl. Also, the formation of NaCl can be considered in 5 steps. The sum of the enthalpy changes of these steps is equal to the enthalpy change for the overall reaction from which the lattice enthalpy of NaCl is calculated.

Let us calculate the lattice energy of sodium chloride using Born-Haber cycle



ΔH_f = heat of formation of sodium chloride = $-411.3 \text{ kJ mol}^{-1}$

ΔH_1 = heat of sublimation of Na(g) = $108.7 \text{ kJ mol}^{-1}$

ΔH_2 = ionisation energy of Na(g) = $495.0 \text{ kJ mol}^{-1}$

ΔH_3 = dissociation energy of $\text{Cl}_2(\text{g})$ = 244 kJ mol^{-1}

ΔH_4 = Electron affinity of Cl(S) = $-349.0 \text{ kJ mol}^{-1}$

U = lattice energy of NaCl

$$\Delta H_f = \Delta H_1 + \Delta H_2 + \frac{1}{2} \Delta H_3 + \Delta H_4 + U$$

$$\therefore U = (\Delta H_f) - (\Delta H_1 + \Delta H_2 + \frac{1}{2} \Delta H_3 + \Delta H_4)$$

$$\Rightarrow U = (-411.3) - (108.7 + 495.0 + 122 - 349)$$

$$U = (-411.3) - (376.7)$$

$$\therefore U = -788 \text{ kJ mol}^{-1}$$

This negative sign in lattice energy indicates that the energy is released when sodium is formed from its constituent gaseous ions Na^+ and Cl^-

Evaluate Yourself - 4



When a mole of magnesium bromide is prepared from 1 mole of magnesium and 1 mole of liquid bromine, 524 kJ of energy is released. The heat of sublimation of Mg metal is 148 kJ mol^{-1} . The heat of dissociation of bromine gas into atoms is 193 kJ mol^{-1} . The heat of vapourisation of liquid bromine is 31 kJ mol^{-1} . The first and second ionisation energies of magnesium are $\text{IE}_1 = 737.5 \text{ kJ mol}^{-1}$ and $\text{IE}_2 = 1450.5 \text{ kJ mol}^{-1}$ and the electron affinity of bromine is $-324.5 \text{ kJ mol}^{-1}$. Calculate the lattice energy of magnesium bromide.

7.10. Second Law of thermodynamics:

Need for the second law of thermodynamics:

We know from the first law of thermodynamics, the energy of the universe is conserved. Let us consider the following processes:

1. A glass of hot water over time loses heat energy to the surrounding and becomes cold.
2. When you mix hydrochloric acid with sodium hydroxide, it forms sodium chloride and water with evolution of heat.

In both these processes, the total energy is conserved and are consistent with the first law of thermodynamics. However, the reverse process i.e. cold water becoming hot water by absorbing heat from surrounding on its own does not occur spontaneously even though the energy change involved in this process is also consistent with the first law. However, if the heat energy is supplied to cold water, then it will become hot. i.e. the change that does not occur spontaneously and can be driven by supplying energy.

Similarly, a solution of sodium chloride does not absorb heat energy on its own, to form hydrochloric acid and sodium hydroxide. But, this process can not be driven even by supplying energy. From these kinds of our natural experiences, we have come to know that certain processes are spontaneous while the others are not, and some processes have a preferred direction. In order to explain the feasibility of a process, we need the second law of thermodynamics.

7.10.1 Various statements of the second law of thermodynamics

Entropy

The second law of thermodynamics introduces another state function called entropy. Entropy is a measure of the

molecular disorder (randomness) of a system. But thermodynamic definition of entropy is concerned with the change in entropy that occurs as a result of a process.

It is defined as, $dS = dq_{\text{rev}} / T$

Entropy statement:

The second law of thermodynamics can be expressed in terms of entropy. i.e. “the entropy of an isolated system increases during a spontaneous process”.

For an irreversible process such as spontaneous expansion of a gas,

$$\Delta S_{\text{total}} > 0$$

$$\Delta S_{\text{total}} > \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

$$\text{i.e. } \Delta S_{\text{total}} > \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

For a reversible process such as melting of ice,

$$\Delta S_{\text{system}} = - \Delta S_{\text{surrounding}}$$

$$\Delta S_{\text{total}} = 0$$

Kelvin-Planck statement:

It is impossible to construct a machine that absorbs heat from a hot source and converts it completely into work by a cyclic process without transferring a part of heat to a cold sink. The second law of thermodynamics explains why even an ideal, frictionless engine cannot convert 100% of its input heat into work. Carnot on his analysis of heat engines, found that the maximum efficiency of a heat engine which operates reversibly, depends only on the two temperatures between which it is operated.

Efficiency = work performed / heat absorbed

$$\eta = \frac{|q_h| - |q_c|}{|q_h|}$$

q_h - heat absorbed from the hot reservoir

q_c - heat transferred to cold reservoir

$$\eta = 1 - \frac{|q_c|}{|q_h|} \quad \text{--- (7.27)}$$

For a reversible cyclic process

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

$$\Delta S_{\text{system}} = -\Delta S_{\text{surroundings}}$$

$$\frac{q_h}{T_h} = \frac{-q_c}{T_c}$$

$$\frac{T_c}{T_h} = \frac{-q_c}{q_h}$$

$$\frac{T_c}{T_h} = \frac{|q_c|}{|q_h|} \quad \text{--- 7.28}$$

Substituting 7.28 in 7.27

$$\Rightarrow \eta = 1 - \frac{T_c}{T_h} \quad \text{--- 7.29}$$

$$T_h \gg T_c$$

Hence, $\eta < 1$

efficiency in percentage can be expressed as

$$\text{Efficiency in percentage} = \left[1 - \frac{T_c}{T_h} \right] \times 100$$

Clausius statement:

It is impossible to transfer heat from a cold reservoir to a hot reservoir without doing some work.

Problem: 7.10

If an automobile engine burns petrol at a temperature of 816°C and if the surrounding temperature is 21°C , calculate its maximum possible efficiency.

Solution:

$$\% \text{ Efficiency} = \left[\frac{T_h - T_c}{T_h} \right] \times 100$$

Here

$$T_h = 816 + 273 = 1089 \text{ K};$$

$$T_c = 21 + 273 = 294 \text{ K}$$

$$\% \text{ Efficiency} = \left(\frac{1089 - 294}{1089} \right) \times 100$$

$$\% \text{ Efficiency} = 73\%$$

Evaluate Yourself - 5



An engine operating between 127°C and 47°C takes some specified amount of heat from a high temperature reservoir. Assuming that there are no frictional losses, calculate the percentage efficiency of an engine.

Unit of entropy:

The entropy (S) is equal to heat energy exchanged (q) divided by the temperature (T) at which the exchange takes place. Therefore, The SI unit of entropy is JK^{-1} .

Spontaneity and Randomness

Careful examination shows that in each of the processes viz., melting of ice and evaporation of water, there is an increase in randomness or disorder of the system. The water molecules in ice

are arranged in a highly organised crystal pattern which permits little movement. As the ice melts, the water molecules become disorganised and can move more freely. The movement of molecules becomes freer in the liquid phase and even more free in the vapour phase. In other words, we can say that the randomness of the water molecules increases, as ice melts into water or water evaporates. Both are spontaneous processes which result in an increase in randomness (entropy).

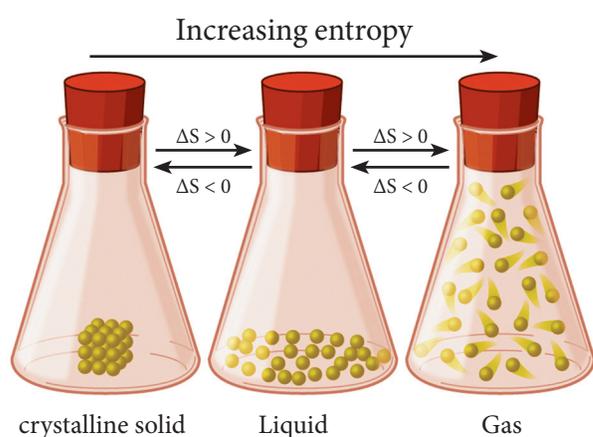


Figure 7.8 Illustration showing an increase in disorder.

Standard Entropy Change (ΔS°):

It is possible to calculate the actual entropy of a substance at any temperature above 0 K. The absolute entropy of a substance at 298 K and one bar pressure is called the standard entropy S° . The third law of thermodynamics states, according to Nernst, that the absolute entropy of elements is zero only at 0 K in a perfect crystal, and standard entropies of all substances at any temperature above 0 K always have positive values. Once we know the entropies of different substances, we can calculate the standard entropy change (ΔS_r°) for chemical reactions.

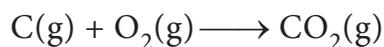
$$\Delta S_r^\circ = \sum S_{\text{products}}^\circ - \sum S_{\text{reactants}}^\circ \quad \text{----- (7.30)}$$

Standard Entropy of Formation:

Standard entropy of formation is defined as “the entropy of formation of 1 mole of a compound from the elements under standard conditions”. It is denoted as ΔS_f° . We can calculate the value of entropy of a given compound from the values of S° of elements.

Problem: 7.6

Calculate the standard entropy change for the following reaction (ΔS_f°), given the standard entropies of $\text{CO}_2(\text{g})$, $\text{C}(\text{s})$, $\text{O}_2(\text{g})$ as 213.6, 5.740 and 205 JK^{-1} respectively.



$$\Delta S_r^\circ = \sum S_{\text{products}}^\circ - \sum S_{\text{reactants}}^\circ$$

$$\Delta S_r^\circ = \{S_{\text{CO}_2}^\circ\} - \{S_{\text{C}}^\circ + S_{\text{O}_2}^\circ\}$$

$$\Delta S_r^\circ = 213.6 - [5.74 + 205]$$

$$\Delta S_r^\circ = 213.6 - [210.74]$$

$$\Delta S_r^\circ = 2.86 \text{ JK}^{-1}$$

Evaluate Yourself- 6



Urea on hydrolysis produces ammonia and carbon dioxide. The standard entropies of urea, H_2O , CO_2 , NH_3 are 173.8, 70, 213.5 and 192.5 $\text{J mole}^{-1}\text{K}^{-1}$ respectively. Calculate the entropy change for this reaction.

Entropy change accompanying change of phase

When there is a change of state from solid to liquid (melting), liquid to

vapour (evaporation) or solid to vapour (sublimation) there is a change in entropy. This change may be carried out at constant temperature reversibly as two phases are in equilibrium during the change.

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{\Delta H_{\text{rev}}}{T} \quad \text{----- (7.31)}$$

Entropy of fusion:

The heat absorbed, when one mole of a solid melts at its melting point reversibly, is called molar heat of fusion. The entropy change for this process is given by

$$\Delta S_{\text{rev}} = \frac{dq_{\text{rev}}}{T}$$

$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_f} \quad \text{----- (7.32)}$$

where ΔH_{fusion} is Molar heat of fusion. T_f is the melting point.

Entropy of vapourisation:

The heat absorbed, when one mole of liquid is boiled at its boiling point reversibly, is called molar heat of vapourisation. The entropy change is given by

$$\Delta S_v = \frac{\Delta H_v}{T_b} \quad \text{----- (7.33)}$$

where ΔH_v is Molar heat of vaporisation. T_b is the boiling point.

Entropy of transition:

The heat change, when one mole of a solid changes reversibly from one allotropic form to another at its transition temperature is called enthalpy of transition. The entropy change is given

$$\Delta S_t = \frac{\Delta H_t}{T_t} \quad \text{----- (7.34)}$$

where ΔH_t is the molar heat of transition, T_t is the transition temperature.

Problem: 7.7

Calculate the entropy change during the melting of one mole of ice into water at 0°C and 1 atm pressure. Enthalpy of fusion of ice is 6008 J mol^{-1}

Given:

$$\Delta H_{\text{fusion}} = 6008\text{ J mol}^{-1}$$

$$T_f = 0^\circ\text{C} = 273\text{ K}$$

$$\text{H}_2\text{O(S)} \xrightarrow{273\text{ K}} \text{H}_2\text{O (l)}$$

$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_f}$$

$$\Delta S_{\text{fusion}} = \frac{6008}{273}$$

$$\Delta S_{\text{fusion}} = 22.007\text{ J K}^{-1}\text{ mole}^{-1}$$

Evaluate Yourself - 7



Calculate the entropy change when 1 mole of ethanol is evaporated at 351 K . The molar heat of vaporisation of ethanol is 39.84 kJ mol^{-1}

7.11 Gibbs free energy (G)

One of the important applications of the second law of thermodynamics is to predict the spontaneity of a reaction under a specific set of conditions. A reaction that occurs under the given set of conditions without any external driving force is called a spontaneous reaction. Otherwise, it is said to be non-spontaneous. In our day today life, we observe many spontaneous physical and chemical processes, which includes the following examples.

1. A waterfall runs downhill, but never uphill, spontaneously.
2. A lump of sugar dissolves spontaneously in a cup of coffee, but never reappears in its original form spontaneously.
3. Heat flows from hotter object to a colder one, but never flows from colder to hotter object spontaneously.
4. The expansion of a gas into an evacuated bulb is a spontaneous process, the reverse process that is gathering of all molecules into one bulb is not spontaneous.

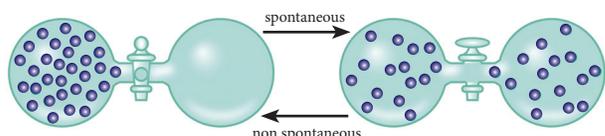
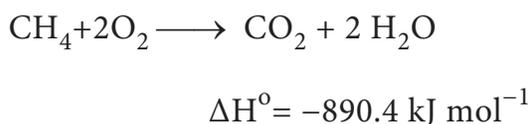


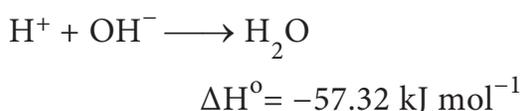
Figure 7.9 Spontaneous process illustration

These examples show that the processes that occur spontaneously in one direction, cannot take place in opposite direction spontaneously.

Similarly a large number of exothermic reactions are spontaneous. An example is combustion of methane.

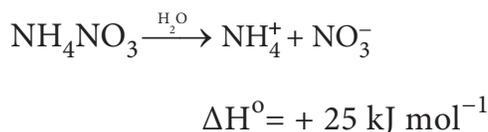


Another example is acid-base neutralization reaction:



However, some endothermic processes are also spontaneous. For

example ammonium nitrate dissolves in water spontaneously though this dissolution is endothermic.



From the above examples we can come to the conclusion that exothermicity favors the spontaneity but does not guarantee it. We cannot decide whether or not a chemical reaction will occur spontaneously solely on the basis of energy changes in the system. We know from second law of thermodynamics that in a spontaneous process, the entropy increases. But not all the processes which are accompanied by an increase in entropy are spontaneous. In order to predict the spontaneity of a reaction, we need some other thermodynamic function.

The second law of thermodynamics introduces another thermodynamic function called Gibbs free energy which finds useful in predicting the spontaneity of a reaction. The Gibbs free energy (G) was developed in the 1870's by Josiah Willard Gibbs. He originally termed this energy as the "available energy" to do work in a system. This quantity is the energy associated with a chemical reaction that can be used to do work.

Gibbs free energy is defined as below

$$G = H - TS \text{ ----- (7.35)}$$

Gibbs free energy (G) is an extensive property and it is a single valued state function.

Let us consider a system which undergoes a change of state from state (1) to state (2) at constant temperature.

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$$

$$\Delta G = \Delta H - T \Delta S \text{-----(7.36)}$$

Now let us consider how ΔG is related to reaction spontaneity.

We know that

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

For a reversible process (equilibrium), the change in entropy of universe is zero. $\Delta S_{\text{total}} = 0$ [$\because \Delta S_{\text{sys}} = -\Delta S_{\text{surr}}$]

Similarly, for an equilibrium process $\Delta G = 0$

For spontaneous process, $\Delta S_{\text{total}} > 0$

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

$$\Delta S_{\text{sys}} + \frac{dq_{\text{surr}}}{T} > 0$$

$$\Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0$$

$$T\Delta S_{\text{sys}} - \Delta H_{\text{sys}} > 0$$

$$-(\Delta H_{\text{sys}} - T\Delta S_{\text{sys}}) > 0$$

$$-\Delta G > 0$$

hence for a spontaneous process,

$$\Delta G < 0$$

$$\text{i.e. } \Delta H - T \Delta S < 0 \text{-----(7.37)}$$

ΔH_{sys} is the enthalpy change of a reaction, $T\Delta S_{\text{sys}}$ is the energy which is not available to do useful work. So ΔG is the net energy available to do useful work and is thus a measure of the 'free energy'. For this reason, it is also known as the free energy of the reaction. For non spontaneous process, $\Delta G > 0$

Gibbs free energy and the net work done by the system:

For any system at constant pressure and temperature

$$\Delta G = \Delta H - T \Delta S \text{----- (7.36)}$$

We know that,

$$\Delta H = \Delta U + P\Delta V$$

$$\therefore \Delta G = \Delta U + P\Delta V - T\Delta S$$

from first law of thermodynamics

if work is done by the system

$$\Delta U = q - w$$

from second law of thermodynamics

$$\Delta S = \frac{q}{T}$$

$$\Delta G = q - w + P\Delta V - T\left(\frac{q}{T}\right)$$

$$\Delta G = -w + P\Delta V$$

$$-\Delta G = w - P\Delta V \text{.....(7.38)}$$

Here, $-P\Delta V$ represents the work done due to expansion against a constant external pressure. Therefore, it is clear that the decrease in free energy ($-\Delta G$) accompanying a process taking place at constant temperature and pressure is equal to the maximum work obtainable from the system other than the work of expansion.

7.11.1 Criteria for spontaneity of a process

The spontaneity of any process depends on three different factors.

- If the enthalpy change of a process is negative, then the process is exothermic and may be spontaneous. (ΔH is negative)
- If the entropy change of a process is positive, then the process may occur spontaneously. (ΔS is positive)

- The Gibbs free energy which is the combination of the above two ($\Delta H - T\Delta S$) should be negative for a reaction to occur spontaneously, i.e. the necessary condition for a reaction to be spontaneous is $\Delta H - T\Delta S < 0$

Table 7.5 Effect of Temperature on Spontaneity of Reactions:

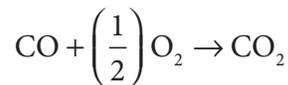
ΔH_r	ΔS_r	$\Delta G_r = \Delta H_r - T\Delta S_r$	Description	Example
-	+	- (at all T)	Spontaneous at all temperature	$2O_3(g) \rightarrow 3O_2(g)$
-	-	- (at low T)	spontaneous at low temperature	Adsorption of gases
		+ (at high T)	non-spontaneous at high temperature	
+	+	+ (at low T)	non-spontaneous at low temperature	Melting of a solid
		- (at high T)	spontaneous at high temperature	
+	-	+ (at all T)	non spontaneous at all temperatures	$2H_2O(g) + O_2(g) \rightarrow 2H_2O_2(l)$

The Table assumes ΔH and ΔS will remain the way indicated for all temperatures. It may not be necessary that way. The spontaneity of a chemical reaction is only the potential for the reaction to proceed as written. The rate of such processes is determined by kinetic factors, outside of thermodynamical prediction.

Problem: 7.8

Show that the reaction $CO + \left(\frac{1}{2}\right)O_2 \rightarrow CO_2$

at 300K is spontaneous. The standard Gibbs free energies of formation of CO_2 and CO are -394.4 and -137.2 kJ mole^{-1} respectively.



$$\Delta G_{(\text{reaction})}^0 = \sum G_{f(\text{products})}^0 - \sum G_{f(\text{reactants})}^0$$

$$\Delta G_{(\text{reaction})}^0 = [G_{CO_2}^0] - \left[G_{CO}^0 + \frac{1}{2} G_{O_2}^0 \right]$$

$$\Delta G_{(\text{reaction})}^0 = -394.4 + [137.2 + 0]$$

$$\Delta G_{(\text{reaction})}^0 = -257.2 \text{ kJ mol}^{-1}$$

$\Delta G_{(\text{reaction})}$ of a reaction at a given temperature is negative hence the reaction is spontaneous.

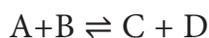
Evaluate Yourself - 8



For a chemical reaction the values of ΔH and ΔS at 300K are -10 kJ mole^{-1} and $-20 \text{ J deg}^{-1} \text{ mole}^{-1}$ respectively. What is the value of ΔG of the reaction? Calculate the ΔG of a reaction at 600 K assuming ΔH and ΔS values are constant. Predict the nature of the reaction.

7.11.2 Relationship between standard free energy change (ΔG^0) and equilibrium constant (K_{eq}):

In a reversible process, the system is in perfect equilibrium with its surroundings at all times. A reversible chemical reaction can proceed in either direction simultaneously, so that a dynamic equilibrium is set up. This means that the reactions in both the directions should proceed with decrease in free energy, which is impossible. It is possible only if at equilibrium, the free energy of a system is minimum. Let's consider a general equilibrium reaction



The free energy change of the above reaction in any state (ΔG) is related to the standard free energy change of the reaction (ΔG^0) according to the following equation.

$$\Delta G = \Delta G^0 + RT \ln Q \text{ -----(7.39)}$$

where Q is reaction quotient and is defined as the ratio of concentration of the products to the concentrations of the reactants under non equilibrium condition.

When equilibrium is attained, there is no further free energy change i.e. $\Delta G = 0$ and Q becomes equal to equilibrium constant. Hence the above equation becomes.

$$\Delta G^0 = -RT \ln K_{eq}$$

This equation is known as Van't Hoff equation.

$$\Delta G^0 = -2.303 RT \log K_{eq} \text{ -----(7.40)}$$

We also know that

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 = -RT \ln K_{eq}$$

Problem: 7.9

Calculate ΔG^0 for conversion of oxygen to ozone $3/2 O_2 \rightleftharpoons O_{3(g)}$ at 298 K, if K_p for this conversion is 2.47×10^{-29} in standard pressure units.

Solution:

$$\Delta G^0 = -2.303 RT \log K_p$$

Where

$$R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$$

$$K_p = 2.47 \times 10^{-29}$$

$$T = 298\text{K}$$

$$\Delta G^0 = -2.303(8.314)(298)\log(2.47 \times 10^{-29})$$

$$\Delta G^0 = 163229 \text{ Jmol}^{-1}$$

$$\Delta G^0 = 163.229 \text{ KJ mol}^{-1}$$

7.12 Third law of Thermodynamics

The entropy of a substance varies directly with temperature. Lower the temperature, lower is the entropy. For example, water above 100°C at one atmosphere exists as a gas and has higher entropy (higher disorder). The water molecules are free to roam about in the entire container. When the system is cooled, the water vapour condenses to form a liquid. The water molecules in liquid phase still can move about somewhat freely. Thus the entropy of the system has decreased. On further cooling, water freezes to form ice crystal. The water molecules in the ice crystal are highly ordered and entropy of the system is very low.

If we cool the solid crystal still further, the vibration of molecules held in the crystal lattice gets slower and they have very little freedom of movement (very little disorder) and hence very small entropy.

At absolute zero $\{0 \text{ K (or) } -273^\circ \text{C}\}$, theoretically all modes of motion stop.

Absolute zero is a temperature that an object can get arbitrarily close to but absolute zero will remain unattainable.

Thus the third law of thermodynamics states that the entropy of pure crystalline substance at absolute zero is zero. Otherwise it can be stated as it is impossible to lower the temperature of an object to absolute zero in a finite number of steps. Mathematically,

$$\lim_{T \rightarrow 0} S = 0 \text{ for a perfectly ordered crystalline state.}$$

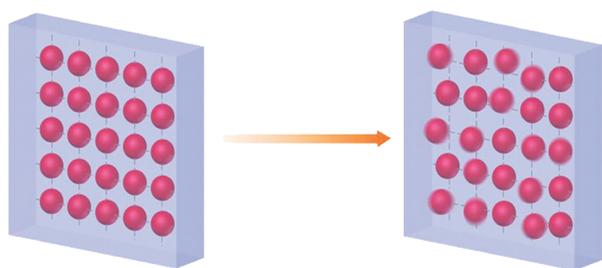


Figure 7.10 Third law of Thermodynamics

Crystals with defects (imperfection) at absolute zero, have entropy greater than zero. Absolute entropy of a substance can never be negative.

SUMMARY

The branch of science which deals the relation between energy, heat and work is called Thermodynamics. The main aim of the study of chemical thermodynamics is to learn (i) transformation of energy from one form into another form (ii) Utilization of various forms of energies.

System: A system is defined as any part of universe under consideration. There are three types of thermodynamic systems. They are (i) isolated system (ii) closed system and (iii) open system.

Surrounding: Everything in the universe that is not the part of the system is called surrounding.

Boundary: Anything which separates the system from its surrounding is called boundary.

Thermodynamic Properties: Any quantity that depends only on the state of system is called thermodynamic property of a system. There are two kinds of thermodynamic properties called (1) intensive - independent of the quantity of material and (2) extensive - directly proportional to the quantity of material. There are five basic thermodynamic properties. (U,H,S and G)

Thermodynamic Processes:

Adiabatic process in which no heat transfer takes place ($q = 0$)

Isothermal process in which

temperature remains constant ($dT = 0$).

Isobaric process in which pressure remains constant ($dP = 0$).

Isochoric process in which volume remains constant ($dV = 0$).

Cyclic process in which the system returns to its original state after completing a series of changes.

Internal energy (U): Internal energy of a system is equal to the energy possessed by all its constituents namely atoms, ions and molecules. The energy of a system of molecules is equal to the sum of its translational energy, vibrational energy, rotational energy, bond energy, electronic energy and energy due to molecular interactions.

Heat: Heat is regarded as the energy in transit across the boundary separating a system from its surrounding. Heat is a path function. The SI unit of heat is joule (J)

Work : Work is defined as the force (F) multiplied by the displacement $-w = F \cdot x$, work is measured in Joules, i.e the SI unit of work is Joule. During expansion or compression of a gas the work done is calculated by the relation $w = -P\Delta V$.

The sign conventions for heat and work are as follows:

If heat is absorbed by the system : +q

If heat is evolved by the system : -q

If work is done by the system : -w

If work is done on the system : +w

Laws of Thermodynamics:

Zerth law : When two systems are separately in equilibrium with a third system, they are in equilibrium with each other.

First law: "Energy can neither be created nor destroyed, but may be converted from one form to another".

$$\Delta U = q + w.$$

Enthalpy is a thermodynamic property of a system. Enthalpy H is defined as the sum of the internal energy and pressure volume work.

$$H=U+PV. \text{ Enthalpy change, } \Delta H = \Delta U + \Delta n_g RT.$$

Hess's law: It states that "the enthalpy change of a reaction either at constant volume or constant pressure is the same whether it takes place in a single or multiple steps". Hess's law can be applied to calculate enthalpies of reactions that are difficult to measure.

Heat capacities: [C_p and C_v]

Heat capacity is defined as the amount of energy required to increase the temperature of one unit quantity of material by one degree, under specific conditions. It can be measured under two different conditions, namely,

(a) constant pressure $C_p = (dH/dT)_p$

(b) constant volume $C_v = (dU/dT)_v$

Second law of thermodynamics:

The second law of thermodynamics helps us to predict whether the reaction is feasible or not and also tells the direction of the flow of heat.

To predict spontaneity of a process, a new thermodynamic quantity namely entropy (S) was introduced. Entropy is a measure of the randomness or disorderliness of the system.

Entropy statement: "whenever a spontaneous process takes place, it is accompanied by an increase in the total entropy of the universe".

Kelvin-Planck statement: It is impossible to take heat from a hotter reservoir and convert it completely into work by a cyclic process without transferring a part of that heat to a colder reservoir.

Clausius statement: This statement recognises that heat flows spontaneously from hot objects to cold objects and to get it flow in the opposite direction, we have to spend some work.

Gibbs Free Energy (G):

G is expressed as $G=H-TS$, free energy change of a process is given by the relation $\Delta G= \Delta H-T\Delta S$.

Standard free energy change and equilibrium constants are related by the equation $\Delta G^0 = -RT\ln K_{eq}$

Third law:

The entropy of a perfectly crystalline material at absolute zero is zero.

EVALUATION



I. Choose the best answer

- The amount of heat exchanged with the surrounding at constant pressure is given by the quantity
 - ΔE
 - ΔH
 - ΔS
 - ΔG
- All the naturally occurring processes proceed spontaneously in a direction which leads to
 - decrease in entropy
 - increase in enthalpy
 - increase in free energy
 - decrease in free energy
- In an adiabatic process, which of the following is true ?
 - $q = w$
 - $q = 0$
 - $\Delta E = q$
 - $P \Delta V = 0$
- In a reversible process, the change in entropy of the universe is
 - > 0
 - ≥ 0
 - < 0
 - $= 0$
- In an adiabatic expansion of an ideal gas
 - $w = -\Delta u$
 - $w = \Delta u + \Delta H$
 - $\Delta u = 0$
 - $w = 0$
- The intensive property among the quantities below is
 - mass
 - volume
 - enthalpy
 - $\frac{\text{mass}}{\text{volume}}$
- An ideal gas expands from the volume of $1 \times 10^{-3} \text{ m}^3$ to $1 \times 10^{-2} \text{ m}^3$ at 300 K against a constant pressure at $1 \times 10^5 \text{ Nm}^{-2}$. The work done is
 - 900 J
 - 900 kJ
 - 270 kJ
 - 900 kJ
- Heat of combustion is always
 - positive
 - negative
 - zero
 - either positive or negative
- The heat of formation of CO and CO₂ are - 26.4 kCal and - 94 kCal, respectively. Heat of combustion of carbon monoxide will be
 - + 26.4 kcal
 - 67.6 kcal
 - 120.6 kcal
 - + 52.8 kcal



10. $C(\text{diamond}) \rightarrow C(\text{graphite})$, $\Delta H = -ve$, this indicates that
- graphite is more stable than diamond
 - graphite has more energy than diamond
 - both are equally stable
 - stability cannot be predicted
11. The enthalpies of formation of Al_2O_3 and Cr_2O_3 are -1596 kJ and -1134 kJ , respectively.
 ΔH for the reaction $2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3$ is
- -1365 kJ
 - 2730 kJ
 - -2730 kJ
 - -462 kJ
12. Which of the following is not a thermodynamic function ?
- internal energy
 - enthalpy
 - entropy
 - frictional energy
13. If one mole of ammonia and one mole of hydrogen chloride are mixed in a closed container to form ammonium chloride gas, then
- $\Delta H > \Delta U$
 - $\Delta H - \Delta U = 0$
 - $\Delta H + \Delta U = 0$
 - $\Delta H < \Delta U$
14. Change in internal energy, when 4 kJ of work is done on the system and 1 kJ of heat is given out by the system is
- $+1 \text{ kJ}$
 - -5 kJ
 - $+3 \text{ kJ}$
 - -3 kJ
15. The work done by the liberated gas when 55.85 g of iron (molar mass 55.85 g mol^{-1}) reacts with hydrochloric acid in an open beaker at 25°C
- -2.48 kJ
 - -2.22 kJ
 - $+2.22 \text{ kJ}$
 - $+2.48 \text{ kJ}$
16. The value of ΔH for cooling 2 moles of an ideal monatomic gas from 125°C to 25°C at constant pressure will be $\left[\text{given } C_p = \frac{5}{2} R \right]$
- $-250 R$
 - $-500 R$
 - $500 R$
 - $+250 R$
17. Given that $C(g) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^0 = -a \text{ kJ}$; $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ $\Delta H^0 = -b \text{ kJ}$; Calculate the ΔH^0 for the reaction $C(g) + \frac{1}{2}O_2(g) \rightarrow CO(g)$
- $\frac{b+2a}{2}$
 - $2a - b$
 - $\frac{2a - b}{2}$
 - $\frac{b - 2a}{2}$



18. When 15.68 litres of a gas mixture of methane and propane are fully combusted at 0°C and 1 atmosphere, 32 litres of oxygen at the same temperature and pressure are consumed. The amount of heat released from this combustion in kJ is ($\Delta H_{\text{C}}(\text{CH}_4) = -890 \text{ kJ mol}^{-1}$ and $\Delta H_{\text{C}}(\text{C}_3\text{H}_8) = -2220 \text{ kJ mol}^{-1}$)
- a) -889 kJ b) -1390 kJ c) -3180 kJ d) -632.68 kJ
19. The bond dissociation energy of methane and ethane are 360 kJ mol^{-1} and 620 kJ mol^{-1} respectively. Then, the bond dissociation energy of C-C bond is
- a) 170 kJ mol^{-1} b) 50 kJ mol^{-1} c) 80 kJ mol^{-1} d) 220 kJ mol^{-1}
20. The correct thermodynamic conditions for the spontaneous reaction at all temperature is (NEET Phase - I)
- a) $\Delta H < 0$ and $\Delta S > 0$
b) $\Delta H < 0$ and $\Delta S < 0$
c) $\Delta H > 0$ and $\Delta S = 0$
d) $\Delta H > 0$ and $\Delta S > 0$
21. The temperature of the system, decreases in an _____
- a) Isothermal expansion b) Isothermal Compression c) adiabatic expansion
d) adiabatic compression
22. In an isothermal reversible compression of an ideal gas the sign of q , ΔS and w are respectively
- a) $+, -, -$ b) $-, +, -$ c) $+, -, +$ d) $-, -, +$
23. Molar heat of vapourisation of a liquid is 4.8 kJ mol^{-1} . If the entropy change is $16 \text{ J mol}^{-1} \text{ K}^{-1}$, the boiling point of the liquid is
- a) 323 K b) 27°C c) 164 K d) 0.3 K
24. ΔS is expected to be maximum for the reaction
- a) $\text{Ca}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CaO}(\text{s})$
b) $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
c) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$
d) $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

25. The values of ΔH and ΔS for a reaction are respectively 30 kJ mol^{-1} and $100 \text{ JK}^{-1} \text{ mol}^{-1}$. Then the temperature above which the reaction will become spontaneous is
- a) 300 K b) 30 K c) 100 K d) 20° C

II. Write brief answer to the following questions:

26. State the first law of thermodynamics.
27. Define Hess's law of constant heat summation.
28. Explain intensive properties with two examples
29. Define the following terms:
- a. isothermal process b. adiabatic process
- c. isobaric process d. isochoric process
30. What is the usual definition of entropy? What is the unit of entropy?
31. Predict the feasibility of a reaction when
- i) both ΔH and ΔS positive ii) both ΔH and ΔS negative
- iii) ΔH decreases but ΔS increases
32. Define is Gibb's free energy.
33. Define enthalpy of combustion.
34. Define molar heat capacity. Give its unit.
35. Define the calorific value of food. What is the unit of calorific value?
36. Define enthalpy of neutralization.
37. What is lattice energy?
38. What are state and path functions? Give two examples.
39. Give Kelvin statement of second law of thermodynamics.
40. The equilibrium constant of a reaction is 10, what will be the sign of ΔG ? Will this reaction be spontaneous?
41. Enthalpy of neutralization is always a constant when a strong acid is neutralized by a strong base: account for the statement.



42. State the third law of thermodynamics.
43. Write down the Born-Haber cycle for the formation of CaCl_2
44. Identify the state and path functions out of the following: a) Enthalpy b) Entropy c) Heat d) Temperature e) Work f) Free energy.
45. State the various statements of second law of thermodynamics.
46. What are spontaneous reactions? What are the conditions for the spontaneity of a process?
47. List the characteristics of internal energy.
48. Explain how heat absorbed at constant volume is measured using bomb calorimeter with a neat diagram.
49. Calculate the work involved in expansion and compression process.
50. Derive the relation between ΔH and ΔU for an ideal gas. Explain each term involved in the equation.
51. Suggest and explain an indirect method to calculate lattice enthalpy of sodium chloride crystal.
52. List the characteristics of Gibbs free energy.
53. Calculate the work done when 2 moles of an ideal gas expands reversibly and isothermally from a volume of 500 ml to a volume of 2 L at 25°C and normal pressure.
54. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298 K. The temperature of the calorimeter was found to increase from 298 K to 298.45 K due to the combustion process. Given that the calorimeter constant is 2.5 kJ K^{-1} . Calculate the enthalpy of combustion of the gas in kJ mol^{-1} .
55. Calculate the entropy change in the system, and surroundings, and the total entropy change in the universe during a process in which 245 J of heat flow out of the system at 77°C to the surrounding at 33°C .
56. 1 mole of an ideal gas, maintained at 4.1 atm and at a certain temperature, absorbs heat 3710J and expands to 2 litres. Calculate the entropy change in expansion process.
57. 30.4 kJ is required to melt one mole of sodium chloride. The entropy change during melting is $28.4 \text{ JK}^{-1} \text{ mol}^{-1}$. Calculate the melting point of sodium chloride.
58. Calculate the standard heat of formation of propane, if its heat of combustion is $-2220.2 \text{ kJ mol}^{-1}$. the heats of formation of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are -393.5 and $-285.8 \text{ kJ mol}^{-1}$ respectively.

59. You are given normal boiling points and standard enthalpies of vapourisation. Calculate the entropy of vapourisation of liquids listed below.

S. No	Liquid	Boiling points ($^{\circ}\text{C}$)	ΔH (kJ mol $^{-1}$)
1.	Ethanol	78.4	+ 42.4
2.	Toluene	110.6	+ 35.2

60. For the reaction $\text{Ag}_2\text{O}(\text{s}) \rightarrow 2\text{Ag}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g})$: $\Delta H = 30.56 \text{ kJ mol}^{-1}$ and $\Delta S = 6.66 \text{ JK}^{-1} \text{ mol}^{-1}$ (at 1 atm). Calculate the temperature at which ΔG is equal to zero. Also predict the direction of the reaction (i) at this temperature and (ii) below this temperature.

61. What is the equilibrium constant K_{eq} for the following reaction at 400K.



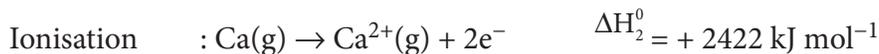
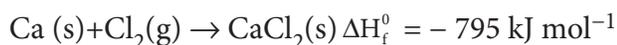
given that $\Delta H^{\circ} = 77.2 \text{ kJ mol}^{-1}$;

and $\Delta S^{\circ} = 122 \text{ JK}^{-1} \text{ mol}^{-1}$.

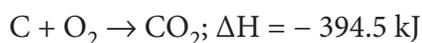
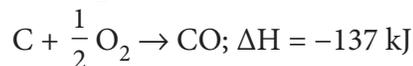
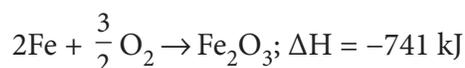
62. Cyanamide (NH_2CN) is completely burnt in excess oxygen in a bomb calorimeter, ΔU was found to be $-742.4 \text{ kJ mol}^{-1}$, calculate the enthalpy change of the reaction at 298K. $\text{NH}_2\text{CN}(\text{s}) + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$ $\Delta H = ?$

63. Calculate the enthalpy of hydrogenation of ethylene from the following data. Bond energies of C - H, C - C, C = C and H - H are 414, 347, 618 and 435 kJ mol^{-1} .

64. Calculate the lattice energy of CaCl_2 from the given data



65. Calculate the enthalpy change for the reaction $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$ from the following data.





66. When 1-pentyne (A) is treated with 4N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne(A) , 95.2% 2-pentyne(B) and 3.5% of 1,2 pentadiene (C) the equilibrium was maintained at 175°C, calculate ΔG^0 for the following equilibria.



67. At 33K, N_2O_4 is fifty percent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.

68. The standard enthalpies of formation of SO_2 and SO_3 are -297 kJ mol^{-1} and -396 kJ mol^{-1} respectively. Calculate the standard enthalpy of reaction for the reaction: $SO_2 + \frac{1}{2} O_2 \rightarrow SO_3$

69. For the reaction at 298 K : $2A + B \rightarrow C$

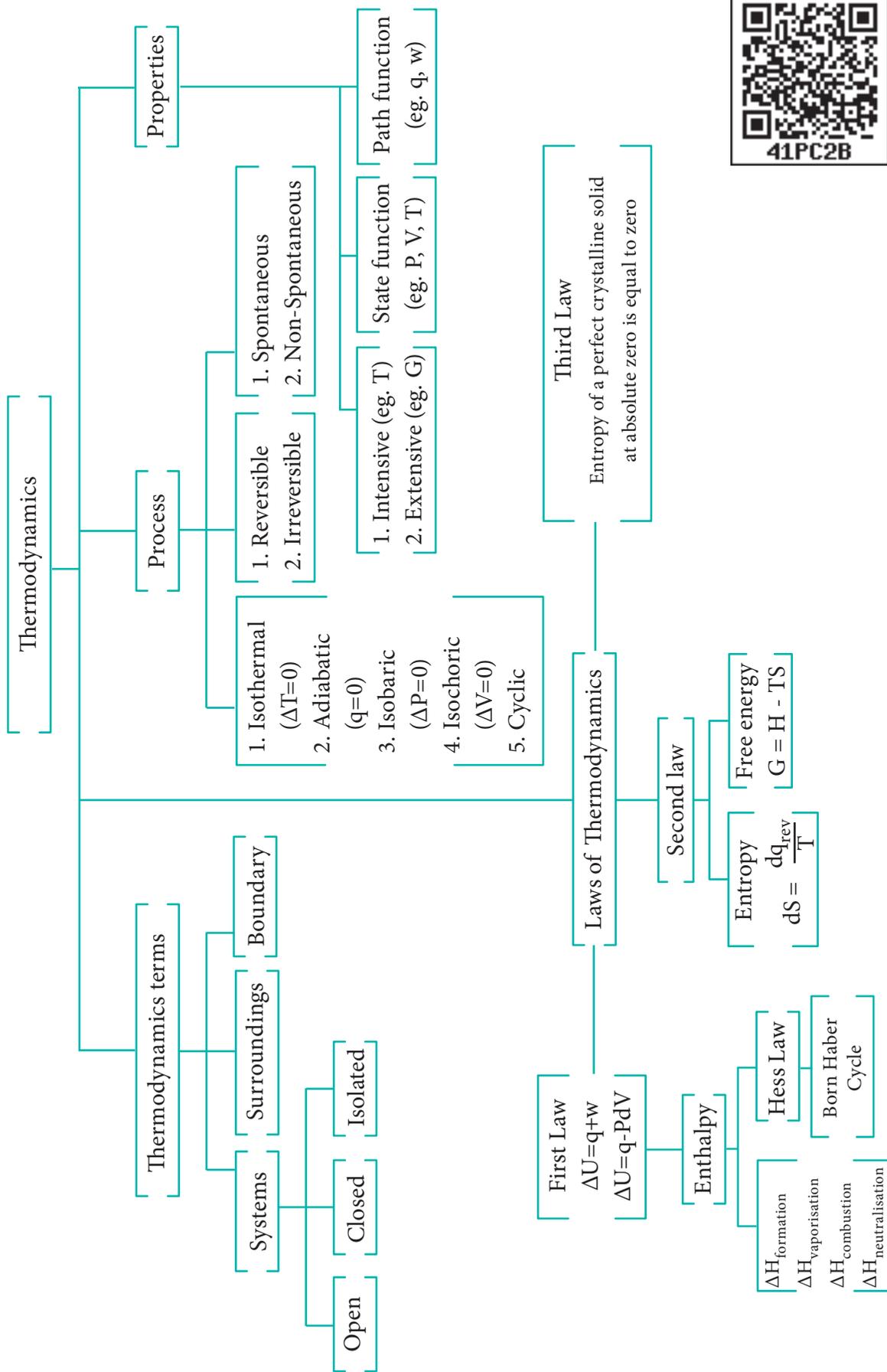
$\Delta H = 400 \text{ kJ mol}^{-1}$; $\Delta S = 0.2 \text{ KJK}^{-1} \text{ mol}^{-1}$ Determine the temperature at which the reaction would be spontaneous.

70. Find out the value of equilibrium constant for the following reaction at 298K, $2 NH_3(g) + CO_2 (g) \rightleftharpoons NH_2CONH_2 (aq) + H_2O (l)$ Standard Gibbs energy change, ΔG_r^0 at the given temperature is $-13.6 \text{ kJ mol}^{-1}$.

71. A gas mixture of 3.67 lit of ethylene and methane on complete combustion at 25°C and at 1 atm pressure produce 6.11 lit of carbondioxide. Find out the amount of heat evolved in kJ, during this combustion. ($\Delta H_C(CH_4) = -890 \text{ kJ mol}^{-1}$ and ($\Delta H_C(C_2H_4) = -1423 \text{ kJ mol}^{-1}$



CONCEPT MAP



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Fundamental constants

Avogadro number	N	6.022×10^{23}
Atomic mass unit (or) Unified atomic mass	amu (or) u	1.660×10^{-27} kg
Speed of light	c	2.997×10^8 m s ⁻¹
Elementary charge (or) Charge of an electron	e	1.602×10^{-19} C
Planck's constant	h	6.626×10^{-34} Js
Mass of electron	m_e	9.109×10^{-31} kg
Mass of proton	m_p	1.672×10^{-27} kg
Mass of neutron	m_n	1.674×10^{-27} kg
Bohr's radius	a_0	0.529 Å
Rydberg constant	R_∞	1.097×10^5 cm ⁻¹
Universal gas constant	R	8.314 J K ⁻¹ mol ⁻¹ 0.082 L atm K ⁻¹ mol ⁻¹ 1.987 cal K ⁻¹ mol ⁻¹ 62.36 L mmHg K ⁻¹ mol ⁻¹ 83.14 L mbar K ⁻¹ mol ⁻¹

Commonly used SI Prefixes

femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
f	p	n	μ	m	c	d	k	M	G
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^3	10^6	10^9

Inter - Conversion of Units

1 Å	=	10^{-10} m	
1 atm	=	101.325 kPa	= 1.01325×10^5 N m ⁻²
1 atm	=	1.01325×10^5 J m ⁻³	= 760 Torr (mmHg)
1 eV	=	1.60219×10^{-19} J	
1 N	=	1 J m ⁻¹	= 10^5 dyne
1 J	=	10^7 erg	= 1 Kg m ² s ⁻²
1 cal	=	4.184 J	

Critical constants of selected gases

Gas	Critical Pressure, P_c (atm)	Critical Volume, V_c (cm ³ mol ⁻¹)	Critical Temperature, T_c (K)
He	2.26	57.76	5.21
Ne	26.86	41.74	44.44
Ar	48.00	75.25	150.72
Kr	54.27	92.24	209.39
Xe	58.0	118.8	289.75
H ₂	12.8	64.99	33.23
N ₂	33.54	90.10	126.3
O ₂	50.14	78.0	154.8
Cl ₂	76.1	124	417.2
Br ₂	102	135	584
HCl	81.5	81.0	324.7
CO ₂	72.85	94.0	304.2
H ₂ O	218.3	55.3	647.4
NH ₃	111.3	72.5	405.5
CH ₄	45.6	98.7	190.6
C ₂ H ₄	50.50	124	283.1
C ₂ H ₆	48.20	148	305.4
C ₆ H ₆	48.6	260	562.7

Van der waals constants for select gases

Name	a (L ² bar mol ⁻²)	b (L mol ⁻¹)
Ammonia	4.225	0.0371
Benzene	18.24	0.1154
Carbon dioxide	3.64	0.04267
Carbon monoxide	1.505	0.03985
Chlorine	6.579	0.05622
Helium	0.0346	0.0238
Hexane	24.71	0.1735
Hydrogen	0.2476	0.02661
Hydrogen bromide	4.51	0.04431
Hydrogen chloride	3.716	0.04081
Hydrogen sulfide	4.49	0.04287
Mercury	8.2	0.01696
Methane	2.283	0.04278
Nitric oxide	1.358	0.02789
Nitrogen	1.37	0.0387
Nitrogen dioxide	5.354	0.04424
Nitrous oxide	3.832	0.04415
Oxygen	1.382	0.03186
Sulfur dioxide	6.803	0.05636
Water	5.536	0.03049

Molar heat capacities of select compounds:

	$C_{v,m}$ (J K ⁻¹ mol ⁻¹)	$C_{p,m}$ (J K ⁻¹ mol ⁻¹)
Gases		
Inert gases	12.48	20.79
H ₂	20.44	28.82
N ₂	20.74	29.12
O ₂	20.95	29.36
CO ₂	28.46	37.11
Liquids		
H ₂ O	-	75.29
CH ₃ OH	-	81.6
C ₂ H ₅ OH	-	111.5
C ₆ H ₆	-	136.1
Solids		
C (diamond)	-	6.11
Cu	-	244.4
Fe	-	25.1
SiO ₂	-	44.4

Standard heat of combustion (ΔH_f^0 , kJ mol⁻¹)

Methane(g)	=	- 890	Ethanol(l)	=	- 1368
Ethane(g)	=	- 1560	Acetic acid (l)	=	- 875
Propane(g)	=	- 2220	Benzoic acid (s)	=	- 3227
Butane(g)	=	- 2878	Glucose (s)	=	- 2808
Benzene(l)	=	- 3268	Sucrose (s)	=	- 5645
Methanol(l)	=	- 726			

Thermodynamic data for select compounds

	ΔH_f^0 (kJ mol ⁻¹)	ΔG_f^0 (kJ mol ⁻¹)	S^0 (J K ⁻¹ mol ⁻¹)
C (s, graphite)	0	0	5.740
H ₂ (g)	0	0	130.684
N ₂ (g)	0	0	191.61
O ₂ (g)	0	0	205.138
Cl ₂ (g)	0	0	223.07
Ag(s)	0	0	42.55
Cu(s)	0	0	33.150
Au(s)	0	0	47.40
Fe(s)	0	0	27.28
Zinc(s)	0	0	41.63
C(s, diamond)	1.895	2.900	2.377
CO(g)	-110.53	-137.17	197.67
CO ₂ (g)	-393.51	-394.36	213.74
HCl(g)	-92.31	-95.30	186.91
H ₂ O(l)	-285.83	-237.13	69.91
H ₂ O(g)	-241.82	-228.57	188.83
NH ₃ (g)	-46.11	-16.45	192.45
Methane(g)	-74.81	-50.72	186.26
Ethane(g)	-84.68	-32.82	229.60
Propane(g)	-103.85	-23.49	269.91
Butane(g)	-126.15	-17.03	310.23
Benzene(l)	49.0	124.3	173.3
Methanol(l)	-238.66	-166.27	126.8
Ethanol(l)	-277.69	-174.78	160.7

Lattice Enthalpies of alkali metal halides ($-\Delta H^0$ Lattice, kJ mol^{-1})

	F	Cl	Br	I
Li	1022	846	800	744
Na	902	771	733	684
K	801	701	670	629
Rb	767	675	647	609
Cs	716	645	619	585

C_p and C_v for Mono, di and tri atomic gases

	C_v Value	C_p Value ($C_p = R + C_v$)
Monatomic gas	$\frac{3}{2}R$	$\frac{5}{2}R$
Diatomic gas	$\frac{5}{2}R$	$\frac{7}{2}R$
Triatomic	$\frac{6}{2}R$	$\frac{8}{2}R$

Unit - 1

Basic Concepts of Chemistry and Chemical Calculations

Evaluate yourself :

1. (i) **Element** - Copper wire, Silver plate
(ii) **Compound** - Sugar, distilled water, carbon dioxide, Table salt, Naphthalene balls
(iii) **Mixture** - Sea water

2. (i) $\text{C}_2\text{H}_5\text{OH}$: $(2 \times 12) + (5 \times 1) + (1 \times 16) + (1 \times 1) = 46 \text{ g}$
(ii) KMnO_4 : $(1 \times 39) + (1 \times 55) + (4 \times 16) = 158 \text{ g}$
(iii) $\text{K}_2\text{Cr}_2\text{O}_7$: $(2 \times 39) + (2 \times 52) + (7 \times 16) = 294 \text{ g}$
(iv) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$: $(12 \times 12) + (22 \times 1) + (11 \times 16) = 342 \text{ g}$

3. (a) Molar mass of ethane, $\text{C}_2\text{H}_6 = (2 \times 12) + (6 \times 1) = 30 \text{ g mol}^{-1}$

$$n = \text{mass} / \text{molar mass} = 9 \text{ g} / 30 \text{ g mol}^{-1} = \mathbf{0.3 \text{ mole}}$$

- (b) At 273 K and 1 atm pressure 1 mole of a gas occupies a volume of 22.4 L

Therefore,

number of moles of oxygen, that occupies a volume of 224 ml at 273 K and 3 atm pressure

$$= \frac{1 \text{ mole}}{273 \text{ K} \times 1 \text{ atm} \times 22.4 \text{ L}} \times 0.224 \text{ L} \times 273 \text{ K} \times 3 \text{ atm}$$

$$= 0.03 \text{ mole}$$

1 mole of oxygen contains 6.022×10^{23} molecules

0.03 mole of oxygen contains $= 6.022 \times 10^{23} \times 0.03$

$$= \mathbf{1.807 \times 10^{22} \text{ molecules of oxygen}}$$

4. (a) Mass of the metal = 0.456 g

Mass of the metal chloride = 0.606 g

0.456 g of the metal combines with 0.15 g of chlorine.

Mass of the metal that combines with 35.5 g of chlorine is $\frac{0.456}{0.15} \times 35.5$

$$= \mathbf{107.92 \text{ g eq}^{-1}}.$$

$$\begin{aligned}
 \text{(b) Equivalent mass of a oxidising agent} &= \frac{\text{molar mass}}{\text{number of moles of electrons gained by one mole of the reducing agent}} \\
 &= \frac{294.2 \text{ g mol}^{-1}}{6 \text{ eq mol}^{-1}} \\
 &= \mathbf{49.0 \text{ g eq}^{-1}}
 \end{aligned}$$

5.

Element	Percentage Composition	Atomic mass	Relative no. of atoms = $\frac{\text{Percentage}}{\text{Atomic mass}}$	Simple ratio
C	54.55 %	12	$54.55/12 = 4.55$	$4.55 / 2.27 = 2$
H	9.09 %	1	$9.09 / 1 = 9.09$	$9.09 / 2.27 = 4$
O	36.36 %	16	$36.36/16 = 2.27$	$2.27/2.27 = 1$
Empirical formula (C₂H₄O)				

6.

Element	Percentage Composition	Relative no. of atoms = $\frac{\text{Percentage}}{\text{Atomic mass}}$	Atomic mass = $\frac{\text{Percentage}}{\text{Relative no. of atoms}}$	Simple ratio
X	32 %	2	16	4
Y	24 %	1	24	2
Z	44 %	0.5	88	1
Empirical formula (X₄Y₂Z)				

$$\begin{aligned}
 \text{Calculated empirical formula mass} &= (16 \times 4) + (24 \times 2) + 88 \\
 &= 64 + 48 + 88 = 200
 \end{aligned}$$

$$\begin{aligned}
 n &= \frac{\text{molar mass}}{\text{calculated empirical formula mass}} \\
 \therefore n &= \frac{400}{200} \\
 &= 2
 \end{aligned}$$

$$\therefore \text{Molecular formula (X}_4\text{Y}_2\text{Z)}_2 = \mathbf{X}_8\text{Y}_4\text{Z}_2$$

7.

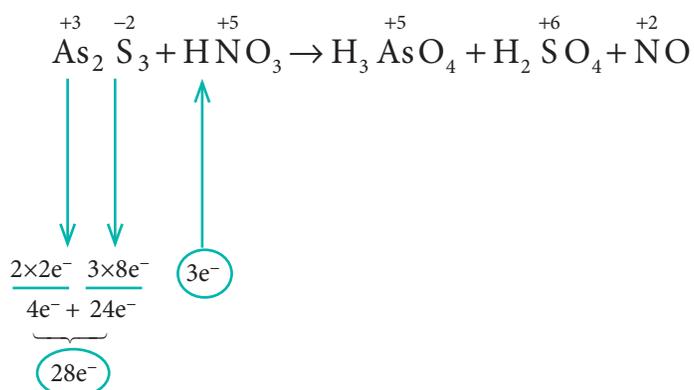
Content	Reactant		Products	
	x	y	l	m
Stoichiometric coefficient	2	3	4	1
No. of moles allowed to react	8	15	-	-
No. of moles of reactant reacted and product formed	8	12	16	4
No. of moles of un-reacted reactants and the product formed	-	3	16	4

Limiting reagent : x

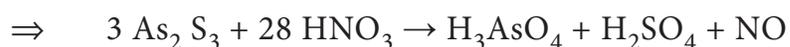
Product formed : 16 moles of l & 4 moles of m

Amount of excess reactant : 3 moles of y

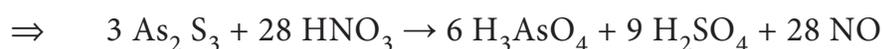
8.



Equate the total no. of electrons in the reactant side by cross multiplying,



Based on reactant side, balance the products



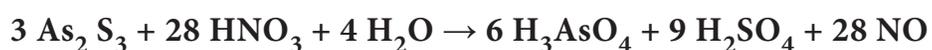
Product side : 36 hydrogen atoms & 88 oxygen atoms

Reactant side : 28 hydrogen atoms & 84 oxygen atoms

Difference is 8 hydrogen atoms & 4 oxygen atoms

∴ Add 4 H₂O molecule on the reactant side.

Balanced equation is,



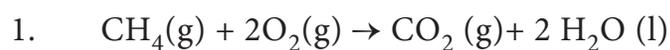
EVALUATION



I Choose the best answer

- (a) 40 ml of CO₂ gas
- (d) 200 u
- (c) assertion is true but reason is false
- (b) oxygen
- (a) 102 g
- (c) 6.022×10^{20}
- (c) 16 %
- (c) 0.075
- (d) 1 mole of HCl
- (c) $\text{BaCl}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + 2 \text{HCl}$
- (b) $\text{P}_4 + 3 \text{NaOH} + 3 \text{H}_2\text{O} \rightarrow \text{PH}_3 + 3 \text{NaH}_2\text{PO}_2$
- (b) 52.7
- (d) 6.022×10^{24} molecules of water
- (a) NO
- (a) 6.022×10^{23}
- (c) $\text{S}_2\text{O}_4^{2-} < \text{SO}_3^{2-} < \text{S}_2\text{O}_6^{2-} < \text{SO}_4^{2-}$
- (c) molar mass of ferrous oxalate / 3
- (d) the mass of one mole of carbon
- (c) the ratio between the number of molecules in A to number of molecules in B is 2:1
- (a) 3.59 g
- (b) 44 g mol^{-1}
- (c) both (a) & (b)
- (a) propene
- (a) relative atomic mass is 12 u
- (a) ${}_6\text{C}^{12}$

Key to the multiple choice questions



Content	CH_4	O_2	CO_2
Stoichiometric coefficient	1	2	1
Volume of reactants allowed to react	40 mL	80 mL	
Volume of reactant reacted and product formed	40 mL	80 mL	40 mL
Volume of gas after cooling to the room temperature	-	-	40 mL

Since the product was cooled to room temperature, water exists mostly as liquid.
Hence, option (a) is correct

2.

$$\frac{(200 \times 90) + (199 \times 8) + (202 \times 2)}{100} = 199.96$$

200 u

3. Correct reason: Total number of entities present in one mole of any substance is equal to 6.022×10^{23} .

4. Reaction 1 : $2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$
 2×12 g carbon combines with 32 g of oxygen. Hence,

$$\text{Equivalent mass of carbon} = \frac{2 \times 12}{32} \times 8 = 6$$

Reaction 2 : $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$

12 g carbon combines with 32 g of oxygen. Hence,

$$\text{Equivalent mass of carbon} = \frac{12}{32} \times 8 = 3$$

5. Let the trivalent metal be M^{3+}

Equivalent mass = mass of the metal / valance factor

9 g eq^{-1} = mass of the metal / 3 eq

Mass of the metal = 27 g

Oxide formed M_2O_3 ;

Mass of the oxide = $(2 \times 27) + (3 \times 16)$

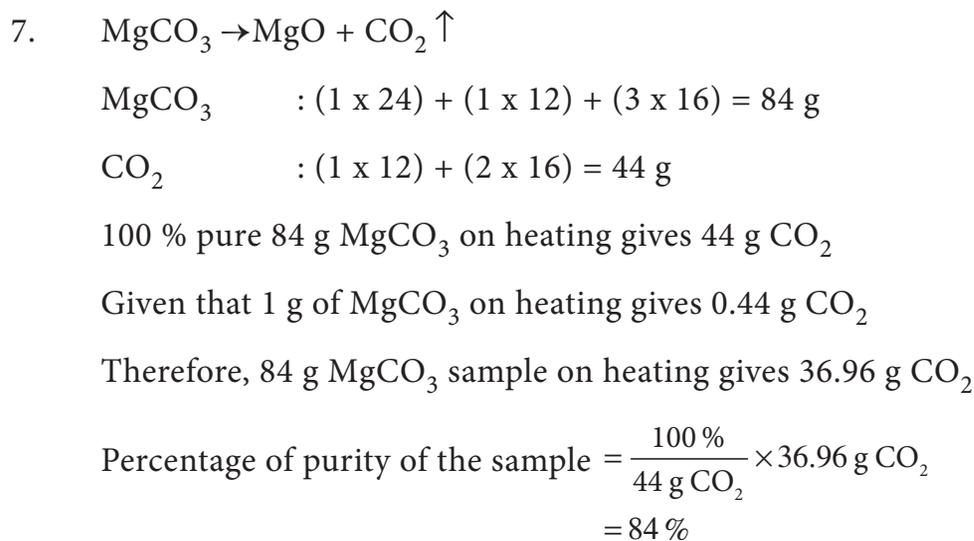
= **102 g**

6. Weight of the water drop = 0.018 g

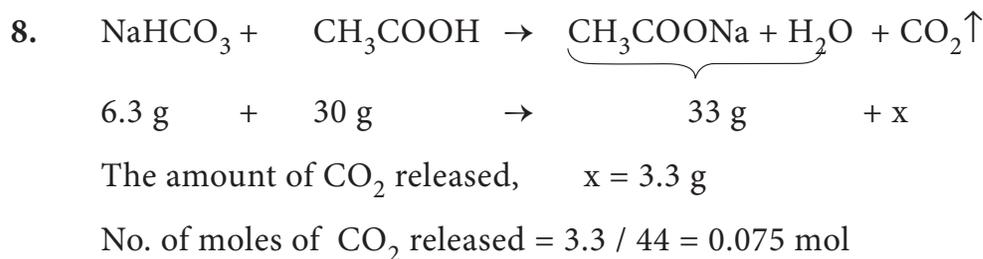
No. of moles of water in the drop = Mass of water / molar mass
 = $0.018 / 18 = 10^{-3}$ mole

No. of water molecules present in 1 mole of water = 6.022×10^{23}

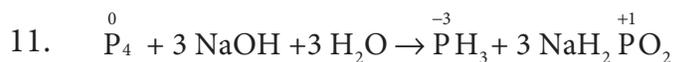
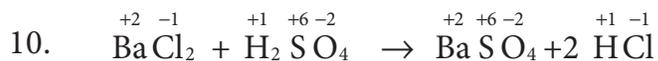
No. water molecules in one drop of water (10^{-3} mole) = $6.022 \times 10^{23} \times 10^{-3}$
 = **6.022×10^{20}**



Percentage of impurity = **16 %**



Content	$\text{H}_2(\text{g})$	$\text{Cl}_2(\text{g})$	$\text{HCl}(\text{g})$
Stoichiometric coefficient	1	1	2
No. of moles of reactants allowed to react at 273 K and 1 atm pressure	22.4 L (1 mol)	11.2 L (0.5 mol)	-
No. of moles of reactant reacted and product formed	0.5	0.5	1
Amount of HCl formed = 1 mol			



12. The reduction reaction of the oxidising agent (MnO_4^-) involves gain of 3 electrons. Hence the equivalent mass = (Molar mass of KMnO_4)/3 = $158.1/3 = 52.7$

13. No. of moles of water present in 180 g
 $= \text{Mass of water} / \text{Molar mass of water}$
 $= 180 \text{ g} / 18 \text{ g mol}^{-1} = 10 \text{ moles}$

One mole of water contains

$$= 6.022 \times 10^{23} \text{ water molecules}$$

10 mole of water contains = $6.022 \times 10^{23} \times 10 = 6.022 \times 10^{24}$ water molecules

14. 7.5 g of gas occupies a volume of 5.6 liters at 273 K and 1 atm pressure Therefore, the mass of gas that occupies a volume of 22.4 liters

$$= \frac{7.5 \text{ g}}{5.6 \text{ L}} \times 22.4 \text{ L} = 30 \text{ g}$$

Molar mass of NO (14+16) = 30 g

15. No. of electrons present in one ammonia (NH_3) molecule (7 + 3) = 10

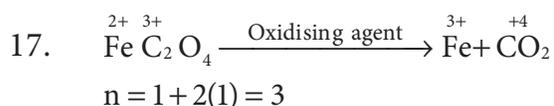
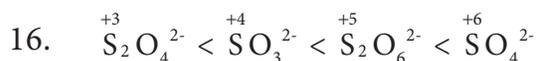
$$\begin{aligned} \text{No. of moles of ammonia} &= \frac{\text{Mass}}{\text{Molar mass}} \\ &= \frac{1.7 \text{ g}}{17 \text{ gmol}^{-1}} \\ &= 0.1 \text{ mol} \end{aligned}$$

No. of molecules present in 0.1 mol of ammonia

$$= 0.1 \times 6.022 \times 10^{23} = 6.022 \times 10^{22}$$

No. of electrons present in 0.1 mol of ammonia

$$= 10 \times 6.022 \times 10^{22} = 6.022 \times 10^{23}$$



18. The mass of one mole of carbon

$$\begin{aligned} 19. \text{ No. of moles of oxygen} &= 8 \text{ g}/32 \text{ g} \\ &= 0.25 \text{ moles of oxygen} \\ \text{No. of moles of sulphur dioxide} &= 8 \text{ g} / 64 \text{ g} \\ &= 0.125 \text{ moles of sulphur dioxide} \\ \text{Ratio between the no. of molecules} &= 0.25: 0.125 \\ &= 2:1 \end{aligned}$$

20. $\text{AgNO}_3 + \text{KCl} \rightarrow \text{KNO}_3 + \text{AgCl}$

50 mL of 8.5 % solution contains 4.25 g of AgNO_3

No. of moles of AgNO_3 present in 50 mL of 8.5 % AgNO_3 solution

$$\begin{aligned} &= \text{Mass} / \text{Molar mass} \\ &= 4.25 / 170 \\ &= 0.025 \text{ moles} \end{aligned}$$

Similarly, No of moles of KCl present in 100 mL of 1.865 % KCl solution

$$\begin{aligned} &= 1.865 / 74.5 \\ &= 0.025 \text{ moles} \end{aligned}$$

So total amount of AgCl formed is 0.025 moles (based on the stoichiometry)

Amount of AgCl present in 0.025 moles of AgCl

$$\begin{aligned} &= \text{no. of moles} \times \text{molar mass} \\ &= \mathbf{0.025 \times 143.5 = 3.59 \text{ g}} \end{aligned}$$

21. No. of moles of a gas that occupies a volume of 612.5 mL at room temperature and pressure (25°C and 1 atm pressure)

$$\begin{aligned} &= 612.5 \times 10^{-3} \text{ L} / 24.5 \text{ Lmol}^{-1} \\ &= 0.025 \text{ moles} \end{aligned}$$

We know that,

$$\begin{aligned} \text{Molar mass} &= \text{Mass} / \text{no. of moles} \\ &= \mathbf{1.1 \text{ g} / 0.025 \text{ mol} = 44 \text{ g mol}^{-1}} \end{aligned}$$

22. No. of moles of carbon present in 6 g of C-12 = Mass / Molar mass

$$= 6/12 = 0.5 \text{ moles} = 0.5 \times 6.022 \times 10^{23} \text{ carbon atoms.}$$

No. of moles in 8 g of methane = $8 / 16 = 0.5$ moles

$$= 0.5 \times 6.022 \times 10^{23} \text{ carbon atoms.}$$

No. of moles in 7.5 g of ethane = $7.5 / 30 = 0.25$ moles

$$= 2 \times 0.25 \times 6.022 \times 10^{23} \text{ carbon atoms.}$$

23. Percentage of carbon in ethylene (C_2H_4) = $\frac{\text{mass of carbon}}{\text{Molar mass}} \times 100$
 $= \frac{24}{28} \times 100 = 85.71\%$

$$\text{Percentage of carbon in propene (C}_3\text{H}_6) = \frac{36}{42} \times 100 = 85.71\%$$

24. (a) relative atomic mass of C-12 is 12 u

25. ${}_6C^{12}$

II Key to brief answer questions:

32. Given :

The density of CO_2 at 273 K and 1 atm pressure = 1.965 kgm^{-3}

Molar mass of $CO_2 = ?$

At 273 K and 1 atm pressure, 1 mole of CO_2 occupies a volume of 22.4 L

$$\begin{aligned} \text{Mass of 1 mole of } CO_2 &= \frac{1.965 \text{ Kg}}{1 \text{ m}^3} \times 22.4 \text{ L} \\ &= \frac{1.965 \times 10^3 \text{ g} \times 22.4 \times 10^{-3} \text{ m}^3}{1 \text{ m}^3} \\ &= 44.01 \text{ g} \end{aligned}$$

Molar mass of $CO_2 = 44 \text{ gmol}^{-1}$

33.

Compound		Given no. of moles	No. of oxygen atoms
Ethanol	- C ₂ H ₅ OH	1	1 × 6.022 × 10 ²³
Formic acid	- HCOOH	1	2 × 6.022 × 10 ²³
Water	- H ₂ O	1	1 × 6.022 × 10 ²³
Answer : Formic acid			

$$\begin{aligned}
 34. \quad \text{Average atomic mass} &= \frac{(78.99 \times 23.99) + (10 \times 24.99) + (11.01 \times 25.98)}{100} \\
 &= \frac{2430.9}{100} \\
 &= 24.31 \text{ u}
 \end{aligned}$$

35. Reaction : $x + y + z_2 \rightarrow xyz_2$

Question	Number of moles of reactants allowed to react			Number of moles of reactants consumed during reaction			Limiting reagent
	x	y	z ₂	x	y	z ₂	
(a)	200 atoms	200 atoms	50 molecules	50 atoms	50 atoms	50 molecules	z ₂
(b)	1 mol	1 mol	3 mol	1 mol	1 mol	1 mol	x and y
(c)	50 atom	25 atom	50 molecules	25 atom	25 atom	25 molecules	y
(d)	2.5 mol	5 mol	5 mol	2.5 mol	2.5 mol	2.5 mol	x

36. Given: mass of one atom = 6.645×10^{-23} g

$$\begin{aligned}
 \therefore \text{mass of 1 mole of atom} &= 6.645 \times 10^{-23} \text{ g} \times 6.022 \times 10^{23} \\
 &= 40 \text{ g}
 \end{aligned}$$

$$\begin{aligned}
 \therefore \text{number of moles of element in 0.320 kg} &= \frac{1 \text{ mole}}{40 \text{ g}} \times 0.320 \text{ kg} \\
 &= \frac{1 \text{ mol} \times 320 \text{ g}}{40 \text{ g}} \\
 &= 8 \text{ mol.}
 \end{aligned}$$

38.

Compound	Molecular formula	Empirical formula
Fructose	C ₆ H ₁₂ O ₆	CH ₂ O
Caffeine	C ₈ H ₁₀ N ₄ O ₂	C ₄ H ₅ N ₂ O

39. Given $2\text{Al} + \text{Fe}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}$

	Reactants		Products	
	Al	Fe_2O_3	Al_2O_3	Fe
Amount of reactant allowed to react	324 g	1.12 kg	-	-
Number of moles allowed to react	$\frac{324}{27} = 12 \text{ mol}$	$\frac{1.12 \times 10^3}{160} = 7 \text{ mol}$	-	-
Stoichiometric Co-efficient	2	1	1	2
Number of moles consumed during reaction	12 mol	6 mol	-	-
Number of moles of reactant unreacted and number of moles of product formed	-	1 mol	6 mol	12 mol

Molar mass of Al_2O_3 formed

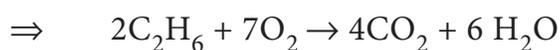
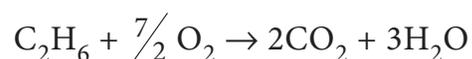
$$= 6 \text{ mol} \times 102 \text{ g mol}^{-1} \left[\begin{array}{l} \text{Al}_2\text{O}_3 \\ (2 \times 27) + 3(\times 16) \\ 54 + 48 = 102 \end{array} \right] = 612 \text{ g}$$

Excess reagent = Fe_2O_3

Amount of excess reagent left at the end of the reaction = $1 \text{ mol} \times 160 \text{ g mol}^{-1}$

$$= 160 \text{ g} \left[\begin{array}{l} \text{Fe}_2\text{O}_3 \\ (2 \times 56) + (3 \times 16) \\ 112 + 48 = 160 \end{array} \right] = 160 \text{ g}$$

40. Balanced equation for the combustion of ethane

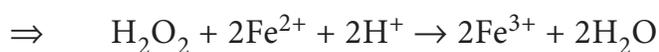
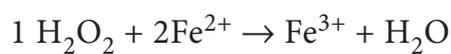
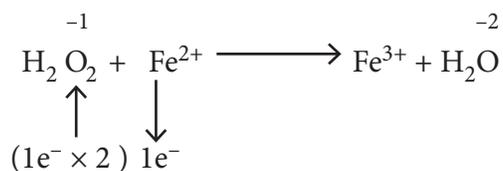


To produce 4 moles of CO_2 , 2 moles of ethane is required

\therefore To produce 1 mole (44 g) of CO_2 required

$$\begin{aligned}
 \text{number of moles of ethane} &= \frac{2 \text{ mol ethane}}{4 \text{ mol CO}_2} \times 1 \text{ mol CO}_2 \\
 &= \frac{1}{2} \text{ mole of ethane} \\
 &= \mathbf{0.5 \text{ mole of ethane}}
 \end{aligned}$$

41.



42.

Element	Percentage	Atomic mass	Relative number of atoms	Simple ratio	Whole no.
C	76.6	12	$\frac{76.6}{12} = 6.38$	$\frac{6.38}{1.06} = 6$	6
H	6.38	1	$\frac{6.38}{1} = 6.38$	$\frac{6.38}{1.06} = 6$	6
O	17.02	16	$\frac{17.02}{16} = 1.06$	$\frac{1.06}{1.06} = 1$	1

$$\text{Empirical formula} = \text{C}_6 \text{H}_6 \text{O}$$

$$n = \frac{\text{Molar mass}}{\text{Calculated empirical formula mass}}$$

$$= \frac{2 \times \text{vapour density}}{94} = \frac{2 \times 47}{94} = 1$$

$$\therefore \text{molecular formula } (\text{C}_6\text{H}_6\text{O}) \times 1 = \text{C}_6\text{H}_6\text{O}$$

43.

Element	%	Relative no. of atoms	Simple ratio
Na	14.31	$\frac{14.31}{23} = 0.62$	$\frac{0.62}{0.31} = 2$
S	9.97	$\frac{9.97}{32} = 0.31$	$\frac{0.31}{0.31} = 1$
H	6.22	$\frac{6.22}{1} = 6.22$	$\frac{6.22}{0.31} = 20$
O	69.5	$\frac{69.5}{16} = 4.34$	$\frac{4.34}{0.31} = 14$

∴ Empirical formula = Na₂ S H₂₀ O₁₄

$$n = \frac{\text{molar mass}}{\text{calculated empirical formula mass}} = \frac{322}{322} = 1$$

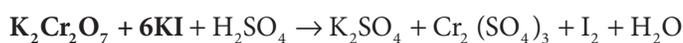
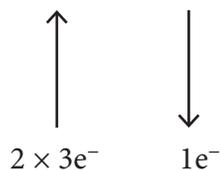
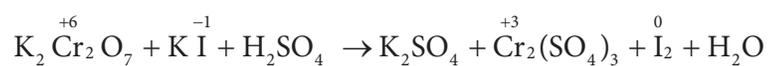
$$\left[\begin{array}{l} \text{Na}_2 \text{S H}_{20} \text{O}_{14} \\ = (2 \times 23) + (1 \times 32) + (20 \times 1) + 14(16) \\ = 46 + 32 + 20 + 224 \\ = 322 \end{array} \right]$$

Molecular formula = Na₂ S H₂₀ O₁₄

Since all the hydrogen in the compound present as water

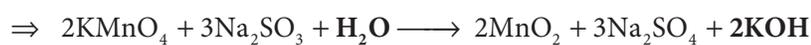
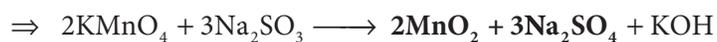
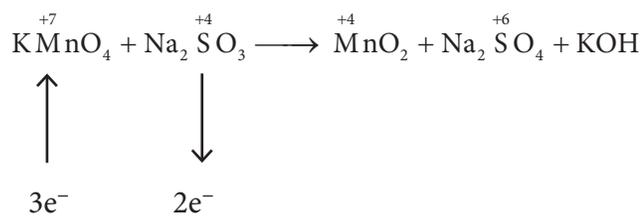
∴ Molecular formula is Na₂ SO₄ · 10H₂O

44. (i)

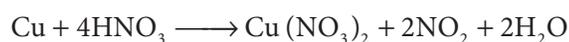
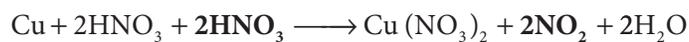
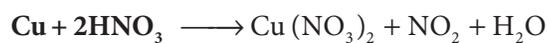
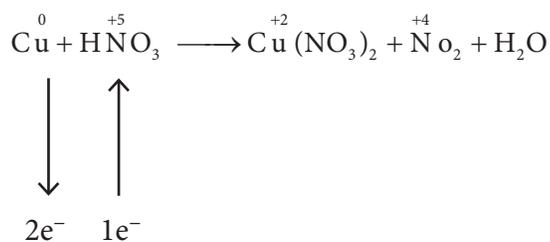




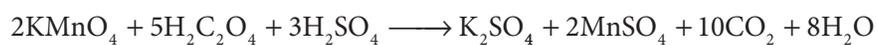
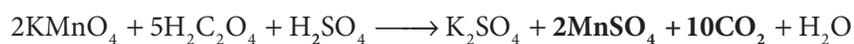
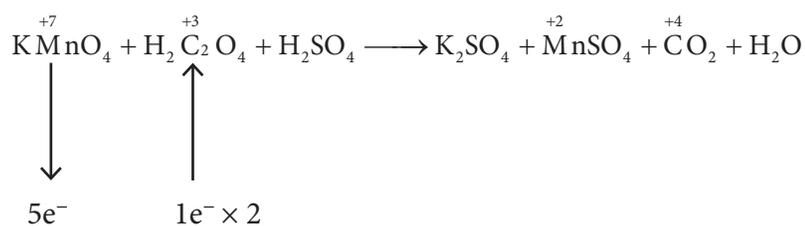
(ii)



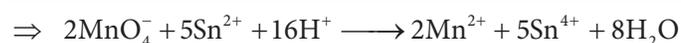
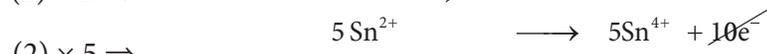
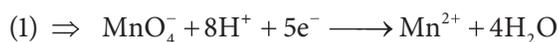
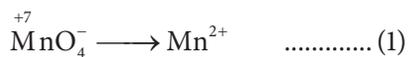
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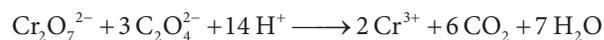
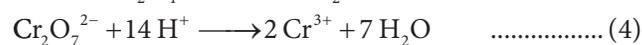
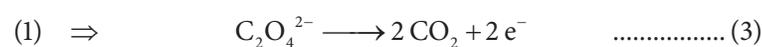
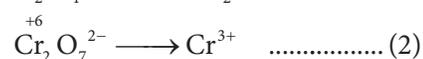
(iv)



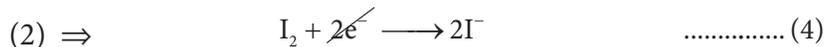
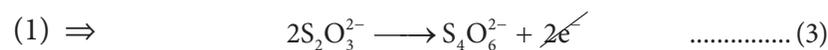
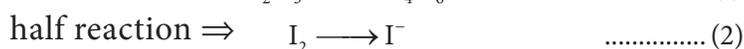
45. (i) Half reaction are



(ii)

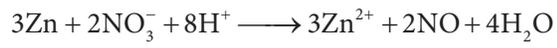
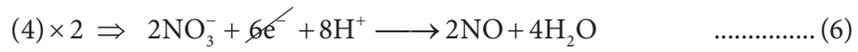
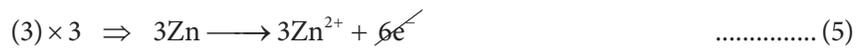
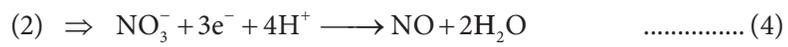


(iii)



(iv) Half reactions are





Unit - 2

Quantum Mechanical Model of Atom

Evaluate yourself:

1) Given: accelerated potential = 1 keV

The kinetic energy of the electron =
the energy due to accelerating potential.

$$\frac{1}{2}mv^2 = eV$$

$$mv^2 = 2eV$$

$$m^2v^2 = 2meV \Rightarrow (mv)^2 = 2meV$$

$$\Rightarrow mv = \sqrt{2meV}$$

$$\text{de Broglie wavelength } \lambda = \frac{h}{mv}$$

$$\Rightarrow \lambda = \frac{h}{\sqrt{2meV}}$$

$$m = \text{mass of the electron} = 9.1 \times 10^{-31} \text{ kg}$$

$$h = \text{Planck constant} = 6.626 \times 10^{-34} \text{ Js}$$

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{6.626 \times 10^{-34} \text{ Js}}{\sqrt{2 \times 9.1 \times 10^{-31} \text{ kg} \times 1 \text{ keV}}}$$

$$\lambda = \frac{6.626 \times 10^{-34} \text{ Js}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 1 \times 10^3 \times 1.6 \times 10^{-19} \text{ kgJ}}}$$

$$\lambda = 3.88 \times 10^{-11} \text{ m}$$

$$[\because \frac{\text{Js}}{\sqrt{\text{J kg}}} = \text{J}^{1/2} \text{kg}^{-1/2} \cdot \text{s}$$

$$= (\text{kgm}^2 \text{s}^{-2})^{1/2} \cdot \text{kg}^{-1/2} \text{ s}$$

$$= \text{m}]$$

2. Given

$$\Delta v = 5.7 \times 10^5 \text{ ms}^{-1} \quad \Delta x = ?$$

According to Heisenberg's uncertainty principle, $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$

$$\frac{h}{4\pi} = \frac{6.626 \times 10^{-34}}{4 \times 3.14} \text{ kgm}^2 \text{ s}^{-1}$$

$$\frac{h}{4\pi} = 5.28 \times 10^{-35}$$

$$\Delta x \cdot \Delta p \geq 5.28 \times 10^{-35}$$

$$\Delta x \cdot m \cdot \Delta v \geq 5.28 \times 10^{-35}$$

$$\Rightarrow \Delta x \geq \frac{5.28 \times 10^{-35} \text{ kgm}^2 \text{ s}^{-1}}{9.1 \times 10^{-31} \text{ kg} \times 5.7 \times 10^5 \text{ ms}^{-1}}$$

$$\Rightarrow \Delta x \geq 1.017 \times 10^{-10} \text{ m}$$

3. $n = 4$

$l = 0, 1, 2, 3$

\therefore 4 sub shells s, p, d & f.

$l = 0 \ m_l = 0 \Rightarrow$ one 4s orbital.

$l = 1 \ m_l = -1, 0, +1 \Rightarrow$ three 4p orbitals.

$l = 2 \ m_l = -2, -1, 0, +1, +2 \Rightarrow$ five 4d orbitals.

$l = 3 \ m_l = -3, -2, -1, 0, +1, +2, +3 \Rightarrow$ seven 4f orbitals.

Over all 16 orbitals are possible.

4.

Orbital	n	l	Radial node $n - l - 1$	Angular node l	Total node $n - 1$
3d	3	2	0	2	2
4f	4	3	0	3	3

5. $E_n = \frac{-13.6}{n^2} \text{eV}$

Second excited state

$n = 3 \quad \therefore E_3 = \frac{-13.6}{9} \text{eV}$
 $E_3 = -1.51 \text{eV}$

6. Electronic configuration of Fe^{3+} is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^5$

Five unpaired electrons.



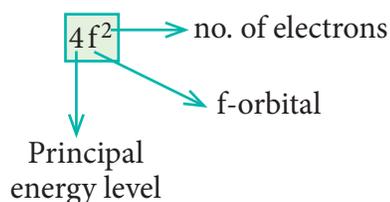
Electronic configuration of Mn^{2+} is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^5$

\therefore **Five unpaired electrons.**

Electronic configuration of Ar: $1s^2 2s^2 2p^6 3s^2 3p^6$

no unpaired electrons.

7.



$$n = 4 ; f \text{ orbital } l = 3 \Rightarrow m_l = -3, -2, -1, 0, +1, +2, +3$$

Out of two electrons, one electron occupies 4f orbital with $m_l = -3$ and another electron occupies 4f orbital with $m_l = -2$.

\therefore All the four quantum numbers for the two electrons are

Electron	n	l	m_l	m_s
$1e^-$	4	3	-3	+1/2
$2e^-$	4	3	-2	+1/2

8.

Electronic configuration of Fe^{3+} : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^5$

Electronic configuration of Ni^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^8$

Fe^{3+} has stable $3d^5$ half filled configuration.

EVALUATION

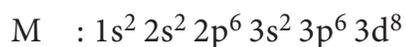
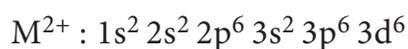


I Choose the best answer:

- (c) 30
- (c) $4.42 \times 10^{-18} \text{ J}$
- (b) $\lambda_1 = 2\lambda_2$
- (d) Stark effect
- (b)
- (d) $n=6$ to $n=5$
- (a)
- (c) $d_{z^2}, d_{x^2-y^2}$
- (b) Spin quantum number
- (b) $[Xe]4f^7 6s^2$; $[Xe]4f^7 5d^1 6s^2$;
 $[Xe]4f^9 6s^2$
- (c) $4l+2$
- (d) $\sqrt{6} h/2\pi$
- (c) 2
- (c)
- (a) 9
- (a) $ns \rightarrow (n-2)f \rightarrow (n-1)d \rightarrow np$
- (b) (ii),(iv) & (v)
- (b) 17
- (a) Zero
- (c) $1/2m \sqrt{h/\pi}$
- (c) $6.6 \times 10^{-31} \text{ cm}$
- (d) 0.4
- (d) $-9E$
- (a) $\hat{H}\psi = E\psi$
- (d) $\Delta E \cdot \Delta X \geq h/4\pi$

Key to multiple choice questions:

1.



Atomic number = 26

Mass number = 56

No. of neutrons = 56 - 26 = 30

2. $E = h\nu = hc/\lambda$

$$= \frac{6.626 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ m s}^{-1}}{45 \times 10^{-9} \text{ m}}$$

$$= 4.42 \times 10^{-18} \text{ J}$$

3.

$$\frac{E_1}{E_2} = \frac{25 \text{ eV}}{50 \text{ eV}} = \frac{1}{2}$$

$$\frac{hc}{\lambda_1} \times \frac{\lambda_2}{hc} = \frac{1}{2}$$

$$2\lambda_2 = \lambda_1$$

4. Splitting of spectral lines in magnetic field is called Zeeman effect and splitting of spectral lines in electric field, is called Stark effect.

5. **Correct statement:** For $n=1$, the electron has more negative energy than it does for $n=6$ which means that the electron is **strongly** bound in the smallest allowed orbit.

6. $n = 6$ to $n=5$

$$E_6 = -13.6 / 6^2; \quad E_5 = -13.6 / 5^2$$

$$E_6 - E_5 = (-13.6 / 6^2) - (-13.6 / 5^2)$$

$$= 0.166 \text{ eV atom}^{-1}$$

$$E_5 - E_4 = (-13.6 / 5^2) - (-13.6 / 4^2)$$

$$= 0.306 \text{ eV atom}^{-1}$$

9. Spin quantum number

For the first electron $m_s = +\frac{1}{2}$

For the second electron $m_s = -\frac{1}{2}$

10. Eu : [Xe] $4f^7, 5d^0, 6s^2$

Gd : [Xe] $4f^7, 5d^1, 6s^2$

Tb: [Xe] $4f^9, 5d^0, 6s^2$

11. $2(2l+1) = 4l+2$

12. Orbital angular momentum = $\sqrt{l(l+1)} h/2\pi$ For d orbital = $\sqrt{(2 \times 3)} h/2\pi = \sqrt{6} h/2\pi$

13. $n = 3; l=1; m = -1$

either $3p_x$ or $3p_y$

i.e., Maximum two electrons can be accommodated either in $3p_x$ or in $3p_y$

14. No. of radial node = $n-l-1$

No. of angular node = l

for $3p$ orbital

No. of angular node = $l = 1$

No. of radial node = $n-l-1 = 3-1-1 = 1$

15. $n = 3; l = 0; m_l = 0$ - one s orbital

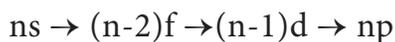
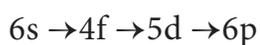
$n = 3; l = 1; m_l = -1, 0, 1$ - three p orbitals

$n = 3; l = 2; m_l = -2, -1, 0, 1, 2$ - five d Orbitals

Overall nine orbitals are possible.

16. $n = 6$

According Aufbau principle,



17 (ii) l can have the values from 0 to $n-1$

$n=2$; possible ' l ' values are 0, 1 hence $l = 2$ is not possible.

(iv) for $l=0$; $m=-1$ not possible

(v) for $n=3$ $l = 4$ and $m = 3$ not possible

18. $n+l = 8$

Electronic configuration of atom with atomic number 105 is $[\text{Rn}] 5f^{14} 6d^3 7s^2$

Orbital	($n+l$)	No. of electrons
5f	$5+3 = 8$	14
6d	$6+2 = 8$	3
7s	$7+0 = 7$	2
No of electrons = $14 + 3 = 17$		

19. Option (a) - Zero (Refer to Figure 2.9)

20.

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

$$\Delta p \cdot \Delta p \geq \frac{h}{4\pi}$$

$$\Delta p^2 \geq \frac{h}{4\pi}$$

$$m^2 (\Delta v)^2 \geq \frac{h}{4\pi}$$

$$(\Delta v) \geq \sqrt{\frac{h}{4\pi m^2}}$$

$$\Delta v \geq \frac{1}{2m} \sqrt{\frac{h}{\pi}}$$

21.

$$m = 100 \text{ g} = 100 \times 10^{-3} \text{ kg}$$

$$v = 100 \text{ cm s}^{-1} = 100 \times 10^{-2} \text{ m s}^{-1}$$

$$\lambda = \frac{h}{mv}$$

$$= \frac{6.626 \times 10^{-34} \text{ J s}^{-1}}{100 \times 10^{-3} \text{ kg} \times 100 \times 10^{-2} \text{ m s}^{-1}}$$

$$= 6.626 \times 10^{-33} \text{ m s}^{-1}$$

$$= 6.626 \times 10^{-31} \text{ cms}^{-1}$$

23.

$$E_n = \frac{-13.6}{n^2} \text{ eV atom}^{-1}$$

$$E_1 = \frac{-13.6}{(1)^2} = -13.6$$

$$E_3 = \frac{-13.6}{(3)^2} = -\frac{13.6}{9}$$

Givethat

$$E_3 = -E$$

$$-\frac{13.6}{9} = -E$$

$$-13.6 = -9E$$

$$\Rightarrow E_1 = -9E$$

II Key to brief answer question:

27. $n = 4$ $l = 0, 1, 2, 3$

four sub-shells \Rightarrow s, p, d, f

$l = 0$ $m_l = 0$; one 4s orbital.

$l = 1$ $m_l = -1, 0, +1$; three 4p orbitals.

$l = 2$ $m_l = -2, -1, 0, +1, +2$; five 4d orbitals.

$l = 3$ $m_l = -3, -2, -1, 0, +1, +2, +3$; seven 4f orbitals

Over all Sixteen orbitals.

28.

Orbital	n	l	Radial node $n - l - 1$	Angular node l
2s	2	0	1	0
4p	4	1	2	1
5d	5	2	2	2
4f	4	3	0	3

30. i) ground state

1	1	1	1	1
---	---	---	---	---

ii) maximum exchange energy

1	1	1	1	1
---	---	---	---	---

32.

Orbital	n	l
$3p_x$	3	1
$4d_{x^2-y^2}$	4	2

34.

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x \cdot \Delta p \geq 5.28 \times 10^{-35} \text{ Kg m}^2 \text{ s}^{-1}$$

$$\Delta x \cdot (m\Delta v) \geq 5.28 \times 10^{-35} \text{ Kg m}^2 \text{ s}^{-1}$$

Given $\Delta v = 0.1\%$

$$v = 2.2 \times 10^6 \text{ ms}^{-1}$$

$$m = 9.1 \times 10^{-31} \text{ Kg}$$

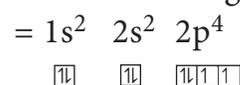
$$\Delta v = \frac{0.1}{100} \times 2.2 \times 10^6 \text{ ms}^{-1}$$

$$= 2.2 \times 10^3 \text{ ms}^{-1}$$

$$\therefore \Delta x \geq \frac{5.28 \times 10^{-35} \text{ Kg m}^2 \text{ s}^{-1}}{9.1 \times 10^{-31} \text{ Kg} \times 2.2 \times 10^3 \text{ ms}^{-1}}$$

$$\Delta x \geq 2.64 \times 10^{-8} \text{ m}$$

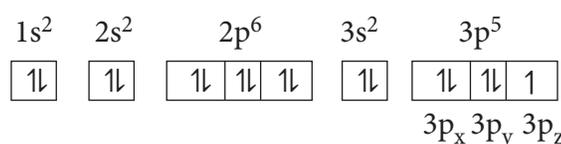
35. Electronic configuration of oxygen



\therefore 8th electron present in $2p_x$ orbital and the quantum numbers are

$$n = 2, l = 1, m_l = \text{either } +1 \text{ or } -1 \text{ and } s = -1/2$$

Electronic configuration of chlorine =



15th electron present in $3p_z$ orbital and the quantum numbers are $n = 3, l = 1, m_l = \text{either } +1 \text{ or } -1$ and $m_s = +1/2$

36.

$$E_n = \frac{-13.6}{n^2} \text{ eV atom}^{-1}$$

$$n = 3 \quad E_3 = \frac{-13.6}{3^2} = \frac{-13.6}{9} = -1.51 \text{ eV atom}^{-1}$$

$$n = 4 \quad E_4 = \frac{-13.6}{4^2} = \frac{-13.6}{16} = -0.85 \text{ eV atom}^{-1}$$

$$\Delta E = (E_4 - E_3) = (-0.85) - (-1.51)$$

$$\text{eV atom}^{-1}$$

$$= (-0.85 + 1.51)$$

$$= \mathbf{0.66 \text{ eV atom}^{-1}}$$

$$(1 \text{ eV} = 1.6 \times 10^{-19} \text{ J})$$

$$\Delta E = 0.66 \times 1.6 \times 10^{-19} \text{ J}$$

$$\Delta E = 1.06 \times 10^{-19} \text{ J}$$

$$h\nu = 1.06 \times 10^{-19} \text{ J}$$

$$\frac{hc}{\lambda} = 1.06 \times 10^{-19} \text{ J}$$

$$\therefore \lambda = \frac{hc}{1.06 \times 10^{-19} \text{ J}}$$

$$= \frac{6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1}}{1.06 \times 10^{-19} \text{ J}}$$

$$\lambda = 1.875 \times 10^{-6} \text{ m}$$

37. Given : de Broglie wavelength of the tennis ball equal to 5400 \AA .

$$m = 54 \text{ g}$$

$$v = ?$$

$$\lambda = \frac{h}{mV}$$

$$V = \frac{h}{m\lambda}$$

$$V = \frac{6.626 \times 10^{-34} \text{ Js}}{54 \times 10^{-3} \text{ Kg} \times 5400 \times 10^{-10} \text{ m}}$$

$$V = 2.27 \times 10^{-26} \text{ ms}^{-1}$$

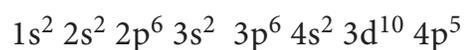
38.

n	l	Sub Energy levels	m_l values	Number of orbitals
4	2	4d	-2, -1, 0, +1, +2	five 4d orbitals
5	3	5f	-3, -2, -1, 0, +1, +2, +3	seven 5f orbitals
7	0	7s	0	one 7s orbitals

41. no. of electrons : 35 (given)

no. of protons : 35

Electronic configuration



last electron present in $4P_y$ orbital

$$n = 4 \quad l = 1 \quad m_l = \text{either } +1 \text{ or } -1 \text{ and } s = -1/2$$

43. $\text{He}^+ \rightarrow \text{He}^{2+} + e^-$

$$E_n = \frac{-13.6Z^2}{n^2}$$

$$E_1 = \frac{-13.6(2)^2}{(1)^2} = -54.4$$

$$E_\infty = \frac{-13.6(2)^2}{(\infty)^2} = 0$$

\therefore Required Energy for the given process = $E_\infty - E_1 = 0 - (-54.4) = 54.4 \text{ eV}$

44.

	Atom	Uni-negative ion
number of electron	$x - 1$	x
number of protons	$x - 1$	$x - 1$
number of neutrons	y	y

Given that, $y = x + 11.1\%$ of x

$$= \left(x + \frac{11.1}{100} x \right) = x + 0.111x$$

$$y = 1.111x$$

mass number = 37

number of protons + number of neutrons = 37

$$(x - 1) + 1.111x = 37$$

$$x + 1.111x = 38$$

$$2.111x = 38$$

$$x = \frac{38}{2.11}$$

$$x = 18.009 \quad x = 18 \text{ (whole number)}$$

$$\therefore \text{Atomic number} = x - 1 = 18 - 1 = 17$$

Mass number = 37

Symbol of the ion ${}_{17}^{37}\text{Cl}^-$

$$45) \quad r_n = \frac{(0.529)n^2}{z} \text{ \AA} \quad E_n = \frac{-13.6(z^2)}{n^2} \text{ eV atom}^{-1}$$

for Li^{2+} $z = 3$

Bohr radius for the third orbit (r_3)

$$= \frac{(0.529)(3)^2}{3}$$

$$= 0.529 \times 3$$

$$= 1.587 \text{ \AA}$$

Energy of an electron in the fourth orbit (E_4)

$$= \frac{-13.6(3)^2}{(4)^2}$$

$$= -7.65 \text{ eV atom}^{-1}$$

46) Given

$$v = 2.85 \times 10^8 \text{ ms}^{-1}$$

$$m_p = 1.673 \times 10^{-27} \text{ Kg}$$

$$\lambda = \frac{h}{mv}$$

$$= \frac{6.626 \times 10^{-34} \text{ kgm}^2 \text{ s}^{-1}}{1.673 \times 10^{-27} \text{ kg} \times 2.85 \times 10^8 \text{ ms}^{-1}}$$

$$\lambda = 1.389 \times 10^{-15} \Rightarrow \lambda = 1.389 \times 10^{-5} \text{ \AA}$$

$$[\because 1 \text{ \AA} = 10^{-10} \text{ m}]$$

47) $m = 160 \text{ g} = 160 \times 10^{-3} \text{ kg}$

$$v = 140 \text{ km hr}^{-1} = \frac{140 \times 10^3}{60 \times 60} \text{ ms}^{-1}$$

$$v = 38.88 \text{ ms}^{-1}$$

$$\lambda = \frac{h}{mv}$$

$$\lambda = \frac{6.626 \times 10^{-34} \text{ Kg m}^2 \text{ s}^{-1}}{160 \times 10^{-3} \text{ Kg} \times 38.88 \text{ ms}^{-1}}$$

$$\lambda = 1.065 \times 10^{-34} \text{ m}$$

48) $\Delta x = 0.6 \text{ \AA} = 0.6 \times 10^{-10} \text{ m}$

$$\Delta p = ?$$

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x \cdot \Delta p \geq 5.28 \times 10^{-35} \text{ kgm}^2 \text{ s}^{-1}$$

$$(0.6 \times 10^{-10}) \Delta p \geq 5.28 \times 10^{-35}$$

$$\Rightarrow \Delta p \geq \frac{5.28 \times 10^{-35} \text{ kgm}^2 \text{ s}^{-1}}{0.6 \times 10^{-10} \text{ m}}$$

$$\Delta p \geq 8.8 \times 10^{-25} \text{ kgms}^{-1}$$

49)

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

$$\lambda \cdot (m\Delta v) \geq \frac{h}{4\pi}$$

$$\Delta v \geq \frac{h}{4\pi(m\lambda)}$$

$$\Delta v \geq \frac{h}{4\pi \times m \times \frac{h}{mv}} \quad \left[\because \lambda = \frac{h}{mv} \right]$$

$$\Delta v \geq \frac{v}{4\pi}$$

Therefore,

$$\text{minimum uncertainty in velocity} = \frac{v}{4\pi}$$

50) Potential difference = 100V

$$= 100 \times 1.6 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{h}{\sqrt{2meV}}$$

$$= \frac{6.626 \times 10^{-34} \text{ Kg m}^2 \text{ s}^{-1}}{\sqrt{2 \times 9.1 \times 10^{-31} \text{ Kg} \times 100 \times 1.6 \times 10^{-19} \text{ J}}}$$

$$\lambda = 1.22 \times 10^{-10} \text{ m}$$

51)

n	l	m_l	sub energy level
4	2	0	4d
3	1	0	3p
5	1	any one value -1, 0, +1	5p
3	2	-2	3d

Unit - 3

Periodic classification of elements

Evaluate yourself

2. Atomic number : 120

IUPAC temporary symbol :
Unbinilium

IUPAC temporary symbol : Ubn

Possible electronic configuration :
:[Og] 8s²

3. Electronic Configuration : (n - 1)d²
ns²

for n = 5, the electronic configuration is,

1s² 2s² 2p⁶ 3s² 3p⁶ 4s² 3d¹⁰ 4p⁶ 4d²
5s² Atomic number : 40

4th group 5th period (d block element)
= Zirconium

4. Electronic Configuration of Aluminium

¹³Al $\underbrace{1s^2}_{(n-2)} \underbrace{2s^2 2p^6}_{(n-1)} \underbrace{3s^2 3p^1}_n$

Group	no. of electrons	Contribution of each electron to 'S' value	Contribution of a particular group
n	2	0.35	0.70
(n - 1)	8	0.85	6.80
(n - 2)	2	1	2.00
			9.50

∴ Effective nuclear charge = Z - S

= 13 - 9.5

(Z_{eff})_{Al} = 3.5

Electronic Configuration of chlorine

$\underbrace{1s^2}_{n-2} \underbrace{2s^2 2p^6}_{n-1} \underbrace{3s^2 3p^5}_n$

Group	no. of electrons	Contribution of each electron to 'S' value	Contribution of a particular group
n	6	0.35	2.1
(n - 1)	8	0.85	6.8
(n - 2)	2	1	2
		S =	10.9

∴ Effective nuclear charge = Z - S

= 17 - 10.9

(Z_{eff})_{Cl} = 6.1

(Z_{eff})_{Cl} > (Z_{eff})_{Al} and. Hence r_{Cl} < r_{Al}.

5.

X³⁺, Y²⁺, Z⁻ are isoelectronic.

∴ Effective nuclear charge is in the order (Z_{eff})_{Z⁻} < (Z_{eff})_{Y²⁺} < (Z_{eff})_{X³⁺} and

Hence, ionic radii should be in the order

r_{Z⁻} > r_{Y²⁺} > r_{X³⁺}

∴ The correct values are,

Species	Ionic radii
Z ⁻	136
Y ²⁺	64
X ³⁺	49

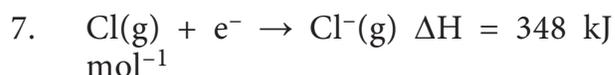
6. **Noble gases** : Ionization energy ranging from 2372 KJmol⁻¹ to 1037 kJ mol⁻¹.

For element X, the IE₁, value is in the

range of noble gas, moreover for this element both IE_1 and IE_2 are higher and hence X is the noble gas.

For Y, the first ionisation energy is low and second ionisation energy is very high and hence Y is most reactive metal.

For Z, both IE_1 and IE_2 are higher and hence it is least reactive.



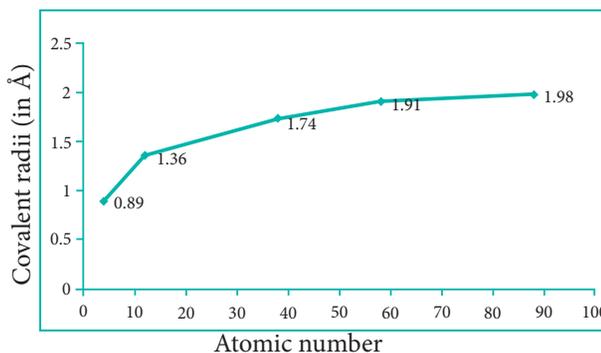
For one mole (35.5g) 348 kJ is released.

\therefore For 17.75g chlorine,
 $\frac{348 \text{ kJ}}{35.5 \text{ g}} \times 17.75 \text{ g}$ energy leased.

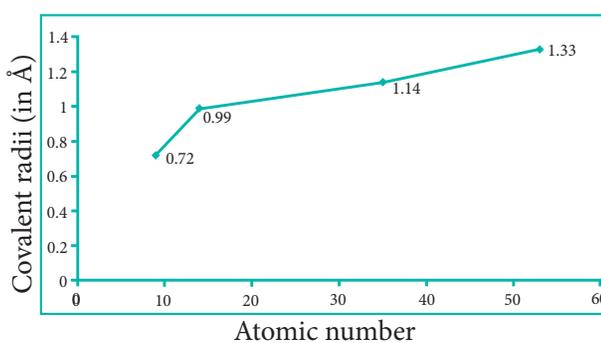
$$\therefore \text{The amount of energy released} = \frac{348}{2} = 174 \text{ kJ}$$

Activity : 3.1

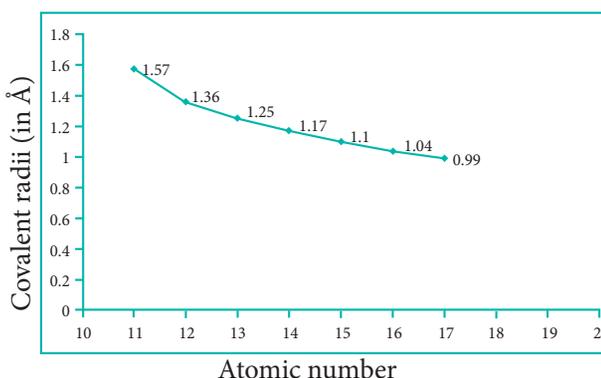
Covalent radii - 2nd group elements



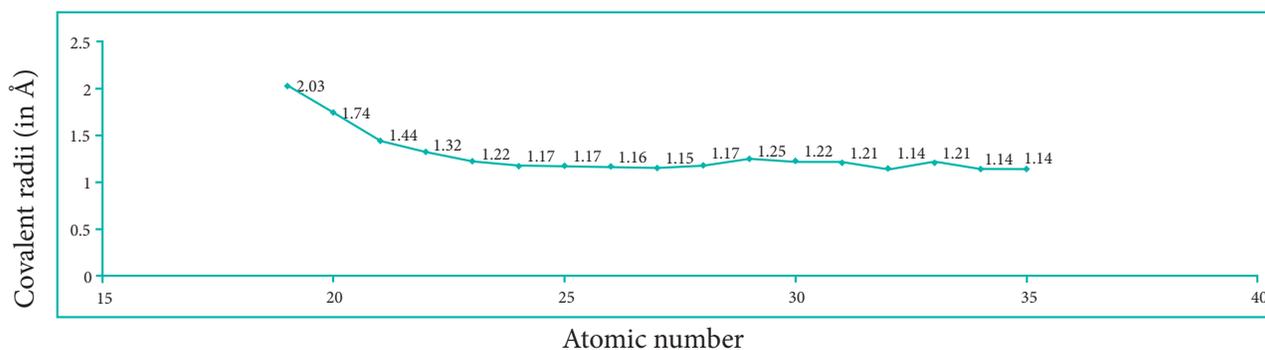
Covalent radii - 17th group elements



Covalent radii - 3rd period elements



Covalent radii - 4th period elements





EVALUATION



I Choose the best answer:

- (d) bismuth
- (b) AB_2
- (d) f-block elements
- (a) $I < Br < Cl < F$ (increasing electron gain enthalpy)
- (d) fluorine
- (c) Aluminium
- (b) $Na < Al < Mg < Si < P$
- (a)
- (d) $Ca < Al < C < O < F$
- (c) $Cl > F > Br > I$
- (d) Hydrogen
- (c) Argon
- (a) $Y > Z > X > A$
- (c)
- (a) $1s^2, 2s^2, 2p^6, 3s^1$
- (c) Oxygen
- (c) $+527 \text{ kcal mol}^{-1}$
- (a) $s > p > d > f$
- (d) None of these
- (b) 575 kJ mol^{-1}
- (a)
- (a) Generally increases
- (d) Be and Al

Unit - 4

Hydrogen

EVALUATION



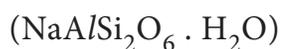
I Choose the best answer:

- (c)
- (c) $\text{CO} + \text{H}_2$
- (b)
- (d) group one elements
- (c) $1p+2n$
- (a) Palladium, Vanadium
- (a)
- (a) 1.2 g
- (d) EDTA
- (c) CaCl_2
- (a) sodium aluminium silicate
- (a)
- (c) $\text{CrO}(\text{O}_2)_2$
- (c) 5/2
- (d) 8.4
- (d) sp^3 and sp^3
- (c) monobasic acid
- (a) tetrahedrally by 4-H atoms
- (b) intra-molecular hydrogen bonding and inter molecular hydrogen bonding
- (c) both (a) & (b)
- (c) amphoteric oxide

Key for multiple choice questions:

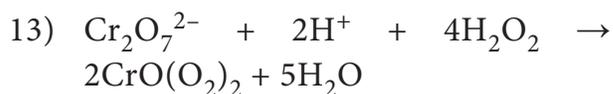
- Option (c)
Correct statement : Hydrogen has three isotopes of which **protium** is the most common.
- Option (c)
 $\text{CO} + \text{H}_2$ - Water gas
- Option (b)
Correct statement : Ortho isomer - one nuclear spin
Para isomer - zero nuclear spin
- Option (d)
eg : Sodium hydride ($\text{Na}^+ \text{H}^-$)
- Option (c)
 ${}_1\text{T}^3 (1e^-, 1p, 2n)$
- Option (a)
 $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{Na}^+$
- mass of deuterium = $2 \times$ mass of protium
If all the 1.2 g hydrogen is replaced with deuterium, the weight will become 2.4g. Hence the increase in body weight is $(2.4 - 1.2 = 1.2 \text{ g})$
Option (a)
- EDTA (option (d))
- Permanent hardness of water is due to the presence of the chlorides, nitrates and sulphates of Ca^{2+} and Mg^{2+} ions.
Option (c) CaCl_2

11) Zeolite is sodium aluminium silicate.

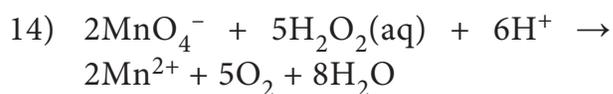


Option (a)

12) (a) 1 mL of H_2O_2 will give 100ml O_2 at STP.



Option (c)



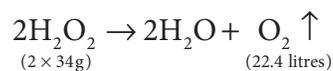
Option (c) 5/2 moles

15) Volume strength of hydrogen peroxide = Normality of hydrogen peroxide $\times 5.6$

$$= 1.5 \times 5.6$$

$$= 8.4$$

Option (d)



Volume strength of Hydrogen peroxide

$$= \frac{\text{Normality} \times \text{Equivalent weight of } \text{H}_2\text{O}_2 \times 22.4}{68}$$

$$= \text{Normality} \times \left(\frac{17 \times 22.4}{68} \right)$$

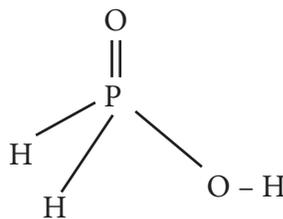
Volume strength of hydrogen peroxide

$$= \text{Normality} \times 5.6$$

16) sp^3 and sp^3

Option (d)

17) Hypophosphorus acid on reaction with D_2O , only one hydrogen is replaced by deuterium and hence it is mono basic

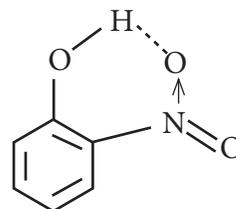


Option (c) monobasic acid

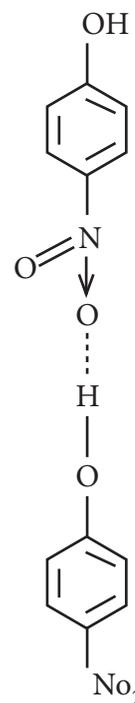
18) (a) tetrahedrally surrounded by 4 hydrogen atoms (refer 4.6 (a) Structure of ice)

19)

o-nitro phenol



p-nitro phenol



Option (b)

20) Heavy water is used as moderator as well as coolant in nuclear reactions.

Option (c)

21) Water is a amphoteric oxide.

Option (c)

Unit - 5

Alkali and Alkaline Earth Metals

EVALUATION



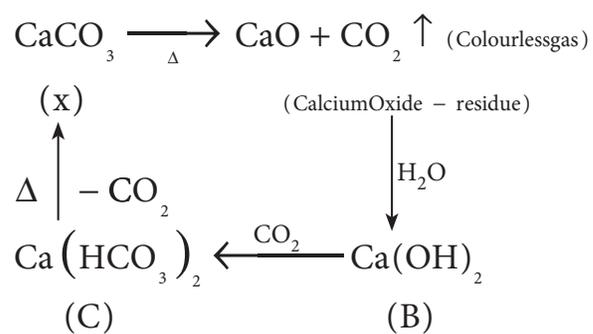
I Choose the best answer.

- (c) Density: $\text{Li} < \text{K} < \text{Na} < \text{Rb} < \text{C}$
- (a) Li^+ has minimum degree of hydration among alkali metal cations
- (d) none of these
- (b) Li
- (c) kerosene
- (a) superoxide and paramagnetic
- (c) Potassium carbonate can be prepared by solvay process
- (b) Magnesium
- (b) $\text{MI} < \text{MBr} < \text{MCl} < \text{MF}$
- (a) Castners process
- (c) $\text{Ca}(\text{CN})_2$
- (a) MgCl_2
- (a) p-2, q-1, r-4, s-5, t-6, u-3
- (d) both assertion and reason are false
- (a)
- (b) $\text{MgCO}_3 > \text{CaCO}_3 > \text{SrCO}_3 > \text{BaCO}_3$
- (c) Its salts are rarely hydrolysed
- (c) milk of lime
- (b) NaHCO_3
- (b) $\text{Ca}(\text{OH})_2$
- (a) Ca^{2+} ions are not important in maintaining the regular beating of the heart.
- (b) CaF_2
- (a) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
- (b) CaNCN
- (d) Li_2CO_3

Keys to multiple choice questions:

- Option (c)
Potassium is lighter than sodium
(Refer table 5.3)
The correct order of density is
 $\text{Li} < \text{K} < \text{Na} < \text{Rb} < \text{Cs}$
 $0.54 < 0.86 < 0.97 < 1.53 < 1.90$ (in g cm^{-3})
- Option (a)
 Li^+ has maximum degree of hydration among alkali metal cations.
 $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$
- All these compounds reacts with alkali metals to evolve hydrogen gas.
(d) none of these.
- hydration energy of Li^+ is more and hence Li^+ is stabilized in aqueous medium.
(b) Li
(c) Kerosene

20)



Option (b)

21) Ca^{2+} ion plays an important role in maintaining regular heart beat.

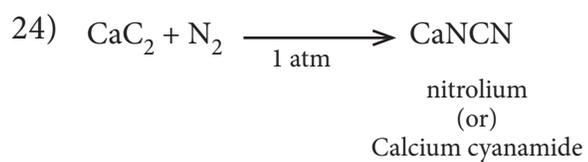
Option (a)

22) 'Blue john' - CaF_2

(A variety of fluorite)

\therefore Option (b)

23) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ \therefore Option (a)



\therefore Option (b)

25) Li_2CO_3 is least stable.

Option (d)

Unit - 6 Gaseous State

Evaluate yourself:

1. Volume of freon (V_1) = 1.5 dm^3

Pressure (P_1) = 0.3 atm

'T' is constant

P_2 = 1.2 atm

V_2 = ?

$\therefore P_1 V_1 = P_2 V_2$

$$\begin{aligned} \Rightarrow V_2 &= \frac{P_1 V_1}{P_2} \\ &= \frac{0.3 \text{ atm} \times 1.5 \text{ dm}^3}{1.2 \text{ atm}} \\ &= 0.375 \text{ dm}^3 \end{aligned}$$

\therefore Volume decreased from 1.5 dm^3
to 0.375 dm^3

2. $V_1 = 0.375 \text{ dm}^3$ $V_2 = 0.125$

$P_1 = 1.05 \text{ atm}$ $P_2 = ?$

'T' - Constant

$P_1 V_1 = P_2 V_2$

$$\begin{aligned} \therefore P_2 &= \frac{P_1 V_1}{V_2} = \frac{1.05 \times 0.375}{0.125} \\ &= 3.15 \text{ atm} \end{aligned}$$

3. $V_1 = 3.8 \text{ dm}^3$ $T_2 = 0^\circ\text{C} = 273 \text{ K}$

$T_1 = ?$ $V_2 = 2.27 \text{ dm}^3$

$$\begin{aligned} \frac{V_1}{T_1} &= \frac{V_2}{T_2} \quad T_1 = \left(\frac{T_2}{V_2} \right) \times V_1 \\ &= \frac{273 \text{ K}}{2.27 \text{ dm}^3} \times 3.8 \text{ dm}^3 \\ T_1 &= 457 \text{ K} \end{aligned}$$

4. $V_1 = 7.05 \text{ dm}^3$ $V_2 = 2.35 \text{ dm}^3$

$n_1 = 0.312 \text{ mol}$ $n_2 = ?$

'P' and 'T' are constant

$$\begin{aligned} \therefore \frac{V_1}{n_1} &= \frac{V_2}{n_2} \\ \Rightarrow n_2 &= \left(\frac{n_1}{V_1} \right) \times V_2 \\ n_2 &= \frac{0.312 \text{ mol}}{7.05 \text{ dm}^3} \times 2.35 \text{ dm}^3 \\ n_2 &= 0.104 \text{ mol} \end{aligned}$$

Number of moles exhaled =

$0.312 - 0.104 = 0.208 \text{ moles}$

5) $T_1 = 8^\circ\text{C} = 8 + 273 = 281 \text{ K}$

$P_1 = 6.4 \text{ atm}$ $V_1 = 2.1 \text{ ml}$

$T_2 = 25^\circ\text{C} = 25 + 273 = 298 \text{ K}$

$P_2 = 1 \text{ atm}$ $V_2 = ?$

$$\begin{aligned} \frac{P_1 V_1}{T_1} &= \frac{P_2 V_2}{T_2} \\ \Rightarrow V_2 &= \left(\frac{P_1 V_1}{T_1} \right) \times \frac{T_2}{P_2} \\ &= \frac{6.4 \text{ atm} \times 2.1 \text{ ml}}{281 \text{ K}} \times \frac{298 \text{ K}}{1 \text{ atm}} \\ V_2 &= 14.25 \text{ ml} \end{aligned}$$

6(a)

$V_{\text{O}_2} = 12 \text{ dm}^3$ $P = 1 \text{ atm}$

$V_{\text{He}} = 46 \text{ dm}^3$

$V_{\text{total}} = 5 \text{ dm}^3$

$$\begin{aligned} P_{\text{O}_2} &= x_{\text{O}_2} \times P_{\text{total}} & n_{\text{O}_2} &= \frac{1 \text{ mol}}{22.4 \text{ L}} \times 12 \text{ L} \\ x_{\text{O}_2} &= \frac{n_{\text{O}_2}}{n_{\text{O}_2} + n_{\text{He}}} & n_{\text{O}_2} &= 0.54 \text{ mol} \\ &= \frac{0.54}{0.54 + 2.05} & n_{\text{He}} &= \frac{1 \text{ mol}}{22.4 \text{ L}} \times 46 \text{ L} \\ &= \frac{0.54}{2.59} = 0.21 & n_{\text{He}} &= 2.05 \text{ mol} \end{aligned}$$

$$P_{\text{total}} \times V_{\text{total}} = 1 \text{ atm} \times 22.4 \text{ l}$$

$$\therefore P_{\text{total}} = \frac{1 \text{ atm} \times 22.4 \cancel{\text{ l}}}{5 \cancel{\text{ l}}}$$

$$P_{\text{total}} = 4.48 \text{ atm}$$

$$\begin{aligned} \therefore P_{\text{O}_2} &= 0.21 \times 4.48 \text{ atm} \\ &= 0.94 \text{ atm} \end{aligned}$$

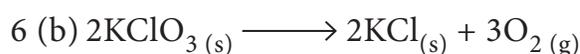
$$P_{\text{He}} = x_{\text{He}} \times P_{\text{total}}$$

$$\begin{aligned} x_{\text{He}} &= \frac{n_{\text{He}}}{n_{\text{O}_2} + n_{\text{He}}} \\ &= \frac{2.05}{0.54 + 2.05} \end{aligned}$$

$$x_{\text{He}} = \frac{2.05}{2.59} = 0.79$$

$$\therefore P_{\text{He}} = 0.79 \times 4.48 \text{ atm}$$

$$P_{\text{He}} = 3.54 \text{ atm}$$



$$P_{\text{total}} = 772 \text{ mm Hg}$$

$$P_{\text{H}_2\text{O}} = 26.7 \text{ mm Hg}$$

$$P_{\text{total}} = P_{\text{O}_2} + P_{\text{H}_2\text{O}}$$

$$\therefore P_{\text{O}_2} = P_{\text{total}} - P_{\text{H}_2\text{O}}$$

$$P_1 = 26.7 \text{ mm Hg} \quad T_2 = 295 \text{ K}$$

$$T_1 = 300 \text{ K} \quad P_2 = ?$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\Rightarrow P_2 = \left(\frac{P_1}{T_1} \right) T_2 = \frac{26.7 \text{ mm Hg}}{300 \text{ K}} \times 295 \text{ K}$$

$$P_2 = 26.26 \text{ mm Hg}$$

$$\therefore P_{\text{O}_2} = 772 - 26.26$$

$$= 745.74 \text{ mm Hg}$$

$$7) \quad t_1 = 1.5 \text{ minutes} \quad (\text{gas})_{\text{hydro carbon}}$$

$$t_2 = 4.73 \text{ minutes} \quad (\text{gas})_{\text{Bromine}}$$

$$\frac{\gamma_{\text{Hydrocarbon}}}{\gamma_{\text{Bromine}}} = \frac{t_{\text{Bromine}}}{t_{\text{Hydrocarbon}}}$$

(\because Volume is constant)

$$= \frac{4.73 \text{ minutes}}{1.5 \text{ minutes}}$$

$$= 3.15$$

$$\frac{\gamma_{\text{Hydrocarbon}}}{\gamma_{\text{Bromine}}} = \sqrt{\frac{M_{\text{Bromine}}}{M_{\text{hydrocarbon}}}}$$

$$3.15 = \sqrt{\frac{159.8 \text{ gmol}^{-1}}{M_{\text{hydro carbon}}}}$$

Squaring on both sides and rearranging,

$$M_{\text{hydro carbon}} = \frac{159.8 \text{ g mol}^{-1}}{(3.15)^2}$$

$$M_{\text{hydro carbon}} = 16.1 \text{ g mol}^{-1}$$

$$\begin{aligned} n(12) + (2n+2)1 &= 16 && \left[\begin{array}{l} \because \text{general formula} \\ \text{for hydrocarbon} \\ \text{C}_n\text{H}_{2n+2} \text{ (alkane)} \end{array} \right] \\ 12n + 2n + 2 &= 16 \end{aligned}$$

$$14n = 16 - 2$$

$$14n = 14$$

$$n = 1$$

$$\therefore \text{The hydro carbon is } \text{C}_1\text{H}_{2(1)+2} = \text{CH}_4$$

8) Critical temperature of a gas is defined as the temperature above which it cannot be liquified even at high pressures.

\therefore When cooling starts from 700 K, H_2O will liquify first, then followed by ammonia and finally carbondioxide will liquify.

EVALUATION



I Choose the correct answer:

1. (d) at high pressure the intermolecular interactions become significant
2. (d) inversely proportional to the square root of its molecular weight
3. (c) $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$
4. (b) exert no attractive forces on each other
5. (a) 1/3
6. (b) Boyle temperature
7. (c) diffusion
8. (b) near the hydrogen chloride bottle
9. (d) units of pressure and volume
10. (c) $8.3 \text{ J mol}^{-1} \text{ K}^{-1}$
11. (a) Boyle's Law
12. (c) NH_3
13. (d) I, II and III
14. (c) 0.41 dm^3
15. (c) P
16. (b) 4
17. (c) 1/8
18. (b) 1/T
19. (a) P
20. (b) NH_3
21. (c) $\text{mol}^{-1} \text{ L}$ and $\text{L}^2 \text{ atm mol}^{-2}$
22. (d) both assertion and reasons are false
23. (c) 3.41 g L^{-1}
24. (c)
25. (d) HI

Keys to multiple choice questions:

5. mass of methane
= mass of oxygen = a

$$\text{number of moles of methane} = \frac{a}{16}$$

$$\text{number of moles of Oxygen} = \frac{a}{32}$$

$$\begin{aligned} \text{mole fraction of Oxygen} &= \frac{\frac{a}{32}}{\frac{a}{16} + \frac{a}{32}} \\ &= \frac{\frac{a}{32}}{\frac{2a}{32} + \frac{a}{32}} \\ &= \frac{\frac{a}{32}}{\frac{3a}{32}} \\ &= \frac{1}{3} \end{aligned}$$

$$\begin{aligned} \text{Partial pressure of oxygen} \\ &= \text{mole fraction} \times \text{Total Pressure} \end{aligned}$$

$$= \frac{1}{3} P$$

6. The temperature at which real gases obey the ideal gas laws over a wide range of pressure is called Boyle temperature

8. Rate of diffusion $\propto 1/\sqrt{M}$

$$M_{\text{NH}_3} = 17 ; M_{\text{HCl}} = 36.5$$

$$\gamma_{\text{NH}_3} > \gamma_{\text{HCl}}$$

Hence white fumes first formed near hydrogen chloride

12. Higher the value of 'a', greater the intermolecular force of attraction, easier the liquefaction.

option (c) is correct

14.

$$\text{Compressibility factor } (z) = \frac{PV}{nRT}$$

$$V = \frac{z \times nRT}{P}$$

$$\begin{aligned} & 0.8697 \times 1 \times 8.314 \\ & \times 10^{-2} \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1} \\ & \times 400 \text{ K} \\ = & \frac{\quad}{71 \text{ bar}} \end{aligned}$$

$$V = 0.41 \text{ dm}^3$$

Option (c)

15. $T_1 \quad T_2 = 2T_1$

$$V_1 \quad V_2 = 2V_1$$

$$P_1 \quad P_2 = ?$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$P_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{V_2} = \frac{P_1 V_1}{T_1} \times \frac{2T_1}{2V_1}$$

$$P_2 = P_1$$

Option (c)

16.

$$\frac{\gamma_{\text{H}_2}}{\gamma_{\text{C}_n\text{H}_{2n+2}}} = \sqrt{\frac{M_{\text{C}_n\text{H}_{2n+2}}}{M_{\text{H}_2}}}$$

$$3\sqrt{3} = \sqrt{\frac{M_{\text{C}_n\text{H}_{2n+2}}}{2}}$$

Squaring on both sides and rearranging

$$27 \times 2 = M_{\text{C}_n\text{H}_{2n+2}}$$

$$54 = n(12) + (2n-2)(1)$$

$$54 = 12n + 2n - 2$$

$$54 = 14n - 2$$

$$n = (54+2)/14 = 56/14 = 4$$

Option (b)

17.

$$\frac{\gamma_{\text{O}_2}}{\gamma_{\text{H}_2}} = \sqrt{\frac{M_{\text{H}_2}}{M_{\text{O}_2}}} = \sqrt{\frac{2}{32}} = \frac{1}{4}$$

$$\gamma_{\text{O}_2} = \frac{1}{4} \gamma_{\text{H}_2}$$

The fraction of oxygen that escapes in the time required for one half of the hydrogen to escape is 1/8

Option (c)

18.

$$\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad [\text{For an ideal gas } PV = nRT]$$

$$= \frac{1}{V} \left(\frac{\partial \left(\frac{nRT}{P} \right)}{\partial T} \right)_P$$

$$= \frac{nR}{PV} \left(\frac{\partial T}{\partial T} \right) = \frac{nR}{nRT} = \frac{1}{T}$$

Option (b)

19. Greater the 'a' value, easier the liquefaction

$$21. \quad an^2/V^2 = \text{atm}$$

$$a = \text{atm L}^2/\text{mol}^2 = \text{L}^2 \text{ mol}^{-2} \text{ atm}$$

$$nb = \text{L}$$

$$b = \text{L/mol} = \text{L mol}^{-1}$$

Option (c)

22. **Correct Statement:** Critical temperature of CO_2 is 304 K. It means that CO_2 cannot be liquefied above 304 K, whatever the pressure may be applied.

Pressure is inversely proportional to volume

Option (d)

23.

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

$$= \frac{m}{\left(\frac{nRT}{P}\right)} = \left(\frac{m}{n}\right) \frac{P}{RT}$$

$$= \text{Molar mass} \times \frac{P}{RT}$$

$$= \frac{28 \text{ g mol}^{-1} \times 5 \text{ atm}}{0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 500 \text{ K}}$$
$$= 3.41 \text{ g L}^{-1}$$

Option (c)

24. For a fixed mass of an ideal gas $V \propto T$
 $P \propto 1/V$
and $PV = \text{Constant}$

Option (c)

25. At a given temperature and pressure

Volume \propto no. of moles

Volume \propto Mass / Molar mass

Volume $\propto 28 / \text{Molar mass}$

i.e. if molar mass is more, volume is less. Hence HI has the least volume

Option (d)

II Key to short answer questions:

$$44. \quad T_1 = 15^\circ \text{C} + 273 \quad T_2 = 38 + 273$$

$$T_1 = 288 \text{ K} \quad T_2 = 311 \text{ K}$$

$$V_1 = 2.58 \text{ dm}^3 \quad V_2 = ?$$

(P = 1 atm constant)

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \left(\frac{V_1}{T_1}\right) \times T_2$$

$$= \frac{2.58 \text{ dm}^3}{288 \text{ K}} \times 311 \text{ K}$$

$V_2 = 2.78 \text{ dm}^3$ i.e. volume increased from 2.58 dm^3 to 2.78 dm^3

$$45. \quad V_1 = 8.5 \text{ dm}^3 \quad V_2 = 6.37 \text{ dm}^3$$

$$T_1 = ? \quad T_2 = 0^\circ \text{C} = 273 \text{ K}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_1 \times \left(\frac{T_2}{V_2}\right) = T_1$$

$$T_1 = 8.5 \text{ dm}^3 \times \frac{273 \text{ K}}{6.37 \text{ dm}^3}$$

$$T_1 = 364.28 \text{ K}$$

$$46. \quad n_A = 1.5 \text{ mol} \quad n_B = ?$$

$$V_A = 37.6 \text{ dm}^3 \quad V_B = 16.5 \text{ dm}^3$$

(T = 298 K constant)

$$\frac{V_A}{n_A} = \frac{V_B}{n_B}$$

$$n_A = \left(\frac{n_B}{V_A}\right) V_B$$

$$= \frac{1.5 \text{ mol}}{37.6 \text{ dm}^3} \times 16.5 \text{ dm}^3$$

$$= 0.66 \text{ mol}$$

47. $n = 1.82 \text{ mole}$

$$V = 5.43 \text{ dm}^3$$

$$T = 69.5 + 273 = 342.5$$

$$P = ?$$

$$PV = nRT$$

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

$$= \frac{1.82 \text{ mol} \times 0.0821 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1} \times 342.5 \text{ K}}{5.43 \text{ dm}^3}$$

$$P = 9.425 \text{ atm}$$

48.

$$P_1 = 1.2 \text{ atm}$$

$$T_1 = 18^\circ \text{C} + 273 = 291 \text{ K}$$

$$T_2 = 85^\circ \text{C} + 273 = 358 \text{ K}$$

$$P_2 = ?$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$P_2 = \left(\frac{P_1}{T_1} \right) \times T_2$$

$$= \frac{1.2 \text{ atm}}{291 \text{ K}} \times 358 \text{ K}$$

$$P_2 = 1.48 \text{ atm}$$

49. $T_1 = 6^\circ \text{C} + 273 = 279 \text{ K}$

$$P_1 = 4 \text{ atm} \quad V_1 = 1.5 \text{ ml}$$

$$T_2 = 25^\circ \text{C} + 273 = 298 \text{ K}$$

$$P_2 = 1 \text{ atm} \quad V_2 = ?$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2}$$

$$= \frac{4 \text{ atm} \times 1.5 \text{ ml} \times 298 \text{ K}}{279 \text{ K} \times 1 \text{ atm}}$$

$$V_2 = 6.41 \text{ ml}$$

50. Given,

$$V = 154.4 \times 10^{-3} \text{ dm}^3,$$

$$P = 742 \text{ mm of Hg}$$

$$T = 298 \text{ K} \quad m = ?$$

$$n = \frac{PV}{RT} = \frac{742 \text{ mm Hg} \times 154.4 \times 10^{-3} \text{ L}}{62 \text{ mm Hg L K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}$$

$$= 0.006 \text{ mol}$$

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

$$\text{Mass} = n \times \text{Molar mass}$$

$$= 0.006 \times 2.016$$

$$= 0.0121 \text{ g} = 12.1 \text{ mg}$$

51.

$$\frac{\gamma_{\text{unknown}}}{\gamma_{\text{N}_2}} = \frac{t_{\text{N}_2}}{t_{\text{unknown}}} = \sqrt{\frac{M_{\text{N}_2}}{M_{\text{unknown}}}}$$

$$\frac{84 \text{ sec}}{192 \text{ sec}} = \sqrt{\frac{28 \text{ g mol}^{-1}}{M_{\text{unknown}}}}$$

On squaring both sides and rearranging

$$\left(\frac{84 \text{ sec}}{192 \text{ sec}} \right)^2 = \frac{28 \text{ g mol}^{-1}}{M_{\text{unknown}}}$$

$$M_{\text{unknown}} = 28 \text{ g mol}^{-1} \times \left(\frac{192 \text{ sec}}{84 \text{ sec}} \right)^2$$

$$M_{\text{unknown}} = 146.28 \text{ g mol}^{-1}$$

$$52. \quad m_{\text{O}_2} = 52.5 \text{ g} \quad P_{\text{O}_2} = ?$$

$$m_{\text{CO}_2} = 65.1 \text{ g} \quad P_{\text{CO}_2} = ?$$

$$T = 300 \text{ K} \quad P = 9.21 \text{ atm}$$

$$P_{\text{O}_2} = X_{\text{O}_2} \times \text{Total Pressure}$$

$$X_{\text{O}_2} = \frac{n_{\text{O}_2}}{n_{\text{O}_2} + n_{\text{CO}_2}}$$

$$n_{\text{O}_2} = \frac{\text{Mass of O}_2}{\text{Molar mass of O}_2}$$

$$= \frac{52.5 \text{ g}}{32 \text{ g mol}^{-1}} = 1.64 \text{ mol}$$

$$n_{\text{CO}_2} = \frac{\text{Mass of CO}_2}{\text{Molar mass of CO}_2}$$

$$= \frac{65.1 \text{ g}}{44 \text{ g mol}^{-1}} = 1.48 \text{ mol}$$

$$X_{\text{O}_2} = \frac{n_{\text{O}_2}}{n_{\text{O}_2} + n_{\text{CO}_2}} = \frac{1.64}{3.12} = 0.53$$

$$X_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{n_{\text{O}_2} + n_{\text{CO}_2}} = \frac{1.48}{3.12} = 0.47$$

$$P_{\text{O}_2} = X_{\text{O}_2} \times \text{Total pressure}$$

$$= 0.53 \times 9.21 \text{ atm} = 4.88 \text{ atm}$$

$$P_{\text{CO}_2} = X_{\text{CO}_2} \times \text{Total pressure}$$

$$= 0.47 \times 9.21 \text{ atm} = 4.33 \text{ atm}$$

53. Pressure of the gas in the tank at its melting point

$$T_1 = 298 \text{ K}; P_1 = 2.98 \text{ atm}; T_2 = 1100 \text{ K}; P_2 = ?$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\Rightarrow P_2 = \frac{P_1}{T_1} \times T_2$$

$$= \frac{2.98 \text{ atm}}{298 \text{ K}} \times 1100 \text{ K} = 11 \text{ atm}$$

At 1100 K the pressure of the gas inside the tank will become 11 atm. Given that tank can withstand a maximum pressure of 12 atm, the tank will start melting first.

Unit - 7 Thermodynamics

Evaluation Yourself

1.

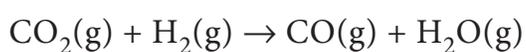
Solution :

Given

$$\Delta H_f^0 \text{ CO}_2 = -393.5 \text{ kJ mol}^{-1}$$

$$\Delta H_f^0 \text{ CO} = -111.31 \text{ kJ mol}^{-1}$$

$$\Delta H_f^0 (\text{H}_2\text{O}) = -242 \text{ kJ mol}^{-1}$$



$$\Delta H_r^0 = ?$$

$$\Delta H_r^0 = \sum (\Delta H_f^0)_{\text{products}} - \sum (\Delta H_f^0)_{\text{reactants}}$$

$$\Delta H_r^0 = [\Delta H_f^0 (\text{CO}) + \Delta H_f^0 (\text{H}_2\text{O})] - [\Delta H_f^0 (\text{CO}_2) + \Delta H_f^0 (\text{H}_2)]$$

$$\Delta H_r^0 = [-111.31 + (-242)] - [-393.5 + (0)]$$

$$\Delta H_r^0 = [-353.31] + 393.5$$

$$\Delta H_r^0 = 40.19$$

$$\Delta H_r^0 = +40.19 \text{ kJ mol}^{-1}$$

2.

Solution :

Given :

number of moles of water n

$$= \frac{180 \text{ g}}{18 \text{ g mol}^{-1}} = 10 \text{ mol}$$

molar heat capacity of water

$$C_p = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T_2 = 100^\circ \text{C} = 373 \text{ K}$$

$$T_1 = 25^\circ \text{C} = 298 \text{ K}$$

$$\Delta H = ?$$

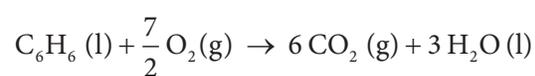
$$\Delta H = nC_p (T_2 - T_1)$$

$$\Delta H = 10 \text{ mol} \times 75.3 \text{ J mol}^{-1} \text{ K}^{-1} \times (373 - 298) \text{ K}$$

$$\Delta H = 56475 \text{ J}$$

$$\Delta H = 56.475 \text{ kJ}$$

3.



$$\Delta U \text{ at } 25^\circ \text{C} = -3268.12 \text{ kJ}$$

Solution :

Given

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

$$\Delta U = -3268.12 \text{ kJ mol}^{-1}$$

$$\Delta H = ?$$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\Delta H = \Delta U + (n_p - n_r) RT$$

$$\Delta H = -3268.12 + \left(6 - \frac{15}{2}\right) \times 8.314 \times 10^{-3} \times 298$$

$$\Delta H = -3268.12$$

$$- (1.5 \times 8.314 \times 10^{-3} \times 298)$$

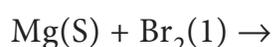
$$\Delta H = -3268.12 - 3.72$$

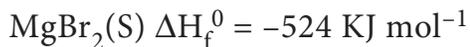
$$\Delta H = -3271.84 \text{ kJ mol}^{-1}$$

4.

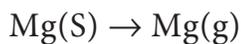
Solution :

Given :

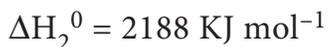




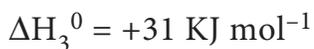
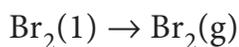
Sublimation :



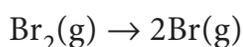
Ionisation :



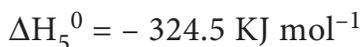
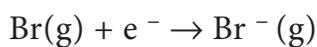
Vapourisation :



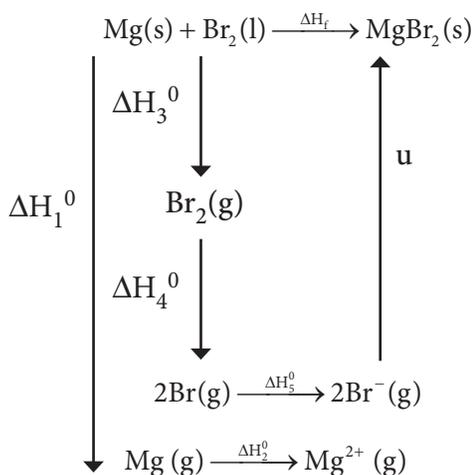
Dissociation :



Electron affinity :



Solution :



$$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + 2\Delta H_5 + u$$

$$-524 = 148 + 2188 + 31 + 193$$

$$+ (2 \times -324.5) + u$$

$$-524 = 1911 + u$$

$$u = -524 - 1911$$

$$u = -2435 \text{ kJ mol}^{-1}$$

5.

Solution:

Given

$$T_h = 127^\circ \text{C} = 127 + 273 = 400 \text{ K}$$

$$T_c = 47^\circ \text{C} = 47 + 273 = 320 \text{ K}$$

% efficiency $\eta = ?$

$$\eta = \left[\frac{T_h - T_c}{T_h} \right] \times 100$$

$$\eta = \left[\frac{400 - 320}{400} \right] \times 100$$

$$\eta = \left[\frac{80}{400} \right] \times 100$$

$$\eta = 20\%$$

6.

Solution:

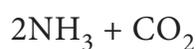
Given:

$$S^0(\text{urea}) = 173.8 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S^0(\text{H}_2\text{O}) = 70 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S^0(\text{CO}_2) = 213.5 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S^0(\text{NH}_3) = 192.5 \text{ J mol}^{-1} \text{ K}^{-1}$$



$$\Delta S_r^0 = \sum (S^0)_{\text{products}} - \sum (S^0)_{\text{reactants}}$$

$$\Delta S_r^0 = [2 S^0(\text{NH}_3) + S^0(\text{CO}_2)]$$



$$- [S^0(\text{urea}) + S^0(\text{H}_2\text{O})]$$

$$\Delta S_r^0 = [2 \times 192.5 + 213.5]$$

$$- [173.8 + 70]$$

$$\Delta S_r^0 = [598.5] - [243.8]$$

$$\Delta S_r^0 = 354.7 \text{ J mol}^{-1} \text{ K}^{-1}$$

7.

Solution:

Given:

$$T_b = 351 \text{ K}$$

$$\Delta H_{\text{vap}} = 39840 \text{ J mol}^{-1}$$

$$\Delta S_v = ?$$

$$\Delta S_v = \frac{\Delta H_{\text{vap}}}{T_b}$$

$$\Delta S_v = \frac{39840}{351}$$

$$\Delta S_v = 113.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

8.

Solution:

Given:

$$\Delta H = -10 \text{ kJ mol}^{-1} = -10000 \text{ J mol}^{-1}$$

$$\Delta S = -20 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = 300 \text{ K}$$

$$\Delta G = ?$$

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

$$\Delta G = -10 \text{ kJ mol}^{-1} - 300 \text{ K} \times (-20 \times 10^{-3}) \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\Delta G = (-10 + 6) \text{ kJ mol}^{-1}$$

$$\Delta G = -4 \text{ kJ mol}^{-1}$$

At 600 K

$$\Delta G = -10 \text{ kJ mol}^{-1} - 600 \text{ K}$$

$$\times (-20 \times 10^{-3}) \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\Delta G = (-10 + 12) \text{ kJ mol}^{-1}$$

$$\Delta G = +2 \text{ kJ mol}^{-1}$$

The value of ΔG is negative at 300K and the reaction is spontaneous, but at 600K the value ΔG becomes positive and the reaction is non spontaneous.

EVALUATION



I Choose the best answer:

- (b) ΔH
- (d) decrease in free energy
- (b) $q = 0$
- (d) $= 0$
- (a) $w = -\Delta U$
- (d) $\frac{\text{mass}}{\text{volume}}$
- (a) -900 J
- (b) negative
- (b) -67.6 kcal
- (a) graphite is more stable than diamond
- (d) -462 kJ
- (d) frictional energy
- (d) $\Delta H < \Delta U$
- (c) $+3 \text{ kJ}$
- (a) -2.48 kJ
- (b) -500 R
- (d) $\frac{b-2a}{2}$

18. (d) -635.66 kJ
 19. (c) 80 kJ mol^{-1}
 20. (a) $\Delta H < 0$ and $\Delta S > 0$
 21. (c) adiabatic expansion
 22. (d) $(-, -, +)$
 23. (b) 27°C
 24. (d) $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
 25. (a) 300K

Keys to multiple choice questions:

7.

$$w = -P \Delta V$$

$$w = -(1 \times 10^5 \text{ Nm}^{-2})$$

$$(1 \times 10^{-2} \text{ m}^3 - 1 \times 10^{-3} \text{ m}^3)$$

$$w = -10^5 (10^{-2} - 10^{-3}) \text{ Nm}$$

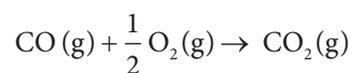
$$w = -10^5 (10 - 1) 10^{-3} \text{ J}$$

$$w = -10^5 (9 \times 10^{-3}) \text{ J}$$

$$w = -9 \times 10^2 \text{ J}$$

$$w = -900 \text{ J}$$

9.



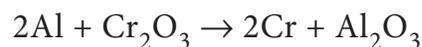
$$\Delta H_C^0(\text{CO}) = \Delta H_f(\text{CO}_2) - \Delta H_f(\text{CO}) + \Delta H_f(\text{O}_2)]$$

$$\Delta H_C^0(\text{CO}) = -94 \text{ KCal} - [-26.4 \text{ KCal} + 0]$$

$$\Delta H_C^0(\text{CO}) = -94 \text{ KCal} + 26.4 \text{ KCal}$$

$$\Delta H_C^0(\text{CO}) = -67.6 \text{ KCal}$$

11.



$$\Delta H_r^0 = [2\Delta H_f(\text{Cr}) + \Delta H_f(\text{Al}_2\text{O}_3)]$$

$$- [2\Delta H_f(\text{Al}) + \Delta H_f(\text{Cr}_2\text{O}_3)]$$

$$\Delta H_r^0 = [0 + (-1596 \text{ kJ})]$$

$$- [0 + (-1134)]$$

$$\Delta H_r^0 = -1596 \text{ kJ} + 1134 \text{ kJ}$$

$$\Delta H_r^0 = -462 \text{ kJ}$$

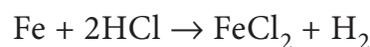
14.

$$\Delta U = q + w$$

$$\Delta U = -1 \text{ kJ} + 4 \text{ kJ}$$

$$\Delta U = +3 \text{ kJ}$$

15.



1 mole of Iron liberates 1 mole of Hydrogen gas

$$55.85 \text{ g Iron} = 1 \text{ mole Iron}$$

$$\therefore n = 1$$

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

$$w = -P \Delta V$$

$$w = -P \left(\frac{nRT}{P} \right)$$

$$w = -nRT$$

$$w = -1 \times 8.314 \times 298 \text{ J}$$

$$w = -2477.57 \text{ J}$$

$$w = -2.48 \text{ kJ}$$

16.

$$T_i = 125^\circ\text{C} = 398 \text{ K}$$

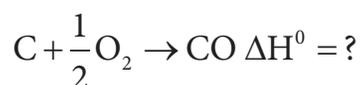
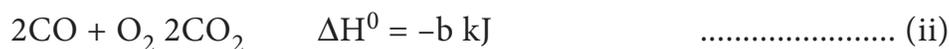
$$T_f = 25^\circ\text{C} = 298 \text{ K}$$

$$\Delta H = nC_p (T_f - T_i)$$

$$\Delta H = 2 \times \frac{5}{2} R (298 - 398)$$

$$\Delta H = - 500 R$$

17.



(i) $\times 2$



Reverse of equation (ii) will be



(iii) + (iv)



(v) $\div 2$



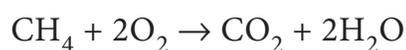
18.

Given :

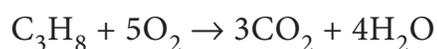
$$\Delta H_C (\text{CH}_4) = - 890 \text{ kJ mol}^{-1}$$

$$\Delta H_C (\text{C}_3\text{H}_8) = - 2220 \text{ kJ mol}^{-1}$$

Let the mixture contain x lit of CH_4 and $5(15.68 - x)$ lit of propane.



$$x \quad 2x$$



$$(15.68 - x) \quad 5(15.68 - x)$$

$$\text{Volume of oxygen consumed} = 2x + 5(15.68 - x) = 32 \text{ lit}$$

$$2x + 78.4 - 5x = 32 \text{ l}$$

$$78.4 - 3x = 32$$

$$3x = 46.4 \text{ l}$$

$$x = 15.47 \text{ l}$$

Given mixture contains 15.47 lit of methane and 0.213 lit of propane, hence

$$\Delta H_c = \left[\left(\frac{\Delta H_c (\text{CH}_4)}{22.4 \text{ lit}} \right) x \text{ lit} \right] + \left[\left(\frac{\Delta H_c (\text{C}_3\text{H}_8)}{22.4 \text{ lit}} \right) (15.68 - x) \text{ lit} \right]$$

$$\Delta H_c = \left[\left(\frac{-890 \text{ kJ mol}^{-1}}{22.4 \text{ lit}} \right) 15.47 \text{ lit} \right] + \left[\left(\frac{-2220}{22.4 \text{ lit}} \right) 0.21 \text{ lit} \right]$$

$$\Delta H_c = [-611.87 \text{ kJ mol}^{-1}] + [-20.81 \text{ kJ mol}^{-1}]$$

$$\Delta H_c = -632.68 \text{ KJ mol}^{-1}$$

19.

$$4E_{\text{C-H}} = 360 \text{ kJ mol}^{-1}$$

$$E_{\text{C-H}} = 90 \text{ kJ mol}^{-1}$$

$$E_{\text{C-C}} + 6 E_{\text{C-H}} = 620 \text{ kJ mol}^{-1}$$

$$E_{\text{C-C}} + 6 \times 90 = 620 \text{ kJ mol}^{-1}$$

$$E_{\text{C-C}} + 540 = 620 \text{ kJ mol}^{-1}$$

$$E_{\text{C-C}} = 80 \text{ kJ mol}^{-1}$$

22. During compression, energy of the system increases, in isothermal condition, to maintain temperature constant, heat is liberated from the system. Hence q is negative.

During compression entropy decreases.

During compression work is done on the system, hence w is positive

23.

$$\Delta S_v = \frac{\Delta H_v}{T_b}$$

$$T_b = \frac{\Delta H_v}{\Delta S_v} = \frac{4800 \text{ J mol}^{-1}}{16 \text{ J mol}^{-1} \text{ K}^{-1}} = 300 \text{ K} = 27^\circ \text{C}$$

24. In $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$, entropy change is positive. **in option d, A solid reactant gives a gaseous product. Hence the entropy change is expected to be maximum for this process.**

25.

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

At 300K

$$\Delta G = 30000 \text{ J mol}^{-1} - 300 \text{ K} \\ \times 100 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta G = 0$$

above 300 K ; ΔG will be negative and reaction becomes spontaneous.

I Keys to the short answer questions:

53.

SOLUTION :

Given :

$$n = 2 \text{ moles}$$

$$V_i = 500 \text{ ml} = 0.5 \text{ lit}$$

$$V_f = 2 \text{ lit}$$

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

$$w = -2.303 nRT \log \left(\frac{V_f}{V_i} \right)$$

$$w = -2.303 \times 2 \times 8.314 \times 298 \\ \times \log \left(\frac{2}{0.5} \right)$$

$$w = -2.303 \times 2 \times 8.314 \\ \times 298 \times \log(4)$$

$$w = -2.303 \times 2 \times 8.314 \\ \times 298 \times 0.6021$$

$$w = -6871 \text{ J}$$

$$w = -6.871 \text{ kJ}$$

54.

SOLUTION :**Given :**

$$T_i = 298 \text{ K}$$

$$T_f = 298.45 \text{ K}$$

$$k = 2.5 \text{ kJ K}^{-1}$$

$$m = 3.5 \text{ g}$$

$$M_m = 28$$

$$\text{heat evolved} = k \Delta T$$

$$= k (T_f - T_i)$$

$$= 2.5 \text{ kJ K}^{-1} (298.45 - 298) \text{ K}$$

$$= 1.125 \text{ kJ}$$

$$\Delta H_c = \frac{1.125}{3.5} \times 28 \text{ kJ mol}^{-1}$$

$$\Delta H_c = 9 \text{ kJ mol}^{-1}$$

55.

SOLUTION :**Given :**

$$T_{\text{sys}} = 77^\circ \text{C} = (77 + 273) = 350 \text{ K}$$

$$T_{\text{surr}} = 33^\circ \text{C} = (33 + 273) = 306 \text{ K}$$

$$q = 245 \text{ J}$$

$$\Delta S_{\text{sys}} = \frac{q}{T_{\text{sys}}} = \frac{-245}{350} = -0.7 \text{ JK}^{-1}$$

$$\Delta S_{\text{surr}} = \frac{q}{T_{\text{surr}}} = \frac{+245}{306} = +0.8 \text{ JK}^{-1}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$\Delta S_{\text{univ}} = -0.7 \text{ JK}^{-1} + 0.8 \text{ JK}^{-1}$$

$$\Delta S_{\text{univ}} = 0.1 \text{ JK}^{-1}$$

56.

SOLUTION :**Given :**

$$n = 1 \text{ mole}$$

$$P = 4.1 \text{ atm}$$

$$V = 2 \text{ Lit}$$

$$T = ?$$

$$q = 3710 \text{ J}$$

$$\Delta S = \frac{q}{T}$$

$$\Delta S = \frac{q}{\left(\frac{PV}{nR}\right)}$$

$$\Delta S = \frac{nRq}{PV}$$

$$\Delta S = \frac{1 \times 0.082 \text{ lit atm K}^{-1} \times 3710 \text{ J}}{4.1 \text{ atm} \times 2 \text{ lit}}$$

$$\Delta S = \frac{1 \times 0.082 \text{ lit atm K}^{-1} \times 3710 \text{ J}}{4.1 \text{ atm} \times 2 \text{ lit}}$$

$$\Delta S = 37.10 \text{ JK}^{-1}$$

57.

SOLUTION:**Given :**

$$\Delta H_f(\text{NaCl}) = 30.4 \text{ kJ} = 30400 \text{ J mol}^{-1}$$

$$\Delta S_f(\text{NaCl}) = 28.4 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$T_f = ?$$

$$\Delta S_f = \frac{\Delta H_f}{T_f}$$

$$T_f = \frac{\Delta H_f}{\Delta S_f}$$

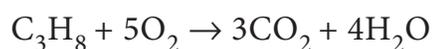
$$T_f = \frac{30400 \text{ J mol}^{-1}}{28.4 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$T_f = 1070.4 \text{ K}$$

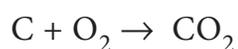
58.

SOLUTION :

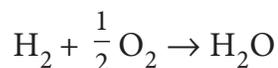
Given



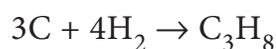
$$\Delta H_c^\circ = -2220.2 \text{ kJ mol}^{-1} \text{ -----(1)}$$



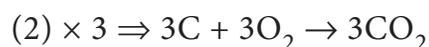
$$\Delta H_f^\circ = -393.5 \text{ kJ mol}^{-1} \text{ -----(2)}$$



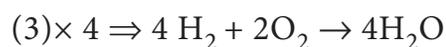
$$\Delta H_f^\circ = -285.8 \text{ kJ mol}^{-1} \text{ ----- (3)}$$



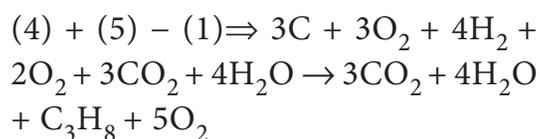
$$\Delta H_c^\circ = ?$$



$$\Delta H_f^\circ = -1180.5 \text{ kJ} \text{ -----(4)}$$

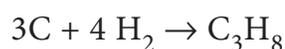


$$\Delta H_f^\circ = -1143.2 \text{ kJ} \text{ -----(5)}$$



$$\Delta H_f^\circ = -1180.5 - 1143.2$$

$$- (-2220.2) \text{ kJ}$$



$$\Delta H_f^\circ = -103.5 \text{ kJ}$$

Standard heat of formation of propane is $\Delta H_f^\circ (\text{C}_3\text{H}_8) = -103.5 \text{ kJ}$

59.

S. No	Liquid	Boiling points ($^\circ\text{C}$)	ΔH (kJ mol $^{-1}$)
1.	Ethanol	78.4	+ 42.4
2.	Toluene	110.6	+ 35.2

SOLUTION :

For ethanol :

Given :

$$T_b = 78.4^\circ \text{C} = (78.4 + 273)$$

$$= 351.4 \text{ K}$$

$$\Delta H_V(\text{ethanol}) = + 42.4 \text{ kJ mol}^{-1}$$

$$\Delta S_V = \frac{\Delta H_V}{T_b}$$

$$\Delta S_V = \frac{+ 42.4 \text{ kJ mol}^{-1}}{351.4 \text{ K}}$$

$$\Delta S_V = \frac{+ 42400 \text{ J mol}^{-1}}{351.4 \text{ K}}$$

$$\Delta S_V = +120.66 \text{ J K}^{-1} \text{ mol}^{-1}$$

For Toluene :

Given :

$$T_b = 110.6^\circ \text{C} = (110.6 + 273)$$

$$= 383.6 \text{ K}$$

$$\Delta H_V(\text{toluene}) = + 35.2 \text{ kJ mol}^{-1}$$

$$\Delta S_V = \frac{\Delta H_V}{T_b}$$

$$\Delta S_V = \frac{+ 35.2 \text{ kJ mol}^{-1}}{383.6 \text{ K}}$$

$$\Delta S_v = \frac{+35200 \text{ J mol}^{-1}}{383.6 \text{ K}}$$

$$\Delta S_v = +91.76 \text{ J K}^{-1} \text{ mol}^{-1}$$

60.

Solution :

Given :

$$\Delta H = 30.56 \text{ kJ mol}^{-1}$$

$$= 30560 \text{ J mol}^{-1}$$

$$\Delta S = 6.66 \times 10^{-3} \text{ kJK}^{-1} \text{ mol}^{-1}$$

T = ? at which $\Delta G = 0$

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

$$0 = \Delta H - T\Delta S$$

$$T = \frac{\Delta H}{\Delta S}$$

$$T = \frac{30.56 \text{ kJ mol}^{-1}}{6.66 \times 10^{-3} \text{ kJK}^{-1} \text{ mol}^{-1}}$$

$$T = 4589 \text{ K}$$

(i) At 4589K ; $\Delta G = 0$ the reaction is in equilibrium.

(ii) at temperature below 4598 K , $\Delta H > T \Delta S$

$\Delta G = \Delta H - T \Delta S > 0$, the reaction in the forward direction, is non spontaneous. In other words the reaction occurs in the backward direction.

61.

Solution :

Given

$$T = 400\text{K}; \Delta H^0 = 77.2 \text{ kJ mol}^{-1} = 77200$$

$$\text{J mol}^{-1}; \Delta S^0 = 122 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta G^0 = -2.303 RT \log K_{\text{eq}}$$

$$\log K_{\text{eq}} = \frac{-\Delta G^0}{2.303 RT}$$

$$\log K_{\text{eq}} = -\frac{(\Delta H^0 - T\Delta S^0)}{2.303 RT}$$

$$\log K_{\text{eq}} = -\left(\frac{77200 - 400 \times 122}{2.303 \times 8.314 \times 400}\right)$$

$$\log K_{\text{eq}} = -\left(\frac{28400}{7659}\right)$$

$$\log K_{\text{eq}} = -3.7080$$

$$K_{\text{eq}} = \text{antilog}(-3.7080)$$

$$K_{\text{eq}} = 1.95 \times 10^{-4}$$

62.

Solution :

Given

$$T = 298\text{K}; \Delta U = -742.4 \text{ kJ mol}^{-1}$$

$$\Delta H = ?$$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\Delta H = \Delta U + (n_p - n_r) RT$$

$$\Delta H = -742.4 + \left(2 - \frac{3}{2}\right)$$

$$\times 8.314 \times 10^{-3} \times 298$$

$$= -742.4 + (0.5 \times 8.314 \times 10^{-3} \times 298)$$

$$= -742.4 + 1.24$$

$$= -741.16 \text{ kJ mol}^{-1}$$

63.

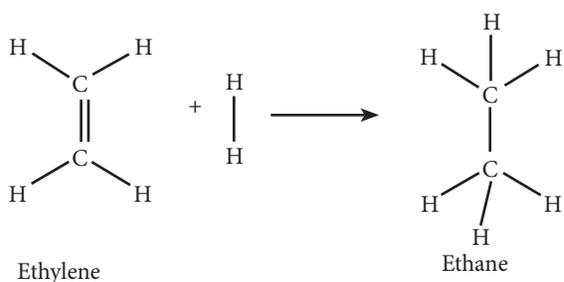
Solution :**Given :**

$$E_{\text{C-H}} = 414 \text{ kJ mol}^{-1}$$

$$E_{\text{C-C}} = 347 \text{ kJ mol}^{-1}$$

$$E_{\text{C=C}} = 618 \text{ kJ mol}^{-1}$$

$$E_{\text{H-H}} = 435 \text{ kJ mol}^{-1}$$



$$\Delta H_r = \Sigma (\text{Bond energy})_r - \Sigma (\text{Bond energy})_p$$

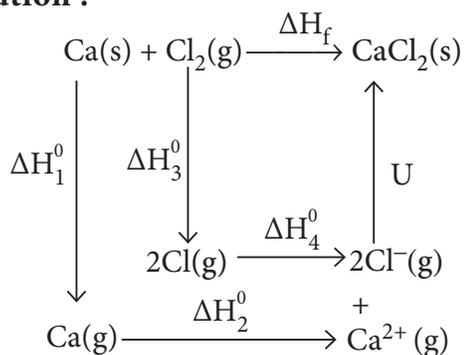
$$\Delta H_r = (E_{\text{C=C}} + 4E_{\text{C-H}} + E_{\text{H-H}}) - (E_{\text{C-C}} + 6E_{\text{C-H}})$$

$$\Delta H_r = (618 + (4 \times 414) + 435) - (347 + (6 \times 414))$$

$$\Delta H_r = 2709 - 2831$$

$$\Delta H_r = -122 \text{ kJ mol}^{-1}$$

64.

Solution :

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

$$+ 2 \Delta H_4 + u$$

$$-795 = 121 + 2422 + 242.8$$

$$+ (2 \times -355) + u$$

$$-795 = 2785.8 - 710 + u$$

$$-795 = 2075.8 + u$$

$$u = -795 - 2075.8$$

$$u = -2870.8 \text{ kJ mol}^{-1}$$

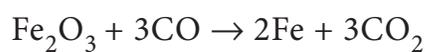
65.

Solution :**Given :**

$$\Delta H_f(\text{Fe}_2\text{O}_3) = -741 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{CO}) = -137 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{CO}_2) = -394.5 \text{ kJ mol}^{-1}$$



$$\Delta H_r = ?$$

$$\Delta H_r = \Sigma (\Delta H_f)_{\text{products}}$$

$$- \Sigma (\Delta H_f)_{\text{reactants}}$$

$$\Delta H_r = [2 \Delta H_f(\text{Fe}) + 3 \Delta H_f(\text{CO}_2)]$$

$$- [\Delta H_f(\text{Fe}_2\text{O}_3) + 3 \Delta H_f(\text{CO})]$$

$$\Delta H_r = [0 + 3(-394.5)]$$

$$- [-741 + 3(-137)]$$

$$\Delta H_r = [-1183.5] - [-1152]$$

$$\Delta H_r = -1183.5 + 1152$$

$$\Delta H_r = -31.5 \text{ kJ mol}^{-1}$$

66.

Solution:**Given :**

$$T = 175^{\circ}C = 175 + 273 = 448K$$

Concentration of 1-pentyne

$$[A] = 1.3\%$$

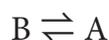
Concentration of 2-pentyne

$$[B] = 95.2\%$$

Concentration of 1, 2-pentadiene

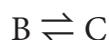
$$[C] = 3.5\%$$

At equilibrium



$$95.2\% \quad 1.3\% \Rightarrow$$

$$K_1 = \frac{1.3}{95.2} = 0.0136$$



$$95.2\% \quad 3.5\% \Rightarrow$$

$$K_2 = \frac{3.5}{95.2} = 0.0367$$

$$\Rightarrow \Delta G_1^{\circ} = -2.303 RT \log K_1$$

$$\Delta G_1^{\circ} = -2.303 \times 8.314 \times 448 \\ \times \log 0.0136$$

$$\Delta G_1^{\circ} = +16010 \text{ J}$$

$$\Delta G_1^{\circ} = +16 \text{ kJ}$$

$$\Rightarrow \Delta G_2^{\circ} = -2.303 RT \log K_2$$

$$\Delta G_2^{\circ} = -2.303 \times 8.314 \times 448 \\ \times \log 0.0367$$

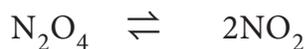
$$\Delta G_2^{\circ} = +12312 \text{ J}$$

$$\Delta G_2^{\circ} = +12.312 \text{ kJ}$$

67.

Solution:**Given :**

$$T = 33K$$



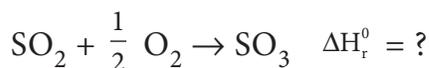
	N_2O_4	\rightleftharpoons	$2NO_2$
Initial no of moles	100		0
Number of moles dissociated	50		-
No of moles remaining	50		100
Total no of moles	150 moles		
$P_{N_2O_4} = \frac{n_{N_2O_4}}{n_{N_2O_4} + n_{NO_2}} \cdot P$	$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}}$		
$P_{N_2O_4} = \frac{50 \text{ mol}}{150 \text{ mol}} \cdot 1 \text{ atm}$	$K_p = \frac{(0.667)^2 \text{ atm}^2}{0.333 \text{ atm}}$		
$P_{N_2O_4} = 0.333 \text{ atm}$	$K_p = 1.336 \text{ atm}$		
$P_{NO_2} = \frac{n_{NO_2}}{n_{N_2O_4} + n_{NO_2}} \cdot P$	$\Delta G^{\circ} = -2.303 RT \log K_p$		
$P_{NO_2} = \frac{100 \text{ mol}}{150 \text{ mol}} \cdot 1 \text{ atm}$	$\Delta G^{\circ} = -2.303 \times 8.314 \times 33 \times \log 1.336$		
$P_{NO_2} = 0.667 \text{ atm}$	$\Delta G^{\circ} = -79.49 \text{ J mol}^{-1}$		

68.

Solution :**Given :**

$$\Delta H_f^{\circ} (\text{SO}_2) = -297 \text{ kJ mol}^{-1}$$

$$\Delta H_f^{\circ} (\text{SO}_3) = -396 \text{ kJ mol}^{-1}$$



$$\Delta H_r^{\circ} = (\Delta H_f^{\circ})_{\text{compound}}$$

$$- \sum (\Delta H_f^{\circ})_{\text{elements}}$$

$$\Delta H_r^{\circ} = \Delta H_f^{\circ} (\text{SO}_3) - \left(\Delta H_f^{\circ} (\text{SO}_2) + \frac{1}{2} \Delta H_f^{\circ} (\text{O}_2) \right)$$

$$\Delta H_r^{\circ} = -396 \text{ kJ mol}^{-1}$$

$$- (-297 \text{ kJ mol}^{-1} + 0)$$

$$\Delta H_r^{\circ} = -396 \text{ kJ mol}^{-1} + 297$$

$$\Delta H_r^{\circ} = -99 \text{ kJ mol}^{-1}$$

69.

Solution:

Given :

$$T = 298 \text{ K}$$

$$\Delta H = 400 \text{ KJ mol}^{-1}$$

$$\Delta S = 0.2 \text{ KJ K}^{-1} \text{ mol}^{-1}$$

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

$$\text{if } T = 2000 \text{ K}$$

$$\Delta G = 400 - (0.2 \times 2000) = 0$$

$$\Delta H = 400 \text{ KJ mol}^{-1} \text{ if } T > 2000 \text{ K}$$

ΔG will be negative.

The reaction would be spontaneous only beyond 2000K

70.

Solution :

Given :

$$T = 298\text{K}$$

$$\Delta G_r^0 = -13.6 \text{ kJ mol}^{-1}$$

$$= -13600 \text{ J mol}^{-1}$$

$$\Delta G^0 = -2.303 RT \log K_{\text{eq}}$$

$$\log K_{\text{eq}} = \frac{-\Delta G^0}{2.303 RT} \quad \log K_{\text{eq}} = \frac{13.6 \text{ kJ mol}^{-1}}{2.303 \times 8.314 \times 10^{-3} \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}$$

$$\log K_{\text{eq}} = 2.38$$

$$K_{\text{eq}} = \text{antilog}(2.38)$$

$$K_{\text{eq}} = 239.88$$

71.

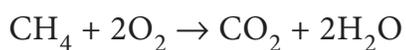
Solution :

Given :

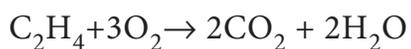
$$\Delta H_C(\text{CH}_4) = -890 \text{ kJ mol}^{-1}$$

$$\Delta H_C(\text{C}_2\text{H}_4) = -1423 \text{ kJ mol}^{-1}$$

Let the mixture contain x lit of CH_4 and $(3.67 - x)$ lit of ethylene.



$$x \text{ lit} \qquad \qquad x \text{ lit}$$



$$(3.67 - x) \text{ lit} \quad 2(3.67 - x) \text{ lit}$$

$$\text{Volume of Carbondioxide formed} = x + 2(3.67 - x) = 6.11 \text{ lit}$$

$$x + 7.34 - 2x = 6.11$$

$$7.34 - x = 6.11$$

$$x = 1.23 \text{ lit}$$

Given mixture contains 1.23 lit of methane and 2.44 lit of ethylene, hence

$$\begin{aligned} \Delta H_C &= \left[\frac{\Delta H_C(\text{CH}_4)}{22.4 \text{ lit}} \times (x) \text{ lit} \right] \\ &+ \left[\frac{\Delta H_C(\text{C}_2\text{H}_4)}{22.4 \text{ lit}} \times (3.67 - x) \text{ lit} \right] \\ \Delta H_C &= \left[\frac{-890 \text{ kJ mol}^{-1}}{22.4 \text{ lit}} \times 1.23 \text{ lit} \right] \\ &+ \left[\frac{-1423}{22.4 \text{ lit}} \times (3.67 - 1.23) \text{ lit} \right] \end{aligned}$$

$$\Delta H_C = [-48.87 \text{ kJ mol}^{-1}]$$

$$+ [-155 \text{ kJ mol}^{-1}]$$

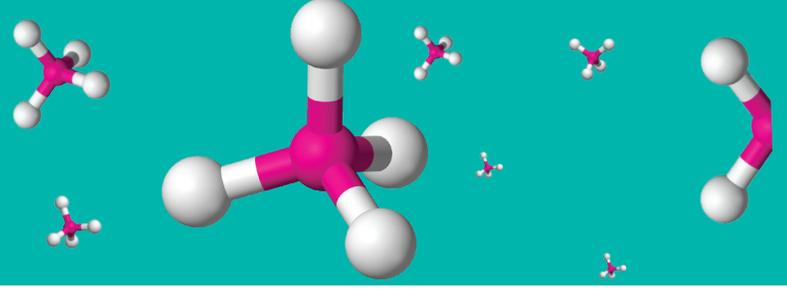
$$\Delta H_C = -203.87 \text{ kJ mol}^{-1}$$

Books for Reference

1. Basic concept of chemistry, L. J. Malone, T. O. Dolter, 8th Edition.
2. Chemistry in your life, Colin Baird, 2nd Edition.
3. Chemistry structure and properties, N. J. Tro, 2nd Edition.
4. General chemistry, R. Chang, 5th Edition.
5. Introductory chemistry for today, S. L. Seagal, M. R. Slabaugh, 8th Edition.
6. Basic Inorganic Chemistry, F. A. Cotton, G. Wilkinson and P. L. Gaus, 3rd Edition.
7. Inorganic chemistry principles structure and reactivity, O. K. Medhi, E. A. Keiter, J. E. Huheey, R. L. Keiter, 4th Edition.
8. Inorganic chemistry, A. K. De.
9. Inorganic chemistry, Holleman-wiberg, 1st Edition.
10. Elements of physical chemistry, P. Atkins, 7th Edition.
11. Physical chemistry, I. Levine, 6th Edition..
12. Physical chemistry, G. Mortimer, 3rd Edition.
13. Advanced organic chemistry, Reactions, Mechanism and structure, J. March, 4th Edition.
14. Advanced organic chemistry, A. Bahl.
15. Introduction to organic chemistry, J. McMurry, 7th Edition.
16. Organic Chemistry, I.L Finar, 5th Edition.
17. Organic chemistry, R. T. Morrison, R. N. Boyd, 7th Edition.
18. Organic chemistry, L. G. Wade, 8th Edition.
19. Organic chemistry, J. McMurry, 9th Edition.
20. Organic chemistry, F. A. Carey, 10th Edition.
21. Environmental chemistry, R. P. Schwarzenbach, P. M. Gschwend, D. M. Imboden, 3rd Edition.

GLOSSARY

A-Z



Absolute zero	தனிச்சூழி
Absorption spectra	உட்கவர் நிறமாலை
Adiabatic process	வெப்பம் மாறாச் செயல்முறை
Alkali metals	கார உலோகங்கள்
Alkaline earth metals	காரமண் உலோகங்கள்
Allotropes	புறவேற்றுமை வடிவங்கள்
Amphoteric	ஈரியல்புள்ள
amu	அணு நிறை அலகு
Anion	எதிர்மின் அயனி
Anode ray	நேர்மின்வாய்க் கதிர்
Anomalous	அசாதாரண
Aqueous solution	நீர்க் கரைசல்
Armor plates	கவச தட்டு
Artificial silk	செயற்கைப் பட்டு
Baking soda	சமையல் சோடா
Boundary	எல்லை
Bunsen flame	புன்சன் சுடர்
Catalyst	வினையூக்கி
Cathode ray	எதிர்மின்வாய்க் கதிர்
Cation	நேர் மின் அயனி
Caustic soda	எரிசோடா
Combustion	எரிதல்
Compression	சுருங்கச் செய்தல்
Concept	கொள்கை
Covalent radius	சகப்பிணைப்பு ஆரம்
Critical constants	நிலைமாறு மாறிலிகள்
Decomposition	சிதைதல்
Diagonal relation	மூலைவிட்டத் தொடர்பு
Diffusion	விரவுதல்
Dipole moment	இருமுனைத் திருப்புத்திறன்

Direct proportion	நேர்விகிதத் தொடர்பு
Discharge tube	மின்னிறக்க குழாய்
Disproportionation	விகிதச் சிதைவு
Dual behavior	ஈரியல்புத் தன்மை
Efficiency	திறன்
Electron affinity	எலக்ட்ரான் நாட்டம்
Electronegativity	எலக்ட்ரான் கவர்திறன்
Electrostatic attraction	நிலைமின்னியல் கவர்ச்சி
Emission spectra	உமிழ் நிறமாலை
Empirical formula	எளிய விகித வாய்ப்பாடு
Equivalent mass	சமான நிறை
Excited state	கிளர்வு நிலை
Expansion	விரிவடைதல்
Fertilizers	உரங்கள்
Formation	உருவாக்கம்
Gaseous state	வாயு நிலை
Ground state	அடிநிலை (சாதாரண நிலை)
Hard water	கடின நீர்
Hardness	கடினத்தன்மை
Heat capacity	வெப்ப ஏற்புத்திறன்
Heavy water	கன நீர்
Heterogeneous mixture	பலபடித்தான கலவை
Homogeneous mixture	ஒருபடித்தான கலவை
Hydrogen bonding	ஹைட்ரஜன் பிணைப்பு
Ideal gases	நல்லியல்பு வாயுக்கள்
Inter molecular	மூலக்கூறுகளுக்கிடையிட்ட
Inner transition metals	உள் இடைநிலைத் தனிமங்கள்
Insoluble	கரையாத் தன்மை
Internal energy	அக ஆற்றல்
Ion exchange	அயனிப் பரிமாற்றம்
Ionic radius	அயனி ஆரம்
Ionisation energy	அயனியாக்கும் ஆற்றல்
Irreversible	மீளாச் செயல்முறை
Isobaric process	அழுத்தம் மாறாச் செயல்முறை
Isochoric process	கனஅளவு மாறாச் செயல்முறை
Isoelectronic species	ஒத்த எலக்ட்ரான் அமைப்பு கொண்ட கூறுகள்
IUPAC	<i>International Union of Pure and Applied Chemistry</i>
Lather	நுரை

Lattice energy	படிசுக் கூடு ஆற்றல்
Laundering	சலவை செய்தல்
Lime stone	சுண்ணாம்புக் கல் $CaCO_3$
Linear	நேர்கோட்டு வடிவம்
Lone pair	தனித்த இரட்டை
Matter	பொருண்மை
Milk of lime	சுண்ணப்பால்- $Ca(OH)_2$
Milk of magnesia	மெக்னீஷியா பால்மம் $Mg(OH)_2$
Naphthalene balls	நாஃப்தலீன் உருண்டை (இரசக் கற்பூரம்)
Negligible	புறக்கணிக்கத்தக்க
Neutralisation	நடுநிலையாக்கல்
nm	நேநோ மீட்டர்
Non-spontaneous process	தன்னிச்சையற்ற செயல்முறை
Octahedron	எண்முகி
Octaves	எட்டு எண்ணிக்கை கொண்ட தொகுதி (a group of eight)
Octet rule	எண்ம விதி
Operator	செயலி
Oxidation	ஆக்ஸிஜனேற்றம்
Oxidation number	ஆக்ஸிஜனேற்ற எண்
Path function	வழிச் சார்பு
Periodic table	ஆவர்த்தன அட்டவணை
Photoelectric effect	ஒளிமின் விளைவு
Plaster of Paris	பாரீஸ் சாந்து
pm	பிகோ மீட்டர்
Polarisation	முனைவாக்கல்
Polarisibility	முனைவாக்கும் திறன்
Polyatomic molecule	பல்லணு மூலக்கூறு
Precipitate	வீழ்ப்படிவு
Quantity	பொருளின் அளவு
Quick lime	சுட்ட சுண்ணாம்பு- CaO
Radioactive elements	கதிரியக்கத் தனிமங்கள்
Reagent	வினைக் கரணி
Redox	ஆக்ஸிஜனேற்ற-ஒடுக்கம்
Reduction	ஒடுக்கம்
Relative atomic mass	ஒப்பு அணு நிறை
Reversible process	மீள் செயல்முறை
Saturated solution	நிறைவுற்ற கரைசல்
Scattering	சிதறடித்தல்

Shielding effect	மறைத்தல் விளைவு
SI unit	System International அலகு
Slaked lime - Ca(OH) ₂	நீர்த்த சுண்ணாம்பு
Soluble	கரையக்கூடிய
Sparingly soluble	பகுதியாக கரையும் தன்மை
Spin	தற்சுழற்சி
Spontaneous process	தன்னிச்சைச் செயல்முறை
State function	நிலைச்சார்பு
Sublimation	பதங்கமாதல்
Surroundings	சுற்றுப்புறம்
Synthesis	தொகுத்தல்
Tetrahedron	நான்முகி
Thermal equilibrium	வெப்பச் சமநிலை
Trans uranium elements	யுரேனியத்தை தொடர்ந்து வரும் தனிமங்கள்
Transition metals	இடைநிலைத் தனிமங்கள்
Triads	மும்மைகள்
Uncertainty	நிச்சயமற்ற தன்மை
Unified mass	வரையறுக்கப்பட்ட நிறை
Universe	அண்டம்
Unsaturated compound	நிறைவுறாச் சேர்மம்
Valence electrons	இணைதிறன் எலக்ட்ரான்கள்
Valency	இணைதிறன்
Vapour pressure	ஆவி அழுத்தம்
Vapourisation	ஆவியாதல்
Viscosity	பாகுநிலைத்தன்மை
Wave function	அலைச் சார்பு

Chemistry – Class XI

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	Books for Reference	List of relevant books for further reading	
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	Glossary	Important terms are enlisted with equivalent Tamil words	
	Appendix	Comprises fundamental constants and Data tables	

CONTENTS

CHEMISTRY

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Claude Louis Berthollet, a Savoyard-French chemist, studied the mechanism of reversible chemical reaction and developed the theory of chemical equilibria. He also contributed to modern chemical nomenclature. He was the first to demonstrate the bleaching action of chlorine gas, and developed a solution of sodium hypochlorite that acts as a bleaching agent.

Learning Objectives

After studying this unit, the students will be able to

- describe the meaning of equilibrium
- explain the dynamic nature of equilibrium involved in physical and chemical processes
- state the law of mass action
- deduce the expression for equilibrium constants, K_c and K_p
- establish the relationship between K_p and K_c
- predict the extent of reaction using equilibrium constant
- state Le-Chatelier's principle
- explain the effect of various factors that affect a system at equilibrium.
- derive Van't Hoff equation.

8.1 Introduction

In our daily life, we observe several chemical and physical changes. For example, a banana gets ripened after few days, silver gets tarnished in few months and iron gets rusted slowly. These processes proceed in one direction. Now let us consider the transport of oxygen by hemoglobin in our body as an illustration for a reversible change. The hemoglobin combines with oxygen in lungs to form oxyhemoglobin. The oxyhemoglobin has a tendency to form hemoglobin by

releasing oxygen. In fact, in our lungs all the three species coexist.

Few chemical reactions proceed in only one direction whereas many reactions proceed in both the directions and these reactions are called reversible reactions.

In chemical reactions, the concentration of the reactants decreases and that of the products increases with time. In reversible reactions, initially the reaction proceeds towards the formation of the product. Upon formation of the product, the reverse reaction begins to take place. At a particular stage, the rate of the reverse reaction is equal to that of the forward reaction indicating a state of equilibrium.

It is desirable to know the three crucial aspects of chemical reactions namely the feasibility, the rate of the reaction and the extent of reaction. We know that the feasibility of a reaction is given by thermodynamics. Chemical kinetics will tell about the rate of the reaction. The equilibrium constant tells about the extent of a reaction which we will discuss in this chapter. We will also discuss the types of equilibrium, the significance of equilibrium constant and its relationship to thermodynamic quantities and the response of chemical equilibrium to change in the reaction conditions.

8.2. Physical and chemical equilibrium:

There are different types of equilibrium. For example, if two persons with same weight sit on opposite sides of a see-saw at equal distance from the fulcrum, then the see-saw will be stationary and straight and it is said to be in equilibrium.

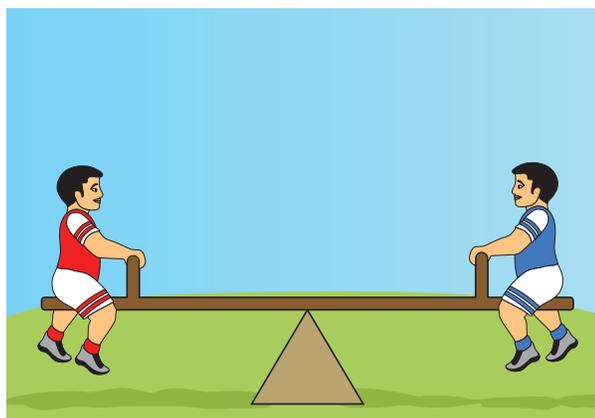


Fig. 8.1 Illustration of equilibrium

Another example of a state of equilibrium is the game of "tug-of-war." In this game a rope is pulled taut between two teams. There may be a situation when both the teams are pulling the rope with equal force and the rope is not moving in either direction. This state is said to be in equilibrium.



Fig. 8.2. Tug-of War

In reversible processes, the rate of two opposing reactions equals at a particular stage. At this stage the concentration of reactants and products do not change with time. This condition is not static and is dynamic, because both the forward and reverse reactions are still occurring with the same rate.

8.2.1 Physical equilibrium

A system in which the amount of matter constituting different phases does not change with time is said to be in physical equilibrium. This involves no perceptible physical change in the system. To understand the physical equilibrium let us analyse the following phase changes.

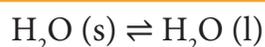
Solid-liquid equilibrium

Let us consider the melting of ice in a closed container at 273 K. This system will reach a state of physical equilibrium in which the amount of water in the solid phase and liquid phase does not change with time. In the process the total number of water molecules leaving from and returning to the solid phase at any instant are equal.

If some ice-cubes and water are placed in a thermos flask (at 273K and 1 atm pressure), then there will be no change in the mass of ice and water.

At equilibrium,

$$\text{Rate of melting of ice} = \text{Rate of freezing of water}$$

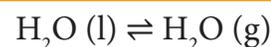


The above equilibrium exists only at a particular temperature and pressure. The temperature at which the solid and liquid phases of a substance are at equilibrium is called the melting point or freezing point of that substance.

Liquid - Vapour equilibrium

Similarly, there exists an equilibrium

between the liquid phase and the vapour phase of a substance. For example, liquid water is in equilibrium with its vapour at 373 K and 1 atm pressure in a closed vessel.



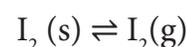
Here

Rate of evaporation = Rate of condensation

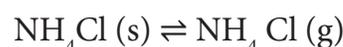
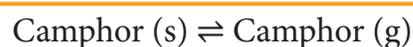
The temperature at which the liquid and vapour phases of a substance are at equilibrium is called the boiling point and condensation point of that substance.

Solid - Vapour equilibrium

Consider a closed system in which the solid sublimes to vapour. In this process also, equilibrium can be established between these two phases. When solid iodine is placed in a closed transparent vessel, after sometime, the vessel gets filled up with violet vapour due to sublimation of iodine. Initially, the intensity of the violet colour increases, after sometime it decreases and finally it becomes constant, as the following equilibrium is attained.



More examples

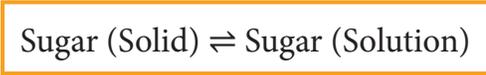


8.2.2 Equilibrium involving dissolution of solids or gases in liquids

Solid in liquids

When you add sugar to water at a particular temperature, it dissolves to form sugar solution. If you continue to

add much sugar, you will reach a stage at which the added sugar remains as solid and the resulting solution is called a saturated solution. Here, as in the previous cases a dynamic equilibrium is established between the solute molecules in the solid phase and in the solution phase.



In this process

$$\text{Rate of dissolution of solute} = \text{Rate of crystallisation of solute}$$

Gas in liquids

When a gas dissolves in a liquid under a given pressure, there will be an equilibrium between gas molecules in the gaseous state and those dissolved in the liquid.

Example:

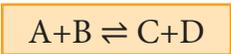
In carbonated beverages the following equilibrium exists.



Henry's law is used to explain such gas-solution equilibrium processes.

8.3. Chemical Equilibrium

Similar to physical processes chemical reactions gradually attain a state of equilibrium after sometime. Let us consider a general reversible reaction.



Initially only A and B are present.

Soon, a few molecules of the products C and D are formed by the forward reaction. As the concentration of the products increases, more products collide and react in the backward direction. This leads to an increase in the rate of backward reaction. As the rate of reverse reaction increases, the rate of the forward reaction decreases. Eventually, the rate of both reactions becomes equal.

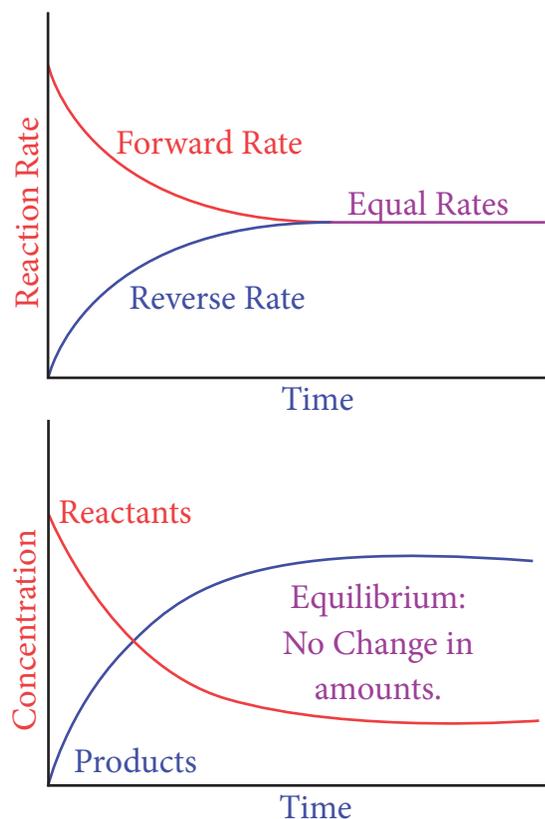


Figure: 8.3 Attainment of equilibrium state for the variation of the rates of forward and backward reactions with time.

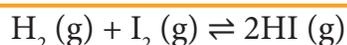
8.4. Dynamic nature of equilibrium:

Let us consider, a situation in multi storey building, people are moving from first floor to second floor and vice versa. Assume that a certain number people moves up from first floor to second floor in a specific time, and the same number of people moves down from second floor to the first floor in the same time. Now, the rate of movement of people from first to second floor equals the

rate of movement of people from second to first floor, and hence the number of people in each floor will remain the same. Thus the population of people on the two floors is in a dynamic equilibrium. Let us extend this analogy to understand dynamic nature of equilibrium.

Chemical reactions which are reversible do not cease, when equilibrium is attained. At equilibrium the forward and the backward reactions are proceeding at the same rate and no macroscopic change is observed. So chemical equilibrium is in a state of dynamic equilibrium.

For example,

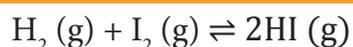


8.5 Homogeneous and heterogeneous equilibria

8.5.1 Homogeneous equilibrium

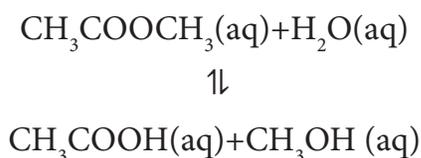
In a homogeneous equilibrium, all the reactants and products are in the same phase.

For example:



In the above equilibrium, H_2 , I_2 and HI are in the gaseous state.

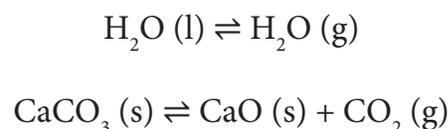
Similarly, for the following reaction, all the reactants and products are in homogeneous solution phase.



8.5.2 Heterogeneous equilibrium

If the reactants and products of a reaction in equilibrium, are in different phases, then it is called as heterogeneous equilibrium.

Example:



8.6 Law of mass action

In 1864 two Norwegian chemists namely Maximilian Guldberg and Peter Waage formulated the law of mass action, based on the experimental studies of many reversible reactions. The law states that,

“At any instant, the rate of a chemical reaction at a given temperature is directly proportional to the product of the active masses of the reactants at that instant”.

$$\text{Rate} \propto [\text{Reactant}]^x$$

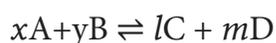
where, x is the stoichiometric coefficient of the reactant and the square bracket represents the active mass (concentration) of the reactants.

$$\text{Active mass} = \left(\frac{n}{V} \right) \text{ mol dm}^{-3} \text{ (or) mol L}^{-1}$$

where n is the number of moles and V is the volume of the container (dm^3 or L)

8.6.1 Equilibrium constants (K_p and K_c):

Let us consider a reversible reaction,



where, A and B are the reactants, C and D are the products and x, y, l and m are the stoichiometric coefficients of A, B, C and D , respectively.

Applying the law of mass action, the rate of the forward reaction,

$$r_f \propto [A]^x [B]^y \quad (\text{or}) \quad r_f = k_f [A]^x [B]^y$$

Similarly, the rate of the backward reaction,

$$r_b \propto [C]^l [D]^m$$

(or)

$$r_b = k_b [C]^l [D]^m$$

where k_f and k_b are proportionality constants

At equilibrium,

$$\begin{aligned} &\text{Rate of forward reaction } (r_f) \\ &= \text{Rate of backward reaction } (r_b) \\ &k_f [A]^x [B]^y = k_b [C]^l [D]^m \\ \text{or } &\frac{k_f}{k_b} = \frac{[C]^l [D]^m}{[A]^x [B]^y} = K_c \end{aligned}$$

where, K_c is the equilibrium constant in terms of concentration (active mass).

At a given temperature, the ratio of the product of active masses of reaction products raised to the respective stoichiometric coefficients in the balanced chemical equation to that of the reactants is a constant, known as equilibrium constant. Later when we study chemical kinetics we will learn that this is only approximately true.

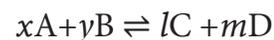
If the reactants and products of the above reaction are in gas phase, then the equilibrium constant can be written in terms of partial pressures as indicated below,

$$K_p = \frac{p_C^l \times p_D^m}{p_A^x \times p_B^y}$$

Where, p_A, p_B, p_C and p_D are the partial pressures of the gas A, B, C and D , respectively.

8.6.2 Relation between K_p and K_c

Let us consider the general reaction in which all reactants and products are ideal gases.



The equilibrium constant, K_c is

$$K_c = \frac{[C]^l [D]^m}{[A]^x [B]^y} \quad (1)$$

and K_p is,

$$K_p = \frac{p_C^l \times p_D^m}{p_A^x \times p_B^y} \quad (2)$$

The ideal gas equation is

$$PV = nRT$$

or

$$P = \frac{n}{V}RT$$

Since

Active mass = molar concentration = n/V

$P = \text{active mass} \times (RT)$

Based on the above expression the partial pressure of the reactants and products can be expressed as,

$$p_A^x = [A]^x (RT)^x$$

$$p_B^y = [B]^y (RT)^y$$

$$p_C^l = [C]^l (RT)^l$$

$$p_D^m = [D]^m (RT)^m$$

On substitution in Eqn. 2,

$$K_p = \frac{[C]^l [RT]^l [D]^m (RT)^m}{[A]^x [RT]^x [B]^y (RT)^y} \quad (3)$$

$$K_p = \frac{[C]^l [D]^m (RT)^{l+m}}{[A]^x [B]^y (RT)^{x+y}}$$

$$K_p = \frac{[C]^l [D]^m}{[A]^x [B]^y} (RT)^{(l+m) - (x+y)} \quad (4)$$

By comparing equation (1) and (4), we get

$$K_p = K_c (RT)^{\Delta n_g} \quad (5)$$

where, Δn_g is the difference between the sum of number of moles of products and the sum of number of moles of reactants in the gas phase.

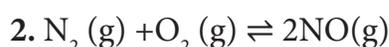
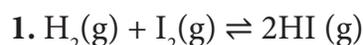
The following relations become immediately obvious.

When $\Delta n_g = 0$

$$K_p = K_c (RT)^0$$

$$K_p = K_c$$

Examples:



When $\Delta n_g = +ve$

$$K_p = K_c (RT)^{+ve}$$

$$K_p > K_c$$

Examples:



When $\Delta n_g = -ve$

$$K_p = K_c (RT)^{-ve}$$

$$K_p < K_c$$

Examples:

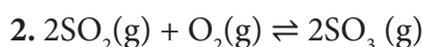
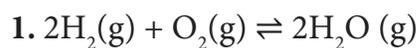


Table 8.1 Relation between equilibrium constants for some reversible reactions

Reversible reactions	Equilibrium constant
For the forward reaction $x\text{A} + y\text{B} \rightleftharpoons l\text{C} + m\text{D}$	K_c



If the reaction is reversed, $lC+mB \rightleftharpoons xA+yB$	$K'_c = \frac{1}{K_c}$
$A \xrightleftharpoons{K_1} B \quad B \xrightleftharpoons{K_2} C$ $C \xrightleftharpoons{K_3} D \quad A \xrightleftharpoons{K_4} D$	$K_4 = K_1 K_2 K_3$

8.6.3 Equilibrium constants for heterogeneous equilibrium

Consider the following heterogeneous equilibrium.



The equilibrium constant for the above reaction can be written as

$$K_c = \frac{[\text{CaO}(\text{s})][\text{CO}_2(\text{g})]}{[\text{CaCO}_3(\text{s})]}$$

A pure solid always has the same concentration at a given temperature, as it does not expand to fill its container. i.e. it has same number of moles L^{-1} of its volume. Therefore, the concentration of a pure solid is a constant. The above expression can be modified as follows

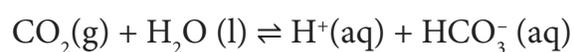
$$K_c = [\text{CO}_2]$$

or

$$K_p = p_{\text{CO}_2}$$

The equilibrium constant for the above reaction depends only the concentration of carbon dioxide and not the calcium carbonate or calcium oxide. Similarly, the active mass (concentration) of the pure liquid does not change at a given temperature. Consequently, the concentration terms of pure liquids can also be excluded from the expression of the equilibrium constant.

For example,



Since, $\text{H}_2\text{O}(\text{l})$ is a pure liquid the K_c can be expressed as

$$K_c = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]}$$

Example

Write the K_p and K_c for the following reactions

1. $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
2. $2\text{CO}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{C}(\text{s})$

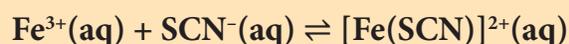
$$1) \quad K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$$

$$K_p = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \times P_{\text{O}_2}}$$

$$2) \quad K_c = \frac{[\text{CO}_2]}{[\text{CO}]^2} \quad \text{and} \quad K_p = \frac{P_{\text{CO}_2}}{P_{\text{CO}}^2}$$

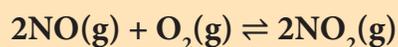
Evaluate Yourself

- 1) Consider the following reaction



A solution is made with initial Fe^{3+} , SCN^{-} concentration of $1 \times 10^{-3}\text{M}$ and $8 \times 10^{-4}\text{M}$ respectively. At equilibrium $[\text{Fe}(\text{SCN})]^{2+}$ concentration is $2 \times 10^{-4}\text{M}$. Calculate the value of equilibrium constant.

- 2) The atmospheric oxidation of NO



was studied with initial pressure of 1 atm of NO and 1 atm of O_2 . At equilibrium, partial pressure of oxygen is 0.52 atm calculate K_p of the reaction.

8.7 Application of equilibrium constant

The knowledge of equilibrium constant helps us to

1. predict the direction in which the net reaction will take place
2. predict the extent of the reaction and
3. calculate the equilibrium concentrations of the reactants and products.

It is to be noted that these constants do not provide any information regarding the rates of the forward or reverse reactions.

8.7.1 Predicting the extent of a reaction

The value of equilibrium constant, K_c tells us the extent of a reaction, i.e., it indicates how far the reaction has proceeded towards product formation at a given temperature.

A large value of K_c indicates that the reaction reaches equilibrium with high product yield. On the other hand, a low value of K_c indicates that the reaction reaches equilibrium with low product yield. In general, if the K_c is greater than the 10^3 , the reaction proceeds nearly to completion. If it is less than 10^{-3} , the reaction rarely proceeds. If K_c is in the range 10^{-3} to 10^3 , significant amount of both reactants and products are present at equilibrium.

Table 8.2 Dependence of extent of reaction on K_c

Value of K_c	$K_c < 10^{-3}$	$10^{-3} < K_c < 10^3$	$K_c > 10^3$
Relative concentrations of reactants and products	[Products] \ll [Reactants]	Significant quantity of Products and Reactants	[Products] \gg [Reactants]
Extent of reaction	Reaction makes a little progress in the forward direction	Both the forward and backward reactions make significant progress	Reaction nearly goes to completion
Prediction	Reverse reaction is favoured	Neither forward nor reverse reaction predominates	Forward reaction is favoured
Examples	Decomposition of water at 500 K $2\text{H}_2\text{O}(\text{g}) \rightleftharpoons 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$ $K_c = 4.1 \times 10^{-48}$ Oxidation of nitrogen at 1000 K $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ $K_c = 1 \times 10^{-30}$	Dissociation of bromine monochloride at 1000 K $2\text{BrCl}(\text{g}) \rightleftharpoons \text{Br}_2(\text{g}) + \text{Cl}_2(\text{g})$ $K_c = 5$ Formation of HI at 700K $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ $K_c = 57.0$	Formation of HCl at 300K $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$ $K_c = 4 \times 10^{31}$ Oxidation of carbon monoxide at 1000 K $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}_2(\text{g})$ $K_c = 2.2 \times 10^{22}$

Example

Consider the following equilibrium reactions and relate their equilibrium constants

- $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO} ; K_1$
- $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2 ; K_2$
- $\text{N}_2 + 2\text{O}_2 \rightleftharpoons 2\text{NO}_2 ; K_3$



$$K_1 = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

$$K_2 = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$$

$$\text{Now } K_1 \times K_2 = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \times \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$$

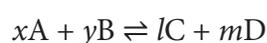
$$= \frac{[\text{NO}_2]^2}{[\text{N}_2][\text{O}_2]^2} = K_3$$

$$\therefore K_3 = K_1 \times K_2$$

8.7.2 Predicting the direction of a reaction

From the knowledge of equilibrium constant, it is possible to predict the direction in which the net reaction is taking place for a given concentration or partial pressure of reactants and products.

Consider a general homogeneous reversible reaction,



For the above reaction under non-equilibrium conditions, reaction quotient 'Q' is defined as the ratio of the product of active masses of reaction products raised to the respective stoichiometric coefficients in the balanced chemical equation to that of the reactants.

Under non-equilibrium conditions, the reaction quotient Q can be calculated using the following expression.

$$Q = \frac{[\text{C}]^l [\text{D}]^m}{[\text{A}]^x [\text{B}]^y}$$

As the reaction proceeds, there is a continuous change in the concentration of

reactants and products and also the Q value until the reaction reaches the equilibrium. At equilibrium Q is equal to K_c at a particular temperature. Once the equilibrium is attained, there is no change in the Q value. By knowing the Q value, we can predict the direction of the reaction by comparing it with K_c .

- If $Q = K_c$, the reaction is in equilibrium state.
- If $Q > K_c$, the reaction will proceed in the reverse direction i.e., formation of reactants.
- If $Q < K_c$, the reaction will proceed in the forward direction i.e., formation of products.

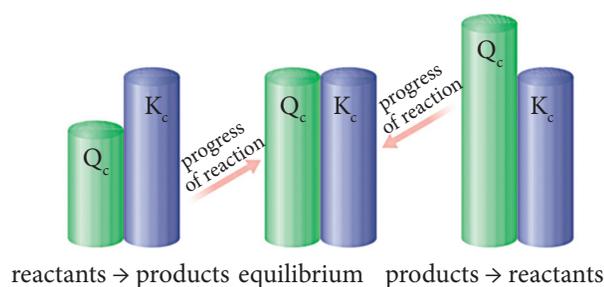
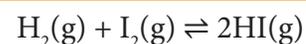


Fig: 8.4 Predicting the direction of a reaction

Example 1

The value of K_c for the following reaction at 717 K is 48.



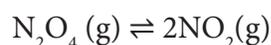
At a particular instant, the concentration of H_2 , I_2 and HI are found to be 0.2 mol L^{-1} , 0.2 mol L^{-1} and 0.6 mol L^{-1} respectively. From the above information we can predict the direction of reaction as follows.

$$Q = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{0.6 \times 0.6}{0.2 \times 0.2} = 9$$

Since $Q < K_c$, the reaction will proceed in the forward direction.

Example 2

The value of K_c for the reaction



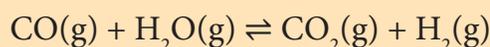
$K_c = 0.21$ at 373 K. The concentrations N_2O_4 and NO_2 are found to be $0.125 \text{ mol dm}^{-3}$ and 0.5 mol dm^{-3} respectively at a given time. From the above information we can predict the direction of reaction as follows.

$$Q = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{0.5 \times 0.5}{0.125} = 2$$

The Q value is greater than K_c . Hence, the reaction will proceed in the reverse direction until the Q value reaches 0.21

Evaluate Yourself

3) The following water gas shift reaction is an important industrial process for the production of hydrogen gas.

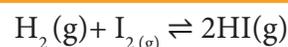


At a given temperature $K_p = 2.7$. If 0.13 mol of CO, 0.56 mol of water, 0.78 mol of CO_2 and 0.28 mol of H_2 are introduced into a 2 L flask, and find out in which direction must the reaction proceed to reach equilibrium

8.7.3 Calculation of concentration of reactants and products at equilibrium

If the equilibrium concentrations of reactants and products are known for a reaction, then the equilibrium constant can be calculated and vice versa.

Let us consider the formation of HI in which, 'a' moles of hydrogen and 'b' moles of iodine gas are allowed to react in a container of volume V . Let 'x' moles of each of H_2 and I_2 react together to form $2x$ moles of HI.



	H_2	I_2	HI
Initial number of moles	a	b	0
number of moles reacted	x	x	0
Number of moles at equilibrium	a-x	b-x	2x
Active mass or molar concentration at equilibrium	$\frac{a-x}{V}$	$\frac{b-x}{V}$	$\frac{2x}{V}$

Applying law of mass action,

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)} = \frac{4x^2}{(a-x)(b-x)}$$

The equilibrium constant K_p can also be calculated as follows:

We know the relationship between the K_c and K_p

$$K_p = K_c (RT)^{\Delta n_g}$$

Here the

$$\Delta n_g = n_p - n_r = 2 - 2 = 0$$

Hence $K_p = K_c$

$$K_p = \frac{4x^2}{(a-x)(b-x)}$$

Solved Problem

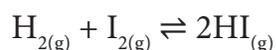
One mole of H_2 and one mole of I_2 are allowed to attain equilibrium in 1 lit container. If the equilibrium mixture contains 0.4 mole of HI. Calculate the equilibrium constant.

Given data:

$$[H_2] = 1 \text{ mol L}^{-1} \quad [I_2] = 1 \text{ mol L}^{-1}$$

At equilibrium, $[HI] = 0.4 \text{ mol L}^{-1}$ $K_c = ?$

Solution:



	H_2	I_2	HI
Initial number of moles	1	1	–
Number of moles at equilibrium	1-x	1-x	2x = 0.4. x=0.2
	0.8	0.8	0.4

$$\therefore K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{0.4 \times 0.4}{0.8 \times 0.8} = 0.25$$

Dissociation of PCl_5 :

Consider that 'a' moles of PCl_5 is taken in a container of volume V. Let 'x' moles of PCl_5 be dissociated into x moles of PCl_3 and x moles of Cl_2 .



	PCl_5	PCl_3	Cl_2
Initial number of moles	a	0	0
number of moles dissociated	x	0	0
Number of moles at equilibrium	a-x	x	x
Active mass or molar concentration at equilibrium	$\frac{a-x}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

Applying law of mass action,

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{a-x}{V}\right)} = \frac{x^2}{(a-x)V}$$

The equilibrium constant K_p can also be calculated as follows:

We know the relationship between the K_c and K_p

$$K_p = K_c (RT)^{\Delta n_g}$$

Here the

$$\Delta n_g = n_p - n_r = 2 - 1 = 1$$

Hence $K_p = K_c (RT)$

We know that $PV = nRT$

$$RT = \frac{PV}{n}$$

Where n is the total number of moles at equilibrium.

$$n = (a-x) + x + x = (a+x)$$



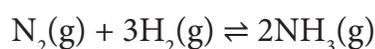
$$K_p = \frac{x^2}{(a-x)V} \frac{PV}{n}$$

$$K_p = \frac{x^2}{(a-x)V} \frac{PV}{(a+x)}$$

$$K_p = \frac{x^2 P}{(a-x)(a+x)}$$

Synthesis of ammonia:

Let us consider the formation of ammonia in which, 'a' moles nitrogen and 'b' moles hydrogen gas are allowed to react in a container of volume V. Let 'x' moles of nitrogen react with 3x moles of hydrogen to give 2x moles of ammonia.



	N_2	H_2	NH_3
Initial number of moles	a	b	0
number of moles reacted	x	3x	0
Number of moles at equilibrium	a-x	b-3x	2x
Active mass or molar concentration at equilibrium	$\frac{a-x}{V}$	$\frac{b-3x}{V}$	$\frac{2x}{V}$

Applying law of mass action,

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3}$$

$$= \frac{\left(\frac{4x^2}{V^2}\right)}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3}$$

$$K_c = \frac{4x^2 V^2}{(a-x)(b-3x)^3}$$

The equilibrium constant K_p can also be calculated as follows:

$$K_p = K_c (RT)^{\Delta n_g}$$

$$\Delta n_g = n_p - n_r = 2 - 4 = -2$$

$$K_p = \frac{4x^2 V^2}{(a-x)(b-3x)^3} (RT)^{-2}$$

Total number of moles at equilibrium,

$$n = a-x + b-3x + 2x = a+b-2x$$

$$K_p = \frac{4x^2 V^2}{(a-x)(b-3x)^3} \times \left[\frac{PV}{n}\right]^{-2}$$

$$K_p = \frac{4x^2 V^2}{(a-x)(b-3x)^3} \times \left[\frac{n}{PV}\right]^2$$

$$K_p = \frac{4x^2 V^2}{(a-x)(b-3x)^3} \times \left[\frac{a+b-2x}{PV}\right]^2$$

$$K_p = \frac{4x^2 (a+b-2x)^2}{P^2 (a-x)(b-3x)^3}$$

Solved Problems:

- The equilibrium concentrations of NH_3 , N_2 and H_2 are $1.8 \times 10^{-2} M$, $1.2 \times 10^{-2} M$ and $3 \times 10^{-2} M$ respectively. Calculate the equilibrium constant for the formation of NH_3 from N_2 and H_2 .
[Hint: $M = \text{mol lit}^{-1}$]

Given data:

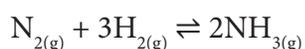
$$[\text{NH}_3] = 1.8 \times 10^{-2} \text{ M}$$

$$[\text{N}_2] = 1.2 \times 10^{-2} \text{ M}$$

$$[\text{H}_2] = 3 \times 10^{-2} \text{ M}$$

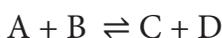
$$K_c = ?$$

Solution:



$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{1.8 \times 10^{-2} \times 1.8 \times 10^{-2}}{1.2 \times 10^{-2} \times 3 \times 10^{-2} \times 3 \times 10^{-2} \times 3 \times 10^{-2}} \\ = 1 \times 10^3 \text{ L}^2 \text{ mol}^{-2}$$

2. The equilibrium constant at 298 K for a reaction is 100.



If the initial concentration of all the four species is 1 M, the equilibrium concentration of D (in mol lit⁻¹) will be

Given data:

$$[\text{A}] = [\text{B}] = [\text{C}] = [\text{D}] = 1 \text{ M}$$

$$K_c = 100$$

$$[\text{D}]_{\text{eq}} = ?$$

Solution:

Let x be the no moles of reactants reacted

	A	B	C	D
Initial concentration	1	1	1	1
At equilibrium (as per reaction stoichiometry)	1-x	1-x	1+x	1+x

$$K_c = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]}$$

$$100 = \frac{(1+x)(1+x)}{(1-x)(1-x)}$$

$$\sqrt{100} = \sqrt{\frac{(1+x)(1+x)}{(1-x)(1-x)}}$$

$$10 = \frac{1+x}{1-x}$$

$$10(1-x) = 1+x$$

$$10 - 10x - 1 - x = 0$$

$$9 - 11x = 0$$

$$11x = 9$$

$$x = \frac{9}{11} = 0.818$$

$$[\text{D}]_{\text{eq}} = 1+x = 1 + 0.818 = 1.818 \text{ M}$$

Evaluate Yourself

- 4) 1 mol of PCl_5 kept in a closed container of volume 1 dm³ and was allowed to attain equilibrium at 423 K. Calculate the equilibrium composition of reaction mixture. (The K_c value for PCl_5 dissociation at 423 K is 2)

8.8 Le-Chatelier's Principle

Many chemical reactions that have industrial importance such as synthesis of ammonia are reversible in nature. It is important to know the reaction conditions to produce maximum yield. If a system at equilibrium is disturbed by modifying the reaction conditions, then the system adjusts itself the new conditions to re-establish the equilibrium.

The effect of change in reaction conditions such as temperature, pressure and concentration etc. on a system at equilibrium can be predicted by Le Chatelier-Braun principle.

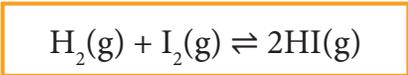
It states that “If a system at equilibrium is disturbed, then the system shifts itself in a direction that nullifies the effect of that disturbance.”

8.8. 1 Effect of concentration

At equilibrium, the concentration of the reactants and the products does not change. The addition of more reactants or products to the reacting system at equilibrium causes an increase in their respective concentrations.

According to Le Chatelier’s principle, the effect of increase in concentration of a substance is to shift the equilibrium in a direction that consumes the added substance.

Let us consider the reaction



The addition of H_2 or I_2 to the equilibrium mixture, disturbs the equilibrium. In order to minimize the stress, the system shifts the reaction in a direction where H_2 and I_2 are consumed. i.e., the formation of additional HI would balance the effect of added reactant. Hence, the equilibrium shifts to the right (forward direction) i.e. the forward reaction takes place until the equilibrium is re-established. Similarly, removal of HI (product) also favours the forward reaction.

If HI is added to the equilibrium mixture, the concentration HI is increased, and system proceeds in the reverse direction to nullify the effect of increase in concentration of HI .

Let us explain the effect change in concentration by considering the formation of HI from H_2 and I_2 . At equilibrium, the concentrations of HI, H_2 and I_2 are 1 M, 0.2 M and 0.1 M respectively.

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{1 \times 1}{0.2 \times 0.1} = 50$$

The equilibrium was disturbed by adding 0.1 M iodine to the reaction mixture. After sometime, the concentration of HI is found to be 1.092 M. Let us verify whether the system proceeds to re-establish the equilibrium according to Le Chatelier’s principle.

	H_2	I_2	HI
Concentration at equilibrium	0.2	0.1	1
Disturbance (Addition of 0.1 M iodine)		+0.1	
Concentration immediately after the addition of iodine	0.2	0.2	1
Change in concentration	-x	-x	2x
New concentration	0.2-x	0.2-x	1+2x

Now,

$$\text{Concentration of HI} = 1 + 2x = 1.092 \text{ M}$$

$$2x = 0.092$$

$$x = 0.046 \text{ M}$$

Therefore, the concentration of hydrogen and iodine at this stage,

$$[\text{H}_2] = 0.2 - X = 0.2 - 0.046 = 0.154$$

$$[\text{I}_2] = 0.2 - X = 0.2 - 0.046 = 0.154$$

The reaction quotient Q at this stage,

$$Q = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{1.092 \times 1.092}{0.154 \times 0.154} \approx 50$$

The Q value is equal to K_c value.

So, we can conclude that the system has reestablished the equilibrium at this stage and the addition of iodine results in the increase in the HI concentration.

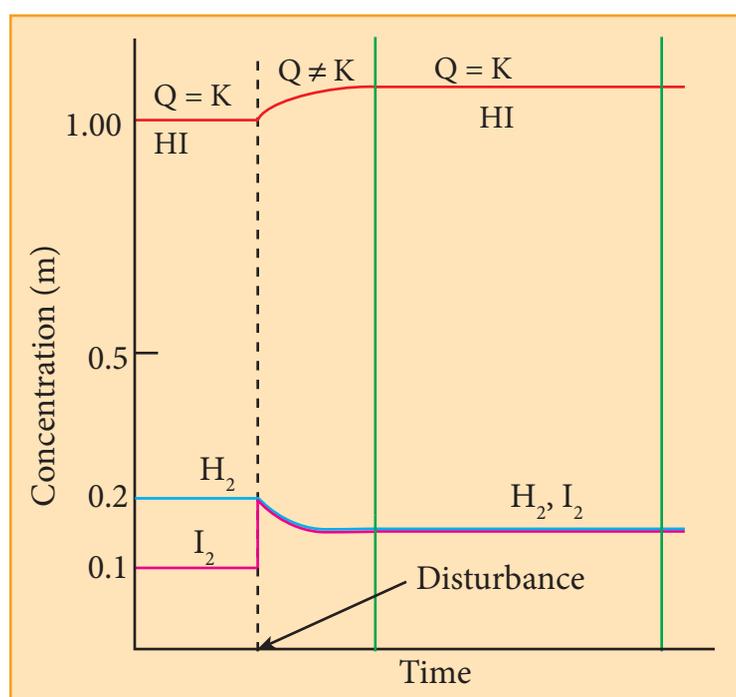


Figure 8.5 Effect of addition of iodine on formation of HI

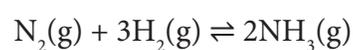


In the large scale of production of CaO from CaCO_3 , constant removal of CO_2 from the kiln drives the reaction to completion. As in the case of manufacture of NH_3 by the Haber's process, NH_3 is liquefied and removed so that the reaction keeps moving in forward direction.

8.8.2 Effect of pressure

The change in pressure has significant effect only on equilibrium systems with gaseous components. When the pressure on the system is increased, the volume decreases proportionately and the system responds by shifting the equilibrium in a direction that has fewer moles of gaseous molecules.

Let us consider the synthesis of ammonia from nitrogen and hydrogen.





Let the system be allowed to attain equilibrium in a cylinder with a piston. If we press the piston down to increase the pressure, the volume decreases. The system responds to this effect by reducing the number of gas molecules. i.e. it favours the formation of ammonia. If we pull the piston upwards to reduce the pressure, the volume increases. It favours the decomposition of ammonia

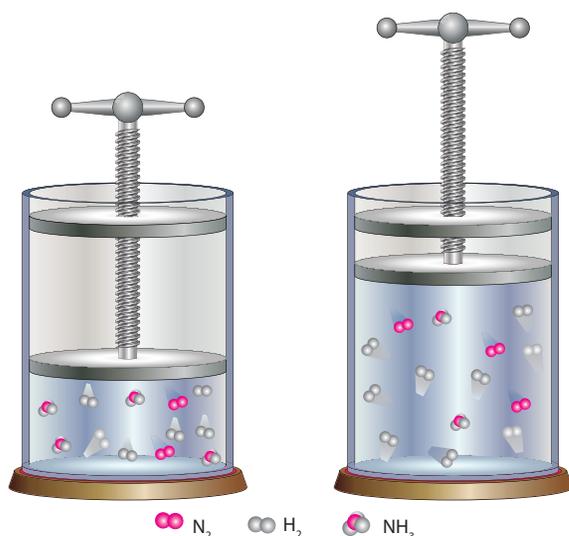
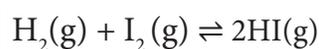


Figure 8.6 Effect of pressure on ammonia synthesis.

However, when the total number of the moles of the gaseous reactants and the gaseous products are equal, the change in pressure has no effect on system at equilibrium.

Let us consider the following reaction



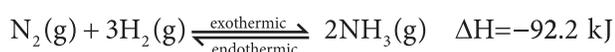
2 moles of reactants \Rightarrow 2 moles of products

Here, the number of moles of reactants and products are equal. So, the pressure has no effect on such equilibrium with $\Delta n_g = 0$.

8.8.3 Effect of temperature

If the temperature of a system at equilibrium is changed, the system responds by shifting the equilibrium in the direction that attempts to nullify the effect of temperature.

Let us consider the formation of ammonia.



In this equilibrium, the forward reaction is exothermic i.e. heat is liberated while the reverse reaction is endothermic i.e. heat is absorbed.

If the temperature of the system is increased (by supplying heat energy), the system responds by decomposing some of the ammonia molecules to nitrogen and hydrogen by absorbing the supplied heat energy. Similarly, the system responds to a drop in the temperature by forming more ammonia molecules from nitrogen and hydrogen, which releases heat energy.

We have already learnt that the change in pressure or concentration causes a change in the equilibrium concentration such that the equilibrium constant remains the same. However, in case of change in temperature, the equilibrium is reestablished with a different equilibrium constant.

8.8.4 Effect of a catalyst

Addition of a catalyst does not affect the state of the equilibrium. The catalyst increases the rate of both the forward and the reverse reactions to the same extent. Hence, it does not change the equilibrium composition of the reaction mixture.

However, it speeds up the attainment of equilibrium by providing a new pathway having a lower activation energy.

For example, in the synthesis of NH_3 by the Haber's process iron is used as a catalyst. Similarly, in the contact process of manufacturing SO_3 , platinum or V_2O_5 is used as a catalyst.

8.8.5 Effect of inert gas

When an inert gas (i.e, a gas which does not react with any other species involved in equilibrium) is added to an equilibrium system at constant volume, the total number of moles of gases present in the container increases, that is, the total pressure of gases increases. the partial pressure of the reactants and the products are unchanged. Hence at constant volume, addition of inert gas has no effect on equilibrium.

Table 8.3: Effect of concentration, pressure, temperature, catalyst and Inert gas on equilibrium

Condition	Stress	Direction in which equilibrium shifts
Concentration	Addition of reactants (increase in reactant concentration)	Forward reaction
	Removal of products (decrease in product concentration)	
	Addition of products (increase in product concentration)	Reverse reaction
	Removal of reactants (decrease in reactant concentration)	
Pressure	Increase of pressure (Decrease in volume)	Reaction that favours fewer moles of the gaseous molecules
	Decrease of pressure (Increase in volume)	Reaction that favours more moles of the gaseous molecules
Temperature (Alters equilibrium constants)	Increase (High T)	Towards endothermic reaction
	decrease (Low T)	Towards exothermic reaction
Catalyst (Speeds up the attainment of equilibrium)	Addition of catalyst	No effect
Inert gas	Addition of inert gas at constant volume	No effect

8.9 Van't Hoff Equation

This equation gives the quantitative temperature dependence of equilibrium constant (K). The relation between standard free energy change (ΔG°) and equilibrium constant is

$$\Delta G^\circ = -RT \ln K \quad (1)$$

We know that

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2)$$

Substituting (1) in equation (2)

$$-RT \ln K = \Delta H^\circ - T\Delta S^\circ$$

Rearranging

$$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (3)$$

Differentiating equation (3) with respect to temperature,

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (4)$$

Equation 4 is known as differential form of van't Hoff equation.

On integrating the equation 4, between T_1 and T_2 with their respective equilibrium constants K_1 and K_2 .

$$\int_{K_1}^{K_2} d(\ln K) = \frac{\Delta H^\circ}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$[\ln K]_{K_1}^{K_2} = \frac{\Delta H^\circ}{R} \left[-\frac{1}{T} \right]_{T_1}^{T_2}$$

$$\ln K_2 - \ln K_1 = \frac{\Delta H^\circ}{R} \left[-\frac{1}{T_2} + \frac{1}{T_1} \right]$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303 R} \left[\frac{T_2 - T_1}{T_2 T_1} \right] \dots\dots\dots (5)$$

Equation 5 is known as integrated form of van't Hoff equation.

Problem:

For an equilibrium reaction $K_p = 0.0260$ at 25°C , $\Delta H = 32.4 \text{ kJ mol}^{-1}$, calculate K_p at 37°C

Solution :

$$T_1 = 25 + 273 = 298 \text{ K}$$

$$T_2 = 37 + 273 = 310 \text{ K}$$

$$\Delta H = 32.4 \text{ kJ mol}^{-1} = 32400 \text{ J mol}^{-1}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_{p_1} = 0.0260$$

$$K_{p_2} = ?$$

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H^\circ}{2.303 R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{32400}{2.303 \times 8.314} \left(\frac{310 - 298}{310 \times 298} \right)$$

$$= \frac{32400 \times 12}{2.303 \times 8.314 \times 310 \times 298}$$

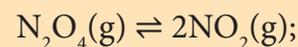
$$= 0.2198$$

$$\frac{K_{p_2}}{K_{p_1}} = \text{anti log } 0.2198 = 1.6588$$

$$K_{p_2} = 1.6588 \times 0.026 = 0.0431$$

Evaluate Yourself

5) The equilibrium constant for the following reaction is 0.15 at 298 K and 1 atm pressure.



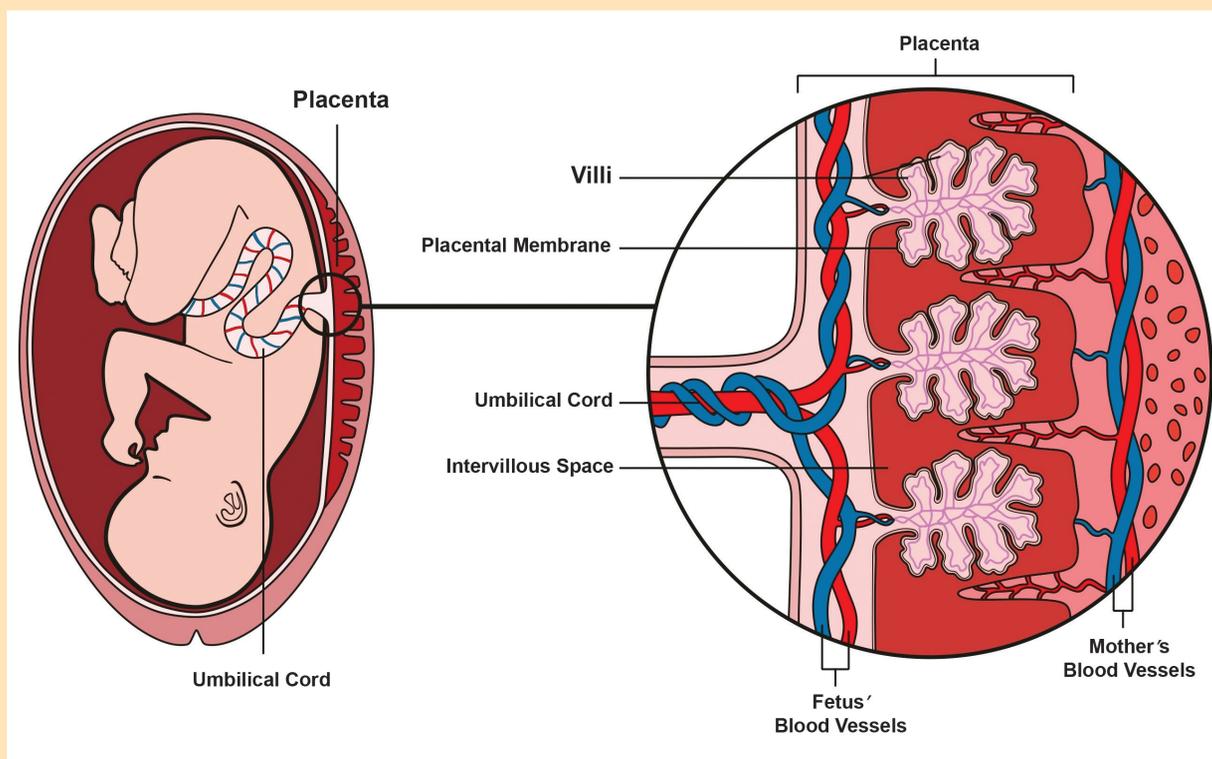
$$\Delta H_f^\circ = 57.32 \text{ kJ mol}^{-1}$$

The reaction conditions are altered as follows.

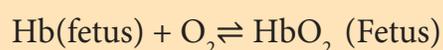
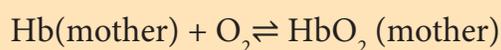
a) The reaction temperature is altered to 100°C keeping the pressure at 1 atm, Calculate the equilibrium constant.



How does oxygen exchanges between maternal and fetal blood in pregnant women?



In a pregnant women, the oxygen supply for fetus is provided by the maternal blood in the placenta where the blood vessels of both mother and fetus are in close proximity. Both fetal and maternal hemoglobin binds to oxygen reversibly as follows.



In the above two equilibriums, the equilibrium constant value for the oxygenation of fetal hemoglobin is higher, which is due to its higher affinity for oxygen compared to the adult hemoglobin. Hence in placenta, the oxygen from the mother's blood is effectively transferred to the fetal hemoglobin

SUMMARY

- In our daily life, we observe several chemical and physical changes.
- In some chemical reactions, at a particular stage, the rate of the reverse reaction is equal to that of the forward reaction indicating a state of equilibrium.

There are different types of equilibrium.

Physical equilibrium

Chemical Equilibrium

- Chemical reactions which are reversible do not cease, when equilibrium is attained. At equilibrium the forward and the backward reactions are proceeding at the same rate and no macroscopic change is observed. So chemical equilibrium is in a state of dynamic equilibrium.
- The rate law states that, "At any instant, the rate of a chemical reaction at a given temperature is directly proportional to the product of the active masses of the reactants at that instant".
- The value of equilibrium constant, K_c tells us the extent of a reaction, i.e., it indicates how far the reaction has proceeded towards product formation at a given temperature.
- Under non-equilibrium conditions, reaction quotient 'Q' is defined as the ratio of the product of active masses of reaction products raised to the respective stoichiometric coefficients in the balanced chemical equation to that of the reactants.
- Le-Chatelier's Principle "If a system at equilibrium is disturbed, then the system shifts itself in a

direction that nullifies the effect of that disturbance."

- The effect of change in reaction conditions such as temperature, pressure and concentration etc... on a system at equilibrium can be predicted by Le Chatelier-Braun principle.
- vant Hoff equation This equation gives the quantitative temperature dependence of equilibrium constant (K).

Evaluation

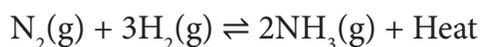


I. Choose the best answer.

1. If K_b and K_f for a reversible reaction are 0.8×10^{-5} and 1.6×10^{-4} respectively, the value of the equilibrium constant is,
a) 20 b) 0.2×10^{-1}
c) 0.05 d) none of these
2. At a given temperature and pressure, the equilibrium constant values for the equilibria
$$3A_2 + B_2 + 2C \xrightleftharpoons{K_1} 2A_3BC$$
 and
$$A_3BC \xrightleftharpoons{K_2} \frac{3}{2} A_2 + \frac{1}{2} B_2 + C$$
The relation between K_1 and K_2 is
a) $K_1 = \frac{1}{\sqrt{K_2}}$ b) $K_2 = K_1^{-1/2}$
c) $K_1^2 = 2K_2$ d) $\frac{K_1}{2} = K_2$
3. The equilibrium constant for a reaction at room temperature is K_1 and that at 700 K is K_2 . If $K_1 > K_2$, then
a) The forward reaction is exothermic

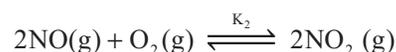
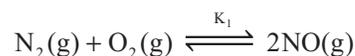


- b) The forward reaction is endothermic
 c) The reaction does not attain equilibrium
 d) The reverse reaction is exothermic
4. The formation of ammonia from $N_2(g)$ and $H_2(g)$ is a reversible reaction



What is the effect of increase of temperature on this equilibrium reaction

- a) equilibrium is unaltered
 b) formation of ammonia is favoured
 c) equilibrium is shifted to the left
 d) reaction rate does not change
5. Solubility of carbon dioxide gas in cold water can be increased by
- a) increase in pressure
 b) decrease in pressure
 c) increase in volume
 d) none of these
6. Which one of the following is incorrect statement ?
- a) for a system at equilibrium, Q is always less than the equilibrium constant
 b) equilibrium can be attained from either side of the reaction
 c) presence of catalyst affects both the forward reaction and reverse reaction to the same extent
 d) Equilibrium constant varied with temperature
7. K_1 and K_2 are the equilibrium constants for the reactions respectively.



What is the equilibrium constant for the reaction $NO_2(g) \rightleftharpoons \frac{1}{2}N_2(g) + O_2(g)$

- a) $\frac{1}{\sqrt{K_1 K_2}}$ b) $(K_1 = K_2)^{1/2}$
 c) $\frac{1}{2K_1 K_2}$ d) $\left(\frac{1}{K_1 K_2}\right)^{3/2}$

8. In the equilibrium,



the equilibrium concentrations of A, B and C_2 at 400 K are 1×10^{-4} M, 2.0×10^{-3} M, 1.5×10^{-4} M respectively. The value of K_C for the equilibrium at 400 K is

- a) 0.06 b) 0.09
 c) 0.62 d) 3×10^{-2}
9. An equilibrium constant of 3.2×10^{-6} for a reaction means, the equilibrium is
- a) largely towards forward direction
 b) largely towards reverse direction
 c) never established
 d) none of these
10. $\frac{K_C}{K_P}$ for the reaction,
 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is
- a) $\frac{1}{RT}$ b) \sqrt{RT}
 c) RT d) $(RT)^2$
11. For the reaction $AB(g) \rightleftharpoons A(g) + B(g)$, at equilibrium, AB is 20% dissociated at a total pressure of P, The equilibrium

constant K_p is related to the total pressure by the expression

- a) $P = 24 K_p$ b) $P = 8 K_p$
c) $24 P = K_p$ d) none of these

12. In which of the following equilibrium, K_p and K_c are not equal?

- a) $2 \text{NO}(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + \text{O}_2(\text{g})$
b) $\text{SO}_2(\text{g}) + \text{NO}_2 \rightleftharpoons \text{SO}_3(\text{g}) + \text{NO}(\text{g})$
c) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
d) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

13. If x is the fraction of PCl_5 dissociated at equilibrium in the reaction



then starting with 0.5 mole of PCl_5 , the total number of moles of reactants and products at equilibrium is

- a) $0.5 - x$ b) $x + 0.5$
c) $2x + 0.5$ d) $x + 1$

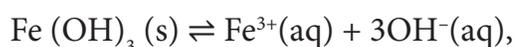
14. The values of K_{p_1} and K_{p_2} for the reactions



$\text{A} \rightleftharpoons 2\text{B}$ are in the ratio 9 : 1 if degree of dissociation and initial concentration of X and A be equal then total pressure at equilibrium P_1 , and P_2 are in the ratio

- a) 36 : 1 b) 1 : 1
c) 3 : 1 d) 1 : 9

15. In the reaction,



if the concentration of OH^{-} ions is decreased by $\frac{1}{4}$ times, then the

equilibrium concentration of Fe^{3+} will

- a) not changed
b) also decreased by $\frac{1}{4}$ times
c) increase by 4 times
d) increase by 64 times

16. Consider the reaction where $K_p = 0.5$ at a particular temperature



if the three gases are mixed in a container so that the partial pressure of each gas is initially 1 atm, then which one of the following is true

- a) more PCl_3 will be produced
b) more Cl_2 will be produced
c) more PCl_5 will be produced
d) none of these

17. Equimolar concentrations of H_2 and I_2 are heated to equilibrium in a 1 litre flask. What percentage of initial concentration of H_2 has reacted at equilibrium if rate constant for both forward and reverse reactions are equal

- a) 33% b) 66%
c) $(33)^2\%$ d) 16.5 %

18. In a chemical equilibrium, the rate constant for the forward reaction is 2.5×10^2 and the equilibrium constant is 50. The rate constant for the reverse reaction is,

- a) 11.5 b) 5
c) 2×10^2 d) 2×10^{-3}

19. Which of the following is not a general



characteristic of equilibrium involving physical process

- a) Equilibrium is possible only in a closed system at a given temperature
- b) The opposing processes occur at the same rate and there is a dynamic but stable condition
- c) All the physical processes stop at equilibrium
- d) All measurable properties of the system remains constant
20. For the formation of Two moles of $\text{SO}_3(\text{g})$ from SO_2 and O_2 , the equilibrium constant is K_1 . The equilibrium constant for the dissociation of one mole of SO_3 into SO_2 and O_2 is

- a) $\frac{1}{K_1}$ b) K_1^2
- c) $\left(\frac{1}{K_1}\right)^{\frac{1}{2}}$ d) $\frac{K_1}{2}$

21. Match the equilibria with the corresponding conditions,

- i) Liquid \rightleftharpoons Vapour
- ii) Solid \rightleftharpoons Liquid
- iii) Solid \rightleftharpoons Vapour
- iv) Solute (s) \rightleftharpoons Solute (Solution)
- 1) melting point
- 2) Saturated solution
- 3) Boiling point
- 4) Sublimation point
- 5) Unsaturated solution

	(i)	(ii)	(iii)	(iv)
(a)	1	2	3	4
(b)	3	1	4	2
(c)	2	1	3	4
(d)	3	2	4	5

22. Consider the following reversible reaction at equilibrium, $\text{A} + \text{B} \rightleftharpoons \text{C}$, If the concentration of the reactants A and B are doubled, then the equilibrium constant will

- a) be doubled b) become one fourth
- c) be halved d) remain the same

23. $[\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ (pink) + $4\text{Cl}^-(\text{aq}) \rightleftharpoons [\text{CoCl}_4]^{2-}(\text{aq})$ (blue) + $6\text{H}_2\text{O}(\text{l})$

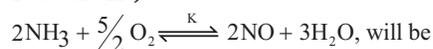
In the above reaction at equilibrium, the reaction mixture is blue in colour at room temperature. On cooling this mixture, it becomes pink in colour. On the basis of this information, which one of the following is true ?

- a) $\Delta H > 0$ for the forward reaction
- b) $\Delta H = 0$ for the reverse reaction
- c) $\Delta H < 0$ for the forward reaction
- d) Sign of the ΔH cannot be predicted based on this information.

24. The equilibrium constants of the following reactions are :



The equilibrium constant (K) for the reaction ;





- a) $K_2^3 K_3 / K_1$ b) $K_1 K_3^3 / K_2$
 c) $K_2 K_3^3 / K_1$ d) $K_2 K_3 / K_1$

25. A 20 litre container at 400 K contains CO_2 (g) at pressure 0.4 atm and an excess of SrO (neglect the volume of solid SrO). The volume of the container is now decreased by moving the movable piston fitted in the container. The maximum volume of the container, when pressure of CO_2 attains its maximum value will be :

Given that : $\text{SrCO}_3 (\text{s}) \rightleftharpoons \text{SrO} (\text{s}) + \text{CO}_2 (\text{g})$

$K_p = 1.6 \text{ atm}$ (NEET 2017)

- a) 2 litre b) 5 litre
 c) 10 litre d) 4 litre

II. Write brief answer to the following questions.

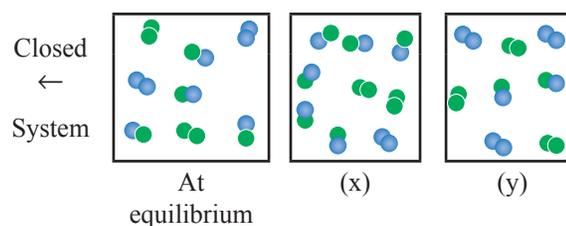
26. If there is no change in concentration, why is the equilibrium state considered dynamic ?
27. For a given reaction at a particular temperature, the equilibrium constant has constant value. Is the value of Q also constant ? Explain.
28. What is the relation between K_p and K_c . Give one example for which K_p is equal to K_c .
29. For a gaseous homogeneous reaction at equilibrium, number of moles of products are greater than the number of moles of reactants. Is K_c is larger or smaller than K_p .
30. When the numerical value of the reaction quotient (Q) is greater than

the equilibrium constant (K), in which direction does the reaction proceed to reach equilibrium ?

31. For the reaction,



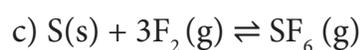
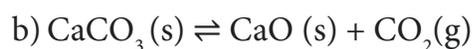
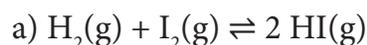
the following molecular scenes represent different reaction mixture (A – green, B – blue)



- i) Calculate the equilibrium constant K_p and (K_c).
- ii) For the reaction mixture represented by scene (x), (y) the reaction proceed in which directions ?
- iii) What is the effect of increase in pressure for the mixture at equilibrium.

32. State Le-Chatelier principle.

33. Consider the following reactions,



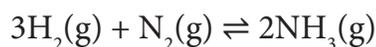
In each of the above reaction find out whether you have to increase (or) decrease the volume to increase the yield of the product.

34. State law of mass action.

35. Explain how will you predict the direction of a equilibrium reaction.



36. Derive a general expression for the equilibrium constant K_p and K_c for the reaction



37. Write a balanced chemical equation for the equilibrium reaction for which the equilibrium constant is given by expression

$$K_c = \frac{[\text{NH}_3]^4 [\text{O}_2]^5}{[\text{NO}]^4 [\text{H}_2\text{O}]^6}$$

38. What is the effect of added inert gas on the reaction at equilibrium at constant volume.
39. Derive the relation between K_p and K_c .
40. One mole of PCl_5 is heated in one litre closed container. If 0.6 mole of chlorine is found at equilibrium, calculate the value of equilibrium constant.
41. For the reaction

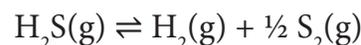


the value of equilibrium constant $K_p = 2.2 \times 10^{-4}$ at 1002 K. Calculate K_c for the reaction.

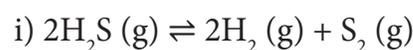
42. To study the decomposition of hydrogen iodide, a student fills an evacuated 3 litre flask with 0.3 mol of HI gas and allows the reaction to proceed at 500 °C. At equilibrium he found the concentration of HI which is equal to 0.05 M. Calculate K_c and K_p for this reaction.
43. 1 mol of CH_4 , 1 mole of CS_2 and 2 mol of H_2S are 2 mol of H_2 are mixed in a 500 ml flask. The equilibrium constant for the reaction $K_c = 4 \times 10^{-2} \text{ mol}^2 \text{ lit}^{-2}$.

In which direction will the reaction proceed to reach equilibrium ?

44. At particular temperature $K_c = 4 \times 10^{-2}$ for the reaction



Calculate K_c for each of the following reaction



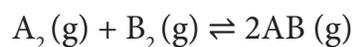
45. 28 g of Nitrogen and 6 g of hydrogen were mixed in a 1 litre closed container. At equilibrium 17 g NH_3 was produced. Calculate the weight of nitrogen, hydrogen at equilibrium.
46. The equilibrium for the dissociation of XY_2 is given as,



if the degree of dissociation x is so small compared to one. Show that

$2 K_p = P X^3$ where P is the total pressure and K_p is the dissociation equilibrium constant of XY_2 .

47. A sealed container was filled with 1 mol of $\text{A}_2(\text{g})$, 1 mol $\text{B}_2(\text{g})$ at 800 K and total pressure 1.00 bar. Calculate the amounts of the components in the mixture at equilibrium given that $K = 1$ for the reaction



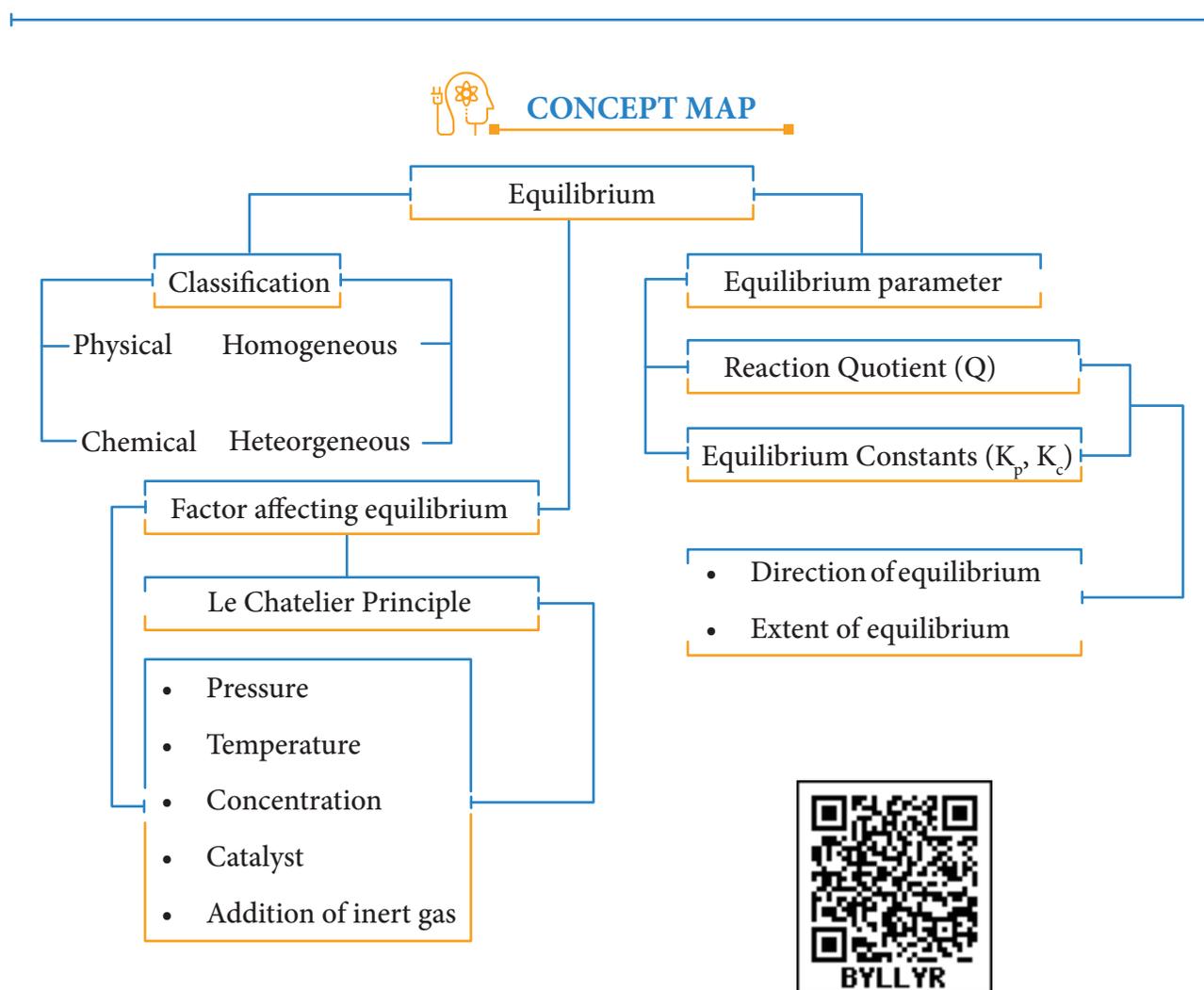
48. Deduce the Vant Hoff equation.
49. The equilibrium constant K_p for the reaction



$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ is 8.19×10^2 at 298 K and 4.6×10^{-1} at 498 K. Calculate ΔH° for the reaction.

50. The partial pressure of carbon dioxide in the reaction

$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ is 1.017×10^{-3} atm at 500°C . Calculate K_p at 600°C for the reaction. ΔH for the reaction is 181 kJ mol^{-1} and does not change in the given range of temperature.





ICT Corner

Effect of temperature and pressure in an equilibrium process

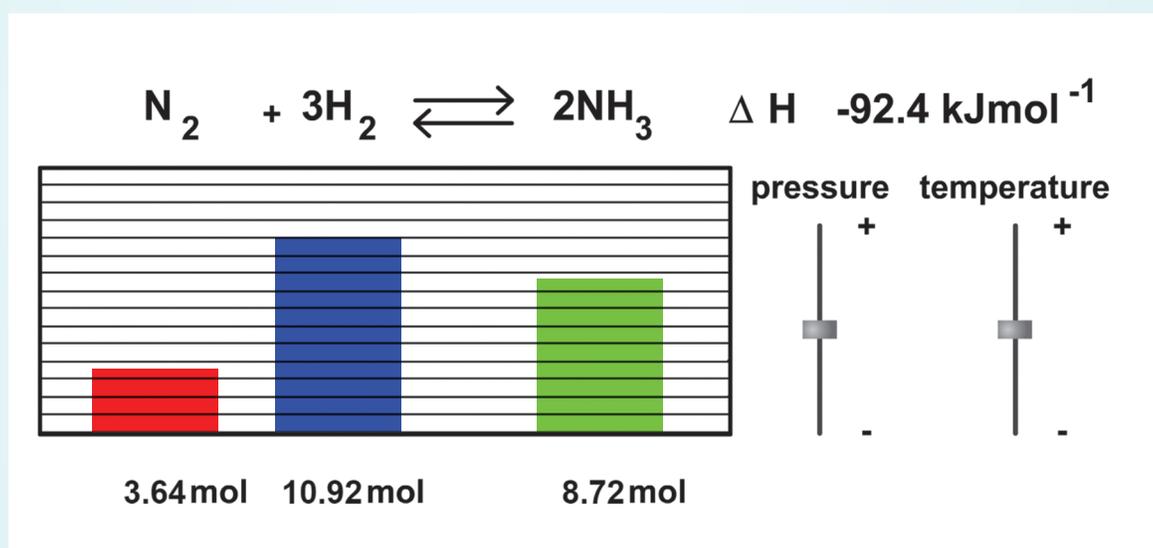
By using this tool, we can determine the effect of pressure and temperature in the equilibrium concentration of the components in ammonia synthesis (Haber process)

Please go to the URL
<http://www.freezeray.com/flashFiles/ammoniaConditions.htm>
(or) Scan the QR code on the right side

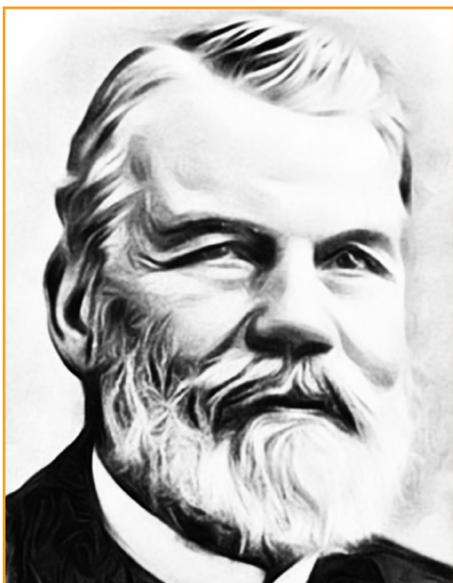


Steps

- Open the Browser and type the URL given (or) Scan the QR Code.
- The website will show the equilibrium reaction involved in ammonia synthesis and the relative concentration of the components. The visual representation and the actual concentration values are given in the box 1.
- Now change the pressure or temperature using the corresponding slider indicated in the box2.
- As you move the slider you will be able to see the change in the equilibrium concentration of reactants and products.
- Now you can understand that if a stress is applied on the system at equilibrium, the system will adjust itself to nullify the effect of the stress.



Unit 9 Solutions



François - Marie Raoult

François - Marie Raoult was a French chemist who conducted research into the behaviour of solutions, especially their physical properties.

In his first research paper, he described the action of solutes in depressing the freezing point of the solutions. He also gave a relation between the vapour pressure of the solution with the molecular weight of the solute.

Learning Objectives

After studying this unit students will be able to

- describe the formation of different types of solutions
- express the concentration of a solution in different units
- prepare solutions of required concentrations by diluting the stock solution
- state Henry's and Raoult's Law
- explain the deviation of real solutions from Raoult's Law
- correlate colligative properties of solutions with the molar masses of their solutes
- explain the abnormal colligative properties
- define Van't Hoff factor and calculate degree of dissociation / association

9.1 INTRODUCTION

There are many chemicals that play an important role in our daily life. All these chemicals are in different physical forms, viz solid, liquid and gas. If we do close examination on their composition, we could find that most of them are mixtures and rarely pure substances. One more interesting aspect is that most of the mixtures are homogeneous irrespective of their physical state and such homogeneous mixtures are called as solutions.

Sea water is one of the naturally existing solutions which covers more than 70% of the earth's surface. We cannot imagine life on earth without sea water. It contains many dissolved solids, mostly NaCl. Another important naturally occurring solution is air. Air is a homogeneous mixture of nitrogen, oxygen, carbon dioxide, and other trace gases. Even solid material such as brass is a homogeneous mixture of copper and zinc.

In the above examples the solutions are in different physical states viz... liquid (sea water), gas (air) and solid (alloys), and one common property of all the above is their homogeneity. The homogeneity implies uniform distribution of their constituents or components throughout the mixture. In this chapter, we learn about the solutions and their properties.

9.2 Types of solutions

A solution is a homogeneous mixture of two or more substances, consisting of atoms, ions or molecules. The compound that is present in largest amount in a homogeneous mixture is called the solvent, and others are solutes. For example, when a small amount of NaCl is dissolved in water, a homogeneous solution is obtained. In this solution, Na^+ and Cl^- ions are uniformly distributed in water. Here water is the solvent as the amount of water is more compared to the amount of NaCl present in this solution, and NaCl is the solute.

The commonly used solutions are the solutions in which a solid solute is dissolved in a liquid solvent. However, solute or solvent can be in any of the three states of matter (solid, liquid, gas). If water is used as

the solvent, the resultant solution is called as an aqueous solution. If solvents (Benzene, CCl_4 , ether etc.,) other than water is used, then the resultant solution is called as a non-aqueous solution.

The following table illustrates the different types of solutions based on the physical state of the solute and solvent.

Table 9.1 Types and examples of solutions

S. No.	State of solution	Solute	Solvent	Examples
1	Gaseous solution	Gas	Gas	Air (A mixture of nitrogen, oxygen and other gases)
		Liquid	Gas	Humid oxygen (Oxygen containing water)
		Solid	Gas	Camphor in nitrogen gas
2	Liquid solutions	Gas	Liquid	CO_2 dissolved in water (carbonated water)
		Liquid	Liquid	Ethanol dissolved in water
		Solid	Liquid	Salt water
3	Solid solutions	Gas	Solid	Solution of H_2 in palladium
		Liquid	Solid	Amalgam of potassium (used for dental filling)
		Solid	Solid	Gold alloy (of copper used in making Jewelry)

9.3 Expressing concentration of solutions

In our life we have come across many solutions of varying strengths or

concentrations such as mouthwash, antiseptic solutions, household disinfectants etc... Have you ever noticed the concentration of the ingredients present in those solutions? For example, chlorhexidine mouthwash solution contains 0.2 % (w/v) chlorhexidine gluconate; The concentration of the commercially available hydrogen peroxide is 3% (w/v). Similarly, other terms such as ppm (TDS of water), molar and normal (laboratory reagents) are used to express the concentration of the solution. The concentration of a solution gives the amount of solute present in a given quantity of solvent. As we have seen, there are different ways of expressing the concentration of a solution. Let us learn the different concentration terms and to prepare a solution of a specific concentration.

Table 9.2 Different concentration units and their illustrations

S. No.	Concentration term	Expression	Illustration
1	Molality (m)	$\frac{\text{Number of moles of solute}}{\text{Mass of the solvent (in kg)}}$	<p>The molality of the solution containing 45 g of glucose dissolved in 2 kg of water</p> $\frac{\text{Number of moles of solute}}{\text{Mass of the solvent (in kg)}} = \frac{\left(\frac{45}{180}\right)}{2}$ $= \frac{0.25}{2} = 0.125 \text{ m}$
2	Molarity (M)	$\frac{\text{Number of moles of solute}}{\text{Volume of solution (in L)}}$	<p>5.845 g of sodium chloride is dissolved in water and the solution was made up to 500 mL using a standard flask. The strength of the solution in molarity is</p> $\frac{\text{Number of moles of solute}}{\text{Volume of solution (in L)}} = \frac{\left(\frac{5.845}{58.45}\right)}{0.5}$ $\frac{0.1}{0.5} = 0.2 \text{ M}$
3	Normality (N)	$\frac{\text{Number of gram equivalents of solute}}{\text{Volume of solution (in L)}}$	<p>3.15 g of oxalic acid dihydrate, is dissolved in water and the solution was made up to 100 mL using a standard flask. The strength of the solution in normality is</p> $= \frac{\text{Number of gram equivalents of solute}}{\text{Volume of solution (in L)}}$ $= \frac{\left(\frac{\text{mass of oxalic acid}}{\text{Equivalent mass of oxalic acid}}\right)}{\text{volume of solution (inL)}} = \frac{\left(\frac{3.15}{63}\right)}{0.1}$ $= \frac{0.05}{0.1} = 0.5 \text{ N}$

S. No.	Concentration term	Expression	Illustration
4	Formality (F)	$\frac{\text{Number of Formula mass of solute}}{\text{Volume of solution (in L)}}$	<p>5.85g of sodium chloride is dissolved in water and the solution was made up to 500 mL using a standard flask. The strength of the solution in formality is</p> $\text{formality} = \frac{\text{Number of Formula mass of solute}}{\text{Volume of solution (in L)}}$ $= \frac{5.85}{58.5 \times 0.5L}$ $= 0.2 F$
5	Mole fraction (of a component) (x)	<p>$\frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components present in solution}}$</p> <p>Consider a solution containing two components A and B whose mole fractions are x_A and x_B, respectively. Let the number of moles of the two components A and B be n_A and n_B, respectively.</p> $x_A = \frac{n_A}{n_A + n_B} \text{ and } x_B = \frac{n_B}{n_A + n_B}$ <p>Now,</p> $x_A + x_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1$	<p>0.5 mole of ethanol is mixed with 1.5 moles of water.</p> <p>The mole fraction of ethanol in the above solution is</p> $= \frac{\text{Number of moles of the ethanol}}{\text{Total number of moles of ethanol and water}}$ $= \frac{0.5}{1.5+0.5} = \frac{0.5}{2.0} = 0.25$ <p>The mole fraction of water in the above solution is</p> $= \frac{\text{Number of moles of water}}{\text{Total number of moles of ethanol and water}}$ $= \frac{1.5}{2.0} = 0.75$ <p>The mole fraction of water can also be calculated as follows mole fraction of water + mole fraction of ethanol = 1; mole fraction of water = 1 – mole fraction of ethanol = 1-0.25 = 0.75</p>
6	Mass percentage (% w/w)	$\frac{\text{Mass of the solute (in g)}}{\text{Mass of solution (in g)}} \times 100$	<p>Neomycin, aminoglycoside antibiotic cream contains 300 mg of neomycin sulphate the active ingredient, in 30g of ointment base. The mass percentage of neomycin is</p> $\frac{\text{Mass of the neomycin sulphate (in g)}}{\text{Mass of solution (in g)}} \times 100$ $= \frac{0.3 \text{ g}}{30 \text{ g}} \times 100 = 1\% \text{ w / w}$

S. No.	Concentration term	Expression	Illustration
7	Volume percentage (% v/v)	$\frac{\text{Volume of the solute (in mL)}}{\text{Volume of solution (in mL)}} \times 100$	<p>50 mL of tincture of benzoin, an antiseptic solution contains 10 mL of benzoin. The volume percentage of benzoin</p> $= \frac{\text{Volume of the benzoin (in mL)}}{\text{Volume of solution (in mL)}} \times 100$ $= \frac{10}{50} \times 100 = 20\% \text{ v / v}$
8	Mass by volume percentage (% w/v)	$\frac{\text{Mass of the solute (in g)}}{\text{Volume of solution (in mL)}} \times 100$	<p>A 60 mL of paracetamol paediatric oral suspension contains 3g of paracetamol. The mass percentage of paracetamol is</p> $\frac{\text{Mass of the paracetamol (in g)}}{\text{Volume of solution (in mL)}} \times 100 =$ $= \frac{3}{60} \times 100 = 5\% \text{ w / v}$
9	Parts per million (ppm)	$\frac{\text{Number of parts of the component}}{\text{Total number of parts of all components}} \times 10^6$ $= \frac{\text{Mass of the solute}}{\text{Mass of the solution}} \times 10^6$	<p>50 g of tap water contains 20 mg of dissolved solids. The TDS value in ppm is</p> $\frac{\text{Mass of the dissolved solids}}{\text{Mass of the water}} \times 10^6$ $\frac{20 \times 10^{-3} \text{ g}}{50 \text{ g}} \times 10^6 = 400 \text{ ppm}$

Evaluate Yourself

- 1) If 5.6 g of KOH is present in (a) 500 mL and (b) 1 litre of solution, calculate the molarity of each of these solutions.
- 2) 2.82 g of glucose is dissolved in 30 g of water. Calculate the mole fraction of glucose and water.
- 3) The antiseptic solution of iodopovidone for the use of external application contains 10 % w/v of iodopovidone. Calculate the amount of iodopovidone present in a typical dose of 1.5 mL.
- 4) A litre of sea water weighing about 1.05 kg contains 5 mg of dissolved oxygen (O₂). Express the concentration of dissolved oxygen in ppm.

The concentration of a solution is expressed in different units. The choice of unit depends on the type of measurement applied. For example, in complexometric titrations involving

EDTA, the reaction between EDTA and the metal ions takes place in the 1:1 mole ratio and hence molar solutions are used in this titrations. In the redox and neutralisation titrations we use normal solutions. The mole fraction is used to calculate the partial pressure of gases and the vapour pressure of solutions. The percentage units are used to express the active ingredients present in therapeutics, and the ppm is used to express the quantity of solutes present in small amounts in solutions.

9.3.1 Standard solutions and working standards

A standard solution or a stock solution is a solution whose concentration is accurately known. A standard solution of required concentration can be prepared by dissolving a required amount of a solute, in a suitable amount of solvent. Its done by

- (i) transforming a known amount of a solute to a standard flask of definite volume.
- (ii) a small amount of water is added to the flask and shaken well to dissolve the solute.
- (iii) then water is added to the flask to bring the solution level to the mark indicated at the top end of the flask.
- (iv) the flask is stoppered and shaken well to make concentration uniform.

At the time of experiment, the solution with required concentration is prepared by diluting the stock solution. This diluted solution is usually called working standard. A known volume of stock solution is transferred to a new container and brought to the calculated volume. The necessary volumes of the stock solution and final volume can be calculated using the following expression.

$$C_s V_s = C_w V_w \text{ -----(9.1)}$$

Where the C_s & V_s are concentration and volume of the stock solution and C_w & V_w are concentration and volume of the working standard, respectively.

9.3.2 Advantages of using standard solutions:

1. The error in weighing the solute can be minimised by using concentrated stock solution that requires large quantity of solute.
2. We can prepare working standards of different concentrations by diluting the stock solution, which is more efficient since consistency is maintained.
3. Some of the concentrated solutions are more stable and are less likely to support microbial growth than working standards used in the experiments.

Example Problem 1

1. What volume of 4M HCl and 2M HCl should be mixed to get 500 mL of 2.5 M HCl?

Let the volume of 4M HCl required to prepare 500 mL of 2.5 MHCl = x mL

Therefore, the required volume of 2M HCl = (500 - x) mL

We know from the equation (9.1)

$$C_1 V_1 + C_2 V_2 = C_3 V_3$$

$$(4x) + 2(500 - x) = 2.5 \times 500$$

$$4x + 1000 - 2x = 1250$$

$$2x = 1250 - 1000$$

$$x = \frac{250}{2}$$

$$= 125 \text{ mL}$$

Hence, volume of 4M HCl required = 125 mL

Volume of 2M HCl required = (500 - 125) mL = 375 mL

Evaluate Yourself

- 5) Describe how would you prepare the following solution from pure solute and solvent
- 1 L of aqueous solution of 1.5 M CoCl_2 .
 - 500 mL of 6.0 % (V/V) aqueous methanol solution.
- 6) How much volume of 6 M solution of NaOH is required to prepare 500 mL of 0.250 M NaOH solution.

9.4 Solubility of the solutes

Solubility of a solute is the maximum amount of solute that can be dissolved in a specific amount of solvent at a specified temperature. When maximum amount of solute is dissolved in a solvent, any more addition of solute will result in precipitation at a given temperature and pressure. Such a solution is called as a saturated solution. The solubility of a substance at a given temperature is defined as the amount of the solute that can be dissolved in 100 g of the solvent at a given temperature to form a saturated solution.

9.4.1 Factors influencing the solubility

The solubility of a solute generally depends on the nature of the solute and the solvent in which it is dissolved. It also depends on the temperature and pressure of the solution.

Nature of solute and solvent:

Sodium chloride, an ionic compound, dissolves readily in a polar solvent such as water, but it does not dissolve in non-polar organic solvents such as benzene or toluene. Many organic compounds dissolve readily in organic solvents and do not dissolve in water. Different gases dissolve in water to different extents: for example, ammonia is more soluble than oxygen in water.

Effect of temperature:

Solid solute in liquid solvent:

Generally, the solubility of a solid solute in a liquid solvent increases with increase in temperature. When the temperature is increased, the average kinetic energy of the molecules of the solute and the solvent increases. The increase in kinetic energy facilitates the solvent molecules to break the intermolecular attractive forces that keep the solute molecules together and hence the solubility increases.

When a solid is added to a solvent, it begins to dissolve. i.e. the solute leaves from the solid state (dissolution). After some time, some of the dissolved solute returns back to the solid state (recrystallisation). If there is excess of solid present, the rate of both these processes becomes equal at a particular stage. At this stage an equilibrium is established between the solid solute molecules and dissolved solute molecules.



According to Le-Chatelier principle, if the dissolution process is endothermic, the increase in temperature will shift the equilibrium towards right i.e solubility increases. for an exothermic reaction, the increase in temperature decreases the solubility. The solubilities of ammonium nitrate, calcium chloride, ceric sulphate nano-hydrate and sodium chloride in water at different temperatures are given in the following graph.

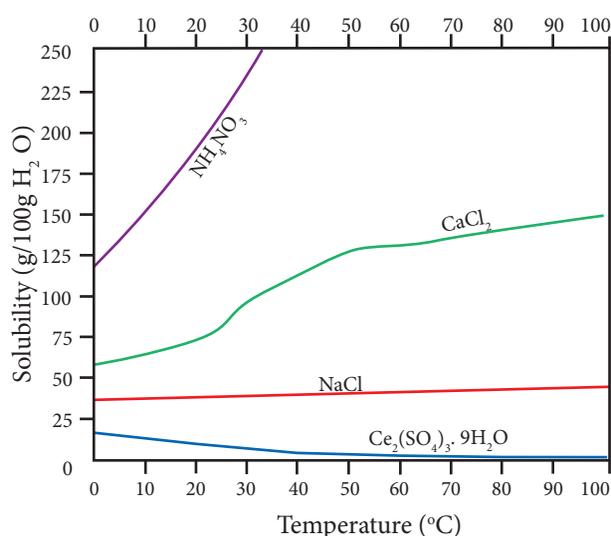


Figure 9. 1 Plot of solubility versus temperature for selective compounds

The following conclusions are drawn from the above graph.

- ▶ The solubility of sodium chloride does not vary appreciable as the maximum solubility is achieved at normal temperature. In fact, there is only 10 % increase in solubility between 0 ° to 100 °C.
- ▶ The dissolution process of ammonium nitrate is endothermic, the solubility increases steeply with increase in temperature.
- ▶ In the case of ceric sulphate, the dissolution is exothermic and the solubility decreases with increase in temperature.
- ▶ Even though the dissolution of calcium chloride is exothermic, the solubility increases moderately with increase in temperature. Here, the entropy factor also plays a significant role in deciding the position of the equilibrium.

Gaseous solute in liquid solvent:

In the case of gaseous solute in liquid solvent, the solubility decreases with increase in temperature. When a gaseous solute dissolves in a liquid solvent, its molecules interact with solvent molecules with weak intermolecular forces. When the temperature increases, the average kinetic energy of the molecules present in the solution also increases. The increase in kinetic energy breaks the weak intermolecular forces between the gaseous solute and liquid solvent which results in the release of the dissolved gas molecules to the gaseous state. Moreover, the dissolution of most of the gases in liquid solvents is an exothermic process, and in such processes, the increase in temperature decreases the dissolution of gaseous molecules.

Activity:

Open the soda bottle and put a balloon over it. The balloon will inflate with the released carbon dioxide from the soda. Carry out the same experiment by placing the soda bottle in a container of hot water. You will observe the balloon is inflated much faster now. This shows the decrease in solubility of gases in solution with increase in temperature. In the rivers where hot water is discharged from industrial plants, the aquatic lives are less sustained due to the decreased availability of dissolved oxygen.

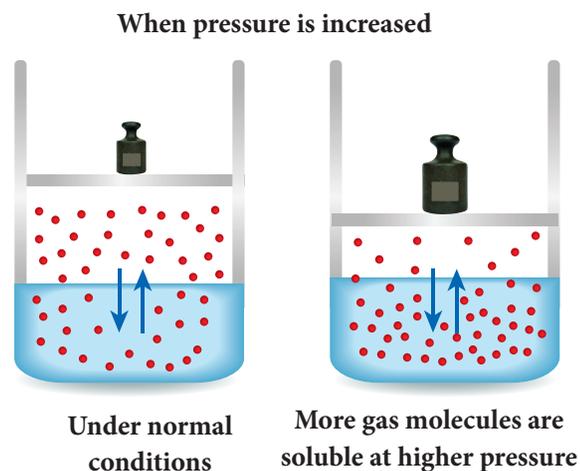


Figure 9.2 Effect of pressure on solubility

Effect of pressure:

Generally the change in pressure does not have any significant effect in the solubility of solids and liquids as they are not compressible. However, the solubility of gases generally increases with increase of pressure.

Consider a saturated solution of a gaseous solute dissolved in a liquid solvent in a closed container. In such a system, the following equilibrium exists.



According to Le-Chatelier principle, the increase in pressure will shift the equilibrium in the direction which will reduce the pressure. Therefore, more number of gaseous molecules dissolves in the solvent and the solubility increases.

9.5 Henry's law

William Henry investigated the relationship between pressure and solubility of a gaseous solute in a particular solvent. According to him, "the partial pressure of the gas in vapour phase (vapour pressure of

the solute) is directly proportional to the mole fraction(x) of the gaseous solute in the solution at low concentrations”. This statement is known as Henry’s law.

Henry’s law can be expressed as,

$$p_{\text{solute}} \propto x_{\text{solute in solution}}$$

$$p_{\text{solute}} = K_{\text{H}} x_{\text{solute in solution}}$$

Here, p_{solute} represents the partial pressure of the gas in vapour state which is commonly called as vapour pressure. x_{solute} in solution represents the mole fraction of solute in the solution. K_{H} is a empirical constant with the dimensions of pressure. The value of ‘ K_{H} ’ depends on the nature of the gaseous solute and solvent. The above equation is a straight-line in the form of $y=mx$. The plot partial pressure of the gas against its mole fraction in a solution will give a straight line as shown in fig 9.3. The slope of the straight line gives the value of K_{H} .

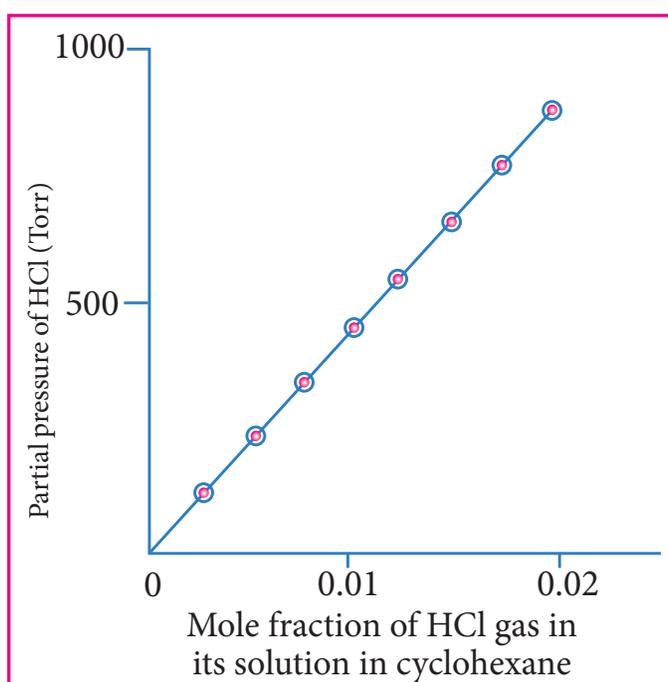


Figure 9.3 Solubility of HCl gas in cyclohexane at 293 K.



Why the carbonated drinks are stored in a pressurized container?

We all know that the carbonated beverages contain carbon dioxide dissolved in them. To dissolve the carbon dioxide in these drinks, the CO_2 gas is bubbled through them under high pressure. These containers are sealed to maintain the pressure. When we open these containers at atmospheric pressure, the pressure of the CO_2 drops to the atmospheric level and hence bubbles of CO_2 rapidly escape from the solution and show effervescence. The burst of bubbles is even more noticeable, if the soda bottle is in warm condition.

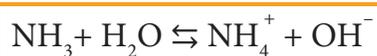


Why deep-sea divers use air diluted with helium gas in their air tanks?

The professional deep-sea divers carry a compressed air tank for breathing at high pressure under water. The normal compressed air contains nitrogen and oxygen and these gases are not very soluble in blood and other body fluids at normal pressure. As the pressure at that depth is far greater than the surface atmospheric pressure, more nitrogen dissolves in the blood and other body fluids when the diver breathes from tank. When the diver ascends to the surface, the pressure decreases, the dissolved nitrogen comes out of the blood and other body fluids quickly forming bubbles in the blood stream. These bubbles restrict blood flow, affect the transmission of nerve impulses and can even burst the capillaries or block them. This condition is called “the bends”, which are painful and dangerous to life. Now a days, to avoid such dangerous condition, the professional divers, use air diluted with helium gas (about 11.7% Helium, 56.2% Nitrogen and 32.1% Oxygen), because of lower solubility of helium in the blood than nitrogen. Moreover, because of small size of helium atoms they can pass through cell walls without damaging them. The excess oxygen dissolved in the blood is used in metabolism and does not cause the condition of bends

9.5.1 Limitations of Henry’s law

- Henry’s law is applicable at moderate temperature and pressure only.
- Only the less soluble gases obeys Henry’s law
- The gases reacting with the solvent do not obey Henry’s law. For example, ammonia or HCl reacts with water and hence does not obey this law.



- The gases obeying Henry’s law should not associate or dissociate while dissolving in the solvent.

Example Problem 2:

0.24 g of a gas dissolves in 1 L of water at 1.5 atm pressure. Calculate the amount of dissolved gas when the pressure is raised to 6.0 atm at constant temperature.

$$p_{\text{solute}} = K_{\text{H}} x_{\text{solute in solution}}$$

At pressure 1.5 atm,

$$p_1 = K_H x_1 \text{-----(1)}$$

At pressure 6.0 atm,

$$p_2 = K_H x_2 \text{-----(2)}$$

Dividing equation (1) by (2)

$$\text{From equation } p_1/p_2 = x_1/x_2$$

$$1.5/6.0 = 0.24/x_2$$

Therefore $x_2 = 0.24 \times 6.0/1.5 = 0.96 \text{ g/L}$

Evaluate Yourself

- 7) Calculate the proportion of O_2 and N_2 dissolved in water at 298 K. When air containing 20% O_2 and 80% N_2 by volume is in equilibrium with water at 1 atm pressure. Henry's law constants for two gases are $K_H(O_2) = 4.6 \times 10^4 \text{ atm}$ and $K_H(N_2) = 8.5 \times 10^4 \text{ atm}$.
- 8) Explain why the aquatic species are more comfortable in cold water during winter season rather than warm water during the summer.

9.6 Vapour pressure of liquid

Generally, liquids have a tendency to evaporate. If the kinetic energy of molecules in the liquid state overcomes the intermolecular force of attraction between them, then the molecules will escape from the liquid state. This process is called 'evaporation' and it happens on the surface of the liquid.

If evaporation is carried out in a closed container then the vapour remains in contact with the surface of the liquid. These vapour molecules are in continuous random motion during which they collide with each other and also with the walls of the container. As the collision is inelastic, they lose their energy and as result the vapour returns back to liquid state. This process is called as 'condensation'.

Evaporation and condensation are continuous processes. If the process is carried out in a closed system, a stage is reached when the rate of evaporation becomes equal to the rate of condensation. Thus, an equilibrium is established between liquid and its vapour. The pressure of the vapour in equilibrium with its liquid is called vapour pressure of the liquid at the given temperature. The vapour pressure of a liquid depends on its nature, temperature and the surface area. The following simple apparatus demonstrates the measurement of vapour pressure of a liquid.

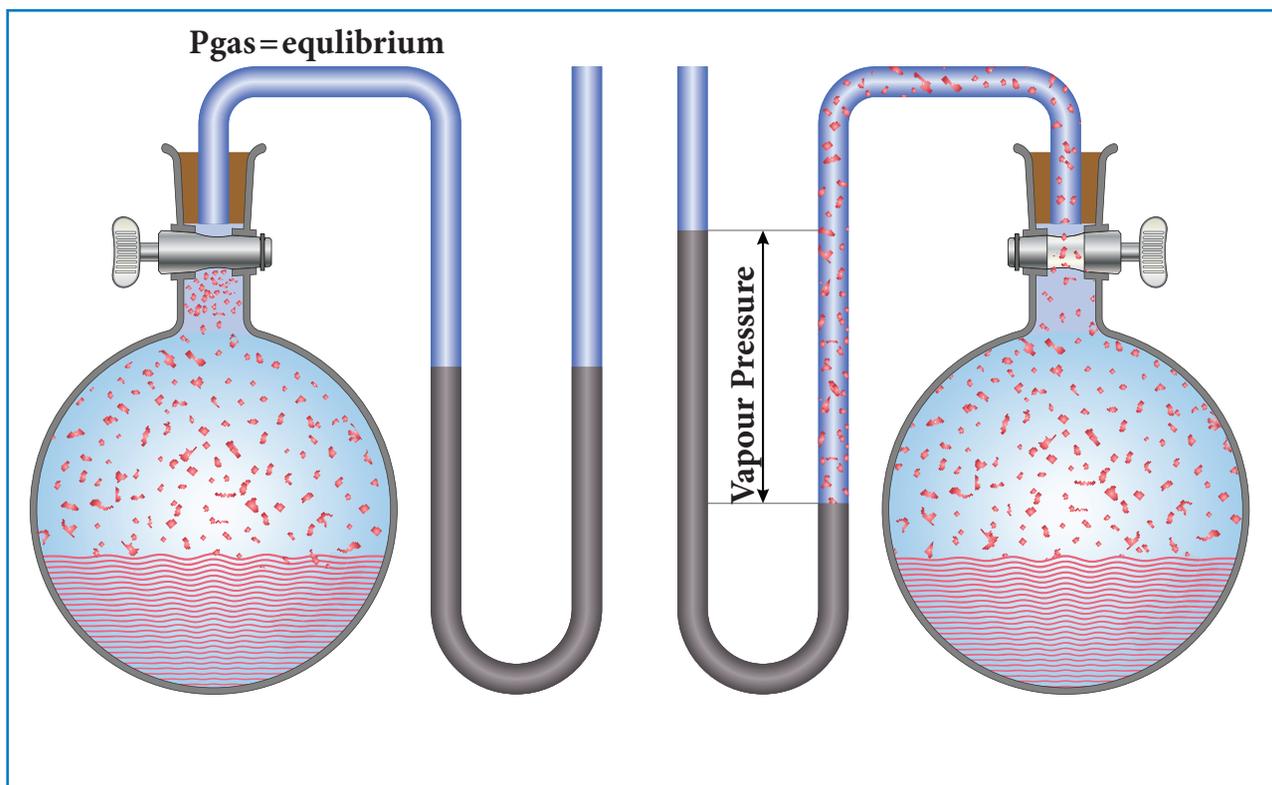


Figure 9.4 : a) A closed round bottomed flask in which ethanol is in equilibrium with its vapour. b) In the same setup the vapour is allowed to escape through a U tube filled with mercury. The escaped vapour pushes the mercury in the U tube and the difference in mercury level gives the vapour pressure of ethanol present in the RB flask.

9.7 Vapour pressure of liquid solutions

When a solute (of any physical state - solid, liquid or gas) is dissolved in a liquid solvent the resultant solution is called a liquid solution. The solution which contains only two components (one solvent and one solute) is called a binary solution. We have already discussed the solution of a gaseous solute in liquid solvent under Henry's law.

9.7.1 Vapour pressure of binary solution of liquid in liquids

Now, let us consider a binary liquid solution formed by dissolving a liquid solute 'A' in a pure solvent 'B' in a closed vessel. Both the components A and B present in the solution would evaporate and an equilibrium will be established between the liquid and vapour phases of the components A and B.

The French chemist Raoult, proposed a quantitative relationship between the partial

pressures and the mole fractions of two components A & B, which is known as Raoult's Law. This law states that "in the case of a solution of volatile liquids, the partial vapour pressure of each component (A & B) of the solution is directly proportional to its mole fraction".

According to Raoult's law,

$$p_A \propto x_A \text{ -----(9.3)}$$

$$p_A = k x_A$$

when $x_A = 1$, $k = p_A^\circ$

where p_A° is the vapour pressure of pure component 'A' at the same temperature.

Therefore,

$$p_A = p_A^\circ x_A \text{ ----- (9.4)}$$

Similarly, for component 'B'

$$p_B = p_B^\circ x_B \text{ -----(9.5)}$$

x_A and x_B are the mole fraction of the components A and B respectively.

According to Dalton's law of partial pressure the total pressure in a closed vessel will be equal to the sum of the partial pressures of the individual components.

Hence,

$$P_{\text{total}} = p_A + p_B \text{ -----(9.6)}$$

Substituting the values of p_A and p_B from equations (9.4) and (9.5) in the above equation,

$$P_{\text{total}} = x_A p_A^\circ + x_B p_B^\circ \quad (9.7)$$

We know that $x_A + x_B = 1$ or $x_A = 1 - x_B$

Therefore,

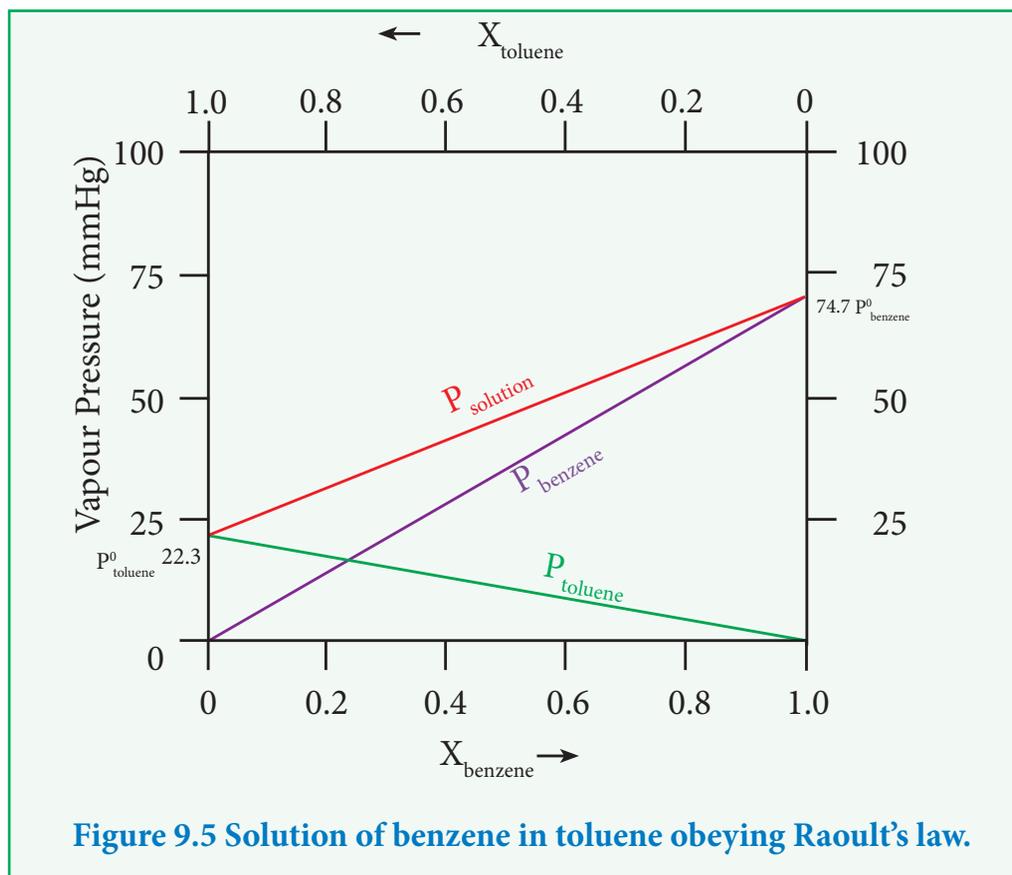
$$P_{\text{total}} = (1 - x_B) p_A^\circ + x_B p_B^\circ \text{ -----(9.8)}$$

$$P_{\text{total}} = p_A^\circ + x_B (p_B^\circ - p_A^\circ) \text{ -----(9.9)}$$

The above equation is of the straight-line equation form $y = mx+c$. The plot of P_{total} versus x_B will give a straight line with $(p_B^\circ - p_A^\circ)$ as slope and p_A° as the y intercept.

Let us consider the liquid solution containing toluene (solute) in benzene (solvent).

The variation of vapour pressure of pure benzene and toluene with its mole fraction is given in the graph.



The vapour pressures of pure toluene and pure benzene are 22.3 and 74.7 mmHg, respectively. The above graph shows, the partial vapour pressure of the pure components increases linearly with the increase in the mole fraction of the respective components. The total pressure at any composition of the solute and solvent is given by the following straight line (represented as red line) equation.

$$P_{\text{solution}} = p_{\text{toluene}}^{\circ} + x_{\text{benzene}} (p_{\text{benzene}}^{\circ} - p_{\text{toluene}}^{\circ}) \text{----- (9.10)}$$

9.7.2 Vapour pressure of binary solution of solids in liquids

When a nonvolatile solute is dissolved in a pure solvent, the vapour pressure of the pure solvent will decrease. In such solutions, the vapour pressure of the solution will depend only on the solvent molecules as the solute is nonvolatile.

For example, when sodium chloride is added to the water, the vapour pressure of the salt solution is lowered. The vapour pressure of the solution is determined by the number of molecules of the solvent present in the surface at any time and is proportional to the mole fraction of the solvent.

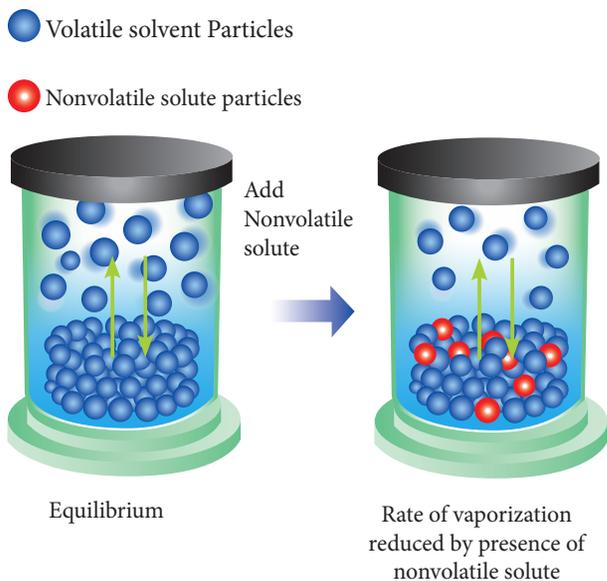


Fig 9.6 Rate of vapourization reduced by presence of nonvolatile solute.

$$P_{\text{solution}} \propto x_A \quad \text{----- (9.11)}$$

Where x_A is the mole fraction of the solvent

$$P_{\text{solution}} = k x_A \quad \text{----- (9.12)}$$

When $x_A = 1$, $K = P_{\text{solvent}}^{\circ}$

($P_{\text{solvent}}^{\circ}$ is the partial pressure of pure solvent)

$$P_{\text{solution}} = P_{\text{solvent}}^{\circ} x_A \quad \text{----- (9.13)}$$

$$\frac{P_{\text{solution}}}{P_{\text{solvent}}^{\circ}} = x_A \quad \text{----- (9.14)}$$

$$1 - \frac{P_{\text{solution}}}{P_{\text{solvent}}^{\circ}} = 1 - x_A \quad \text{----- (9.15)}$$

$$\frac{P_{\text{solvent}}^{\circ} - P_{\text{solution}}}{P_{\text{solvent}}^{\circ}} = x_B \quad \text{----- (9.16)}$$

Where x_B is the mole fraction of the solute

$$(\because x_A + x_B = 1, x_B = 1 - x_A)$$

The above expression gives the relative lowering of vapour pressure. Based

on this expression, Raoult's Law can also be stated as "the relative lowering of vapour pressure of an ideal solution containing the nonvolatile solute is equal to the mole fraction of the solute at a given temperature".

Comparison of Raoult's law and Henry's law

According to Raoult's law, for a solution containing a nonvolatile solute

$$P_{\text{solute}} = P_{\text{solute}}^{\circ} x_{\text{solute}} \quad \text{----- (9.17)}$$

According to Henry's law:

$$P_{\text{solute}} = K_H x_{\text{solute in solution}} \quad \text{----- (9.18)}$$

The difference between the above two expressions is the proportionality constant P_A° (Raoult's Law) and K_H (Henry's Law). Henry's law is applicable to solution containing gaseous solute in liquid solvent, while the Raoult's Law is applicable to nonvolatile solid solute in a liquid solvent. If the solute is non volatile then the Henry's law constant will become equal to the vapour pressure of the pure solvent (P_A°) and thus, Raoult's law becomes a special case of Henry's law. For very dilute solutions the solvent obeys Raoult's law and the solute obeys Henry's law.

9.8 Ideal and non-ideal solutions

9.8.1 Ideal Solutions:

An ideal solution is a solution in which each component i.e. the solute as well as the solvent obeys the Raoult's law over the entire range of concentration. Practically no solution is ideal over the entire range of concentration. However,

when the concentration of solute is very low, the dilute solution behaves ideally. If the two components present in the solution (A and B) are identical in size, structure, and having almost similar intermolecular attractive forces between them (i.e. between A-A, B-B and B-A) and then the solution tends to behave like an ideal solution.

For an ideal solution

1. There is no change in the volume on mixing the two components (solute & solvents). ($\Delta V_{\text{mixing}} = 0$)
2. There is no exchange of heat when the solute is dissolved in solvent ($\Delta H_{\text{mixing}} = 0$).
3. Escaping tendency of the solute and the solvent present in it should be same as in pure liquids.

Examples for ideal solutions: (Benzene & Toluene) ; (n-hexane & n-heptane) ; (Ethyl bromide & Ethyl iodide) ; (Chlorobenzene & Bromobenzene).

9.8.2 Non-ideal solutions

The solutions which do not obey Raoult's law over the entire range of concentration, are called non-ideal solutions. For a non-ideal solution, there is a change in the volume and enthalpy upon mixing. i.e. $\Delta H_{\text{mixing}} \neq 0$ & $\Delta V_{\text{mixing}} \neq 0$. The deviation of the non-ideal solutions from the Raoult's law can either be positive or negative.

Non-ideal solutions - positive deviation from Raoult's Law:

The nature of the deviation from the Raoult's law can be explained in terms of the

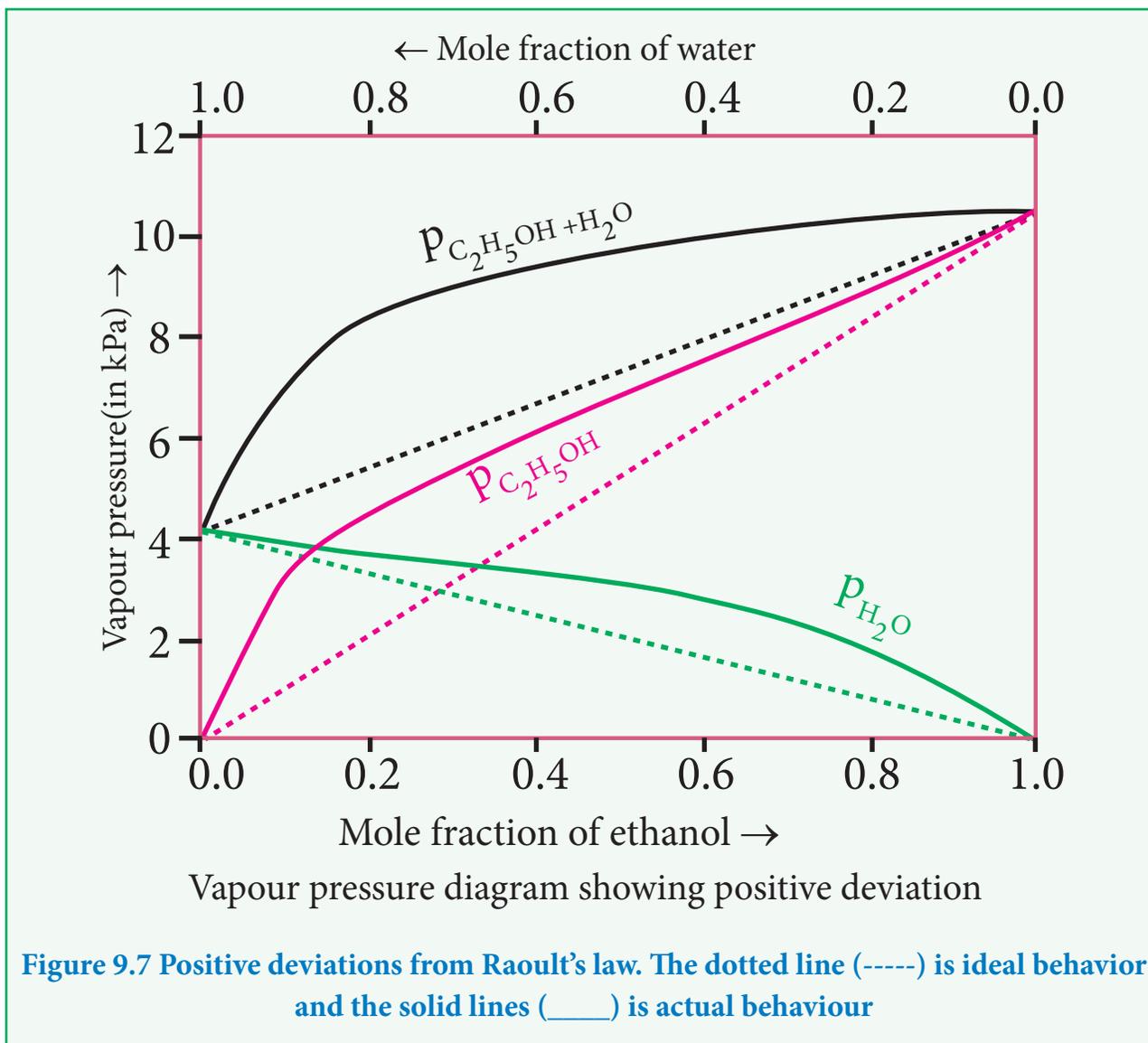
intermolecular interactions between solute (B) and solvent (A). Consider a case in which the intermolecular attractive forces between A and B are weaker than those between the molecules of A (A-A) and molecules of B (B-B). The molecules present in such a solution have a greater tendency to escape from the solution when compared to the ideal solution formed by A and B, in which the intermolecular attractive forces (A-A, B-B, A-B) are almost similar. Consequently, the vapour pressure of such non-ideal solution increases and it is greater than the sum of the vapour pressure of A and B as predicted by the Raoult's law. This type of deviation is called positive deviation.

Here, $p_A > p_A^\circ x_A$ and $p_B > p_B^\circ x_B$.

Hence $p_{\text{total}} > p_A^\circ x_A + p_B^\circ x_B$ -----(9.19)

Let us understand the positive deviation by considering a solution of ethyl alcohol and water. In this solution the hydrogen bonding interaction between ethanol and water is weaker than those hydrogen bonding interactions amongst themselves (ethyl alcohol-ethyl alcohol and water-water interactions). This results in the increased evaporation of both components (H_2O and $\text{C}_2\text{H}_5\text{OH}$) from the aqueous solution of ethanol. Consequently, the vapour pressure of the solution is greater than the vapour pressure predicted by Raoult's law. Here, the mixing process is endothermic i.e. $\Delta H_{\text{mixing}} > 0$ and there will be a slight increase in volume ($\Delta V_{\text{mixing}} > 0$).

Examples for non-ideal solutions showing positive deviations: Ethyl alcohol & cyclohexane, Benzene & acetone, Carbon tetrachloride & chloroform, Acetone & ethyl alcohol, Ethyl alcohol & water.



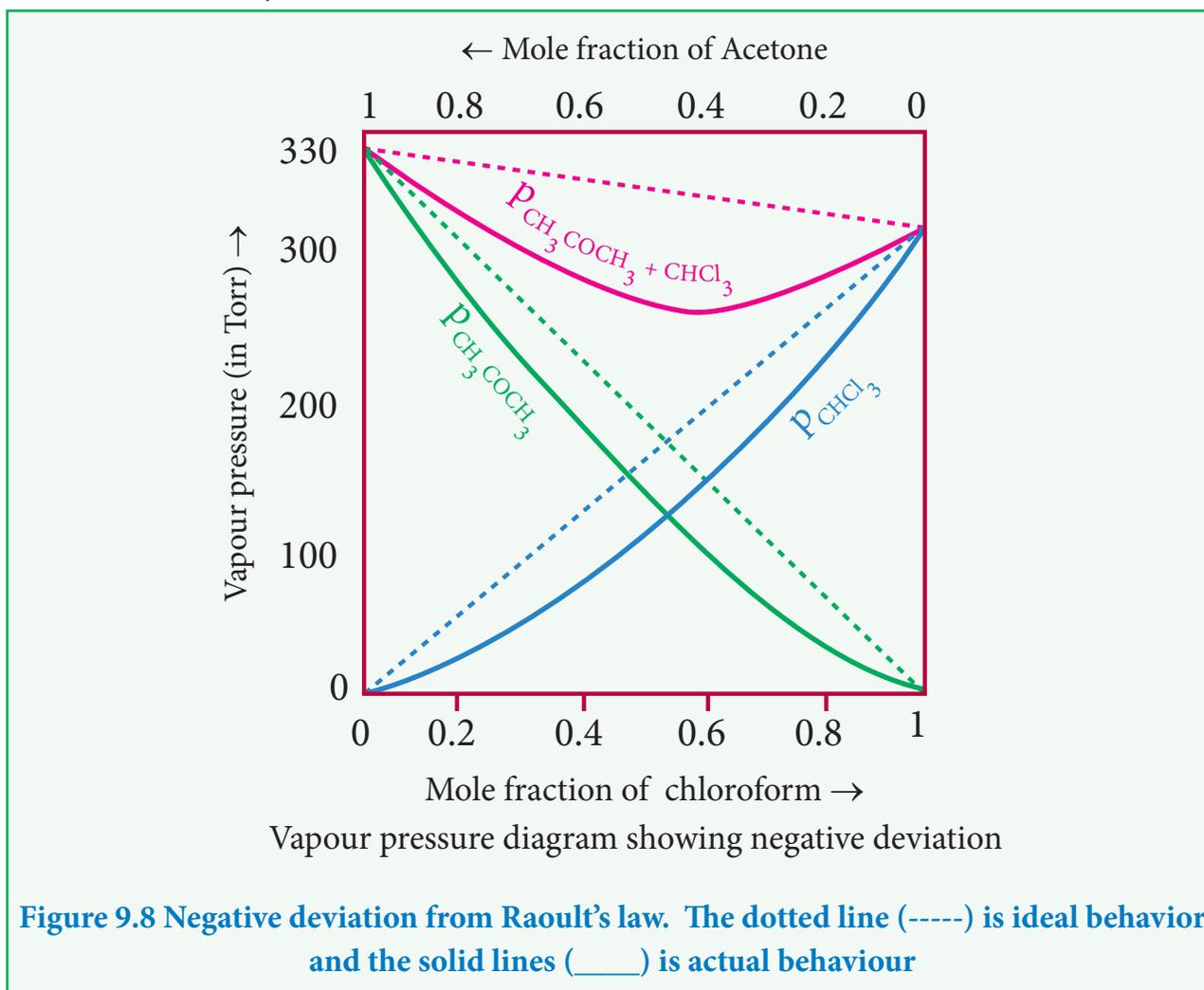
Non-ideal solutions - negative deviation from Raoult's Law:

Let us consider a case where the attractive forces between solute (A) and solvent (B) are stronger than the intermolecular attractive forces between the individual components (A-A & B-B). Here, the escaping tendency of A and B will be lower when compared with an ideal solution formed by A and B. Hence, the vapour pressure of such solutions will be lower than the sum of the vapour pressure of A and B. This type of deviation is called negative deviation. For the negative deviation $p_A < p_A^\circ x_A$ and $p_B < p_B^\circ x_B$.

Let us consider a solution of phenol and aniline. Both phenol and aniline form hydrogen bonding interactions amongst themselves. However, when mixed with aniline, the phenol molecule forms hydrogen bonding interactions with aniline, which are stronger than the hydrogen bonds formed amongst themselves. Formation of new hydrogen bonds considerably reduce the escaping tendency of phenol and aniline from the solution. As a result, the vapour pressure of the solution is less and there is a slight decrease in volume ($\Delta V_{\text{mixing}} < 0$) on mixing. During this process evolution of heat takes place i.e. $\Delta H_{\text{mixing}} < 0$ (exothermic)



Examples for non-ideal solutions showing negative deviation: Acetone + chloroform, Chloroform + diethyl ether, Acetone + aniline, Chloroform + Benzene.



9.8.3 Factors responsible for deviation from Raoult's law

The deviation of solution from ideal behavior is attributed to the following factors.

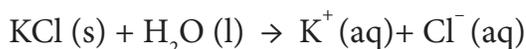
i) Solute-solvent interactions

For an ideal solution, the interaction between the solvent molecules (A-A), the solute molecules (B-B) and between the solvent & solute molecules (A-B) are expected to be similar. If these interactions are dissimilar, then there will be a deviation from ideal behavior.

ii) Dissociation of solute

When a solute present in a solution dissociates to give its constituent ions, the resultant ions interact strongly with the solvent and cause deviation from Raoult's law.

For example, a solution of potassium chloride in water deviates from ideal behavior because the solute dissociates to give K^+ and Cl^- ion which form strong ion-dipole interaction with water molecules.



iii) Association of solute

Association of solute molecules can also cause deviation from ideal behaviour. For example, in solution, acetic acid exists as a dimer by forming intermolecular hydrogen bonds, and hence deviates from Raoult's law.

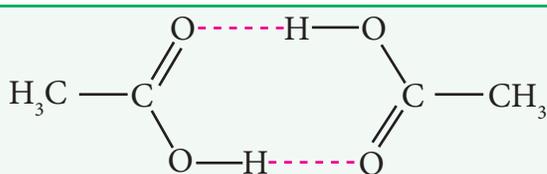


Fig 9.9 Acetic acid (dimer)

iv) Temperature

An increase in temperature of the solution increases the average kinetic energy of the molecules present in the solution which causes decrease in the attractive force between them. As a result, the solution deviates from ideal behaviour.

v) Pressure

At high pressure the molecules tend to stay close to each other and therefore there will be an increase in their intermolecular attraction. Thus, a solution deviates from Raoult's law at high pressure.

vi) Concentration

If a solution is sufficiently dilute there is no pronounced solvent-solute interaction because the number of solute molecules are very low compared to the solvent. When the concentration is increased by adding solute, the solvent-solute interaction becomes significant. This causes deviation from the Raoult's law.

Evaluate Yourself



- 9) Calculate the mole fractions of benzene and naphthalene in the vapour phase when an ideal liquid solution is formed by mixing 128 g of naphthalene with 39 g of benzene. It is given that the vapour pressure of pure benzene is 50.71 mmHg and the vapour pressure of pure naphthalene is 32.06 mmHg at 300 K.

9.9 Colligative properties

Pure water is tasteless. When you add sugar it becomes sweet, while addition of salt makes it salty. It implies that the properties of a solution depend on the nature of solute particles present in the solution. However, for an ideal dilute solution, the properties, namely, relative lowering of vapour pressure, elevation of boiling point, depression in freezing point and osmotic pressure do not depend on the chemical nature of the solute but depends only on the number of solute particles (ions/molecules) present in the solution. These four properties are known as colligative properties. Though the magnitude of these properties are small, they have plenty of practical applications. For example the osmotic pressure is important for some vital biological systems.

Relative lowering of vapour pressure

The vapour pressure of a solution containing a nonvolatile, non-electrolyte solute is always lower than the vapour pressure of the pure solvent. Consider a closed system in which a pure solvent is in equilibrium with its vapour. At equilibrium the molar Gibbs free energies of solvent in the liquid and gaseous phase are equal ($\Delta G = 0$). When a solute is added to this solvent, the dissolution takes place and its free energy (G) decreases due to increase in entropy. In order to maintain the equilibrium, the free energy of the vapour phase must also decrease. At a given temperature, the only way to lower the free energy of the vapour is to reduce its pressure. Thus the vapour pressure of the solution must decrease to maintain the equilibrium.

We know that from the Raoult's law the relative lowering of the vapour pressure is equal to the mole fraction of the solute (equation 9.16)

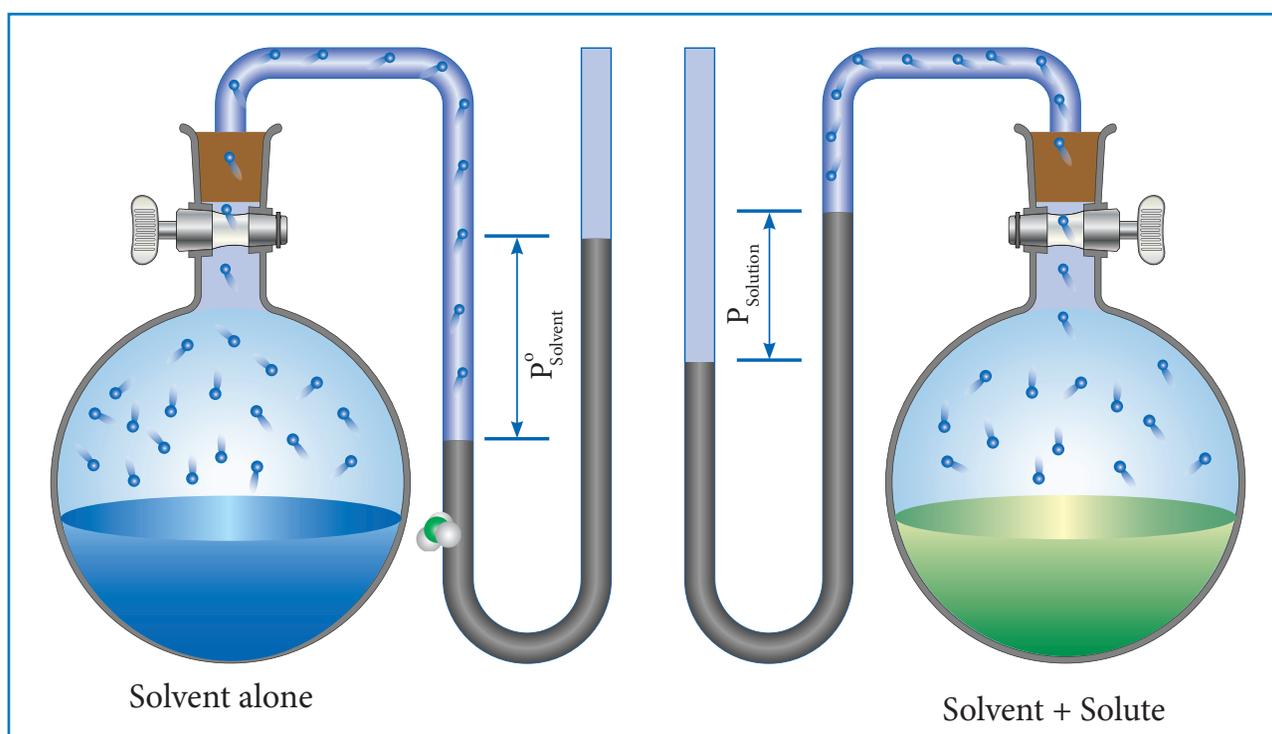


Figure 9.10 Measuring relative lowering of vapour pressure

From the above equation, it is clear that the relative lowering of vapour pressure depends only on the mole fraction of the solute (x_B) and is independent of its nature. Therefore, relative lowering of vapour pressure is a colligative property.

Determination of molar mass from relative lowering of vapour pressure

The measurement of relative lowering of vapour pressure can be used to determine the molar mass of a nonvolatile solute. In this method, a known mass of the solute is dissolved in a known quantity of solvent. The relative lowering of vapour pressure is measured experimentally.

According to Raoult's law the relative lowering of vapor pressure is,

$$\frac{P_{\text{solvent}}^{\circ} - P_{\text{solution}}}{P_{\text{solvent}}^{\circ}} = x_B$$

Let w_A and w_B be the weights of the solvent and solute respectively and their corresponding molar masses are M_A and M_B , then the mole fraction of the solute x_B is

$$x_B = \frac{n_B}{n_A + n_B} \quad (9.20)$$

Here, n_A & n_B are the moles of the solvent and the solute respectively. For dilute solutions $n_A \gg n_B$. Hence $n_A + n_B \approx n_A$. Now

$$x_B = \frac{n_B}{n_A}$$

Number of moles of solvent and the solute are,

$$n_A = \frac{w_A}{M_A}, n_B = \frac{w_B}{M_B}$$

$$\text{Therefore, } x_B = \frac{\frac{w_B}{M_B}}{\frac{w_A}{M_A}} \quad \text{----- (9.21)}$$

Thus,

$$\frac{P_{\text{solvent}}^{\circ} - P_{\text{solution}}}{P_{\text{solvent}}^{\circ}} = \frac{\frac{w_B}{M_B}}{\frac{w_A}{M_A}}$$

$$\frac{\Delta P}{P_A^{\circ}} = \frac{w_B \times M_A}{w_A \times M_B} \quad \text{----- (9.22)}$$

From the equation (9.22) the molar mass of the solute (M_B) can be calculated using the known values of w_A , w_B , M_A and the measured relative lowering of vapour pressure.

Example Problem3:

An aqueous solution of 2 % nonvolatile solute exerts a pressure of 1.004

bar at the boiling point of the solvent. What is the molar mass of the solute when P_A° is 1.013 bar?

$$\frac{\Delta P}{P_A^{\circ}} = \frac{W_B \times M_A}{M_B \times W_A}$$

In a 2 % solution weight of the solute is 2 g and solvent is 98 g

$$\Delta P = P_A^{\circ} - P_{\text{solution}} = 1.013 - 1.004 \text{ bar} = 0.009 \text{ bar}$$

$$M_B = \frac{P_A^{\circ} \times W_B \times M_A}{\Delta P \times W_A}$$

$$M_B = 2 \times 18 \times 1.013 / (98 \times 0.009)$$

$$= 41.3 \text{ g mol}^{-1}$$

Evaluate Yourself

10) Vapour pressure of a pure liquid A is 10.0 torr at 27°C . The vapour pressure is lowered to 9.0 torr on dissolving one gram of B in 20 g of A. If the molar mass of A is 200 g mol⁻¹ then calculate the molar mass of B.

Elevation of boiling point

Boiling point is an important physical property of a liquid. The boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure (1 atm). When a nonvolatile solute is added to a pure solvent at its boiling point, the vapour pressure of the solution is lowered below 1 atm. To bring the vapour pressure again to 1 atm, the temperature of the solution has to be increased. As a result, the solution boils at a higher temperature (T_b) than the boiling point of the pure solvent (T_b°). This increase

in the boiling point is known as elevation of boiling point. A plot of vapour pressure versus temperature for water and an aqueous solution is given below

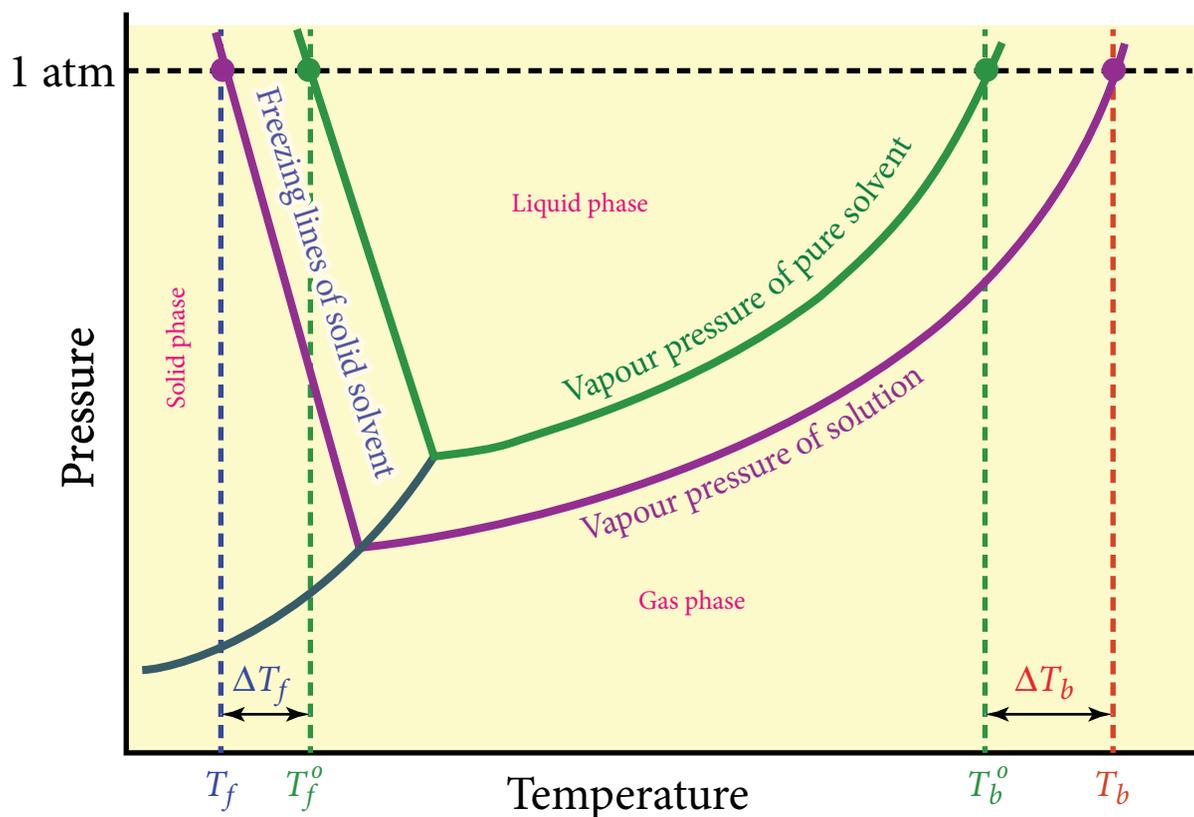


Figure 9.11 Elevation of boiling point and depression in freezing point

The vapour pressure of the solution increases with increase in temperature as shown in the above figure. The variation of vapour pressure with respect to temperature for pure water is given by the violet coloured curve. At 100 °C the vapour pressure of water is equal to 1 atm. Hence the boiling point of water is 100 °C (T_b^0). When a solute is added to water, the vapour pressure of the resultant solution is lowered. The variation of vapour pressure with respect to temperature for the solution is given by green curve. From the graph, it is evident the vapour pressure of the solution is equal to 1 atm pressure at the temperature T_b which is greater than T_b^0 . The difference between these two temperatures ($T_b - T_b^0$) gives the elevation of boiling point.

The elevation of boiling point (ΔT_b) = $T_b - T_b^0$

The elevation of boiling point is directly proportional to the concentration of the solute particles.

$$\Delta T_b \propto m \quad \text{----- (9.23)}$$

m is the concentration of solution expressed in molality.

$$\Delta T_b = K_b m \quad \text{----- (9.24)}$$

Where K_b = molal boiling point elevation constant or Ebullioscopic constant.

$$\text{If } m=1, \text{ then } \Delta T_b = K_b;$$

Hence, K_b is equal to the elevation in boiling point for 1 molal solution. K_b is calculated by the following expression

$$K_b = \frac{RT^2 M_{\text{solvent}}}{\Delta H_{\text{vapourisation}}}$$

Determination of molar mass of solute from elevation of boiling point

If the solution is prepared by dissolving w_B g of solute in w_A g of solvent, then the molality is,

$$m = \frac{\text{Number of moles of solute} \times 1000}{\text{weight of solvent in grams}} \quad \dots\dots\dots (9.25)$$

$$\text{Number of moles of solute} = \frac{w_B}{M_B} \quad \dots\dots\dots (9.26)$$

Where, M_B = molar mass of the solute

Therefore,

$$m = \frac{w_B \times 1000}{M_B \times w_A} \quad \dots\dots\dots (9.27)$$

and

$$\Delta T_b = \frac{K_b \times w_B \times 1000}{M_B \times w_A} \quad \dots\dots\dots (9.28)$$

Molar mass can be calculated by using (9.28)

$$M_B = \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_A} \quad \dots\dots\dots (9.29)$$

Table 9.3 Molal boiling point elevation constant ' K_b ' for some solvents

S. No.	Solvent	T_b° (K)	K_b (K kg mol ⁻¹)
1.	Water	373.15	0.52
2.	Ethanol	351.5	1.20
3.	Benzene	353.3	2.53
4.	Chloroform	334.4	3.63
5.	Ether	307.8	2.02
6.	Carbon tetrachloride	350.0	5.03
7.	Carbon disulphide	319.4	2.42
8.	Acetic acid	391.1	2.93
9.	Cyclohexane	353.74	2.79

Example Problem 4

0.75 g of an unknown substance is dissolved in 200 g solvent. If the elevation of boiling point is 0.15 K and molal elevation constant is 7.5 K Kg mol⁻¹ then, calculate the molar mass of unknown substance

$$\begin{aligned} \Delta T_b &= K_b m \\ &= K_b \times W_2 \times 1000 / M_2 \times W_1 \\ M_2 &= K_b \times W_2 \times 1000 / \Delta T_b \times W_1 \\ &= 7.5 \times 0.75 \times 1000 / 0.15 \times 200 \\ &= 187.5 \text{ g mol}^{-1} \end{aligned}$$

Evaluate Yourself

11) 2.56 g of Sulphur is dissolved in 100g of carbon disulphide. The solution boils at 319.692 K. What is the molar mass of Sulphur in solution The boiling point of CS₂ is 319.450K. Given that K_b for CS₂ = 2.42 K Kg mol⁻¹

Depression in freezing point

Freezing point of a substance is another important physical property like boiling point. Freezing point is defined as “the temperature at which the solid and the liquid states of the substance have the same vapour pressure”. At freezing point, the solid and liquid phases of the substance are in equilibrium. For example, the freezing point of water is 0 °C. At this temperature the ice and water are in equilibrium. When a nonvolatile solute is added to water at its freezing point, the freezing point of the solution is lowered from 0 °C. The lowering of the freezing point of the solvent when a solute is added is called depression in freezing point (ΔT_f).

From the above graph, we infer that the freezing point (T_f^0) is 0 °C as the vapour pressure at this temperature is 1 atm (atmospheric pressure). The vapour pressure versus temperature curve for the solution indicates that the freezing point (T_f) is lower than the 0 °C. The depression in freezing temperature (ΔT_f) can be expressed as,

$$\Delta T_f = T_f^0 - T_f$$

The experimental results show that the depression in freezing point is directly proportional to the molal concentration of the solute particles.

Hence,

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m \quad \dots\dots\dots(9.30)$$

Here, ‘m’ = is the molality of the solution

K_f = molal freezing point depression constant or cryoscopic constant.

If $m=1$ then $\Delta T_f = K_f$

The K_f is equal to the depression in freezing point for 1 molal solution

Table 9.4 Molal freezing point depression constant for some solvents

S. No.	Solvent	Freezing point (K)	K_f (K.kg. mol ⁻¹)
1.	Water	273.0	1.86
2.	Ethanol	155.7	1.99
3.	Benzene	278.6	5.12
4.	Chloroform	209.6	4.79
5.	Carbon disulphide	164.2	3.83
6.	Ether	156.9	1.79
7.	Cyclohexane	279.5	20.0
8.	Acetic acid	290.0	3.90

Determination of molar mass of solute from depression in freezing point

If the solution is prepared by dissolving w_B g of solute in w_A g of solvent, then depression in freezing point is given by (9.31)

$$\Delta T_f = \frac{K_f \times w_B \times 1000}{M_B \times w_A} \quad \dots\dots\dots(9.31)$$

molar mass of a solute can be calculated using (9.31)

$$M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A} \quad \dots\dots\dots(9.32)$$

Example Problem - 5

Ethylene glycol ($C_2H_6O_2$) can be used as an antifreeze in the radiator of a car. Calculate the temperature when ice will begin to separate from a mixture with 20 mass percent of glycol in water used in the car radiator. K_f for water = 1.86 K Kg mol⁻¹

and molar mass of ethylene glycol is 62 g mol^{-1} .

Weight of solute (W_2) = 20 mass percent of solution means 20 g of ethylene glycol

Weight of solvent (water) $W_1 = 100 - 20 = 80 \text{ g}$

$$\Delta T_f = K_f m$$

$$= \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$= \frac{1.86 \times 20 \times 1000}{62 \times 80}$$

$$= 7.5 \text{ K}$$

The temperature at which ice will begin to separate is the freezing point of water after the addition of solute i.e 7.5 K lower than the normal freezing point of water ($273 - 7.5 \text{ K}$) = 265.5 K

Evaluate Yourself

12) 2g of a non electrolyte solute dissolved in 75 g of benzene lowered the freezing point of benzene by 0.20 K. The freezing point depression constant of benzene is $5.12 \text{ K Kg mol}^{-1}$. Find the molar mass of the solute.

Osmosis and osmotic pressure

Many biological processes depend on osmosis, which is a spontaneous process by which the solvent molecules pass through a semi permeable membrane from a solution of lower concentration to a solution of higher concentration. The name osmosis is derived from the Greek word 'osmos' which means 'to push'. It is also important to know that the semipermeable membrane selectively

allows certain molecules in the solution to pass through it but not others.

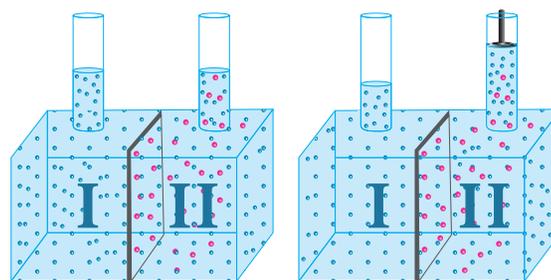


Figure 9.12 Osmosis and osmotic pressure

Let us consider a simple apparatus as shown in the above figure. A semipermeable membrane separates a chamber into two compartments. Water (pure solvent) is added to the first compartment and the aqueous NaCl (solution) is added to the second compartment such that the liquid levels on the both sides are equal. Since there is a difference in concentration between the liquids present in the two compartments, the water molecules move from first compartment to second compartment through the semipermeable membrane. The membrane allows only water molecules to pass through it in either direction but not NaCl. The net flow of water is into the sodium chloride solution and hence increases its volume. This decreases its concentration and also creates a pressure difference between the compartments. This pressure difference, push some of the water molecules back to the solvent side through the semipermeable membrane until an equilibrium is established. At the equilibrium, the rate of movement of solvent molecules on both directions are equal. The pressure difference at the equilibrium is called osmotic pressure (π). Thus, osmotic pressure can be defined as "the pressure

that must be applied to the solution to stop the influx of the solvent (to stop osmosis) through the semipermeable membrane”

van't Hoff found out that for dilute solutions, the osmotic pressure is directly proportional to the molar concentration of the solute and the temperature of the solution. He proposed the following equation to calculate osmotic pressure which is now called as van't Hoff equation.

$$\pi = CRT \text{ ----- 9.31}$$

Here,

C = Concentration of the solution in molarity

T = Temperature

R = Gas constant

Determination of molar mass from osmotic pressure

According to van't Hoff equation

$$\pi = CRT$$

$$C = \frac{n}{V}$$

Here, n= number of moles of solute dissolved in 'V' litre of the solution.

Therefore, $\pi = \frac{n}{V} RT$ or

$$\pi V = nRT \text{ ----- (9.33)}$$

If the solution is prepared by dissolving w_B g of nonvolatile solute in w_A g of solvent, then the number of moles of solute (n) is,

$$n = \frac{w_B}{M_B}$$

Here, M_B = molar mass of the solute

Substituting the 'n' in (9.33), we get,

$$\pi = \frac{w_B}{V} \frac{RT}{M_B}$$

$$M_B = \frac{w_B}{V} \frac{RT}{\pi} \text{ ----- (9.34)}$$

From the equation 9.33, molar mass of the solute can be calculated.

Significances of osmotic pressure over other colligative properties

Unlike elevation of boiling point (for 1 molal solution the elevation in boiling point is 0.512 °C for water) and the depression in freezing point (for 1 molal solution the depression in freezing point is 1.86 °C for water), the magnitude of osmotic pressure is large.

The osmotic pressure can be measured at room temperature enables to determine the molecular mass of biomolecules which are unstable at higher temperatures.

Even for a very dilute solution, the osmotic pressure is large.

Isotonic solutions

Two solutions having same osmotic pressure at a given temperature are called isotonic solutions. When such solutions are separated by a semipermeable membrane, solvent flow between one to the other in either direction is same, i.e. the net solvent flow between the two isotonic solutions is zero.

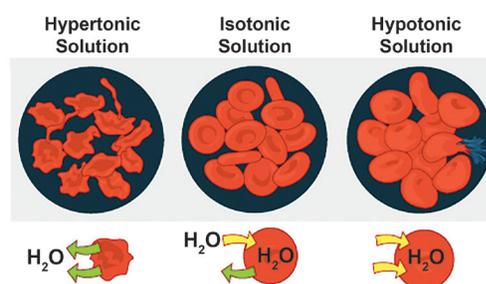


Figure 9.13 Isotonic solutions

The osmotic pressure of the blood cells is approximately equal to 7 atm at 37°C. The intravenous injections should have same osmotic pressure as that of

the blood (isotonic with blood). If the Intravenous solutions are too dilute that is hypotonic, the solvent from outside of the cells will flow into the cell to normalise the osmotic pressure and this process which is called hemolysis, causes the cells to burst. On the other hand, if the solution is too concentrated, that is hypertonic, the solvent molecules will flow out of the cells, which causes the cells to shrink and die. For this reason, the Intravenous fluids are prepared such they are isotonic to blood (0.9 % mass/volume sodium chloride solution).

9.10 Reverse osmosis (RO):

Let us consider the experimental setup (Figure 9.15) discussed in the osmosis. The pure water moves through the semipermeable membrane to the NaCl solution due to osmosis. This process can be reversed by applying pressure greater than the osmotic pressure to the solution side. Now the pure water moves from the solution side to the solvent side and this process is called reverse osmosis. It can be defined as a process in which a solvent passes through a semipermeable membrane in the opposite direction of osmosis, when subjected to a hydrostatic pressure greater than the osmotic pressure.

Application of Reverse osmosis in water purification:

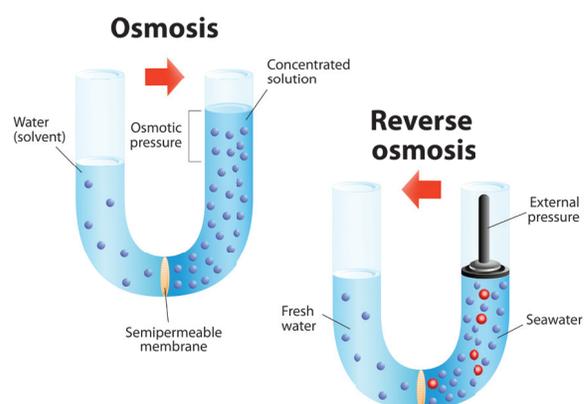


Figure 9.14 Osmosis & Reverse osmosis

Reverse osmosis is used in the desalination of sea water and also in the purification of drinking water. A simple set up used in both the process is shown in the figure 9.15. When a pressure higher than the osmotic pressure is applied on the solution side (sea water) the water molecules moves from solution side to the solvent side through semipermeable membrane (Opposite to the Osmotic flow). Pure water can be collected. There are different types of semipermeable membranes used in this process. The membrane used for reverse osmosis has to withstand high pressures. Generally, cellulose acetate or polyamide membranes are commonly used in commercial systems. The selection of membrane used for reverse osmosis will be decided based on the nature of the input water.

Example Problem-6 :

At 400K 1.5 g of an unknown substance is dissolved in a solvent and the solution is made to 1.5 L. Its osmotic pressure is found to be 0.3 bar. Calculate the molar mass of the unknown substance.

$$\begin{aligned} \text{Molar mass} &= \frac{\text{mass of unknown solute} \times RT}{\text{osmotic pressure} \times \text{volume of solution}} \\ &= \frac{1.5 \times 8.314 \times 10^{-2} \times 400}{0.3 \times 1.5} \\ &= 110.85 \text{ gram mol}^{-1} \end{aligned}$$

Evaluate Yourself

13) What is the mass of glucose ($C_6H_{12}O_6$) in one litre solution which is isotonic with 6 g L^{-1} of urea ($NH_2CO NH_2$) ?

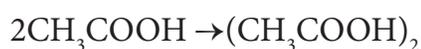
9.11 Abnormal molar mass

The molar masses of the nonvolatile solutes can be calculated accurately using the experimentally determined colligative properties. In this method, we assume that the solution is very dilute and there is no dissociation or association of solute particles in the solution.

In a concentrated solution, the interaction between the solute and solvent becomes significant and reflected in the measured colligative properties. Similarly, the dissociation or association of solute molecules would alter the total number of particles present in the solution and hence affect the results of measured colligative properties. In such solutions, the value of the molar mass of the solute determined using colligative properties would be different from the actual molar mass, and it is called abnormal molar mass.

Association or dissociation of solute molecules:

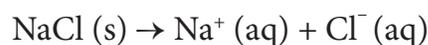
Normally, the molar mass determination using measured colligative properties assumes that the solute does not dissociate or associate. In certain solvents, solute molecules associate to form a dimer or trimer etc... This reduces the total number of particles (molecules) formed in solution and as a result the calculated molar mass will be higher than the actual molar mass. Let us consider a solution of acetic acid in benzene. It is already established that acetic acid forms inter molecular hydrogen bonds as shown in the figure 9.9 and exists as a dimer in benzene.



The molar mass of acetic acid calculated using colligative properties is

found to be around 120 g mol^{-1} is two times the actual molar mass (60 g mol^{-1}).

The electrolytes such as KCl or NaCl dissociates completely into its constituent ions in their aqueous solution. This causes an increase in the total number of particles (ions) present in the solution. The calculated molar mass using colligative property measurement for this type of solutions will be lower than the actual molar mass. For example, sodium chloride dissociates into Na^+ ions and Cl^- ions in aqueous solution, as shown below.



When we dissolve 1 mole of NaCl (58.4 g) in water, it dissociates and gives 1 mole of Na^+ and 1 mole of Cl^- . Hence, the solution will have 2 moles of particles. Thus, the colligative properties would be double the expected value.

van't Hoff factor

We have learnt that the dissociation or association of solute molecules in a solution will result in the increase or decrease in the calculated molar mass using the colligative property. This variation is proportional to the extent of association or dissociation. To quantify the extent of association or dissociation of solutes in solution, van't Hoff introduced a term 'i' which is now called van't Hoff factor. It is defined as the ratio of the actual molar mass to the abnormal (calculated) molar mass of the solute. Here, the abnormal molar mass is the molar mass calculated using the experimentally determined colligative property.

$$i = \frac{\text{Normal (actual) molar mass}}{\text{Observed (abnormal) molar mass}}$$
$$= \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

The estimated Van't Hoff factor for acetic acid solution in Benzene is 0.5 and that of sodium chloride solution in water is 2. The degree of dissociation or association can be related to Van't Hoff factor (i) using the following relationships

$$\alpha_{\text{dissociation}} = \frac{i-1}{n-1}$$

(Where n is number ions /species formed by the dissociation of a single molecule)

$$\alpha_{\text{association}} = \frac{(1-i)n}{n-1}$$

(here, n is the number of solute involved in association.

The equations relating the four colligative properties with the concentration of the solutes can be rewritten as follows by incorporating the van't Hoff factor

Relative lowering of vapour pressure,

$$= \frac{p_{\text{solvent}}^{\circ} - p_{\text{solution}}}{p_{\text{solvent}}^{\circ}} = i \frac{n_{\text{solute}}}{n_{\text{solvent}}}$$

Elevation of boiling point,

$$\Delta T_b = iK_b m$$

Depression in the freezing point,

$$\Delta T_f = iK_f m$$

Osmotic pressure,

$$\pi = i \frac{w_{\text{solute}}}{V} \frac{RT}{M_{\text{solute}}}$$

For a solute that does not dissociate or associate the van't Hoff factor is equal to 1 ($i = 1$) and the molar mass will be close to the actual molar mass.

For the solutes that associate to form higher oligomers in solution the van't Hoff factor will be less than one ($i < 1$) and the observed molar mass will be greater than the actual molar mass.

For solutes that dissociates into their constituent ions the van't Hoff factor will be more than one ($i > 1$) and the observed molar mass will be less than the normal molar mass.

Example Problem - 7

The depression in freezing point is 0.24K obtained by dissolving 1g NaCl in 200g water. Calculate van't-Hoff factor. The molal depression constant is 1.86 K Kg mol⁻¹

Molar mass of solute

$$\begin{aligned} &= \frac{1000 \times K_f \times \text{mass of NaCl}}{\Delta T_f \times \text{mass of solvent}} \\ &= \frac{1000 \times 1.86 \times 1}{0.24 \times 200} \\ &= 38.75 \text{ g mol}^{-1} \\ &= 38.75 \text{ g mol}^{-1} \end{aligned}$$

Theoretical molar mass of NaCl is =

$$\begin{aligned} i &= \frac{\text{Theoretical molar mass}}{\text{Experimental molar mass}} = \frac{58.5}{38.75} \\ &= 1.50 \end{aligned}$$

Evaluate Yourself

14. 0.2 m aqueous solution of KCl freezes at -0.68°C calculate van't Hoff factor. k_f for water is 1.86 K kg mol⁻¹.

SUMMARY

- A solution is a homogeneous mixture of two or more chemically non-reacting substances mixed uniformly. The proportion of component which is more in the solution is called solvent and the lesser component is called solute.
- The different concentration units used to prepare the solutions are formality, molality, normality, molarity, molefraction, %w/w solution, %w/v solution, %v/v solution. If the solute quantity is very minimum then ppm unit is used to express its concentration.
- The standard solutions are prepared and diluted to desired concentration (working standards). This helps in overcoming the error due to weighing and maintain efficiency and consistency in the preparation of solution.
- Solubility is defined as the amount of solute in a saturated solution per 100g of a solvent. Solubility of a solute in a solvent depends on the nature of the solute and solvent, temperature.
- The solubility of a gas in a liquid depends upon, the nature of the gas and the nature of the liquid, the temperature of the system, and the pressure of the gas.
- The effect of pressure on the solubility of a gas in a liquid is governed by Henry's Law. It states that the solubility of a gas in a liquid at a given temperature is directly proportional to the partial pressure of the gas.
- The vapour pressure of a liquid is the pressure exerted by its vapour when it is in dynamic equilibrium with its liquid, in a closed container. According to Raoult's Law, the vapour pressure of a solution containing a non-volatile solute is directly proportional to the mole fraction of the solvent (X_A). The proportionality constant being the vapour pressure of the pure solvent.
- The solution shows positive deviation from Raoult's Law if its vapour pressure is higher than that predicted by Raoult's Law for example ethyl alcohol and cyclohexane.
- The solution shows negative deviation if its vapour pressure is lower than that predicted by Raoult's Law for example acetone and chloroform.
- Colligative properties of solutions are those properties which depend only upon the number of solute particles in the solution and not on their nature. Such properties are
 - (a) Relative lowering in vapour pressure: On addition of a non volatile solute it is observed that the vapour pressure of the solution is lesser than the solvent. According to Raoult's law relative lowering of vapour pressure is equal to the mole fraction of the solute.
 - (b) Elevation of boiling point ΔT_b : The solution boils at a higher temperature than the pure solvent. This is due to the decreased vapour pressure of solution and the temperature it reaches the atmospheric pressure on heating to boil is much higher than the solvent.
 - (c) Depression of freezing point:

The freezing point of the solution is much lower than the solvent as the temperature at which the solid and the liquid have the same vapour pressure is much lower than the solvent.

- (d) Osmotic pressure: The spontaneous flow of solvent molecules from a dilute solution into a concentrated solution when the two are separated by a perfect semipermeable membrane is called osmosis.
- Osmotic pressure (π) is the pressure which must be applied to the solution side (more concentrated solution) to just prevent the passage of pure solvent into it through a semipermeable membrane.
- Abnormal colligative properties
- If solutes undergo any association or dissociation in a solution, they exhibit abnormal colligative properties. Van't Hoff factor explains quantitatively the extent of association or dissociation of solutes in solvent.

Evaluation



I. Choose the best answer.

- The molality of a solution containing 1.8g of glucose dissolved in 250g of water is
 - 0.2 M
 - 0.01 M
 - 0.02 M
 - 0.04 M
- Which of the following concentration terms is / are independent of temperature
 - molality
 - molarity
 - mole fraction
 - (a) and (c)
- Stomach acid, a dilute solution of HCl can be neutralised by reaction with Aluminium hydroxide

$$\text{Al}(\text{OH})_3 + 3\text{HCl}(\text{aq}) \rightarrow \text{AlCl}_3 + 3\text{H}_2\text{O}$$
 How many millilitres of 0.1 M $\text{Al}(\text{OH})_3$ solution are needed to neutralise 21 mL of 0.1 M HCl ?
 - 14 mL
 - 7 mL
 - 21 mL
 - none of these
- The partial pressure of nitrogen in air is 0.76 atm and its Henry's law constant is 7.6×10^4 atm at 300K. What is the molefraction of nitrogen gas in the solution obtained when air is bubbled through water at 300K ?
 - 1×10^{-4}
 - 1×10^{-6}
 - 2×10^{-5}
 - 1×10^{-5}
- The Henry's law constant for the solubility of Nitrogen gas in water at 350 K is 8×10^4 atm. The mole fraction of nitrogen in air is 0.5. The number of moles of Nitrogen from air dissolved in 10 moles of water at 350K and 4 atm pressure is
 - 4×10^{-4}
 - 4×10^4
 - 2×10^{-2}
 - 2.5×10^{-4}
- Which one of the following is incorrect for ideal solution ?
 - $\Delta H_{\text{mix}} = 0$
 - $\Delta U_{\text{mix}} = 0$
 - $\Delta P = P_{\text{observed}} - P_{\text{Calculated by Raoult's law}} = 0$
 - $\Delta G_{\text{mix}} = 0$
- Which one of the following gases has the lowest value of Henry's law constant ?
 - N_2
 - He
 - CO_2
 - H_2



8. P_1 and P_2 are the vapour pressures of pure liquid components, 1 and 2 respectively of an ideal binary solution if x_1 represents the mole fraction of component 1, the total pressure of the solution formed by 1 and 2 will be
- $P_1 + x_1 (P_2 - P_1)$
 - $P_2 - x_1 (P_2 + P_1)$
 - $P_1 - x_2 (P_1 - P_2)$
 - $P_1 + x_2 (P_1 - P_2)$
9. Osmotic pressure (π) of a solution is given by the relation
- $\pi = nRT$
 - $\pi V = nRT$
 - $\pi RT = n$
 - none of these
10. Which one of the following binary liquid mixtures exhibits positive deviation from Raoult's law?
- Acetone + chloroform
 - Water + nitric acid
 - HCl + water
 - ethanol + water
11. The Henry's law constants for two gases A and B are x and y respectively. The ratio of mole fractions of A to B is 0.2. The ratio of mole fraction of B and A dissolved in water will be
- $\frac{2x}{y}$
 - $\frac{y}{0.2x}$
 - $\frac{0.2x}{y}$
 - $\frac{5x}{y}$
12. At 100°C the vapour pressure of a solution containing 6.5g a solute in 100g water is 732mm. If $K_b = 0.52$, the boiling point of this solution will be
- 102°C
 - 100°C
 - 101°C
 - 100.52°C
13. According to Raoult's law, the relative lowering of vapour pressure for a solution is equal to
- mole fraction of solvent
 - mole fraction of solute
 - number of moles of solute
 - number of moles of solvent
14. At same temperature, which pair of the following solutions are isotonic?
- 0.2 M BaCl_2 and 0.2M urea
 - 0.1 M glucose and 0.2 M urea
 - 0.1 M NaCl and 0.1 M K_2SO_4
 - 0.1 M $\text{Ba}(\text{NO}_3)_2$ and 0.1 M Na_2SO_4
15. The empirical formula of a non-electrolyte(X) is CH_2O . A solution containing six gram of X exerts the same osmotic pressure as that of 0.025M glucose solution at the same temperature. The molecular formula of X is
- $\text{C}_2\text{H}_4\text{O}_2$
 - $\text{C}_8\text{H}_{16}\text{O}_8$
 - $\text{C}_4\text{H}_8\text{O}_4$
 - CH_2O
16. The K_H for the solution of oxygen dissolved in water is 4×10^4 atm at a given temperature. If the partial pressure of oxygen in air is 0.4 atm, the mole fraction of oxygen in solution is
- 4.6×10^3
 - 1.6×10^4
 - 1×10^{-5}
 - 1×10^5
17. Normality of 1.25M sulphuric acid is
- 1.25 N
 - 3.75 N
 - 2.5 N
 - 2.25 N



18. Two liquids X and Y on mixing gives a warm solution. The solution is
- ideal
 - non-ideal and shows positive deviation from Raoult's law
 - ideal and shows negative deviation from Raoult's Law
 - non-ideal and shows negative deviation from Raoult's Law
19. The relative lowering of vapour pressure of a sugar solution in water is 3.5×10^{-3} . The mole fraction of water in that solution is
- 0.0035
 - 0.35
 - $0.0035 / 18$
 - 0.9965
20. The mass of a non-volatile solute (molar mass 80 g mol^{-1}) which should be dissolved in 92g of toluene to reduce its vapour pressure to 90%
- 10g
 - 20g
 - 9.2 g
 - 8.89g
21. For a solution, the plot of osmotic pressure (π) versus the concentration (c in mol L^{-1}) gives a straight line with slope $310R$ where 'R' is the gas constant. The temperature at which osmotic pressure measured is
- $310 \times 0.082 \text{ K}$
 - 310°C
 - 37°C
 - $\frac{310}{0.082} \text{ K}$
22. 200ml of an aqueous solution of a protein contains 1.26g of protein. At 300K, the osmotic pressure of this solution is found to be 2.52×10^{-3} bar. The molar mass of protein will be ($R = 0.083 \text{ L bar mol}^{-1} \text{ K}^{-1}$)
- $62.22 \text{ Kg mol}^{-1}$
 - 12444 g mol^{-1}
 - 300 g mol^{-1}
 - none of these
23. The Van't Hoff factor (i) for a dilute aqueous solution of the strong electrolyte barium hydroxide is (NEET)
- 0
 - 1
 - 2
 - 3
24. What is the molality of a 10% W/W aqueous sodium hydroxide solution ?
- 2.778
 - 2.5
 - 10
 - 0.4
25. The correct equation for the degree of an associating solute, 'n' molecules of which undergoes association in solution, is
- $\alpha = \frac{n(i-1)}{n-1}$
 - $\alpha^2 = \frac{n(1-i)}{(n-1)}$
 - $\alpha = \frac{n(i-1)}{1-n}$
 - $\alpha = \frac{n(1-i)}{n(1-i)}$
26. Which of the following aqueous solutions has the highest boiling point ?
- 0.1M KNO_3
 - 0.1 MNa_3PO_4
 - 0.1 M BaCl_2
 - 0.1 M K_2SO_4
27. The freezing point depression constant for water is $1.86^\circ \text{K Kg mol}^{-1}$. If 5g Na_2SO_4 is dissolved in 45g water, the depression in freezing point is 3.64°C . The Vant Hoff factor for Na_2SO_4 is
- 2.50
 - 2.63
 - 3.64
 - 5.50
28. Equimolar aqueous solutions of NaCl and KCl are prepared. If the freezing point of NaCl is -2°C , the freezing point of KCl solution is expected to be
- -2°C
 - -4°C
 - -1°C
 - 0°C



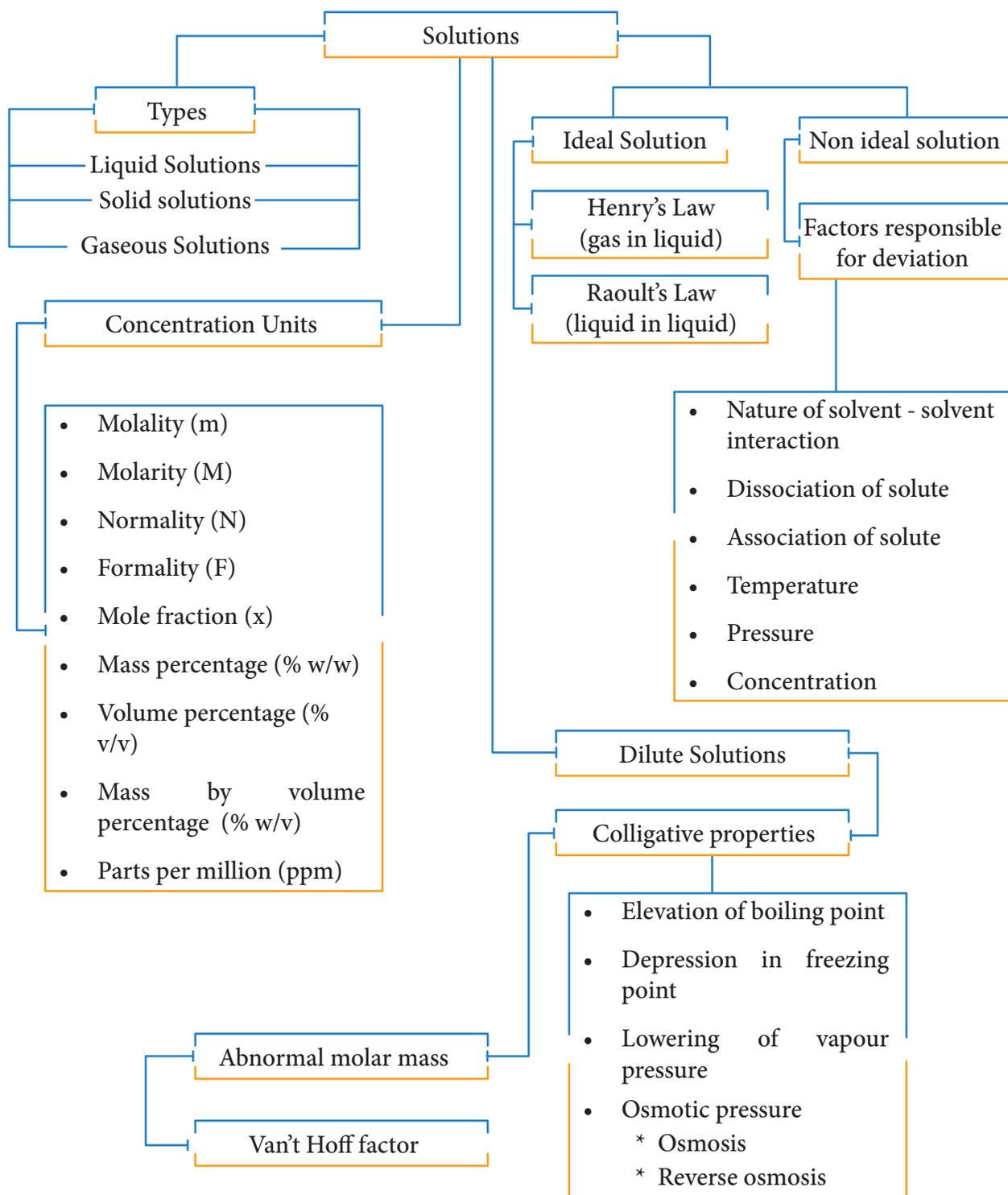
29. Phenol dimerises in benzene having van't Hoff factor 0.54. What is the degree of association ?
- a) 0.46 b) 92
c) 46 d) 0.92
30. Assertion : An ideal solution obeys Raoult's Law
- Reason : In an ideal solution, solvent-solvent as well as solute-solute interactions are similar to solute-solvent interactions.
- a) both assertion and reason are true and reason is the correct explanation of assertion
b) both assertion and reason are true but reason is not the correct explanation of assertion
c) assertion is true but reason is false
d) both assertion and reason are false

II. Write brief answer to the following questions.

31. Define (i) molality (ii) Normality
32. What is a vapour pressure of liquid?
What is relative lowering of vapour pressure?
33. State and explain Henry's law
34. State Raoult's law and obtain expression for lowering of vapour pressure when nonvolatile solute is dissolved in solvent.
35. What is molal depression constant? Does it depend on nature of the solute ?
36. What is osmosis?
37. Define the term 'isotonic solution'.
38. You are provided with a solid 'A' and three solutions of A dissolved in water - one saturated, one unsaturated, and one super saturated. How would you determine which solution is which ?
39. Explain the effect of pressure on the solubility.
40. A sample of 12 M Concentrated hydrochloric acid has a density 1.2 gL^{-1} . Calculate the molality
41. A 0.25 M glucose solution at 370.28 K has approximately the pressure as blood does what is the osmotic pressure of blood ?
42. Calculate the molality of a solution containing 7.5 g of glycine ($\text{NH}_2\text{-CH}_2\text{-COOH}$) dissolved in 500 g of water.
43. Which solution has the lower freezing point? 10 g of methanol (CH_3OH) in 100 g of water (or) 20 g of ethanol ($\text{C}_2\text{H}_5\text{OH}$) in 200 g of water.
44. How many moles of solute particles are present in one litre of 10^{-4} M potassium sulphate?
45. Henry's law constant for solubility of methane in benzene is $4.2 \times 10^{-5} \text{ mm Hg}$ at a particular constant temperature. At this temperature. Calculate the solubility of methane at i) 750 mm Hg ii) 840 mm Hg
46. The observed depression in freezing point of water for a particular solution is 0.093°C . Calculate the concentration of the solution in molality. Given that molal depression constant for water is $1.86 \text{ K Kg mol}^{-1}$
47. The vapour pressure of pure benzene (C_6H_6) at a given temperature is 640 mm Hg. 2.2 g of non-volatile solute is added to 40 g of benzene. The vapour pressure of the solution is 600 mm Hg. Calculate the molar mass of the solute?



FLOW CHART





Osmosis

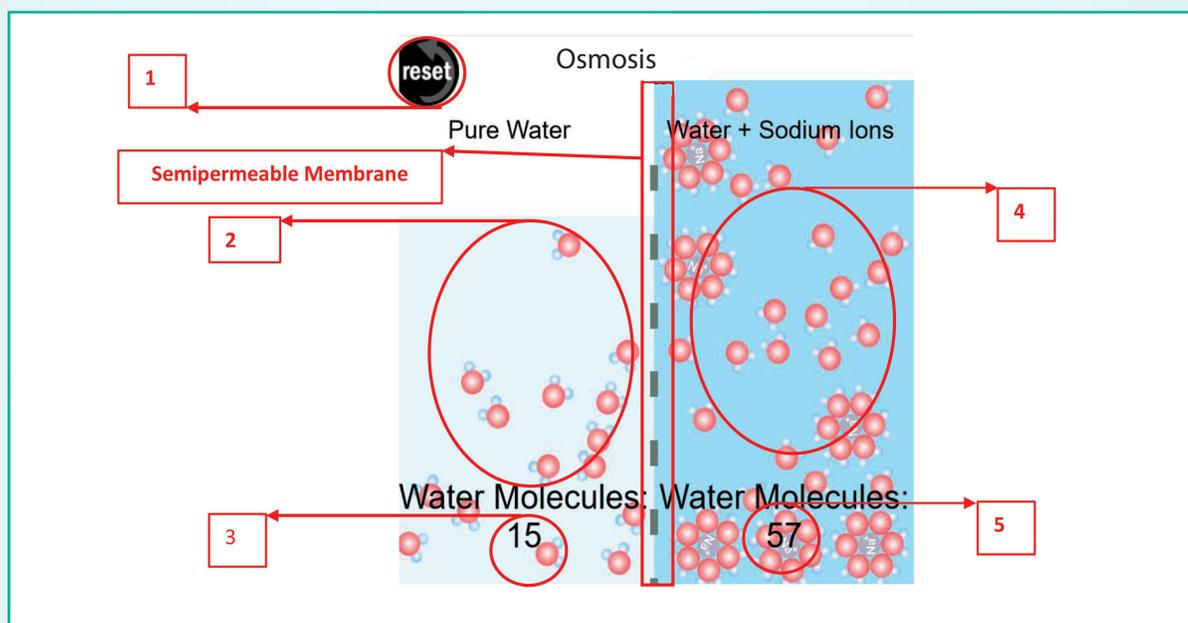
By using this tool, you will be able to visualise the process of osmosis which gives a clear understating of this process.

Please go to the URL
<https://pbslm-contrib.s3.amazonaws.com/WGBH/arct15/SimBucket/Simulations/osmosis/content/index.html>
(or)
Scan the QR code on the right side



Steps

- Open the Browser and type the URL given (or) Scan the QR Code.
- Now you will see the webpage as shown below.
- The two compartments were separated by a semipermeable membrane.
- On the left side (Box 2) contains pure solvent (water) and right side contains solution (solute + water).
- The number of solvent molecules (water) on each side is shown in the area designated by box 3 and 5.
- Now you can see the water molecules moving from solvent side to solution side through the membrane. It reflects in the change in number of water molecules on either side.
- You can restart the simulation by clicking the reset button in box 1





Linus Carl Pauling was an American chemist, biochemist, peace activist, author and educator. In addition to his contribution to chemistry and he also worked with many biologists.

He received the Nobel Prize in Chemistry in 1954 for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances.

Learning Objectives

After studying this unit students will be able to

- describe Kossel – Lewis approach to chemical bonding
- explain the octet rule
- sketch the Lewis structures of simple molecules
- describe the formation of different types of bonds and bond parameters
- sketch the resonance structures for simple molecules
- apply the concept of electronegativity to explain the polarity of covalent bonds
- describe VSEPR theory and predict the shapes of simple molecules
- explain the valence bond approach for the formation of covalent bonds
- explain the different types of hybridisation involving s, p & d orbitals and sketch shapes of simple covalent molecules
- explain the molecular orbital theory, calculate the bond order and explain the magnetic properties of H_2 , O_2 , N_2 , CO and NO
- describe metallic bonding briefly.

10.1 Introduction

Diamond is very hard while its allotrope graphite is very soft. Gases like hydrogen and oxygen are diatomic while the inert gases are monoatomic.

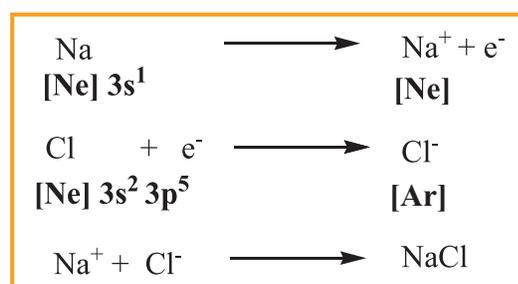
Carbon combines with chlorine to form carbon tetrachloride, which is a liquid and insoluble (immiscible) in water. Sodium combines with chlorine atom to form sodium chloride, a hard and brittle compound that readily dissolves in water. The possible reason for these observations lies in the type of interaction that exists between the atoms of these molecules and these interactions are responsible for holding the atoms/ions together. The interatomic attractive forces which hold the constituent atoms/ions together in a molecule are called chemical bonds.

Why do atoms combine only in certain combinations to form molecules? For example oxygen combines with hydrogen to give water (H_2O) and with carbon it gives carbon dioxide (CO_2). The structure of water is 'V' shaped while that of the carbon dioxide is linear. Such questions can be answered using the principles of chemical bonding. In this unit we will analyse the various theories and their principles, which were developed over the years to explain the nature of chemical bonding.

10.1.1 Kossel – Lewis approach to chemical bonding

A logical explanation for chemical bonding was provided by Kossel and Lewis in 1916. Their approach to chemical bonding is based on the inertness of the noble gases which have little or no tendency to combine with other atoms. They proposed that the noble gases are stable due to their completely filled outer shell electronic configuration. Elements other than noble gases, try to attain the completely filled electronic configurations by losing, gaining

or sharing one or more electrons from their outer shell. For example, sodium loses one electron to form Na^+ ion and chlorine accepts that electron to give chloride ion (Cl^-), enabling both atoms to attain the nearest noble gas configuration. The resultant ions, Na^+ and Cl^- are held together by electrostatic attractive forces and the attractive force is called a chemical bond, more specifically an electrovalent bond.



G. N. Lewis proposed that the attainment of stable electronic configuration in molecules such as diatomic nitrogen, oxygen etc... is achieved by mutual sharing of the electrons. He introduced a simple scheme to represent the chemical bond and the electrons present in the outer shell of an atom, called Lewis dot structure. In this scheme, the valence electrons (outer shell electrons) of an element are represented as small dots around the symbol of the element. The first four valence electrons are denoted as single dots around the four sides of the atomic symbol and then the fifth onwards, the electrons are denoted as pairs. For example, the electronic configuration of nitrogen is $1s^2, 2s^2, 2p^3$. It has 5 electrons in its outer shell (valence shell). The Lewis structure of nitrogen is as follows.



Fig 10.1 Lewis Structure of Nitrogen atom

Similarly, Lewis dot structure of carbon, oxygen can be drawn as shown below.



Fig 10.2 Lewis Structures of C & O atoms

Only exception to this is helium which has only two electrons in its valence shell which is represented as a pair of dots (duet).



Fig 10.3 Lewis Structures of He atom

Octet rule

The idea of Kossel – Lewis approach to chemical bond lead to the octet rule, which states that *“the atoms transfer or share electrons so that all atoms involved in chemical bonding obtain 8 electrons in their outer shell (valence shell)”*.

10.2 Types of chemical bonds

The chemical bonds can be classified based on the nature of the interaction between the bonded atoms. Two major types of chemical bonds are covalent bonds and ionic bonds. Generally metals reacts with non-metals to form ionic compounds, and the covalent bonds are present in the compounds formed by nonmetals.

10.2.1 Covalent bonds:

Do you know all elements (except noble gases) occurs either as compounds or as polyatomic molecules? Let us consider hydrogen gas in which two hydrogen atoms bind to give a dihydrogen molecule. Each hydrogen atom has one electron and it requires one more electron to attain the electronic configuration of the nearest noble gas helium. Lewis suggested that both hydrogen atoms will attain the stable

configuration by mutually sharing the electrons available with them. Similarly, in the case of oxygen molecule, both the oxygen atoms share two electron pairs between them and in nitrogen molecule three electron pairs are shared between two nitrogen atoms. *This type of mutual sharing of one or more pairs of electrons between two combining atoms results in the formation of a chemical bond called a covalent bond.* If two atoms share just one pair of electron a single covalent bond is formed as in the case of hydrogen molecule. If two or three electron pairs are shared between the two combining atoms, then the covalent bond is called a double bond or a triple bond, respectively.

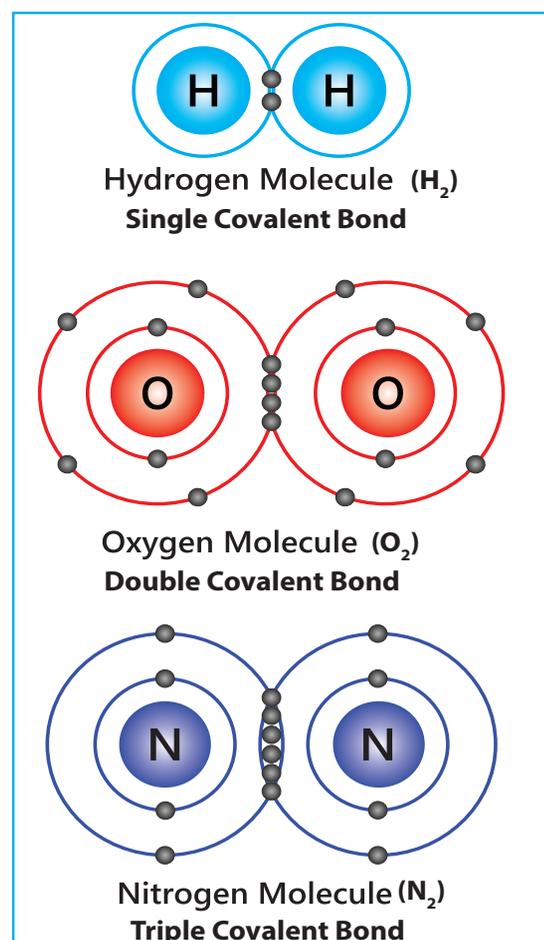


Fig 10. 4 Representation of Lewis Structures of covalent bonds

10.2.2 Representing a covalent bond - Lewis structure (Lewis dot structure)

Lewis structure (Lewis dot structure) is a pictorial representation of covalent bonding between the combining atoms. In this structure the shared valence electrons are represented as a pair of dots between the combining atoms and the unshared electrons of the atoms are represented as a pair of dots (lone pair) on the respective individual atoms.

The Lewis dot structure for a given compound can be written by following the steps given below. Let us understand these steps by writing the Lewis structure for water.

1. **Draw the skeletal structure of the molecule.** In general, the less electronegative atom is placed at the centre. Hydrogen and fluorine atoms should be placed at the terminal positions. For water, the skeletal structure is



2. **Calculate the total number of valence electrons of all the atoms in the molecule.** In case of polyatomic ions the charge on ion should also be considered during the calculation of the total number of valence electrons. In case of anions the number of negative charges should be added to the number of valence electrons. For positive ions the total number of positive charges should be subtracted from the total number of valence electrons.

In water, total number of valence electron = $[2 \times 1$ (valence electron of

hydrogen)] + $[1 \times 6$ (valence electrons of oxygen)] = $2 + 6 = 8$.

3. **Draw a single bond between the atoms in the skeletal structure of the molecule.** Each bond will account for two valence electrons (a bond pair). For water, we can draw two bonds accounting for four valence electrons as follows.



4. **Distribute the remaining valence electrons as pairs (lone pair), giving octet (only duet for hydrogen) to the atoms in the molecule.** The distribution of lone pairs starts with the most electronegative atoms followed by other atoms.

In case of water, the remaining four electrons (two lone pairs) are placed on the most electronegative central oxygen, giving octet.



5. **Verify whether all the atoms satisfy the octet rule (for hydrogen duet).** If not, use the lone pairs of electrons to form additional bond to satisfy the octet rule.

In case of water, oxygen has octet and the hydrogens have duets, hence there is no need for shifting the lone pairs. The Lewis structure of water is as follows

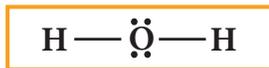


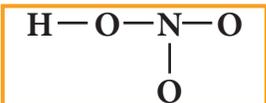
Fig 10.5 Lewis structure of water

Let us draw the Lewis structure for nitric acid.

1. Skeletal structure

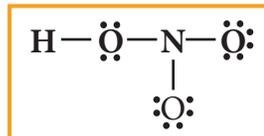


- Total number of valence electrons in HNO_3
 $= [1 \times 1(\text{hydrogen})] + [1 \times 5(\text{nitrogen})] + [3 \times 6(\text{oxygen})] = 1 + 5 + 18 = 24$
- Draw single bonds between atoms. Four bonds can be drawn as shown in the figure for HNO_3 which account for eight electrons (4 bond pairs).



- Distribute the remaining sixteen ($24 - 8 = 16$) electrons as eight lone pairs starting from most electronegative atom, the oxygen. Six lone pairs are distributed to the two terminal oxygens

(three each) to satisfy their octet and two pairs are distributed to the oxygen that is connected to hydrogen to satisfy its octet.



- Verify whether all the atoms have octet configuration. In the above distribution, the nitrogen has one pair short for octet. Therefore, move one of the lone pair from the terminal oxygen to form another bond with nitrogen.

The Lewis structure of nitric acid is given as

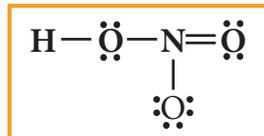


Fig 10. 6 Lewis structure of Nitric acid

Table 10.1 : The Lewis dot structures for some molecules

S. No	Molecule	Lewis Structure	
1.	Sulphur trioxide (SO_3)	$\begin{array}{c} \ddot{\text{O}} \\ \\ \ddot{\text{O}} - \text{S} = \ddot{\text{O}} \end{array}$	$\begin{array}{c} \ddot{\text{O}} \\ \ddot{\text{O}} : \text{S} : \ddot{\text{O}} \end{array}$
2.	Ammonia (NH_3)	$\begin{array}{c} \text{H} \\ \\ \text{H} - \text{N} - \text{H} \\ \vdots \end{array}$	$\begin{array}{c} \text{H} \\ \text{H} : \text{N} : \text{H} \\ \vdots \end{array}$
3.	Methane (CH_4)	$\begin{array}{c} \text{H} \\ \\ \text{H} - \text{C} - \text{H} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \text{H} : \text{C} : \text{H} \\ \vdots \\ \text{H} \end{array}$
4.	Dinitrogen Pentoxide (N_2O_5)	$\begin{array}{c} \ddot{\text{O}} = \text{N} - \ddot{\text{O}} - \text{N} = \ddot{\text{O}} \\ \quad \quad \\ \ddot{\text{O}} \quad \quad \ddot{\text{O}} \end{array}$	$\begin{array}{c} \ddot{\text{O}} : \text{N} : \ddot{\text{O}} : \text{N} : \ddot{\text{O}} \\ \ddot{\text{O}} \quad \quad \ddot{\text{O}} \end{array}$

Note

It is to be noted that nearly in all their compounds, certain elements form a fixed number of bonds. For example, Fluorine forms only one bond. Hydrogen, oxygen, nitrogen and carbon atoms form one, two, three and four bonds, respectively.

Evaluate Yourself

- 1) Draw the Lewis structures for
 - i) Nitrous acid (HNO_2)
 - ii) Phosphoric acid
 - iii) Sulphur trioxide (SO_3)

10.2.3 Formal charge:

Let us draw the Lewis structure for carbon dioxide.

1. Skeletal structure



2. Total number of valence electrons in CO_2

$$= [1 \times 4(\text{carbon})] + [2 \times 6(\text{oxygen})] = 4 + 12 = 16$$

3. Draw single bonds between atoms. Two bonds can be drawn as shown in the figure for CO_2 which accounts for four electrons (2 bond pairs).



4. Distribute the remaining twelve electrons ($16 - 4 = 12$) as six lone pairs starting from most electronegative atom, the oxygen. Six lone pairs are distributed to the two terminal oxygens (three each) to satisfy their octet.



5. Verify whether all the atoms have octet configuration. In the above distribution, the central carbon has two pair short

for octet. Therefore, to satisfy the octet rule two lone pairs from one oxygen or one pair from each oxygen can be moved to form multiple bonds, leading the formation of two possible structures for carbon dioxide as shown below



Fig 10.7 (a) two possible structures for carbon dioxide

Similarly, the Lewis structure for many molecules drawn using the above steps gives more than one acceptable structure. Let us consider the above mentioned two structures of carbon dioxide.

Which one the above forms represents the best distribution of electrons in the molecule. To find an answer, we need to know the formal charge of each atom in the Lewis structures. Formal charge of an atom in a molecule, is the electrical charge difference between the valence electron in an isolated atom and the number of electrons assigned to that atom in the Lewis structure.

$$\text{Formal charge of an atom} = N_v - \left(N_l + \frac{N_b}{2} \right)$$

Where,

N_v - Number of valence electron of atom in its isolated state.

N_l - Number of electrons present as lone pairs around the atom in the Lewis structure

N_b - Number of electrons present in bonds around the atom (bond pairs) in the Lewis structure]

Now let us calculate the formal charge on all atoms in both structures,

For Structure 1,

$$\begin{aligned}\text{Formal charge on carbon} &= N_v - \left(N_l + \frac{N_b}{2} \right) \\ &= 4 - \left(0 + \frac{8}{2} \right) = 0\end{aligned}$$

$$\begin{aligned}\text{Formal charge on oxygen} &= 6 - \left(4 + \frac{4}{2} \right) \\ &= 0 \text{ (for both oxygens)}\end{aligned}$$

For structure 2

Formal charge on carbon

$$\begin{aligned}&= N_v - \left(N_l + \frac{N_b}{2} \right) \\ &= 4 - \left(0 + \frac{8}{2} \right) = 0\end{aligned}$$

Formal charge on singly bonded oxygen

$$= 6 - \left(6 + \frac{2}{2} \right) = -1$$

Formal charge on triply bonded oxygen

$$= 6 - \left(2 + \frac{6}{2} \right) = +1$$

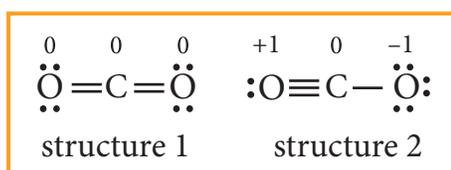


Fig 10. 7 (b) two possible structures for carbon dioxide (with formal charges)

After calculating the formal charges, the best representation of Lewis structure can be selected by using following guidelines.

1. A structure in which all formal charges are zero preferred over the one with charges.

2. A structure with small formal charges is preferred over the one with higher formal charges.
3. A structure in which negative formal charges are placed on the most electronegative atom is preferred.

In case of CO_2 structures, the structure one is preferred over the structure 2 as it has zero formal charges for all atoms.

10.2.4 Lewis structures for exceptions to octet rule

The octet rule is useful for writing Lewis structures for molecules with second period element as central atoms. In some molecules, the central atoms have less than eight electrons around them while some others have more than eight electrons. Exception to the octet rule can be categorized into following three types.

1. Molecules with electron deficient central atoms
2. Molecules containing odd electrons
3. Molecules with expanded valence shells

Molecules with electron deficient central atoms

Let us consider boron trifluoride, as an example. The central atom boron has three valence electron and each fluorine has seven valence electrons. The Lewis structure is

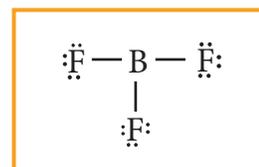


Fig 10. 8 (a) Lewis structure of BF_3

In the above structure, only six electrons around boron atom. Moving a

lone pair from one of the fluorine to form additional bond as shown below.

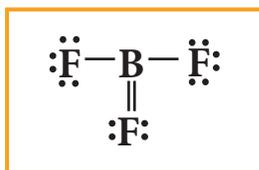


Fig 10. 8 (b) Lewis structure of BF_3

However, the above structure is unfavourable as the most electronegative atom fluorine shows positive formal charge and hence the structure with incomplete octet is the favourable one. Molecules such as BCl_3 , BeCl_2 , etc... also have incomplete octets.

Molecules containing odd electrons

Few molecules have a central atom with an odd number of valence electrons. For example, in nitrogen dioxide and nitric oxide all the atoms does not have octet configuration. The lewis structure of the above molecules are shown in the figure.

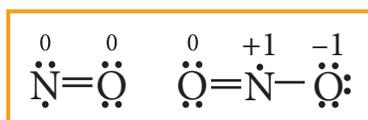


Fig 10. 9 Lewis structures of Nitric oxide and Nitrogen dioxide (with formal charges)

Molecules with expanded valence shells

In molecules such as sulphur hexafluoride (SF_6), phosphorous pentachloride (PCl_5) the central atom has more than eight valence electrons around them. Here the central atom can accommodate additional electron pairs by using outer vacant d orbitals. In SF_6 the central atom sulphur is surrounded by six bonding pair of electrons or twelve electrons.

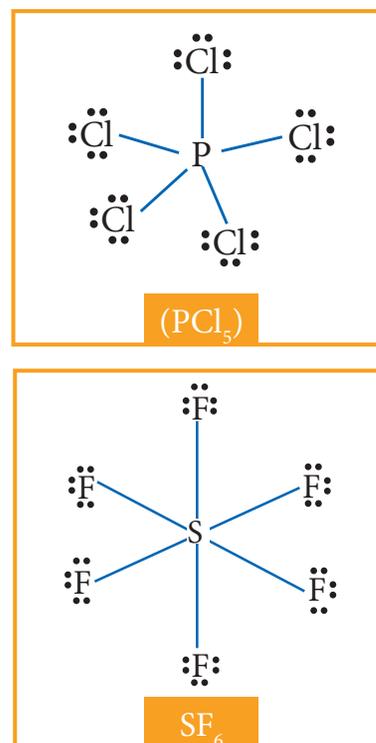


Fig 10. 10 Lewis structures for SF_6 and PCl_5

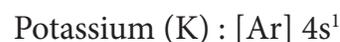
Evaluate Yourself

- Calculate the formal charge on each atom of carbonyl chloride (COCl_2)

10.3 Ionic or electrovalent bond

When the electronegativity difference between the two combining atoms is large, the least electronegative atom completely transfers one or more of its valence electrons to the other combining atom so that both atoms can attain the nearest inert gas electronic configuration. The complete transfer of electron leads to the formation of a cation and an anion. Both these ions are held together by the electrostatic attractive force which is known as ionic bond.

Let us consider the formation potassium chloride. The electronic configuration of potassium and chlorine are



Chlorine (Cl) : [Ne]3s², 3p⁵

Potassium has one electron in its valence shell and chlorine has seven electron in its valence shell. By losing one electron potassium attains the inert gas electronic configuration of argon and becomes a unipositive cation (K⁺) and chlorine accepts this electron to become uninegative chloride ion (Cl⁻) there by attaining the stable electronic configuration of argon. These two ions combine to form an ionic crystal in which they are held together by electrostatic attractive force. The energy required for the formation of one mole of K⁺ is 418.81 kJ (ionization energy) and the energy released during the formation of one mole of Cl⁻ is -348.56 kJ (electron gain enthalpy). The sum of these two energies is positive (70.25 kJ) However, during the formation of one mole potassium chloride crystal from its constituent ions, 718 kJ energy is released. This favours the formation of KCl and its stability.

Evaluate Yourself

- 3) Explain the ionic bond formation in MgO and CaF₂

10.4 Coordinate covalent bond

In the formation of a covalent bond, both the combining atoms contribute one electron each and these electrons are mutually shared among them. However, in certain bond formation, one of the combining atoms donates a pair of electrons i.e. two electrons which are necessary for the covalent bond formation, and these electrons are shared by both the combining atoms. These type of bonds are called coordinate

covalent bond or coordinate bond. The combining atom which donates the pair of electron is called a donor atom and the other atom an acceptor atom. This bond is denoted by an arrow starting from the donor atom pointing towards the acceptor atom. (Later in coordination compound, we will refer the donor atom as ligand and the acceptor atom as central-metal atom/ion.

For Example, in ferrocyanide ion [Fe(CN)₆]⁴⁻, each cyanide ion (CN⁻) donates a pair of electrons to form a coordinate bond with iron (Fe²⁺) and these electrons are shared by Fe²⁺ and CN⁻.

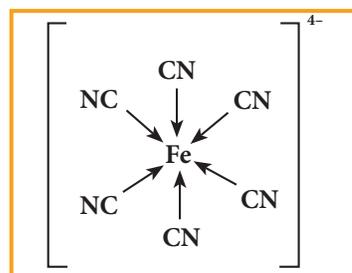


Fig 10.11 Structure of Ferrocyanide ion

In certain cases, molecules having a lone pair of electrons such as ammonia donates its pair to an electron deficient molecules such as BF₃. to form a coordinate

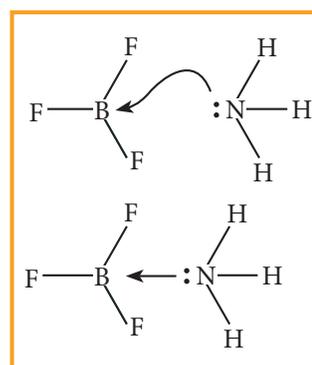


Fig 10.12 Structure of BF₃ → NH₃

10.5 Bond parameters

A covalent bond is characterised by parameters such as bond length, bond angle, bond order etc... A brief description of some of the bond parameters is given below.

10.5.1 Bond length

The distance between the nuclei of the two covalently bonded atoms is called bond length. Consider a covalent molecule A-B. The bond length is given by the sum of the radii of the bonded atoms ($r_A + r_B$). The length of a bond can be determined by spectroscopic, x-ray diffraction and electron-diffraction techniques. The bond length depends on the size of the atom and the number of bonds (multiplicity) between the combining atoms.

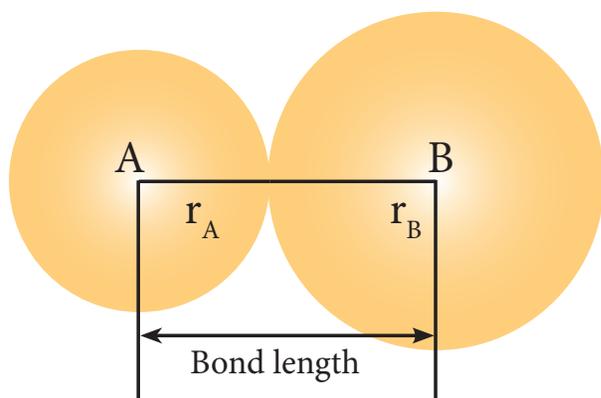


Fig 10.13 Bond length of covalent molecule A-B

Greater the size of the atom, greater will be the bond length. For example, carbon-carbon single bond length (1.54 \AA) is longer than the carbon-nitrogen single bond length (1.43 \AA).

Increase in the number of bonds between the two atoms decreases the bond

length. For example, the carbon-carbon single bond is longer than the carbon-carbon double bond (1.33 \AA) and the carbon-carbon triple bond (1.20 \AA).

10.5.2 Bond order

The number of bonds formed between the two bonded atoms in a molecule is called the bond order. In Lewis theory, the bond order is equal to the number of shared pair of electrons between the two bonded atoms. For example in hydrogen molecules, there is only one shared pair of electrons and hence, the bond order is one. Similarly, in H_2O , HCl , Methane, etc the central atom forms single bonds with bond order of one.

Table 10.2 Bond order of some common bonds:

S. No.	Molecule	Bonded atoms	Bond order (No. of shared pair of electrons between bonded atoms)
1	H_2	H-H	1
2	O_2	O=O	2
3	N_2	$\text{N}\equiv\text{N}$	3
4	HCN	$\text{C}\equiv\text{N}$	3
5	HCHO	C=O	2
6	CH_4	C-H	1
7	C_2H_4	C=C	2

10.5.3 Bond angle

Covalent bonds are directional in nature and are oriented in specific directions in space. This directional nature creates a fixed angle between two covalent bonds in a molecule and this angle is termed as bond angle. It is usually expressed in degrees. The bond angle can be determined by spectroscopic methods and it can give some idea about the shape of the molecule.

Table 10.3 Bond angles for some common molecules

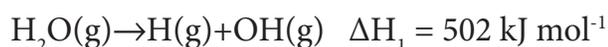
S. No.	Molecule	Atoms defining the angle	Bond angle (°)
1	CH ₄	H-C-H	109° 28'
2	NH ₃	H-N-H	107° 18'
3	H ₂ O	H-O-H	104° 35'

10.5.4 Bond enthalpy

The bond enthalpy is defined as the minimum amount of energy required to break one mole of a particular bond in molecules in their gaseous state. The unit of bond enthalpy is kJ mol⁻¹. Larger the bond enthalpy, stronger will be the bond. The bond energy value depends on the size of the atoms and the number of bonds between the bonded atoms. Larger the size of the atom involved in the bond, lesser is the bond enthalpy.

In case of polyatomic molecules with, two or more same bond types, in the term average bond enthalpy is used. For such

bonds, the arithmetic mean of the bond energy values of the same type of bonds is considered as average bond enthalpy. For example in water, there are two OH bonds present and the energy needed to break them are not same.



The average bond enthalpy of OH bond in water = $\frac{502+427}{2} = 464.5 \text{ kJ mol}^{-1}$

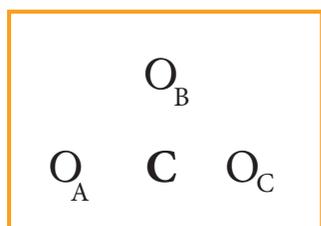
Table 10.4 Bond lengths and bond enthalpies of some common bonds:

S. No.	Bond type	Bond Enthalpy (kJ mol ⁻¹)	Bond Length (Å)
1	H-H	432	0.74
2	H-F	565	0.92
3	H-Cl	427	1.27
4	H-Br	363	1.41
5	H-I	295	1.61
6	C-H	413	1.09
7	C-C	347	1.54
8	C-Si	301	1.86
9	C-N	305	1.47
10	C-O	358	1.43
11	C-P	264	1.87
12	C-S	259	1.81
13	C-F	453	1.33
14	C-Cl	339	1.77
15	C-Br	276	1.94
16	C-I	216	2.13

10.5.5 Resonance

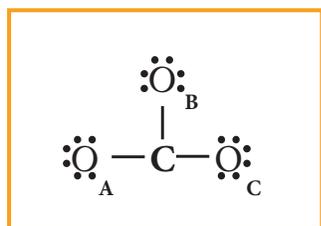
When we write Lewis structures for a molecule, more than one valid Lewis structures are possible in certain cases. For example let us consider the Lewis structure of carbonate ion $[\text{CO}_3]^{2-}$.

The skeletal structure of carbonate ion (The oxygen atoms are denoted as O_A , O_B & O_C



Total number of valence electrons = $[1 \times 4(\text{carbon})] + [3 \times 6(\text{oxygen})] + [2(\text{charge})] = 24$ electrons.

Distribution of these valence electrons gives us the following structure.



Complete the octet for carbon by moving a lone pair from one of the oxygens (O_A) and write the charge of the ion ($2-$) on the upper right side as shown in the figure.

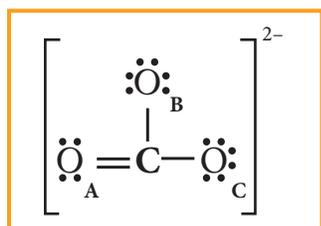


Fig 10.14 (a) Lewis Structure of CO_3^{2-}

In this case, we can draw two additional Lewis structures by moving the lone pairs from the other two oxygens

(O_B and O_C) thus creating three similar structures as shown below in which the relative position of the atoms are same. They only differ in the position of bonding and lone pair of electrons. Such structures are called resonance structures (canonical structures) and this phenomenon is called resonance.

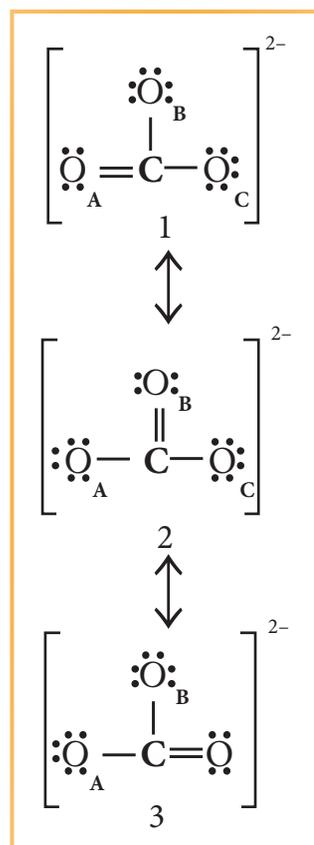


Fig 10.14 (b) Resonance structures of CO_3^{2-}

It is evident from the experimental results that all carbon-oxygen bonds in carbonate ion are equivalent. The actual structure of the molecules is said to be the resonance hybrid, an average of these three resonance forms. It is important to note that carbonate ion does not change from one structure to another and vice versa. It is not possible to picturise the resonance hybrid by drawing a single Lewis structure. However, the following structure gives a qualitative idea about the correct structure.

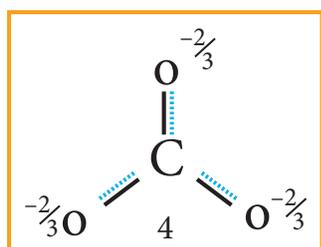


Fig 10. 14 (c) Resonance Hybrid structures of CO_3^{2-}

It is found that the energy of the resonance hybrid (structure 4) is lower than that of all possible canonical structures (Structure 1, 2 & 3). The difference in energy between structure 1 or 2 or 3, (most stable canonical structure) and structure 4 (resonance hybrid) is called resonance energy.

Evaluate Yourself

- 4) Write the resonance structures for
i) Ozone molecule ii) N_2O

10.5.6 Polarity of Bonds

Partial ionic character in covalent bond:

When a covalent bond is formed between two identical atoms (as in the case of H_2 , O_2 , Cl_2 etc...) both atoms have equal tendency to attract the shared pair of electrons and hence the shared pair of electrons lies exactly in the middle of the nuclei of two atoms. However, in the case of covalent bond formed between atoms having different electronegativities, the atom with higher electronegativity will have greater tendency to attract the shared pair of electrons more towards itself than the other atom. As a result the cloud of shared electron pair gets distorted.

Let us consider the covalent bond between hydrogen and fluorine in hydrogen

fluoride. The electronegativities of hydrogen and fluorine on Pauling's scale are 2.1 and 4 respectively. It means that fluorine attracts the shared pair of electrons approximately twice as much as the hydrogen which leads to partial negative charge on fluorine and partial positive charge on hydrogen. Hence, the H-F bond is said to be polar covalent bond.

Here, a very small, equal and opposite charges are separated by a small distance (91 pm) and is referred to as a dipole.

Dipole moment:

The polarity of a covalent bond can be measured in terms of dipole moment which is defined as

$$\mu = q \times 2d$$

Where μ is the dipole moment, q is the charge and $2d$ is the distance between the two charges. The dipole moment is a vector and the direction of the dipole moment vector points from the negative charge to positive charge.

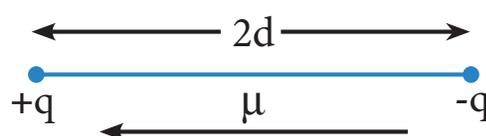
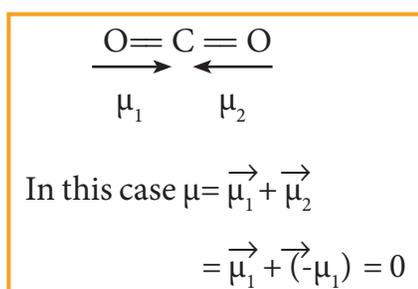


Fig 10. 15 Representation of Dipole

The unit for dipole moment is coulomb meter (C m). It is usually expressed in Debye unit (D). The conversion factor is $1 \text{ Debye} = 3.336 \times 10^{-30} \text{ C m}$

Diatomic molecules such as H_2 , O_2 , F_2 etc... have zero dipole moment and are called non polar molecules and molecules such as HF, HCl, CO, NO etc... have non zero dipole moments and are called polar molecules.

Molecules having polar bonds will not necessarily have a dipole moment. For example, the linear form of carbon dioxide has zero dipole moment, even though it has two polar bonds. In CO_2 , the dipole moments of two polar bonds (CO) are equal in magnitude but have opposite direction. Hence, the net dipole moment of the CO_2 is, $\mu = \mu_1 + \mu_2 = \mu_1 + (-\mu_1) = 0$



In case of water net dipole moment is the vector sum of $\mu_1 + \mu_2$ as shown.

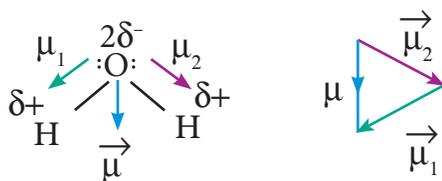


Fig 10. 16 Dipole moment in water

Dipole moment in water is found to be 1.85D

Table 10. 5 Dipole moments of common molecules

S. No.	Molecule	Dipole moment (in D)
1	HF	1.91
2	HCl	1.03
3	H_2O	1.85
4	NH_3	1.47
5	CHCl_3	1.04

The extent of ionic character in a covalent bond can be related to the electronegativity difference to the bonded atoms. In a typical polar molecule, $\text{A}^{\delta-}\text{-B}^{\delta+}$, the electronegativity difference ($\chi_A - \chi_B$) can be used to predict the percentage of ionic character as follows.

If the electronegativity difference ($\chi_A - \chi_B$), is

equal to 1.7, then the bond A-B has 50% ionic character

if it is greater than 1.7, then the bond A-B has more than 50% ionic character,

and if it is lesser than 1.7, then the bond A-B has less than 50% ionic character.

Evaluate Yourself

- 5) Of the two molecules OCS and CS_2 which one has higher dipole moment value? why?

Partial covalent character in ionic bonds:

Like the partial ionic character in covalent compounds, ionic compounds show partial covalent character. For example, the ionic compound, lithium chloride shows covalent character and is soluble in organic solvents such as ethanol.

The partial covalent character in ionic compounds can be explained on the basis of a phenomenon called polarisation. We know that in an ionic compound, there is an electrostatic attractive force between the cation and anion. The positively charged cation attracts the valence electrons of anion while repelling the nucleus. This causes a distortion in the electron cloud of the anion and its electron density drifts towards the cation, which results in some sharing of the

valence electrons between these ions. Thus, a partial covalent character is developed between them. This phenomenon is called polarisation.

The ability of a cation to polarise an anion is called its polarising ability and the tendency of an anion to get polarised is called its polarisability. The extent of polarisation in an ionic compound is given by the Fajans rules

Fajans Rules

- (i) To show greater covalent character, both the cation and anion should have high charge on them. Higher the positive charge on the cation, greater will be the attraction on the electron cloud of the anion. Similarly higher the magnitude of negative charge on the anion, greater is its polarisability. Hence, the increase in charge on cation or in anion increases the covalent character

Let us consider three ionic compounds aluminum chloride, magnesium chloride and sodium chloride. Since the charge of the cation increase in the order $\text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$, the covalent character also follows the same order $\text{NaCl} < \text{MgCl}_2 < \text{AlCl}_3$.

- (ii) The smaller cation and larger anion show greater covalent character due to the greater extent of polarisation.

Lithium chloride is more covalent than sodium chloride. The size of Li^+ is smaller than Na^+ and hence the polarising power of Li^+ is more. Lithium iodide is more covalent than lithium chloride as the size of I^- is larger than the Cl^- . Hence I^- will be more polarised than Cl^- by the cation, Li^+ .

- (iii) Cations having $ns^2 np^6 nd^{10}$ configuration show greater polarising power than the cations with $ns^2 np^6$ configuration. Hence, they show greater covalent character.

CuCl is more covalent than NaCl . Compared to Na^+ (1.13 Å). Cu^+ (0.6 Å) is small and have $3s^2 3p^6 3d^{10}$ configuration.

Electronic configuration of Cu^+
[Ar] $3d^{10}$

Electronic Configuration of Na^+
[He] $2s^2, 2p^6$

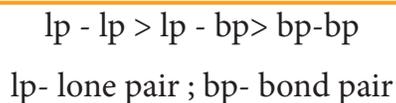
10.6 Valence Shell Electron Pair Repulsion (VSEPR) theory

Lewis concept of structure of molecules deals with the relative position of atoms in the molecules and sharing of electron pairs between them. However, we cannot predict the shape of the molecule using Lewis concept. Lewis theory in combination with VSEPR theory will be useful in predicting the shape of molecules.

Important principles of VSEPR Theory are as follows:

1. The shape of the molecules depends on the number of valence shell electron pair around the central atom.
2. There are two types of electron pairs namely bond pairs and lone pairs. The bond pair of electrons are those shared between two atoms, while the lone pairs are the valence electron pairs that are not involved in bonding.
3. Each pair of valence electrons around the central atom repels each other and hence, they are located as far away as possible in three dimensional space to minimize the repulsion between them.

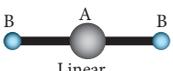
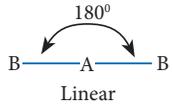
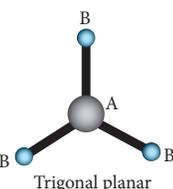
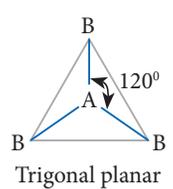
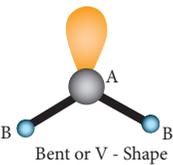
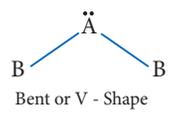
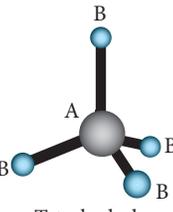
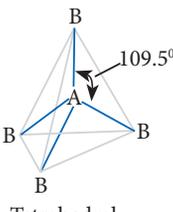
4. The repulsive interaction between the different types of electron pairs is in the following order.

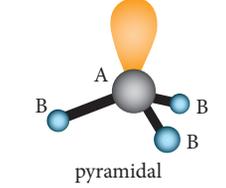
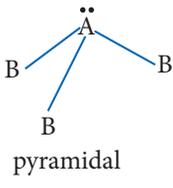
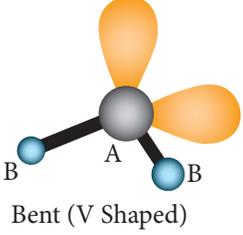
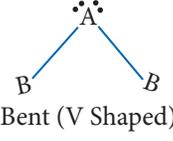
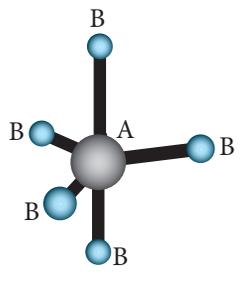
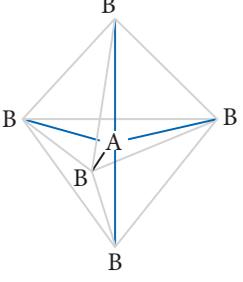
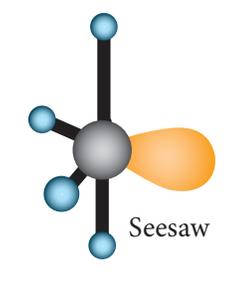
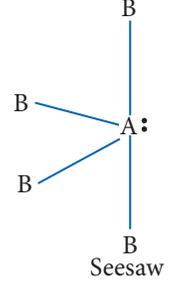
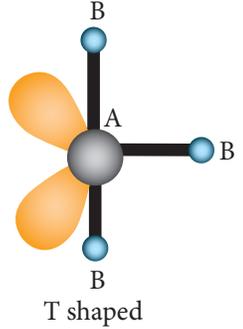
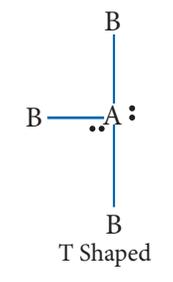


The lone pair of electrons are localised only on the central atom and interacts with only one nucleus whereas the bond pairs are shared between two atoms and they interact with two nuclei. Because of this the lone pairs occupy more space and have greater repulsive power than the bond pairs in a molecule.

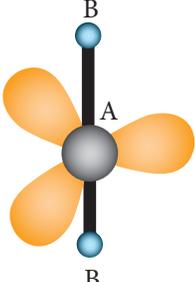
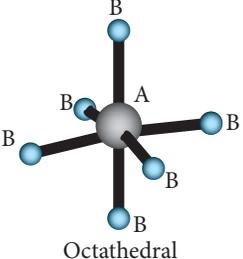
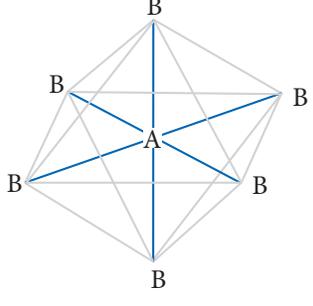
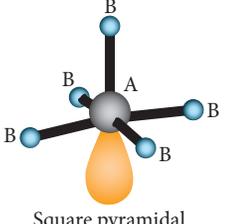
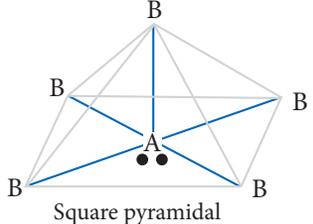
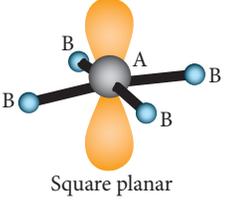
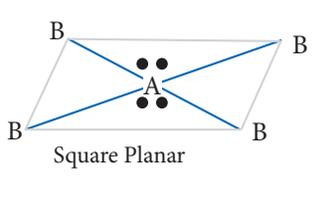
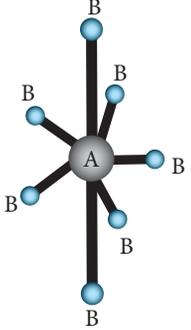
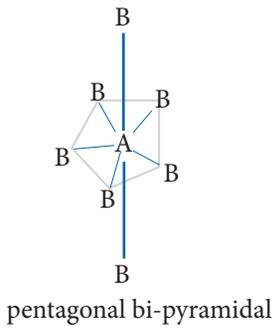
The following Table illustrates the shapes of molecules predicted by VSEPR theory. Consider a molecule AB_x where A is the central atom and x represents the number of atoms of B covalently bonded to the central atom A. The lone pairs present in the atoms are denoted as L.

Table 10. 6 Shapes of molecules predicted by VSEPR theory.

Number of electron Pairs	Molecule	No.of bond pairs	No.of. lone pairs	Shape	Molecular geometry	Examples
2	AB_2	2	-	 Linear	 Linear	$BeCl_2$, $HgCl_2$, CO_2 , CS_2 , HCN , BeF_2
3	AB_3	3	-	 Trigonal planar	 Trigonal planar	BF_3 , BCl_3 , NO_3^- , BF_3 , CO_3^{2-} , $HCHO$
	AB_2L	2	1	 Bent or V - Shape	 Bent or V - Shape	SO_2 , O_3 , $PbCl_2$, $SnBr_2$
4	AB_4	4	-	 Tetrahedral	 Tetrahedral	CH_4 , CCl_4 , CCl_2F_2 , SO_4^{2-} , ClO_4^- , NH_4^+

Number of electron Pairs	Molecule	No. of bond pairs	No. of lone pairs	Shape	Molecular geometry	Examples
	AB_3L	3	1	 <p>pyramidal</p>	 <p>pyramidal</p>	$NH_3, PF_3,$ $ClO_3^-, H_3O^+,$
	AB_2L_2	2	2	 <p>Bent (V Shaped)</p>	 <p>Bent (V Shaped)</p>	$H_2O, OF_2,$ SCl_2
5	AB_5	5	-	 <p>Trigonal bipyramidal</p>	 <p>Trigonal bipyramidal</p>	$PCl_5, ASF_5,$ SOF_4
	AB_4L	4	1	 <p>Seesaw</p>	 <p>Seesaw</p>	$SF_4, XeO_2F_2,$ $IF_4^+, IO_2F_2^-$
	AB_3L_2	3	2	 <p>T shaped</p>	 <p>T Shaped</p>	$BrF_3, ClF_3,$



Number of electron Pairs	Molecule	No. of bond pairs	No. of lone pairs	Shape	Molecular geometry	Examples
	AB_2L_3	2	3	 <p>Linear</p>	 <p>Linear</p>	XeF_2, I_3^-, IF_2^-
	AB_6	6	-	 <p>Octahedral</p>	 <p>Octahedral</p>	SF_6, IOF_5
6	AB_5L	5	1	 <p>Square pyramidal</p>	 <p>Square pyramidal</p>	$BrF_5, IF_5, TeF_5^-, XeOF_4$
	AB_4L_2	4	2	 <p>Square planar</p>	 <p>Square Planar</p>	XeF_4, ICl_4^-
7	AB_7	7	-		 <p>pentagonal bi-pyramidal</p>	IF_7



Evaluate Yourself

6) Arrange the following in the decreasing order of Bond angle

- i) $\text{CH}_4, \text{H}_2\text{O}, \text{NH}_3$ ii) $\text{C}_2\text{H}_2, \text{BF}_3, \text{CCl}_4$

10.7 Valence Bond Theory

Heitler and London gave a theoretical treatment to explain the formation of covalent bond in hydrogen molecule on the basis of wave mechanics of electrons. It was further developed by Pauling and Slater. The wave mechanical treatment of VB theory is beyond the scope of this textbook. A simple qualitative treatment of VB theory for the formation of hydrogen molecule is discussed below.

Consider a situation wherein two hydrogen atoms (H_a and H_b) are separated by infinite distance. At this stage there is no interaction between these two atoms and the potential energy of this system is arbitrarily taken as zero. As these two atoms approach each other, in addition to the electrostatic attractive force between the nucleus and its own electron (purple arrows), the following new forces begins to operate.

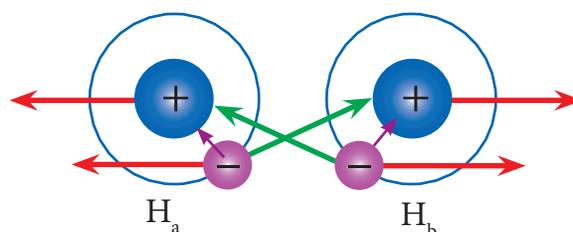


Fig 10. 17 (a) VB theory for the formation of hydrogen molecule

The new attractive forces (green arrows) arise between

- nucleus of H_a and valence electron of H_b
- nucleus of H_b and the valence electron of H_a .

The new repulsive forces (red arrows) arise between

- the nucleus of H_a and H_b
- valence electrons of H_a and H_b .

The attractive forces tend to bring H_a and H_b together whereas the repulsive forces tends to push them apart. At the initial stage, as the two hydrogen atoms approach each other, the attractive forces are stronger than the repulsive forces and the potential energy decreases. A stage is reached where the net attractive forces are exactly balanced by repulsive forces and the potential energy of the system acquires a minimum energy.

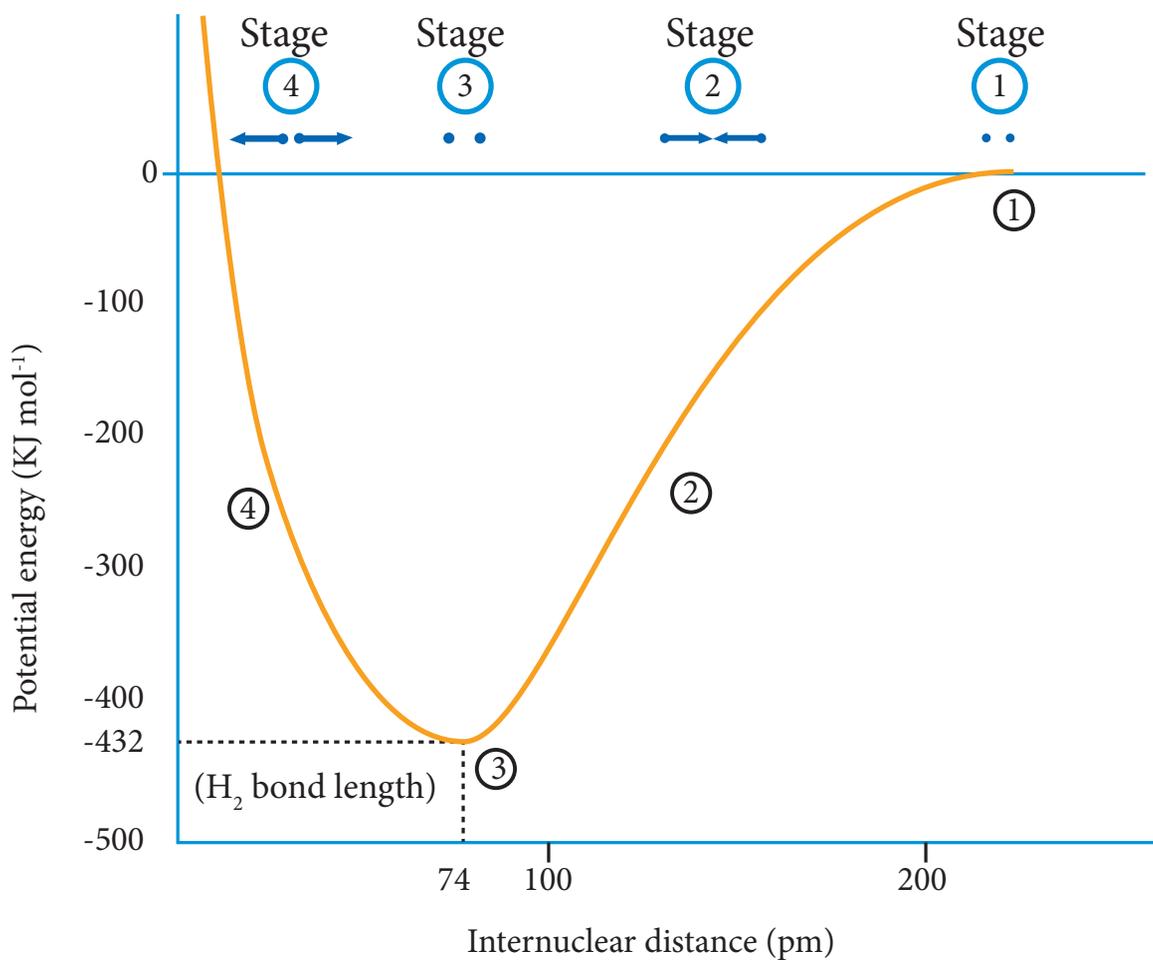


Fig 10. 17 (b) VB theory for the formation of hydrogen molecule

At this stage, there is a maximum overlap between the atomic orbitals of H_a and H_b , and the atoms H_a and H_b are now said to be bonded together by a covalent bond. The internuclear distance at this stage gives the H-H bond length and is equal to 74 pm. The liberated energy is 436 kJ mol^{-1} and is known as bond energy. Since the energy is released during the bond formation, the resultant molecule is more stable. If the distance between the two atoms is decreased further, the repulsive forces dominate the attractive forces and the potential energy of the system sharply increases

10.7.1 Salient features of VB Theory:

- (i) When half filled orbitals of two atoms overlap, a covalent bond will be formed between them.
- (ii) The resultant overlapping orbital is occupied by the two electrons with opposite spins. For example, when H_2 is formed, the two 1s electrons of two hydrogen atoms get paired up and occupy the overlapped orbital.
- (iii) The strength of a covalent bond depends upon the extent of overlap of atomic orbitals. Greater the overlap, larger is the energy released and stronger will be the bond formed.

- (iv) Each atomic orbital has a specific direction (except s-orbital which is spherical) and hence orbital overlap takes place in the direction that maximizes overlap

Let us explain the covalent bond formation in hydrogen, fluorine and hydrogen fluoride using VB theory.

10.8 Orbital Overlap

When atoms combine to form a covalent molecule, the atomic orbitals of the combining atoms overlap to form a covalent bond. The bond pair of electrons will occupy the overlapped region of the orbitals. Depending upon the nature of overlap we can classify the covalent bonding between the two atoms as sigma (σ) and pi (π) bonds.

10.8.1 Sigma and Pi bonds

When two atomic orbitals overlap linearly along the axis, the resultant bond is called a sigma (σ) bond. This overlap is also called 'head-on overlap' or 'axial overlap'. Overlap involving an s orbital (s-s and s-p overlaps) will always result in a sigma bond as the s orbital is spherical. Overlap between two p orbitals along the molecular axis will also result in sigma bond formation. When we consider x-axis as molecular axis, the p_x - p_x overlap will result in σ -bond.

When two atomic orbitals overlap sideways, the resultant covalent bond is called a pi (π) bond. When we consider x-axis as molecular axis, the p_y - p_y and p_z - p_z overlaps will result in the formation of a π -bond.

Following examples will be useful to understand the overlap:

10.8.2 Formation of hydrogen (H_2) Molecule

Electronic configuration of hydrogen atom is $1s^1$

During the formation of H_2 molecule, the 1s orbitals of two hydrogen atoms containing one unpaired electron with opposite spin overlap with each other along the internuclear axis. This overlap is called s-s overlap. Such axial overlap results in the formation of a σ -covalent bond.

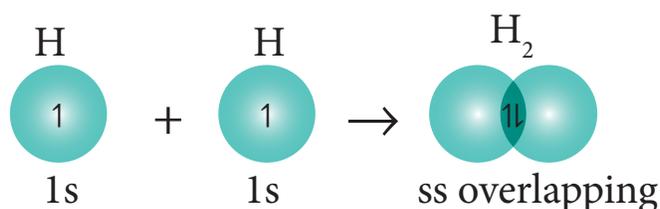


Fig 10. 18 Formation of hydrogen molecule

Formation of fluorine molecule (F₂):

Valence shell electronic configuration of fluorine atom : $2s^2 2p_x^2, 2p_y^2, 2p_z^1$

When the half filled p_z orbitals of two fluorine overlaps along the z-axis, a σ -covalent bond is formed between them.

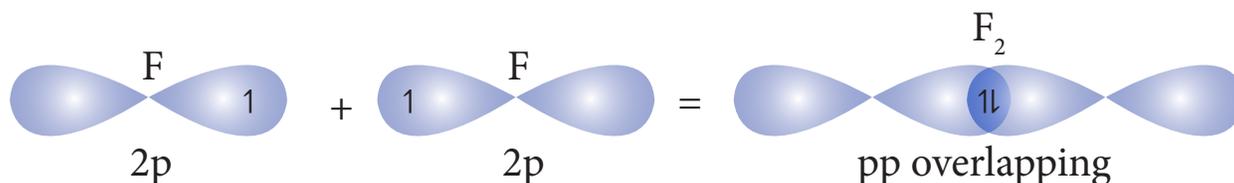


Fig 10.19 Formation of F₂ Molecule

Formation of HF molecule:

Electronic configuration of hydrogen atom is $1s^1$

Valence shell electronic configuration of fluorine atom : $2s^2 2p_x^2, 2p_y^2, 2p_z^1$

When half filled $1s$ orbital of hydrogen linearly overlaps with a half filled $2p_z$ orbital of fluorine, a σ -covalent bond is formed between hydrogen and fluorine.

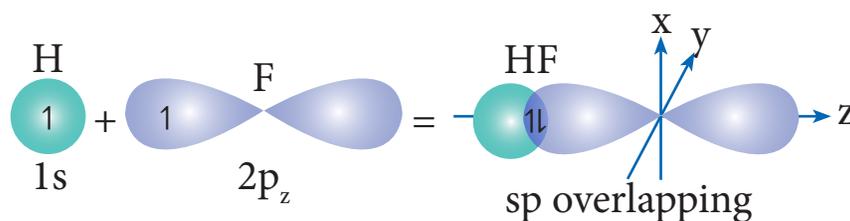


Fig 10.20 Formation of HF Molecule

Formation of oxygen molecule (O₂):

Valence shell electronic configuration of oxygen atom : $2s^2 2p_x^2, 2p_y^1, 2p_z^1$

		π bond	σ bond
Oxygen 1	$1\downarrow$	$1\downarrow$	1
	$2s^2$	$2p_x^2$	$2p_y^1$ $2p_z^1$
Oxygen 2	$1\downarrow$	$1\downarrow$	1
	$2s^2$	$2p_x^2$	$2p_y^1$ $2p_z^1$

When the half filled p_z orbitals of two oxygen overlaps along the z-axis (considering molecular axis as z axis), a σ -covalent bond is formed between them. Other two half filled p_y orbitals of two oxygen atoms overlap laterally (sideways) to form a π -covalent bond between

the oxygen atoms. Thus, in oxygen molecule, two oxygen atoms are connected by two covalent bonds (double bond). The other two pair of electrons present in the 2s and $2p_x$ orbital do not involve in bonding and remains as lone pairs on the respective oxygen.

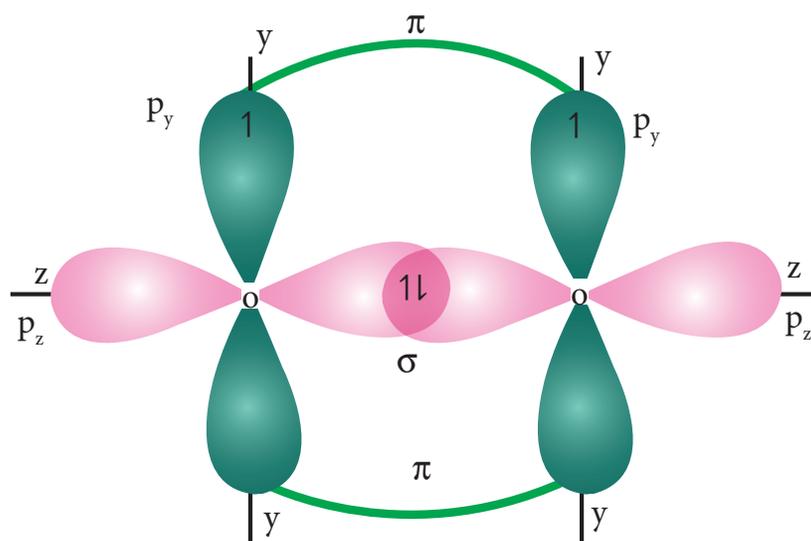


Fig 10. 21 Formation of π bond in O_2 Molecule

Evaluate Yourself

7) Bond angle in PH_4^+ is higher than in PH_3 why?

10.9 Hybridisation

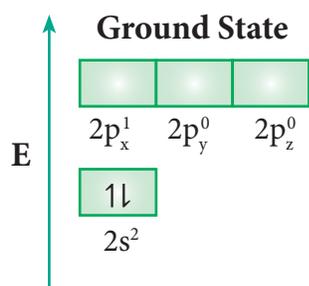
Bonding in simple molecules such as hydrogen and fluorine can easily be explained on the basis of overlap of the respective atomic orbitals of the combining atoms. But the observed properties of polyatomic molecules such as methane, ammonia, beryllium chloride etc... cannot be explained on the basis of simple overlap of atomic orbitals. For example, it was experimentally proved that methane has a tetrahedral structure and the four C-H bonds are equivalent. This fact cannot be explained on the basis of overlap of atomic orbitals of hydrogen (1s) and the atomic orbitals of carbon with different energies ($2s^2 2p_x^2 2p_y 2p_z$).

In order to explain these observed facts, Linus Pauling proposed that the valence atomic orbitals in the molecules are different from those in isolated atom and he introduced the concept of hybridisation. Hybridisation is the process of mixing of atomic orbitals of the same atom with comparable energy to form equal number of new equivalent orbitals with same energy. The resultant orbitals are called hybridised orbitals and they possess maximum symmetry and definite orientation in space so as to minimize the force of repulsion between their electrons.

10.9.1 Types of hybridisation and geometry of molecules

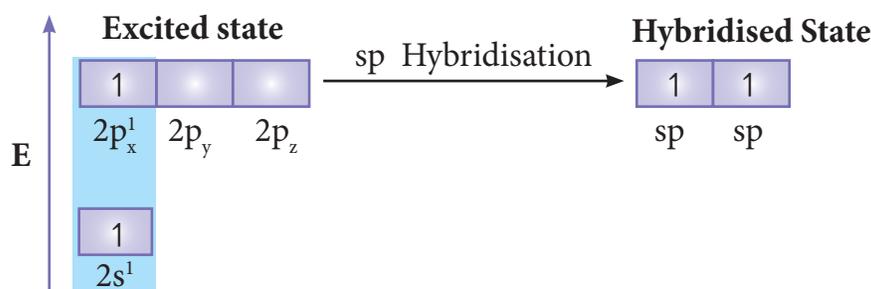
sp Hybridisation:

Consider the bond formation in beryllium chloride. The ground state valence shell electronic configuration of Beryllium atom is $[\text{He}]2s^2 2p^0$



In BeCl_2 both the Be-Cl bonds are equivalent and it was observed that the molecule is linear. VB theory explain this observed behaviour by sp hybridisation. One of the paired electrons in the 2s orbital gets excited to 2p orbital and the electronic configuration at the excited state is shown.

Now, the 2s and 2p orbitals hybridise and produce two equivalent sp hybridised orbitals which have 50 % s-character and 50 % p-character. These sp hybridised orbitals are oriented in opposite direction as shown in the figure.



Overlap with orbital of chlorine

Each of the sp hybridized orbitals linearly overlap with $3p_z$ orbital of the chlorine to form a covalent bond between Be and Cl as shown in the Figure.

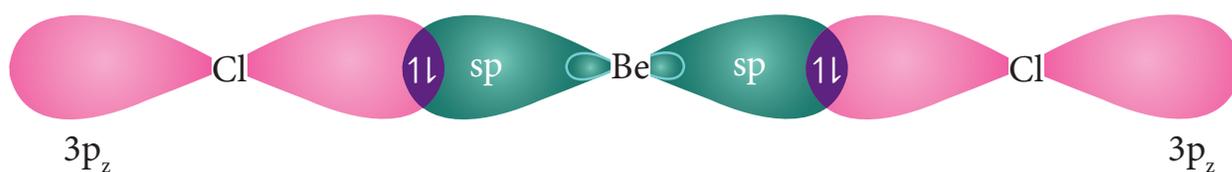
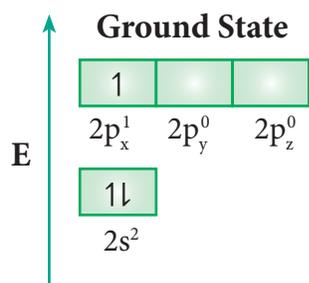


Fig 10.22 sp Hybridisation : BeCl_2

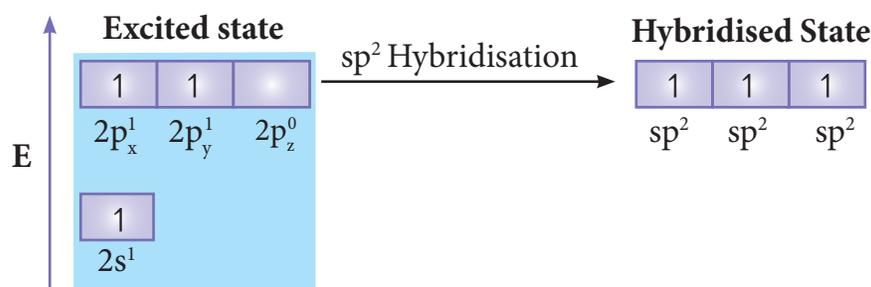
sp² Hybridisation:

Consider the bond formation in boron trifluoride. The ground state valence shell electronic configuration of Boron atom is [He]2s² 2p¹.



In the ground state boron has only one unpaired electron in the valence shell. In order to form three covalent bonds with fluorine atoms, three unpaired electrons are required. To achieve this, one of the paired electrons in the 2s orbital is promoted to the 2p_y orbital in the excited state.

In boron, the s orbital and two p orbitals (p_x and p_y) in the valence shell hybridises, to generate three equivalent sp² orbitals as shown in the Figure. These three orbitals lie in the same xy plane and the angle between any two orbitals is equal to 120°



Overlap with 2p_z orbitals of fluorine:

The three sp² hybridised orbitals of boron now overlap with the 2p_z orbitals of fluorine (3 atoms). This overlap takes place along the axis as shown below.

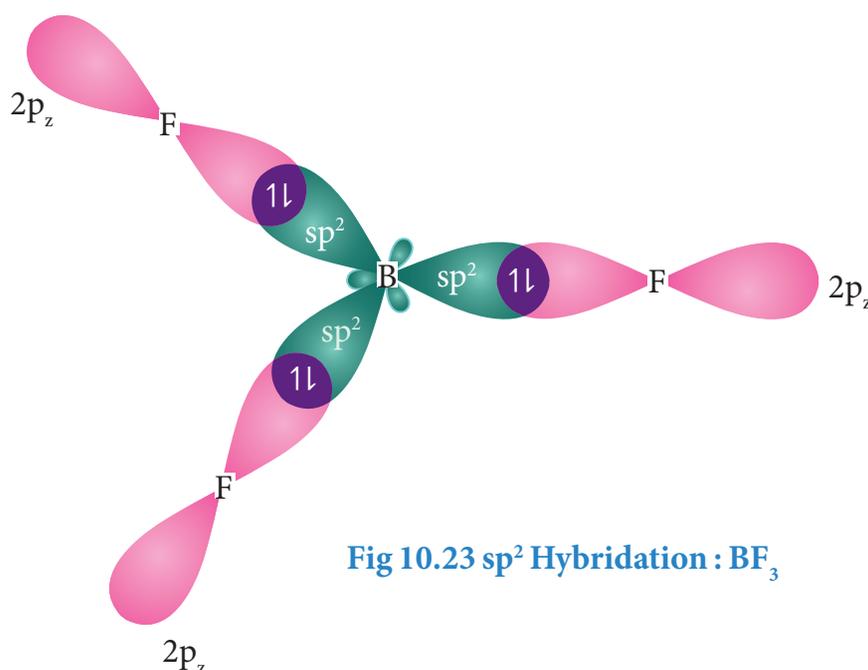
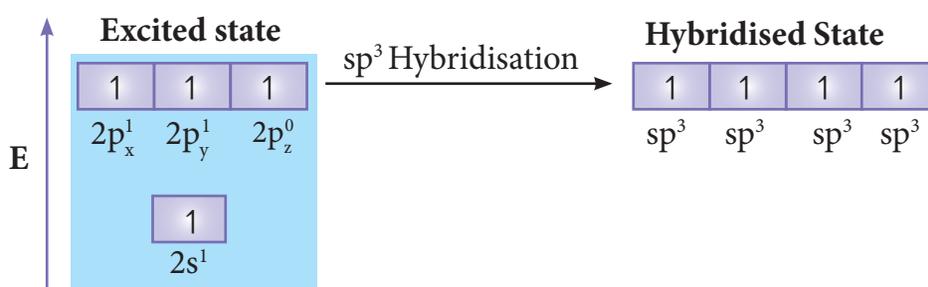
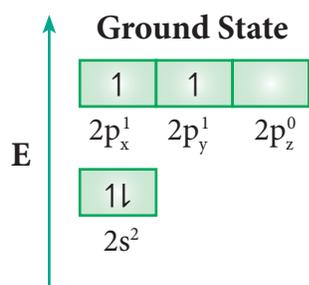


Fig 10.23 sp² Hybridisation : BF₃

sp³ Hybridisation:

sp³ hybridisation can be explained by considering methane as an example. In methane molecule the central carbon atom is bound to four hydrogen atoms. The ground state valence shell electronic configuration of carbon is [He]2s² 2p_x¹ 2p_y¹ 2p_z⁰.



In order to form four covalent bonds with the four hydrogen atoms, one of the paired electrons in the 2s orbital of carbon is promoted to its 2p_z orbital in the excited state. The one 2s orbital and the three 2p orbitals of carbon mix to give four equivalent sp³ hybridised orbitals. The angle between any two sp³ hybridised orbitals is 109° 28'

Overlap with 1s orbitals of hydrogen:

The 1s orbitals of the four hydrogen atoms overlap linearly with the four sp³ hybridised orbitals of carbon to form four C-H σ-bonds in the methane molecule, as shown below.

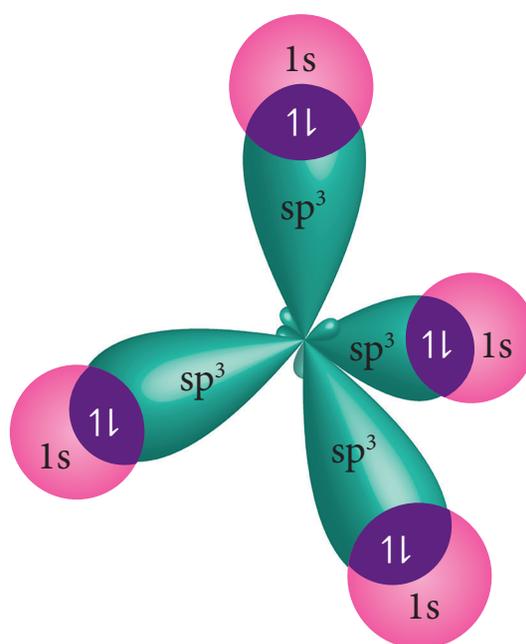


Fig 10.24 sp³ Hybridisation : CH₄

sp³d Hybridisation:

In the molecules such as PCl₅, the central atom phosphorus is covalently bound to five chlorine atoms. Here the atomic orbitals of phosphorous undergoes sp³d hybridisation which involves its one 3s orbital, three 3p orbitals and one vacant 3d orbital (d_{z²}). The ground state electronic configuration of phosphorous is [Ne]3s² 3p_x¹ 3p_y¹ 3p_z¹ as shown below.

One of the paired electrons in the 3s orbital of phosphorous is promoted to one of its vacant 3d orbital (d_{z²}) in the excited state. One 3s orbital, three 3p orbitals and one 3d_{z²} orbital of phosphorus atom mixes to give five equivalent sp³d hybridised orbitals. The orbital geometry of sp³d hybridised orbitals is trigonal bi-pyramidal as shown in the figure 10.25.

Overlap with 3p_z orbitals of chlorine:

The 3p_z orbitals of the five chlorine atoms linearly overlap along the axis with the five sp³d hybridised orbitals of phosphorous to form the five P-Cl σ-bonds, as shown below.

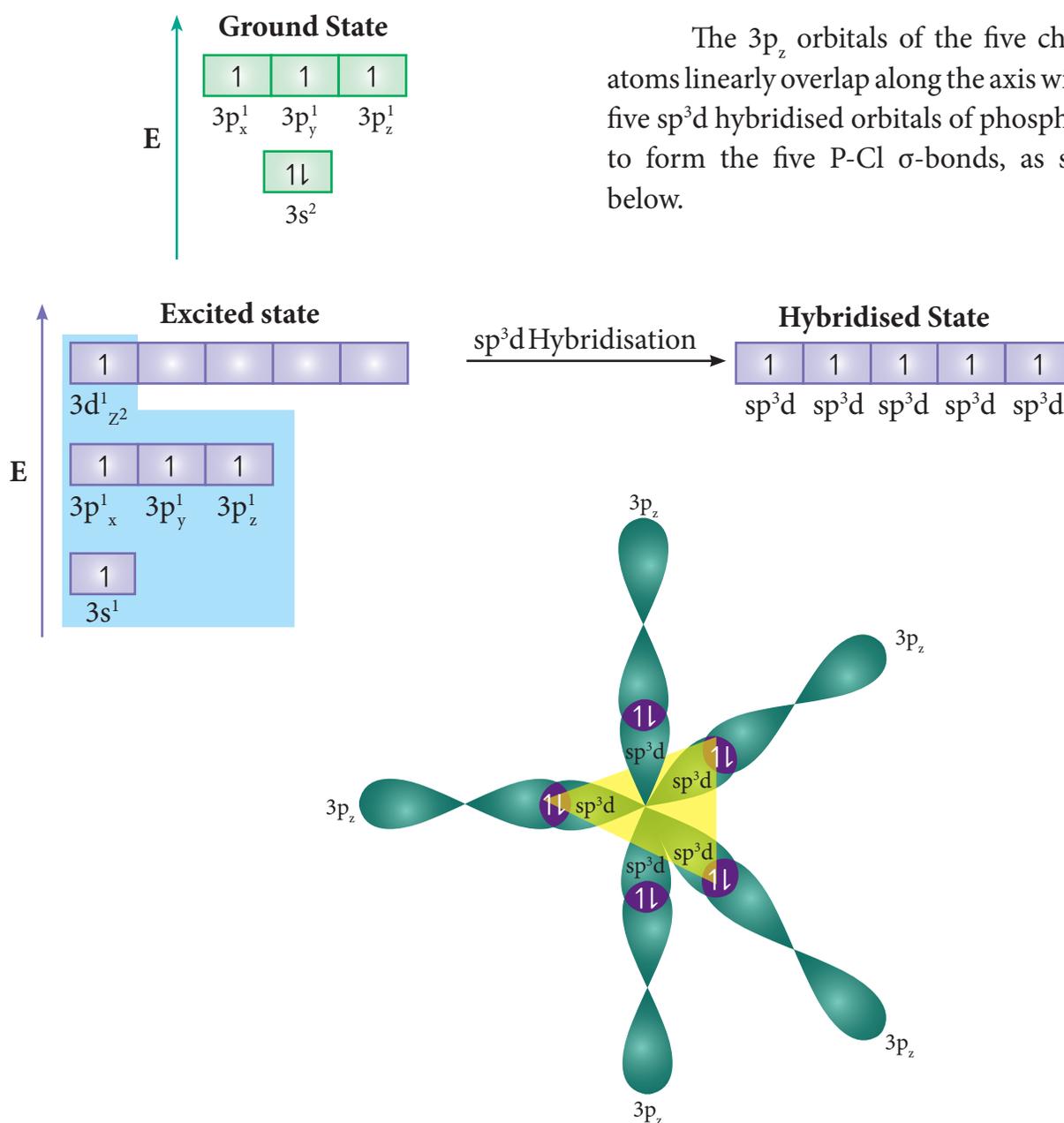


Fig 10.25 sp³d Hybridisation : PCl₅

sp³d² Hybridisation:

In sulphur hexafluoride (SF₆) the central atom sulphur extends its octet to undergo sp³d² hybridisation to generate six sp³d² hybridised orbitals which accounts for six equivalent S-F bonds. The ground state electronic configuration of sulphur is [Ne]3s² 3p_x² 3p_y¹ 3p_z¹.

One electron each from 3s orbital and 3p orbital of sulphur is promoted to its two vacant 3d orbitals (d_{z²} and d_{x²-y²}) in the excited state. A total of six valence orbitals from sulphur (one 3s orbital, three 3p orbitals and two 3d orbitals) mixes to give six equivalent sp³d² hybridised orbitals. The orbital geometry is octahedral as shown in the figure.

Overlap with 2p_z orbitals of fluorine:

The six sp³d² hybridised orbitals of sulphur overlap linearly with 2p_z orbitals of six fluorine atoms to form the six S-F bonds in the sulphur hexafluoride molecule.

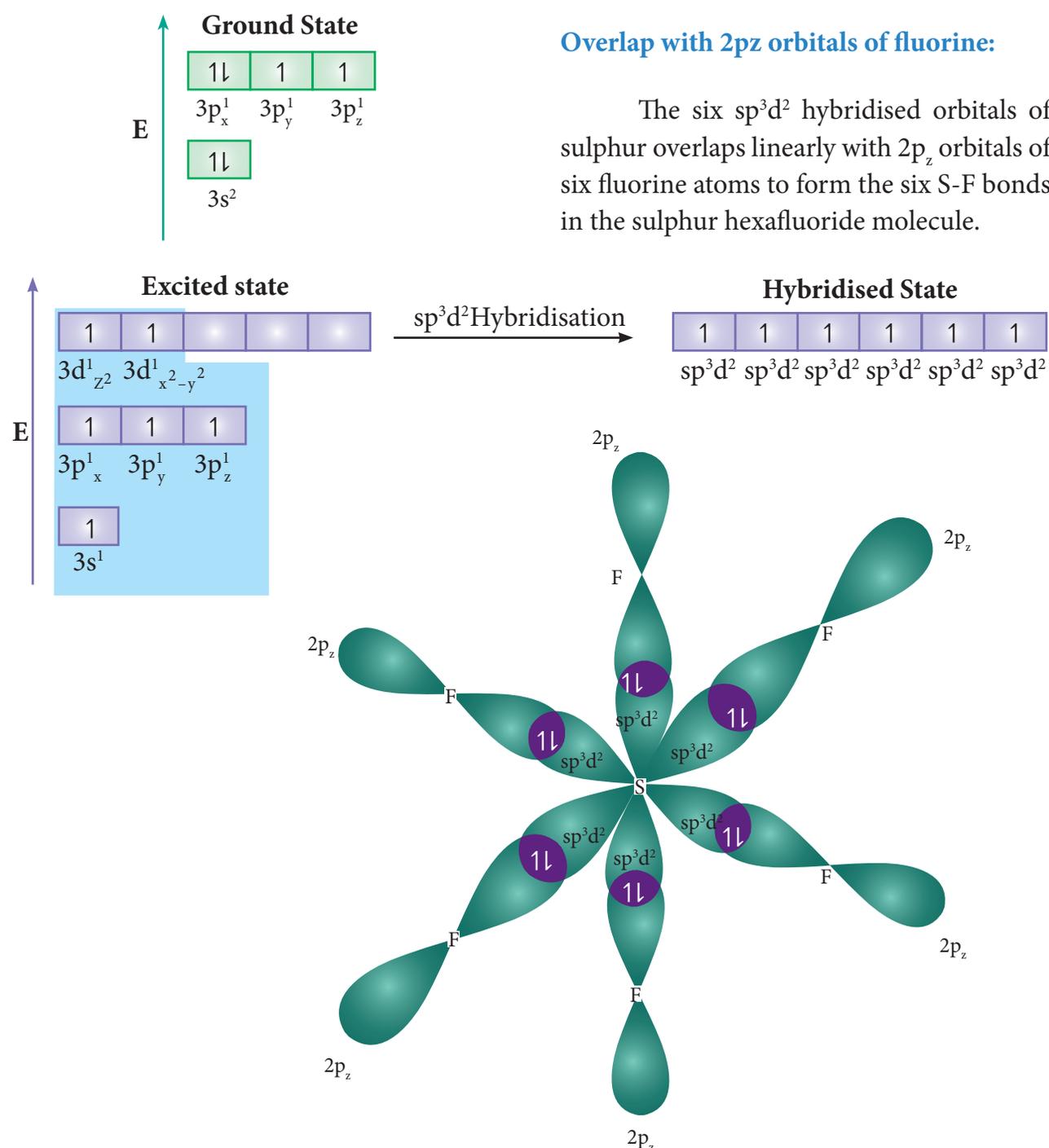
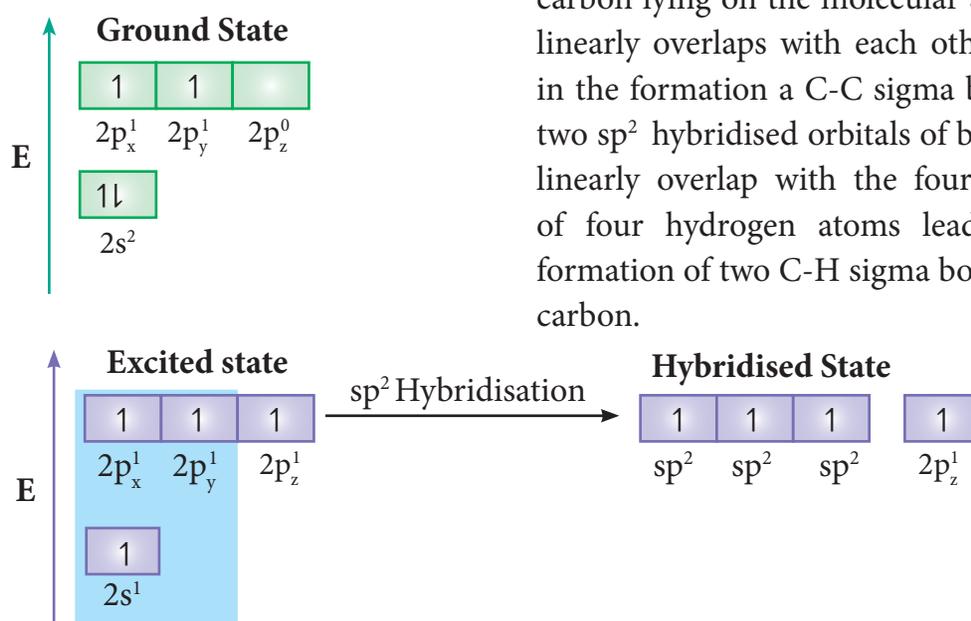


Fig 10.26 sp³d² Hybridisation : SF₆

Bonding in Ethylene:

The bonding in ethylene can be explained using hybridisation concept. The molecular formula of ethylene is C_2H_4 . The valency of carbon is 4. The electronic configuration of valence shell of carbon in ground state is $[He]2s^2 2p_x^1 2p_y^1 2p_z^0$. To satisfy the valency of carbon promote an electron from $2s$ orbital to $2p_z$ orbital in the excited state.



In ethylene both the carbon atoms undergoes sp^2 hybridisation involving $2s$, $2p_x$ and $2p_y$ orbitals, resulting in three equivalent sp^2 hybridised orbitals lying in the xy plane at an angle of 120° to each other. The unhybridised $2p_z$ orbital lies perpendicular to the xy plane.

Formation of sigma bond:

One of the sp^2 hybridised orbitals of each carbon lying on the molecular axis (x -axis) linearly overlaps with each other resulting in the formation a C-C sigma bond. Other two sp^2 hybridised orbitals of both carbons linearly overlap with the four $1s$ orbitals of four hydrogen atoms leading to the formation of two C-H sigma bonds on each carbon.

Formation of Pi (π) bond:

The unhybridised $2p_z$ orbital of both carbon atoms can overlap only sideways as they are not in the molecular axis. This lateral overlap results in the formation a pi(π) bond between the two carbon atoms as shown in the figure.

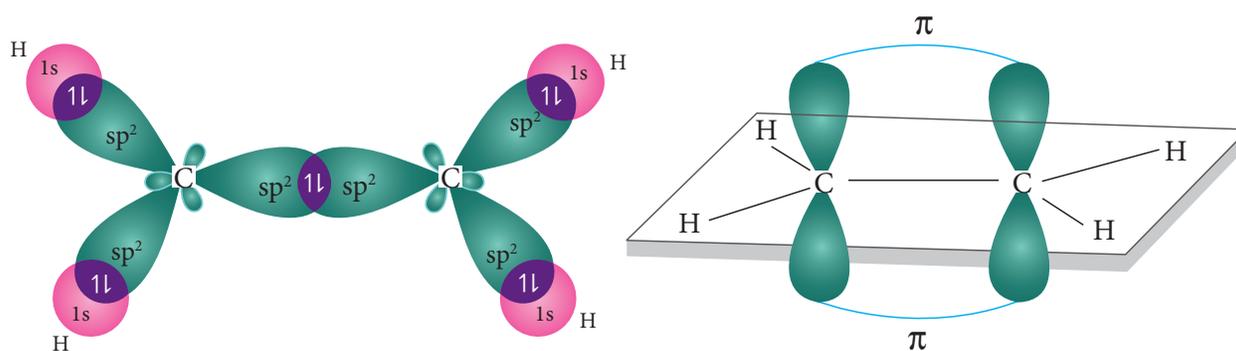


Fig 10.27 sp^2 Hybridisation : C_2H_4

Bonding in acetylene:

Similar to ethylene, the bonding in acetylene can also be explained using hybridisation concept. The molecular formula of acetylene is C_2H_2 . The electronic configuration of valence shell of carbon in ground state is $[He]2s^2 2p_x^1 2p_y^1 2p_z^0$. To satisfy the valency of carbon promote an electron from 2s orbital to $2p_z$ orbital in the excited state.

In acetylene molecule, both the carbon atoms are in sp hybridised state. The 2s and $2p_x$ orbitals, resulting in two equivalent sp hybridised orbitals lying in a straight line along the molecular axis (x-axis). The unhybridised $2p_y$ and $2p_z$ orbitals lie perpendicular to the molecular axis.

Formation of sigma bond:

One of the two sp hybridised orbitals of each carbon linearly overlaps with each other resulting in the formation a C-C sigma bond. The other sp hybridised orbital of both carbons linearly overlap with the two 1s orbitals of two hydrogen atoms leading to the formation of one C-H sigma bonds on each carbon.

Formation of pi bond:

The unhybridised $2p_y$ and $2p_z$ orbitals of each carbon overlap sideways. This lateral overlap results in the formation of two pi bonds (p_y-p_y and p_z-p_z) between the two carbon atoms as shown in the figure.

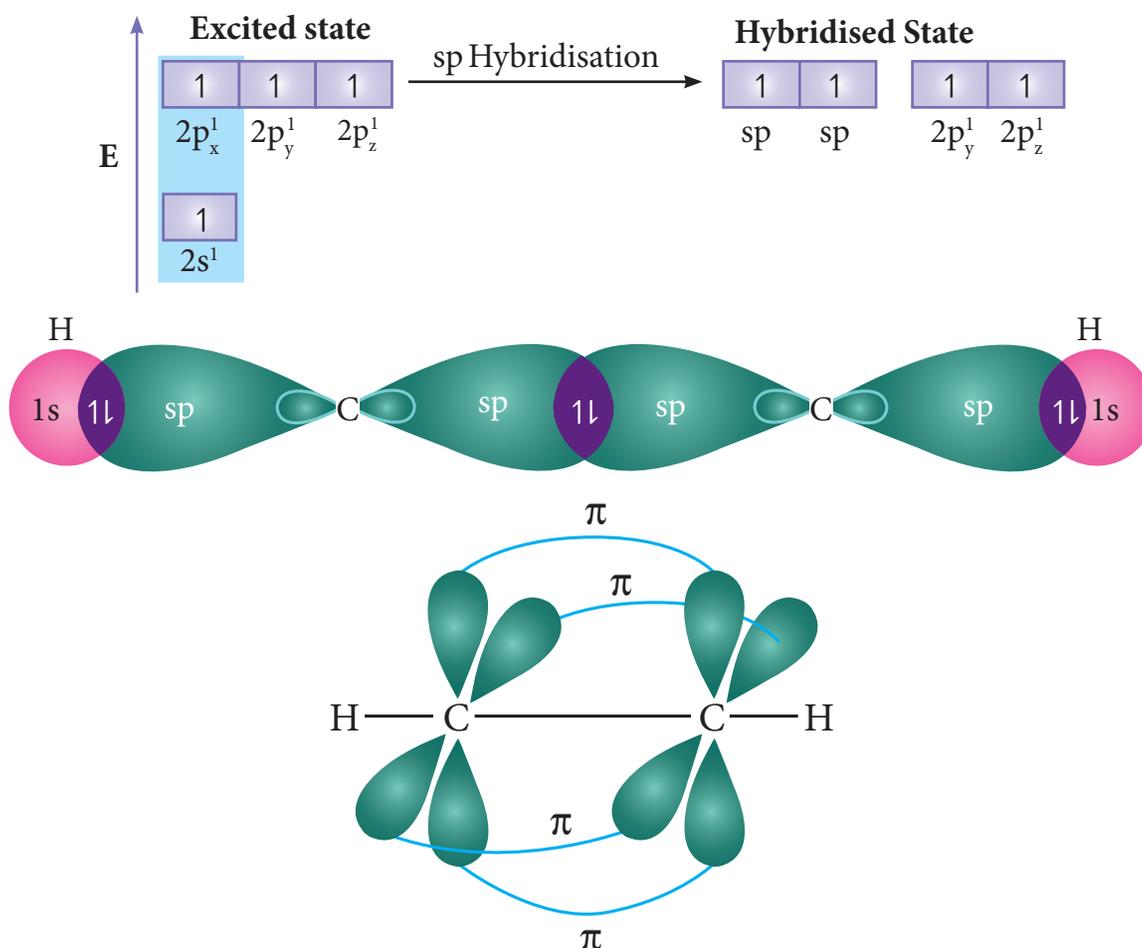


Fig 10.28 sp Hybridisation in acetylene: C_2H_2

Evaluate Yourself



- 8) Explain the bond formation in SF₄ and CCl₄ using hybridisation concept.

Evaluate Yourself



- 9) The observed bond length of N₂⁺ is larger than N₂ while the bond length in NO⁺ is less than in NO. Why?

10.10 Molecular orbital theory

Lewis concept and valence bond theory qualitatively explains the chemical bonding and molecular structure. Both approaches are inadequate to describe some of the observed properties of molecules. For example, these theories predict that oxygen is diamagnetic. However, it was observed that oxygen in liquid form was attracted towards the poles of strong magnet, indicating that oxygen is paramagnetic. As both these theories treated the bond formation in terms of electron pairs and hence they fail to explain the bonding nature of paramagnetic molecules. F. Hund and Robert. S. Mulliken developed a bonding theory called molecular orbital theory which explains the magnetic behaviour of molecules.

The salient features of Molecular orbital Theory (MOT):

1. When atoms combine to form molecules, their individual atomic orbitals lose their identity and form new orbitals called molecular orbitals.
2. The shapes of molecular orbitals depend upon the shapes of combining atomic orbitals.
3. The number of molecular orbitals formed is the same as the number of combining atomic orbitals. Half the number of molecular orbitals formed will have lower energy than the corresponding atomic orbital, while the remaining molecular orbitals will have higher energy. The molecular orbital with lower energy is called bonding molecular orbital and the one with higher energy is called anti-bonding molecular orbital. The bonding molecular orbitals are represented as σ (Sigma), π (pi), δ (delta) and the corresponding antibonding orbitals are denoted as σ^* , π^* and δ^* .
4. The electrons in a molecule are accommodated in the newly formed molecular orbitals. The filling of electrons in these orbitals follows Aufbau's principle, Pauli's exclusion principle and Hund's rule as in the case of filling of electrons in atomic orbitals.
5. Bond order gives the number of covalent bonds between the two combining atoms. The bond order of a molecule can be calculated using the following equation

$$\text{Bond order} = \frac{N_b - N_a}{2}$$

Where,

N_b = Total number of electrons present in the bonding molecular orbitals

N_a = Total number of electrons present in the antibonding molecular orbitals and

A bond order of zero value indicates that the molecule doesn't exist.

10.10.1 Linear combination of atomic orbitals

The wave functions for the molecular orbitals can be obtained by solving Schrödinger wave equation for the molecule. Since solving the Schrödinger equation is too complex, approximation methods are used to obtain the wave function for molecular orbitals. The most common method is the linear combination of atomic orbitals (LCAO).

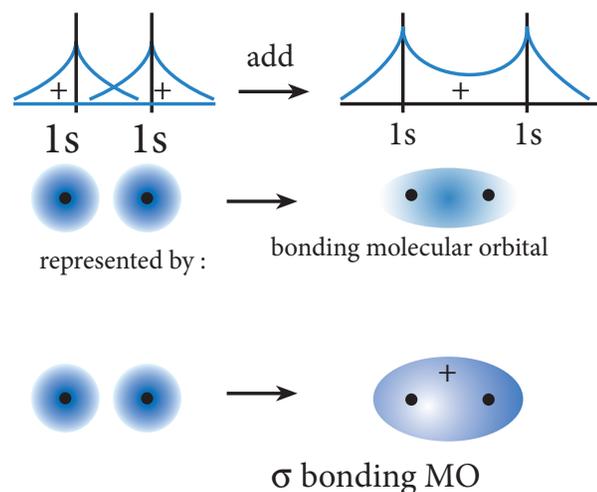
We know that the atomic orbitals are represented by the wave function Ψ . Let us consider two atomic orbitals represented by the wave function ψ_A and ψ_B with comparable energy, combines to form two molecular orbitals. One is bonding molecular orbital (ψ_{bonding}) and the other is antibonding molecular orbital ($\psi_{\text{antibonding}}$). The wave functions for these two molecular orbitals can be obtained by the linear combination of the atomic orbitals ψ_A and ψ_B as below.

$$\Psi_{\text{bonding}} = \psi_A + \psi_B$$

$$\Psi_{\text{antibonding}} = \psi_A - \psi_B$$

The formation of bonding molecular orbital can be considered as the result of constructive interference of the atomic orbitals and the formation of anti-bonding molecular orbital can be the result of the destructive interference of the atomic orbitals. The formation of the two molecular orbitals from two 1s orbitals is shown below.

Constructive interaction: The two 1s orbitals are in phase and have the same sign.



Destructive interaction The two 1s Orbitals are out phase

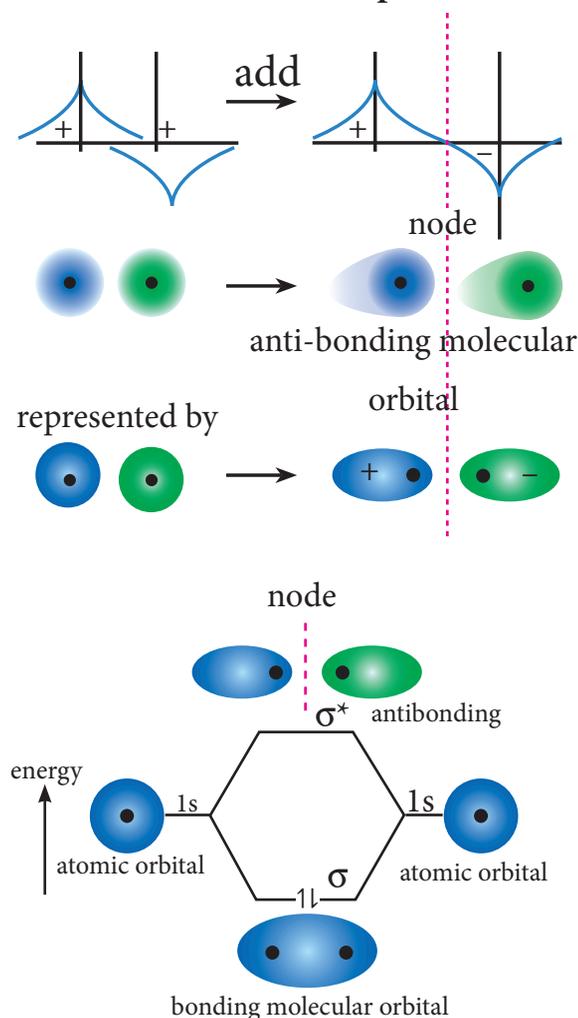


Fig 10.29 Linear Combination of atomic orbitals

10.10.2 Bonding in some Homonuclear di-atomic molecules:

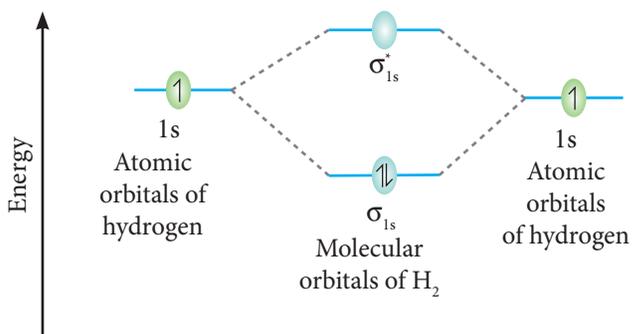


Fig 10.30 MO Diagram for H₂ molecule

Molecular orbital diagram of hydrogen molecule (H₂)

Electronic configuration of H atom is 1s¹

Electronic configuration of H₂ molecule

σ_{1s}^2

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1$$

Molecule has *no unpaired electrons*.

Hence, it is **diamagnetic**.

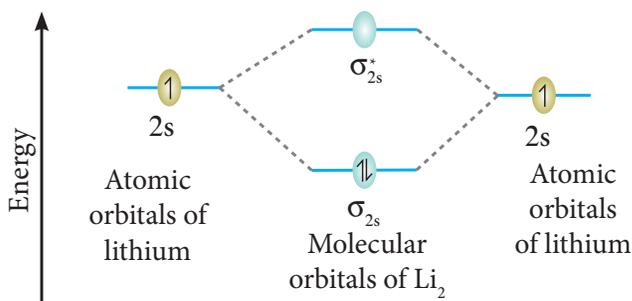


Fig 10.31 MO Diagram for Li₂ molecule

Molecular orbital diagram of lithium molecule (Li₂)

Electronic configuration of Li atom is

1s²2s¹

Electronic configuration of Li₂ molecule

$\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{4 - 2}{2} = 1$$

Molecule has *no unpaired electrons*.

Hence it is **diamagnetic**.

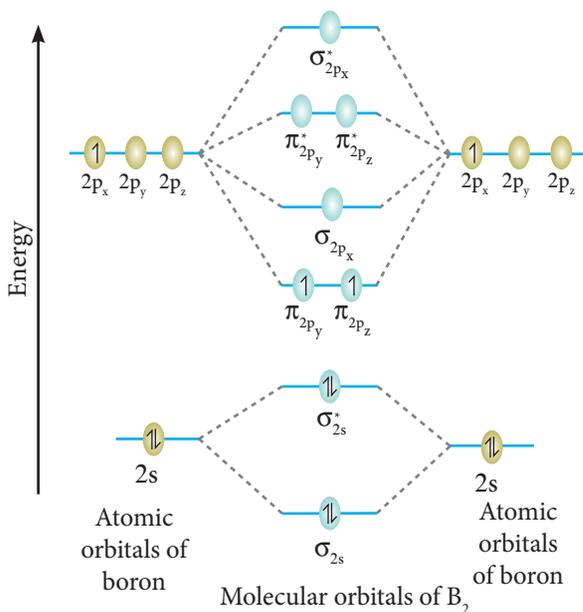


Fig 10.32 MO Diagram for B₂ molecule

Molecular orbital diagram of boron molecule (B₂)

Electronic configuration of B atom is

1s²2s²2p¹

Electronic configuration of B₂ molecule

$\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi_{2p_y}^1, \pi_{2p_z}^1$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{6 - 4}{2} = 1$$

Molecule has *two unpaired electrons*.

Hence it is **paramagnetic**.

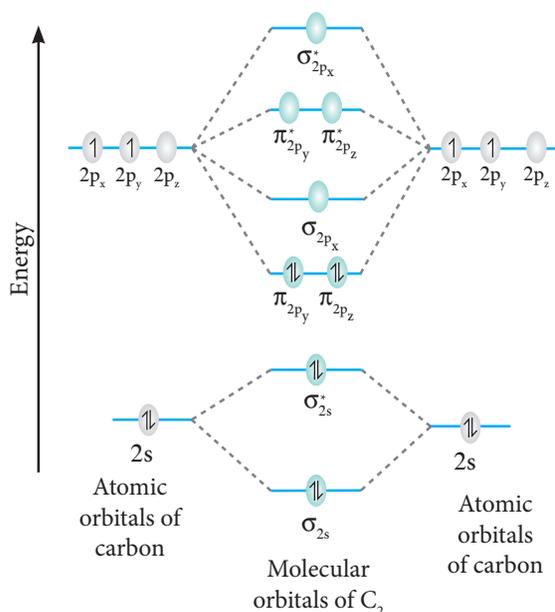


Fig 10.33 MO Diagram for C₂ molecule

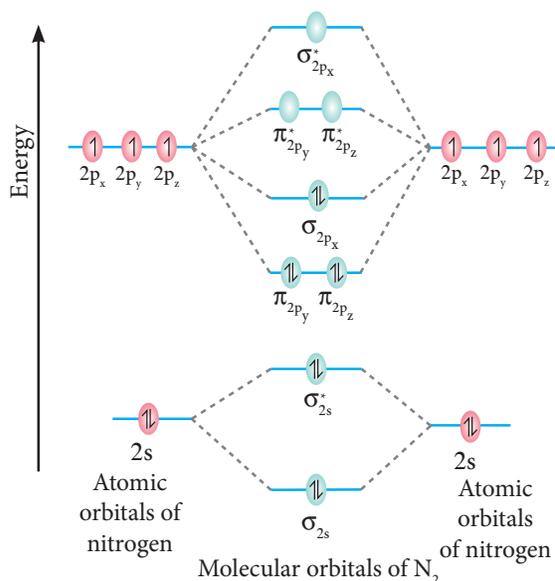


Fig 10.34 MO Diagram for N₂ molecule

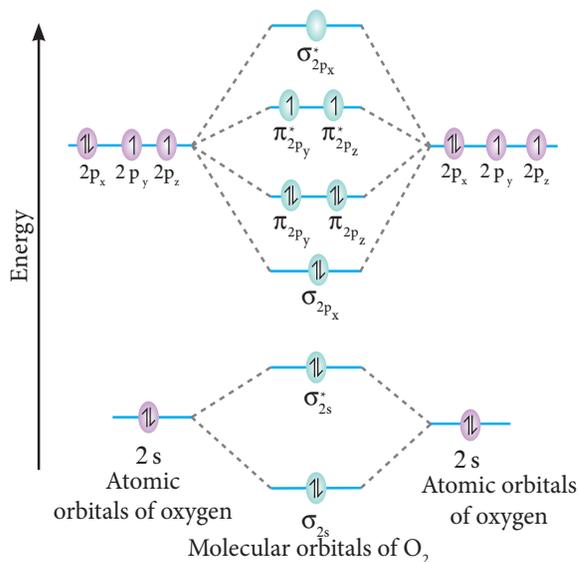
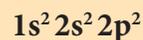


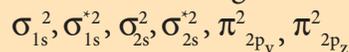
Fig 10.35 MO Diagram for O₂ molecule

Molecular orbital diagram of carbon molecule (C₂)

Electronic configuration of C atom is



Electronic configuration of C₂ molecule

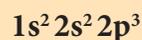


$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{8 - 4}{2} = 2$$

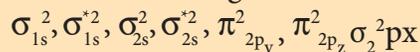
Molecule has *no unpaired electrons*. Hence, it is **diamagnetic**.

Molecular orbital diagram of nitrogen molecule (N₂)

Electronic configuration of N atom is



Electronic configuration of N₂ molecule

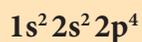


$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 4}{2} = 3$$

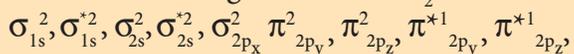
Molecule has *no unpaired electrons*. Hence, it is **diamagnetic**.

Molecular orbital diagram of oxygen molecule (O₂)

Electronic configuration of O atom is



Electronic configuration of O₂ molecule



$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 6}{2} = 2$$

Molecule has *two unpaired electrons*. Hence, it is **paramagnetic**.

10.10.3 Bonding in some Heteronuclear di-atomic molecules

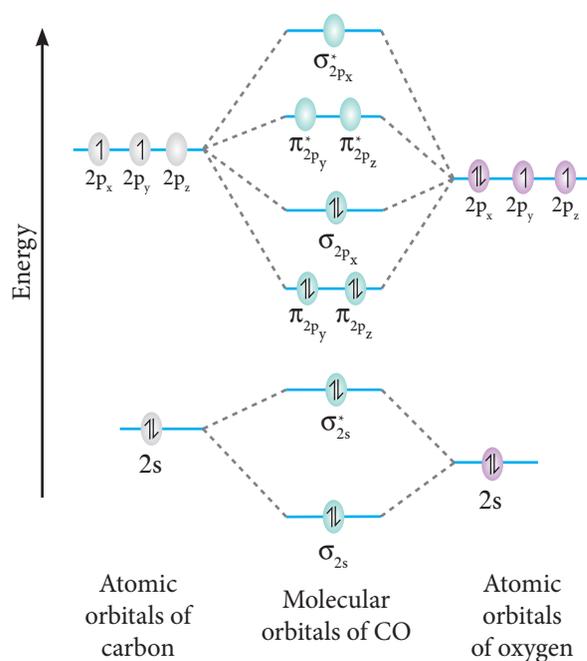


Fig 10.36 MO Diagram for CO molecule

Molecular orbital diagram of Carbon monoxide molecule (CO)

Electronic configuration of C atom is $1s^2 2s^2 2p^2$

Electronic configuration of O atom is $1s^2 2s^2 2p^4$

Electronic configuration of CO molecule $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi_{2p_y}^2, \pi_{2p_z}^2, \sigma_{2p_x}^2$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 4}{2} = 3$$

Molecule has *no unpaired electrons*. Hence, it is **diamagnetic**.

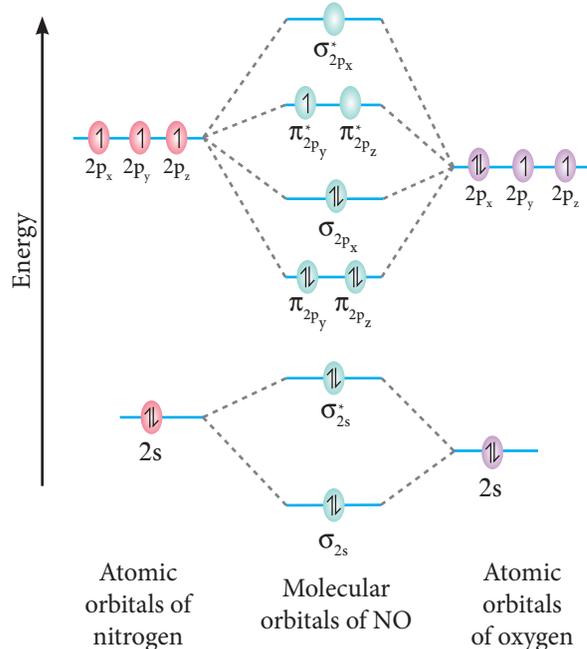


Fig 10.36 MO Diagram for NO molecule

Molecular orbital diagram of Nitric oxide molecule (NO)

Electronic configuration of N atom is $1s^2 2s^2 2p^3$

Electronic configuration of O atom is $1s^2 2s^2 2p^4$

Electronic configuration of NO molecule $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi_{2p_y}^2, \pi_{2p_z}^2, \sigma_{2p_x}^2, \pi_{2p_y}^{*1}$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 5}{2} = 2.5$$

Molecule has *one unpaired electron*. Hence, it is **paramagnetic**.

Evaluate Yourself

10) Draw the MO diagram for acetylide ion C_2^{2-} and calculate its bond order.

Metallic bonding

Metals have some special properties of lustre, high density, high electrical and thermal conductivity, malleability and ductility, and high melting and boiling points. The forces that keep the atoms of the metal so closely in a metallic crystal constitute what is generally known as the metallic bond. The metallic bond is not just an electrovalent bond(ionic bond), as the latter is formed between atoms of different electro negativities. Similarly, the metallic bond is not a covalent bond,as the metal atoms do not have sufficient number of valence electrons for mutual sharing with 8 or 12 neighboring metal atoms in a crystal. So, we have to search for a new theory to explain metallic bond. The first successful theory is due to Drude and Lorentz, which regards metallic crystal as an assemblage of positive ions immersed in a gas of free electrons. The free electrons are due to ionization of the valence electrons of the atoms of the metal. As the valence electrons of the atoms are freely shared by all the ions in the crystal, the metallic bonding is also referred to as electronic bonding. As the free electrons repel each other, they are uniformly distributed around the metal ions. Many physical properties of the metals can be explained by this theory, nevertheless there are exceptions.

The electrostatic attraction between the metal ions and the free electrons yields a three-dimensional close packed crystal with a large number of nearest metal ions. So, metals have high density. As the close packed structure contains many slip planes along which movement can occur during mechanical loading, the metal acquires

ductility. Pure metals can undergo 40 to 60% elongation prior to rupturing under mechanical loading. As each metal ion is surrounded by electron cloud in all directions, the metallic bonding has no directional properties.

As the electrons are free to move around the positive ions, the metals exhibit high electrical and thermal conductivity. The metallic luster is due to reflection of light by the electron cloud. As the metallic bond is strong enough, the metal atoms are reluctant to break apart into a liquid or gas, so the metals have high melting and boiling points.

The bonding in metal is better treated by Molecular orbital theory. As per this theory, the atomic orbitals of large number of atoms in a crystal overlap to form numerous bonding and antibonding molecular orbitals without any band gap. The bonding molecular orbitals are completely filled with an electron pair in each, and the antibonding molecular orbitals are empty. Absence of band gap accounts for high electrical conductivity of metals. High thermal conductivity is due to thermal excitation of many electrons from the valence band to the conductance band. With an increase in temperature, the electrical conductivity decreases due to vigorous thermal motion of lattice ions that disrupts the uniform lattice structure, that is required for free motion of electrons within the crystal. Most metals are black except copper, silver and gold. It is due to absorption of light of all wavelengths. Absorption of light of all wavelengths is due to absence of bandgap in metals.

SUMMARY

In molecules, atoms are held together by attractive forces, called chemical bonds. Kossel and Lewis are the first people to provide a logical explanation for chemical bonding. They proposed that atoms try to attain the nearest noble gas electronic configuration by losing, gaining or sharing one or more electrons during the bond formation. The noble gases contain eight electrons in their valance shell which is considered to be stable electronic configuration. The idea of Kossel – Lewis approach to chemical bond lead to the octet rule, which states that “the atoms transfer or share electrons so that all atoms involved in chemical bonding obtain 8 electrons in their outer shell (valance shell)”.

There are different types of chemical bonds. In compounds such as sodium chloride, the sodium atom loses an electron which is accepted by the chlorine atom resulting in the formation of Na^+ and Cl^- ions. These two ions are held together by the electrostatic attractive forces. This type of chemical bond is known as ionic bonds or electrovalent bonds. In certain compounds, instead of the complete transfer of electrons, the electrons are shared by both the bonding atoms. The two combining atoms are held together by their mutual attraction towards the shared electrons. This type of bond is called covalent bonding. In addition, there also another bond type known as coordinate covalent bonds, where the shared electrons of a covalent bond are provided by only one of the combining atoms. Metallic bonding is another type of bonding which is observed in metals.

Lewis theory in combination with VSEPR theory will be useful in predicting the shape of molecules. According to this theory, the shape of the molecules depends on the number of valance shell electron pair (lone pairs and bond pairs) around the central atom. Each pair of valance electrons around the central atom repels each other and hence, they are located as far away as possible in three-dimensional space to minimise the repulsion between them.

Heitler and London gave a theoretical treatment to explain the formation of covalent bond in hydrogen molecule on the basis of wave mechanics of electrons. It was further developed by Pauling and Slater. According to this theory when half-filled orbitals of two atoms overlap, a covalent bond will be formed between them. Linus Pauling introduced the concept of hybridisation. Hybridisation is the process of mixing of atomic orbitals of the same atom with comparable energy to form equal number of new equivalent orbitals with same energy. There are different types of hybridization such as sp , sp^2 , sp^3 , sp^3d^2 etc..

F. Hund and Robert. S. Mulliken developed a bonding theory called molecular orbital theory. According to this theory, when atoms combines to form molecules, their individual atomic orbitals lose their identity and forms new orbitals called molecular orbitals. The filling of electrons in these orbitals follows Aufbau's principle, Pauli's exclusion principle and Hund's rule as in the case of filling of electrons in atomic orbitals.

Evaluation



I. Choose the best answer.

- In which of the following Compounds does the central atom obey the octet rule?
a) XeF_4 b) AlCl_3
c) SF_6 d) SCl_2
- In the molecule $\text{O}_A = \text{C} = \text{O}_B$, the formal charge on O_A , C and O_B are respectively.
a) -1, 0, +1 b) +1, 0, -1
c) -2, 0, +2 d) 0, 0, 0
- Which of the following is electron deficient?
a) PH_3 b) $(\text{CH}_3)_2$
c) BH_3 d) NH_3
- Which of the following molecule contain no π bond?
a) SO_2 b) NO_2
c) CO_2 d) H_2O
- The ratio of number of sigma (σ) and pi (π) bonds in 2- butynal is
a) 8/3 b) 5/3
c) 8/2 d) 9/2
- Which one of the following is the likely bond angles of sulphur tetrafluoride molecule?
a) $120^\circ, 80^\circ$ b) $109^\circ, 28'$
c) 90° d) $89^\circ, 117'$
- Assertion:** Oxygen molecule is paramagnetic.
Reason : It has two unpaired electron in its bonding molecular orbital
a) both assertion and reason are true and reason is the correct explanation of assertion
b) both assertion and reason are true but reason is not the correct explanation of assertion
c) assertion is true but reason is false
d) Both assertion and reason are false
- According to Valence bond theory, a bond between two atoms is formed when
a) fully filled atomic orbitals overlap
b) half filled atomic orbitals overlap
c) non- bonding atomic orbitals overlap
d) empty atomic orbitals overlap
- In ClF_3 , NF_3 and BF_3 molecules the chlorine, nitrogen and boron atoms are
a) sp^3 hybridised
b) sp^3 , sp^3 and sp^2 respectively
c) sp^2 hybridised
d) sp^3d , sp^3 and sp^2 hybridised respectively
- When one s and three p orbitals hybridise,
a) four equivalent orbitals at 90° to each other will be formed
b) four equivalent orbitals at $109^\circ 28'$ to each other will be formed.



- c) four equivalent orbitals, that are lying the same plane will be formed
d) none of these
11. Which of these represents the correct order of their increasing bond order.
- a) $C_2 < C_2^{2-} < O_2^{2-} < O_2$
b) $C_2^{2-} < C_2^+ < O_2 < O_2^{2-}$
c) $O_2^{2-} < O_2 < C_2^{2-} < C_2^+$
d) $O_2^{2-} < C_2^+ < O_2 < C_2^{2-}$
12. Hybridisation of central atom in PCl_5 involves the mixing of orbitals.
- a) s, p_x , p_y , d_{x^2} , $d_{x^2-y^2}$
b) s, p_x , p_y , p_{xy} , $d_{x^2-y^2}$
c) s, p_x , p_y , p_z , $d_{x^2-y^2}$
d) s, p_x , p_y , d_{xy} , $d_{x^2-y^2}$
13. The correct order of O-O bond length in hydrogen peroxide, ozone and oxygen is
- a) $H_2O_2 > O_3 > O_2$
b) $O_2 > O_3 > H_2O_2$
c) $O_2 > H_2O_2 > O_3$
d) $O_3 > O_2 > H_2O_2$
14. Which one of the following is diamagnetic.?
- a) O_2 b) O_2^{2-}
c) O_2^+ d) None of these
15. Bond order of a species is 2.5 and the number of electrons in its bonding molecular orbital is found to be 8. The no. of electrons in its antibonding molecular orbital is
- a) three b) four
c) Zero d) can not be calculated from the given information.
16. Shape and hybridisation of IF_5 are
- a) Trigonal bipyramidal, sp^3d^2
b) Trigonal bipyramidal, sp^3d
c) Square pyramidal, sp^3d^2
d) Octahedral, sp^3d^2
17. Pick out the incorrect statement from the following
- a) sp^3 hybrid orbitals are equivalent and are at an angle of $109^\circ 28'$ with each other
b) dsp^2 hybrid orbitals are equivalent and bond angle between any two of them is 90°
c) All five sp^3d hybrid orbitals are not equivalent out of these five sp^3d hybrid orbitals, three are at an angle of 120° , remain two are perpendicular to the plane containing the other three
d) none of these
18. The molecules having same hybridisation, shape and number of lone pairs of electrons are
- a) SeF_4 , XeO_2F_2 b) SF_4 , XeF_2
c) $XeOF_4$, TeF_4 d) $SeCl_4$, XeF_4
19. In which of the following molecules / ions BF_3 , NO_2^- , H_2O the central atom is sp^2 hybridised?
- a) NH_2^- and H_2O
b) NO_2^- and H_2O
c) BF_3 and NO_2^-
d) BF_3 and NH_2^-



20. Some of the following properties of two species, NO_3^- and H_3O^+ are described below. which one of them is correct?
- dissimilar in hybridisation for the central atom with different structure.
 - isostructural with same hybridisation for the Central atom.
 - different hybridisation for the central atom with same structure
 - none of these
21. The types of hybridisation on the five carbon atom from right to left in the, 2,3 pentadiene.
- $\text{sp}^3, \text{sp}^2, \text{sp}, \text{sp}^2, \text{sp}^3$
 - $\text{sp}^3, \text{sp}, \text{sp}, \text{sp}, \text{sp}^3$
 - $\text{sp}^2, \text{sp}, \text{sp}^2, \text{sp}^2, \text{sp}^3$
 - $\text{sp}^3, \text{sp}^3, \text{sp}^2, \text{sp}^3, \text{sp}^3$
22. Xe F_2 is isostructural with
- SbCl_2
 - BaCl_2
 - TeF_2
 - ICl_2^-
23. The percentage of s-character of the hybrid orbitals in methane, ethane, ethene and ethyne are respectively
- 25, 25, 33.3, 50
 - 50, 50, 33.3, 25
 - 50, 25, 33.3, 50
 - 50, 25, 25, 50
24. Of the following molecules, which have shape similar to carbon dioxide?
- SnCl_2
 - NO_2
 - C_2H_2
 - All of these.
25. According to VSEPR theory, the repulsion between different parts of electrons obey the order.
- $\text{l.p} - \text{l.p} > \text{b.p} - \text{b.p} > \text{l.p} - \text{b.p}$
 - $\text{b.p} - \text{b.p} > \text{b.p} - \text{l.p} > \text{l.p} - \text{b.p}$
 - $\text{l.p} - \text{l.p} > \text{b.p} - \text{l.p} > \text{b.p} - \text{b.p}$
 - $\text{b.p} - \text{b.p} > \text{l.p} - \text{l.p} > \text{b.p} - \text{l.p}$
26. Shape of ClF_3 is
- Planar triangular
 - Pyramidal
 - "T" Shaped
 - none of these
27. Non- Zero dipole moment is shown by
- CO_2
 - p-dichlorobenzene
 - carbontetrachloride
 - water.
28. Which of the following conditions is not correct for resonating structures?
- the contributing structure must have the same number of unpaired electrons
 - the contributing structures should have similar energies
 - the resonance hybrid should have higher energy than any of the contributing structure.
 - none of these
29. Among the following, the compound that contains, ionic, covalent and Coordinate linkage is
- NH_4Cl
 - NH_3
 - NaCl
 - none of these



30. CaO and NaCl have the same crystal structure and approximately the same radii. If U is the lattice energy of NaCl, the approximate lattice energy of CaO is

- a) U b) $2U$
c) $U/2$ d) $4U$

II. Write brief answer to the following questions.

31. Define the following

- i) Bond order
ii) Hybridisation
iii) σ - bond

32. What is a pi bond?

33. In CH_4 , NH_3 and H_2O , the central atom undergoes sp^3 hybridisation - yet their bond angles are different. why?

34. Explain sp^2 hybridisation in BF_3

35. Draw the M.O diagram for oxygen molecule calculate its bond order and show that O_2 is paramagnetic.

36. Draw MO diagram of CO and calculate its bond order.

37. What do you understand by Linear combination of atomic orbitals in MO theory.

38. Discuss the formation of N_2 molecule using MO Theory

39. What is dipole moment?

40. Linear form of carbondioxide molecule has two polar bonds. yet the molecule has Zero dipole moment why?

41. Draw the Lewis structures for the following species.

- i) NO_3^- ii) SO_4^{2-}
iii) HNO_3 iv) O_3

42. Explain the bond formation in BeCl_2 and MgCl_2 .

43. Which bond is stronger σ or π ? Why?

44. Define bond energy.

45. Hydrogen gas is diatomic where as inert gases are monoatomic - explain on the basis of MO theory.

46. What is Polar Covalent bond? explain with example.

47. Considering x- axis as molecular axis, which out of the following will form a sigma bond.

- i) $1s$ and $2p_y$ ii) $2p_x$ and $2p_x$
iii) $2p_x$ and $2p_z$ iv) $1s$ and $2p_z$

48. Explain resonance with reference to carbonate ion?

49. Explain the bond formation in ethylene and acetylene.

50. What type of hybridisations are possible in the following geometries?

- a) octahedral
b) tetrahedral
c) square planer.

51. Explain VSEPR theory. Applying this theory to predict the shapes of IF_7 and SF_6

52. CO_2 and H_2O both are triatomic molecule but their dipole moment values are different. Why?

53. Which one of the following has highest bond order?

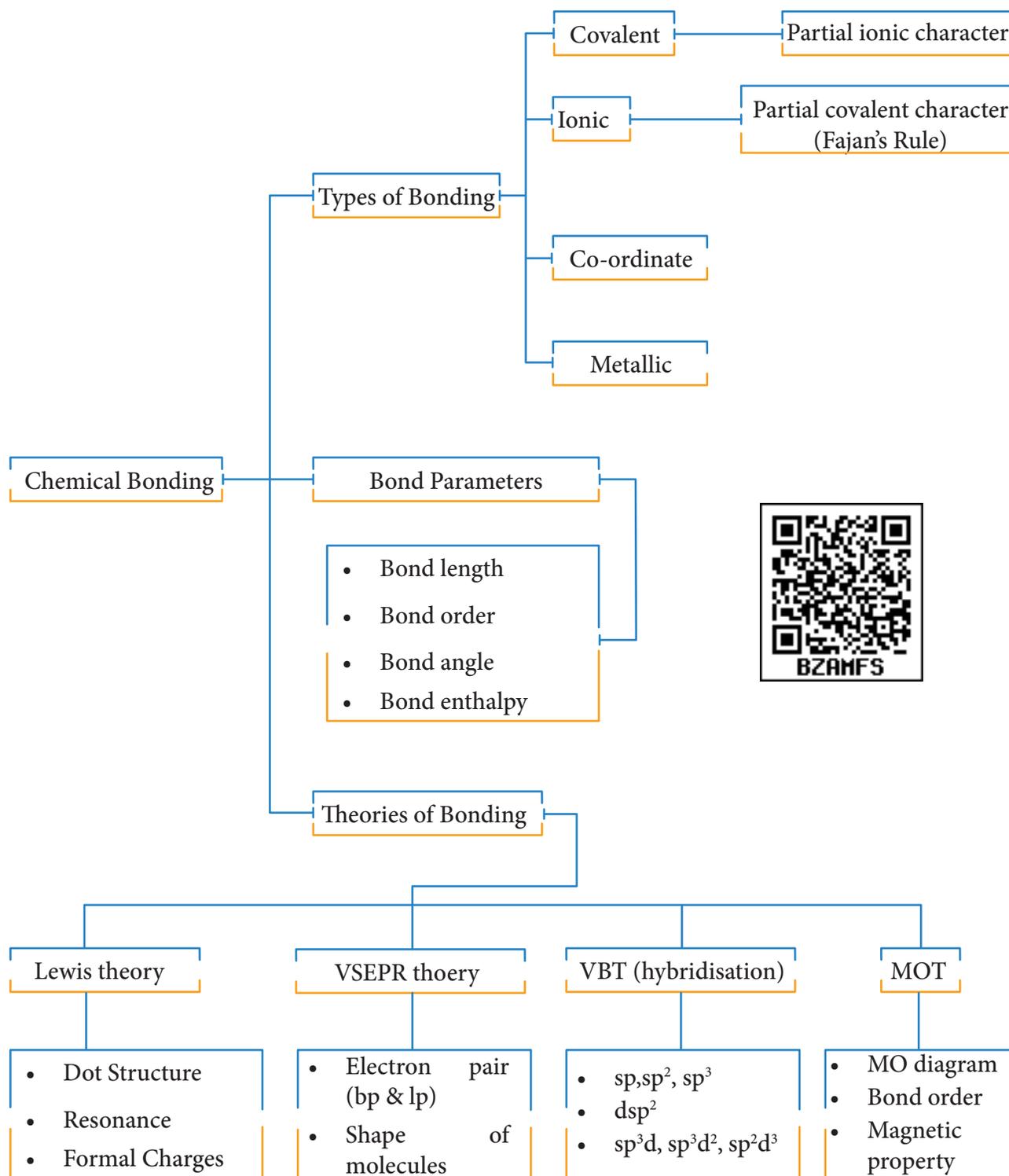
- N_2 , N_2^+ or N_2^-

54. Explain the covalent character in ionic bond.

55. Describe fajan's rule.



CONCEPT MAP





Shapes of Molecule (VSEPR Theory)

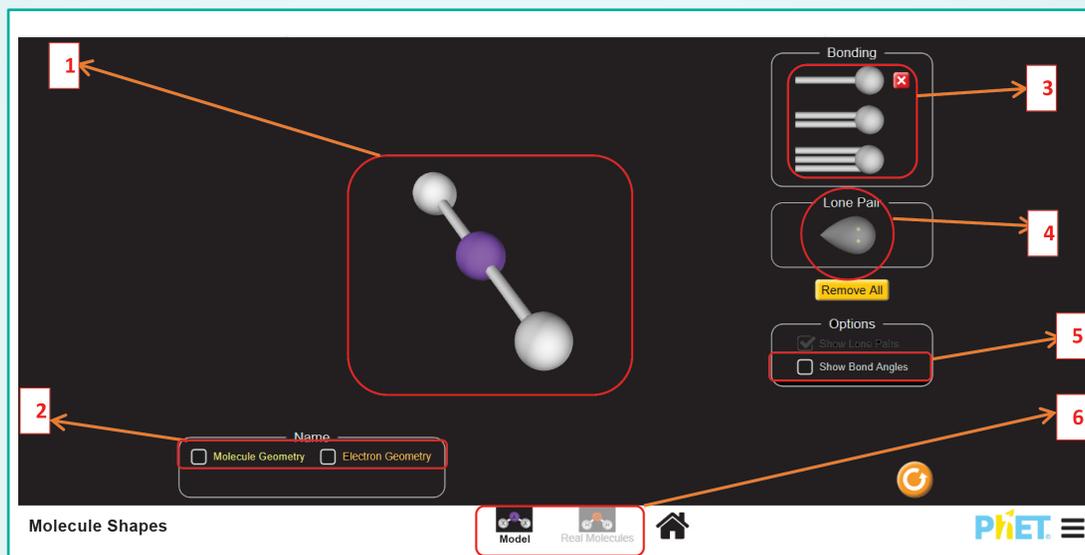
By using this tool, you will be able to create and visualise molecules with different number of bonds and lone pairs.

Please go to the URL
https://phet.colorado.edu/sims/html/molecule-shapes/latest/molecule-shapes_en.html
(or)
Scan the QR code on the right side



Steps

- Open the Browser and type the URL given (or) Scan the QR Code.
- Double click the 'models' icon given in this page. Now you will see the web page as shown in the figure.
- Now, by selecting the number of bond pairs and lone pairs using the options in the box 3 and 4 effectively, you visualize the corresponding molecular geometry.
- You can see the angles between the bonds selecting the "Show bond angles" indicated in box 5.
- You can also visualize the molecular geometry and the electron geometry by selecting corresponding option in box 2.



Structure of simple molecules:

By selecting the real molecules icon in indicated in the box 6, you will be able to see a screen as shown below. In this screen, use the dropdown menu indicated in box 7 you can select a molecule. Use the option in the box 8 you can visualise the lone pairs and bond pairs in the molecules.



Friedrich Wöhler, was a German pioneer in organic chemistry. He is best known for his synthesis of urea an the organic compound from the inorganic compound, ammonium cyanate. This finding went against the mainstream theory of that time called *vitalism* which stated that organic matter possessed a special force or vital force inherent to all living things. He is also the first to isolate several chemical elements. He is the discoverer of the element aluminum and also the co-discoverer of yttrium, beryllium, and titanium.

Learning Objectives

After studying this unit students will be able to

- understand the reason for the tetra valency of carbon and shapes of organic molecules
- classify the organic compounds
- name the organic compounds according to IUPAC nomenclature and derive the structure from the IUPAC name
- describe various types of isomerism
- explain the principles of detection and estimation of elements in organic compounds
- describe various techniques used in the purification of organic compounds

11.1 Introduction

Organic chemistry is the study of compounds of carbon. Carbon has a tendency to form more compounds with itself and other atoms (H, O, N, S and halogens) than any other elements. The tendency of an atom to form a chain of bonds with the atoms of the same element is called catenation. The high strength of C-C bond is responsible for its catenation property.

The word 'organic' means 'derived from living organisms'. Organic compounds were thought to be found only in living things. Cell the basic unit of living things, consumes, creates and consists of mainly organic compounds. DNA, the genetic material, the

lipids, that forms our cell membrane and the glycogen the energy reserve stored in our liver are all organic compounds. Except few inorganic compounds like salt, water etc... all others such as food, medicine, clothing, cosmetics, fuel etc... are compounds of carbon. All the essential biochemical reactions are also organic in nature leading to the formation of various essential bioorganic molecules such as lipoproteins, phospholipids, glycolipids etc...

Synthesis of acetic acid by Kolbe and methane by Berthelot, confirmed that organic compounds can be synthesized in laboratory. Since then, millions of organic compounds were synthesised and characterised. The field of organic chemistry is very vast and its principles find applications in many industries including food, textile, petrochemical, pharmaceutical, dye, polymers, fertilizer, cosmetics etc... Discussing the importance of organic chemistry is just like describing a drop of water in a mighty ocean.

The knowledge of chemical bonding and molecular structure will help in understanding the properties of organic compounds. We know that, the carbon has four valence electrons and its ground state electronic configuration is $1s^2 2s^2 2p^2$. An atom can attain noble gas electronic configuration either by transferring or sharing of electrons. It is not possible for the carbon to form either C^{4+} or C^{4-} ions to attain the nearest noble gas configuration, as it requires large amount of energy. This implies that carbon cannot form ionic bond. Almost in all compounds of carbon, it forms four covalent bonds.

The formation of four covalent bonds can be explained as below. During bond formation, one of the electrons from $2s$ orbital is promoted to $2p_z$ orbital. The formation of four sigma bonds by carbon can be explained on the basis of sp^3 hybridisation of carbon. Carbon forms multiple (double and triple) bonds in certain compounds. These can be explained by sp^2 and sp hybridisation of carbon. The carbon forms relatively short bonds which enable the lateral overlap of unhybridised $2p$ orbitals of sp^2 and sp hybridised carbon to form one and two pi bonds respectively.

Molecular structure can be derived from the type of hybridisation. An sp^3 hybridised carbon will have a tetrahedral geometry, a sp^2 hybridised carbon will have trigonal planar geometry, and sp hybridised carbon will have a linear geometry.

Characteristics of organic compounds:

All organic compounds have the following characteristic properties.

1. They are covalent compounds of carbon and generally insoluble in water and readily soluble in organic solvent such as benzene, toluene, ether, chloroform etc...
2. Many of the organic compounds are inflammable (except CCl_4). They possess low boiling and melting points due to their covalent nature
3. Organic compounds are characterised by functional groups. A functional group is an atom or a specific combination of bonded atoms that

react in a characteristic way, irrespective of the organic molecule in which it is present. In almost all the cases, the reaction of an organic compound takes place at the functional group. They exhibit isomerism which is a unique phenomenon.

4. **Homologous series:** A series of organic compounds each containing a characteristic functional group and the successive members differ from each other in molecular formula by a CH_2 group is called homologous series. Eg.

Alkanes: Methane (CH_4), Ethane (C_2H_6), Propane (C_3H_8) etc.

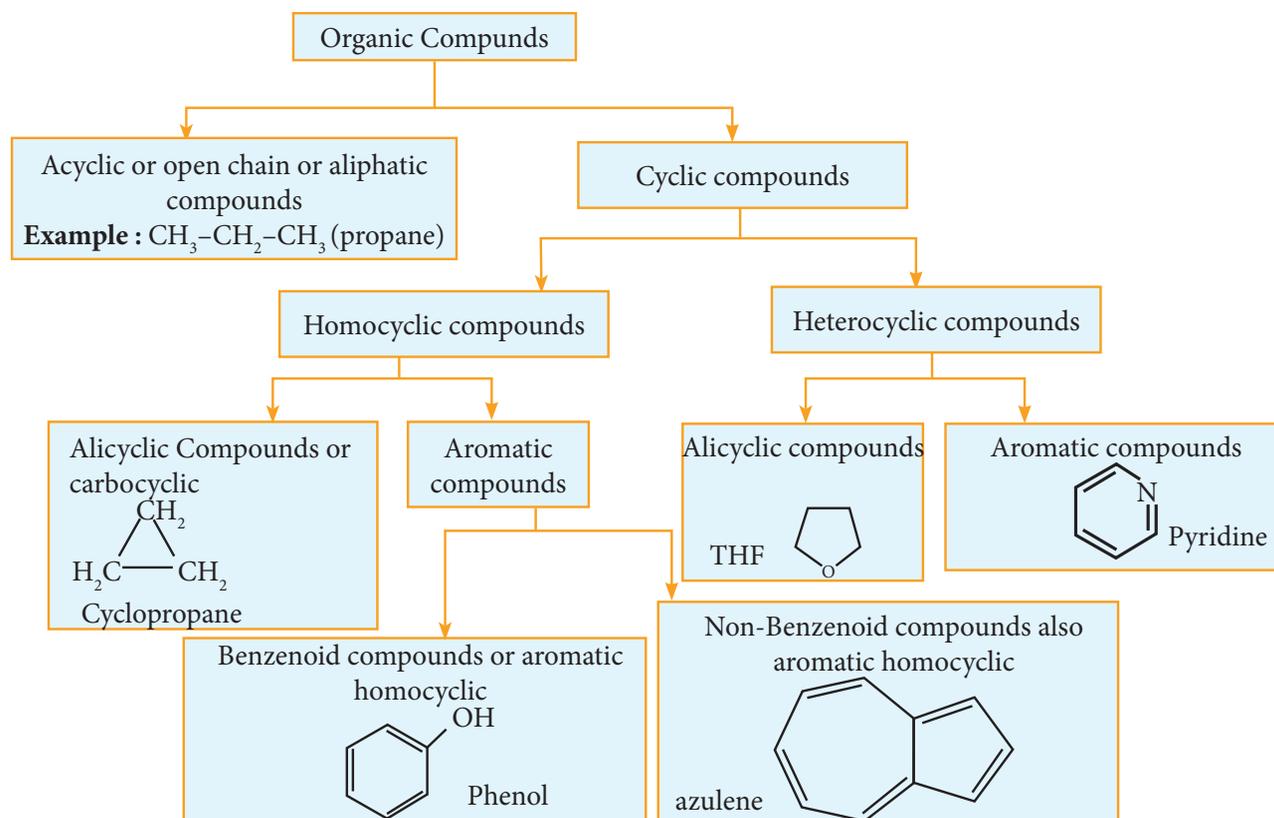
Alcohols: Methanol (CH_3OH), Ethanol ($\text{C}_2\text{H}_5\text{OH}$) Propanol ($\text{C}_3\text{H}_7\text{OH}$) etc.)

Compounds of the homologous series are represented by a general formula Alkanes $\text{C}_n\text{H}_{2n+2}$, Alkenes C_nH_{2n} , Alkynes $\text{C}_n\text{H}_{2n-2}$ and can be prepared by general methods. They show regular gradation in physical properties but have almost similar chemical property.

11.2 Classification of organic compounds

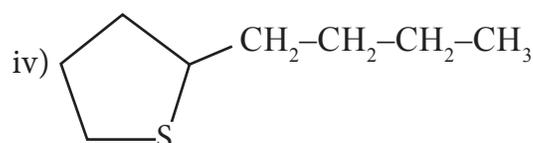
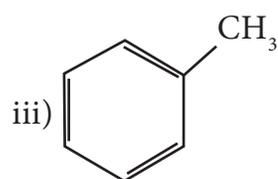
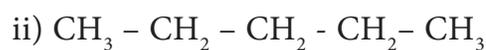
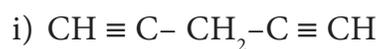
The existing large number of organic compounds and ever-increasing number have made it necessary to classify them. They may be classified based on their structure or the functional group.

11.2.1 Classification based on the structure:



Based on the above classification let us classify the following compounds.

1. Classify the following compounds based on the structure



Solutions:

- (i) Unsaturated open chain compound
- (ii) saturated open chain compound
- (iii) aromatic benzenoid compound
- (iv) alicyclic compound

Evaluate Yourself 

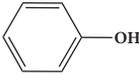
1) Give two examples for each of the following type of organic compounds.

- (i) non-benzenoid aromatic,
- (ii) aromatic heterocyclic,
- (iii) alicyclic and
- (iv) aliphatic open chain.

11.2.2 Classification based on functional groups:

Table 11.1 Class of compounds and their functional group

S. No.	Class of compounds	Functional group	General formula (R - Alkyl group)
1	Alkene	-	C_nH_{2n}
2	Alkyne	-	$\text{C}_n\text{H}_{2n-2}$
3	Alkyl halide	$\begin{array}{l} \text{---F, ---Br,} \\ \text{---Cl, ---I} \end{array}$	R-X
4	Alcohol	---OH	R-OH
5	Ether	---O---	R-O-R'
6	Aldehyde	$\begin{array}{c} \text{O} \\ \parallel \\ \text{---C---H} \end{array}$	R-CHO
7	Ketone	$\begin{array}{c} \diagup \\ \text{C=O} \\ \diagdown \end{array}$	R-CO-R'
8	Carboxylic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{---C---OH} \end{array}$	R-COOH
9	Ester	$\begin{array}{c} \text{O} \\ \parallel \\ \text{---C---OR} \end{array}$	RCOOR'
10	Acid anhydride	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{---C---O---C---} \end{array}$	R-CO-O-CO-R'
11	Acyl halide	$\begin{array}{c} \text{O} \\ \parallel \\ \text{---C---X} \end{array}$	R-COX
12	Sulphonic acid	$\text{---SO}_3\text{H}$	R-SO ₃ H
13	Nitro alkane	---NO_2	R-NO ₂
14	Amine	---NH_2	R-NH ₂
15	Amide	$\begin{array}{c} \text{O} \\ \parallel \\ \text{---C---NH}_2 \end{array}$	R-CO-NH ₂

S. No.	Class of compounds	Functional group	General formula (R - Alkyl group)
16	Cyanide (Nitrile)	$\text{—C}\equiv\text{N}$	R-CN
17	Isocyanide	—NC	R-NC
18	Cyanate	—OCN	R-OCN
19	Isocyanate	—NCO	R-NCO
20	Thiocyanate	—SCN	R-SCN
21	Isothiocyanate	—NCS	R-NCS
23	Thioalcohols or thiols	—SH	R-SH
24	Thioethers	—S—R	R-S-R'
25	Imines	=NH	R-CH=NH
26	Nitroso compounds	—NO	R-NO
27	Hydrazines	—NH—NH_2	R-NH-NH ₂
28	Hydrazo compounds	—NH—NH—	R-NH-NH-R
29	Phenols		C ₆ H ₅ OH
30	Imide		RCON(R')COR''

11.3 Nomenclature of organic compounds:

The International Union of Pure and Applied Chemistry (IUPAC) is the world authority on chemical nomenclature and terminology, naming of new elements in the periodic table standardized methods

for measurement; atomic weights, and many other critically-evaluated data. According to IUPAC recommendations to name any organic compound, it is considered as a derivative of its parent saturated hydrocarbon. The IUPAC name of an organic compound consists of three parts.

prefix + root word + suffix

Root word denotes the number of carbon atoms in the longest continuous chain in molecules. Prefix denotes the group(s) attached to the main chain which is placed before the root. Suffix denotes the functional group and is placed after the root word.

Table 11.2 Number of carbons in parent chain and the corresponding root words

Chain length (or) no. of carbon atoms	Root word	Chain length (or) no. of carbon atom	Root word
C ₁	Meth-	C ₁₇	Heptadec-
C ₂	Eth-	C ₁₈	Octadec-
C ₃	Prop-	C ₁₉	Nonadec-
C ₄	But-	C ₂₀	Icos-
C ₅	Pent-	C ₂₁	Henicos
C ₆	Hex-	C ₂₂	Docos
C ₇	Hept-	C ₃₀	Triacont-
C ₈	Oct-	C ₃₁	Hentriacont
C ₉	Non-	C ₃₂	Dotriacont
C ₁₀	Dec-	C ₄₀	Tetracont-
C ₁₁	Undec-	C ₅₀	Pentacont-

Chain length(or) no. of carbon atoms	Root word	Chain length(or) no. of carbon atom	Root word
C ₁₂	Dodec-	C ₆₀	Hexacont-
C ₁₃	Tridec -	C ₇₀	Heptacont-
C ₁₄	Tetradec-	C ₈₀	Octacont-
C ₁₅	Pentadec-	C ₉₀	Nonacont-
C ₁₆	Hexadec-	C ₁₀₀	Hect-

Suffix: There are two types of suffix. They are primary suffix and secondary suffix

Primary suffix: It denotes the saturation/unsaturation of organic compounds. It is added immediately after the root word. Primary suffix for various saturated and unsaturated carbon chains are as follows:

Table 11.3 Primary suffix for various saturated and unsaturated carbon chains

Name & type of carbon chain	Primary suffix
Saturated, C-C	ane
Unsaturated carbon chain	
one C=C bond	ene
Two C=C bonds	diene
Three C=C bonds	triene
One C≡C bond	yne
Two C≡C bonds	diyne

Secondary suffix: It is used to denote the nature of functional group present in the organic compound. It is added to the primary suffix by removing its terminal 'e'. Secondary suffix names for some functional groups is listed below in table 11.4

Table 11.4 Secondary suffix and prefixes for some functional groups:

Class of organic compounds	Functional group	Prefix	Secondary suffix
Alcohols	—OH	hydroxy-	-ol
Thioalcohols	—SH	mercapto	-thiol
Aldehydes	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—H} \end{array}$	formyl-	-al
Ketones	$\begin{array}{c} \diagup \\ \text{C}=\text{O} \\ \diagdown \end{array}$	oxo-	-one
Carboxylic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—OH} \end{array}$	carboxy-	-oic acid
Esters	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—OR} \end{array}$	Alkoxy-Carbonyl	-oate
Acid chlorids	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—Cl} \end{array}$	chloro-carbonyl	-oyl chloride
Acid amides	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—NH}_2 \end{array}$	Carbamoyl	-amide
Amines	—NH ₂	amino-	-amine
Nitriles	—C≡N	cyano-	-nitrile
Sulphonic acid	—SO ₃ H	sulpho-	-sulphonic acid

Prefix: Substituents that are attached to the parent carbon chain are denoted by adding prefix names before the root word. The prefix names for some common substituents are listed below. If the functional groups are not part of the parent chain, they are considered as substituents. In such cases its prefix name is added before the root word. Prefix names for some functional groups mentioned along with their secondary prefix are listed in table 11.4

Table 11.5 List of substituents and their Prefix names

Substituent group	Prefix
-F	Fluoro
-Cl	Chloro
-Br	Bromo
-I	Iodo
-NO ₂	Nitro
-NO	Nitroso
-N=N-	Diazo
-OR	Alkoxy
-OCH ₃ (or) -OMe	Methoxy
-OC ₂ H ₅ (or) -OEt	Ethoxy
-CH ₃ (or) -Me	Methyl
-C ₂ H ₅ (or) -Et	Ethyl
-CH ₂ -CH ₂ -CH ₃	Propyl
-CH(CH ₃) ₂	Propan-2-yl (isopropyl)
-CH ₂ -CH ₂ -CH ₂ -CH ₃	Butyl

Substituent group	Prefix
-CH ₂ -CH(CH ₃)-CH ₃	2-methyl propyl (isobutyl)
-C(CH ₃) ₃	2-methylpropan-2-yl (tertbutyl)
-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	Pentyl
-CH ₂ -CH(CH ₃)-CH ₂ -CH ₃	2-methyl butyl
-CH ₂ -C(CH ₃) ₃	2,2-dimethyl propyl (neopentyl)

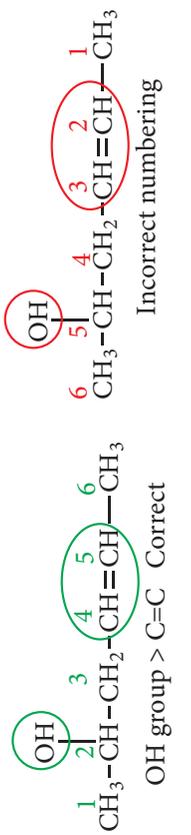
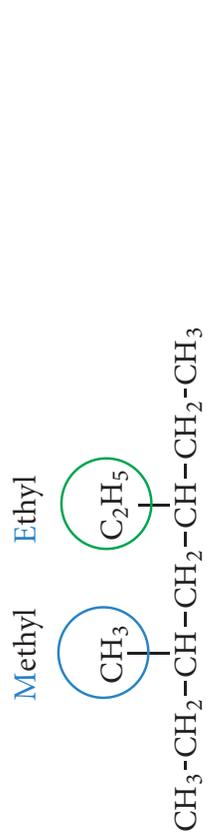
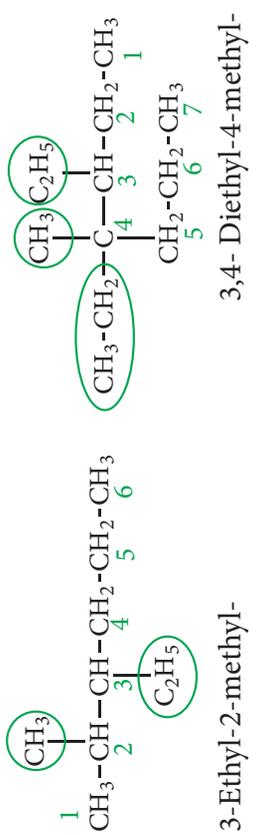
11.3.1 IUPAC rules for nomenclature of organic compounds

The following steps should be followed for naming an organic compound as per IUPAC nomenclature.

1. Choose the longest carbon chain. (Root word). Consider all the other groups attached to this chain as substituents.
2. Numbering of the longest carbon chain
3. Naming of the substituents (prefixes or suffixes)
4. Arrange the substituents in the alphabetical order
5. Write the name of the compound as below

"prefix + root word + primary suffix + secondary suffix"

Step No.	Conditions	Rule	Illustrations
Choose the longest carbon chain (parent chain)			<p>longest chain of 7 C atom</p>
Two chains of equal lengths.	Choose the chain with maximum number of substituents		<p>One Substituent Correct</p>
Compound contains functional group or multiple bond or both	i) If any of the functional groups (-OH, -CHO, -COOH, -CN, -COOR, CONH ₂ , -NH ₂ , COR, COX, -SO ₃ H, -SH, -SR) are present, choose the longest carbon chain in such a way that it contains functional groups.		<p>Correct 4C Chain with COOH and double bond, Correct 4C Chain with CHO 5C Chain without COOH Wrong 5C Chain with COOH Correct 4C Chain with COOH - Wrong</p>
	ii) If more than one functional group is present, the one with highest precedence should be part of the parent chain. Order of precedence of functional group is -COOH > -SO ₃ H > -COOR, > -COX > CONH ₂ > -CN > -CHO > -CO- > -OH > -SH > -NH ₂		<p>Correct 7C chain with COOH Group Correct 7C chain without COOH group 4C Chain with COOH - Wrong</p>

Step No.	Conditions	Rule	Illustrations
	When more than one functional group have same locant the following order of priority should be followed.	Order of precedence of functional group is -COOH > -SO ₃ H > -COOR, > -COX > CONH ₂ > -CN > -CHO > -CO- > -OH > -SH > -NH ₂ > -C=C- > -C≡C- > C-C > -O- > -X > -NO ₂ .	 <p>OH group > C=C Correct</p> <p>Incorrect numbering</p>
	Two substituents are present on identical position with respect to the parent chain end.	Assign the lowest number according to the alphabetical order of the name of the substituent.	 <p>Methyl Ethyl</p> <p>OH group > C=C Correct</p>
Naming the substituents / functional group / side chain using the prefixes / suffixes given in table 1.1.3 primary suffix for various saturated and unsaturated carbon chains, Table 1.1.4 Secondary suffix and prefixes for some functional groups and table 1.1.5 prefix name for some substituents.			
4. Arrange the substituents in the alphabetical order	Two or more substituents are present on the parent chain,	These substituent prefixed with their position number are arranged in alphabetical order (irrespective of the position number) before root word (The prefixes di-, tri-, etc. are not taken into consideration for grouping alphabetically)	 <p>3-Ethyl-2-methyl-3,4-Diethyl-4-methyl-</p>



The following are guide lines for writing IUPAC of the organic compound.

1. The IUPAC names are always written as single word, with notable exception of organic salts, acids and acid derivatives.
2. Commas are used between two adjacent number or letter symbols, and hypens are used to separate numbers and letter symbol in names **Eg: 2,2-Dimethyl-3-hexene**
N,N-Dimethyl methanamide
3. Structural prefix such as, meso-, cis-, trans-, are italicised and joined to the name by a hyphen. These prefixes are omitted in alphabetising compound names or in capitalising names at the beginning of a sentence. **Eg: trans-2-Butene**
4. Structural prefixes such as di, tri, tetra are treated as a part of the basic name and therefore are neither italicised nor separated by a hyphen. These prefixes are not taken into account in alphabetising compound names **eg: 4-Ethyl -2,2-dimethyl hexane.**
5. To name alicyclic compounds, the additional rules should be followed as illustrated in the table 11.6

Table 11.6 Rules for naming of alicyclic compounds:

Rule	Illustration
In the naming of such compounds a prefix cyclo is added to the word root	 cyclobutane cyclopentane cyclobutene cyclooctane
If only one substituent is present on the ring, then it is not required to give its position	 ethylcyclobutane methylcyclohexane cyclohexanol
If two or more substituents are present on the ring, the numbering of ring is done according to lowest set of locant rule. Alicyclic compounds also follow the numbering rules of acyclic compounds	 1-ethyl-2-methylcyclopentane 1-ethyl-2,3-dimethylcyclohexane 2-ethyl-1,1-dimethylcyclopentane 4-ethyl-1-methylcyclohex-1-ene





Rule	Illustration
If the ring contains lesser number of carbon atoms than that of alkyl group attached to it, the compound is named as derivative of alkane and the ring is considered as a substituent group to the alkane, otherwise it is named as derivative of cycloalkane	<p>Propan-2-ylcyclobutane (derivative of cycloalkane)</p> <p>2-Cyclopropylbutane (derivative of alkane)</p> <p>Chlorocyclobut-1-ene Double bond get preference over substituent-Cl for numbering)</p>
If the side chain contains a multiple bond or a functional group, then the alicyclic ring is treated as the substituent irrespective of the size of the ring	<p>2-cyclobutylpropanal</p> <p>3-cyclohexylpentan-2-one</p>
If the alicyclic ring contains a multiple bond and the side chain contains a functional group the compound is named as derivative of the side chain and the ring is treated as substituent	<p>2-(cyclobut-2-en-1-yl)-propanal</p> <p>4-(cyclopent-3-en-1-yl)-3-methylbutanoic acid</p>
If both ring as well as the side chain contain the functional group, then parent hydrocarbon is decided on the basis of principal group which is further based on preferential order of functional groups	<p>3-(3-nitrocyclopentyl) - prop-2-enoic acid</p>



Rule	Illustration
If both alicyclic ring and the side chain contain same functional group, the parent hydrocarbon is selected on the basis of number of carbon atoms in the ring and side chain	<p>2-(2-hydroxypropyl)cyclohexan-1-ol</p>
If more than one alicyclic rings are attached to the single chain of carbon atoms, the compound is named as a derivative of alkane and alicyclic rings are treated as substituent irrespective of the number of atom in the ring or chain	<p>1-(cyclobutyl)-2-(cyclopropyl)ethane</p>
If the alicyclic ring is directly attached to the benzene ring the compound is named as a derivative of benzene	<p>cyclopentylbenzene</p>
If the alicyclic ring has a functional group along with some substituent on the ring, then the appropriate prefixes and suffixes are used to represent such groups, and numbering is done in such a way that the functional group is not counted for word root rather appropriate suffixes are used to represent such groups	<p>cyclohexanecarboxylic acid</p> <p>2-carbamoylcyclobutane-1-carboxylic acid</p>

Evaluate Yourself

2) Write structural formula for the following compounds

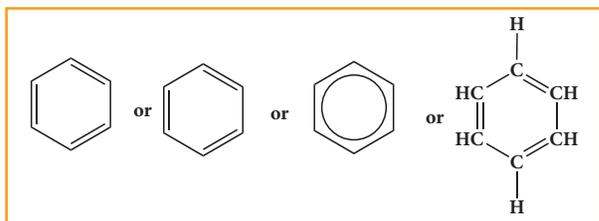
(i) Cyclohexa-1, 4-diene (ii) Ethynyl cyclohexane

NOMENCLATURE OF AROMATIC COMPOUNDS:

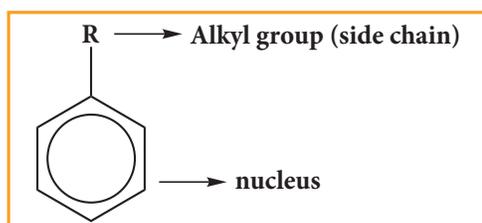
An aromatic compound consists of two parts nucleus and side chain

(A) Nucleus: The benzene ring present in aromatic compound is called nucleus. It is represented as follows



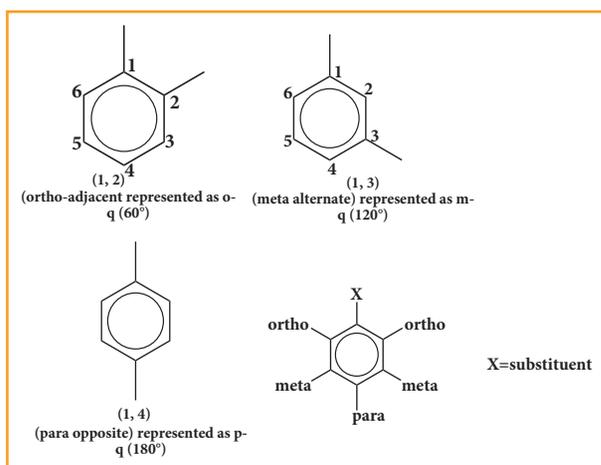
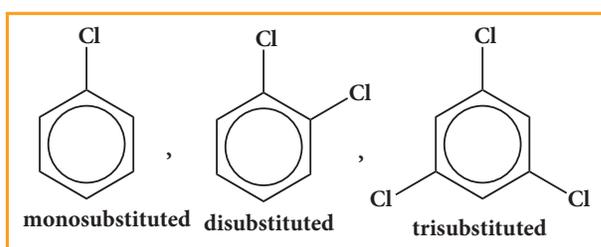


(B) Side chain: Alkyl or any other aliphatic group attached to the benzene nucleus by replacing one or more hydrogen atom is called the side chain



If one hydrogen atom, (or) two hydrogen atoms or three hydrogen atoms are replaced in the benzene ring by some other groups, they are termed as mono substituted, di substituted or tri substituted derivative respectively.

Example

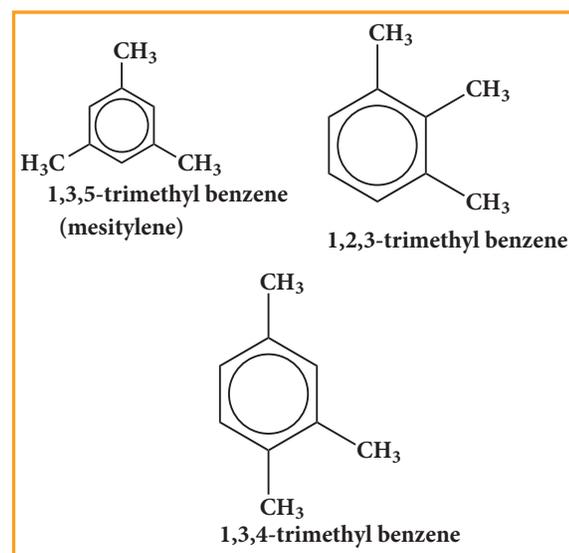
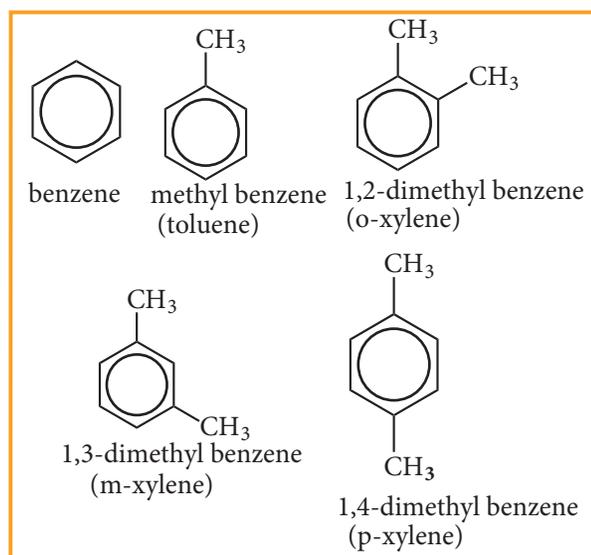


If more than one hydrogen atom of benzene ring is replaced by some other atom or group, then their position is mentioned by Arabic numerals 1,2,3 In case of disubstitution, respective position of two groups can also be mentioned as follows.

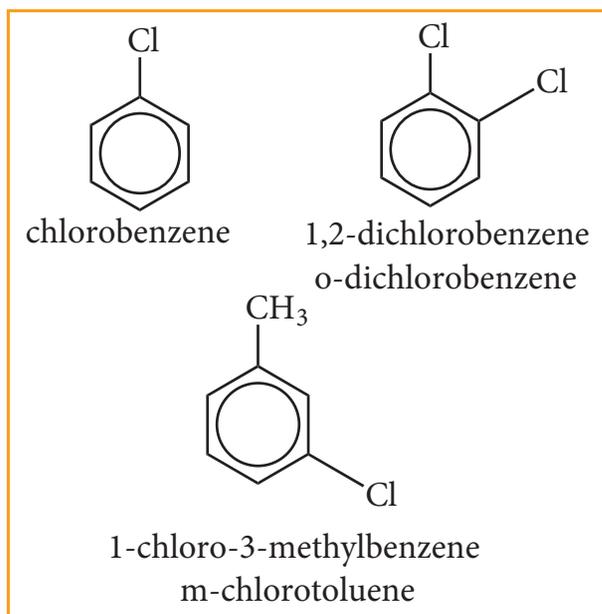
ortho - adjacent; represented as - o
meta - alternate; represented as - m
Para - opposite; represented as - p

Aromatic compounds are basically of two types:

1. Nuclear substituted aromatic compounds: These are the compounds in which the functional group is directly attached to the benzene ring. They are named as derivatives of benzene.

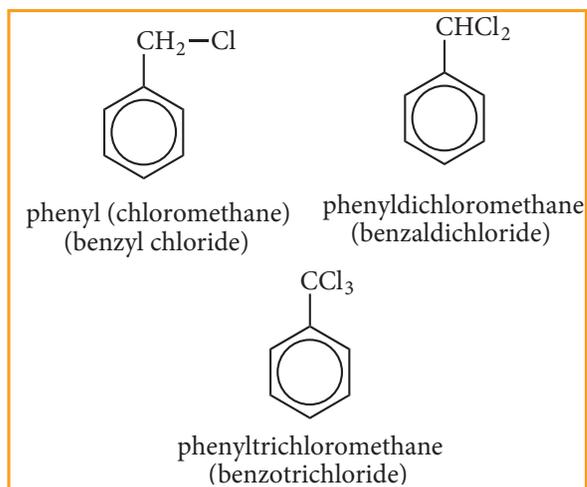


Nuclear substituted aromatic Halogen derivatives compounds.

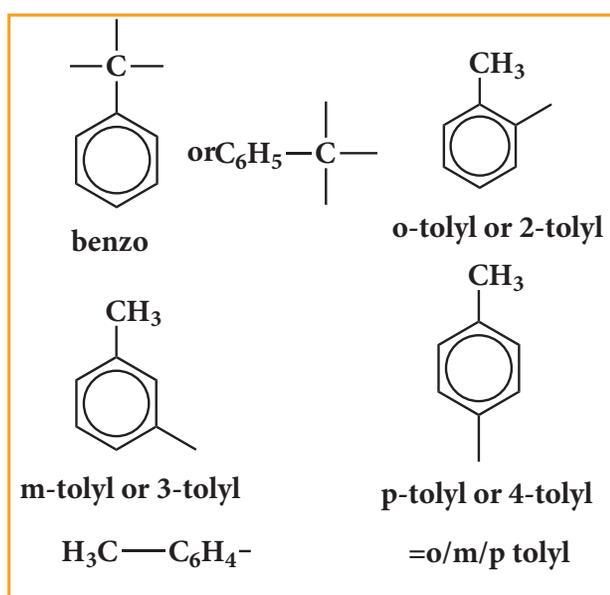
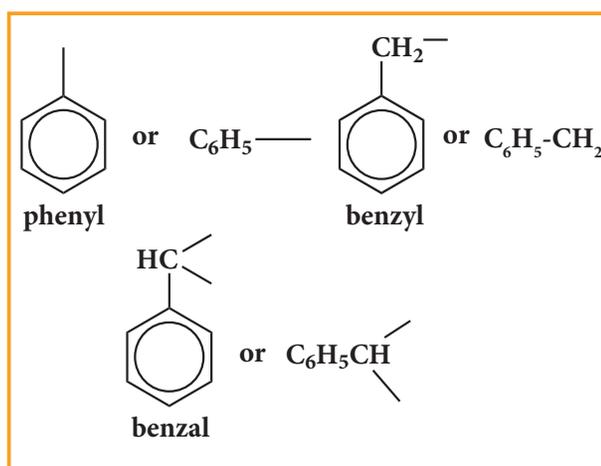


2. Side chain substituted aromatic compounds: These are the compounds in which the functional group is present in the side chain of the benzene ring. These are named as phenyl derivatives of the corresponding aliphatic compounds.

Side chain substituted



Aryl groups



Selection of parent hydrocarbon out of side chain and benzene ring is based on (more or less) some rule as for the alicyclic compounds.

Evaluate Yourself

3) Write structural formula for the following compounds

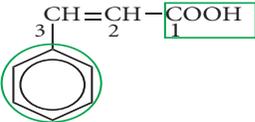
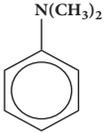
- (i) m - dinitrobenzene (ii) p-dichloro benzene (iii) 1, 3, 5- Trimethyl benzene

Table 11.3.1. 2

Compound Structure and IUPAC Name	Prefix with position number	Root word	Primary suffix	Secondary suffix
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_3 \\ \text{1} \quad \text{2} \quad \text{3} \quad \text{4} \quad \text{5} \end{array}$ <p>3-methylpentane</p>	3-methyl	pent	ane	-
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_3 \\ \quad \quad \quad \quad \quad \quad \\ \text{CH}_3 \quad \quad \quad \text{6 CH}_2 \\ \quad \quad \quad \quad \\ \quad \quad \quad \quad \text{7 CH}_3 \end{array}$ <p>2,2,5-trimethylheptane</p>	2,2,5- trimethyl	Hept	ane	-
$\begin{array}{c} \text{1} \quad \text{2} \quad \text{3} \quad \text{4} \quad \text{5} \\ \text{CH}_3-\text{CH}-\text{CH}-\text{CH}_2-\text{CH}_3 \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_2-\text{CH}_3 \end{array}$ <p>3-ethyl-2-methylpentane</p>	3-ethyl- -2-methyl	pent	ane	-
$\begin{array}{c} \text{2} \quad \text{3} \quad \text{4} \\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_3 \\ \\ \text{1} \\ \text{CHO} \end{array}$ <p>2-methylbutanal</p>	2-methyl	but	ane	al
$\begin{array}{c} \text{2} \quad \text{3} \quad \text{4} \\ \text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}=\text{CH}_2 \\ \\ \text{1} \\ \text{COOH} \end{array}$ <p>2-ethylbut-3-enoic acid</p>	2-ethyl	but	ene	oic acid
$\begin{array}{c} \text{CHO} \\ \\ \text{1} \quad \text{2} \quad \text{3} \quad \text{4} \quad \text{5} \\ \text{HOOC}-\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2 \\ \quad \quad \quad \\ \text{CH}_3 \quad \quad \quad \text{6 CH}_2 \\ \quad \quad \quad \quad \\ \quad \quad \quad \quad \text{7 CH}_3 \end{array}$ <p>Primary Functional group</p> <p>2-formyl-2-methylheptanoic acid</p>	2-formyl-2-methyl	hept	ane	oic acid
$\begin{array}{c} \text{CH}_3 \\ \\ \text{HOOC}-\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}-\text{OH} \\ \quad \quad \quad \\ \text{CH}_3 \quad \quad \quad \text{6 CH}_2 \\ \quad \quad \quad \quad \\ \quad \quad \quad \quad \text{7 CH}_3 \end{array}$ <p>5-hydroxy-2,2-dimethylheptanoic acid</p>	5-hydroxy-2,2- dimethyl	hept	ane	oic acid
$\begin{array}{c} \text{1} \quad \quad \quad \text{5} \\ \text{COOH} \quad \text{COOH} \\ \quad \quad \quad \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \\ \quad \quad \quad \quad \quad \quad \\ \quad \quad \quad \text{2} \quad \quad \quad \text{4} \end{array}$ <p>2-ethyl-4-propylpentanedioic acid</p>	2-ethyl- 4-propyl	pent	ane	oic acid

Compound Structure and IUPAC Name	Prefix with position number	Root word	Primary suffix	Secondary suffix
$\begin{array}{cccccc} \text{CH}_3 & -\text{CH}_2 & -\text{CH}_2 & -\text{CH} & -\text{CH}_2 & -\text{CH}_3 \\ 6 & 5 & 4 & 3 & 2 & 1 \\ & & & & & \\ & & & \text{CH}_3 & & \end{array}$ <p>3-methylhexane</p>	3-methyl	hex	ane	-
$\begin{array}{cccc} \text{CH}_3 & -\text{CH} & -\text{CH}_2 & -\text{CH}_3 \\ 2 & 3 & 4 & \\ & & & \\ \text{CHO} & & & \\ 1 & & & \end{array}$ <p>2-methylbutanal</p>	2-Methyl	but	ane	al
$\begin{array}{cccc} \text{CH}_3 & -\text{CH}_2 & -\text{CH} & -\text{CH}=\text{CH}_2 \\ 2 & 3 & 4 & \\ & & & \\ \text{COOH} & & & \\ 1 & & & \end{array}$ <p>2-ethylbut-3-enoic acid</p>	2-ethyl	but	3-ene	oic acid
$\begin{array}{cccccc} \text{CH}_3 & -\text{CH}_2 & -\text{CH} & -\text{CH}_2 & -\text{CH}_2 & \text{CN} \\ 6 & 5 & 4 & 3 & 2 & 1 \\ & & & & & \\ & & \text{CH}_3 & & & \end{array}$ <p>4-methylhexanenitrile</p>	4-methyl	hex	ane	nitrile
$\begin{array}{cccc} \text{CH}_2=\text{CH} & -\text{CH} & -\text{CH}_3 \\ 4 & 3 & 2 \\ & & \\ \text{CONH}_2 & & \\ 1 & & \end{array}$ <p>2-methylbut-3-enamide</p>	2-methyl	but	3-ene	amide
$\begin{array}{cccccc} \text{OH} & & & & & \\ & & & & & \\ \text{CH}_3 & -\text{CH} & -\text{CH}_2 & -\text{CH}=\text{CH} & -\text{CH}_3 \\ 1 & 2 & 3 & 4 & 5 & 6 \end{array}$ <p>hex-4-en-2-ol</p>		hex	4-ene	2-ol
$\begin{array}{cccccc} \text{CH}_3 & & \text{C}_2\text{H}_5 & & & \\ & & & & & \\ \text{CH}_3 & -\text{CH}_2 & -\text{CH} & -\text{CH}_2 & -\text{CH} & -\text{CH}_2 & -\text{CH}_3 \\ 7 & 6 & 5 & 4 & 3 & 2 & 1 \end{array}$ <p>3-ethyl-5-methylheptane</p>	3-ethyl 5-methyl	hept	ane	-
$\begin{array}{cccccc} \text{CH}_3 & & & & & \\ & & & & & \\ \text{CH}_3 & -\text{CH} & -\text{CH} & -\text{CH}_2 & -\text{CH}_2 & -\text{CH}_3 \\ 1 & 2 & 3 & 4 & 5 & 6 \\ & & & & & \\ & & \text{C}_2\text{H}_5 & & & \end{array}$ <p>3-ethyl-2-methylhexane</p>	3-ethyl-2-methyl	hex	ane	-
$\begin{array}{cccccc} \text{CH}_3 & & \text{C}_2\text{H}_5 & & & \\ & & & & & \\ \text{CH}_3 & -\text{CH}_2 & -\text{C} & -\text{CH} & -\text{CH}_2 & -\text{CH}_3 \\ & & & & & \\ & & \text{CH}_2 & -\text{CH}_2 & -\text{CH}_3 \\ & & 5 & 6 & 7 \end{array}$ <p>3,4-diethyl-4-methylheptane</p>	3,4-diethyl- 4-methyl	hept	ane	-
$\begin{array}{cccccc} \text{CH}_3 & & & & \text{CH}_3 & \\ & & & & & \\ \text{CH}_3 & -\text{C} & =\text{CH} & -\text{CH} & -\text{CH}_3 \\ 1 & 2 & 3 & 4 & 5 \end{array}$ <p>2,4-dimethylpent-2-ene</p>	2,4-dimethyl	pent	2-ene	-

Compound Structure and IUPAC Name	Prefix with position number	Root word	Primary suffix	Secondary suffix
$\overset{7}{\text{CH}_3}-\overset{6}{\text{CH}}=\overset{5}{\text{CH}}-\overset{4}{\text{CH}}=\overset{3}{\underset{\text{CH}_3}{\text{C}}}-\overset{2}{\text{CH}}=\overset{1}{\text{CH}_2}$ <p>3-methylhepta-1,3,5-triene</p>	3-methyl	hept	1, 3, 5 - triene	-
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{CH}$ $\overset{5}{\text{CH}_3}-\overset{4}{\text{CH}_2}-\overset{3}{\text{CH}_2}-\overset{2}{\text{C}}\equiv\overset{1}{\text{CH}}$ <p>1-pentyne (or) pent -1- yne</p>	-	pent	1- yne	-
<p>2-methyl propan-2-ol</p>	2-methyl	prop	ane	2-ol
$\text{H}_3\text{C}-\text{CH}-\text{CH}_2-\text{CH}_2$ $\overset{5}{\text{H}_3\text{C}}-\overset{4}{\text{CH}}-\overset{3}{\text{CH}_2}-\overset{2}{\text{CH}_2}$ <p>4-methylpentan -1- ol</p>	4-methyl	pent	ane	1-ol
<p>2,2-dimethyl propan -1- ol</p>	2,2-dimethyl	prop	ane	1-ol
$\text{CH}_3-\text{CH}_2-\text{C}(=\text{O})-\text{OH}$ $\overset{3}{\text{CH}_3}-\overset{2}{\text{CH}_2}-\overset{1}{\text{C}}(=\text{O})-\text{OH}$ <p>propanoic acid</p>		prop	ane	oic acid
<p>3-methyl-5-(1,3-dimethylcyclobutyl)pentanal</p>		pent	ane	al
$\text{CH}_3-\text{CH}-\text{CHO}$ <p>2-cyclopentylpropanal</p>	2-cyclopentyl	prop	ane	al
$\text{CH}_3-\text{CH}-\text{CHO}$ <p>2-(cyclobut-2-enyl)propanal</p>	2-(cyclobut-2-enyl)	prop	ane	al
$\text{CH}_3-\text{CH}_2-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_3$ $\overset{1}{\text{CH}_3}-\overset{2}{\text{CH}_2}-\overset{3}{\text{C}}(=\text{O})-\overset{4}{\text{CH}_2}-\overset{5}{\text{CH}_3}$ <p>pentan-3-one</p>	-	pent	ane	3 - one

Compound Structure and IUPAC Name	Prefix with position number	Root word	Primary suffix	Secondary suffix
$\begin{array}{ccccccc} 5 & 4 & 3 & 2 & 1 \\ \text{CH}_3 & -\text{C} & =\text{CH} & -\text{C} & -\text{CH}_3 \\ & & & & \\ & \text{CH}_3 & & \text{O} & \end{array}$ <p>4-methylpent-3-en-2-one</p>	4-methyl	pent	3-ene	2-one
$\begin{array}{ccccccc} 5 & 4 & 3 & 2 & 1 \\ \text{CH}_3 & -\text{CH}_2 & -\text{C} & -\text{C} & \equiv\text{CH} \\ & & & & \\ & & \text{O} & & \end{array}$ <p>pent-1-yn-3-one</p>	-	pent	1-yne	3-one
 <p>3-phenylprop-2-enoic acid</p>	3-phenyl	prop	2-ene	oic acid
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_3$ <p>N-methylpropan-1-amine</p>	N-methyl	prop	ane	1-amine
$\begin{array}{c} 1 \\ \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{NH}-\text{CH}_3 \\ 3 \quad 2 \end{array}$ <p>N-methylpropan-2-amine</p>	N-methyl	prop	ane	2-amine
$\begin{array}{ccccccc} & & & \text{CH}_3 & & & \\ & & & & & & \\ 3 & 2 & 1 & \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{N} & -\text{CH}_3 & & \end{array}$ <p>N,N-dimethylpropan-1-amine</p>	N,N-dimethyl	prop	ane	1-amine
$\begin{array}{ccccccc} & & & \text{CH}_3 & & & \\ & & & & & & \\ 3 & 2 & 1 & \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{N} & -\text{CH}_2-\text{CH}_3 & & \end{array}$ <p>N-ethyl-N-methylpropan-1-amine</p>	N-ethyl-N-methyl	prop	ane	1-amine
 <p>N,N-dimethylbenzenamine</p>	N,N-dimethyl	benzene		amine
$\begin{array}{ccccccc} & & & \text{CH}_2\text{OH} & & & \\ & & & & & & \\ 6 & 5 & 4 & 3 & 2 & 1 \\ \text{CH}_3 & -\text{CH}_2 & -\text{CH} & -\text{CH} & -\text{CH}_2 & -\text{COOH} \\ & & & & & \\ & & \text{OH} & & & \end{array}$ <p>4-hydroxy-3-(2-hydroxyethyl)hexanoic acid</p>	4-hydroxy-3-(2-hydroxyethyl)	hexa	ane	oic acid

11.4 Structural representation of organic compounds

Molecular formula of a compound is the simplest, least informative representation, showing the ratio of atoms present. The structure of an organic compound can be represented using any one of the below mentioned methods.

1. Lewis structure or dot structure,
2. Dash structure or line bond structure,
3. Condensed structure
4. Bond line structure

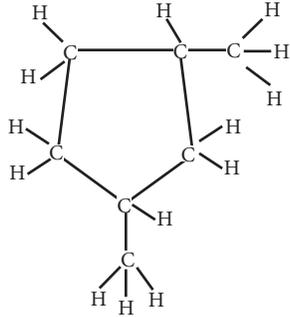
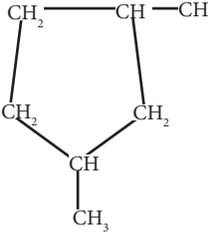
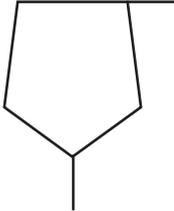
We know how to draw the Lewis structure for a molecule. The line bond structure is obtained by representing the two electron covalent bond by a dash or line (-) in a Lewis structure. A single line or dash represents single σ covalent bond, double line represents double bond (1σ bond, 1π bond) and a triple line represents

triple bond (1σ bond, 2π bond). Lone pair of electrons on heteroatoms may or may not be shown. This represents the complete structural formula.

This structural formula can be further abbreviated by omitting some or all of the dashes representing covalent bonds and by indicating the number of identical groups attached to an atom by a subscript. The resulting expression of the compound is called a condensed structural formula.

For further simplification, organic chemists use another way of representing the structures in which only lines are used. In this type of representation of organic compounds, carbon and hydrogen atoms are not shown and the lines representing carbon-carbon bonds are shown in a zigzag fashion. The only atoms specifically written are oxygen, chlorine, nitrogen etc. These representations can be easily understood by the following illustration.

Molecular formula	Complete structural formula (dash line structure)	Condensed Structure	Bond line Structure
n-propanol C_3H_8O	$\begin{array}{ccccccc} & H & & H & & H & \\ & & & & & & \\ H & -C & - & C & - & C & -OH \\ & & & & & & \\ & H & & H & & H & \end{array}$	$CH_3-CH_2-CH_2-OH$	
1,3-butadiene C_4H_6	$\begin{array}{ccccccc} & H & & H & & H & & H \\ & & & & & & & \\ H & -C & = & C & - & C & = & C-H \\ & & & & & & & \end{array}$	$CH_2=CH-CH=CH_2$	
t-butyl chloride C_4H_9Cl	$\begin{array}{c} & H & & H & \\ & & & & \\ & C & & & \\ & & & & \\ H & & & C & -Cl \\ / & & & & \\ H & & & C & \\ \backslash & & & & \\ & & & H & \\ & & & & \\ & & & H & \end{array}$	$\begin{array}{c} CH_3 \\ \\ CH_3-C-Cl \\ \\ CH_3 \end{array}$	

Molecular formula	Complete structural formula (dash line structure)	Condensed Structure	Bond line Structure
1,3-dimethyl cyclopentane C_7H_{14}			

Molecular models

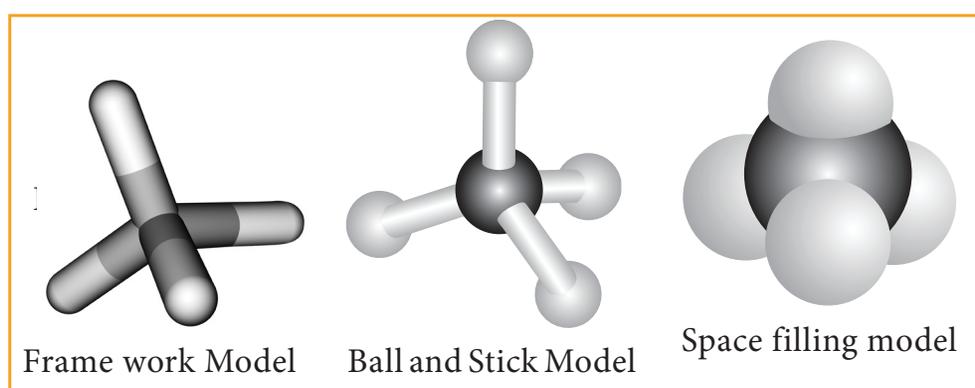


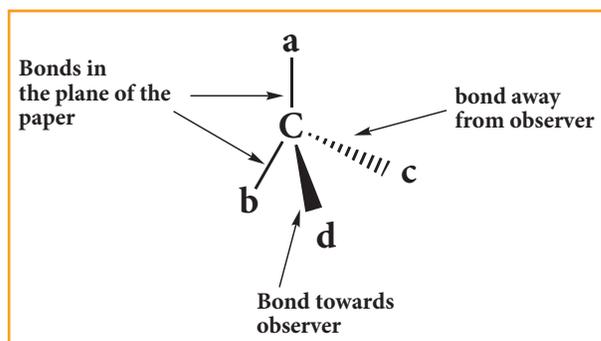
Fig 11.3 Methane - Molecular Models

Molecular models are physical devices that are used for a better visualisation and perception of three dimensional shapes of organic molecules. These are made of wood, plastic or metal and are commercially available. (i) Frame work model (ii) Ball and stick model & (iii) space filling model. In the frame work model only the bonds connecting the atoms themselves are shown. This model emphasizes the pattern of bonds of a molecule while ignoring the size of the atom. In the ball and stick model, both the atoms and the bonds are shown. Ball represent atoms and the stick a bond. Compounds containing $C=C$ can be best represented by using springs in place of sticks and this model is termed as ball and spring model. The space filling model emphasizes the relative size of each atom based on its vander-waals radius.

Three dimensional representation of organic molecules:

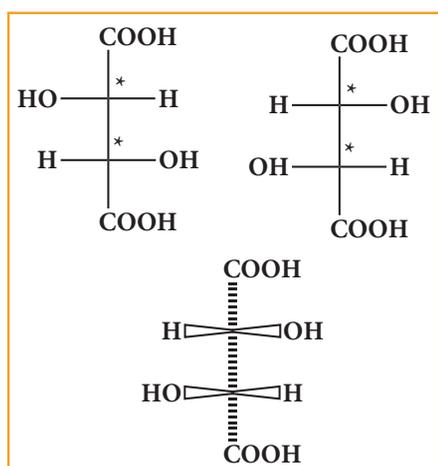
The simplest convention is solid and dashed wedge formula in which 3-D image of a molecule can be perceived from two dimensional picture. In this representation a tetrahedral molecule with four atoms or group a,b,c and d bonded to it can be represented by a wedge formula as follows. A solid wedge (\blacksquare) (or a heavy line) is used to indicate a bond projecting

above the plane of the paper and the dashed wedge ($\cdots\diagup$) (or a dashed line) is used to depict the bond below the plane. The bonds lying in the plane of the paper are shown by normal lines.



Fisher projection formula:

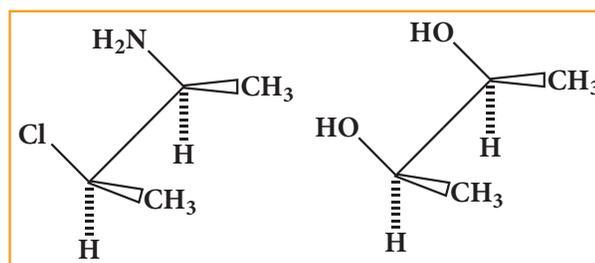
This is a method of representing three dimensional structures in two dimension. In this method, the chiral atom(s) lies in the plane of paper. The horizontal substituents are pointing towards the observer and the vertical substituents are away from the observer. Fisher projection formula for tartaric acid is given below.



Sawhorse projection formula:

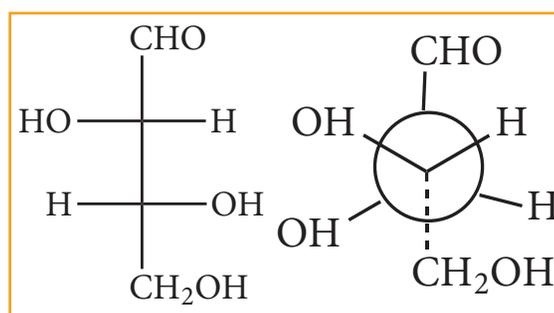
Here the bond between two carbon atoms is drawn diagonally and slightly elongated. The lower left hand carbon is considered lying towards the front and

the upper right hand carbon towards the back. The Fischer projection inadequately portrays the spatial relationship between ligands attached to adjacent atoms. The sawhorse projection attempts to clarify the relative location of the groups.



Newman projection formula:

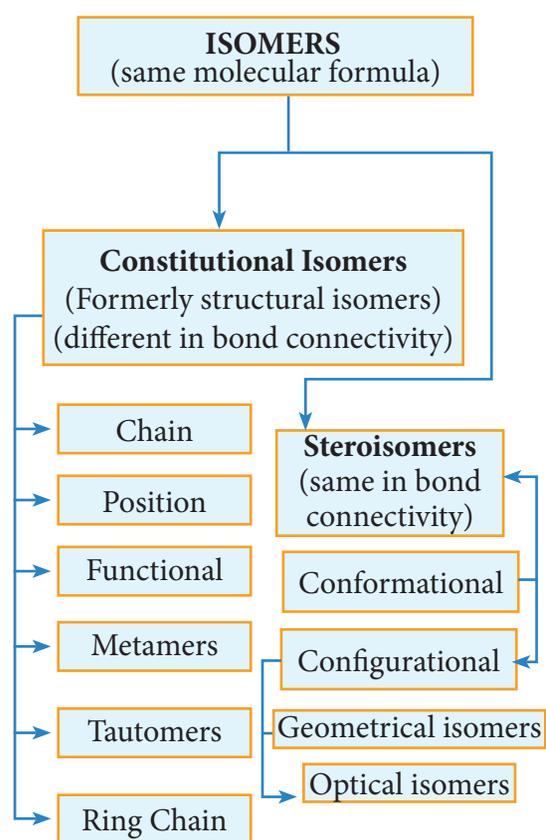
In this method the molecules are viewed from the front along the carbon-carbon bond axis. The two carbon atom forming the σ bond is represented by two circles. One behind the other so that only the front carbon is seen. The front carbon atom is shown by a point where as the carbon lying further from the eye is represented by the origin of the circle. Therefore, the C-H bonds of the front carbon are depicted from the circle while C-H bonds of the back carbon are drawn from the circumference of the circle with an angle of 120° to each other.



11.5. Isomerism in organic compounds:

The term 'isomerism' was given by Berzelius, and its represents of existence

of two or more compounds with the same molecular formula but different structure and properties (physical, chemical, or both). Compounds exhibiting this isomerism are called isomers. The difference in properties of two isomers is due to difference in (bond connectivity or spatial arrangement) the arrangement of atoms within their molecules. Isomerism is broadly divided into two types. i. Constitutional isomerism, ii. stereoisomerism.

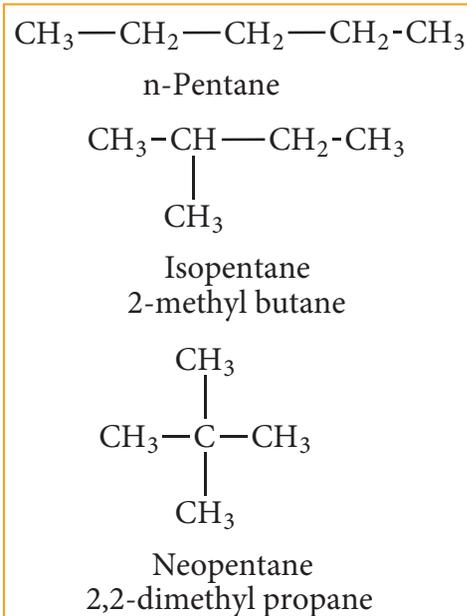


11.5.1 Constitutional isomers (Formerly structural isomers):

This type of isomers have same molecular formula but differ in their bonding sequence. Structural or constitutional isomerism is further classified into following types.

(a) Chain or nuclear or skeletal isomerism:

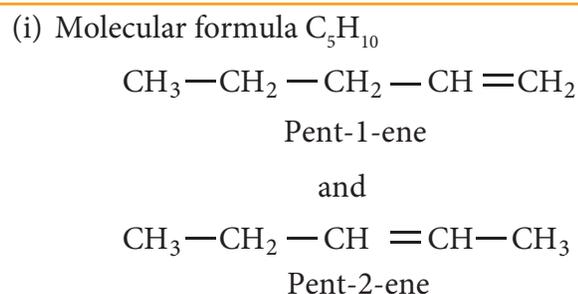
These isomers differ in the way in which the carbon atoms are bonded to each other in a carbon chain or in other words isomers have similar molecular formula but differ in the nature of the carbon skeleton (ie. Straight or branched)



(b) Position isomerism:

If different compounds belonging to same homologous series with the same molecular formula and carbon skeleton, but differ in the position of substituent or functional group or an unsaturated linkage are said to exhibit position isomerism.

Example:

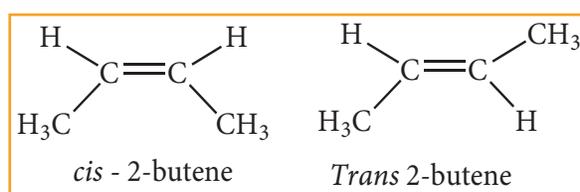


Stereoisomerism:

11.5.3 Geometrical isomerism:

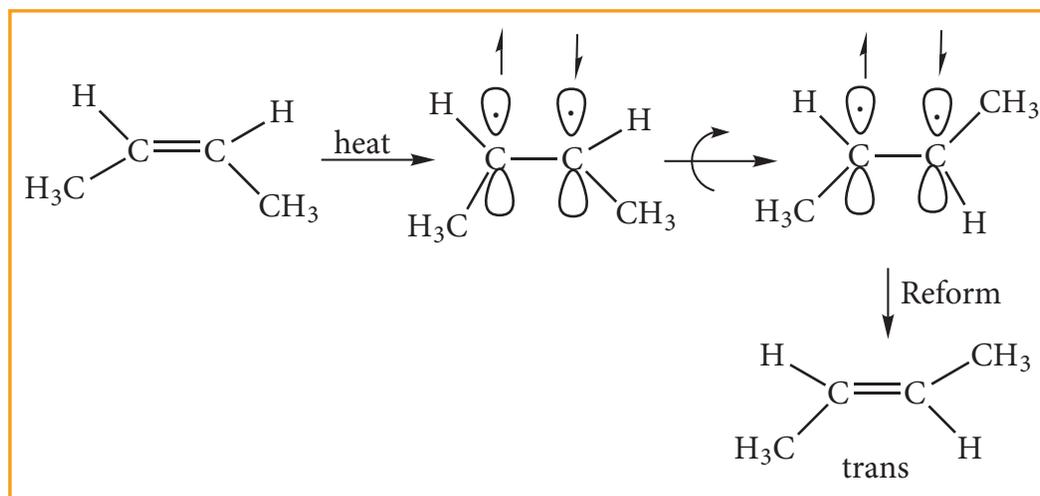
Geometrical isomers are the stereoisomers which have different arrangement of groups or atoms around a rigid frame work of double bonds. This type of isomerism occurs due to restricted rotation of double bonds, or about single bonds in cyclic compounds.

In alkenes, the carbon-carbon double bond is sp^2 hybridized. The carbon-carbon double bond consists of a σ bond and a π bond. The σ bond is formed by the head on overlap of sp^2 hybrid orbitals. The π bond is formed by the side wise overlap of 'p' orbitals. The presence of the π bond lock the molecule in one position. Hence, rotation around C=C bond is not possible. This restriction of rotation about C-C double bond is responsible for geometrical isomerism in alkenes.



These two compounds are termed as geometrical isomers and are distinguished from each other by the terms *cis* and *trans*. The *cis* isomer is one in which two similar groups are on the same side of the double bond. The *trans* isomers is that in which the two similar groups are on the opposite side of the double bond, hence this type of isomerism is often called *cis-trans* isomerism.

The *cis*-isomer can be converted to *trans* isomer or vice versa is only if either isomer is heated to a high temperature or absorbs light. The heat supplies the energy (about 62kcal/mole) to break the π bond so that rotation about σ bond becomes possible. Upon cooling, the reformation of the π bond can take place in two ways giving a mixture both *cis* and *trans* forms of *trans*-2-butene and *cis*-2-butene.

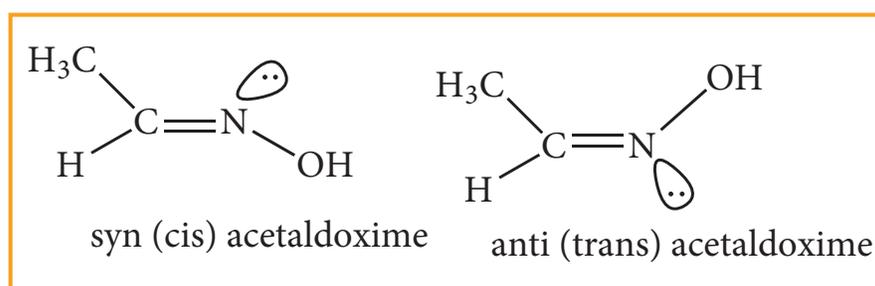


Generally the trans isomer is more stable than the corresponding *cis* isomers. This is because in the *cis* isomer, the bulky groups are on the same side of the double bond. The steric repulsion of the groups makes the *cis* isomers less stable than the *trans* isomers in which bulky groups are on the opposite side. These *cis* and *trans* isomers have different chemical property is. They can be separated by fractional distillation, gas chromatography etc., All alkenes with identical substrate do not show geometrical isomerism. Geometrical isomerism is possible only when each double bonded C atom is attached to two different atoms or groups eg. In propene no geometrical isomers are possible because one of the double bonded carbon has two identical H atoms.

Cis-trans isomerism is also seen around single bond. For eg: 1,3-butadiene has two double bonds in conjugation. $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$. It can exist in infinite number of conformations, but the following two extreme conformations are important.

ii) Oximes and azo compounds:

Restricted rotation around C=N (oximes) gives rise to geometrical isomerism in oximes. Here 'syn' and 'anti' are used instead of *cis* and *trans* respectively. In the *syn* isomer the H atom of a doubly bonded carbon and -OH group of doubly bonded nitrogen lie on the same side of the double bond, while in the *anti* isomer, they lie on the opposite side of the double bond. For eg:



11.5.4 Optical Isomerism

Compounds having same physical and chemical property but differ only in the rotation of plane of the polarized light are known as optical isomers and the phenomenon is known as optical isomerism.

Some organic compounds such as glucose have the ability to rotate the plane of the plane polarized light and they are said to be optically active compounds and this property of a compound is called optical activity. The optical isomer, which rotates the plane of the plane polarised light to the right or in clockwise direction is said to be dextro rotatory (dexter means right) denoted by the sign (+), whereas the compound which rotates to the left or anticlockwise is said to be leavo rotatory (leaves means left) denoted by sign (-). Dextrorotatory compounds are represented as 'd' or by sign (+) and levorotatory compounds are represented as 'l' or by sign (-).

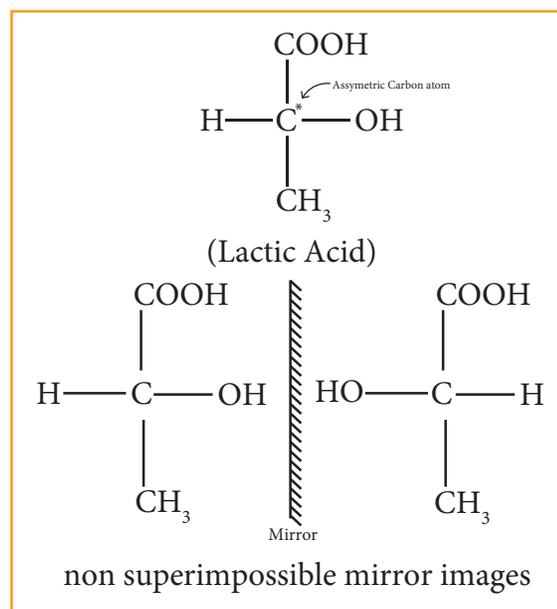
Enantiomerism and optical activity

An optically active substance may exist in two or more isomeric forms which have same physical and chemical properties but differ in terms of direction of rotation of plane polarized light, such optical isomers which rotate the plane of polarized light with equal angle but in opposite direction are known as enantiomers and the phenomenon is known as enantiomerism. Isomers which are non-super impossible mirror images of each other are called enantiomers.

Conditions for enantiomerism or optical isomerism

A carbon atom whose tetra valency

is satisfied by four different substituents (atoms or groups) is called asymmetric carbon or chiral carbon. It is indicated by an asterisk as C*. A molecule possessing chiral carbon atom and non-super impossible to its own mirror image is said to be a chiral molecule or asymmetric, and the property is called chirality or dissymmetry.



11.6 Detection of elements in organic compounds

Introduction

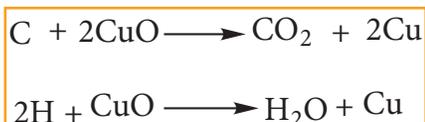
The first step in the analysis of an organic compound is the detection of elements present in it. The principal elements are carbon, hydrogen and oxygen. In addition to these they may contain nitrogen, sulphur and halogens. Phosphorous. Metals like Li, Mg, Zn are present in certain organometallic compounds.

Detection of carbon and hydrogen

If the compound under investigation is organic, there is no need to test for carbon. This test is performed only to establish whether a

given compound is organic or not. With the exception of few compounds like CCl_4 , CS_2 all organic compounds also contain hydrogen. The presence of both these elements is confirmed by the following common test.

Copper(II)oxide test: The organic substance is mixed with about three times its weight of dry copper oxide by grinding. The mixture is then placed in a hard glass test tube fitted with a bent delivery tube. The other end of which is dipping into lime water in an another test tube. The mixture is heated strongly and the following reaction take place.



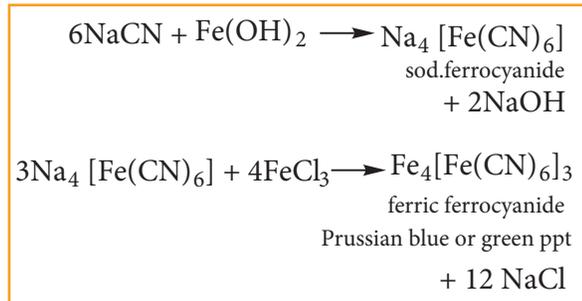
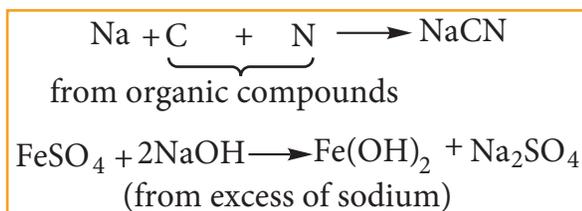
Thus if carbon is present, it is oxidized to CO_2 which turns lime water milky. If hydrogen is also present, it will be oxidized to water which condenses in small droplets on the cooler wall of the test tube and inside the bulb. Water is collected on anhydrous CuSO_4 which turns anhydrous CuSO_4 blue. This confirms the presence of C and H in the compound.

Detection of nitrogen by lassaing sodium fusion test: This is a good test for the detection of nitrogen in all classes of nitrogenous compound and it involves the preparation of sodium fusion extract

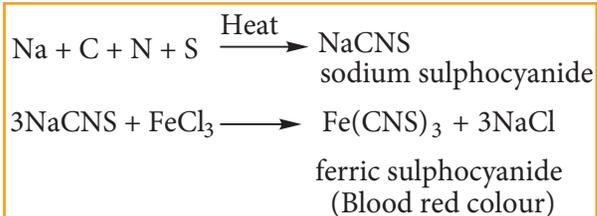
This method involves the conversion of covalently bonded N, S or halogen present in the organic compounds to corresponding water soluble ions in the form of sodium salts For this purpose a small piece of Na dried by pressing between the folds of a filter paper is taken in a fusion tube and it is gently heated.

When it melts to a shining globule, put a pinch of the organic compound on it. Heat the tube till reaction ceases and becomes red hot. Plunge it in about 50 mL of distilled water taken in a china dish and break the bottom of the tube by striking against the dish. Boil the contents of the dish for about 10 mts and filter. This filtrate is known as lassaing extract or sodium fusion extract and it used for detection of nitrogen, sulfur and halogens present in organic compounds.

ii) Test for Nitrogen: If nitrogen is present it gets converted to sodium cyanide which reacts with freshly prepared ferrous sulphate and ferric ion followed by conc. HCl and gives a Prussian blue color or green colour or precipitate. It confirms the presence of nitrogen. HCl is added to dissolve the greenish precipitate of ferrous hydroxide produced by the excess of NaOH on FeSO_4 which would otherwise mark the Prussian blue precipitate. The following reaction takes part in the formation of Prussian blue.

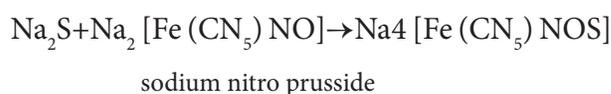


Incase if both N & S are present, a blood red colour is obtained due to the following reactions.

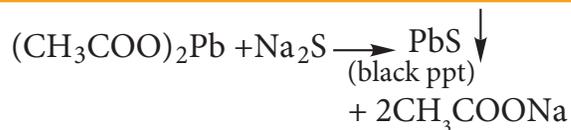


iii) Test for sulphur:

- a) To a portion of the lassaig's extract, add freshly prepared sodium nitro prusside solution. A deep violet or purple colouration is obtained. This test is also used to detect S^{2-} in inorganic salt analysis



- b) Acidify another portion of lassaig's extract with acetic acid and add lead acetate solution. A black precipitate is obtained.



c) **Oxidation test:** The organic substances are fused with a mixture of KNO_3 and Na_2CO_3 . The sulphur, if present is oxidized to sulphate.

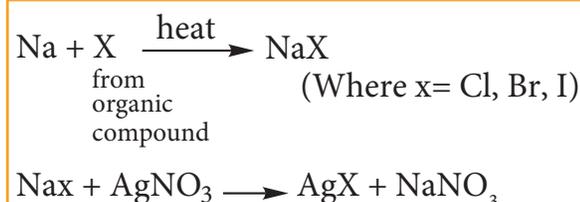


The fused mass is extracted with water, acidified with HCl and then BaCl_2 solution is added to it. A white precipitate indicates the presence of sulphur.

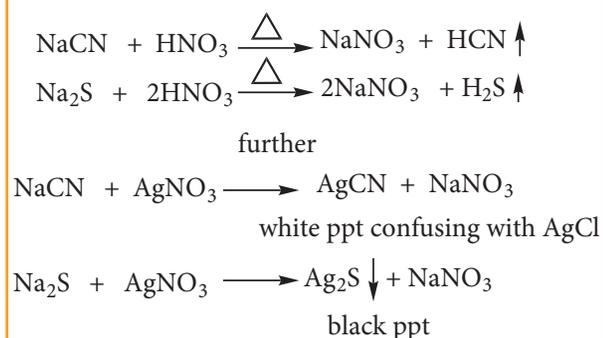


- iv) **Test for halogens:** To another portion of the lassaig's filtrate add dil HNO_3 warm gently and add AgNO_3 solution.

- a) Appearance of curdy white precipitate soluble in ammonia solution indicates the presence of chlorine.
- b) Appearance of pale yellow precipitate sparingly soluble in ammonia solution indicates the presence of bromine.
- c) Appearance of a yellow precipitate insoluble in ammonia solution indicates the presence of iodine.



If N or S is present in the compound along with the halogen, we might obtain NaCN and Na_2S in the solution, which interfere with the detection of the halogen in the AgNO_3 test. Therefore we boil the lassaig's extract with HNO_3 which decomposes NaCN and Na_2S as



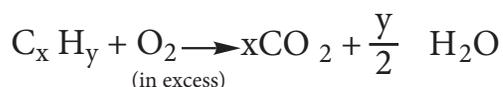
V) Test for phosphorous: A solid compound is strongly heated with a mixture of Na_2CO_3 & KNO_3 . Phosphorous present in the compound is oxidized to sodium phosphate. The residue is extracted with water and boiled with Conc. HNO_3 . A solution of ammonium molybdate is added to the above solution. A canary yellow coloration or precipitate shows the presence of phosphorous.

11.7 Estimation of elements

After detecting the various elements present in a given organic compound by qualitative analysis it is necessary to determine their composition by weight. The estimation of carbon, hydrogen, nitrogen, sulphur halogens are discussed here. No dependable method is however available for determination oxygen and hence its amount is always determined by difference.

Estimation of carbon and hydrogen:

Both carbon and hydrogen are estimated by the same method. A known weight of the organic substance is burnt in excess of oxygen and the carbon and hydrogen present in it are oxidized to carbon dioxide and water, respectively.



The weight of carbon dioxide and water thus formed are determined and the amount of carbon and hydrogen in the organic substance is calculated.

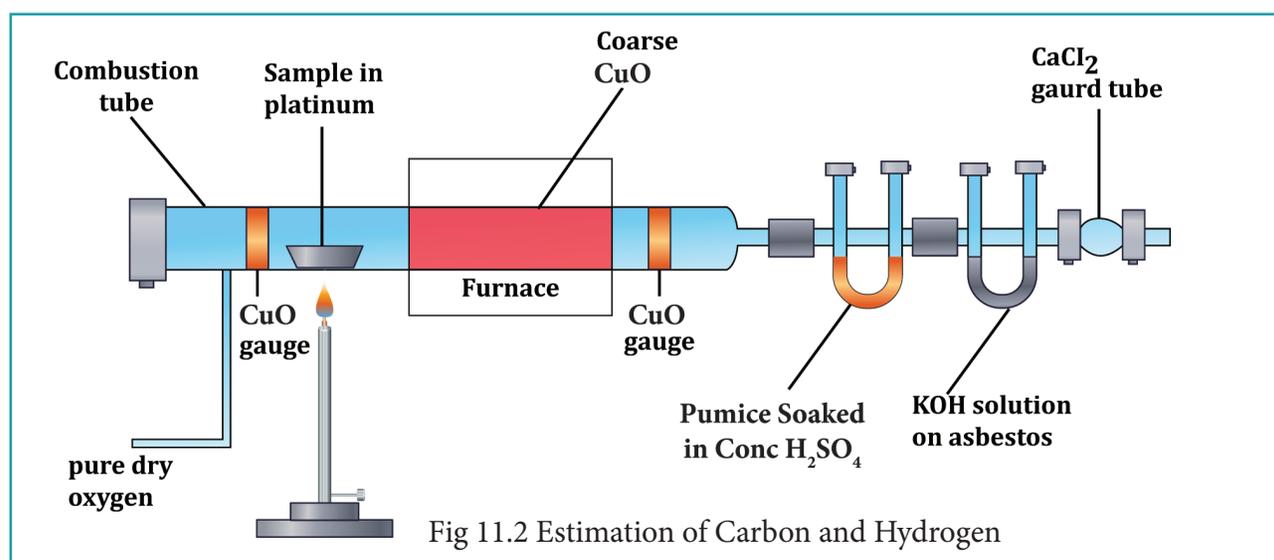
The apparatus employed for the purpose consists of three units (i) oxygen

supply (2) combustion tube (3) absorption apparatus. (see Fig. 11.2)

(1) **Oxygen supply:** To remove the moisture from oxygen it is allowed to bubble through sulphuric acid and then passed through a U-tube containing sodalime to remove CO_2 . The oxygen gas free from moisture and carbon dioxide enters the combustion tube.

(2) **Combustion tube:** A hard glass tube open at both ends is used for the combustion of the organic substance. It contains (i) an oxidized copper gauze to prevent the backward diffusion of the products of combustion (ii) a porcelain boat containing a known weight of the organic substance (iii) coarse copper oxide on either side and (iv) an oxidized copper gauze placed towards the end of the combustion tube. The combustion tube is heated by a gas burner.

(3) **Absorption Apparatus:** The combustion products containing moisture and carbon-dioxide are then passed through the absorption apparatus which consists of (1) a weighed U-tube



packed with pumice soaked in Conc. H_2SO_4 to absorb water (ii) a set of bulbs containing a strong solution of KOH to absorb CO_2 and finally (iii) a guard tube filled with anhydrous CaCl_2 to prevent the entry of moisture from atmosphere.

Procedure: The combustion tube is heated strongly to dry its content. It is then cooled slightly and connected to the absorption apparatus. The other end of the combustion tube is open for a while and the boat containing weighed organic substance is introduced. The tube is again heated strongly till the substance in the boat is burnt away. This takes about 2 hours. Finally, a strong current of oxygen is passed through the combustion tube to sweep away any traces of carbon dioxide or moisture which may be left in it. The U-tube and the potash bulbs are then detached and the increase in weight of each of them is determined.

Calculation:

Weight of the organic substance taken = w g

Increase in weight of H_2O = x g

Increase in weight of CO_2 = y g

18 g of H_2O contains 2g of hydrogen

$\therefore x$ g of H_2O contains $\left(\frac{2}{18}x\right)$ g of hydrogen

Percentage of hydrogen = $\left(\frac{2}{18} \times \frac{x}{w} \times 100\right)\%$

44g of CO_2 contains 12g of carbon

$\therefore y$ g of CO_2 contains $\left(\frac{12}{44}y\right)$ g of carbon

Percentage of Carbon = $\left(\frac{12}{44} \times \frac{y}{w} \times 100\right)\%$

Note:

1. If the organic substance under investigation also contain N, it will produce oxides of nitrogen on combustion. A spiral of copper is introduced at the combustion tube, to reduce the oxides of nitrogen to nitrogen which escapes unabsorbed.
2. If the compound contains halogen as well, a spiral of silver is also introduced in the combustion tube. It converts halogen into silver halide.
3. In case if the substance also contains sulphur, the copper oxide in the combustion tube is replaced by lead chromate. The SO_2 formed during combustion is thus converted to lead sulphate and prevented from passing into the absorption unit.

Worked out example: 1

0.26g of an organic compound gave 0.039 g of water and 0.245 g of carbon dioxide on combustion. Calculate the percentage of C & H

Weight of organic compound = 0.26g

Weight of water = 0.039g

Weight of CO_2 = 0.245g

Percentage of hydrogen

18 g of water contain 2 g of hydrogen

0.039 g of water contain $\frac{2}{18} \times \frac{0.039}{0.26}$

% of hydrogen = $\frac{0.039}{0.26} \times \frac{2}{18} \times 100 = 1.66\%$

Percentage of carbon

44 g of CO₂ contain 12 g of C

0.245 g of CO₂ contains $\frac{12}{44} \times \frac{0.245}{0.26}$ g of C

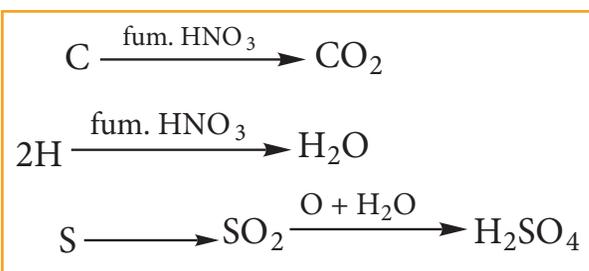
% of Carbon = $\frac{12}{44} \times \frac{0.245}{0.26} \times 100 = 25.69\%$

Evaluate Yourself

5) 0.2346g of an organic compound containing C, H & O, on combustion gives 0.2754g of H₂O and 0.4488g CO₂. Calculate the % composition of C, H & O in the organic compound [C=52.17, H = 13.04, O = 34.79]

Estimation of sulphur:

Carius method: A known mass of the organic substance is heated strongly with fuming HNO₃. C & H get oxidized to CO₂ & H₂O while sulphur is oxidized to sulphuric acid as per the following reaction.



The resulting solution is treated with excess of BaCl₂ solution H₂SO₄ present in the solution is quantitatively converted into BaSO₄, from the mass of BaSO₄, the mass of sulphur and hence the percentage of sulphur in the compound can be calculated.

Procedure:

A known mass of the organic compound is taken in clean carius tube and

added a few mL of fuming HNO₃. The tube is sealed. It is then placed in an iron tube and heated for about 5 hours. The tube is allowed to cool to room temperature and a small hole is made to allow gases produced inside to escape. The carius tube is broken and the content collected in a beaker. Excess of BaCl₂ is added to the beaker contains H₂SO₄ acid as a result of the reaction is converted to BaSO₄. The precipitate of BaSO₄ is filtered, washed, dried and weighed. From the mass of BaSO₄, percentage of S is found.

Mass of the organic compound = w g

Mass of the BaSO₄ formed = x g

233g of BaSO₄ contains 32 g of Sulphur

∴ x g of BaSO₄ contains $\left(\frac{32}{233} x\right)$ g of S

Percentage of Sulphur = $\left(\frac{32}{233} \times \frac{x}{w} \times 100\right)\%$

Example -2

In an estimation of sulphur by carius method, 0.2175 g of the substance gave 0.5825 g of BaSO₄ calculate the percentage composition of S in the compound.

Weight of organic compound 0.2175 g

Weight of BaSO₄ 0.5825 g

233 g of BaSO₄ contains 32 g of S

0.5825 g of BaSO₄ contains $\frac{32}{233} \times \frac{0.5825}{0.2175}$

Percentage of S = $\frac{32}{233} \times \frac{0.5825}{0.2175} \times 100$

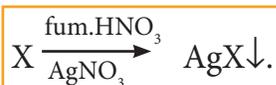
= 36.78 %

Evaluate Yourself

6) 0.16 g of an organic compound was heated in a carius tube and H_2SO_4 acid formed was precipitated with BaCl_2 . The mass of BaSO_4 was 0.35g. Find the percentage of sulphur

Estimation of halogens: carius method:

A known mass of the organic compound is heated with fuming HNO_3 and AgNO_3 . C,H & S get oxidized to CO_2 , H_2O & SO_2 and halogen combines with AgNO_3 to form a precipitate of silver halide.



The ppt of AgX is filtered,

washed, dried and weighed. From the mass of AgX and the mass of the organic compound taken, percentage of halogens are calculated.

A known mass of the substance is taken along with fuming HNO_3 and AgNO_3 is taken in a clean carius tube. The open end of the Carius tube is sealed and placed in a iron tube for 5 hours in the range at 530-540 K Then the tube is allowed to cool and a small hole is made in the tube to allow gases produced to escape. The tube is broken and the ppt is filtered, washed, dried and weighed. From the mass of AgX obtained, percentage of halogen in the organic compound is calculated.

Weight of the organic compound: w g

Weight of AgCl precipitate = a g

143.5 g of AgCl contains 35.5 g of Cl

\therefore a g of AgCl contains $\frac{35.5}{143.5} \times a$

w g Organic compound gives a g AgCl

Percentage of Cl in w g = $\left(\frac{35.5}{143.5} \times \frac{a}{w} \times 100\right)\%$
organic compound

Let Weight of silver Bromide be 'b'g

188g of AgBr contains 80 g of Br

\therefore b g of AgBr contains $\left(\frac{80}{188} b\right)$ g of Br

w g Organic compound gives b g AgBr

Percentage of Br in w g = $\left(\frac{80}{188} \times \frac{b}{w} \times 100\right)\%$
organic compound

Let Weight of silver Iodide be 'c'g

235g of AgI contains 127 g of I

\therefore C g of AgI contains $\left(\frac{127}{235} c\right)$ g of I

w g Organic compound gives c g AgI

Percentage of I in w g = $\left(\frac{127}{235} \times \frac{c}{w} \times 100\right)\%$
organic compound

EXAMPLE : 0.284 g of an organic substance gave 0.287 g AgCl in a carius method for the estimation of halogen. Find the Percentage of Cl in the compound.

Weight of the organic substance = 0.284 g

Weight of AgCl is = 0.287 g

143.5 g of AgCl contains 35.5 g of chlorine

0.287 g of AgCl contains $\frac{35.5}{143.5} \times \frac{0.287}{0.284}$

% of chlorine is $\frac{35.5}{143.5} \times \frac{0.287}{0.284} \times 100 = 24.98\%$

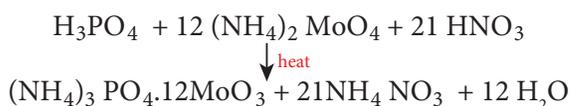
Evaluate Yourself

7) 0.185 g of an organic compound when treated with Conc. HNO_3 and silver nitrate gave 0.320 g of silver bromide. Calculate the % of bromine in the compound. ($\text{Ag} = 108$, $\text{Br} = 80$) Ans: 73.6

8) 0.40 g of an iodo-substituted organic compound gave 0.235 g of AgI by carius method. Calculate the percentage of iodine in the compound. ($\text{Ag} = 108$, $\text{I} = 127$) (Ans = 31.75)

Estimation of phosphorus:

Carius method: A known mass of the organic compound (w) containing phosphorous is heated with fuming HNO_3 in a sealed tube where C is converted into CO_2 and H to H_2O . phosphorous present in organic compound is oxidized to phosphoric acid which is precipitated, as ammonium phosphomolybdate by heating with Conc. HNO_3 and then adding ammonium molybdate.



The precipitate of ammonium phosphomolybdate thus formed is filtered washed, dried and weighed.

In an alternative method, the phosphoric acid is precipitated as magnesium-ammonium phosphate by adding magnesia mixture (a mixture containing MgCl_2 , NH_4Cl and ammonia) This ppt is washed, dried and ignited to get magnesium pyrophosphate which is washed, dried and weighed. The following are the reaction that takes place.

By knowing the mass of the organic compound and the mass of ammonium phosphomolybdate or magnesium pyrophosphate formed, the percentage of P is calculated.

Mass of organic compound is w g

Weight of ammonium

phosphomolybdate = x g

Weight of magnesium pyrophosphate = y g

Mole mass of $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ is = 1877g

$[3 \times (14 + 4) + 31 + 4(16)] + 12 (96 + 3 \times 16)$

Molar mass of $\text{Mg}_2\text{P}_2\text{O}_7$ is 222 g

$(2 \times 24) + (31 \times 2) + (7 \times 16)$

1877g of $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ contains 31g of P

x g of $(\text{NH}_4)_3\text{PO}_4 \cdot 12 \text{MoO}_3$ in w g of organic compound contains $\frac{31}{1877} \times \frac{x}{w}$ of phosphorous

Percentage of Phosphorous = $\frac{31}{1877} \times \frac{x}{w} \times 100\%$

(or)

222 of $\text{Mg}_2\text{P}_2\text{O}_7$ contains 62 g of P

Y g of $\text{Mg}_2\text{P}_2\text{O}_7$ in w g of Organic compound contains $\frac{62}{222} \times \frac{Y}{w}$ of P.

Percentage Phosphorous = $\frac{62}{222} \times \frac{Y}{w} \times 100\%$

Example 4: 0.24 g of organic compound containing phosphorous gave 0.66 g of $\text{Mg}_2\text{P}_2\text{O}_7$ by the usual analysis. Calculate the percentage of phosphorous in the compound

Weight of an organic compound = 0.24 g

Weight of $\text{Mg}_2\text{P}_2\text{O}_7$ = 0.66 g

222 g of $\text{Mg}_2\text{P}_2\text{O}_7$ contains 62 g of P
 0.66 g contains $\left(\frac{62}{222} \times 0.66\right)$ g of P
 Percentage of P $\frac{62}{222} \times \frac{0.66}{0.24} \times 100 = 76.80\%$

Evaluate Yourself

9) 0.33 g of an organic compound containing phosphorous gave 0.397 g of $\text{Mg}_2\text{P}_2\text{O}_7$ by the analysis. Calculate the percentage of P in the compound (Ans: 23.21) (MFW of $\text{Mg}_2\text{P}_2\text{O}_7$ is 222 P = 31)

Estimation of nitrogen: There are two methods for the estimation of nitrogen in an organic compound. They are 1. Dumas method 2. Kjeldahls method

1. Dumas method:

This method is based upon the fact that nitrogenous compound when heated with cupric oxide in an atmosphere of CO_2 yields free nitrogen. Thus



Traces of oxide of nitrogen, which may be formed in some cases, are reduced to elemental nitrogen by passing over heated copper spiral.

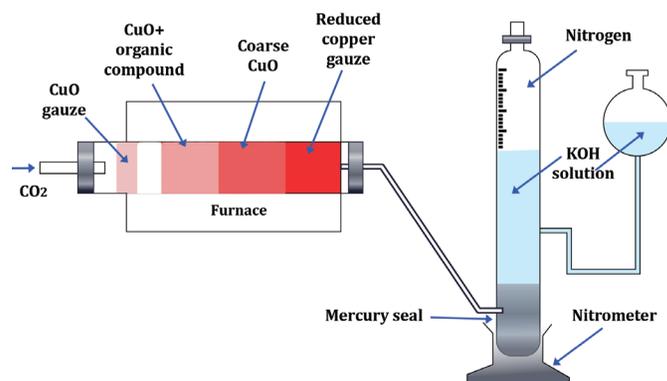


Fig 11.4 Dumas Method

The apparatus used in Dumas method consists of CO_2 generator, combustion tube, Schiff's nitrometer. (See Fig. 11.4)

CO_2 generator:

CO_2 needed in this process is prepared by heating magnetite or sodium bicarbonate contained in a hard glass tube or by the action of dil. HCl on marble in a kipp's apparatus. The gas is passed through the combustion tube after being dried by bubbling through Conc. H_2SO_4 .

Combustion Tube: The combustion tube is heated in a furnace is charged with a) A roll of oxidized copper gauze to prevent the back diffusion of the products of combustion and to heat the organic substance mixed with CuO by radiation b) a weighed amount of the organic substance mixed with excess of CuO, c) a layer of coarse CuO packed in about 2/3 of the entire length of the tube and kept in position by loose asbestos plug on either side; this oxidizes the organic vapors passing through it, and d) a reduced copper spiral which reduces any oxides of nitrogen formed during combustion to nitrogen.

Schiff's nitro meter: The nitrogen gas obtained by the decomposition of the substance in the combustion tube is mixed with considerable excess of CO_2 . It is estimated by passing nitrometer when CO_2 is absorbed by KOH and the nitrogen gets collected in the upper part of graduated tube.

Procedure: To start with the tap of nitro meter is left open. CO_2 is passed through the combustion tube to expel the air in it. When the gas bubbles rising through, the



potash solution fails to reach the top of it and is completely absorbed it shows that only CO_2 is coming and that all air has been expelled from the combustion tube. The nitrometer is then filled with KOH solution by lowering the reservoir and the tap is closed. The combustion tube is now heated in the furnace and the temperature rises gradually. The nitrogen set free from the compound collects in the nitro meter. When the combustion is complete a strong current of CO_2 is sent through, the apparatus in order to sweep the last trace of nitrogen from it. The volume of the gas gets collected is noted after adjusting the reservoir so that the solution in it and the graduated tube is the same. The atmospheric pressure and the temperature are also recorded.

Calculations:

Weight of the substance taken = w g

Volume of nitrogen = V_1 L

Room Temperature = T_1 K

Atmospheric Pressure = P mm of Hg

Aqueous tension at

room temperature = P^1 mm of Hg

Pressure of dry nitrogen = $(P - P^1) = P_1$ mm of Hg.

Let p_0 , V_0 and T_0 be the pressure, Volume and temperature respectively of dry nitrogen at STP,

$$\text{Then, } \frac{P_0 V_0}{T_0} = \frac{P_1 V_1}{T_1}$$

$$\therefore V_0 = \frac{P_1 V_1}{T_1} \times \frac{T_0}{P_0}$$

$$V_0 = \left(\frac{P_1 V_1}{T_1} \times \frac{273\text{K}}{760} \right) \text{ mmHg}$$

Calculation of percentage of nitrogen.
22.4 L of N_2 at STP weigh 28g of N_2

$$\therefore V_0 \text{ L of } \text{N}_2 \text{ at S.T.P weigh } \frac{28}{22.4} \times V_0$$

Wg of Organic compound contain
 $\left(\frac{28}{22.4} \times \frac{V_0}{W} \right)$ g of nitrogen

\therefore Percentage of nitrogen =

$$\left(\frac{28}{22.4} \times \frac{V_0}{W} \right) \times 100$$

Problem: 0.1688 g when analyzed by the Dumas method yield 31.7 mL of moist nitrogen measured at 14°C and 758 mm mercury pressure. Determine the % of N in the substance (Aqueous tension at $14^\circ\text{C} = 12$ mm)

Weight of Organic compound = 0.168g

Volume of moist nitrogen (V_1) = 31.7mL
= 31.7×10^{-3} L
Temperature (T_1) = 14°C
= $14 + 273$
= 287K

Pressure of Moist nitrogen (P) = 758 mm Hg
Aqueous tension at 14°C = 14°C
= 12 mm of Hg

\therefore Pressure of dry nitrogen = $(P - P^1)$
= $758 - 12$
= 746 mm of

$$\frac{P_1 V_1}{T_1} = \frac{P_0 V_0}{T_0}$$

$$\therefore V_0 = \frac{746 \times 31.7 \times 10^{-3}}{287} \times \frac{273}{760}$$

$$V_0 = 29.58 \times 10^{-3} \text{ L}$$

Percentage of

$$\begin{aligned}\text{nitrogen} &= \left(\frac{28}{22.4} \times \frac{V_0}{W} \right) \times 100 \\ &= \frac{28}{22.4} \times \frac{29.58 \times 10^{-3}}{0.1688} \times 100 \\ &= 21.90\%\end{aligned}$$



Dumas method is a high precision method and is generally preferred over Kjeldahl's method.

Kjeldahls method:

This method is carried much more easily than the Dumas method. It is used largely in the analysis of foods and fertilizers. Kjeldahls method is based on the fact that when an organic compound containing nitrogen is heated with Conc. H_2SO_4 , the nitrogen in it is quantitatively converted to ammonium sulphate. The resultant liquid is then treated with excess of alkali and then liberated ammonia gas absorbed in excess of standard acid. The amount of ammonia (and hence nitrogen) is determined by finding the amount of acid neutralized by back titration with same standard alkali.

Procedure:

A weighed quantity of the substance (0.3 to 0.5 g) is placed in a special long-necked Kjeldahl flask made of pyrex glass. About 25 mL of Conc. H_2SO_4 together with a little K_2SO_4 and CuSO_4 (catalyst) are added to it the flask is loosely stoppered by a glass bulb and heated gently in an inclined position. The heating is continued till the brown color of the liquid first produced, disappears leaving the contents clear as before. At this point all the nitrogen in the substance is converted to $(\text{NH}_4)_2\text{SO}_4$. The Kjeldahl flask is then cooled and its contents are diluted with distilled water and then carefully transferred into a 1 lit round bottom flask. An excess NaOH solution is poured down the side of the flask and it is fitted with a Kjeldahl trap and a water condenser. The lower end of the condenser dips in a measured volume of excess the $\frac{N}{20}$ H_2SO_4 solution. The liquid in the round bottom flask is then heated and the liberated ammonia is distilled into sulphuric acid. The Kjeldahl trap serves to retain any alkali splashed up on vigorous boiling. (See Fig. 11.3)

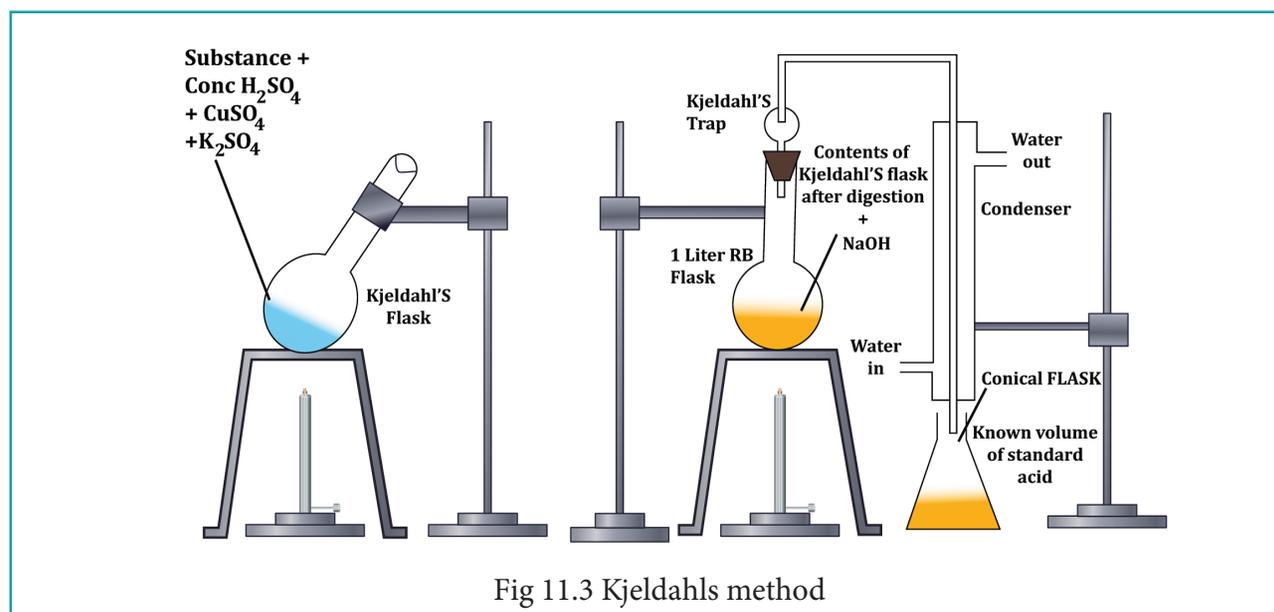


Fig 11.3 Kjeldahls method

When no more ammonia passes over (test the distillate with red litmus) the receiver is removed. The excess of acid is then determined by titration with alkali, using phenolphthalein as the indicator.

Calculation:

Weight of the substance = Wg.

Volume of H_2SO_4 required for the complete neutralisation of evolved $\text{NH}_3 = V$ mL.

Strength of H_2SO_4 used to neutralise $\text{NH}_3 = N$

Let the Volume and the strength of NH_3 formed are V_1 and N_1 respectively

we know that $V_1 N_1 = VN$

The amount of nitrogen present in the w g of Organic Compound = $\frac{14 \times NV}{1 \times 1000 \times w}$

Percentage of Nitrogen = $\left(\frac{14 \times NV}{1000 \times w} \right) \times 100\%$

Example : 0.6 g of an organic compound was Kjeldalised and NH_3 evolved was absorbed into 50 mL of semi-normal solution of H_2SO_4 . The residual acid solution was diluted with distilled water and the volume made up to 150 mL. 20 mL of this diluted solution required 35 mL of $\frac{N}{20}$ NaOH solution for complete neutralization. Calculate the % of N in the compound.

Weight of Organic compound = 0.6g
 Volume of sulphuric acid taken = 50mL
 Strength of sulphuric acid taken = 0.5 N
 20 ml of diluted solution of unreacted sulphuric acid was neutralised by 35 mL of

0.05 N Sodium hydroxide

Strength of the diluted sulphuric acid = $\frac{35 \times 0.05}{20}$
 = 0.0875 N

Volume of the sulphuric acid remaining after reaction with = V_1 mL

Organic compound
 Strength of H_2SO_4 = 0.5N
 Volume of the diluted H_2SO_4 = 150 mL
 Strength of the diluted sulphuric acid = 0.0875 N

$V_1 = \frac{150 \times 0.087}{0.5} = 26.25$ mL

Volume of H_2SO_4 consumed by ammonia = 50 - 26.25
 = 23.75 mL

23.75 mL of 0.5 N $\text{H}_2\text{SO}_4 \equiv 23.75$ mL of 0.5N NH_3

The amount of Nitrogen present in the 0.6 = $\frac{14g}{1000 \text{ mL} \times 1 \text{ N}} \times 23.75 \times 0.5 \text{ N}$
 = 0.166g

Percentage of Nitrogen = $\frac{0.166}{0.6} \times 100$
 = 27.66 %

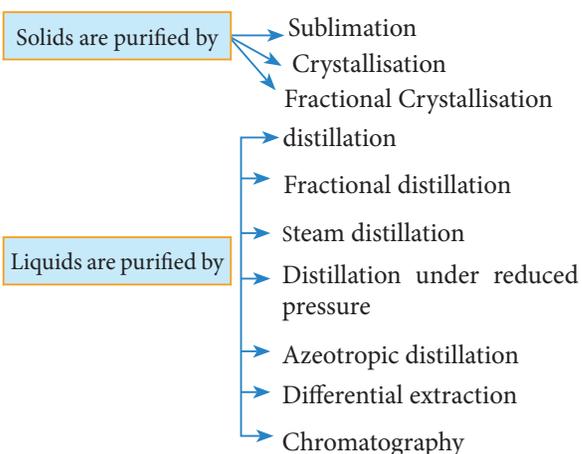
Evaluate Yourself

10) 0.3 g of an organic compound on kjeldahl's analysis gave enough ammonia to just neutralize 30 mL of 0.1N H_2SO_4 . Calculate the percentage of nitrogen in the compound.

11.8 Purification of organic compounds

Need for purification:

In order to study the structure, physical properties, chemical properties and biological properties of organic compounds they must be in the pure state. There are several methods by which organic compounds can be purified. The methods employed for purification depend upon the nature of impurity and the nature of organic compound. The most widely used technique for the separation and purification of organic compounds are: (a) Crystallisation, (b) Sublimation (c) Distillation (d) Fractional distillation (e) Steam distillation (f) Azeotropic distillation (g) Differential extraction and (h) Chromatography.



11.8.1 Sublimation:

Few substances like benzoic acid, naphthalene and camphor when heated pass directly from solid to vapor without melting (ie liquid). On cooling the vapours will give back solids. Such phenomenon is called sublimation. It is a useful technique to separate volatile and non-volatile solid. It has limited application because only a few substance will sublime.

Substances to be purified is taken in a beaker. It is covered with a watch glass. The beaker is heated for a while and the resulting vapours condense on the bottom of the watch glass. Then the watch glass is removed and the crystals are collected. This method is applicable for organic substance which has high vapour pressure at temperature below their melting point. Substances like naphthalene, benzoic acid can be sublimed quickly. Substance which has very small vapour pressure will decompose upon heating are purified by sublimation under reduced pressure. This apparatus consists of large heating and large cooling surface with small distance in between because the amount of the substance in the vapour phase is much too small in case of a substance with low vapour pressure.

11.8.2 Crystallization:

It is the most widely used method for the purification of solid organic compound. This process is carried out in by the following step

(i) **Selection of solvent:** Most of the organic substances being covalent do not dissolve in polar solvents like water, hence selection of solvent (suitable) becomes necessary. Hence the powdered organic substance is taken in a test tube and the solvent is added little by little with constant stirring and heating, till the amount added is just sufficient to dissolve the solute (ie) organic compound. If the solid dissolves upon heating and throws out maximum crystals on cooling, then the solvent is suitable. This process is repeated with other solvents like benzene, ether, acetone and alcohol till the most suitably one is sorted out.



(ii) Preparation of solution: The organic substance is dissolved in a minimum quantity of suitable solvent. Small amount of animal charcoal can be added to decolorize any colored substance. The heating may be done over a wire gauze or water bath depending upon the nature of liquid (ie) whether the solvent is low boiling or high boiling.

(iii) Filtration of hot solution: The hot solution so obtained is filtered through a fluted filter paper placed in a funnel.

(iv) Crystallization: The hot filtrate is then allowed to cool. Most of the impurities are removed on the filter paper, the pure solid substance separate as crystal. When copious amount of crystal has been obtained, then the crystallization is complete. If the rate of crystallization is slow, it is induced either by scratching the walls of the beaker with a glass rod or by adding a few crystals of the pure compounds to the solution.

(v) Isolation and drying of crystals: The crystals are separated from the mother liquor by filtration. Filtration is done under reduced pressure using a Bucher funnel. When the whole of the mother liquor has been drained into the filtration flask, the crystals are washed with small quantities of the pure cold solvent and then dried.

11.8.3 Distillation:

This method is to purify liquids from non-volatile impurities, and used for separating the constituents of a liquid mixture which differ in their boiling points. There are various methods of distillation depending upon the difference in the boiling points of the constituents. The methods

are (i) simple distillation (ii) fractional distillation and (iii) steam distillation. The process of distillation involves the impure liquid when boiled gives out vapour and the vapour so formed is collected and condensed to give back the pure liquid in the receiver. This method is called simple distillation. Liquids with large difference in boiling point (about 40k) and do not decompose under ordinary pressure can be purified by simply distillation eg. The mixture of $C_6H_5NO_2$ (b.p 484k) & C_6H_6 (354k) and mixture of diethyl ether (b.p 308k) and ethyl alcohol (b.p 351k)

Fractional distillation: This is one method to purify and separate liquids present in the mixture having their boiling point close to each other. In the fractional distillation, a fractionating column is fitted with distillation flask and a condenser. A thermometer is fitted in the fractionating column near the mouth of the condenser. This will enable to record the temperature of vapour passing over the condenser. The process of separation of the components in a liquid mixture at their respective boiling points in the form of vapours and the subsequent condensation of those vapours is called fractional distillation. The process of fractional distillation is repeated, if necessary. This method finds a remarkable application in distillation of petroleum, coal-tar and crude oil.

11.8.4 Steam distillation:

This method is applicable for solids and liquids. If the compound to be steam distilled the it should not decompose at the steam temperature, should have a fairly high vapour pressure at 373k, it should be insoluble in water and the impurities present should be non-volatile.

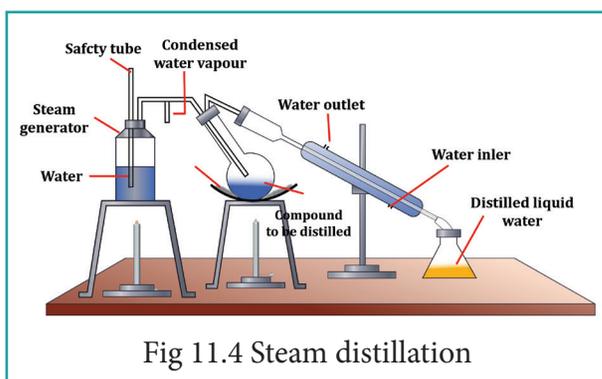


Fig 11.4 Steam distillation

The impure liquid along with little water is taken in a round-bottom flask which is connected to a boiler on one side and water condenser on the other side, the flask is kept in a slanting position so that no droplets of the mixture will enter into the condenser on the brisk boiling and bubbling of steam. The mixture in the flask is heated and then a current of steam passed in to it. The vapours of the compound mix up with steam and escape into the condenser. The condensate obtained is a mixture of water and organic compound which can be separated. This method is used to recover essential oils from plants and flowers, also in the manufacture of aniline and turpentine oil. (see Fig. 11.4)

11.8.5 Azeotropic Distillation

These are the mixture of liquids that cannot be separated by fractional distillation. The mixtures that can be purified only by azeotropic distillation are called as azeotropes. These azeotropes are constant boiling mixtures, which distil as a single component at a fixed temperature. For example ethanol and water in the ratio of 95.87:4.13.

In this method the presence of a third component like C_6H_6 , CCl_4 , ether, glycerol, glycol which act as a dehydrating agent depress the partial pressure of one component of azeotropic mixture and raises

the boiling point of that component and thus other component will distil over.

Substances like C_6H_6 , CCl_4 have low boiling points and reduce the partial vapour pressure of alcohol more than that of water while substances like glycerol & glycol etc. have high boiling point and reduce the partial vapour pressure of water more than that of alcohol.

11.8.6 Differential extraction:

The process of removing a substance from its aqueous solution by shaking with a suitable organic solvent is termed extraction. When an organic substance present as solution in water can be recovered from the solution by means of a separating funnel. The aqueous solution is taken in a separating funnel with little quantity of ether or chloroform ($CHCl_3$). The organic solvent immiscible with water will form a separate layer and the contents are shaken gently. The solute being more soluble in the organic solvent is transferred to it. The solvent layer is then separated by opening the tap of the separating funnel, and the substance is recovered.

11.8.7 Chromatography:

The most valuable method for the separation and purification of small quantity of mixtures. As name implies chroma-colour and graphed writing it was first applied to separation of different colored constituents of chlorophyll in 1906 by M.S Tswett, a Russian botanist. He achieved it by passing a petroleum ether solution of chlorophyll present in leaves through a column of $CaCO_3$ firmly packed into a narrow glass tube. Different components of the pigments got separated into bands or zones of different



colors and now this technique is equally well applied to separation of colorless substances.

The principle behind chromatography is selective distribution of the mixture of organic substances between two phases – a stationary phase and a moving phase. The stationary phase can be a solid or liquid, while the moving phase is a liquid or a gas. When the stationary phase is a solid, the moving phase is a liquid or a gas. If the stationary phase is a solid, the basis is adsorption, and when it is a liquid, the basis is partition. So the Chromatography is defined as a technique for the separation of a mixture brought about by differential movement of the individual compound through porous medium under the influence of moving solvent. The various methods of chromatography are

1. Column chromatography (CC)
2. Thin layer chromatography (TLC)
3. Paper chromatography (PC)
4. Gas-liquid chromatography (GLC)
5. Ion-exchange chromatography

Adsorption chromatography: The principle involved is different compounds are adsorbed on an adsorbent to different degree. Silica gel and alumina are the commonly used adsorbent. The components of the mixture move by varying distances over the stationary phase. Column chromatography and thin layer chromatography are the techniques based on the principle of differential adsorption.

Column chromatography: This is the simplest chromatographic method carried out in long glass column having a stop cock

near the lower end. This method involves separation of a mixture over a column of adsorbent (Stationery phase) packed in a column. In the column a plug of cotton or glass wool is placed at the lower end of the column to support the adsorbent powder. The tube is uniformly packed with suitable adsorbent constitute the stationary phase. (Activated aluminum oxides (alumina), Magnesium oxide, starch are also used as adsorbents).

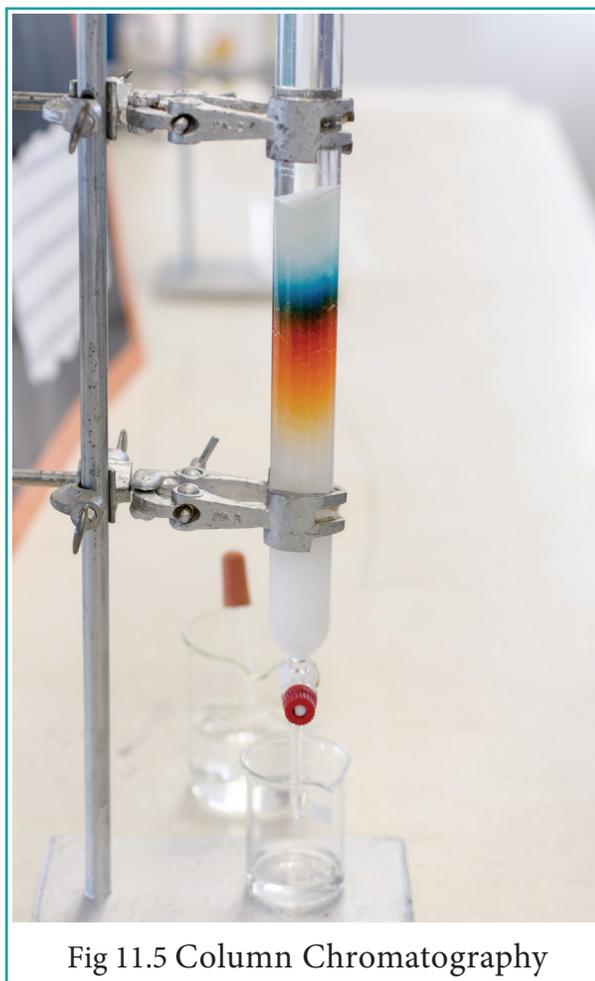


Fig 11.5 Column Chromatography

The mixture to be separated is placed on the top of the adsorbent column. Eluent which is a liquid or a mixture of liquids is allowed to flow down the column slowly. Different components are eluted depending upon the degree to which the components are adsorbed and complete separation takes place. The most readily adsorbed substances

are retained near the top and others come down to various distances in the column.

Thin layer chromatography: This method is another type of adsorption chromatography with this method it is possible to separate even minute quantities of mixtures. A sheet of glass is coated with a thin layer of adsorbent (cellulose, silica gel or alumina). This sheet of glass is called chromoplate or thin layer chromatography plate. After drying the plate, a drop of the mixture is placed just above one edge and the plate is then placed in a closed jar containing eluent (solvent). The eluent is drawn up the adsorbent layer by capillary action. The components of the mixture move up along with the eluent to different distances depending upon their degree of adsorption of each component of the mixture. It is expressed in terms of its retention factor (ie) R_f value

$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

The spots of colored compounds are visible on TLC plate due to their original color. The colorless compounds are viewed under uv light or in another method using iodine crystals or by using appropriate reagent.

Partition chromatography: Paper chromatography (PC) is an example of partition chromatography. The same procedure is followed as in thin layer chromatography except that a strip of paper acts as an adsorbent. This method involves continuous differential partitioning of components of a mixture between stationary and

mobile phase. In paper chromatography, a special quality paper known as chromatography paper is used. This paper act as a stationary phase.

A strip of chromatographic paper spotted at the base with the solution of the mixture is suspended in a suitable solvent which act as the mobile phase. The solvent rises up and flows over the spot. The paper selectively retains different components according to their different partition in the two phases where a chromatogram is developed. The spots of the separated colored compounds are visible at different heights from the position of initial spots on the chromatogram. The spots of the separated colorless compounds may be observed either under ultraviolet light or by the use of an appropriate spray reagent.

Evaluation



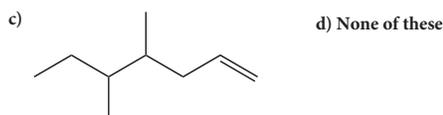
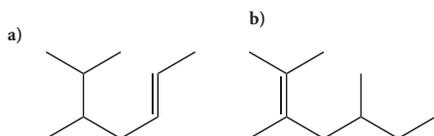
I. Choose the best answer.

- Select the molecule which has only one π bond.
 - $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$
 - $\text{CH}_3 - \text{CH} = \text{CH} - \text{CHO}$
 - $\text{CH}_3 - \text{CH} = \text{CH} - \text{COOH}$
 - All of these
- In the hydrocarbon $\overset{7}{\text{C}}\text{H}_3 - \overset{6}{\text{C}}\text{H}_2 - \overset{5}{\text{C}}\text{H} = \overset{4}{\text{C}}\text{H} - \overset{3}{\text{C}}\text{H}_2 - \overset{2}{\text{C}} \equiv \overset{1}{\text{C}}\text{H}$ the state of hybridisation of carbon 1,2,3,4 and 7 are in the following sequence.
 - $\text{sp}, \text{sp}, \text{sp}^3, \text{sp}^2, \text{sp}^3$
 - $\text{sp}^2, \text{sp}, \text{sp}^3, \text{sp}^2, \text{sp}^3$
 - $\text{sp}, \text{sp}, \text{sp}^2, \text{sp}, \text{sp}^3$
 - none of these
- The general formula for alkadiene is

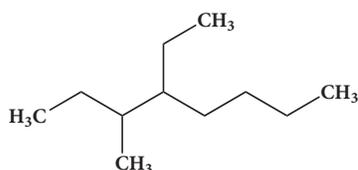
a) C_nH_{2n}	b) $\text{C}_n\text{H}_{2n-1}$
c) $\text{C}_n\text{H}_{2n-2}$	d) C_nH_{n-2}



4. Structure of the compound whose IUPAC name is 5,6 - dimethylhept - 2 - ene is



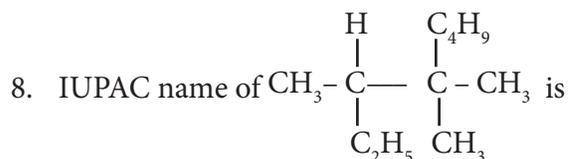
5. The IUPAC name of the Compound is



- a) 2,3 - Dimethylheptane
b) 3- Methyl -4- ethyloctane
c) 5-ethyl -6-methyloctane
d) 4-Ethyl -3 - methyloctane.
6. Which one of the following names does not fit a real name?
- a) 3 - Methyl -3-hexanone
b) 4-Methyl -3- hexanone
c) 3- Methyl -3- hexanol
d) 2- Methyl cyclo hexanone.

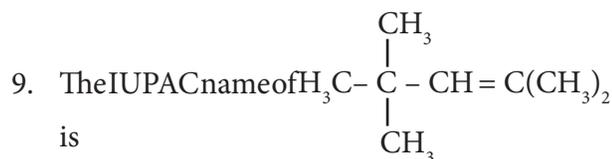
7. The IUPAC name of the compound $\text{CH}_3\text{-CH=CH-C}\equiv\text{CH}$ is

- a) Pent - 4 - yn-2-ene
b) Pent -3-en-1-yne
c) pent - 2- en - 4 - yne
d) Pent - 1 - yn -3 -ene

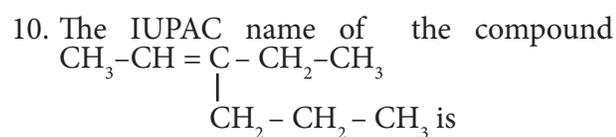


- a) 3,4,4 - Trimethylheptane
b) 2 - Ethyl -3, 3- dimethyl heptane

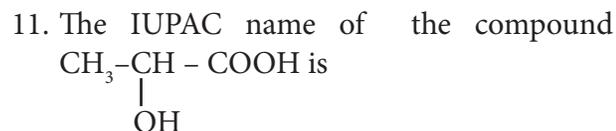
- c) 3, 4,4 - Trimethyloctane
d) 2 - Butyl -2 -methyl - 3 - ethyl-butane.



- a) 2,4,4 - Trimethylpent -2-ene
b) 2,4,4 - Trimethylpent -3-ene
c) 2,2,4 - Trimethylpent -3-ene
d) 2,2,4 - Trimethylpent -2-ene

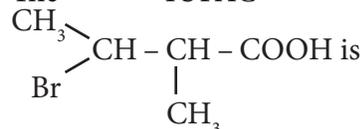


- a) 3 - Ethyl -2- hexene
b) 3 - Propyl -3- hexene
c) 4 - Ethyl - 4 - hexene
d) 3 - Propyl -2-hexene



- a) 2 - Hydroxypropionic acid
b) 2 - Hydroxy Propanoic acid
c) Propan - 2- ol -1 - oic acid
d) 1 - Carboxyethanol.

12. The IUPAC name of



- a) 2 - Bromo -3 - methyl butanoic acid
b) 2 - methyl - 3- bromobutanoic acid
c) 3 - Bromo - 2 - methylbutanoic acid
d) 3 - Bromo - 2, 3 - dimethyl propanoic acid.

13. The structure of isobutyl group in an organic compound is

- a) $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$



- b) $\text{CH}_3 - \overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}$
- c) $\text{CH}_3 - \overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{CH}}} - \text{CH}_2 -$
- d) $\text{CH}_3 - \overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{CH}}} - \text{CH}_2 - \text{CH}_3$
14. The number of stereoisomers of 1, 2 - dihydroxy cyclopentane
a) 1 b) 2 c) 3 d) 4
15. Which of the following is optically active?
a) 3 - Chloropentane
b) 2 Chloro propane
c) Meso - tartaric acid
d) Glucose
16. The isomer of ethanol is
a) acetaldehyde b) dimethylether
c) acetone d) methyl carbinol
17. How many cyclic and acyclic isomers are possible for the molecular formula $\text{C}_3\text{H}_6\text{O}$?
a) 4 b) 5 c) 9 d) 10
18. Which one of the following shows functional isomerism?
a) ethylene b) Propane
c) ethanol d) CH_2Cl_2
19. $\overset{\ominus}{\text{C}}\text{H}_2 - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_3$ and $\text{CH}_2 = \overset{\ominus}{\text{C}} - \text{CH}_3$ are
a) resonating structure b) tautomers
c) Optical isomers d) Conformers.
20. Nitrogen detection in an organic compound is carried out by Lassaigne's test. The blue colour formed is due to the formation of.
a) $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$
b) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
c) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_2$
d) $\text{Fe}_3[\text{Fe}(\text{CN})_6]_3$
21. Lassaigne's test for the detection of nitrogen fails in
a) $\text{H}_2\text{N} - \text{CO} - \text{NH} \cdot \text{NH}_2 \cdot \text{HCl}$
b) $\text{NH}_2 - \text{NH}_2 \cdot \text{HCl}$
c) $\text{C}_6\text{H}_5 - \text{NH} - \text{NH}_2 \cdot \text{HCl}$
d) $\text{C}_6\text{H}_5 \text{CONH}_2$
22. Connect pair of compounds which give blue colouration / precipitate and white precipitate respectively, when their Lassaigne's test is separately done.
a) $\text{NH}_2 \text{NH}_2 \text{HCl}$ and $\text{ClCH}_2 - \text{CHO}$
b) $\text{NH}_2 \text{CS NH}_2$ and $\text{CH}_3 - \text{CH}_2\text{Cl}$
c) $\text{NH}_2 \text{CH}_2 \text{COOH}$ and $\text{NH}_2 \text{CONH}_2$
d) $\text{C}_6\text{H}_5\text{NH}_2$ and $\text{ClCH}_2 - \text{CHO}$.
23. Sodium nitropruside reacts with sulphide ion to give a purple colour due to the formation of
a) $[\text{Fe}(\text{CN})_5 \text{NO}]^{3-}$
b) $[\text{Fe}(\text{NO})_5 \text{CN}]^+$
c) $[\text{Fe}(\text{CN})_5 \text{NOS}]^{4-}$
d) $[\text{Fe}(\text{CN})_5 \text{NOS}]^{3-}$
24. An organic Compound weighing 0.15g gave on carius estimation, 0.12g of silver bromide. The percentage of bromine in the Compound will be close to
a) 46% b) 34%
c) 3.4% d) 4.6%
25. A sample of 0.5g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50mL of 0.5M H_2SO_4 . The remaining acid after neutralisation by ammonia consumed 80mL of 0.5 MNaOH, The percentage of nitrogen in the organic compound is.
a) 14%
b) 28%
c) 42%
d) 56%



26. In an organic compound, phosphorus is estimated as

- a) $\text{Mg}_2\text{P}_2\text{O}_7$ b) $\text{Mg}_3(\text{PO}_4)_2$
c) H_3PO_4 d) P_2O_5

27. Ortho and para-nitro phenol can be separated by

- a) azeotropic distillation
b) destructive distillation
c) steam distillation
d) cannot be separated

28. The purity of an organic compound is determined by

- a) Chromatography
b) Crystallisation
c) melting or boiling point
d) both (a) and (c)

29. A liquid which decomposes at its boiling point can be purified by

- a) distillation at atmospheric pressure
b) distillation under reduced pressure
c) fractional distillation
d) steam distillation.

30. Assertion: $\text{CH}_3 - \underset{\text{COOC}_2\text{H}_5}{\text{C}} = \text{CH} - \text{COOH}$ is

3- carbethoxy -2- butenoic acid.

Reason: The principal functional group gets lowest number followed by double bond (or) triple bond.

- (a) both the assertion and reason are true and the reason is the correct explanation of assertion.
(b) both assertion and reason are true and the reason is not the correct explanation of assertion.
(c) assertion is true but reason is false
(d) both the assertion and reason are false.

II. Write brief answer to the following questions.

31. Give the general characteristics of organic compounds?

32. Describe the classification of organic compounds based on their structure.

33. Write a note on homologous series.

34. What is meant by a functional group? Identify the functional group in the following compounds.

- (a) acetaldehyde (b) oxalic acid
(c) di methyl ether (d) methylamine

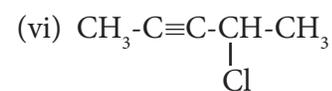
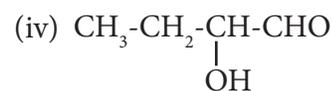
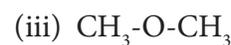
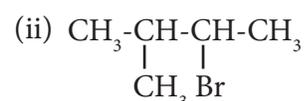
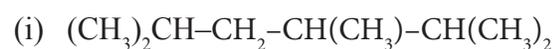
35. Give the general formula for the following classes of organic compounds

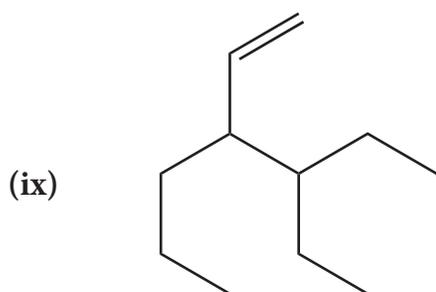
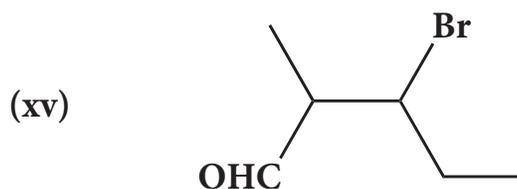
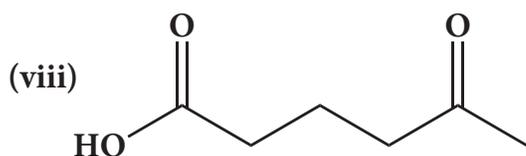
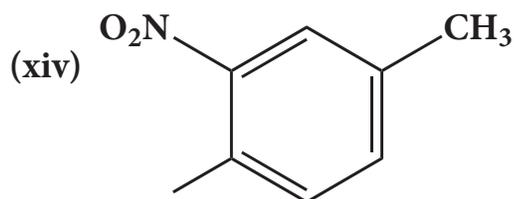
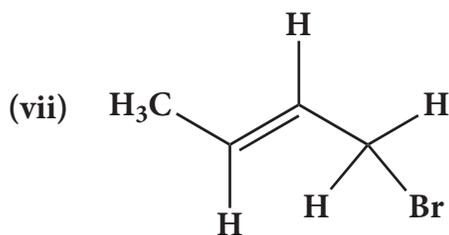
- (a) Aliphatic monohydric alcohol
(b) Aliphatic ketones.
(c) Aliphatic amines.

36. Write the molecular formula of the first six members of homologous series of nitro alkanes.

37. Write the molecular and possible structural formula of the first four members of homologous series of carboxylic acids.

38. Give the IUPAC names of the following compounds.





39) Give the structure for the following compound.



(i) 3-ethyl-2-methyl-1-pentene

(ii) 1,3,5-Trimethylcyclohex-1-ene

(iii) tertiary butyl iodide

(iv) 3-Chlorobutanal

(v) 3-Chlorobutanol

(vi) 2-Chloro-2-methylpropane

(vii) 2,2-dimethyl-1-chloropropane

(viii) 3-methylbut-1-ene

(ix) Butane-2,2-diol

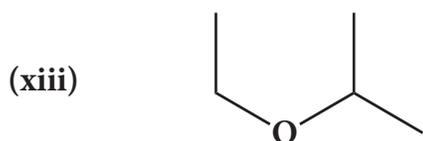
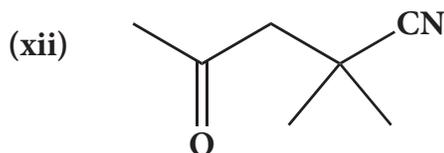
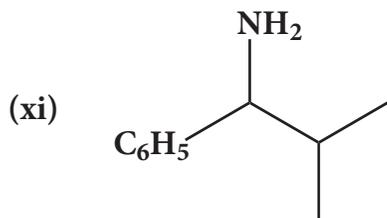
(x) Octane-1,3-diene

(xi) 1,3-Dimethylcyclohexane

(xii) 3-Chlorobut-1-ene

(xiii) 3-methylbutan-2-ol

(xiv) acetaldehyde



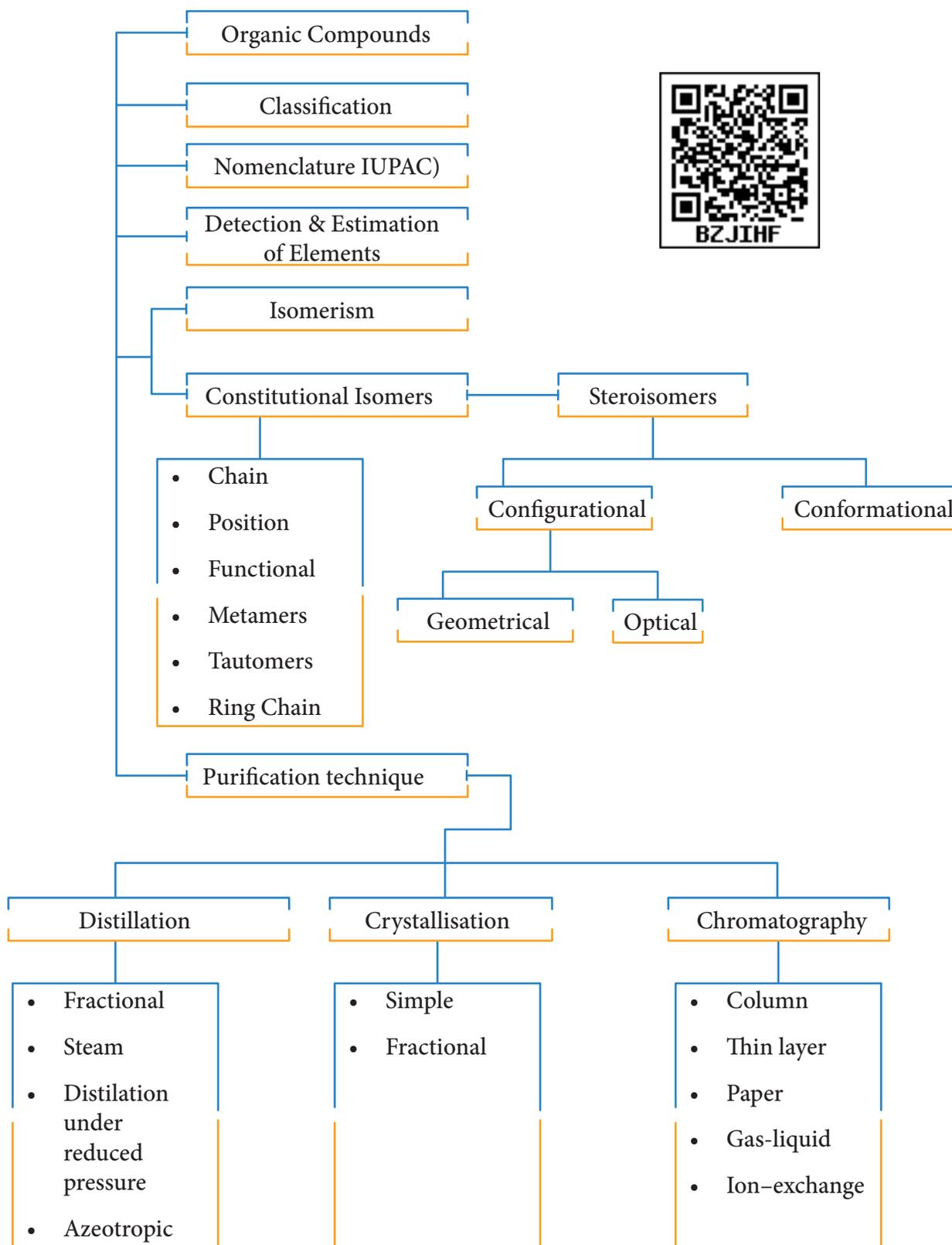
40) Describe the reactions involved in the detection of nitrogen in an organic compound by Lassaigne method.



- 
- 41) Give the principle involved in the estimation of halogen in an organic compound by carius method.
- 42) Give a brief description of the principles of
- Fractional distillation
 - Column Chromatography
- 43) Explain paper chromatography
- 44) Explain various types of constitutional isomerism (structural isomerism) in organic compounds
- 45) Describe optical isomerism with suitable example.
- 46) Briefly explain geometrical isomerism in alkene by considering 2- butene as an example.
- 47) 0.30 g of a substance gives 0.88 g of carbon dioxide and 0.54 g of water calculate the percentage of carbon and hydrogen in it.
- 48) The ammonia evolved from 0.20 g of an organic compound by kjeldahl method neutralised 15ml of N/20 sulphare acid solution. Calculate the percentage of Nitrogen.
- 49) 0.32 g of an organic compound, after heating with fuming nitric acid and barium nitrate crystals in a sealed tube gave 0.466 g of barium sulphate. Determine the percentage of sulphur in the compound.
- 50) 0.24g of an organic compound gave 0.287 g of silver chloride in the carius method. Calculate the percentage of chlorine in the compound.
- 51) In the estimation of nitrogen present in an organic compound by Dumas method 0.35 g yielded 20.7 mL of nitrogen at 150 C and 760 mm pressure. Calculate the percentage of nitrogen in the compound



CONCEPT MAP





Paper Chromatography

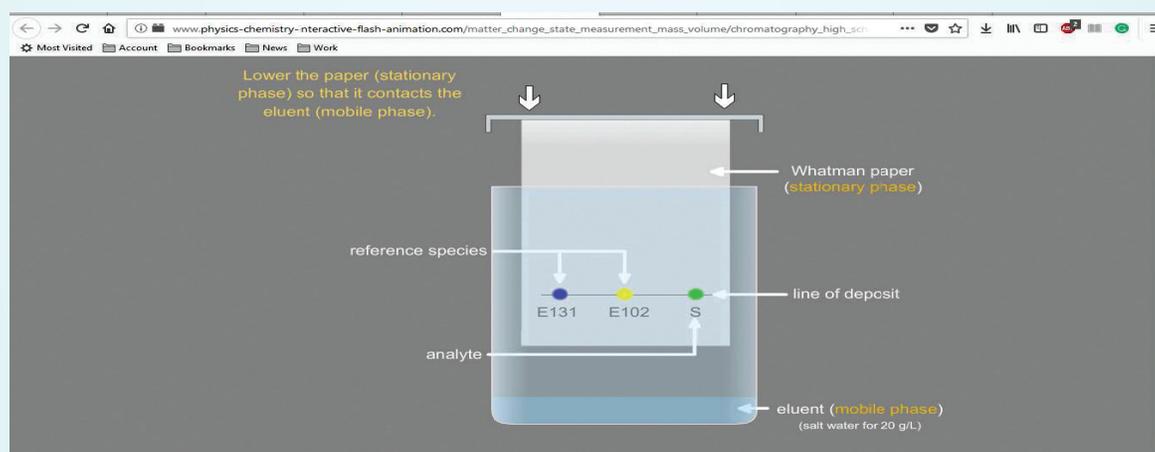
By using this tool you will learn to use a paper chromatography to detect the presence of colouring agents E102 and E131.

Please go to the URL http://www.physics-chemistry-interactive-flash-animation.com/matter_change_state_measurement_mass_volume/chromatography_high_school.htm (or) Scan the QR code on the right side



Steps

- Open the Browser and type the URL given (or) Scan the QR Code. You can see a webpage which displays the term “Chromatography” in the middle and arrow with word “Enter” is present. Now click the arrow.
- Now the page will explain the experimental setup and conditions and arrow at the bottom with the word “Chromatography”. After reading the text click the arrow again.
- Now you can see a page as shown in the figure. Now lower the paper so that it contacts the eluent by clicking the region marked by the red box and move it downwards. Now the experiment starts and you can see the result in few seconds.
- After the simulation you can see few evaluation questions which you can try to answer.





Otto diels and Kurt Alder describe an important reaction mechanism for the reaction between a conjugated diene and a substituted alkene. For this work they were awarded nobel prize in chemistry in 1950 Diels - Alder reaction is a powerful tool in synthetic organic chemistry.

Learning Objectives

After learning this unit, students will be able to

- understand the concept of organic reaction mechanism
- describe homolytic and heterolytic fission of bonds
- identify free radicals, nucleophiles and electrophiles,
- classify organic reactions into substitution, elimination, addition, oxidation and reduction
- describe electron movement in organic reactions
- explain the electronic effects in co-valent bonds

12.1 Introduction

A chemical reaction can be treated as a process by which some existing bonds in the reacting molecules are broken and new bonds are formed. i.e., in a chemical reaction, a reactant is converted into a product. This conversion involves one or more steps. A In general an organic reaction can be represented as



Here the substrate is an organic molecule which undergoes chemical change. The reagent which may be an organic, inorganic or any agent like heat, photons etc., that brings about the chemical change

Many chemical reactions are depicted in one or more simple steps. Each step passes through an energy barrier, leading to the formation of short lived intermediates or transition states. The series of simple steps which collectively represent the chemical change, from substrate to product is called as the mechanism of the reaction. The slowest step in the

mechanism determines the overall rate of the reaction.

12.1.1 Fundamental concepts in organic reaction mechanism

The mechanism is the theoretical pathway which describes the changes occurring in each step during the course of the chemical change. An organic reaction can be understood by following the direction of flow of electrons and the type of intermediate formed during the course of the reaction. The direction of flow of electron is represented by curved arrow. The movement of a pair of electron is represented by a double headed arrow which starts from the negative and ends with the atom to which the electrons needs to be transferred.

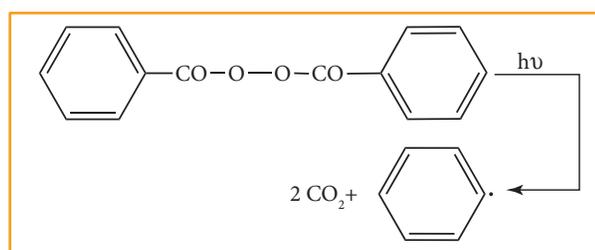
12.1.2 Fission of a covalent bond

All organic molecules contain covalent bonds which are formed by the mutual sharing of electrons between atoms. These covalent bonds break in two different ways, namely homolytic cleavage (symmetrical splitting) and heterolytic cleavage (unsymmetrical splitting). The cleavage of a bond in the substrate is influenced by the nature of the reagent (attacking agent).

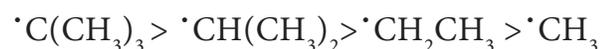
Homolytic Cleavage

Homolytic cleavage is the process in which a covalent bond breaks symmetrically in such way that each of the bonded atoms retains one electron. It is denoted by a half headed arrow (fish hook arrow). This type of cleavage occurs under high temperature or in the presence

of UV light in a compound containing non polar covalent bond formed between atoms of similar electronegativity. In such molecules, the cleavage of bonds results into free radicals. They are short lived and are highly reactive. The type of reagents that promote homolytic cleavage in substrate are called as free radical initiators. For example Azobisisobutyronitrile (AIBN) and peroxides such as benzoyl peroxide are used as free radical initiators in polymerisation reactions.



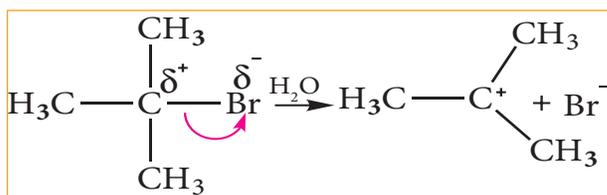
As a free radical with an unpaired electron is neutral and unstable, it has a tendency to gain an electron to attain stability. Organic reactions involve homolytic fission of C-C bonds to form alkyl free radicals. The stability of alkyl free radicals is in the following order



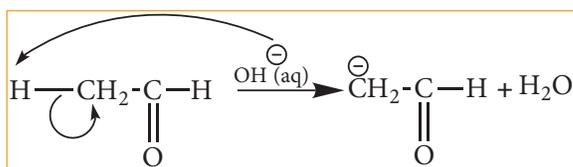
Heterolytic Cleavage

Heterolytic cleavage is the process in which a covalent bond breaks unsymmetrically such that one of the bonded atoms retains the bond pair of electrons. It results in the formation of a cation and an anion. Of the two bonded atoms, the most electronegative atom becomes the anion and the other atom becomes the cation. The cleavage is denoted by a curved arrow pointing towards the more electronegative atom.

For example, in tert-butyl bromide, the C-Br bond is polar as bromine is more electronegative than carbon. The bonding electrons of the C-Br bond are attracted more by bromine than carbon. Hence, the C-Br undergoes heterolytic cleavage to form a tert-butyl cation during hydrolysis.



Let us consider the cleavage in a carbon-hydrogen (C-H) bond of aldehydes or ketones. We know that the carbon is more electronegative than hydrogen and hence the heterolytic cleavage of C-H bonds results in the formation of carbanion (carbon bears a negative charge). For example in aldol condensation the OH^- ion abstracts a α -hydrogen from the aldehyde, which leads to the formation of the below mentioned carbanion.



Hybridisation of carbon in carbocation:

In a carbocation, the carbon bearing positive charge is sp^2 hybridised and hence it has a planar structure. In the reaction involving such a carbocation, the attack of a negatively charged species (nucleophiles) take place on either side of the carbocation as shown below.

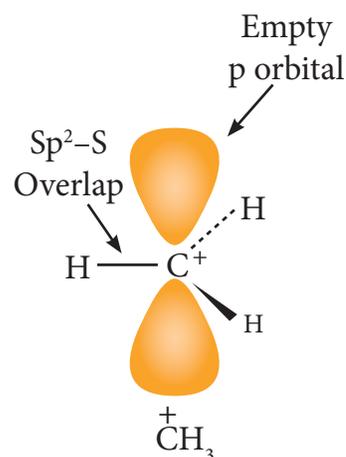


Fig 12.1(a) Shape of Carbocation

The carbanions are generally pyramidal in shape and the lone pair occupies one of the sp^3 hybridised orbitals. An alkyl free radical may be either pyramidal or planar.

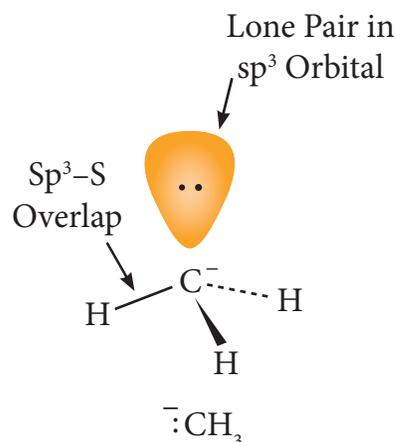


Fig 12.1(b) Shape of Carbanion

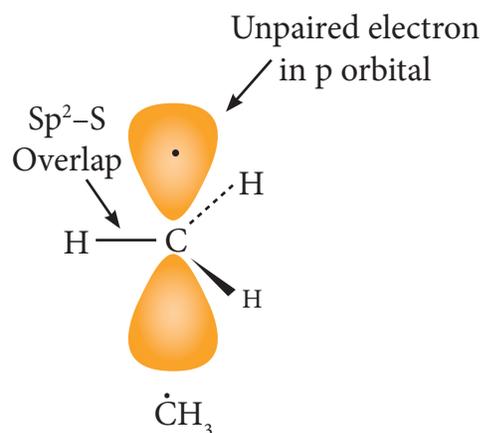
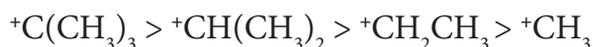


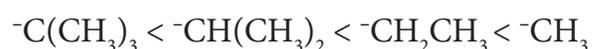
Fig 12.1(c) Shape of Carbon radical

The relative stability of the alkyl carbocations and carbanions are given below.

Relative stability carbocations.



relative stability of carbanions



The energy required to bring about homolytic splitting is greater than that of heterolytic splitting.

12.1.3 Nucleophiles and electrophiles

Nucleophiles are reagents that has high affinity for electro positive centers. They possess an atom has an unshared pair of electrons, and hence it is in search for an electro positive centre where it can have an opportunity to share its electrons to form a covalent bond, and gets stabilised. They are usually negatively charged ions or electron rich neutral molecules (contains one or more lone pair of electrons). All Lewis bases act as nucleophiles.

Types	Examples	Electron rich site
Neutral molecules having unshared pair of electron	Ammonia (NH ₃) and amines (RNH ₂)	N:
	Water (H ₂ O), alcohols (ROH) and ethers (R-O-R)	:O:
	Hydrogen sulphide (H ₂ S) and thiols (RSH)	:S:
Negatively charged nucleophiles	Chlorides (Cl ⁻), bromides (Br ⁻) and iodides (I ⁻)	X ⁻
	Hydroxide (HO ⁻), alkoxide (RO ⁻) and Carboxlate ions (RCOO ⁻)	O ⁻
	Cyanide (CN ⁻)	N ⁻

Electrophiles are reagents that are attracted towards negative charge or electron rich center. They are either positively charged ions or electron deficient neutral molecules. All Lewis acids act as electrophiles. Neutral molecules like SnCl₄ can also act as an electrophile, as it has vacant d-orbitals which can accommodate the electrons from others.

Types	Examples	Electron deficient entity
Neutral electrophiles	Carbon dioxide (CO ₂), dichlorocarbene (:CCl ₂)	C
	Aluminium chloride (AlCl ₃), boron trifluoride (BF ₃) and ferric chloride (FeCl ₃)	Metal (M)
Positively charged electrophiles	Carbocations (R ⁺)	C ⁺
	Proton (H ⁺)	H ⁺
	Alkyl halides (RX)	X ⁺
	Nitrosonium ion (NO ⁺)	O ⁺
	Nitronium ion (⁺ NO ₂)	N ⁺



Human body produces free radicals when it is exposed to x-rays, cigarette smoke, industrial chemicals and air pollutants. Free radicals can disrupt cell membranes, increase the risk of many forms of cancer, damage the interior lining of blood vessels and lead to a high risk of heart disease and stroke. Body uses vitamins and minerals to counter the effects of free radicals. Fruits contains antioxidants which decrease the effects of free radicals.

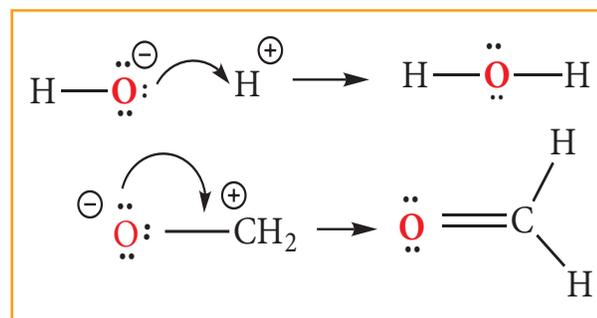
12.1.4 Electron movement in organic reactions

All organic reactions can be understood by following the electron movements, i.e. the electron redistribution during the reaction. The electron movement depends on the nature of the substrate, reagent and the prevailing conditions. The flow of electrons is represented by curved arrows which show how electrons move as shown in the figure. These electron movements result in breaking or formation of a bond (sigma or pi bond). The movement of single electron is indicated by a half-headed curved arrows.

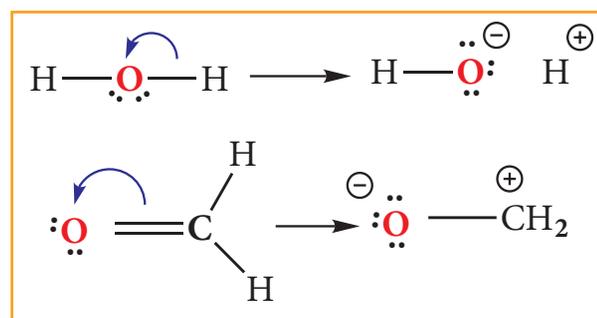
There are three types of electron movement viz.,

- lone pair becomes a bonding pair.
- bonding pair becomes a lone pair
- a bond breaks and becomes another bond.

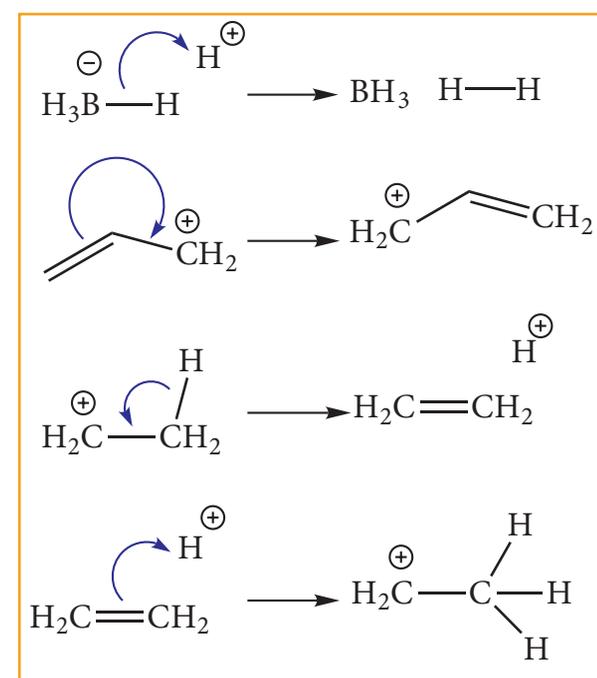
Type 1: A lone pair to a bonding pair



Type 2: A bonding pair to a lone pair



Type 3: A bonding pair to an another bonding pair



12.1.5 Electron displacement effects in co-valent bonds

Some of the properties of organic molecules such as stability, reactivity,

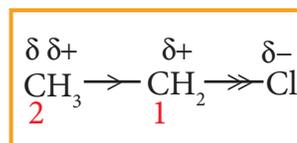
basicity etc., are affected by the displacement of electrons that takes place in its covalent bonds. This movement can be influenced by either the atoms/groups present in close proximity to the bond or when a reagent approaches a molecule. The displacement effects can either be permanent or a temporary. In certain cases, the electron displacement due to an atom or a substituent group present in the molecule cause a permanent polarisation of the bond and it leads to fission of the bond under suitable conditions. The electron displacements are categorised into inductive effect (I), resonance effect (R), electromeric effect (E) and hyper conjugation.

Inductive effect (I)

Inductive effect is defined as the change in the polarisation of a covalent bond due to the presence of adjacent bonds, atoms or groups in the molecule. This is a permanent phenomenon.

Let us explain the inductive effect by considering ethane and ethylchloride as examples. The C-C bond in ethane is non polar while the C-C bond in ethyl chloride is polar. We know that chlorine is more electronegative than carbon, and hence it attracts the shared pair of electron between C-Cl in ethyl chloride towards itself. This develops a slight negative charge on chlorine and a slight positive charge on carbon to which chlorine is attached. To compensate it, the C_1 draws the shared pair of electron between itself and C_2 . This polarisation effect is called inductive effect. This effect is greatest for the adjacent bonds, but they also be felt farther away. However, the magnitude of the charge separation

decreases rapidly, as we move away from C_1 and is observed maximum for 2 carbons and almost insignificant after 4 bonds from the active group.

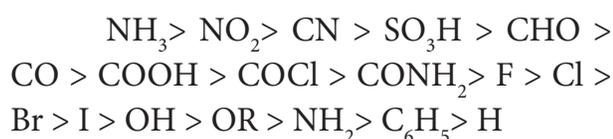


It is important to note that the inductive effect does not transfer electrons from one atom to another but the displacement effect is permanent. The inductive effect represents the ability of a particular atom or a group to either withdraw or donate electron density to the attached carbon. Based on this ability the substituents are classified as +I groups and -I groups. Their ability to release or withdraw the electron through sigma covalent bond is called +I effect and -I effect respectively.

Highly electronegative atoms and groups with an atom carrying a positive charge are electron withdrawing groups or -I groups.

Example: -F, -Cl, -COOH, -NO₂, -NH₂

Higher the electronegativity of the substituent, greater is the -I effect. The order of the -I effect of some groups are given below.



Highly electropositive atoms and atoms are groups which carry a negative charge are electron donating or +I groups.

Example. Alkali metals, alkyl groups such as methyl, ethyl, negatively charged groups such as CH_3O^- , $\text{C}_2\text{H}_5\text{O}^-$, COO^- etc

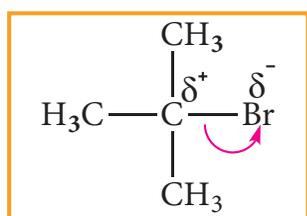
Lesser the electronegativity of the elements, greater is the +I effect. The relative order of +I effect of some alkyl groups is given below



Let us understand the influence of inductive effect on some properties of organic compounds.

Reactivity:

When a highly electronegative atom such as halogen is attached to a carbon then it makes the C-X bond polar. In such cases the -I effect of halogen facilitates the attack of an incoming nucleophile at the polarised carbon, and hence increases the reactivity.



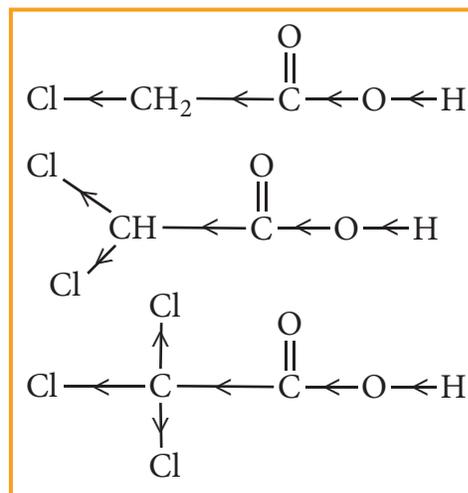
If a -I group is attached nearer to a carbonyl carbon, it decreases the availability of electron density on the carbonyl carbon, and hence increases the rate of the nucleophilic addition reaction.

Acidity of carboxylic acids:

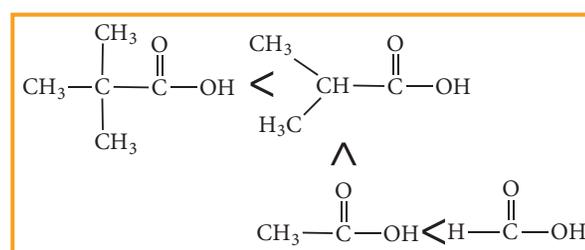
When a halogen atom is attached to the carbon which is nearer to the carboxylic acid group, its -I effect withdraws the bonded electrons towards itself and makes the ionisation of H^+ easy. The acidity of various chloro acetic acid is in the following order. The strength of the acid increases with increase in the -I effect of the group attached

to the carboxyl group.

Trichloro acetic acid > Dichloro acetic acid > Chloro acetic acid > acetic acid



Similarly, the following order of acidity in the carboxylic acids is due to the +I effect of alkyl group.



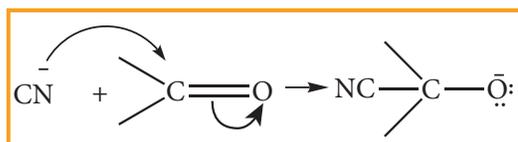
Electromeric effect (E)

Electromeric is a temporary effect which operates in unsaturated compounds (containing $>\text{C}=\text{C}<$, $>\text{C}=\text{O}$, etc...) in the presence of an attacking reagent.

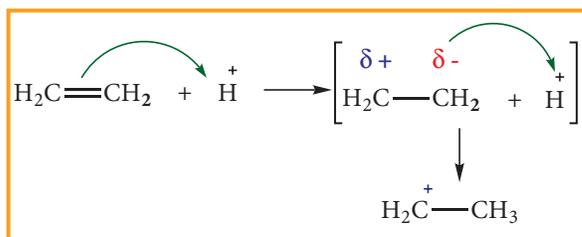
Let us consider two different compounds (i) compounds containing carbonyl group ($>\text{C}=\text{O}$) and (ii) unsaturated compounds such as alkenes ($>\text{C}=\text{C}<$).

When a nucleophile approaches the carbonyl compound, the π electrons between C and O is instantaneously shifted to the more electronegative oxygen. This

makes the carbon electron deficient and thus facilitating the formation of a new bond between the incoming nucleophile and the carbonyl carbon atom.

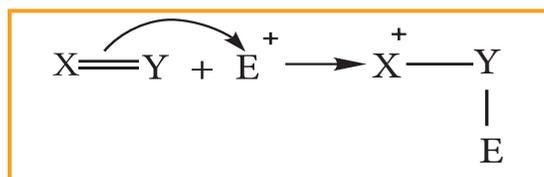


On the other hand when an electrophile such as H^+ approaches an alkene molecule, the π electrons are instantaneously shifted to the electrophile and a new bond is formed between carbon and hydrogen. This makes the other carbon electron deficient and hence it acquires a positive charge.



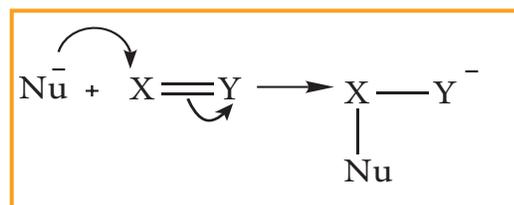
The electromeric effect, is denoted as E effect. Like the inductive effect, the electromeric effect is also classified as +E and -E based on the direction in which the pair of electron is transferred to form a new bond with the attacking agent.

When the π electron is transferred towards the attacking reagent, it is called +E (positive electromeric) effect.



The addition of H^+ to alkene as shown above is an example of +E effect.

When the π electron is transferred away from the attacking reagent, it is called, -E (negative electromeric) effect



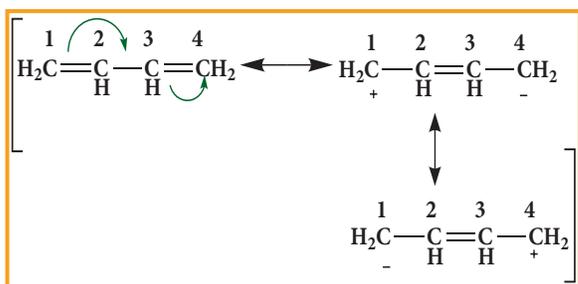
The attack of CN^- on a carbonyl carbon, as shown above, is an example of -E effect.

Resonance or Mesomeric effect

The resonance is a chemical phenomenon which is observed in certain organic compounds possessing double bonds at a suitable position. Certain organic compounds can be represented by more than one structure and they differ only in the position of bonding and lone pair of electrons. Such structures are called resonance structures (canonical structures) and this phenomenon is called resonance. This phenomenon is also called mesomerism or mesomeric effect.

For example, the structure of aromatic compounds such as benzene and conjugated systems like 1,3-butadiene cannot be represented by a single structure, and their observed properties can be explained on the basis of a resonance hybrid.

In 1,3 buta diene, it is expected that the bond between C^1-C^2 and C^3-C^4 should be shorter than that of C^2-C^3 , but the observed bond lengths are of same. This property cannot be explained by a simple structure in which two π bonds localised between C^1-C^2 and C^3-C^4 . Actually the π electrons are delocalised as shown below.



These resonating structures are called canonical forms and the actual structure lies between these three resonating structures, and is called a resonance hybrid. The resonance hybrid is represented as below.



Similar to the other electron displacement effect, mesomeric effect is also classified into positive mesomeric effect (+M or +R) and negative mesomeric effect (-M or -R) based on the nature of the functional group present adjacent to the multiple bond.

Positive Mesomeric Effect:

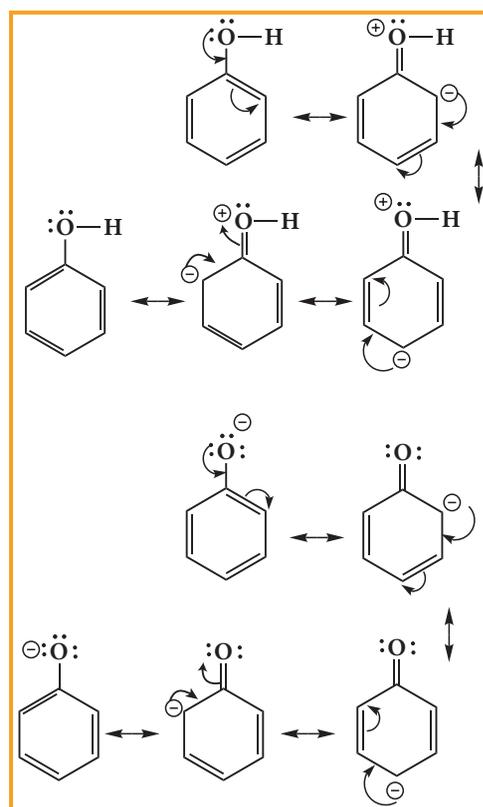
Positive resonance effect occurs, when the electrons move away from substituent attached to the conjugated system. It occurs, if the electron releasing substituents are attached to the conjugated system. In such cases, the attached group has a tendency to release electrons through resonance. These electron releasing groups are usually denoted as +R or +M groups. **Examples :** -OH, -SH, -OR, -SR, -NH₂, -O- etc.

Negative Mesomeric Effect

Negative resonance effect occurs, when the electrons move towards the substituent attached to the conjugated system. It occurs if the electron withdrawing

substituents are attached to the conjugated system. In such cases, the attached group has a tendency to withdraw electrons through resonance. These electron withdrawing groups are usually denoted as -R or -M groups. **Examples :** NO₂, >C=O, -COOH, -C≡N etc

Resonance is useful in explaining certain properties such as acidity of phenol. The phenoxide ion is more stabilised than phenol by resonance effect (+M effect) and hence resonance favours ionisation of phenol to form H⁺ and shows acidity.



The above structures shows that there is a charge separation in the resonance structure of phenol which needs energy, whereas there is no such hybrid structures in the case of phenoxide ion. This increased stability accounts for the acidic character of phenol.

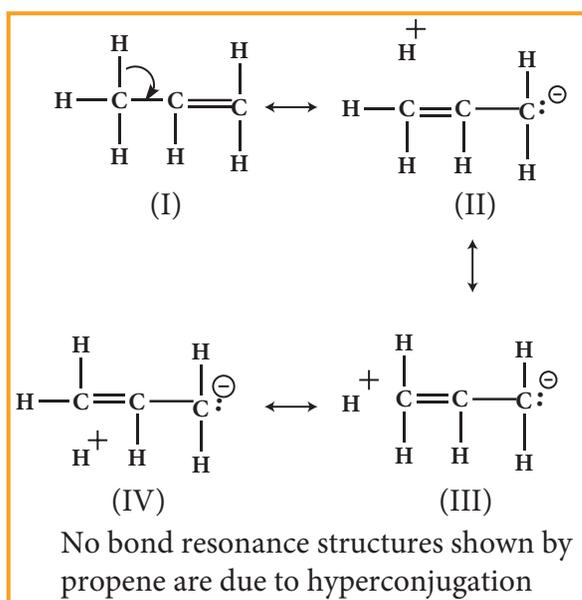
Hyper conjugation

The delocalisation of electrons of σ bond is called as hyper conjugation. It is a special stabilising effect that results due to the interaction of electrons of a σ -bond (usually C-H or C-C) with the adjacent, empty non-bonding p-orbital or an anti-bonding σ^* or π^* -orbitals resulting in an extended molecular orbital. Unlike electromeric effect, hyper conjugation is a permanent effect.

It requires an α -CH group or a lone pair on atom like N, O adjacent to a π bond (sp^2 hybrid carbon). It occurs by the overlapping of the σ -bonding orbital or the orbital containing a lone pair with the adjacent π -orbital or p-orbital.

Example 1:

In propene, the σ -electrons of C-H bond of methyl group can be delocalised into the π -orbital of doubly bonded carbon as represented below.

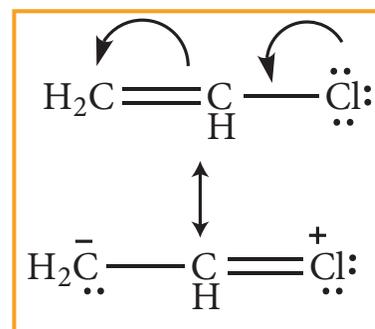


In the above structure the sigma bond is involved in resonance and breaks in

order to supply electrons for delocalisation giving rise to 3 new canonical forms. In the contributing canonical structures: (II), (III) & (IV) of propene, there is no bond between an α -carbon and one of the hydrogen atoms. Hence the hyperconjugation is also known as “no bond resonance” or “Baker-Nathan effect”. The structures (II), (III) & (IV) are polar in nature.

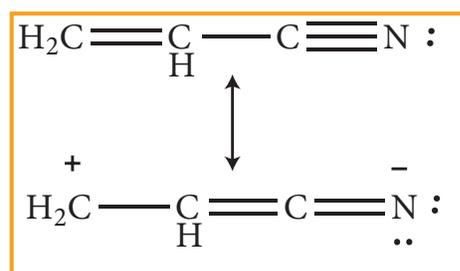
Example 2:

Hyper conjugation effect is also observed when atoms / groups having lone pair of electrons are attached by a single bond, and in conjugation with a π bond. The lone pair of electrons enters into resonance and displaces π electrons resulting in more than one structure



Example 3:

When electronegative atoms or group of atoms are in conjugation with a π -bond, they pull π -electrons from the multiple bond.



In case of carbocations, greater the number of alkyl groups attached to the

carbon bearing positive charge, greater is number of the hyper conjugate structure. thus the stability of various carbocations decreases in the order

3° Carbocation > 2° Carbocation > 1° Carbocation

12.2 Different types of organic reactions

Organic compounds undergo many number of reactions, however in actual sense we can fit all those reactions into the below mentioned six categories.

- Substitution reactions
- Addition reactions
- Elimination reactions
- Oxidation and reduction reactions
- Rearrangement reactions
- Combination of the above

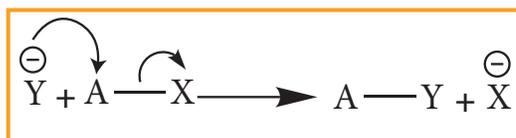
12.2.1 Substitution reaction (Displacement reaction)

In this reaction an atom or a group of atoms attached to a carbon atom is replaced by a new atom or a group of atoms. Based on the nature of the attacking reagent, this reactions can be classified as

- Nucleophilic substitution
- Electrophilic substitution
- Free radical substitution

Nucleophilic substitution:

This reaction can be represented as



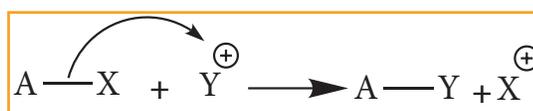
Here Y^- is the incoming nucleophile or attacking species and X^- is the leaving group.

Example: Hydrolysis of alkyl halides



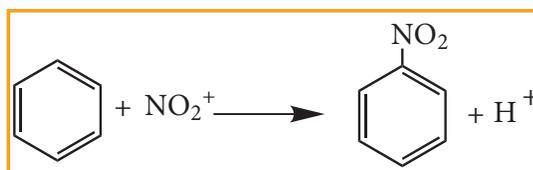
Aliphatic nucleophilic substitution reactions take place either by S_N1 or S_N2 mechanism. Detailed study of the mechanisms is given in unit 14.

Electrophilic Substitution



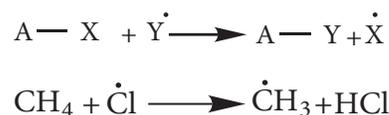
Here Y^+ is an electrophile

Example: Nitration of Benzene



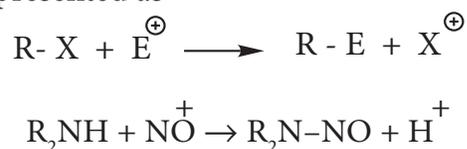
Mechanism of aromatic electrophilic substitution reactions (EAS) is discussed in detail in unit 13.

Free radical substitution



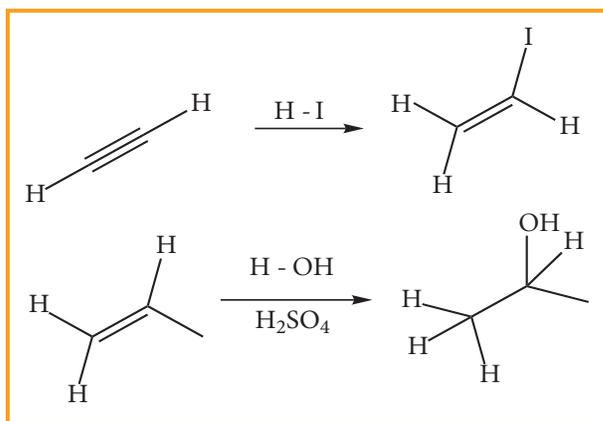
Aliphatic electrophilic substitution

A general aliphatic electrophilic substitution is represented as



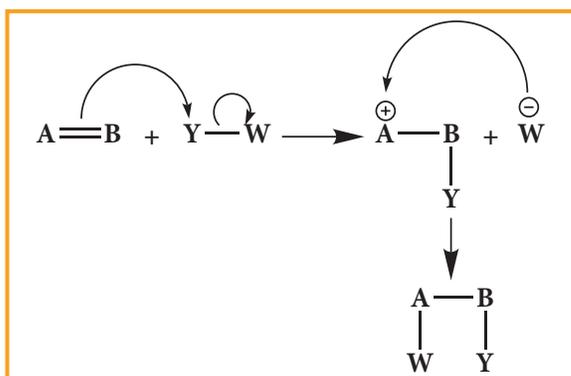
12.2.2 Addition reactions

It is a characteristic reaction of an unsaturated compound (compounds containing C-C localised double or triple bond). In this reaction two molecules combine to give a single product. Like substitution this reaction also can be classified as nucleophilic, electrophilic and freeradical addition reactions depending the type of reagent which initiates the reaction. During the addition reaction the hybridisation of the substrate changes (from $sp^2 \rightarrow sp^3$ in the addition reaction of alkenes or $sp \rightarrow sp^2$ in the addition reaction of alkynes) as only one bond breaks and two new bonds are formed.

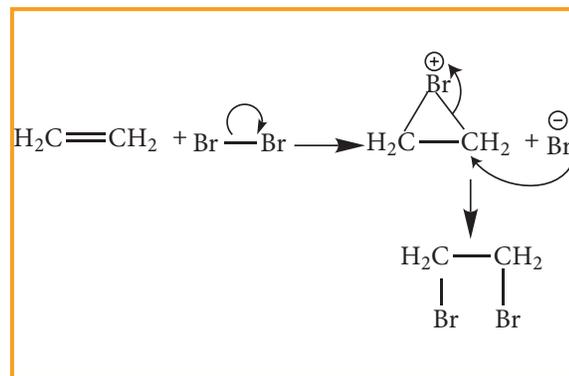


Electrophilic Addition reaction

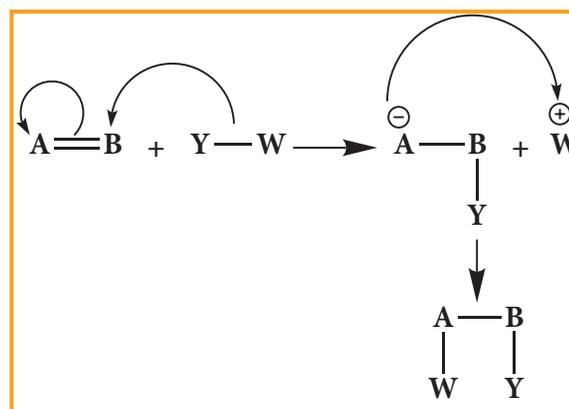
A general electrophilic addition reaction can be represented as below.



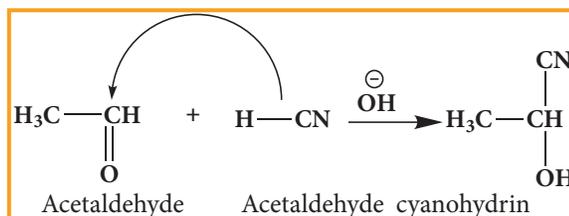
Bromination of alkene to give bromo alkane is an example for this reaction.



Nucleophilic addition reaction

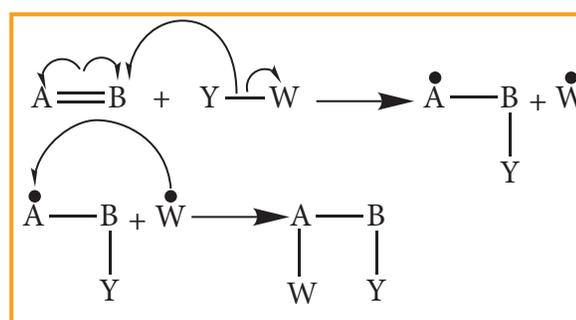


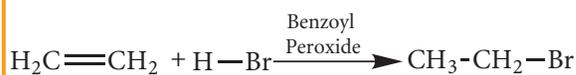
Example: addition of HCN to acetaldehyde



Free radical addition Reaction:

A General freeradical addition reaction can be represented as below.



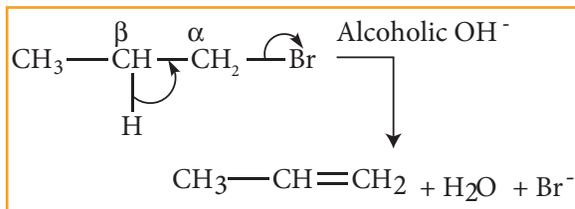


In the above reaction, Benzoyl peroxide acts as a radical initiator. The mechanism involves free radicals.

Elimination reactions:

In this reaction two substituents are eliminated from the molecule, and a new C=C double bond is formed between the carbon atoms to which the eliminated atoms/groups are previously attached. Elimination reaction is always accompanied with change in hybridisation.

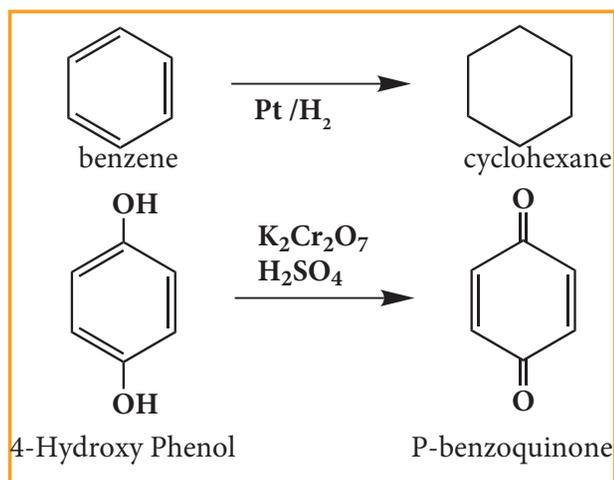
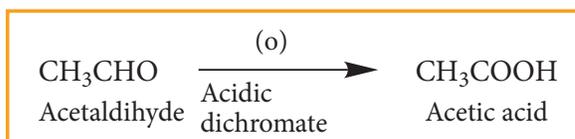
Example: n-Propyl bromide on reaction with alcoholic KOH gives propene. In this reaction hydrogen and Br are eliminated.



Oxidation and reduction reactions:

Many oxidation and reduction reactions of organic compounds fall into one of the four types of reaction that we already discussed but others do not. Most of the oxidation reaction of organic compounds involves gain of oxygen or loss of hydrogen. Reduction involves gain of hydrogen and loss of oxygen.

Examples:

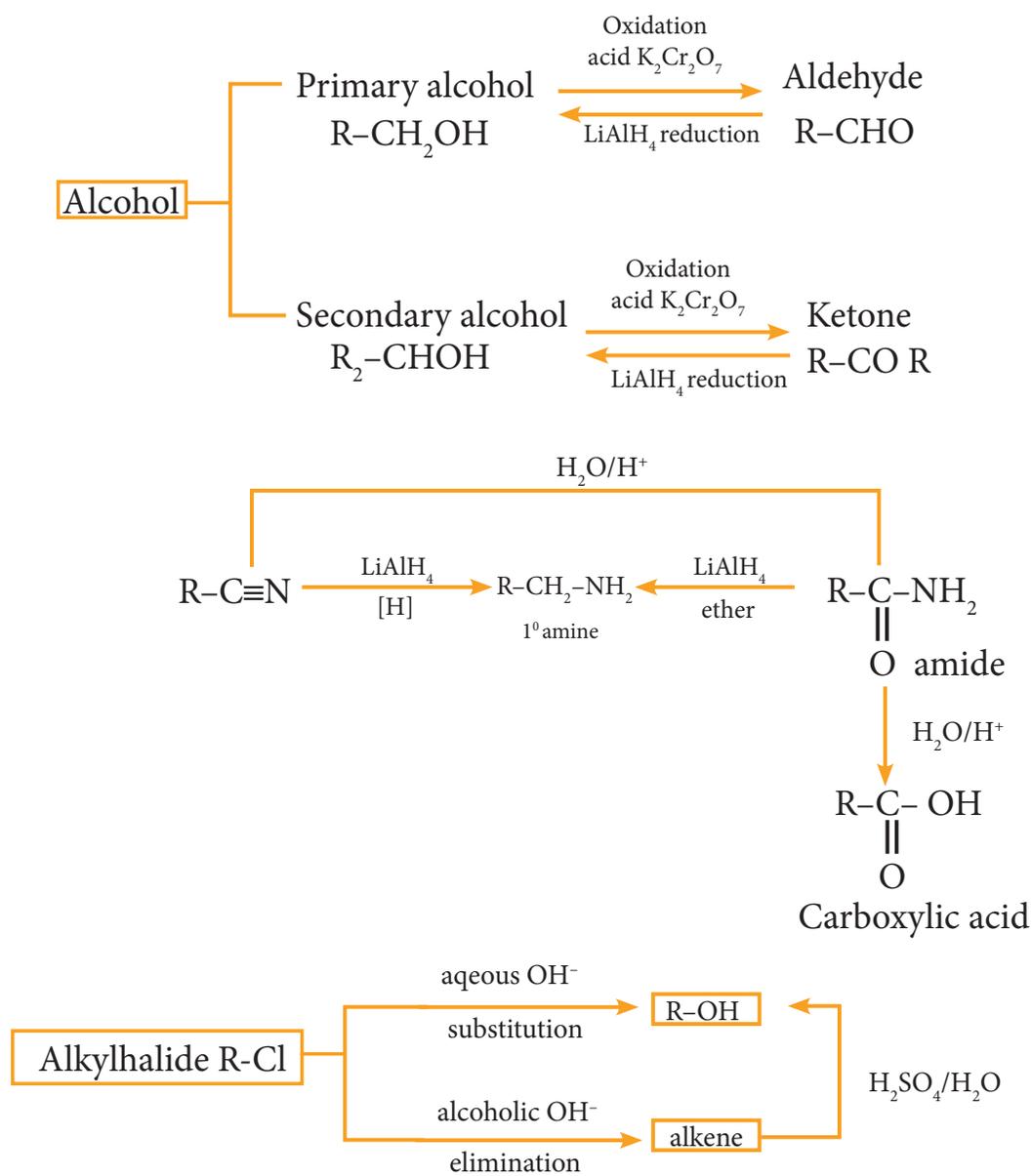


Apples contain an enzyme called polyphenol oxidase (PPO), also known as tyrosinase. Cutting an apple exposes its cells to the atmospheric oxygen and oxidizes the phenolic compounds present in apples. This is called the enzymatic browning that turns a cut apple brown. In addition to apples, enzymatic browning is also evident in bananas, pears, avocados and even potatoes

12.3 Functional Group inter conversion

Organic synthesis involves functional group inter conversions. A particular functional group can be converted into other functional group by reacting it with suitable reagents. For example: The carboxylic acid group (-COOH) presents in organic acids can be transformed to a variety of other functional group such as -CH₂-OH, -CONH₂, -COCl by treating the acid with LiAlH₄, NH₃ and SOCl₂ respectively.

Some of the important functional group interconversions of Organic compounds are summarised in the below mentioned Flow chart.

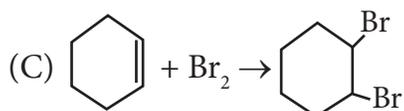
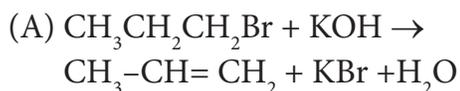


Evaluation



I. Choose the best answer.

1. For the following reactions



Which of the following statement is correct?

- (a) (A) is elimination, (B) and (C) are substitution
- (b) (A) is substitution, (B) and (C) are elimination
- (c) (A) and (B) are elimination and (C) is addition reaction
- (d) (A) is elimination, B is substitution and (C) is addition reaction.
2. What is the hybridisation state of benzyl carbonium ion?
- (a) sp^2 (b) sp^{d^2}
(c) sp^3 (d) sp^{d}
3. Decreasing order of nucleophilicity is
- (a) $\text{OH}^- > \text{NH}_2^- > ^-\text{OCH}_3 > \text{RNH}_2$
(b) $\text{NH}_2^- > \text{OH}^- > ^-\text{OCH}_3 > \text{RNH}_2$
(c) $\text{NH}_2^- > \text{CH}_3\text{O}^- > \text{OH}^- > \text{RNH}_2$
(d) $\text{CH}_3\text{O}^- > \text{NH}_2^- > \text{OH}^- > \text{RNH}_2$
4. Which of the following species is not electrophilic in nature?
- (a) Cl^+ (b) BH_3 (c) H_3O^+ (d) $^+\text{NO}_2$

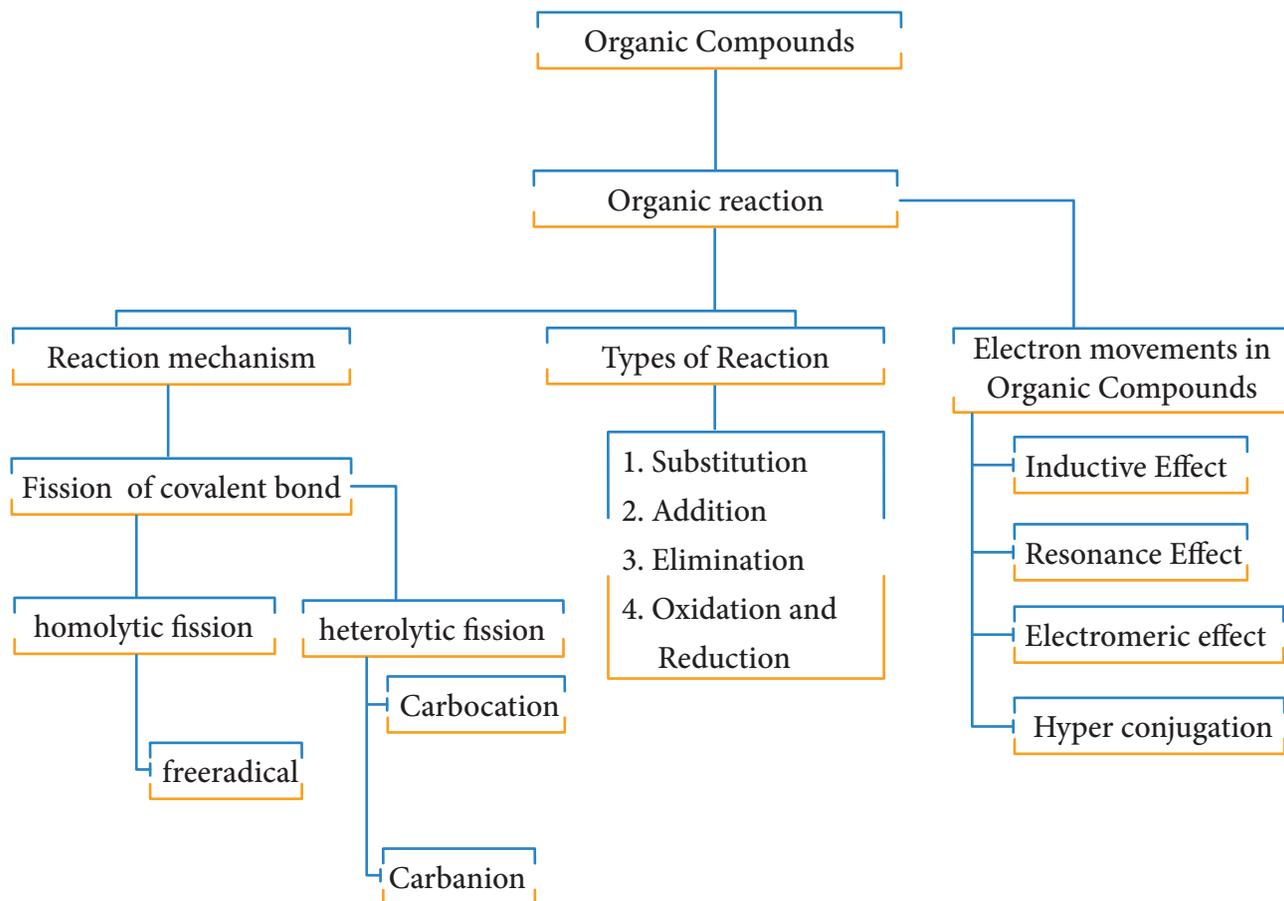
5. Homolytic fission of covalent bond leads to the formation of
- (a) electrophile (b) nucleophile
(c) Carbo cation (d) free radical
6. Hyper Conjugation is also known as
- (a) no bond resonance
(b) Baker - nathan effect
(c) both (a) and (b)
(d) none of these
7. Which of the group has highest +I effect?
- (a) $\text{CH}_3\text{-}$ (b) $\text{CH}_3\text{-CH}_2\text{-}$
(c) $(\text{CH}_3)_2\text{-CH-}$ (d) $(\text{CH}_3)_3\text{-C-}$
8. Which of the following species does not exert a resonance effect?
- (a) $\text{C}_6\text{H}_5\text{OH}$ (b) $\text{C}_6\text{H}_5\text{Cl}$
(c) $\text{C}_6\text{H}_5\text{NH}_2$ (d) $\text{C}_6\text{H}_5\text{NH}_3^+$
9. -I effect is shown by
- (a) -Cl (b) -Br
(c) both (a) and (b) (d) -CH_3
10. Which of the following carbocation will be most stable?
- (a) Ph_3C^+ (b) $\text{CH}_3\text{-}\overset{+}{\text{C}}\text{H}_2\text{-}$
(c) $(\text{CH}_3)_2\text{-}\overset{+}{\text{C}}\text{H}$ (d) $\text{CH}_2=\text{CH-}\overset{+}{\text{C}}\text{H}_2$
11. Assertion: Tertiary Carbocations are generally formed more easily than primary Carbocations ions.
- Reason: Hyper conjugation as well as inductive effect due to additional alkyl group stabilize tertiary carbonium ions.



- (a) both assertion and reason are true and reason is the correct explanation of assertion.
- (b) both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) Assertion is true but reason is false
- (d) Both assertion and reason are false
12. Heterolytic fission of C–C bond results in the formation of
- (a) free radical (b) Carbanion
- (c) Carbocation (d) Carbanion and Carbocation
13. Which of the following represent a set of nucleophiles?
- (a) BF_3 , H_2O , NH_2^-
- (b) AlCl_3 , BF_3 , NH_3
- (c) CN^- , RCH_2^- , ROH
- (d) H^+ , RNH_3^+ , $:\text{CCl}_2$
14. Which of the following species does not act as a nucleophile?
- (a) ROH (b) ROR
- (c) PCl_3 (d) BF_3
15. The geometrical shape of carbocation is
- (a) Linear (b) tetrahedral
- (c) Planar (d) Pyramidal
- II. Write brief answer to the following questions.**
16. Write short notes on
- (a) Resonance
- (b) Hyperconjugation
17. What are electrophiles and nucleophiles? Give suitable examples for each.
18. Show the heterolysis of covalent bond by using curved arrow notation and complete the following equations. Identify the nucleophile in each case.
- (i) $\text{CH}_3 - \text{Br} + \text{KOH} \rightarrow$
- (ii) $\text{CH}_3 - \text{OCH}_3 + \text{HI} \rightarrow$
19. Explain inductive effect with suitable example.
20. Explain electromeric effect.
21. Give examples for the following types of organic reactions
- (i) β - elimination
- (ii) electrophilic substitution.



CONCEPT MAP





Learning Objectives



CHARLES ADOLPHE WURTZ

He is a French organic Chemist. He discovered phosphoryl chlorides. He showed that alkylhalides react with sodium to produce higher alkanes. This reaction was later named as Wurtz reaction. He is also known for his discoveries of ethylamine glycol and aldol condensation reactions.

After studying this unit, the students will be able to

- classify hydrocarbons according to nature of bond between the carbon atoms.
- name hydrocarbons according to IUPAC system of nomenclature.
- describe various methods of preparing hydrocarbon.
- interpret and use the following terminology in organic chemistry like free radicals, initiation, propagation and termination.
- describe chemistry of alkanes by the following reaction of halogenations, combustion, cracking.
- predict the formation of addition products of unsymmetrical alkenes which applies both Markovnikov's rule and peroxide effect.
- deduce acidic hydrogen in alkynes.
- comprehend the structure of benzene, explain aromaticity and understand mechanism of electrophilic substitutions reactions.
- predict the directive influence of substituents on mono substituted benzene.
- recognize the toxicity and carcinogenic nature of aromatic hydrocarbons.

Introduction

The hydrocarbons are compounds composed entirely of Carbon and Hydrogen. They occur widely in nature. The crude oil consists of complex mixtures of hydrocarbons, mangoes contain cyclohexane, a cyclic hydrocarbon, cockroaches secrete a hydrocarbon, undecane which attracts opposite gender of its species. Hydrocarbons are primarily used as fuel. For example, Liquefied mixture of propane and butane is used as Liquefied petroleum gas (LPG). They also find many applications in industries such as solvents etc. In this unit we will study the classification, preparation, properties and uses of aliphatic and aromatic hydrocarbons.

13.1 Introduction and classification of alkanes:

Depending upon the characteristic pattern of bonding between the carbon atoms, hydrocarbons are divided into two main classes: aliphatic and aromatic. The word aliphatic was derived from the Greek word 'aleiphar' meaning fat. Important sources of aliphatic hydrocarbons are oils and fats. The word 'aroma' means odour, which is obtained by chemical treatment of pleasant-smelling plant extracts.

Aliphatic hydrocarbons include three major groups: alkanes, alkenes and alkynes. Alkanes are saturated hydrocarbons in which all the bonds between the carbon atoms are single bonds, alkenes consist of at least one carbon-carbon double bond, and alkynes have at least one carbon-carbon triple bond. Hydrocarbons having localised carbon-carbon multiple bonds are called unsaturated hydrocarbons.

Aromatic hydrocarbons are cyclic compounds which contain characteristic benzene ring or its derivatives. The classification of hydrocarbons is as shown below.

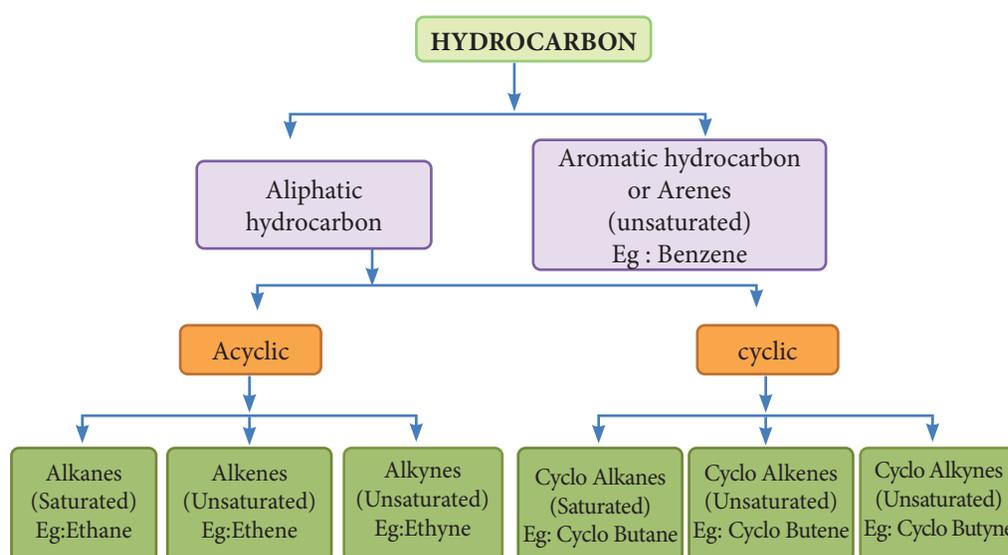


Fig.13.1. Classification of Hydrocarbons

13.2. Alkanes:

Alkanes are saturated hydrocarbons represented by the general formula C_nH_{2n+2} where 'n' is the number of carbon atoms in the molecule. Methane CH_4 , is the first member of alkane family. The successive members are ethane C_2H_6 , propane C_3H_8 , butane C_4H_{10} , pentane C_5H_{12} and so on. It is evident that each member differs from its preceding or succeeding member by a $-CH_2$ group.

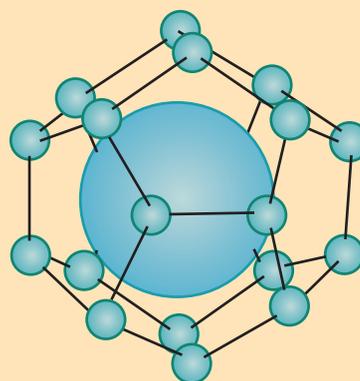
**DO
YOU
KNOW?**

Methane is the major component of the atmosphere of Jupiter, Saturn, Uranus and Neptune but only minor component of earth atmosphere. However, decomposition of plant and animal matter in an oxygen deficient environment like swamps, marshes, bogs and the sediments of lakes produces methane gas. So, it is otherwise known as marsh gas. It is also associated with coal and petroleum deposits.

**DO
YOU
KNOW?**

“FLAMMABLE ICE”

This catchy phrase describes a frozen mixture of water and methane gas chemically known as methane clathrates. The methane molecule which is produced by biological process under the deep-ocean, (at $4^\circ C$ & 50 atm) doesn't simply reach the surface, instead each molecule is trapped inside clusters of 6 to 18 water molecules forming methane clathrates. Many countries are working on how to tap out these vast resources of natural gas but mining and extracting are very difficult.

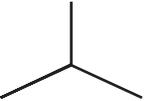


Nomenclature and isomerism:

We have already discussed the nomenclature of organic compound in Unit:11. Let us understand the nomenclature and isomerism in few examples. The first three members methane CH_4 , ethane C_2H_6 and propane C_3H_8 have only one structure.

IUPAC Name	Molecular Formula	Condensed Structural formula
Methane	CH ₄	CH ₄
Ethane	C ₂ H ₆	CH ₃ -CH ₃
Propane	C ₃ H ₈	CH ₃ -CH ₂ -CH ₃

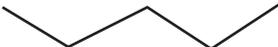
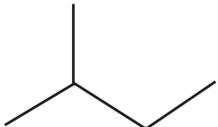
However, higher members can have more than one structure leading to constitutional isomers (differ in connectivity) or structural isomers. For example, an alkane with molecular formula C₄H₁₀ can have two structures. They are n-butane and iso-butane. In n-butane, all the four carbon atoms are arranged in a continuous chain. The 'n' in n-butane stand for 'normal' and means that the carbon chain is unbranched. The second isomer iso-butane has a branched carbon chain. The word iso indicates it is an isomer of butane.

Molecular Formula	Structural Formula	Bond line Formula	IUPAC name	Common Name
C ₄ H ₁₀	CH ₃ -CH ₂ -CH ₂ -CH ₃		butane	n-butane
	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{CH}_3 \end{array}$		2-methylpropane	iso-butane

Though both the structures have same molecular formula but their carbon chains differ leading to chain isomerism

Let us understand the chain isomerism by writing the isomers of pentane C₅H₁₂

Solution:

To begin, draw the carbon backbone of the straight chain-isomer	C—C—C—C—C
Determine the carbon backbone structure of the other isomers by arranging the carbon atoms in the other way	$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array} \quad \begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$
Fill in all the hydrogen atoms so that each carbon forms four bonds	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 \quad \begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_3 \\ \\ \text{CH}_3 \end{array} \quad \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$
	  

Evaluate Yourself

1) Write the structural formula and carbon skeleton formula for all possible chain isomers of C_6H_{14} (Hexane)

IUPAC name for some branched alkanes

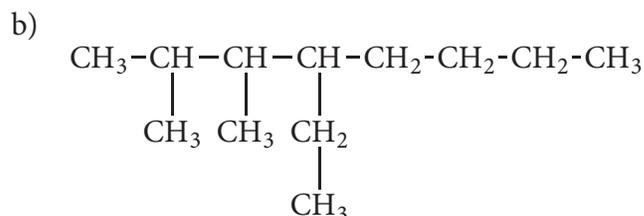
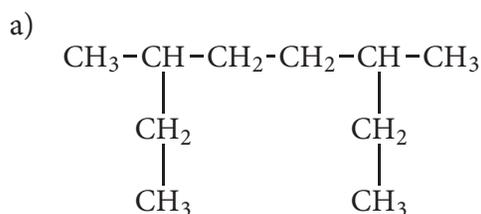
Let us write the IUPAC name for the below mentioned alkanes by applying the general rules of nomenclature that we already discussed in unit No.11

S.NO	COMPOUND	IUPAC NAME
1	$ \begin{array}{cccccc} & 5 & 4 & 3 & 2 & 1 \\ & \text{CH}_3 & -\text{CH}_2 & -\text{CH}_2 & -\text{CH} & -\text{CH}_3 \\ & & & & & \\ & & & & \text{CH}_3 & \end{array} $	2- Methyl pentane
2	$ \begin{array}{cccccc} \text{CH}_3 & -\text{CH} & -\text{CH}_2 & -\text{CH} & -\text{CH}_3 \\ 1 & 2 & 3 & 4 & 5 \\ & & & & \\ & \boxed{\text{CH}_3} & & \boxed{\text{CH}_3} & \end{array} $	2,4- Dimethyl pentane
3	$ \begin{array}{cccccc} & & & \boxed{\text{CH}_3} & & \\ & & & & & \\ \text{CH}_3 & -\text{CH}_2 & -\text{C} & -\text{CH}_2 & -\text{CH}_3 \\ 1 & 2 & 3 & 4 & 5 \\ & & & & \\ & & \boxed{\text{CH}_3} & & \end{array} $	3,3- Dimethyl pentane
4	$ \begin{array}{cccccc} \text{CH}_3 & -\text{CH} & -\text{CH} & -\text{CH}_2 & -\text{CH}_3 \\ 1 & 2 & 3 & 4 & 5 \\ & & & & \\ & \text{CH}_3 & \text{CH}_2 & & \\ & & & & \\ & & \text{CH}_3 & & \end{array} $	3-Ethyl-2-methylpentane
5	$ \begin{array}{cccccccc} \text{CH}_3 & -\text{CH}_2 & -\text{CH} & -\text{CH} & -\text{CH} & -\text{CH}_2 & -\text{CH}_2 & -\text{CH}_3 \\ 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\ & & & & & & & \\ & & \boxed{\text{CH}_2} & \boxed{\text{CH}_2} & \text{CH}_2 & & & \\ & & & & & & & \\ & & \text{CH}_3 & \text{CH}_2 & \text{CH}_2 & & & \\ & & & & & & & \\ & & & \text{CH}_3 & \text{CH}_3 & & & \end{array} $	3-Ethyl-4,5-dipropyl octane
6	$ \begin{array}{cccc} \text{CH}_3 & -\text{CH} & -\text{CH} & -\text{CH}_3 \\ & & & \\ & \text{CH}_2 & \text{CH}_3 & \\ & & & \\ & \text{CH}_3 & & \end{array} $	2,3 - Dimethylpentane

7	$\begin{array}{ccccccc} \text{CH}_3 & -\text{CH} & -\text{CH}_2 & -\text{CH}_2 & -\text{CH} & -\text{CH}_2 & -\text{CH} & -\text{CH}_3 \\ & & & & & & & \\ & \text{CH}_3 & & & \text{CH}_2 & & \text{CH}_3 & \\ & & & & & & & \\ & & & & \text{CH}_3 & & & \end{array}$	4 - Ethyl - 2,7 - Dimethyloctane
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Evaluate Yourself

2) Give the IUPAC name for the following alkane.



How to draw structural formula for given IUPAC name :

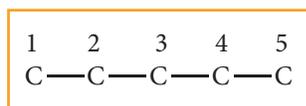
After you learn the rules for naming alkanes, it is relatively easy to reverse the procedure and translate the name of an alkane into a structural formula. The example below show how this is done.

Let us draw the structural formula for

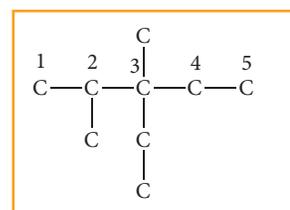
a) 3-ethyl-2,3-dimethyl pentane

Solution:

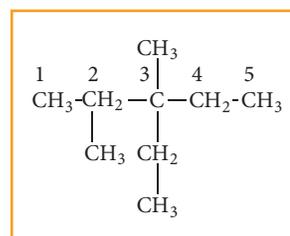
Step: 1 The parent hydrocarbon is pentane. Draw the chain of five carbon atoms and number it.



Step :2 Complete the carbon skeleton by attaching the alkyl group as they are specified in the name. An ethyl group is attached to carbon 3 and two methyl groups are attached to carbon 2 and 3.



Step: 3 Add hydrogen atoms to the carbon skeleton so that each carbon atoms has four bonds



Evaluate Yourself

3) Draw the structural formula for 4,5-diethyl -3,4,5- trimethyl octane

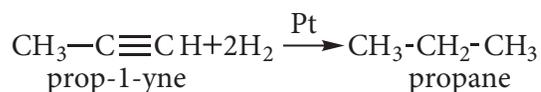
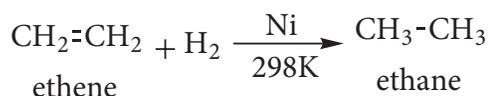
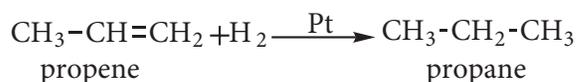
13.2.1 Preparation of alkanes:

Alkanes are not laboratory curiosities but they are extremely important naturally occurring compounds. Natural gas and petroleum (crude oil) are the most important natural sources. However, it can be prepared by the following methods.

1. Preparation of alkanes from catalytic reduction of unsaturated hydrocarbons.

When a mixture hydrogen gas with alkene or alkyne gas is passed over a catalysts such as platinum or palladium at room temperature, an alkane is produced. This process of addition of H_2 to unsaturated compounds is known as hydrogenation. The above process can be catalysed by nickel at 298K. This reaction is known as Sabatier-Sendersens reaction

for example:

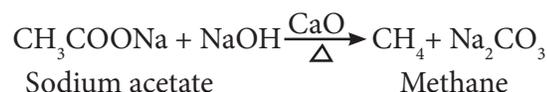


2. Preparation of alkanes from carboxylic acids:

i) Decarboxylation of sodium salt of carboxylic acid

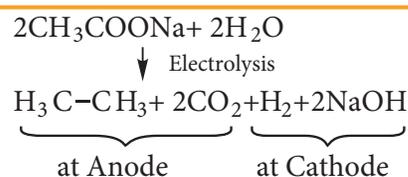
When a mixture of sodium salt of carboxylic acid and soda lime (sodium hydroxide + calcium oxide) is heated, alkane is formed. The alkane formed has one carbon atom less than carboxylic acid. This process of eliminating carboxylic group is known as decarboxylation.

for example:



ii) Kolbe's Electrolytic method

When sodium or potassium salt of carboxylic acid is electrolyzed, a higher alkane is formed. The decarboxylative dimerization of two carboxylic acid occurs. This method is suitable for preparing symmetrical alkanes (R-R).

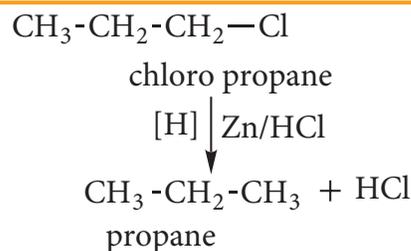


3. Preparation of alkanes using alkyl halides (or) halo alkanes

i) By reduction with nascent hydrogen

Except alkyl fluorides, other alkyl halides can be converted to alkanes by reduction with nascent hydrogen. The hydrogen for reduction may be obtained by using any of the following reducing agents: $\text{Zn} + \text{HCl}$, $\text{Zn} + \text{CH}_3\text{COOH}$, Zn-Cu couple in ethanol, LiAlH_4 etc.,

for example:

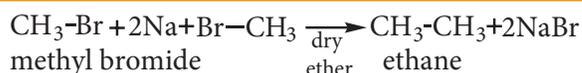


ii) Wurtz reaction

When a solution of halo alkanes in dry ether is treated with sodium metal,

higher alkanes are produced. This reaction is used to prepare higher alkanes with even number of carbon atoms.

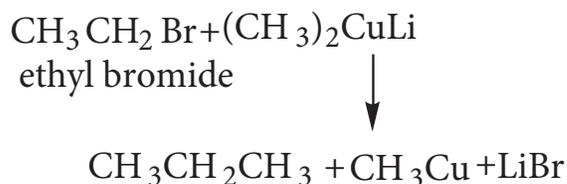
for example:



iii) Corey- House Mechanism

An alkyl halide and lithium dialkyl copper are reacted to give higher alkane.

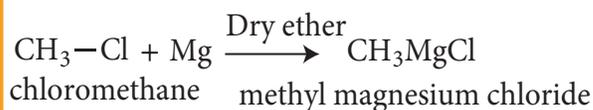
for example:



4) Preparation of Alkanes from Grignard reagents

Halo alkanes reacts with magnesium in the presence of dry ethers to give alkyl magnesium halide which is known as Grignard reagents. Here the alkyl group is directly attached to the magnesium metal make it to behave as carbanion. So, any compound with easily replaceable hydrogen reacts with Grignard reagent to give corresponding alkanes.

for example:

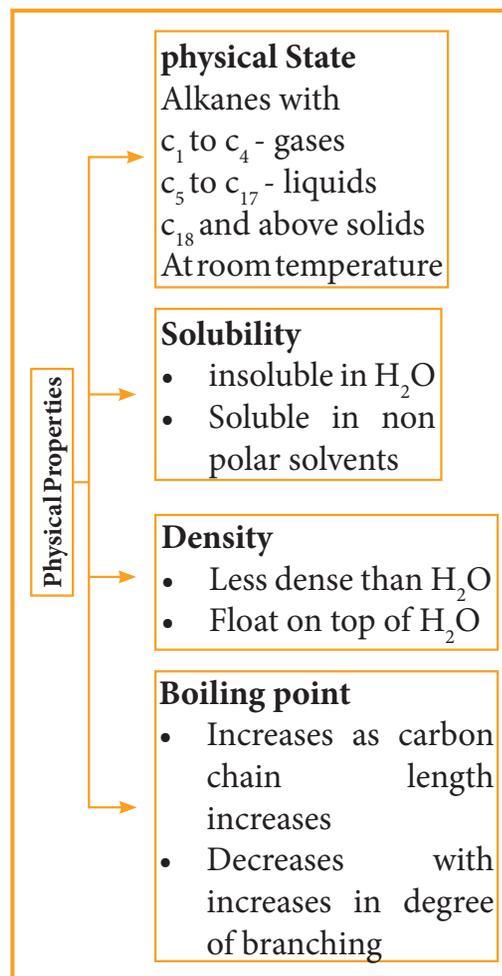


Evaluate Yourself



- 4) Water destroys Grignard reagents why?
- 5) Is it possible to prepare methane by Kolbe's Electrolytic method

13.2.2 Physical Properties:



1) Boiling Point and Physical state

The boiling point of continuous chain alkanes increases with increases in length of carbon chain roughly about 30°C for every added carbon atom to the chain. Being non polar, alkanes have weak Vanderwal's force which depends upon molecular surface area and hence increases with increase molecular size. We observe that with same number of carbon atoms, straight chain isomers have

higher boiling point compared to branch chain isomers. The boiling point decreases with increase in branching as the molecule becomes compact and the area of the contact decreases.

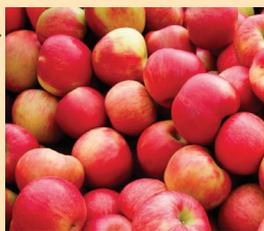
2) Solubility and density

Water molecules are polar and alkanes are non-polar. The insolubility of alkanes in water makes them good water repellent for metals which protects the metal surface from corrosion. Because of their lower density than water, they form two layers and occupy top layer. The density difference between alkanes and water explains why oil spills in aqueous environment spread so quickly.



Apples produce its own wax which contains long unbranched alkanes ($C_{27}H_{56}$ and $C_{29}H_{60}$).

This natural wax helps the apple to resist moisture lost, enhances the fruit firmness and slows down its natural degradation. The consumption of apple with artificial wax coating is harmful to the digestive system

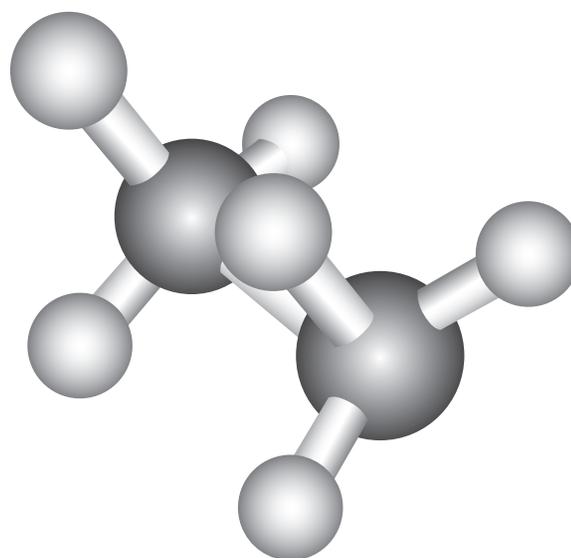


infinite number of readily interconvertible three dimensional arrangements. Such readily interconvertible three dimensional arrangement of a molecule is called conformations.

(i) Conformations of ethane:

The two tetrahedral methyl groups can rotate about the carbon – carbon bond axis yielding several arrangements called conformers. The extreme conformations are staggered and eclipsed conformation. There can be number of other arrangements between staggered and eclipsed forms and their arrangements are known as skew forms.

Eclipsed conformation:

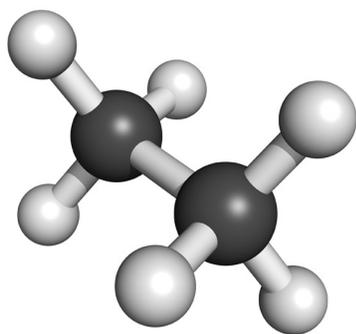


In this conformation, the hydrogen's of one carbon are directly behind those of the other. The repulsion between the atoms is maximum and it is the least stable conformer.

13.2.3 Conformations of alkane:

Each carbon in alkanes is sp^3 hybridized and the four groups or atoms around the carbon are tetrahedrally bonded. In alkanes having two or more carbons, there exists free rotation about C-C single bond. Such rotation leaves all the groups or atoms bonded to each carbon into an

Staggered conformation:



In this conformation, the hydrogens of both the carbon atoms are far apart from each other. The repulsion between the atoms is minimum and it is the most stable conformer.

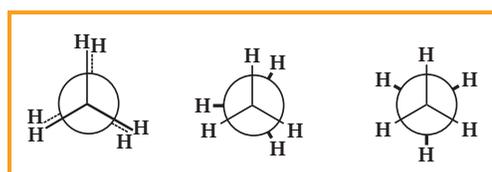
Skew Conformation :

The infinite numbers of possible intermediate conformations between the two extreme conformations are referred as skew conformations.

The stabilities of various conformations of ethane are

Staggered > Skew > Eclipsed

The potential energy difference between the staggered and eclipsed conformation of ethane is around 12.5 KJmol^{-1} . The various conformations can be represented by new man projection formula.



Eclipsed Skew Staggered

Newman projection formula for Ethane

Conformations of n-Butane:

n-Butane may be considered as a derivative of ethane, as one hydrogen

on each carbon is replaced by a methyl group

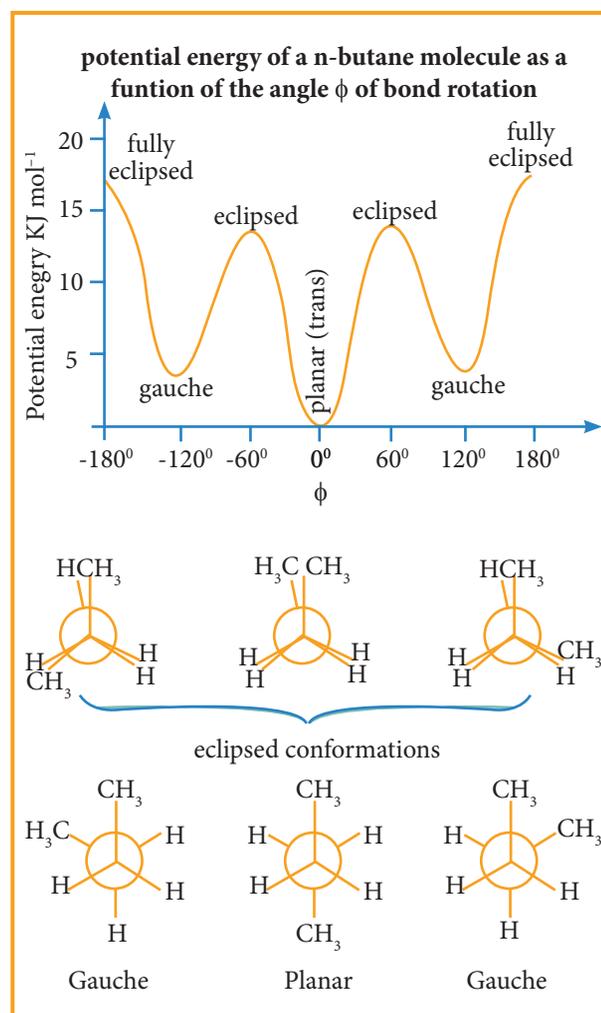
Eclipsed conformation:

In this conformation, the distance between the two methyl group is minimum. So there is maximum repulsion between them and it is the least stable conformer.

Anti or staggered form

In this conformation, the distance between the two methyl groups is maximum and so there is minimum repulsion between them. And it is the most stable conformer.

The following potential energy diagram shows the relative stabilities of various conformers of n-butane.



13.2.4 Chemical properties:

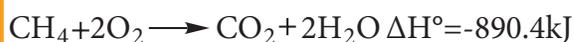
Alkanes are quite unreactive towards most reagents. However under favorable conditions, alkanes undergo the following type of reaction.

Paraffin is the older name for the alkane group family of compounds. This name comes from the Latin which means 'little activity'

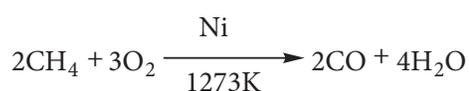
1) Combustion:

A combustion reaction is a chemical reaction between a substance and oxygen with evolution of heat and light (usually as a flame). In the presence of sufficient oxygen, alkanes undergo combustion when ignited and produce carbon dioxide and water.

for example:



When alkanes burn in insufficient supply of oxygen, they form carbon monoxide and carbon black.



Evaluate Yourself

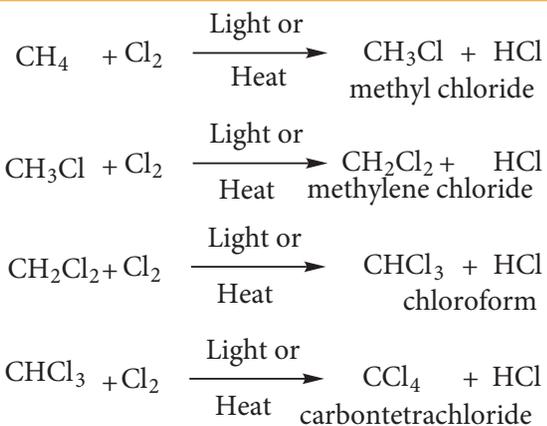
6) Write down the combustion reaction of propane whose $\Delta H^\circ = -2220 \text{ kJ}$

2) Halogenation:

Halogenation reaction is the chemical reaction between an alkane and halogen

in which one or more hydrogen atoms are substituted by the halogens.

Chlorination and Bromination are two widely used halogenation reactions. Fluorination is too quick and iodination is too slow. Methane reacts with chlorine in the presence of light or when heated as follows.



Mechanism:

The reaction proceeds through the free radical chain mechanism. This mechanism is characterized by three steps: initiation, propagation and termination.

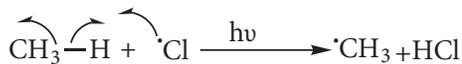
i) **CHAIN INITIATION:** The chain is initiated by UV light leading to homolytic fission of chlorine molecules into free radicals (chlorine atoms).



Here we choose Cl-Cl bond for fission because C-C & C-H bonds are stronger than Cl-Cl.

ii) **PROPAGATION:** It proceeds as follows,

(a) Chlorine free radical attacks the methane molecule and breaks the C-H bond resulting in the generation of methyl free radical



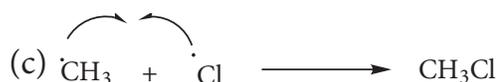
(b) The methyl free radical thus obtained attacks the second molecule of chlorine to give chloromethane (CH_3Cl) and a chlorine free radical as follows.



(c) This chlorine free radical then cycles back to step (a) and both step (a) and (b) are repeated many times and thus chain of reaction is set up.

iii) Chain termination:

After sometimes, the reactions stops due to consumption of reactant and the chain is terminated by the combination of free radicals.



Evaluate Yourself

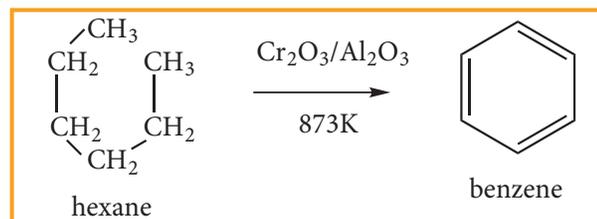
7) Why ethane is produced in chlorination of methane?

3) Aromatisation

Alkanes with six to ten carbon atoms are converted into homologous of benzene at high temperature and in the presence of catalyst. This process is known as aromatization. It occurs by simultaneous

cyclisation followed by dehydrogenation of alkanes.

n-Hexane passed over Cr_2O_3 supported on alumina at 873 K gives benzene.

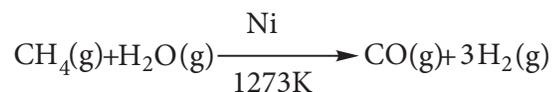


Evaluate Yourself

8) How toluene can be prepared by this method?

4) Reaction With Steam:

Methane reacts with steam at 1273K in the presence of Nickel and decomposes to form carbon monoxide and hydrogen gas.

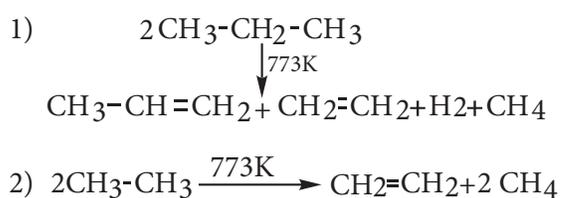


Production of H_2 gas from methane is known as steam reforming process and it is a well-established industrial process for the production of H_2 gas from hydrocarbons.

5) Pyrolysis

Pyrolysis is defined as the thermal decomposition of organic compound into smaller fragments in the absence of air through the application of heat. 'Pyro' means 'fire' and 'lysis' means 'separating'. Pyrolysis of alkanes also named as cracking.

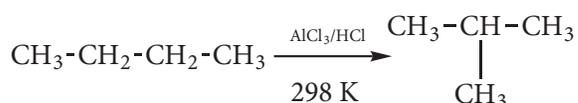
In the absence of air, when alkane vapours are passed through red-hot metal it breaks down into simpler hydrocarbons.



The products depends upon the nature of alkane, temperature, pressure and presence or absence of catalyst. The ease of cracking in alkanes increases with increase in molecular weight and branching in alkanes. Cracking plays an important role in petroleum industry.

6) Isomerisation:

Isomerisation is a chemical process by which a compound is transformed into any of its isomeric forms. Normal alkanes can be converted into branched alkanes in the presence of AlCl_3 and HCl at 298 k.



This process is of great industrial importance. The quality of gasoline is improved by isomerising its components.

Uses

The exothermic nature of alkane combustion reaction explains the extensive use of alkanes as fuels. Methane present in natural gas is used in home heating. Mixture of propane and butane are known as LPG gas which is used for domestic cooking purpose. GASOLINE is a complex mixture of many hydrocarbons used as a fuel for internal-combustion engines.

Carbon black is used in the manufacture of ink, printer ink and black pigments. It is also used as fillers.

No of Carbon Atoms	State at room temperature	Major uses
1-4	Gas	Heating fuel, Cooking fuel
5-7	Low boiling liquid	Solvents, Gasoline
6-12	Liquid	Gasoline
12-24	Liquid	Jet fuel- portable stove fuel
18-50	High boiling liquid	Diesel fuel, lubricant, heating oil
50+	Solid	Petroleum jelly and paraffin wax

13.3. Alkenes:

Alkenes are unsaturated hydrocarbons that contain carbon-carbon double bond. They are represented by the general formulae C_nH_{2n} where 'n' stands for number of carbon atoms in the molecule. Alkenes are also known as olefins (in Latin - oil maker) because the first member ethene combines with chlorine gas to form an oily liquid as a product.

(I) Nomenclature of Alkenes:

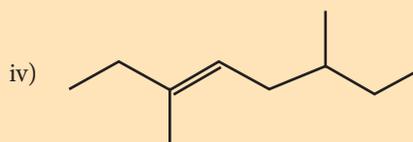
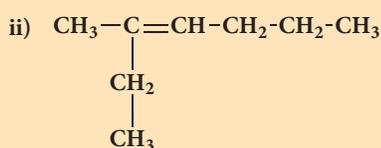
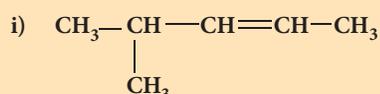
Let us write the IUPAC name for the below mentioned alkanes by applying the general rules of nomenclature that we already discussed in unit No.11

TAB 13.4 IUPAC NAMES FOR ALKENES

S No	Structure	IUPAC name
1	$\text{CH}_3-\text{CH}=\text{CH}_2$	propene
2	$\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$	but-1-ene
3	$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$	but-2-ene
4	$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	2-methyl prop-1-ene
5	$\begin{array}{cccccc} \text{CH}_2 & = & \text{CH} & - & \text{CH} & - & \text{CH}_2 & - & \text{CH}_3 \\ 1 & & 2 & & 3 & & 4 & & 5 \\ & & & & & & & & \\ & & & & \text{CH}_3 & & & & \end{array}$	3-methyl pent-1-ene

Evaluate Yourself

9. Write the IUPAC names for the following alkenes.



10. Draw the structures for the following alkenes.

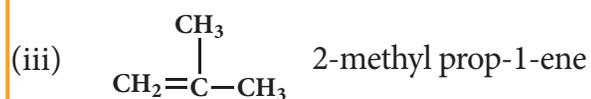
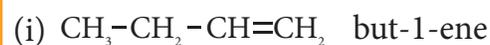
- 6-Bromo-2,3-dimethyl-2-hexene
- 5-Bromo-4-chloro-1-heptene
- 2,5-dimethyl-4-octene
- 4-Methyl-2-pentene

(ii) Isomerism:

Presence of double bond in Alkene provides the possibility of both structural and geometrical isomerism.

Structural Isomerism:

The first two member's ethene C_2H_4 and propene C_3H_6 do not have isomers because the carbon atoms in the molecules can be arranged only one distinct way. However from the third member of alkene family butene C_4H_8 , structural isomerism exists.



structures (i) & (ii) are position isomers. structures (i) & (iii), (ii) & (iii) are chain isomers.

Evaluate Yourself

11) Draw the structure and write down the IUPAC name for the isomerism exhibited by the molecular formulae:



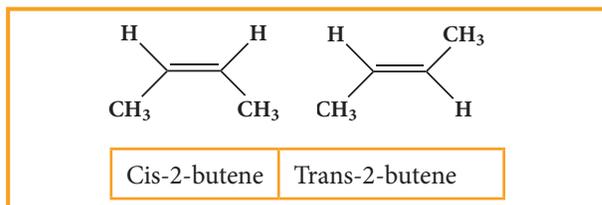
Geometrical isomerism:

It is a type of stereoisomerism and it is also called cis-trans isomerism. Such type of isomerism results due to the restricted rotation of doubly bounded carbon atoms.

If the similar groups lie on the same side, then the geometrical isomers are called Cis-isomers. When the similar groups lie on

the opposite side, it is called a Trans isomer.

for example: the geometrical isomers of 2-Butene is expressed as follows



Evaluate Yourself



12) Determine whether each of the following alkenes can exist in cis-trans isomers?

- (a) 1 - Chloro propene
- (b) 2 - Chloro propene

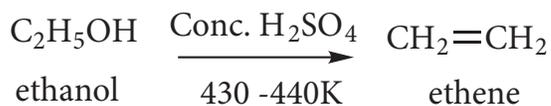
13) Draw cis-trans isomers for the following compounds

- (a) 2- chloro - 2 - butene
- (b) $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH}_3$

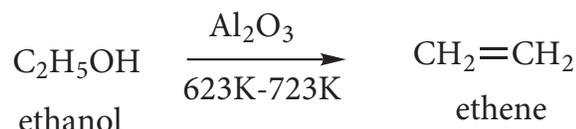
13.3.1: General methods of preparation of alkenes:

(1) Preparation of alkene by dehydration of alcohol:

When an alcohol is heated at 430-440 K with excess of concentrated sulphuric acid, a molecule of water from alcohol is removed and an alkene is formed. This reaction is called elimination reaction.

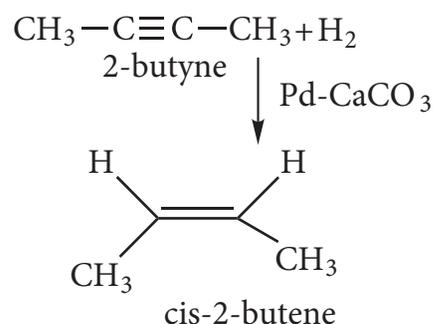


Ethene can also be prepared in laboratory by catalytic dehydration of alcohol.

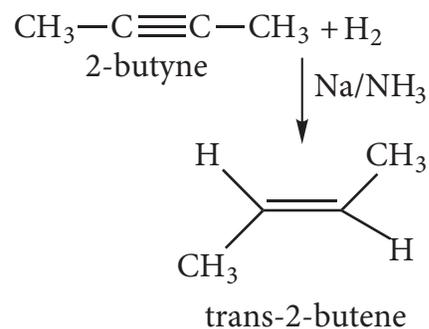


(2) Preparation of alkenes from alkynes:

Alkynes can be reduced to cis-alkenes using Lindlar's catalyst (CaCO_3 supported in palladium partially deactivated with sulphur (or) gasoline). This reaction is stereo specific giving only the cis-alkene.

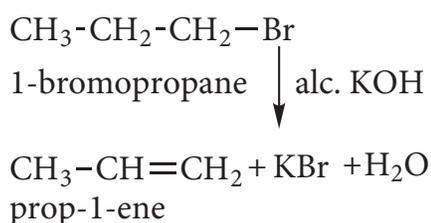


Alkynes can also be reduced to trans-alkenes using sodium in liquid ammonia. This reaction is stereospecific giving only the trans-alkene.



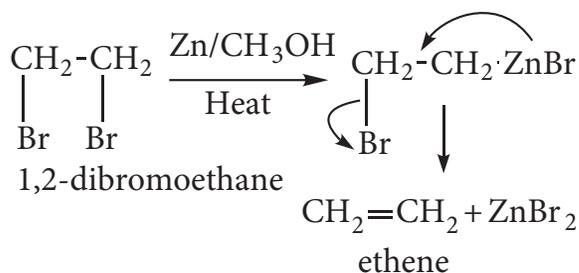
(3) Preparation of alkenes by dehydrohalogenation of halo alkanes.

Halo alkanes react with alcoholic KOH and eliminate hydrohalide resulting in the formation of alkene.



(4) Preparation of alkenes from vicinal dihalogen derivative of alkanes or vicinal dihalides

The compound in which two halogen atoms are attached to adjacent carbon-atoms are called as vicinal dihalides. When vicinal dihalides are warmed with granulated zinc in methanol, they lose a molecule of ZnX_2 to form an alkene.

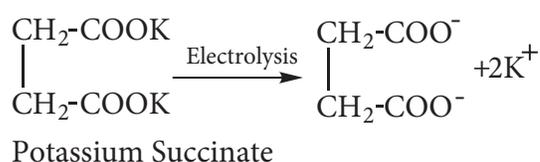


Evaluate Yourself

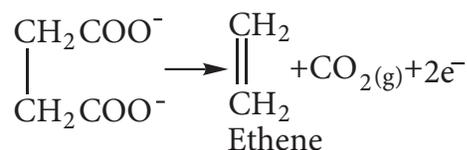
14) How propene is prepared from 1, 2-dichloro propane?

(5) Preparation of ethene by Kolbe's electrolytic method:

When an aqueous solution of potassium succinate is electrolyzed between two platinum electrodes, ethene is produced at the anode.



At anode



13.3.2. Physical properties of alkenes:

The first three members (Ethene, Propene and Butene) are gases, next fourteen members are liquids and the higher alkenes are waxy solids. They are all colourless and odourless except ethene which has a sweet smell.

1. The melting and boiling point of alkenes increases along the homologous series. Like alkanes, straight chain alkenes have high boiling point compared to its isomeric branched alkenes.
2. Alkenes are slightly soluble in water but readily in organic solvents.

13.3.3. Chemical properties of alkenes:

Alkenes are more reactive than alkanes due to the presence of a double bond. The σ -bond is strong but the π -bond is weak. The typical reactions of alkenes involve addition of an electrophile across the double bonds proceeding through ionic mechanism. However addition reactions proceed through free-radical mechanism also. Ozonolysis and polymerization are some of the characteristic reactions of alkenes.

(i) Addition Reactions

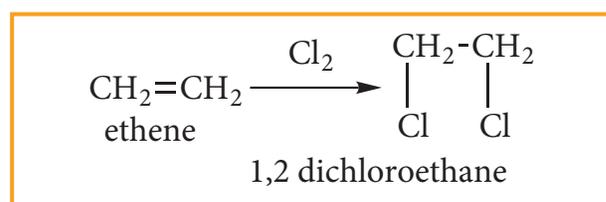
(ii) Addition of hydrogen: (Hydrogenation of alkenes)

Hydrogen adds on to alkenes in the presence of a metal catalyst (Ni, Pd (or) Pt) to yield corresponding alkanes. This is known

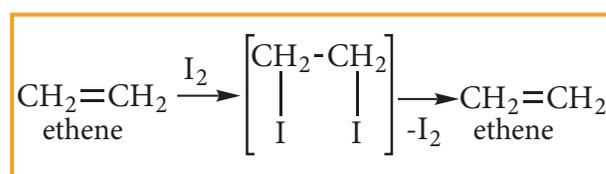
as catalytic hydrogenation. This process is of great importance in the manufacture of vanaspathi from vegetable oil. This helps to prevent rancidity of vegetable oils.

(ii) Addition of halogens: (Halogenation of alkenes)

When alkene is treated with halogens like chlorine or bromine, addition takes place rapidly and forms 1, 2- dihalo alkane (or) vicinal dihalide.



Iodine reacts very slowly to form 1, 2 - diiodo alkane which are unstable and regenerate the original alkene by elimination of iodine.



TEST FOR ALKENE:



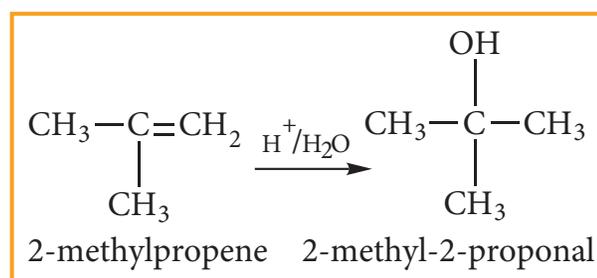
Bromine in water is reddish brown colour. When small amount of bromine water is added to an alkene, the solution is decolourised as it forms dibromo compound. So, this is the characteristic test for unsaturated compounds.

Markovnikoff's rule:

“When an unsymmetrical alkene reacts with hydrogen halide, the hydrogen adds to the carbon that has more number of hydrogen and halogen add to the carbon having fewer hydrogen”. This rule can also be stated as in the addition reaction of alkene / alkyne, the most electro negative part of the reagent adds on to the least hydrogen attached doubly bonded carbon.

(iii) Addition of water:- (Hydration of alkenes)

Normally, water does not react with alkenes. In the presence of concentrated sulphuric acid, alkenes react with water to form alcohols. This reaction follows carbocation mechanism and Markovnikoff's rule.

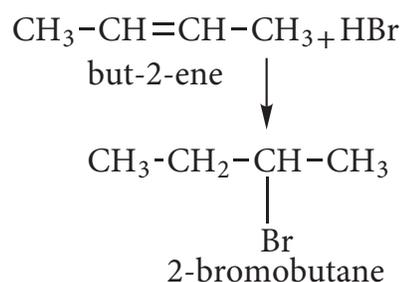
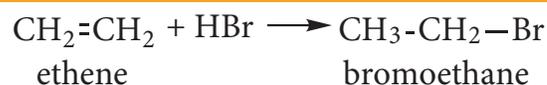


(iv) Addition of hydrohalides: (Hydrohalogenation of Alkenes)

Hydrogen halides (HCl, HBr and HI) add to alkene to yield alkyl halides. The order of reactivity of different hydrogen halides is $\text{HI} > \text{HBr} > \text{HCl}$. It is an example for electrophilic addition.

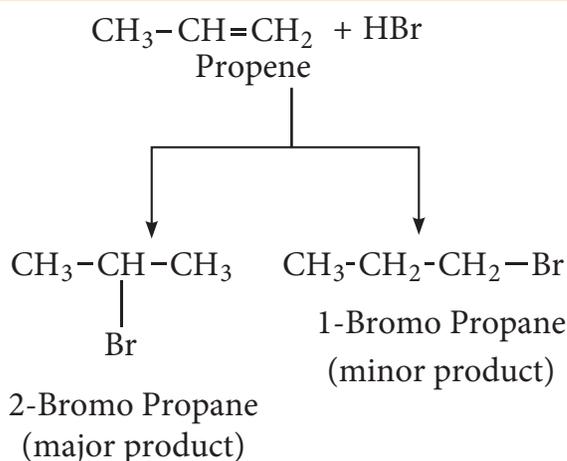
(a) Addition of HBr to symmetrical alkene:

Addition of HBr to symmetrical alkene (similar groups are attached to double bond) yields alkyl halides (haloalkanes)



(b) Addition HBr to unsymmetrical alkene:

In the addition of hydrogen halide to an unsymmetrical alkene, two products are obtained.

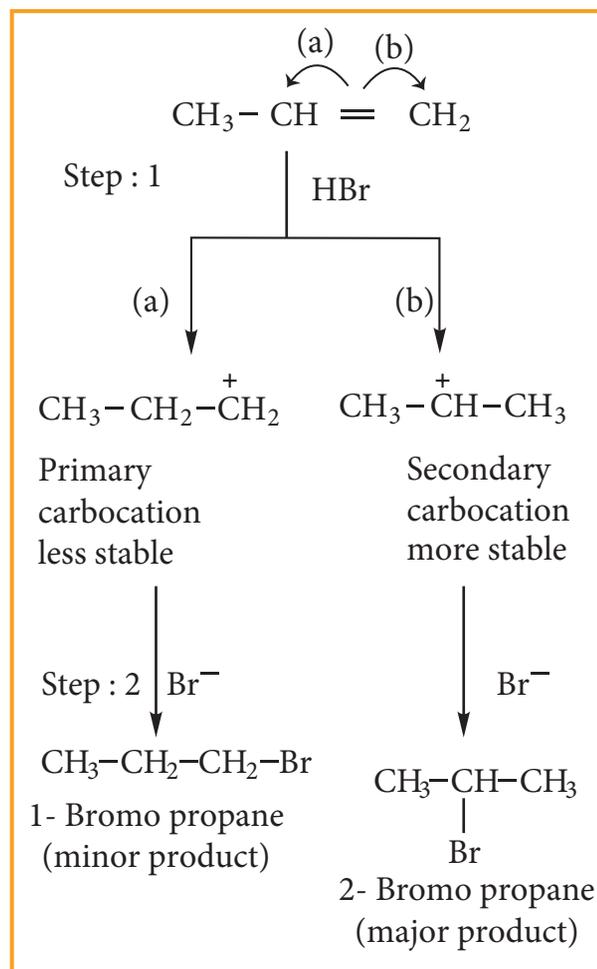


Mechanism:

Consider addition of HBr to propene

Step: 1 Formation of electrophile:

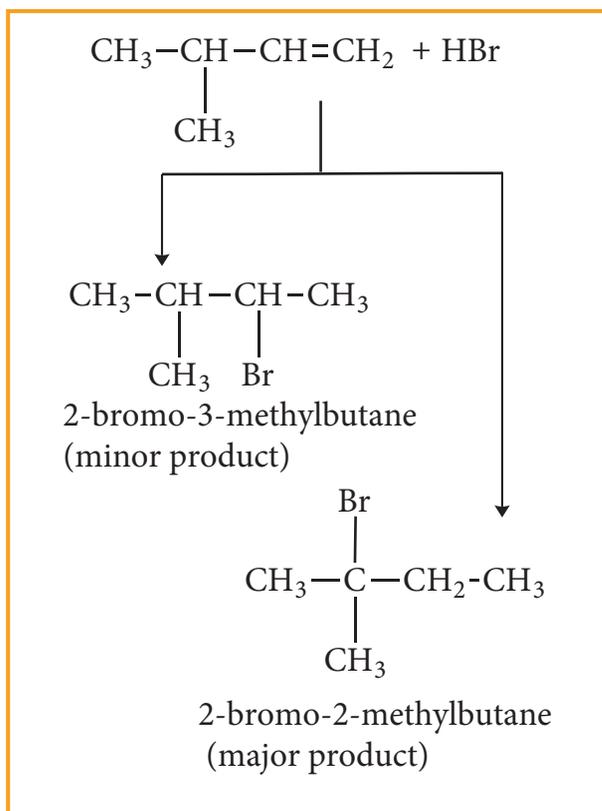
In H-Br, Br is more electronegative than H. When bonded electron moves toward Br, polarity is developed and creates an electrophile H^+ which attacks the double bond to form carbocation, as shown below.



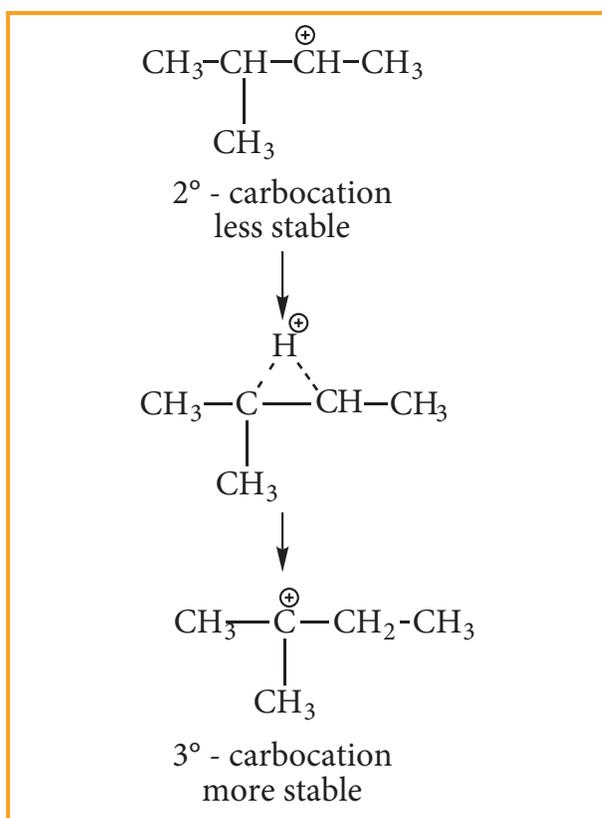
Step:2 Secondary carbocation is more stable than primary carbocation and it predominates over a the primary carbocation.

Step:3 The Br^- ion attacks the 2° carbocation to form 2-Bromo propane, as the major product.

Consider addition of HBr to 3-methyl-1-butene. Here the expected product according to markovnikoff's rule is 2-bromo-3-methyl butane but the actual major product is 2-Bromo-2-methyl butane. This is because, the secondary carbocation formed during the reaction rearranged to more stable tertiary carbocation. Attack of Br^- on this tertiary carbocation gives the major product 2-bromo-2-methyl butane.

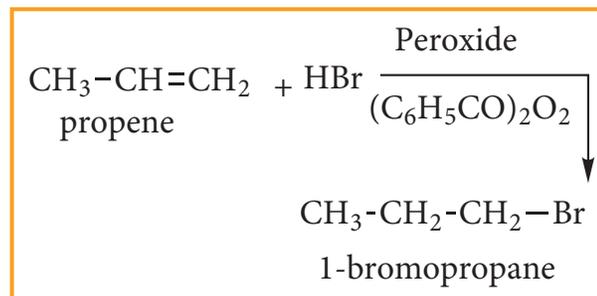


Carbocation rearrangement



Anti-Markovnikoff's Rule (Or) Peroxide Effect (Or) Kharasch Addition

The addition of HBr to an alkene in the presence of organic peroxide, gives the anti Markovnikoff's product. This effect is called peroxide effect.

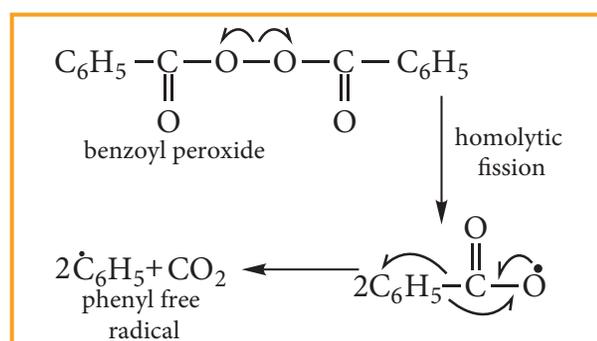


Mechanism:

The reaction proceeds via free radical mechanism.

Step:1

The weak O-O single bond linkages of peroxides undergoes homolytic cleavage to generate free radical.



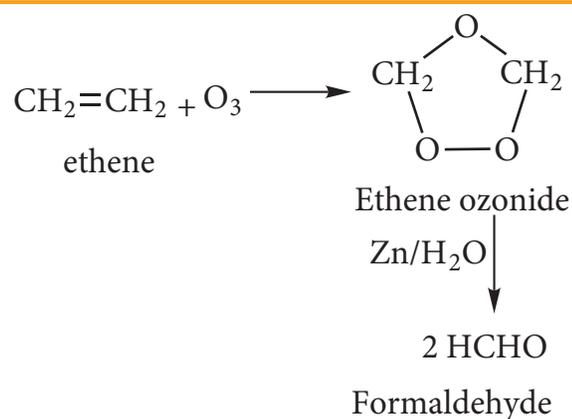
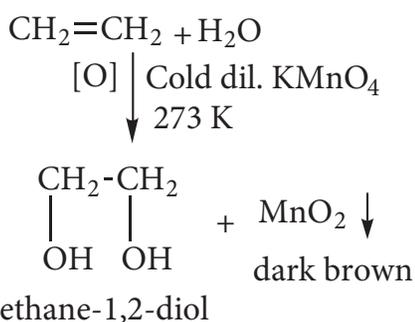
Step:2

The radicals abstracts a hydrogen from HBr thus generating bromine radical.



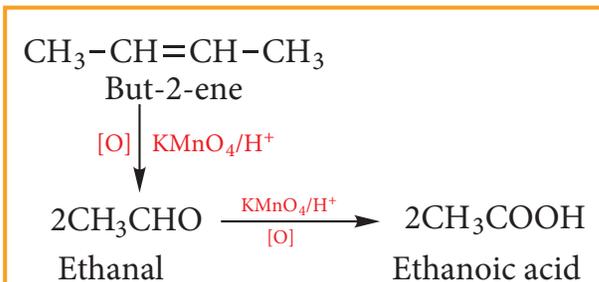
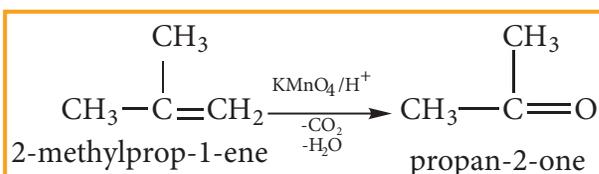
Step:3

The Bromine radical adds to the double bond in the way to form more stable alkyl free radical.



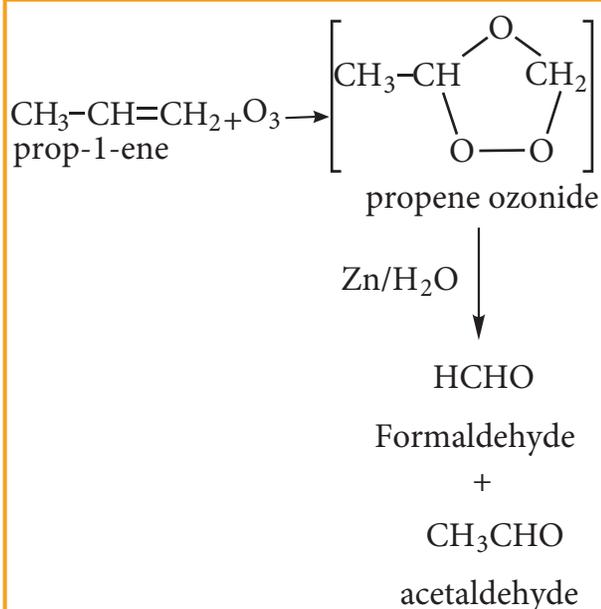
(ii) With acidified KMnO_4 Solution:

Alkenes react with acidified KMnO_4 solution and are oxidised to ketones or carboxylic acid depends on the substituent at the olefinic carbon atom.. The purple solution becomes colourless. This is one of the test for unsaturation.



(iii) Ozonolysis:

Ozonolysis is a method of oxidative cleavage of alkenes or alkynes using ozone and forms two carbonyl compounds. Alkenes react with ozone to form Ozonide and it is cleaved by $\text{Zn}/\text{H}_2\text{O}$ to form smaller molecules. This reaction is often used to identify the structure of unknown alkene or alkyne by detecting the position of double or triple bond.



Evaluate Yourself

15) How ozone reacts with 2-methyl propene?

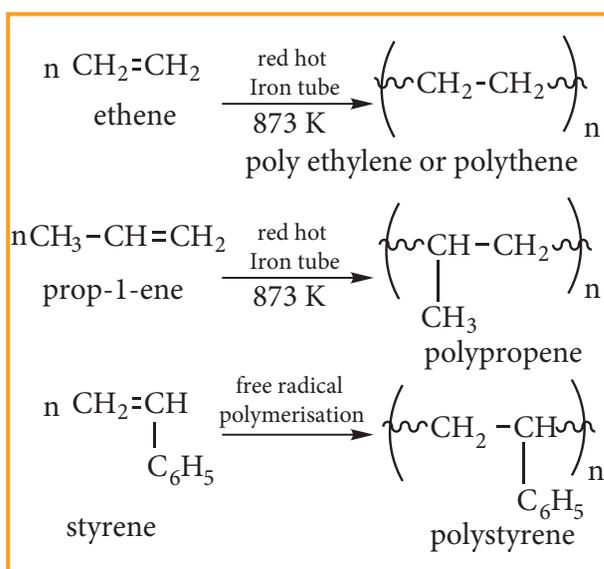
16) An organic compound (A) on ozonolysis gives only acetaldehyde. (A) reacts with Br_2/CCl_4 to give compound (B) Identify the compound (A) and (B). Write the IUPAC name of (A) and (B). Give the Geometrical isomers of (A)

17) An organic compound (A) C_2H_4 decolourises bromine water. (A) on reaction with chlorine gives (B) A reacts with HBr to give (C). identify (A),(B),(C), Explain the reactions.

(iv) Polymerisation:

A polymer is a large molecule formed by the combination of larger number of small molecules. The process is known as polymerisation. Alkenes undergo polymerisation at high temperature and pressure, in the presence of a catalyst.

for example



Recycling plastics

Extensive use of polymers clogs up landfills and pollute the environment. Because of diversity of polymers in consumer products, recycling requires sorting the polymers into various sub-types, labels with codes and symbols, which are then recycled separately.

Table shows the codes and symbols used in recycling of ethene-based addition polymers.

(Lower the number, greater the ease of recycling the material)

CODE	TYPE	NAME	EXAMPLES
PET		Polyethylene terephthalate	Soft drinks bottles, jars, vegetable oil bottle.
HDPE		High-density polyethylene	Milk, water and juice containers
PVC		Polyvinyl chloride	Shampoo bottles, plastic pipes
LDPE		Low density polyethylene	Sandwich bags, grocery bags
PP		Polypropylene	Straws, diaper, toys
PS		Polystyrene	Disposable utensil, foam cups
Other		Multilayer plastics	Various flexible item.

13.3.4. Uses of Alkenes

1) Alkenes find many diverse applications in industry. They are used as starting materials in the synthesis of alcohols, plastics, liquors, detergents and fuels

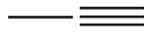
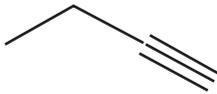
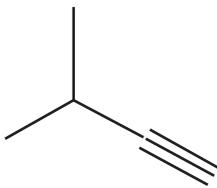
2) Ethene is the most important organic feed stock in the polymer industry. E.g. PVC, Sarans and polyethylene. These polymer are used in the manufacture of floor tiles, shoe soles, synthetic fibres, raincoats, pipes etc.,

13.4. ALKYNES

Alkynes are unsaturated hydrocarbons that contain carbon-carbon triple bonds in their molecules. Their general formula is $C_n H_{2n-2}$. The first member of alkyne series is Ethyne popularly known as acetylene. Oxyacetylene torch is used in welding.

Nomenclature of alkynes:

Let us write the IUPAC name for the below mentioned alkynes by applying the general rules of nomenclature that we already discussed in unit No.11

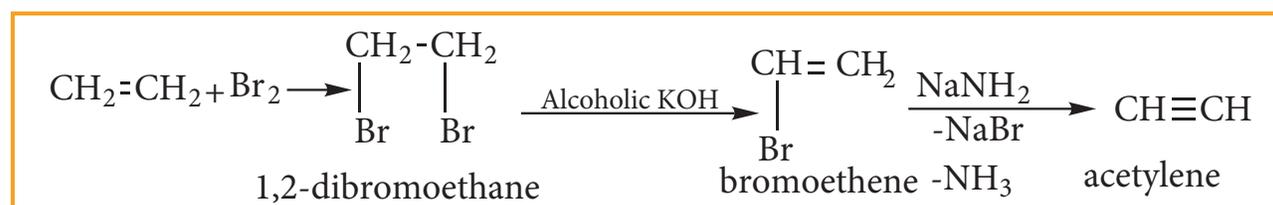
Structure	IUPAC name	Carbon Skeleton Formula
$CH_3-C\equiv CH$	Propyne	
$CH_3-CH_2-C\equiv CH$	but-1-yne	
$CH_3-C\equiv C-CH_3$	but-2-yne	
$CH_3-\underset{\substack{ \\ CH_3}}{CH}-C\equiv CH$	3-methyl but-1-yne	

13.4.1. General Methods Of Preparation Of Alkynes

1. Preparation of alkynes from alkenes:

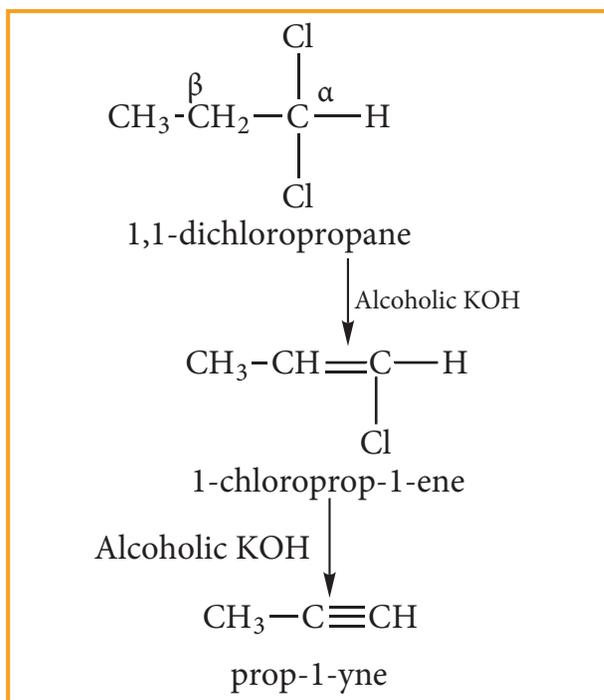
This process involves two steps:

- Halogenation of alkenes to form vicinal dihalides
- Dehalogenation of vicinal dihalides to form alkynes.



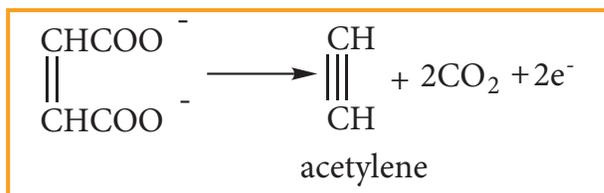
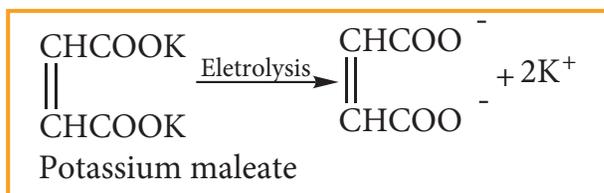
2. Preparation of alkene from gem dihalides:

A compound containing two halogen atoms on the same carbon atom is called gem dihalide (Latin word 'Gemini' means twins). On heating with alcoholic KOH, gem dihalides give alkynes.



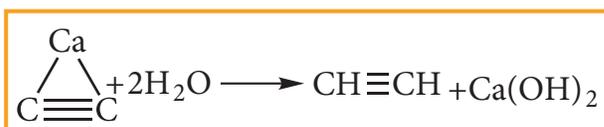
3. Preparation of alkynes from electrolysis of salts of unsaturated dicarboxylic acids. (Kolbe's electrolytic method)

Electrolysis of sodium or potassium salt of maleic or fumaric acid yields alkynes.

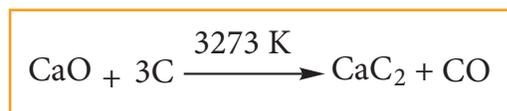


4. Industrial preparation of ethyne:

Ethyne can be manufactured in large scale by action of calcium carbide with water.

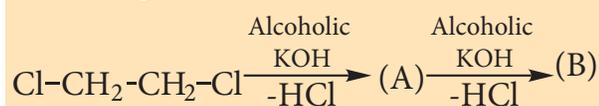


Calcium carbide required for this reaction is prepared by heating quick lime and coke in an electric furnace at 3273 K



Evaluate Yourself

- 18) Prepare propyne from its corresponding alkene.
- 19) Write the products A & B for the following reaction.



13.4.2. Physical properties of alkynes:

1. The first three members are gases, next eight are liquids and the higher alkynes are solids. They are all colourless and odourless except acetylene which has a garlic odour.

2. They are slightly soluble in water but dissolve readily in organic solvents like benzene, acetone and ethyl alcohol

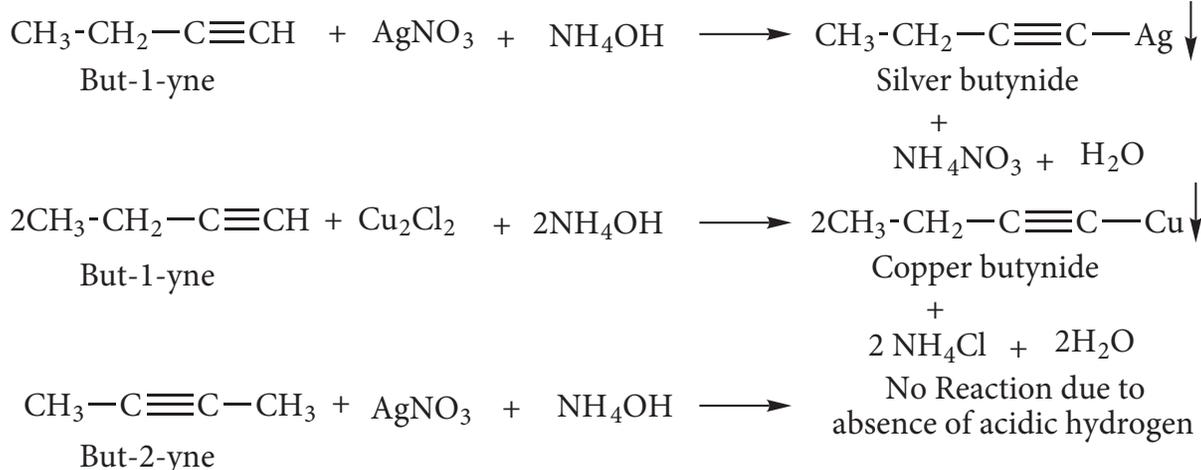
13.4.3. Chemical properties of alkynes

Terminal Alkynes are acidic in nature. It undergoes polymerization and addition reaction.

1. Acidic nature of alkynes:

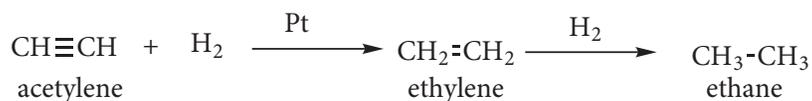
An alkyne shows acidic nature only if it contains terminal hydrogen. This can be explained by considering sp hybrid orbitals of carbon atom in alkynes. The percentage of s-character of sp hybrid orbital (50%) is more than sp² hybrid orbital of alkene (33%) and sp³ hybrid orbital of alkane (25%). Because of this, Carbon becomes more electronegative facilitating donation of H⁺

ions to bases. So hydrogen attached to triply bonded carbon atoms is acidic.



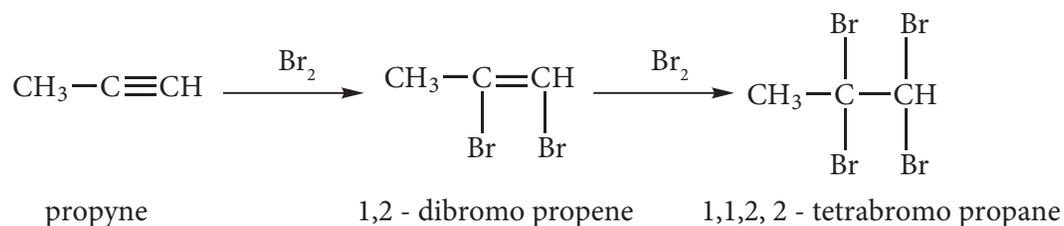
2. Addition reactions of alkynes

i) addition of hydrogen



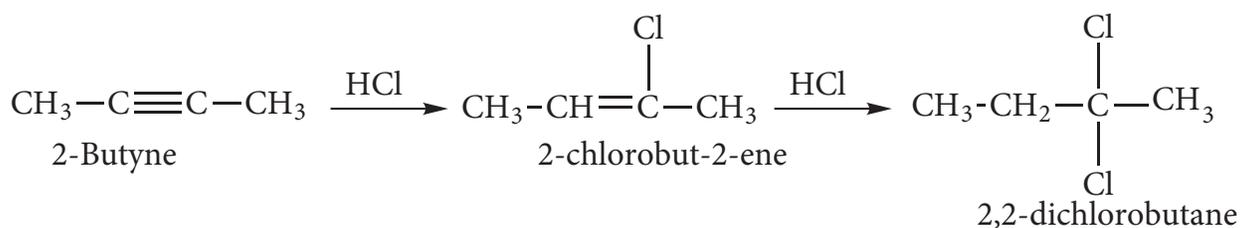
ii) Addition Of Halogens:

When Br_2 in CCl_4 (Reddishbrown) is added to an alkyne, the bromine solution is decolourised. This is the test for unsaturation.



iii) Addition Of Hydrogen Halides:

Reaction of hydrogen halides to symmetrical alkynes is electrophilic addition reaction. This reaction also follows Markovnikoff's rule.

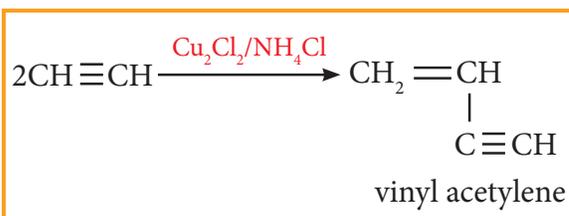


4. Polymerisation:

Alkyne undergoes two types of polymerisation reaction

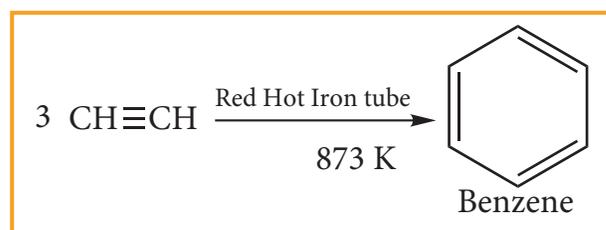
(i) Linear Polymerisation:

Ethyne forms linear polymer, when passed into a solution of cuprous chloride and ammonium chloride.



(ii) Cyclic Polymerisation:

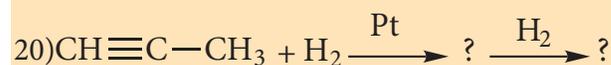
Ethyne undergoes cyclic polymerisation on passing through red hot iron tube. Three molecules of ethynepolymerises to benzene.



13.4.4 Uses of Alkynes

- 1) Acetylene is used in oxy acetylene torch used for welding and cutting metals.
- 2) It is used for manufacture of PVC, polyvinyl acetate, polyvinyl ether, orlon and neoprene rubbers.

Evaluate Yourself



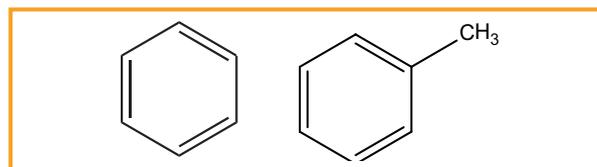
13.5. Aromatic Hydrocarbons

Take a moment and think of substances that have a strong fragrance. What kind of things come to your mind?

Perfume, Vanilla or cinnamon? They smell differently, they have something in common. These substances are made of aromatic compounds [Greek: Aroma-Pleasant smelling]. However, some compounds are chemically aromatic but do not have distinct smell. The aromatic hydrocarbons are classified depending upon number of rings present in it.

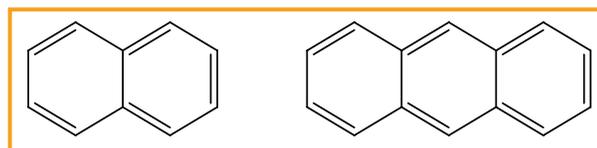
(i) Monocyclic aromatic hydrocarbon (MAH)

(Ex) Benzene (C_6H_6) and Toluene (C_7H_8)



(ii) Polycyclic aromatic hydrocarbon (PAH)

(Ex) Naphthalene (C_{10}H_8) and Anthracene ($\text{C}_{14}\text{H}_{10}$)



Evaluate Yourself

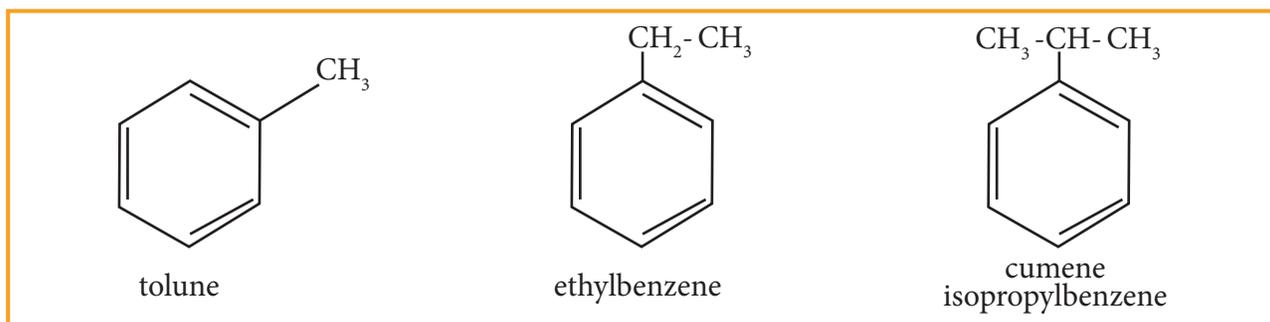
21) Calculate the number of rings present in $\text{C}_{18}\text{H}_{12}$.

13.5.1. Nomenclature and Isomerism

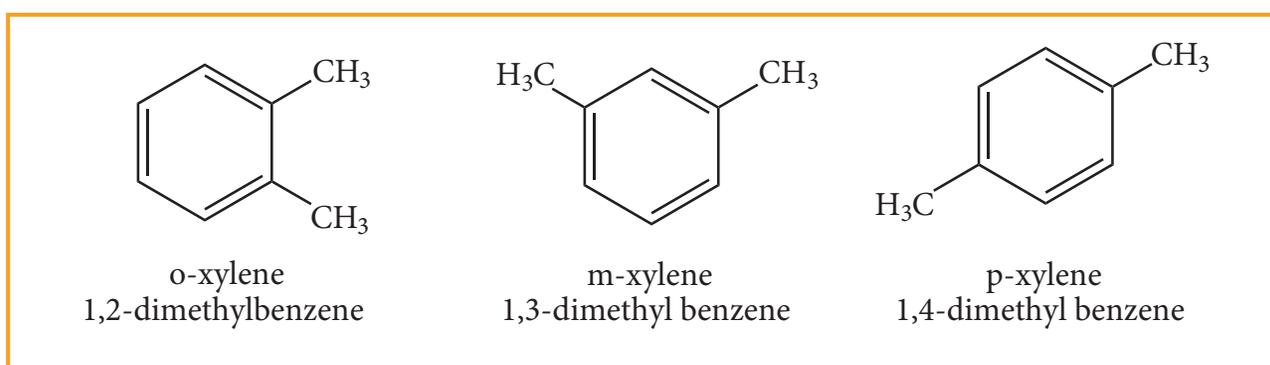
- We have already discussed about nomenclature of aromatic hydrocarbons in Unit:11. The first member of aromatic hydrocarbon is benzene (C_6H_6)

represented by a regular hexagon with a circle inscribed in it.

- Since, all the six hydrogen atom in benzene are equivalent, it can give only one mono-substituted compound (Ex) methyl benzene ($C_6H_5-CH_3$) which named as toluene.



- When di substitution occurs either by a similar monovalent atom or two different atoms or groups in benzene, then three different position isomers are possible. Their relative positions are indicated as ortho (1,2), meta (1,3) and para (1,4). For example, consider dimethyl benzene which is named as xylene.



Evaluate Yourself

- 22) write all possible isomers for an aromatic benzenoid compound having the molecular formula C_8H_{10}
- 23) write all possible isomers for a monosubstituted aromatic benzenoid compound having the molecular formula C_9H_{12}

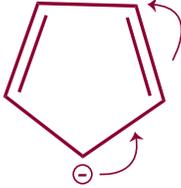
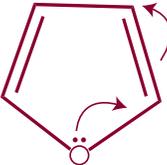
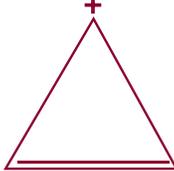
13.5.2. Aromaticity

Huckel proposed that aromaticity is a function of electronic structure. A compound may be aromatic, if it obeys the following rules

- (i) The molecule must be co-planar
- (ii) Complete delocalization of π electron in the ring
- (iii) Presence of $(4n+2)$ π electrons in the ring where n is an integer ($n=0,1,2,\dots$)

This is known as Huckel's rule.

Some of the examples for Huckel rule

1.	 <p>Benzene</p>	<p>(i) The benzene is a planar molecule (ii) It has six delocalised π electrons (iii) $4n + 2 = 6$ $4n = 6 - 2$ $n = 1$ it obeys Huckel's $(4n+2)$ π electron rule with $n = 1$. hence, benzene is aromatic.</p>
2.	 <p>Cyclo penta dienyl anion</p>	<p>(i)cyclopenta dienyl anion a planar ring structure (ii) It has 6 delocalised electrons (iii) $4n + 2 = 6$ $n = 1$ it obeys Huckel's $(4n+2)$ π electron rule with $n = 1$. hence, it is aromatic.</p>
3.	 <p>Furan</p>	<p>(i) Furan has a planar ring structure. (ii) if has 6 delocalised electrons (iii) $4n+2 = 6$ $n=1$ it obeys Huckel's $(4n+2)$ π electron rule with $n = 1$. hence, it is aromatic.</p>
4.	 <p>Cyclo penta diene</p>	<p>(i) It has planar structure (ii) It has four π electron but the π electrons are not delocalised and hence it is not an aromatic compound</p>
5.	 <p>Cyclooctatetraene</p>	<p>molecule is non planar and hence it is not an aromatic compound</p> <p>Cyclooctatetraene</p>
6	 <p>Cyclopropenylcation</p>	<p>(i) cyclopropenyl cation has planar structure (ii) It has 2 delocalised π electron. (ii) $4n + 2 = 2$ $4n = 0$ $n = 0$ (an interger) and hence it is aromatic compound.</p>

13.5.3. Structure of benzene:

1. Molecular formula

Elemental Analysis and molecular weight determination have proved that the molecular formula of benzene is C_6H_6 . This indicates that benzene is a highly unsaturated compound.

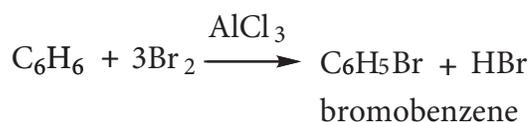
2. Straight chain structure not possible:

Benzene could be constructed as a straight chain or ring compound but it not feasible since it does not show the properties of alkenes or alkynes. For example, it did not decolourise bromine in carbon tetrachloride or acidified $KMnO_4$. It did not react with water in the presence of acid.

3. Evidence of cyclic structure:

I) substitution of benzene:

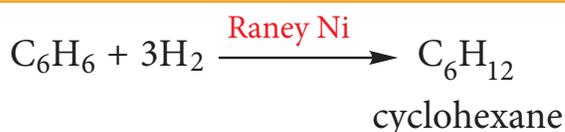
Benzene reacts with bromine in the presence of $AlCl_3$ to form mono bromo benzene.



Formation of only one monobromo compound indicates that all the six hydrogen atoms in benzene were identical. This is possible only if it has a cyclic structure of six carbons each containing one hydrogen.

II) addition of hydrogen:

Benzene can add on to three moles of hydrogen in the presence of nickel catalyst to give cyclohexane.



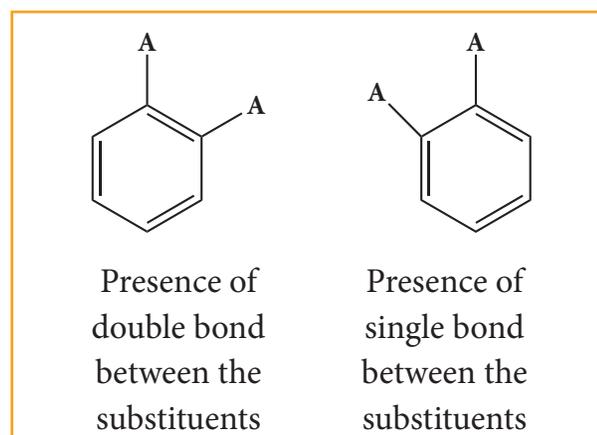
This confirms cyclic structure of benzene and the presence of three carbon-carbon double bond.

4. Kekule's structure of benzene:

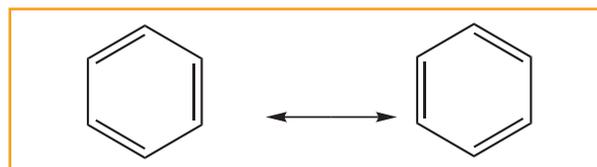
In 1865, August Kekule suggested that benzene consists of a cyclic planar structure of six carbon with alternate single and double bonds.

There were two objections:

- (i) Benzene forms only one ortho disubstituted products whereas the Kekule's structure predicts two o-di substituted products as shown below.



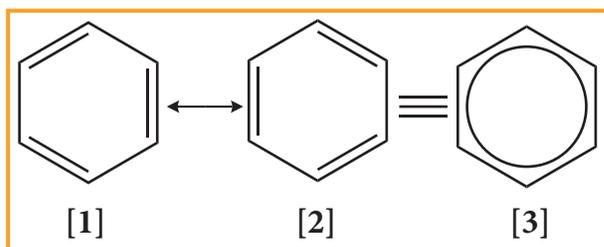
- (ii) Kekule's structure failed to explain why benzene with three double bonds did not give addition reactions like other alkenes. To overcome this objection, Kekule suggested that benzene was mixture of two forms (1 and 2) which are in rapid equilibrium.



5. Resonance description of benzene:

The phenomenon in which two or more structures can be written for a substance which has identical position

of atoms is called resonance. The actual structure of the molecule is said to be resonance hybrid of various possible alternative structures. In benzene, Kekule's structures I & II represented the resonance structure, and structure III is the resonance hybrid of structure I & II



The structures 1 and 2 exist only in theory. The actual structure of benzene is the hybrid of two hypothetical resonance structures.

6. Spectroscopic measurements:

Spectroscopic measurements show that benzene is planar and all of its carbon-carbon bonds are of equal length 1.40Å . This value lies between carbon-carbon single bond length 1.54Å and carbon-carbon double bond length 1.34Å .

7. Molecular orbital structure:

The structure of benzene is best described in terms of the molecular orbital theory. All the six carbon atoms of benzene are sp^2 hybridized. Six sp^2 hybrid orbitals of carbon linearly overlap with six $1s$ orbitals of hydrogen atoms to form six C - H sigma bonds. Overlap between the remaining sp^2 hybrid orbitals of carbon forms six C-C sigma bonds.

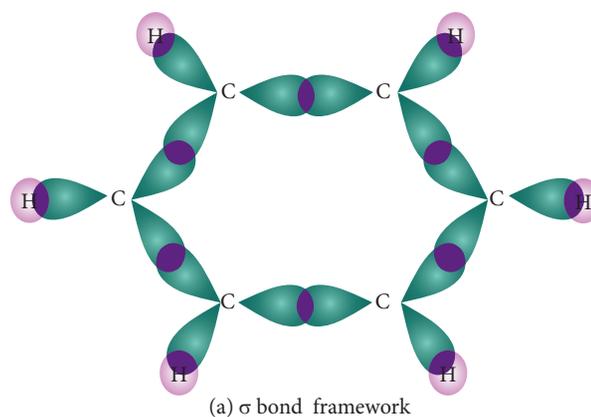


Figure 13.6. Formation of Sigma bond in benzene

All the σ bonds in benzene lie in one plane with bond angle 120° . Each carbon atom in benzene possess an un hybridized p-orbital containing one electron. The lateral overlap of their p-orbital produces 3π - bond The six electrons of the p-orbitals cover all the six carbon atoms and are said to be delocalised. Due to delocalization, strong π -bond is formed which makes the molecule stable. Hence unlike alkenes and alkynes benzene undergoes substitution reactions rather addition reactions under normal conditions.

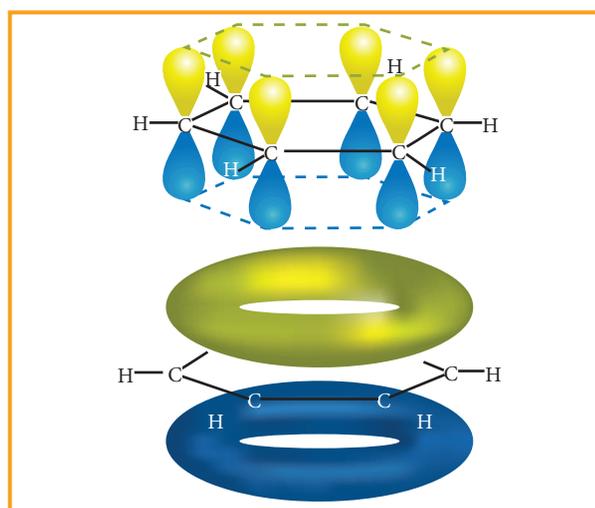
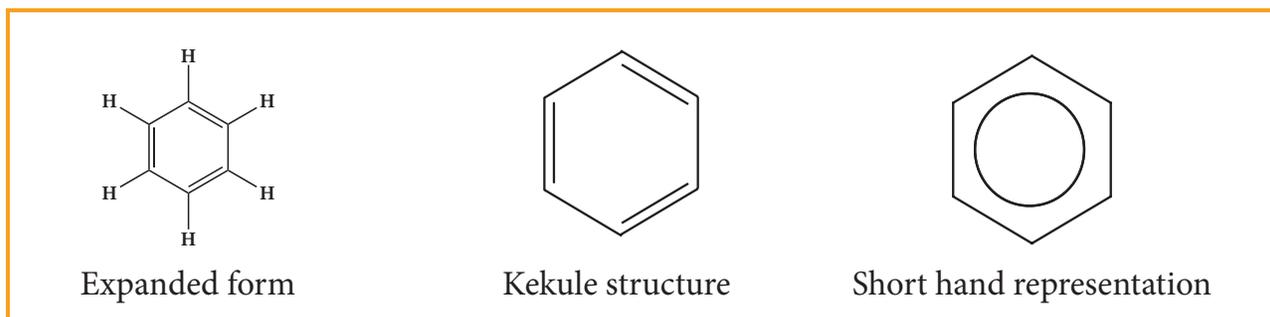


Figure 13.7. All carbon atoms have The delocalized π Mo is formed by p orbitals the overlap of six p-orbitals

8. Representation of benzene:

Hence, there are three ways in which benzene can be represented.



Benzene and its homologous series

Benzene and its homologous series are colorless liquids with pleasant odour. They are lighter than water and insoluble in it. Their vapours are highly flammable, and volatile and toxic in nature.

13.5.4. Sources of aromatic compound:

- Benzene and other aromatic compound are obtained from coal tar and petroleum
- It can also be prepared in laboratory using some simple aliphatic compounds

1. Preparation of benzene

(i) industrial preparation of benzene from coal tar :

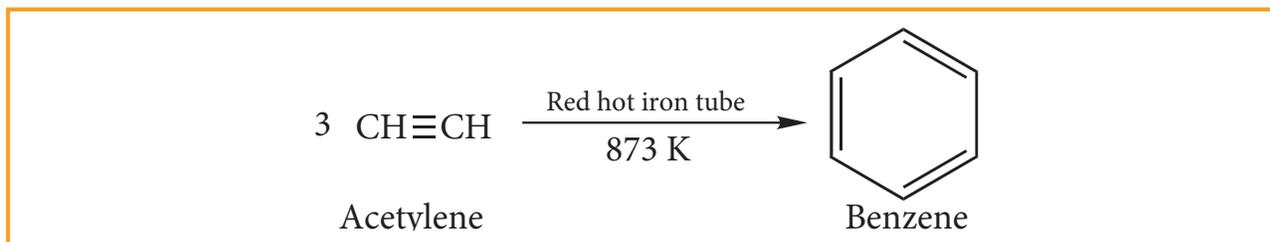
Coal tar is a viscous liquid obtained by the pyrolysis of coal. During fractional distillation, coal tar is heated and distills away its volatile compounds namely benzene, toluene, xylene in the temperature range of 350 to 443 K. These vapours are collected at the upper part of the fractionating column (Table 13.5.)

TABLE.13.5 COMPENENTS OF DISTILLATION OF COAL TAR

NAME OF THE FRACTION	TEMPERATURE RANGE	NAME OF THE COMPENENTS
1. Crude light oil	350 - 443 K	Benzene, Toluene, Xylenes
2. Middle oil	443 - 503 K	Phenol, Naphthalene
3. Heavy oil	503 - 543 K	Naphthalene, Cresol
4. Green oil	543 - 633 K	Anthracene
5. Pitch	Above 633 K	Residue

(ii) from acetylene.

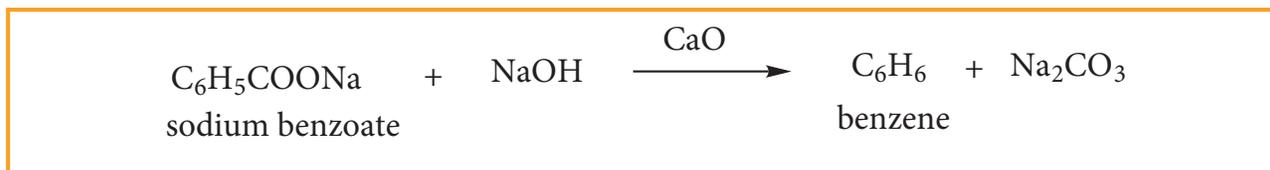
Acetylene on passing through a red-hot tube trimerises to give benzene. We have already studied this concept in polymerization of alkynes.



(iii) Laboratory Methods Of Preparing Benzene And Toluene

(a) Decarboxylation Of Aromatic Acid.

When sodium benzoate is heated with sodalime, benzene vapours distil over.



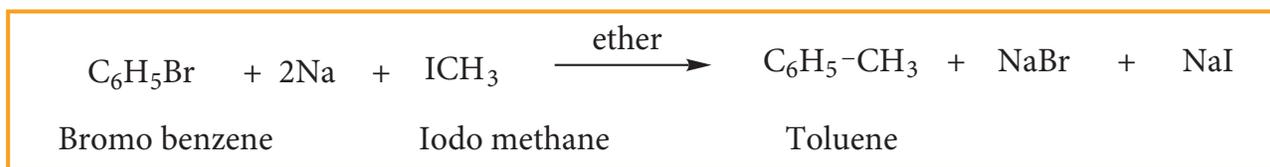
(b) Preparation Of Benzene From Phenol

When phenol vapours are passed over zinc dust, then it is reduced to benzene.



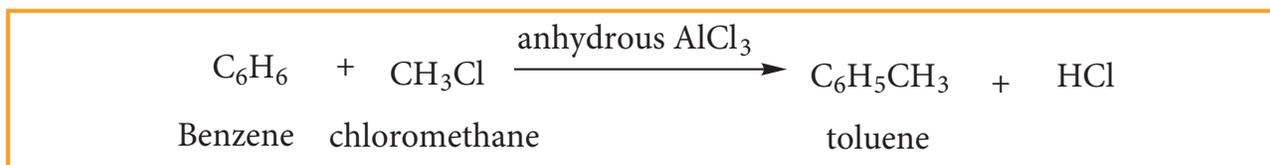
(c) Wurtz - Fittig Reaction:

When a solution of bromo benzene and iodo methane in dry ether is treated with metallic sodium, toluene is formed.



(d) Friedel Craft's Reaction:

When benzene is treated with methyl chloride in the presence of anhydrous aluminium chloride, toluene is formed.



Evaluate Yourself 

24) How benzene can be prepared by Grignard Reagent

13.5.5 Physical Properties:

- Benzene is a colourless liquid, insoluble in water and solution alcohol, ether and chloroform.
- It burns with luminous sooty flame in contrast to alkanes and alkenes which usually burn with bluish flame.
- Their vapours are highly toxic which on inhalation produce loss of consciousness.

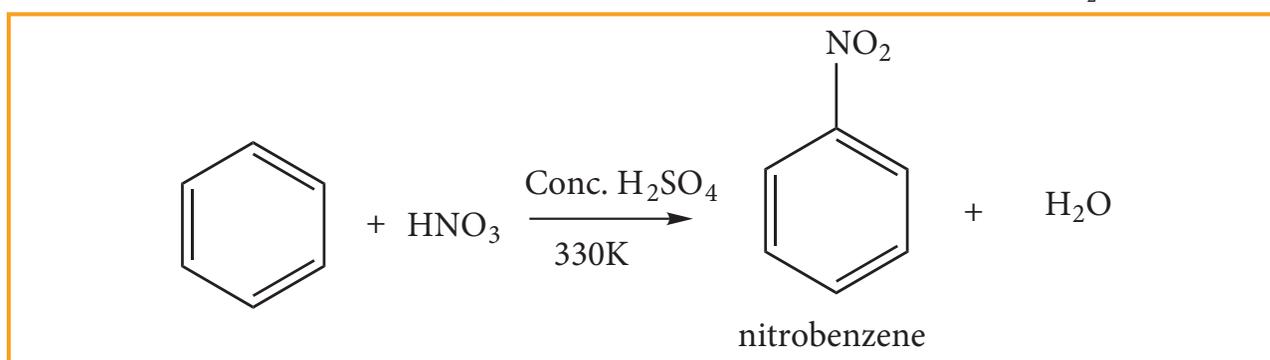
13.5.6 Chemical Properties:

1. Benzene contains delocalized π -electrons which make the ring to act as an electron rich centre. So electrophilic substitution reaction occurs in benzene.
2. Benzene ring is stabilized by delocalized π electrons. Though it is highly stable, it undergoes addition and oxidation reaction under specific conditions.

1. Electrophilic Substitution Reaction

(a) Nitration:

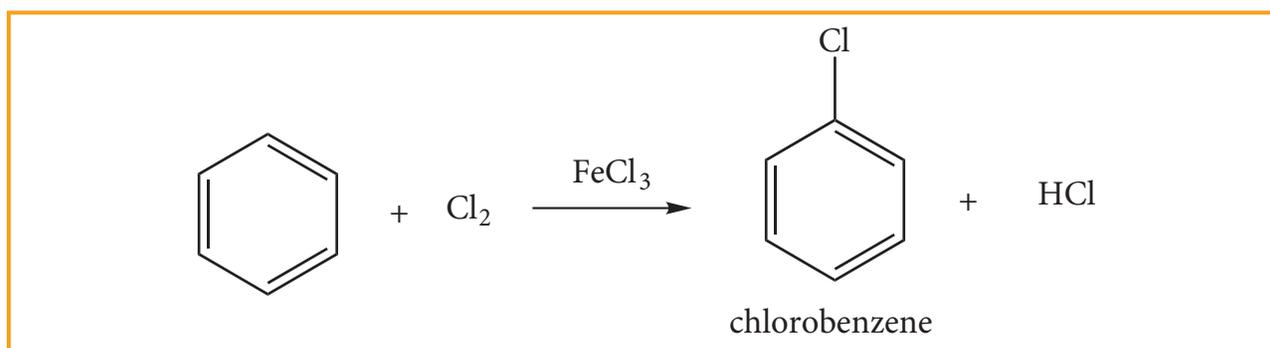
When benzene is heated at 330K with a nitrating mixture (Con. HNO_3 + Con. H_2SO_4), nitro benzene is formed by replacing one hydrogen atom by nitronium ion NO_2^+ (electrophile)



Concentrated H_2SO_4 is added to produce nitronium ion NO_2^+

(b) Halogenation:

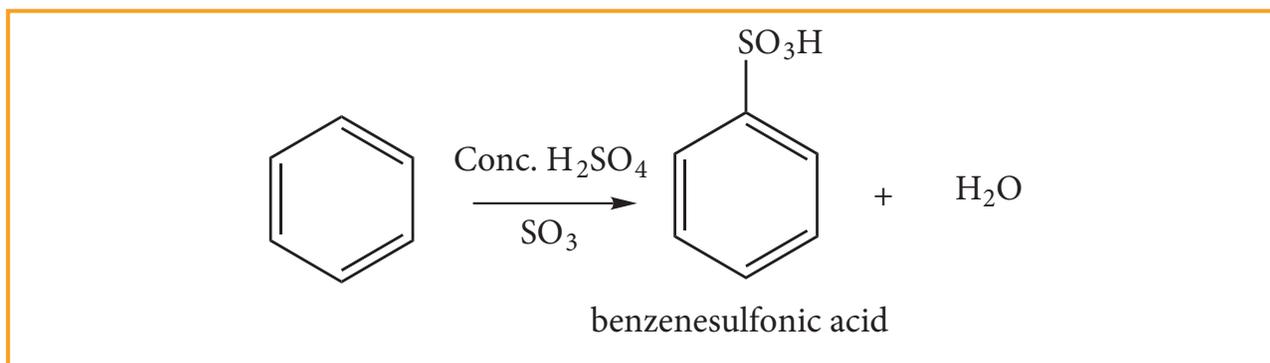
Benzene reacts with halogens ($\text{X}_2 = \text{Cl}_2, \text{Br}_2$) in the presence of Lewis acid such as $\text{FeCl}_3, \text{FeBr}_3$ or AlCl_3 and give corresponding halo benzene. In the absence of catalyst, Fluorine reacts vigorously with benzene even in the absence of catalyst. However iodine is very inactive even in the presence of catalyst



(c) Sulphonation:

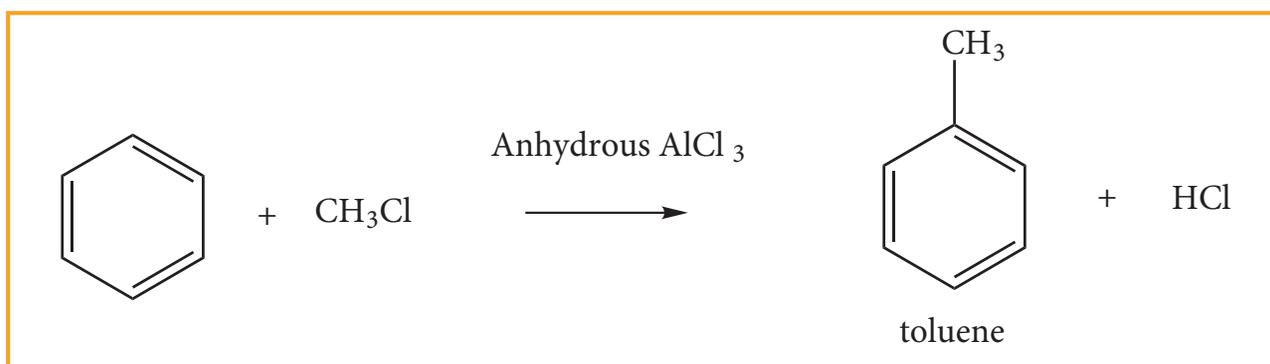
Benzene reacts with fuming sulphuric acid (Con $\text{H}_2\text{SO}_4 + \text{SO}_3$) and gives benzene sulphonic acid. The electrophile SO_3 is a molecule. Although it does not have positive charge, it is a strong electrophile.

This is because the octet of electron around the sulphur atom is not reached. The reaction is reversible and desulphonation occurs readily in aqueous medium.



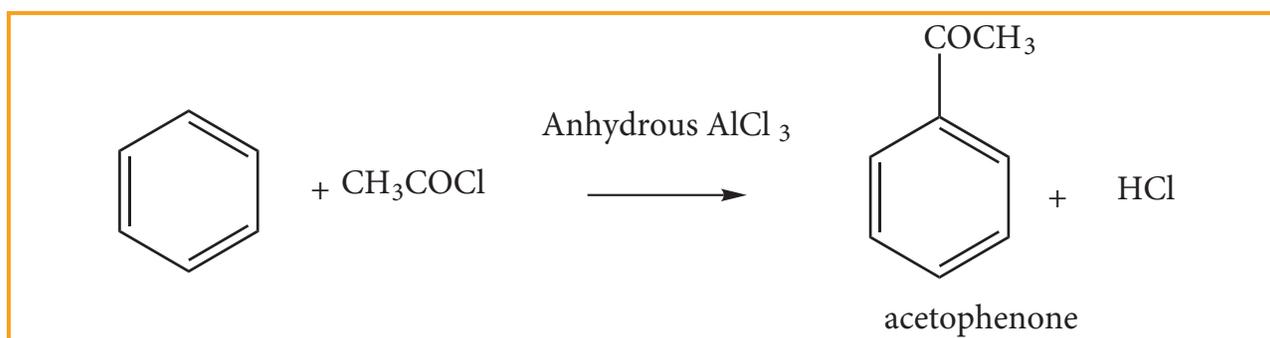
(d) Friedel Craft's Alkylation: (Methylation)

When benzene is treated with an alkyl halide in the presence of only AlCl_3 , alkyl benzene is formed.



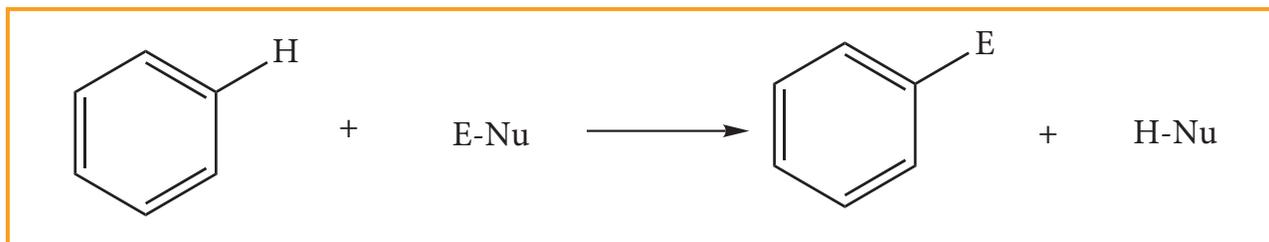
(e) Friedel Craft's Acylation : Acetylation

When benzene is treated with acetyl chloride in the presence of AlCl_3 , acyl benzene is formed.



(f) Electrophilic Substitution Reactions: Mechanism

Benzene undergoes electrophilic substitution reaction because it is an electron-rich system due to delocalised π electron. So it is easily attacked by electrophiles and gives substituted products.



Mechanism:

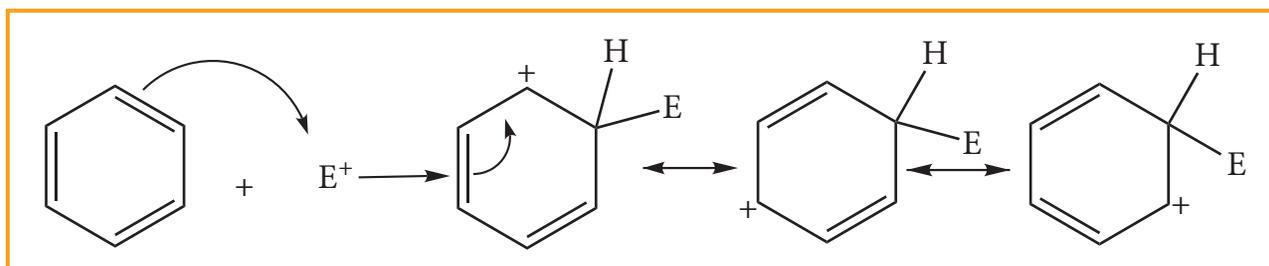
Step: 1

Formulation of the electrophile



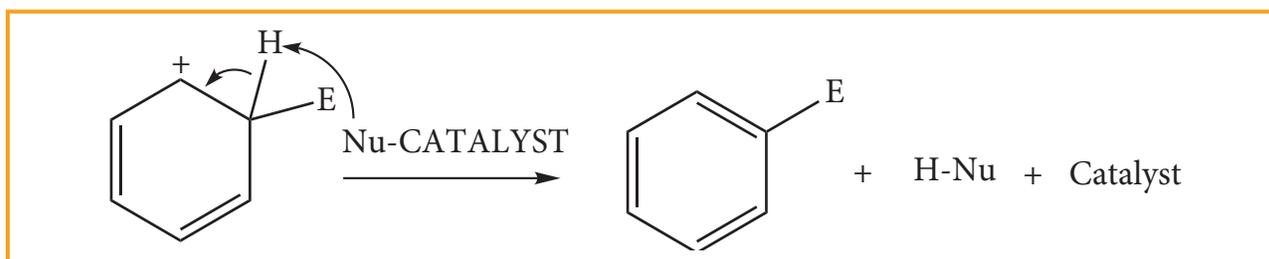
Step:2

The electrophile attacks the aromatic ring to form a carbocation intermediate which is stabilized by resonance.



Step: 3

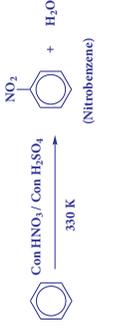
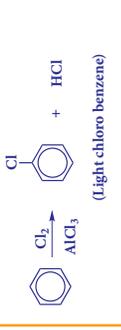
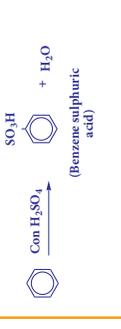
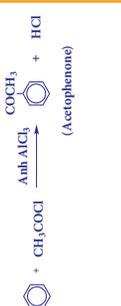
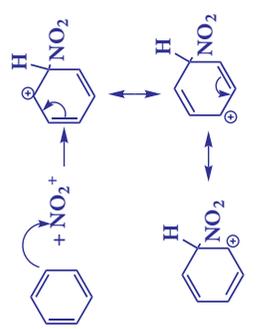
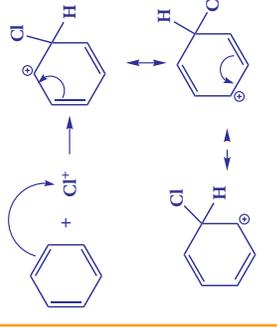
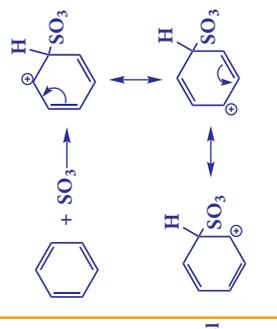
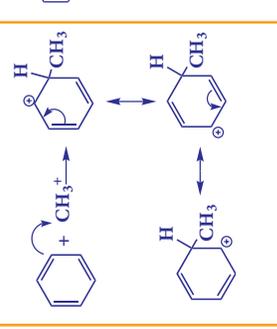
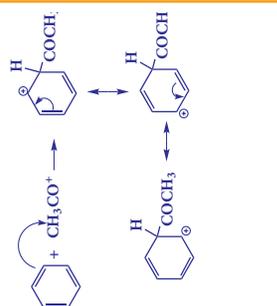
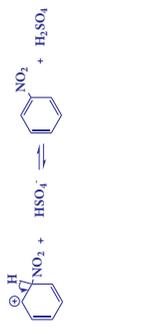
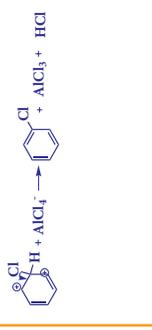
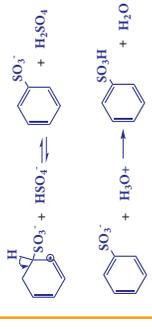
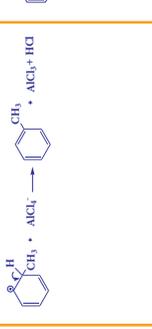
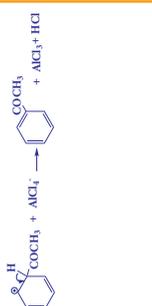
Loss of proton gives the substitution product.



Evaluate Yourself

25) Why benzene undergoes electrophilic substitution reaction whereas alkenes undergoes addition reaction?

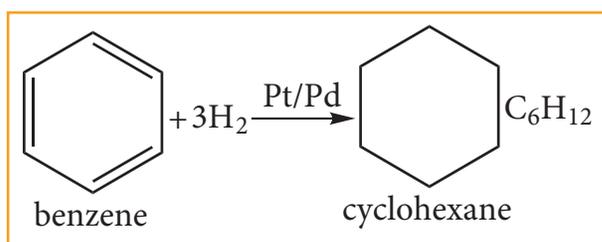


Types of reaction	NITRATION	HALOGENATION	SULPHONATION	FRIEDEL CRAFT'S ALKYLATION	FRIEDEL CRAFT'S ACYLATION
Reagents	Con HNO_3 + Con H_2SO_4	$\text{X}_2 / \text{Al X}_3$	Fuming H_2SO_4	CH_3Cl + anhydrous AlCl_3	CH_3COCl + anhydrous AlCl_3
Electro- phile	$-\text{NO}_2^+$	$-\text{X}^+ (\text{X} = \text{Cl}, \text{Br})$	$-\text{SO}_3$ (Neutral electrophile)	$-\text{CH}_3^+$	$-\text{COCH}_3^+$
Over all reaction					
Mechanism Step 1	$\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O}$	$\text{AlCl}_3 + \text{Cl}_2 \rightarrow \text{Cl}^+ + \text{AlCl}_4^-$	$2\text{H}_2\text{SO}_4 \rightarrow \text{H}_3\text{O}^+ + \text{SO}_3 + \text{HSO}_4^-$	$\text{AlCl}_3 + \text{CH}_3\text{Cl} \rightarrow \text{CH}_3^+ + \text{AlCl}_4^-$	$\text{AlCl}_3 + \text{CH}_3\text{COCl} \rightarrow \text{CH}_3\text{CO}^+ + \text{AlCl}_4^-$
Step 2					
Step 3					

(ii) Addition Reaction:

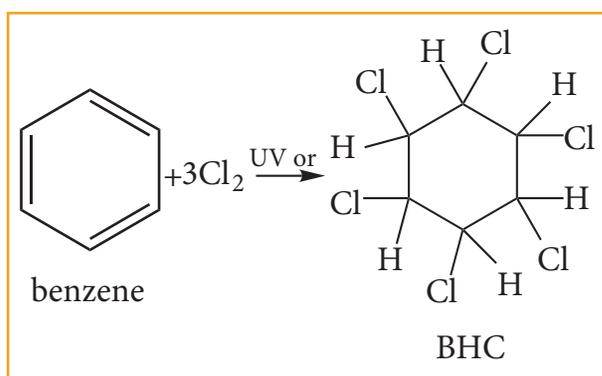
a. Hydrogenation of benzene:

Benzene reacts with hydrogen in the presence of Platinum or Palladium to yield Cyclohexane. This is known as hydrogenation.



b. Chlorination of Benzene:

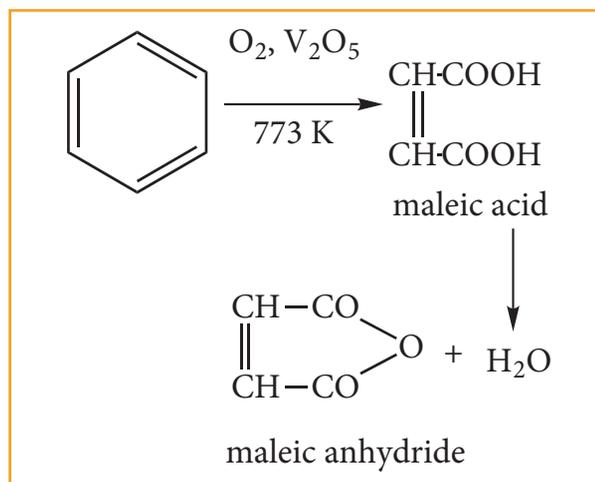
Benzene reacts with three molecules of Cl₂ in the presence of sun light or UV light to yield Benzene Hexa Chloride (BHC) C₆H₆Cl₆. This is known as gammaxane or Lindane which is a powerful insecticide.



(iii) Oxidation:

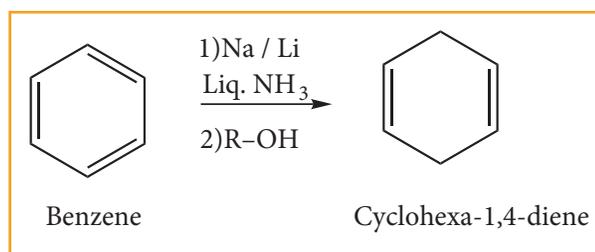
a. Vapour – phase oxidation:-

Although benzene is very stable to strong oxidizing agents, it quickly undergoes vapour phase oxidation by passing its vapour mixed with oxygen over V₂O₅ at 773K. The ring breaks to give maleic anhydride.



b. Birch reduction:

Benzene can be reduced to 1,4-cyclohexadiene by treatment with Na or Li in a mixture of liquid ammonia and alcohol. It is the convenient method to prepare cyclic dienes.



Evaluate Yourself

26) Convert Ethyne to Benzene and name the process.

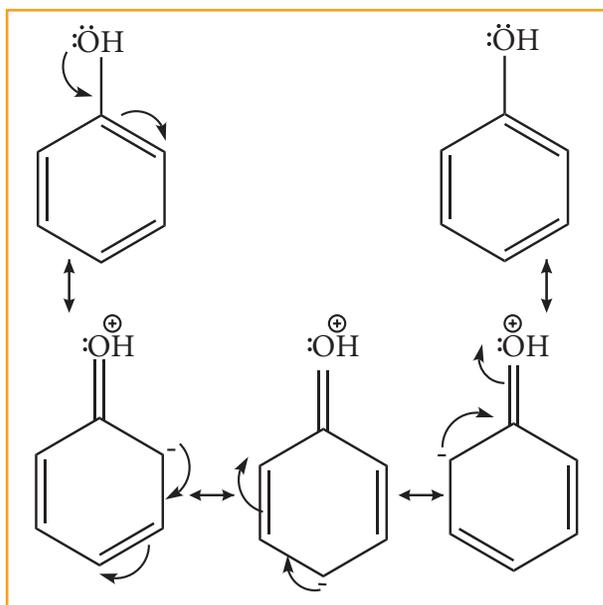
13.5.7 directive influence of a functional group in monosubstituted benzene:

When mono substituted benzene undergoes an electrophilic substitution reaction, the rate of the reaction and the site of attack of the incoming electrophile depends on the functional group already attached to it. Some groups increase the reactivity of benzene ring and are known as activating groups. While others which decrease the reactivity are known as deactivating groups. We further divide

these groups into two categories depending on the way they influence the orientation of attack by the incoming groups. Those which increase electron density at 'ortho' and 'para' position are known as ortho-para directors while those which increase electron density at 'meta' position is known as meta-directors. Some examples of directive influence of functional groups in mono-substituted benzene are explained below.

Ortho and para directing groups

All the activating groups are 'ortho-para' directors. Example $-\text{OH}$, $-\text{NH}_2$, $-\text{NHR}$, $-\text{NHCOCH}_3$, $-\text{OCH}_3$, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$ etc. Let us consider the directive influences of phenolic ($-\text{OH}$) group. Phenol is the resonance hybrid of following structures.



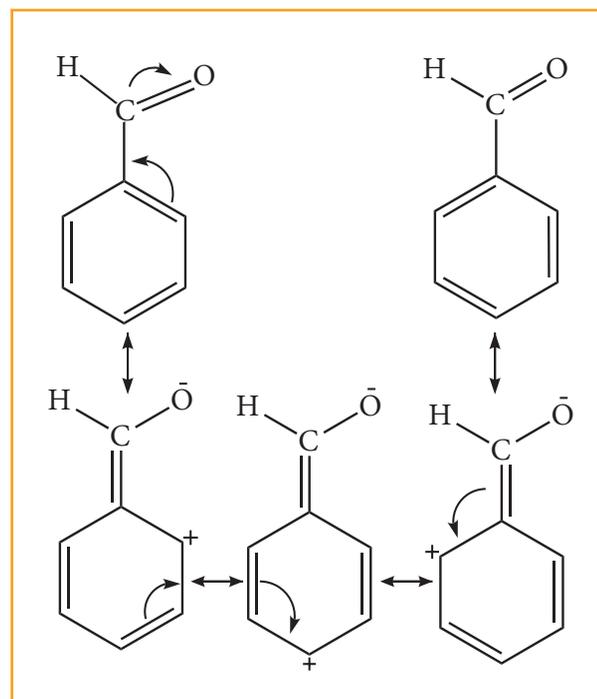
In these resonance structures, the (-) charge residue is present on ortho and para position of ring structure. It is quite evident that the lone pair of electron on the atom which is attached to the ring involves in resonance and makes the ring more electron rich than benzene. The electron

density at ortho and parapositions increases as compared to the meta position. Therefore phenolic group activates the benzene ring for electrophilic attack at 'ortho' and 'para' positions and hence $-\text{OH}$ group is an ortho-para director and activator.

In aryl halides, the strong $-I$ effect of the halogens (electron withdrawing tendency) decreases the electron density of benzene ring, thereby deactivating for electrophilic attack. However the presence of lone pair on halogens involved in the resonance with pi electrons of benzene ring, increases electron density at ortho and para positions. Hence the halogen group is an ortho-para director and deactivator.

META DIRECTING GROUPS

Generally all deactivating groups are meta-directors. For example $-\text{NO}_2$, $-\text{CN}$, $-\text{CHO}$, $-\text{COR}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{SO}_3\text{H}$ etc. Let us consider the directive influence of aldehyde ($-\text{CHO}$) group. Benz aldehyde is the resonance hybrid of following structures.



In these resonance structures, the (+) charge residues is present on the ring structure. It is quite evident that resonance delocalizes the positive charge on the atoms of the ring, making the ring less electron rich than benzene. Here overall density of benzene ring decreases due to -I effect of -CHO group there by deactivating the benzene for electrophilic attack. However resonating structure shows that electron density is more in meta position. Compared to o & p-position. Hence -CHO group is a meta-director and deactivator.

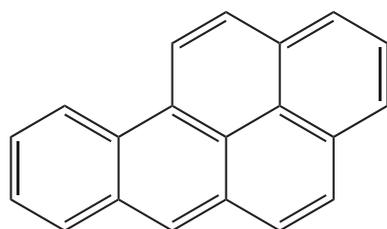
Evaluate Yourself

27) Toluene undergoes nitration easily than benzene. Why?

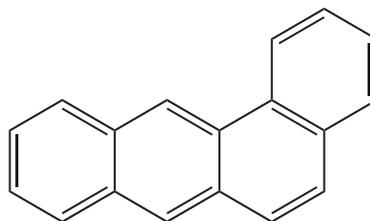
13.5.8. Carcinogenity and toxicity

Benzene and polycyclic aromatic hydrocarbons (PAH) are ubiquitous environmental pollutants generated during incomplete combustion of coal oil, petrol and wood. Some PAH originate from open burning, natural seepage of petroleum and coal deposits and volcanic activities. They are toxic, mutagenic and carcinogenic. It has hematological, immunological and neurological effect on humans. They are radiomimetic and prolonged exposure leads to genetic damage. Some of the examples of PAH are.

“L” shaped polynuclear hydrocarbons are much more toxic & carcinogenic

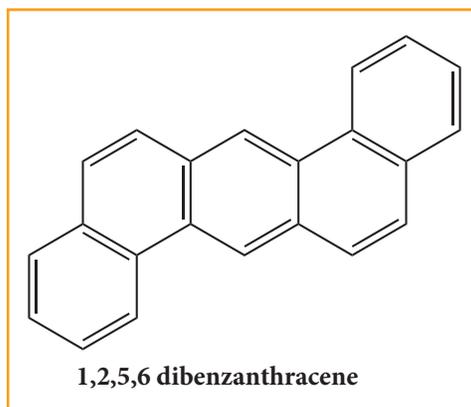


3, 4- Benz[a]pyrene



1, 2- Benzanthracene

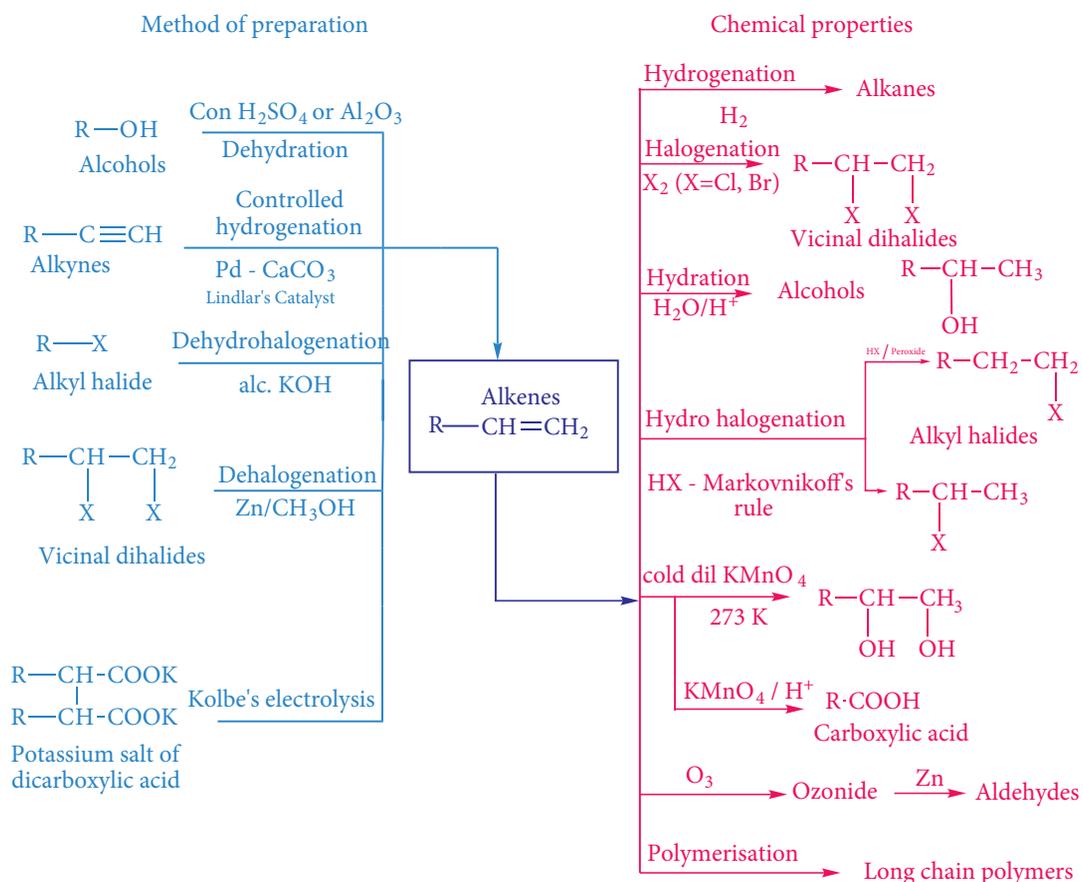
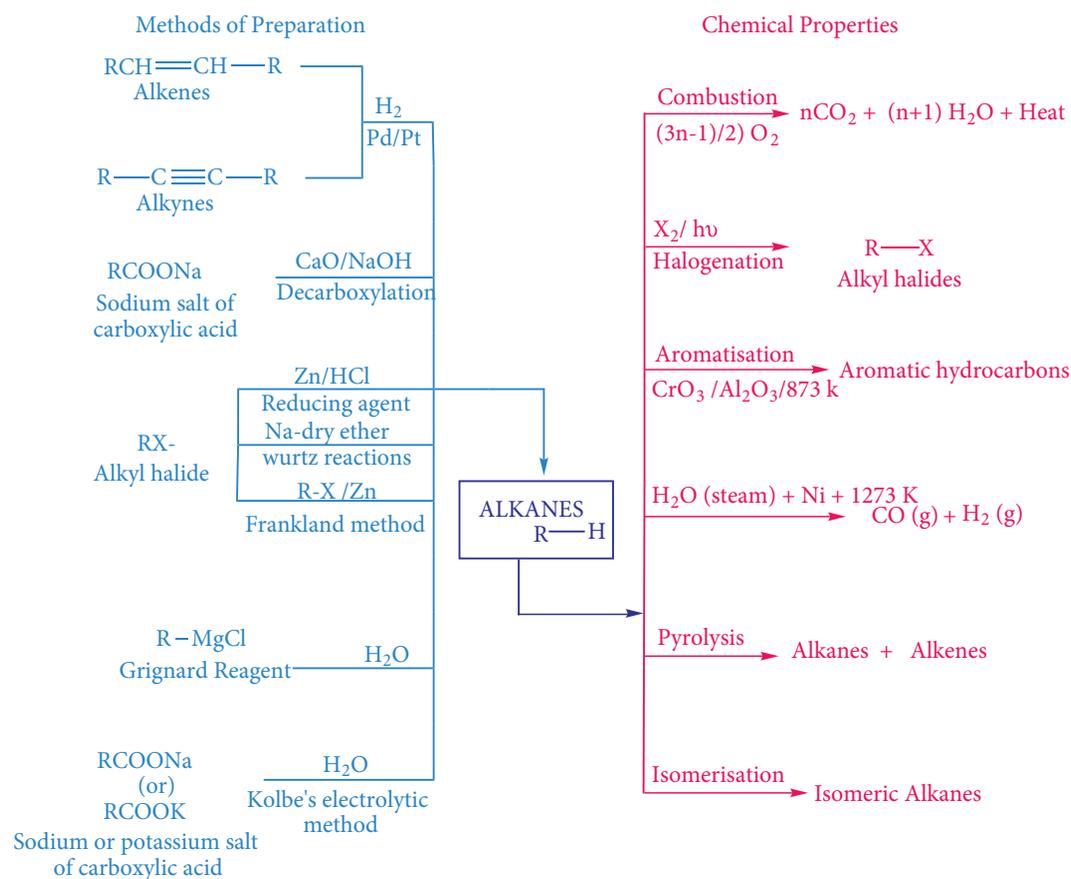
Found in cigarette smoke Found in tobacco and cigarette and charcoal boiled food



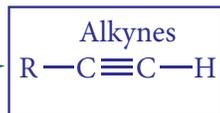
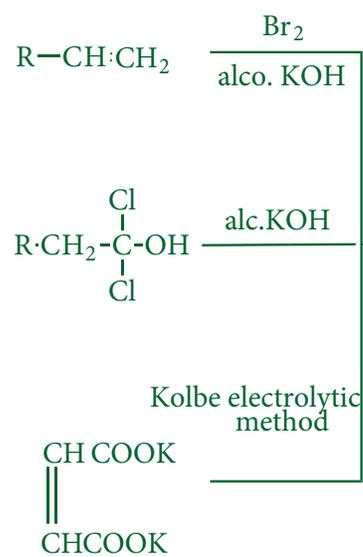
1,2,5,6 dibenzanthracene

Found in gasoline exhaust and barbecued food

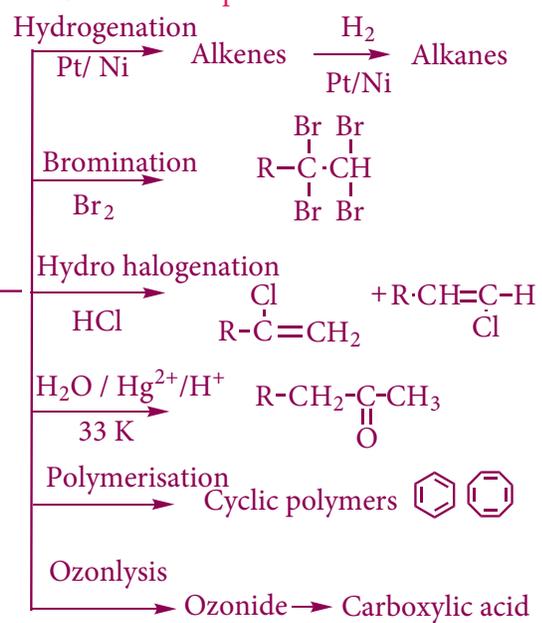
FLOWCHART AND REACTION SUMMARY OF HYDROCARBON



Methods of Preparation



Chemical Properties



Evaluation



I. Choose the best answer.

1. The correct statement regarding the comparison of staggered and eclipsed conformations of ethane, is (NEET)

a) the eclipsed conformation of ethane is more stable than staggered conformation even though the eclipsed conformation has torsional strain.

b) the staggered conformation of ethane is more stable than eclipsed conformation, because staggered conformation has no torsional strain.

c) the staggered conformation of ethane is less stable than eclipsed conformation, because staggered conformation has torsional strain.

d) the staggered conformation of ethane is less stable than eclipsed conformation, because staggered conformation has no torsional strain.

2. $C_2H_5Br + 2Na \xrightarrow{\text{dry ether}} C_4H_{10} + 2NaBr$ The above reaction is an example of which of the following

a) Reimer Tiemann reaction

b) Wurtz reaction

c) Aldol condensation

d) Hoffmann reaction

3. An alkyl bromide (A) reacts with sodium in ether to form 4, 5- diethyloctane, the

compound (A) is

a) $CH_3(CH_2)_3Br$

b) $CH_3(CH_2)_5Br$

c) $CH_3(CH_2)_3CH(Br)CH_3$

d) $CH_3 - (CH_2)_2 - CH(Br) - CH_2 - CH_3$

4. The C - H bond and C - C bond in ethane are formed by which of the following types of overlap

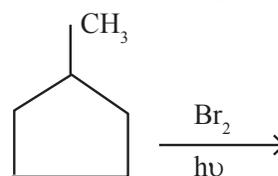
a) $sp^3 - s$ and $sp^3 - sp^3$

b) $sp^2 - s$ and $sp^2 - sp^2$

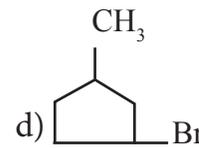
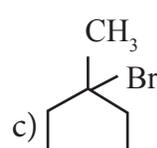
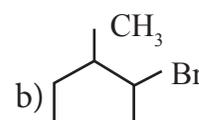
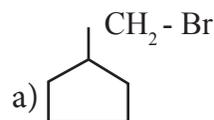
c) $sp - sp$ and $sp - sp$

d) $p - s$ and $p - p$

5. In the following reaction,



The major product obtained is



6. Which of the following is optically active

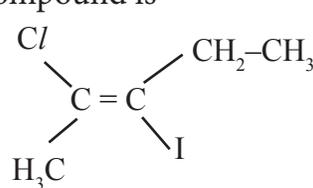
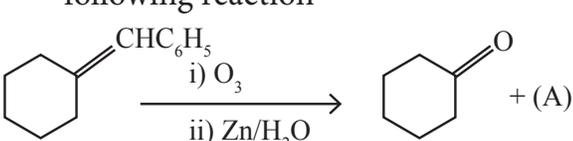
a) 2 - methyl pentane

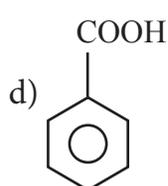
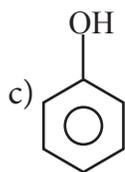
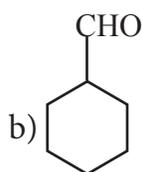
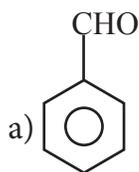
b) citric acid

c) Glycerol

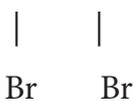
d) none of these



7. The compounds formed at anode in the electrolysis of an aqueous solution of potassium acetate are
- CH_4 and H_2
 - CH_4 and CO_2
 - C_2H_6 and CO_2
 - C_2H_4 and Cl_2
8. The general formula for cyclo alkanes
- C_nH_n
 - C_nH_{2n}
 - $\text{C}_n\text{H}_{2n-2}$
 - $\text{C}_n\text{H}_{2n+2}$
9. The compound that will react most readily with gaseous bromine has the formula (NEET)
- C_3H_6
 - C_2H_2
 - C_4H_{10}
 - C_2H_4
10. Which of the following compounds shall not produce propene by reaction with HBr followed by elimination (or) only direct elimination reaction (NEET)
- ∇
 - $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH}$
 - $\text{H}_2\text{C} = \text{C} = \text{O}$
 - $\text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{Br}$
11. Which among the following alkenes on reductive ozonolysis produces only propanone?
- 2 - Methyl propene
 - 2 - Methyl but - 2 - ene
 - 2, 3 - Dimethyl but - 1 - ene
 - 2, 3 - Dimethyl but - 2 - ene
12. The major product formed when 2 - bromo - 2 - methyl butane is refluxed with ethanolic KOH is
- 2 - methylbut - 2 - ene
 - 2 - methyl butan - 1 - ol
 - 2 - methyl but - 1 - ene
 - 2 - methyl butan - 2 - ol
13. Major product of the below mentioned reaction is,
- $$(\text{CH}_3)_2\text{C} = \text{CH}_2 \xrightarrow{\text{ICl}}$$
- 2-chloro - 1 - iodo - 2 - methyl propane
 - 1-chloro - 2 - iodo - 2 - methylpropane
 - 1,2 - dichloro - 2 - methyl propane
 - 1, 2 - diiodo - 2 - methyl propane
14. The IUPAC name of the following compound is
- 
- trans-2-chloro-3-iodo - 2 - pentene
 - cis-3 - iodo - 4 - chloro - 3 - pentane
 - trans-3-iodo-4-chloro - 3 - pentene
 - cis-2 - chloro - 3 - iodo - 2 - pentene
15. Cis - 2 - butene and trans - 2 - butene are
- conformational isomers
 - structural isomers
 - configurational isomers
 - optical isomers
16. Identify the compound (A) in the following reaction
- 



17. $\text{CH}_2 - \text{CH}_2 \xrightarrow{\text{(A)}} \text{CH} \equiv \text{CH}$, where A is,

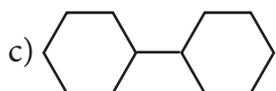
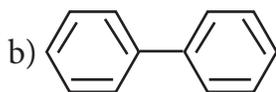
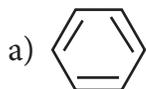


- a) Zn
c) alc. KOH
- b) Conc H_2SO_4
d) dil H_2SO_4

18. Consider the nitration of benzene using mixed con H_2SO_4 and HNO_3 if a large quantity of KHSO_4 is added to the mixture, the rate of nitration will be

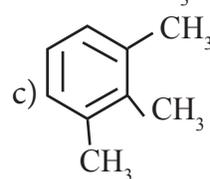
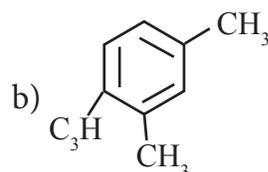
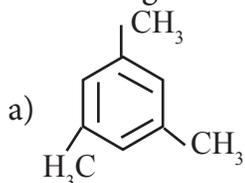
- a) unchanged
c) faster
- b) doubled
d) slower

19. In which of the following molecules, all atoms are co-planar



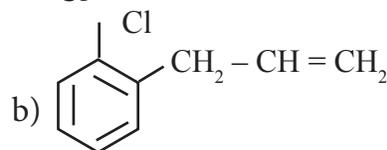
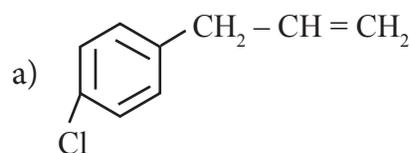
- d) both (a) and (b)

20. Propyne on passing through red hot iron tube gives

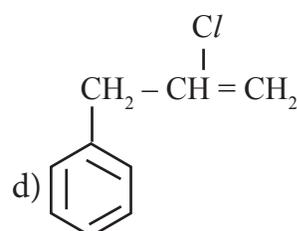


- d) none of these

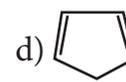
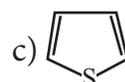
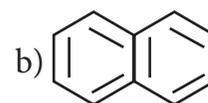
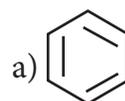
21. $\xrightarrow{\text{HCl}}$ (A) is



- c) both (a) and (b)



22. Which one of the following is non aromatic ?



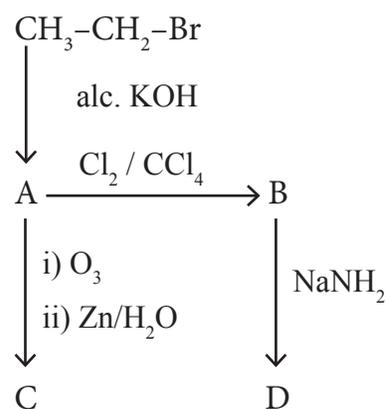
23. Which of the following compounds will not undergo Friedal - crafts reaction easily ? (NEET)

- a) Nitro benzene
c) Cumene
- b) Toluene
d) Xylene





24. Some meta-directing substituents in aromatic substitution are given. Which one is most deactivating ?
- a) - COOH b) - NO₂
c) - C ≡ N d) - SO₃H
25. Which of the following can be used as the halide component for Friedel-Crafts reaction ?
- a) Chloro benzene
b) Bromo benzene
c) chloro ethene
d) isopropyl chloride
26. An alkane is obtained by decarboxylation of sodium propionate. Same alkane can be prepared by
- a) Catalytic hydrogenation of propene
b) action of sodium metal on iodomethane
c) reduction of 1-chloro propane
d) reduction of bromomethane
27. Which of the following is aliphatic saturated hydrocarbon
- a) C₈H₁₈ b) C₉H₁₈
c) C₈H₁₄ d) All of these
28. Identify the compound 'Z' in the following reaction
- $$\text{C}_2\text{H}_6\text{O} \xrightarrow[623\text{K}]{\text{Al}_2\text{O}_3} \text{X} \xrightarrow{\text{O}_3} \text{Y} \xrightarrow{\text{Zn}/\text{H}_2\text{O}} (\text{Z})$$
- a) Formaldehyde
b) Acetaldehyde
c) Formic acid d) none of these
29. Peroxide effect (Kharasch effect) can be studied in case of
- a) Oct - 4 - ene b) hex - 3 - ene
c) pent - 1 - ene d) but - 2 - ene
30. 2 - butyne on chlorination gives
- a) 1 - chloro butane
b) 1, 2 - dichloro butane
c) 1, 1, 2, 2 - tetrachlorobutane
d) 2, 2, 3, 3 - tetra chloro butane
31. Give IUPAC names for the following compounds
- 1) $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{CH}_3$
- $\begin{array}{cc} \text{C}_2\text{H}_5 & \text{CH}_3 \\ | & | \end{array}$
- 2) $\text{CH}_3-\text{C}-\text{C}-\text{C}\equiv\text{C}-\text{CH}_3$
- $\begin{array}{cc} | & | \\ \text{CH}_3 & \text{H} \end{array}$
- 3) $(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{C}-\text{CH}(\text{CH}_3)_2$
- 4) ethyl isopropyl acetylene
- 5) $\text{CH}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{CH}$
32. Identify the compound A, B, C and D in the following series of reactions



33. Write short notes on ortho, para directors in aromatic electrophilic substitution reactions.
34. How is propyne prepared from an alkylene dihalide ?
35. An alkylhalide with molecular formula $C_6H_{13}Br$ on dehydro halogenation gave two isomeric alkenes X and Y with molecular formula C_6H_{12} . On reductive ozonolysis, X and Y gave four compounds CH_3COCH_3 , CH_3CHO , CH_3CH_2CHO and $(CH_3)_2CHCHO$. Find the alkylhalide.
36. Describe the mechanism of Nitration of benzene.
37. How does Huckel rule help to decide the aromatic character of a compound.
38. Suggest the route for the preparation of the following from benzene.
- 1) 3 - chloro nitrobenzene
 - 2) 4 - chlorotoluene
 - 3) Bromo benzene
 - 4) m - dinitro benzene
39. Suggest a simple chemical test to distinguish propane and propene.
40. What happens when isobutylene is treated with acidified potassium permanganate ?
41. How will you convert ethyl chloride in to
- i) ethane
 - ii) n - butane
42. Describe the conformers of n - butane.
43. Write the chemical equations for combustion of propane.
44. Explain Markov nikoff's rule with suitable example.
45. What happens when ethylene is passed through cold dilute alkaline potassium permanganate.
46. Write the structures of following alkanes.
- 1) 2, 3 - Dimethyl - 6 - (2 - methyl propyl) decane
 - 2) 5 - (2 - Ethyl butyl) - 3, 3 - dimethyldecane
 - 3) 5 - (1, 2 - Dimethyl propyl) - 2 - methylnonane
47. How will you prepare propane from a sodium salt of fatty acid ?
48. $CH_3 - CH(CH_3) - CH(OH) - CH_3$
- ↓ $H^+/heat$
- (A) major product \xrightarrow{HBr} (B) major product
- Identify A and B
49. Complete the following :
- i) 2 - butyne $\xrightarrow{\text{Lindlar Catalyst}}$
 - ii) $CH_2 = CH_2 \xrightarrow{I_2}$
 - iii) $\begin{array}{c} CH_2 - CH_2 \\ | \quad | \\ Br \quad Br \end{array} \xrightarrow{Zn/C_2H_5OH}$
 - iv) $CaC_2 \xrightarrow{H_2O}$
50. How will you distinguish 1 - butyne and 2 - butyne?



**Francois Auguste Victor
Grignard**

He a French chemist was awarded the noble prize for chemistry in 1912. He prepared and realised the usefulness of organo magnesium compounds. He took maths degree and eventually switched over organic chemistry while attempting to find the catalyst for the process of Methylation.

Learning Objectives

After learning this unit, students will be able to

- classify the various organic halo compounds.
- name the organic halo compounds according to IUPAC system.
- recognise the nature of C-X bond.
- describe the general methods of preparation of haloalkanes and haloarenes
- explain the physical and chemical properties of haloalkanes and haloarenes.
- describe the mechanism of nucleophilic substitution and elimination reactions of halo organics
- explain the preparation and synthetic uses of grignard reagent.
- highlight the uses of poly halogen compounds.
- comprehend the environmental effect of poly halogen compounds.

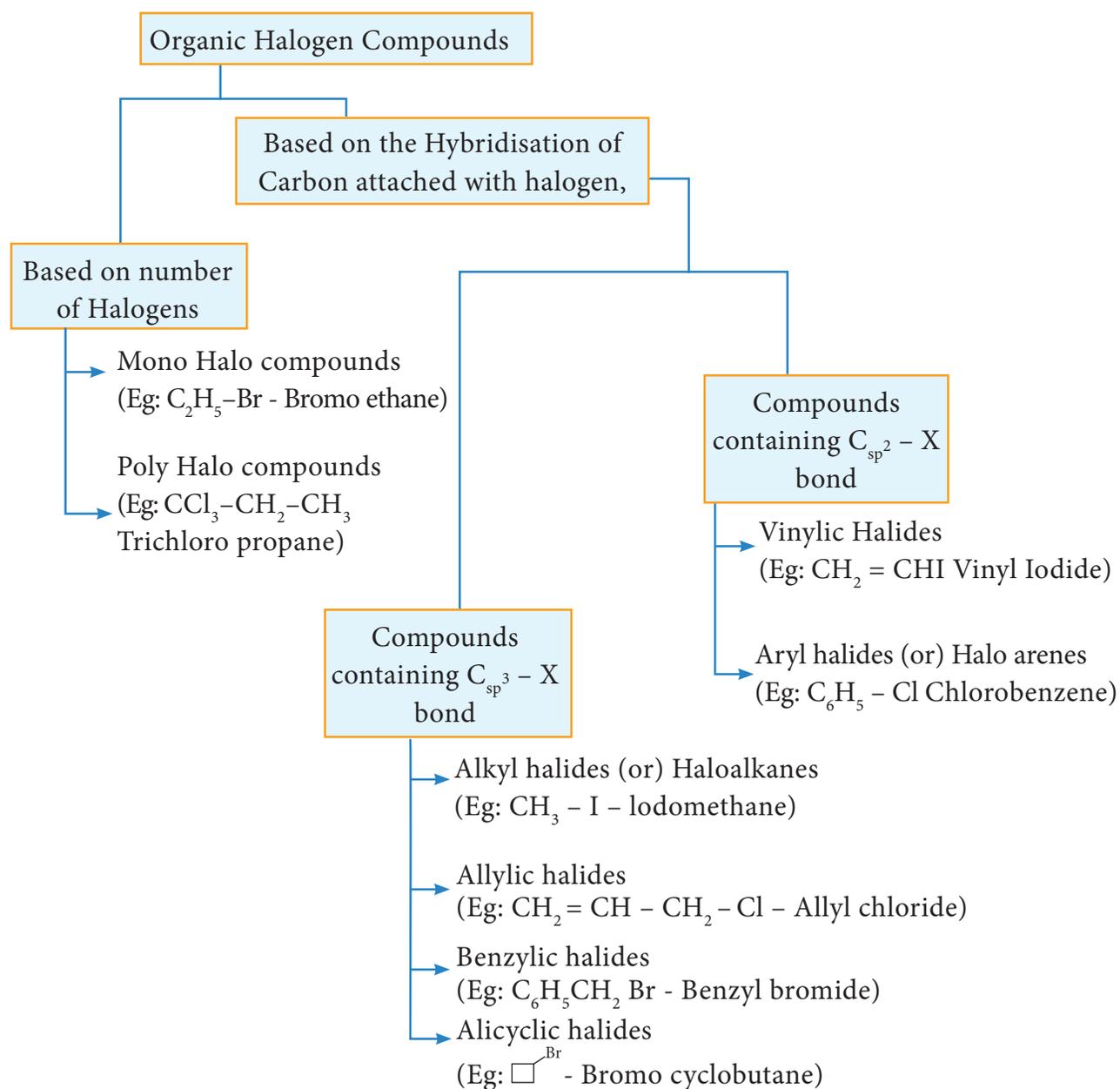
14.1 INTRODUCTION

In the previous unit we learnt about the chemistry of hydrocarbons. In this unit we learn about organic compounds containing halogens. When one or more hydrogen atoms of aliphatic or aromatic hydrocarbons are replaced by the corresponding number of halogens like fluorine, chlorine, bromine

or iodine, the resultant compounds are called either haloalkanes or halo arenes. They serve as starting materials for many organic synthesis.

Halogen substituted organic compounds are widely spread in nature and find application in our day to day life as well as in industry. Certain compounds like chloramphenicol produced by soil microbes are used in the treatment of typhoid; chloroquine is used in the treatment of malaria, halothane is used as an anesthetic, and halogenated solvents like trichloroethylene are used for cleaning electronic equipments.

14.2 Classification of organic halogen compounds

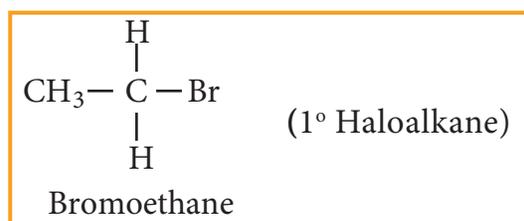


14.3 Haloalkanes

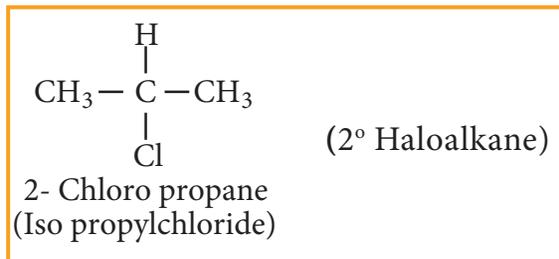
Mono halogen derivatives of alkanes are called haloalkanes. Haloalkanes are represented by general formula $R - X$, Where, R is an alkyl group (C_nH_{2n+1}) – and X is a halogen atom ($X = F, Cl, Br$ or I). Haloalkanes are further classified into primary, secondary, tertiary haloalkane on the basis of type of carbon atom to which the halogen is attached.

Primary haloalkane

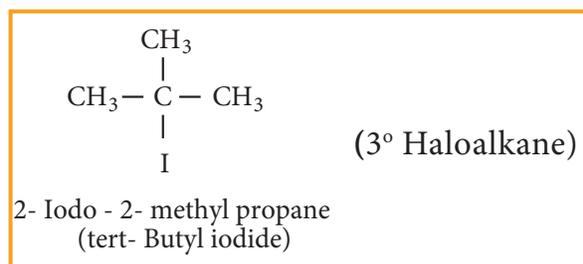
Examples:



Secondary haloalkane



Tertiary haloalkane



14.3.1 Nomenclature

Common system

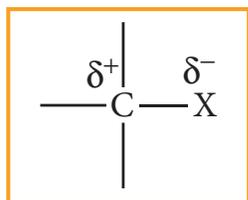
In the common system, haloalkanes are named as alkyl halides. It is derived by naming the alkyl group followed by the halide.

IUPAC system

Let us write the IUPAC name for the below mentioned haloalkanes by applying the general rules of nomenclature that are already discussed in Unit no : 11



S.No	Structural formula	Common name	IUPAC name
1	CH_3I	methyl iodide	Iodomethane
2	$\text{CH}_3\text{CH}_2\text{Br}$	ethyl bromide	Bromoethane
3	$\text{CH}_3\text{CH}_2\text{CH}_2\text{F}$	n-propyl fluoride	1-Fluoropropane
4	$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \\ \text{F} \end{array}$	isopropyl fluoride	2-Fluoropropane
5	$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{Cl}$	n-butyl chloride	1-Chlorobutane
6	$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{Cl} \\ \\ \text{CH}_3 \end{array}$	isobutyl chloride	1-Chloro-2-methylpropane
7	$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 \\ \\ \text{Cl} \end{array}$	sec-butyl chloride	2-Chlorobutane
8	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{Cl} \end{array}$	tert-butyl chloride	2-Chloro-2-methylpropane
9	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{Br} \\ \\ \text{CH}_3 \end{array}$	neo-pentyl bromide	1-Bromo-2,2-dimethylpropane
10	$\text{CH}_2 = \text{CH} - \text{Cl}$	vinyl chloride	Chloroethene
11	$\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{Br}$	allyl bromide	3-Bromopropene



The C - X bond is formed by overlap of sp^3 orbital of carbon atom with half filled p-orbital of the halogen atom. The atomic size of halogen increases from fluorine to iodine, which increases the C - X bond length. Larger the size, greater is the bond length, and weaker is the bond formed. The bond strength of C - X decreases from C - F to C - I in CH_3X . The changes in the value of bond length, bond enthalpy and bond polarity, as we move from C - F to C - I, is given in the table.

Table showing carbon - halogen bond length, bond enthalpy and polarity of bond.

Bond	Bond length (pm)	Bond Enthalpy (kJmol^{-1})	Polarity of bond in terms of dipole moment (Debye)
$CH_3 - F$	139	452	1.847
$CH_3 - Cl$	178	351	1.860
$CH_3 - Br$	193	293	1.830
$CH_3 - I$	214	234	1.636

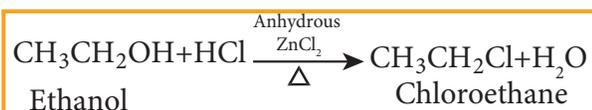
14.3.3 Methods of preparation

Haloalkanes are prepared by the following methods

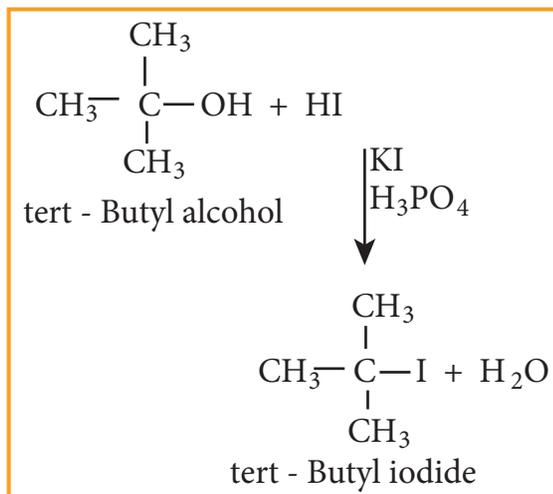
1) From alcohols

Alcohols can be converted into haloalkanes by reacting it with any one of the following reagent 1. hydrogen halide 2. Phosphorous halides 3. Thionyl chloride

a) Reaction with hydrogen halide



Mixture of con.HCl and anhydrous ZnCl_2 is called **Lucas reagent**.

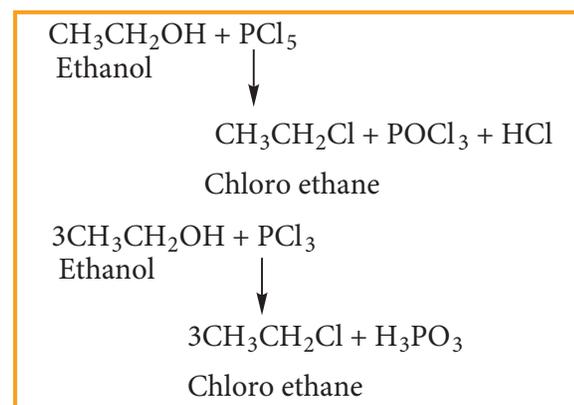


The order of reactivity of halo acids with alcohol is in the order $\text{HI} > \text{HBr} > \text{HCl}$. The order of reactivity of alcohols with halo acid is tertiary $>$ secondary $>$ primary.

b) Reaction with phosphorous halides

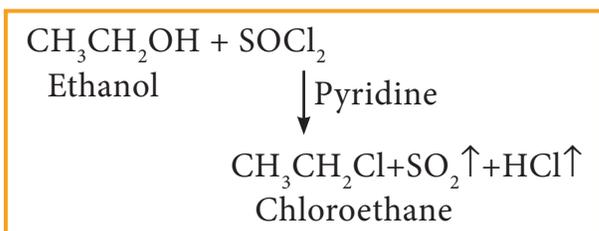
Alcohols react with PX_5 or PX_3 to form haloalkane. PBr_3 and PI_3 are usually generated in situ (produced in the reaction mixture) by the reaction of red phosphorus with bromine and iodine, respectively.

Example



c) Reaction with thionyl chloride (Sulphonyl chloride)

Example



This reaction is known as **Darzen's halogenation**

2) From alkenes

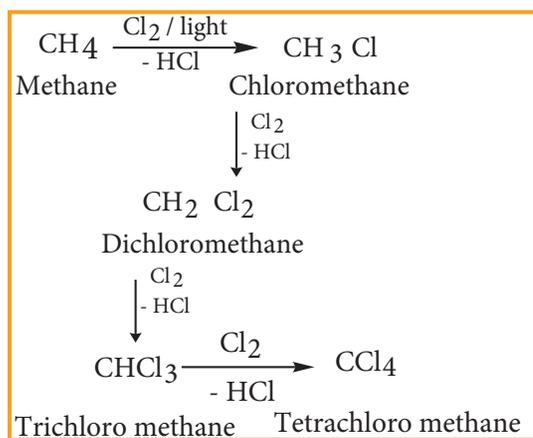
Alkenes react with halogen acids (HCl, HBr, HI) to give haloalkane. The mode of addition follows Markovnikov's rule.

3) From alkanes

Alkanes react with halogens (Cl_2 or Br_2) in the presence of ultra violet light to form haloalkane. This reaction is a free radical substitution reaction and gives a mixture of mono, di or poly substituted haloalkane.

Example

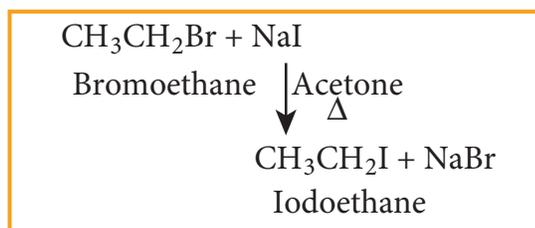
Chlorination of methane gives different products which have differences in the boiling points. Hence, these can be separated by fractional distillation.



4) Halogen exchange reactions

a) Finkelstein reaction

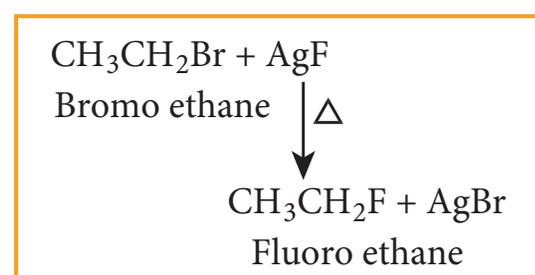
Chloro or bromoalkane on heating with a concentrated solution of sodium iodide in dry acetone gives iodo alkanes. This reaction is called Finkelstein reaction, ($\text{S}_{\text{N}}2$ reaction).



b) Swarts reaction

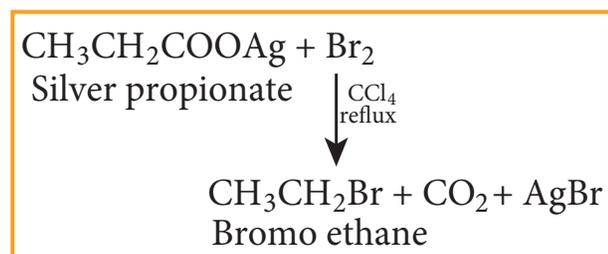
Chloro or bromo alkanes on heating with metallic fluorides like AgF, SbF_3 or Hg_2F_2 gives fluoro alkanes. This reactions is called Swarts reaction.

Example



5) From silver salts of fatty acids (Hunsdiccker reaction)

Silver salts of fatty acids when refluxed with bromine in CCl_4 gives bromo alkane



14.3.4 Physical Properties

1. Pure haloalkanes are colourless. Bromo and iodo alkanes are coloured in the presence of light.

2. Haloalkanes having one, two or three carbon atoms are in the gaseous state at normal temperature. Haloalkanes having more than three carbon atoms are liquids or solids.

3. Boiling point and Melting point

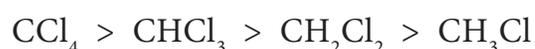
- i) Haloalkanes have higher boiling point and melting point than the parent alkanes having the same number of carbons because the intermolecular forces of attraction (dipole – dipole interaction and vander Waals forces) are stronger in haloalkane.
- ii) The boiling point and melting point of haloalkanes decreases with respect to the halogen in the following order.

Example



- iii) The boiling points of chloro, bromo and iodo alkanes increase with the increase in the number of halogen atoms.

For Example:



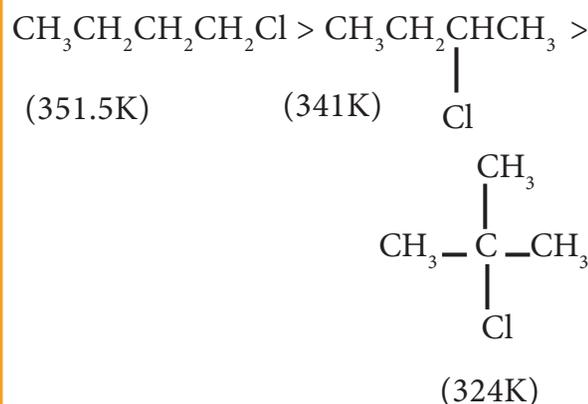
- iv) The boiling point and melting point of mono haloalkane increase with the increase in the number of carbon atoms.

Example



- v) Among isomeric alkyl halides the boiling point decreases with the increase in branching in the alkyl group; with increase in branching, the molecule attains spherical shape with less surface area. As a result the inter molecular forces become weak, resulting in lower boiling points.

Example



4. Solubility

Haloalkanes are polar covalent compounds soluble in organic solvents, but insoluble in water because they cannot form hydrogen bonds with water molecules

5. Density

The density of liquid alkyl halides are higher than these of hydrocarbons of comparable molecular weight.

Evaluate Yourself

3) Write all possible chain isomers with molecular formula $C_5H_{11}Cl$

14.3.5 Chemical properties

Haloalkanes are one of the most reactive classes of organic compounds. Their reactivity is due to the presence of polar carbon – halogen bond in their molecules. The reactions of haloalkane may be divided into the following types

- Nucleophilic substitution reactions
- Elimination reactions
- Reaction with metals
- Reduction

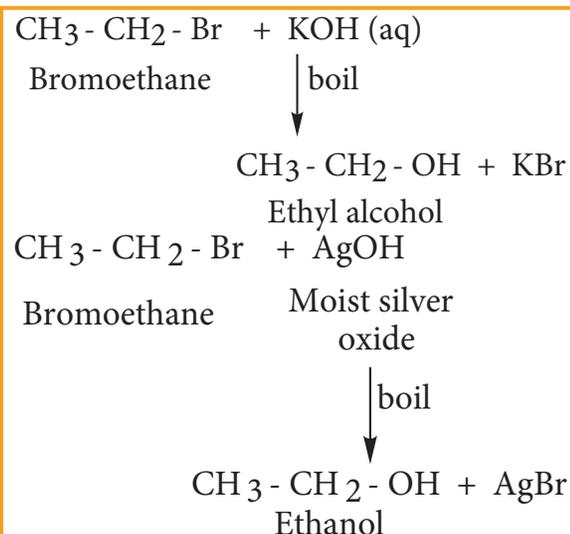
1) Nucleophilic substitution reactions

We know that the $C^{\delta+} - X^{\delta-}$ present in halo alkane is polar and hence the nucleophilic reagents are attracted by partially positively charged carbon atoms resulting in substitution reactions.

Reaction with aqueous alkali or moist silver oxide. (Hydrolysis)

Haloalkane reacts with aqueous solution of KOH or moist silver oxide (Ag_2O/H_2O) to form alcohols.

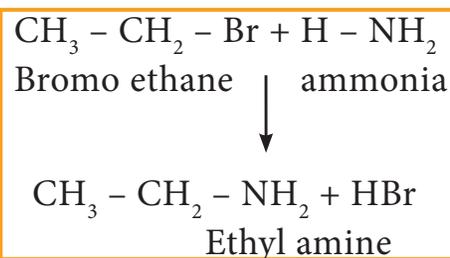
Example



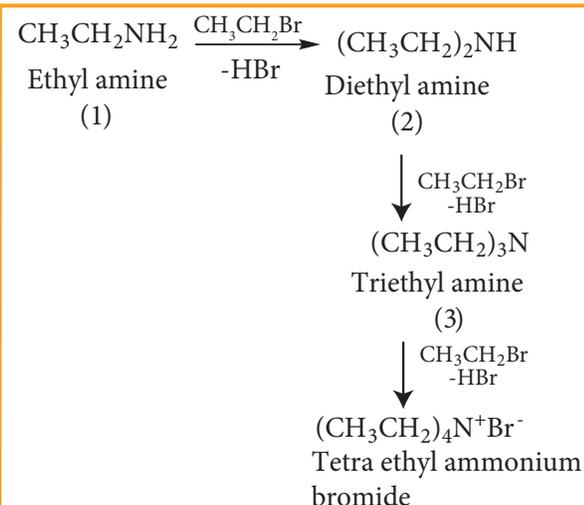
i) Reaction with alcoholic ammonia (Ammonolysis)

Haloalkanes react with alcoholic ammonia solution to form alkyl amines.

Example



However, with excess of halo alkane, secondary and tertiary amines along with quaternary ammonium salts are obtained



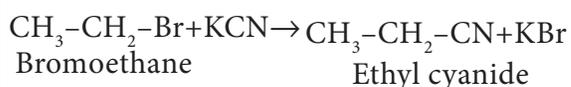
Ambident Nucleophiles

Nucleophiles such as cyanide and nitrite ion which can attack nucleophilic centre from two sides of the nucleophile are called ambident nucleophiles. These nucleophiles can attack with either of the two sides depending upon the reaction conditions and the reagent used.

ii) Reaction with alcoholic KCN

Haloalkanes react with alcoholic KCN solution to form alkyl cyanides.

Example



iii) Reaction with alcoholic AgCN

Haloalkanes react with alcoholic AgCN solution to form alkyl isocyanide.

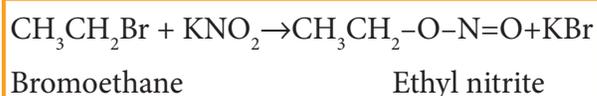
Example



iv) Reaction with sodium or potassium nitrite

Haloalkanes react with alcoholic solution of NaNO_2 or KNO_2 to form alkyl nitrites.

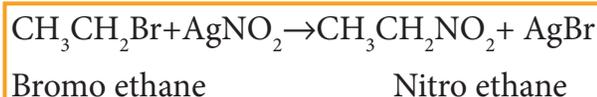
Example



v) Reaction with silver nitrite

Haloalkanes react with alcoholic solution of AgNO_2 to form nitro alkanes.

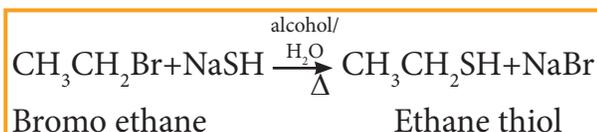
Example



vi) Reaction with sodium or potassium hydrogen sulphide

Haloalkanes react with sodium or potassium hydrogen sulphide to form thio alcohols.

Example

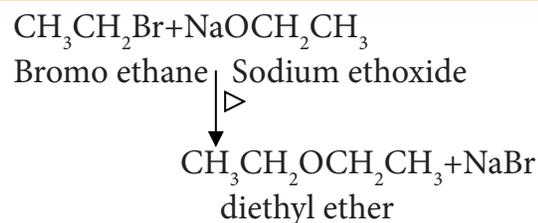


vii) Williamson ether synthesis

Haloalkane, when boiled with sodium alkoxide gives corresponding ethers.

Example

This method can be used to prepare mixed (unsymmetrical) ethers also.



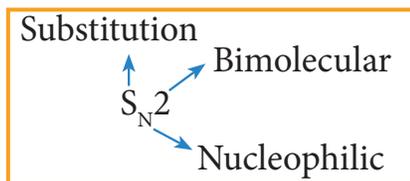
Mechanism of Nucleophilic substitution reaction

The mechanism of nucleophilic substitution reaction is classified as

a) Bimolecular Nucleophilic substitution reaction ($\text{S}_{\text{N}}2$)

b) Unimolecular Nucleophilic substitution reaction (S_N1)

S_N2 Mechanism



The rate of S_N2 reaction depends upon the concentration of both alkyl halide and the nucleophile.

Rate of reaction

$$= k_2 [\text{alkylhalide}][\text{nucleophile}]$$

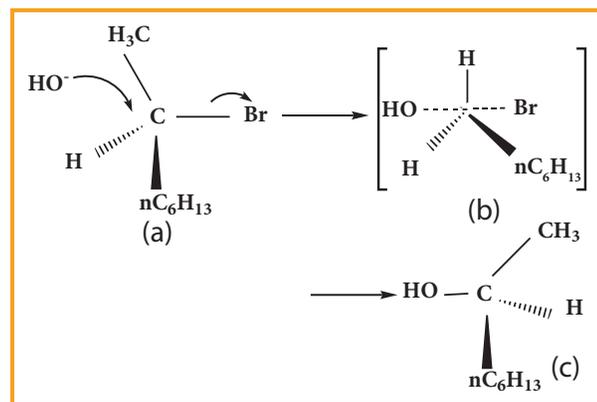
It follows second order kinetics and occurs in one step.

This reaction involves the formation of a transition state in which both the reactant molecules are partially bonded to each other. The attack of nucleophile occurs from the back side (i.e opposite to the side in which the halogen is attached). The carbon at which substitution occurs has inverted configuration during the course of reaction just as an umbrella has tendency to invert in a wind storm. This inversion of configuration is called Walden inversion; after Paul Walden who first discovered the inversion of configuration of a compound in S_N2 reaction.

S_N2 reaction of an optically active haloalkane is always accompanied by inversion of configuration at the asymmetric centre. Let us consider the following example

When 2 - Bromooctane is heated with sodium hydroxide, 2 - octanol is formed with inversion of configuration. (-)

- 2 - Bromo octane is heated with sodium hydroxide (+) - 2 - Octanol is formed in which - OH group occupies a position opposite to what bromine had occupied,



(a) (-) 2 - Bromo octane

(b) Transition State

(c) (+) 2 - Octanol (product)

S_N1 Mechanism

S_N1 stands for unimolecular nucleophilic substitution

'S' stands for substitution

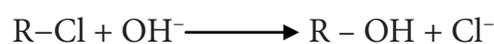
'N' stands for nucleophilic

'1' stands for unimolecular (one molecule is involved in the rate determining step)

The rate of the following S_N1 reaction depends upon the concentration of alkyl halide (RX) and is independent of the concentration of the nucleophile (OH^-).

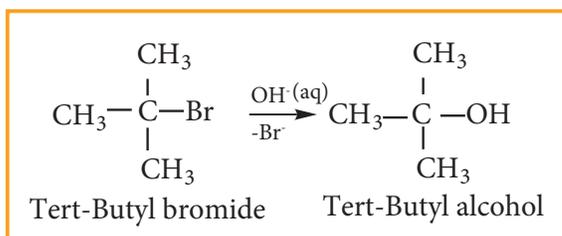
Hence Rate of the reaction

$$= k[\text{alkyl halide}]$$



This S_N1 reaction follows first order kinetics and occurs in two steps.

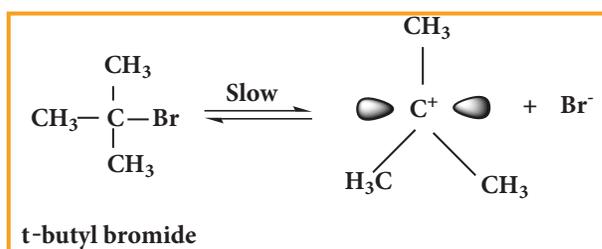
We understand S_N1 reaction mechanism by taking a reaction between tertiary butyl bromide with aqueous KOH.



This reaction takes place in two steps as shown below

Step - 1 Formation of carbocation

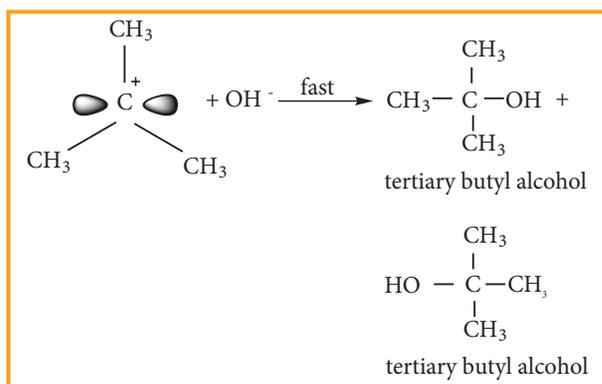
The polar C - Br bond breaks forming a carbocation and bromide ion. This step is slow and hence it is the rate determining step.



The carbocation has 2 equivalent lobes of the vacant 2p orbital, so it can react equally rapidly from either face

Step - 2

The nucleophile immediately reacts with the carbocation. This step is fast and hence does not affect the rate of the reactions.



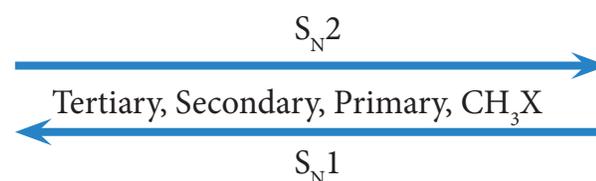
As shown above, the nucleophilic reagent OH^- can attack carbocation from both the sides.

In the above example the substrate tert-butyl bromide is not optically active, hence the obtained product is optically inactive. If halo alkane substrate is optically active then, the product obtained will be optically inactive racemic mixture. As nucleophilic reagent OH^- can attack carbocation from both the sides, to form equal proportion of dextro and levorotatory optically active isomers which results in optically inactive racemic mixture.

Example

Hydrolysis of optically active 2-bromo butane gives racemic mixture of \pm butan-2-ol

The order of reactivity of haloalkanes towards S_N1 and S_N2 reaction is given below.



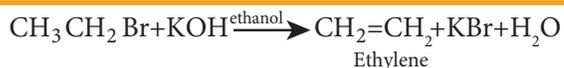
Evaluate Yourself

4) neo-pentyl bromide undergoes nucleophilic substitution reactions very slowly - justify.

2) Elimination reactions

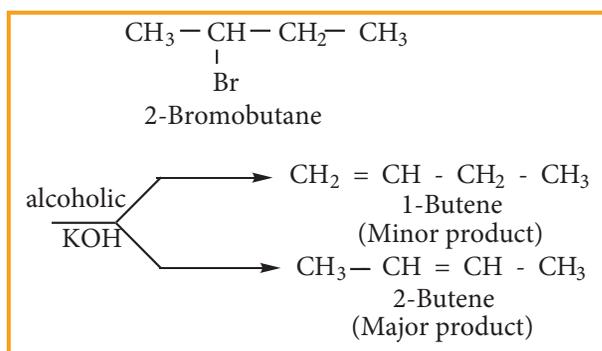
When a haloalkane containing a hydrogen on β carbon is treated with an ethanolic solution of potassium hydroxide, an alkene is formed. In this reaction a double bond between α and β carbon is formed by

releasing a halogen attached to a α carbon and a hydrogen to a β carbon of halo alkane. This reaction is called β elimination reaction. (dehydrohalogenation).



Some haloalkanes yield a mixture of olefins in different amounts. It is explained by Saytzeff's Rule, which states that 'In a dehydrohalogenation reaction, the preferred product is that alkene which has more number of alkyl groups attached to the doubly bonded carbon (more substituted double bond is formed)

Example



Elimination reactions may proceed through two different mechanisms namely E_1 and E_2

E_2 reaction mechanism

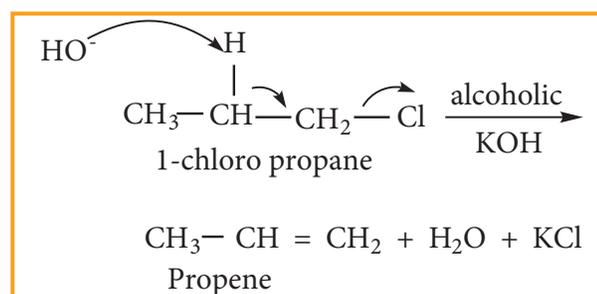
Elimination
 E_2 → bimolecular
(Second order)

The rate of E_2 reaction depends on the concentration of alkyl halide and base

$$\text{Rate} = k [\text{alkyl halide}][\text{base}]$$

It is therefore, a second order reaction. Generally primary alkyl halide undergoes this reaction in the presence of

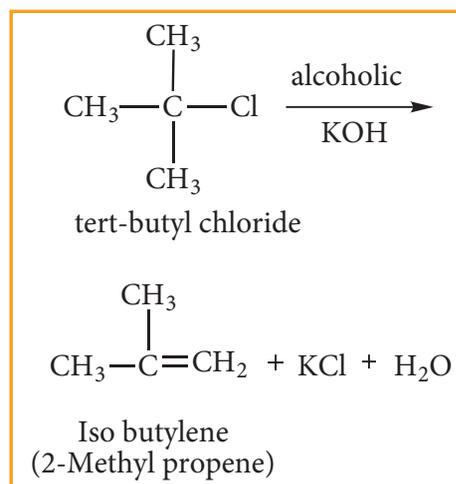
alcoholic KOH. It is a one step process in which the abstraction of the proton from the β carbon and expulsion of halide from the α carbon occur simultaneously. The mechanism is shown below.



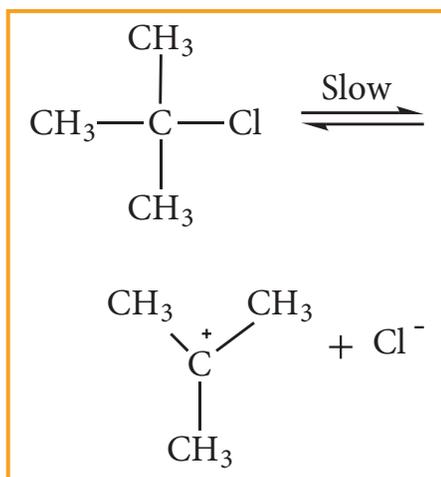
E_1 reaction mechanism

Elimination
 E_1 → Unimolecular

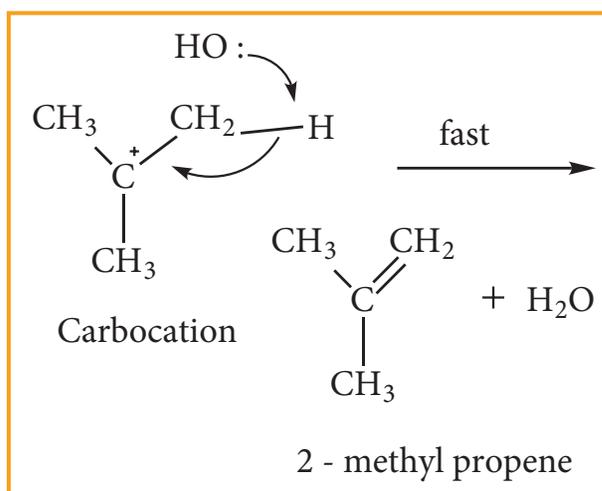
Generally, tertiary alkyl halide which undergoes elimination reaction by this mechanism in the presence of alcoholic KOH. It follows first order kinetics. Let us consider the following elimination reaction.



Step - 1 Heterolytic fission to yield a carbocation



Step - 2 Elimination of a proton from the β - carbon to produce an alkene



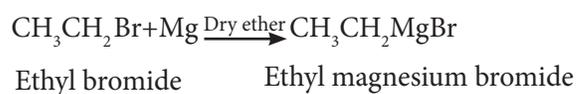
3) Reaction with metals

Haloalkane reacts with metals, to form a compound containing carbon - metal bond known as organometallic compounds.

a) Grignard reaction

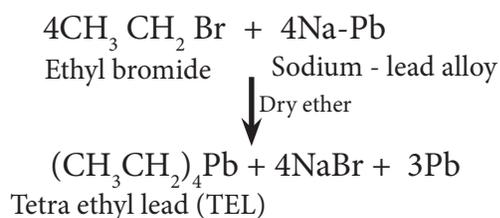
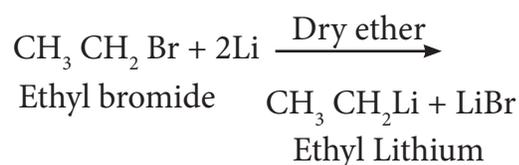
When a solution of halo alkane in ether is treated with magnesium, we get alkyl magnesium halide known as Grignard reagent.

Example



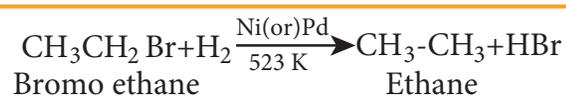
b) Reaction with active metals like sodium, lead etc

Haloalkane reacts with active metals like sodium, lead etc in the presence of dry ether to form organo metallic compounds.



4) Reduction reactions

Haloalkanes are reduced to alkanes by treating with H_2 in the presence of metal catalyst like nickel, palladium etc or with hydroiodic acid in the presence of red phosphorous.



14.3.6 Uses of haloalkane

Chloroform:

1. is used as a solvent in pharmaceutical industry
2. is used for producing pesticides and drugs
3. is used as an anaesthetic.
4. used as a preservative for anatomical specimens.

Iodoform:

1. is used as an antiseptic for dressing wounds.

Carbon tetrachloride:

1. is used as dry cleaning agent
2. is used as a solvent for oils, fats and waxes
3. As the vapour of CCl_4 is non-combustible, it is used under the name pyrene for extinguishing the fire in oil or petrol.

14.4 Organo metallic Compounds

Organo metallic compounds are organic compounds in which there is a direct carbon-metal bond. For Example

CH_3MgI - Methyl magnesium iodide

$\text{CH}_3\text{CH}_2\text{MgBr}$ - Ethyl magnesium bromide

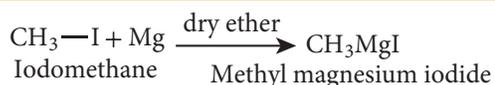
The Carbon - Magnesium bond in Grignard reagent is covalent but highly polar. The carbon atom is more electro negative than magnesium. Hence, the carbon atom has partial negative charge and the magnesium atom has partial positive charge



14.4.1. Preparation

When a solution of alkyl halide in ether is allowed to stand over pieces of magnesium metal, the metal gradually dissolves and alkyl magnesium halide (Grignard reagent) is formed. All the reagents used should be pure and dry

Example



Evaluate Yourself

5) Why Grignard reagent should be prepared in anhydrous condition?

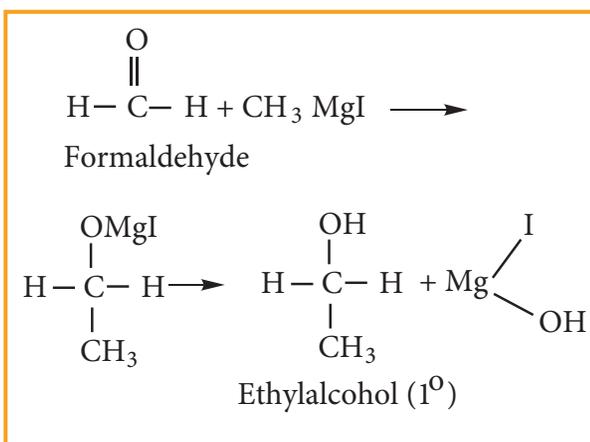
14.4.2. Uses of Grignard reagent

Grignard reagents are synthetically very useful compounds. These reagents are

converted to various organic compounds like alcohols, carboxylic acids, aldehydes and ketones. The alkyl group being electron rich acts as a carbanion or a nucleophile. They would attack polarized molecules at a point of low electron density. The following reactions illustrate the synthetic uses of Grignard reagent.

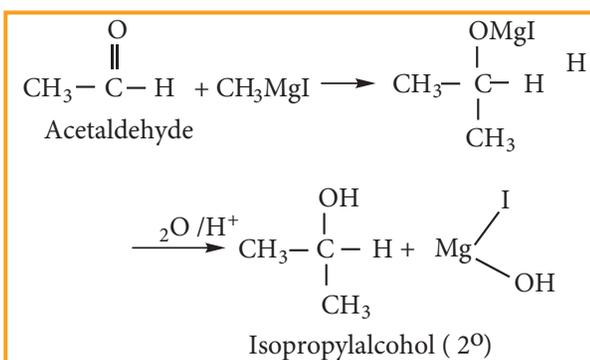
(1) Preparation of primary alcohol

Formaldehyde reacts with Grignard reagent to give addition products which on hydrolysis yields primary alcohol.



2) Preparation of secondary alcohol

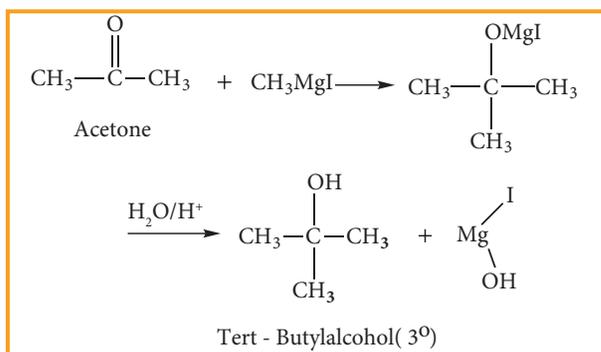
Aldehydes other than formaldehyde, react with Grignard reagent to give addition product which on hydrolysis yields secondary alcohol.



3) Preparation of Tertiary alcohol

Ketone reacts with Grignard reagent to give an addition product which on hydrolysis yields tertiary alcohols.

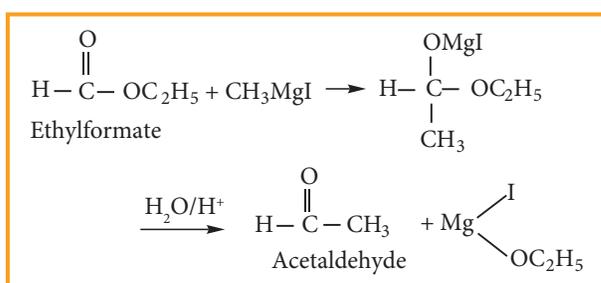
Example



(4) Preparation of aldehyde

Ethyl formate reacts with Grignard reagent to form aldehyde. However, with excess of Grignard reagent it forms secondary alcohol.

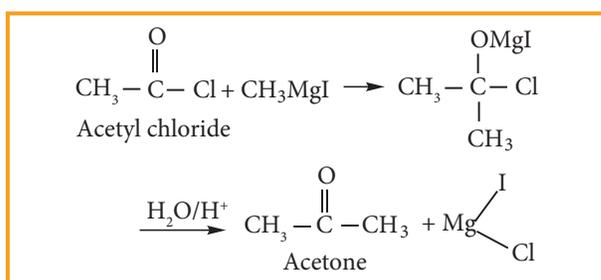
Example



(5) Preparation of ketone

Acid chloride reacts with Grignard reagent to form ketones. However, with excess of Grignard reagent it forms tertiary alcohol.

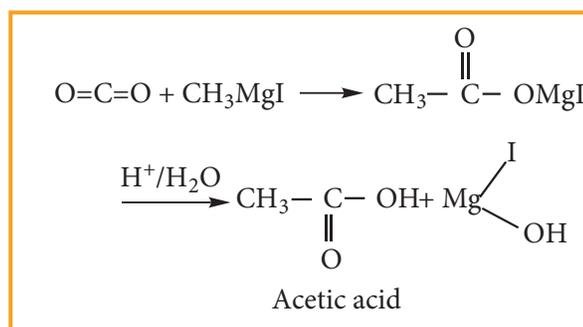
Example



6) Preparation of carboxylic acids

Solid carbon dioxide reacts with Grignard reagent to form addition product which on hydrolysis yields carboxylic acids.

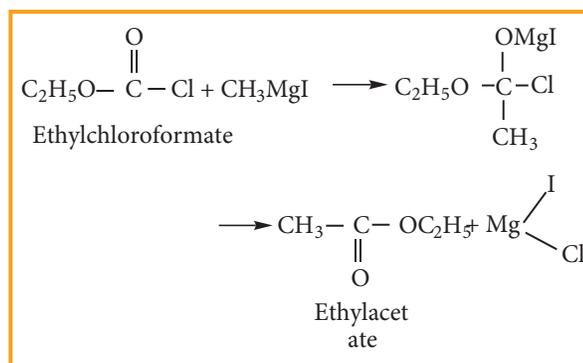
For Example



7) Preparation of esters

Ethylchloroformate reacts with Grignard reagent to form esters.

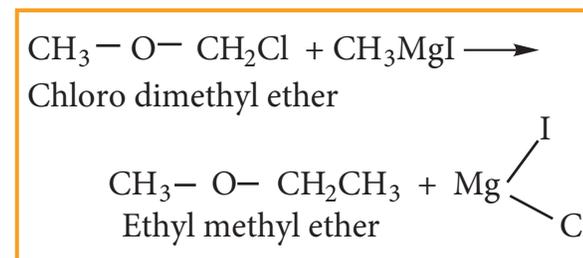
Example



8) Preparation of higher ethers

Lower halogenated ether reacts with Grignard reagent to form higher ethers.

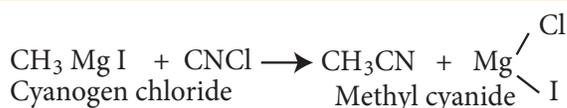
Example



9) Preparation of alkyl cyanide

Grignard reagent reacts with cyanogen chloride to form alkyl cyanide

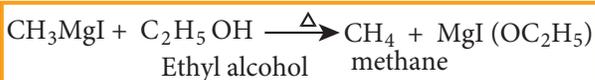
Example



10) Preparation of Alkanes

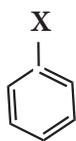
Compounds like water, alcohols and amines which contain active hydrogen atom react with Grignard reagents to form alkanes.

Example



14.5 Haloarenes

Haloarenes are the compounds in which the halogen is directly attached to the benzene ring.



14.5.1. Nomenclature of haloarenes

In the IUPAC nomenclature, the haloarenes are named by adding prefix halo before the name of the aromatic hydrocarbon. For naming disubstituted arenes, the relative position of the substituent 1,2; 1,3 and 1,4 are indicated by the prefixes ortho, meta and para, respectively.

For poly haloarenes the numbering should be done in such a way that the lowest possible number should be given to the substituents and the name of the halogens are arranged in alphabetic order.

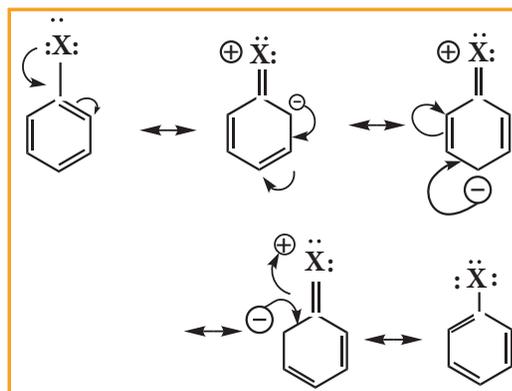
Nomenclature can be well understood from the following examples.

Compound	IUPAC NAME
1	1, 2 - Dichlorobenzene
2	1, 3- Dibromobenzene
3	1,3,5-tri bromobenzene
4	1- Bromo - 4- fluoro -2- iodobenzene
5	1- Bromo -2- chloro-4- iodobenzene

14.5.2 Nature of C- X bond in haloarenes

In halo arenes the carbon atom is sp^2 hybridised. The sp^2 hybridised orbitals are shorter and holds the electron pair of bond more tightly.

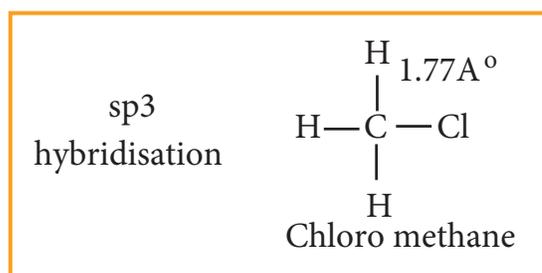
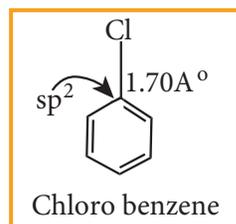
Halogen atom contains P-orbital with lone pair of electrons which interacts with π -orbitals of benzene ring to form extended conjugated system of π - orbitals. The delocalisation of these electrons give double bond character to C - X bond. The resonance structure of halobenzene is given as



Due to this double bond character of C- X bond in haloarenes ,the C-X bond is

shorter in length and stronger than in halo alkanes.

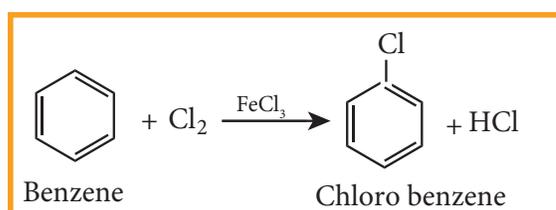
Example



14.5.3 Methods of preparation

1) Direct halogenation

Chlorobenzene is prepared by the direct chlorination of benzene in the presence of lewis acid catalyst like FeCl₃

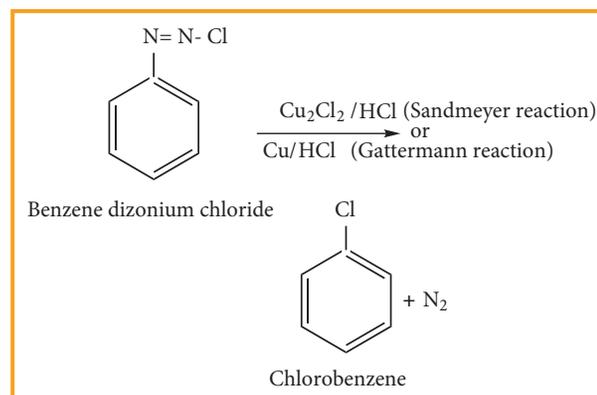


2) From benzene diazonium chloride

Chloro benzene is prepared by Sandmeyer reaction or Gattermann reaction using benzene diazonium chloride.

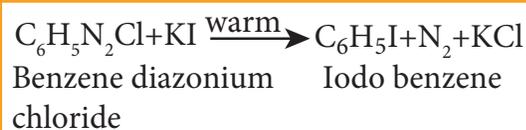
(i) Sandmeyer reaction

When aqueous solution of benzene diazonium chloride is warmed with Cu₂Cl₂ in HCl gives chloro benzene



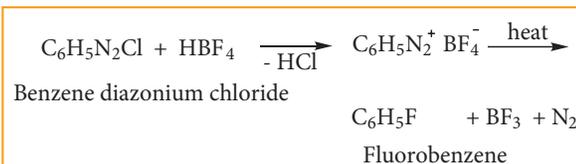
3) Preparation of iodobenzene

Iodobenzene is prepared by warming benzene diazonium chloride with aqueous KI solution.



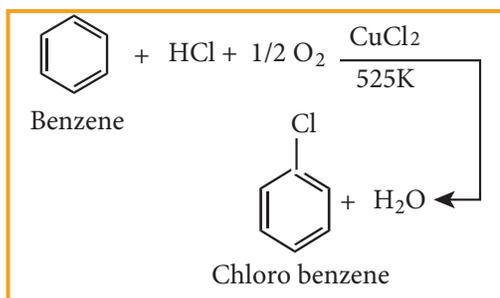
4) Preparation of fluorobenzene

Fluoro benzene is prepared by treating benzenediazonium chloride with fluoro boric acid. This reaction produces diazonium fluoroborate which on heating produces fluorobenzene. This reaction is called Balz – schiemann reaction.



5) Commercial preparation of chloro benzene (Raschig process)

Chloro benzene is commercially prepared by passing a mixture of benzene vapour, air and HCl over heated cupric chloride. This reaction is called Raschig process.



14.5.4 Physical properties

1. Melting and boiling points

The boiling points of monohalo benzene which are all liquids follow the order

Iodo > Bromo > Chloro

The boiling points of isomeric dihalobenzene are nearly the same

The melting point of para isomer is generally higher than the melting points of ortho and meta isomers. The higher melting point of p-isomer is due to its symmetry which leads to more close packing of its molecules in the crystal lattice and consequently strong intermolecular attractive force which requires more energy for melting

p -Dihalo benzene > o-Dichloro benzene > m-Dichloro benzene

2. Solubility

Haloarenes are insoluble in water because they cannot form hydrogen bonds with water, but are soluble in organic solvents

3. Density

Halo arenes are all heavier than water and their densities follow the order.

Iodo benzene > Bromo benzene > Chloro benzene

14.5.5 Chemical properties

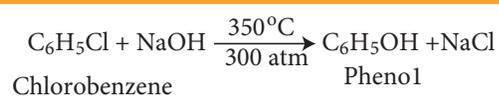
A. Reactions involving halogen atom

1. Aromatic nucleophilic substitution reaction

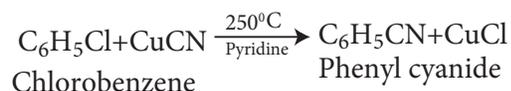
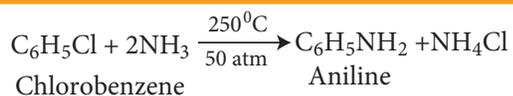
Halo arenes do not undergo nucleophilic substitution reaction readily. This is due to C-X bond in aryl halide is short and strong and also the aromatic ring is a centre of high electron density.

The halogen of haloarenes can be substituted by OH⁻, NH₂⁻, or CN⁻ with appropriate nucleophilic reagents at high temperature and pressure.

For Example



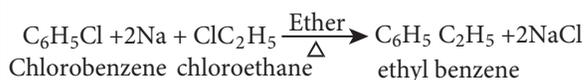
This reaction is known as Dow's Process



2. Reaction with metals

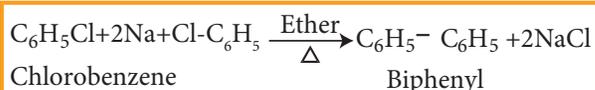
a) Wurtz Fittig reaction

Halo arenes reacts with halo alkanes when heated with sodium in ether solution to form alkyl benzene. This reaction is called Wurtz Fittig reaction.



b) Fittig reaction

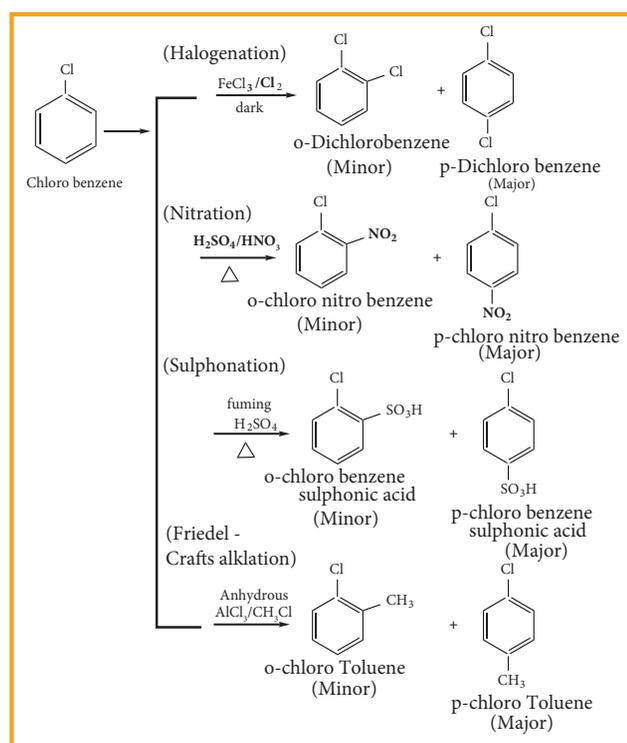
Haloarenes react with sodium metal in dry ether, two aryl groups combine to give biaryl products. This reaction is called Fittig reaction



B) Reaction involving aromatic ring

3. Electrophilic substitution reaction

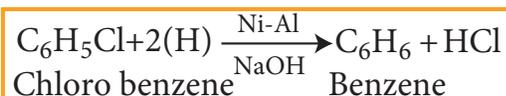
Haloarenes undergo aromatic electrophilic substitution reactions. The rate of electrophilic substitution of halobenzene is lower than that of benzene. Halogen is deactivating due to -I effect of halogen. The lone pair of electrons on the chlorine involves in resonance with the ring. It increases the electron density at ortho and para position (refer figure no 14.1). The halogen attached to the benzene ring withdraws electron and thereby and hence the halogen which is attached to the benzene directs the incoming, electrophile either to ortho or to para position in electrophilic substitution reaction



Toluene

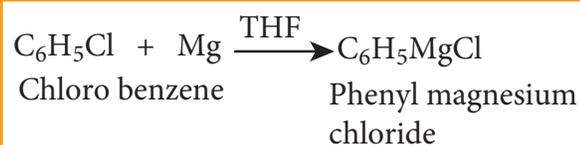
4) Reduction

Haloarenes on reduction with Ni-Al alloy in the presence of NaOH gives corresponding arenes.



5) Formation of Grignard reagent

Haloarenes reacts with magnesium to form Grignard reagent in tetrahydrofuran (THF).



14.5.6 Uses of Chloro benzene

- Chloro benzene is used in the manufacture of pesticides like DDT
- It is used as high boiling solvent in organic synthesis.

iii) It is used as fibre - swelling agent in textile processing.

Evaluate Yourself



6) Haloalkanes undergo nucleophilic substitution reaction whereas haloarenes undergo electrophilic substitution reaction. comment.

14.6 Poly halogen compounds

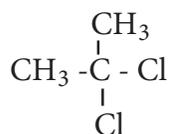
Carbon compounds containing more than one halogen atoms are called poly halogen compounds. Some of the important poly halogen compounds are described below.

They are classified as

a) gem - dihalides



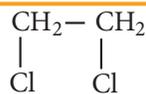
Ethylidene chloride
1,1 - Dichloro ethane



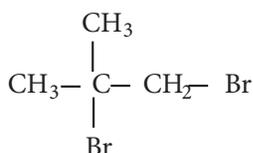
Isopropylidene chloride (or)
Isopropylidene dichloride
2,2-Dichloropropane

b) vic - dihalides

For Example



Ethylene dichloride (or) Ethylene chloride
1, 2 - Dichloro ethane



Isobutylene dibromide (or) Isobutylene bromide
1, 2-Dibromo-2-methyl propane

14.6.1 Preparation

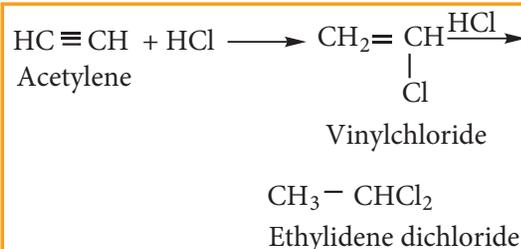
a) gem- dihalides

Ethylidene dichloride (1, 1 - Dichloro ethane) is prepared by

(i) Treating acetaldehyde with PCl_5



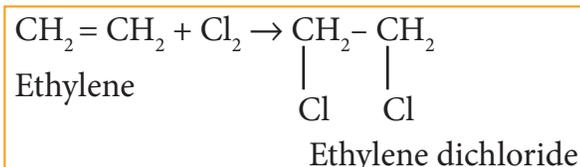
(ii) Adding hydrogen chloride to acetylene



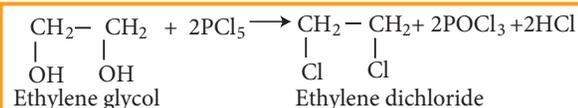
b) vic- dihalides

Ethylene dichloride (1, 2 - Dichloro ethane) is prepared by the following methods.

i) Addition of chlorine to ethylene



ii) Action of PCl_5 (or HCl) on ethylene glycol



Properties

Physical Properties

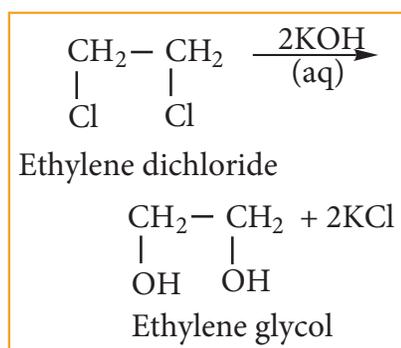
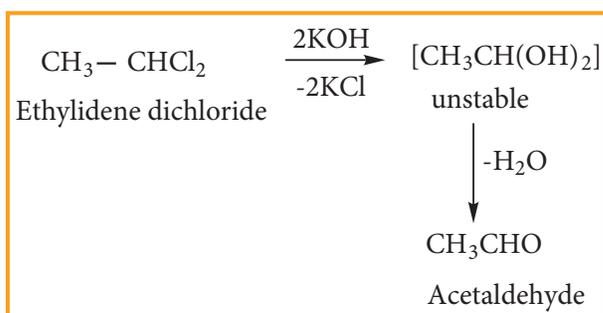
i) They are sweet smelling, colourless liquids having relatively high boiling points.

ii) The boiling point of ethylidene chloride is less than that of ethylene dichloride.

Chemical properties

1) Hydrolysis with aqueous NaOH or KOH

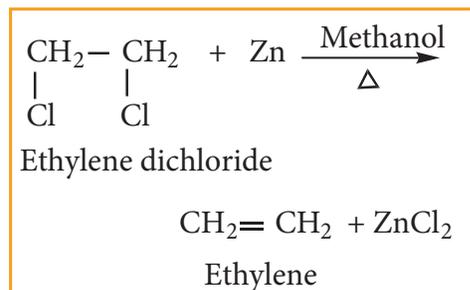
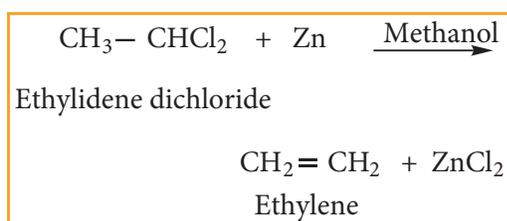
Gem-Dihalides, on hydrolysis with aqueous KOH give an aldehyde or a ketone
vic-Dihalides, on hydrolysis with aqueous KOH gives glycols.



This reaction can be used to distinguish the gem- Dihalides and vic- Dihalides.

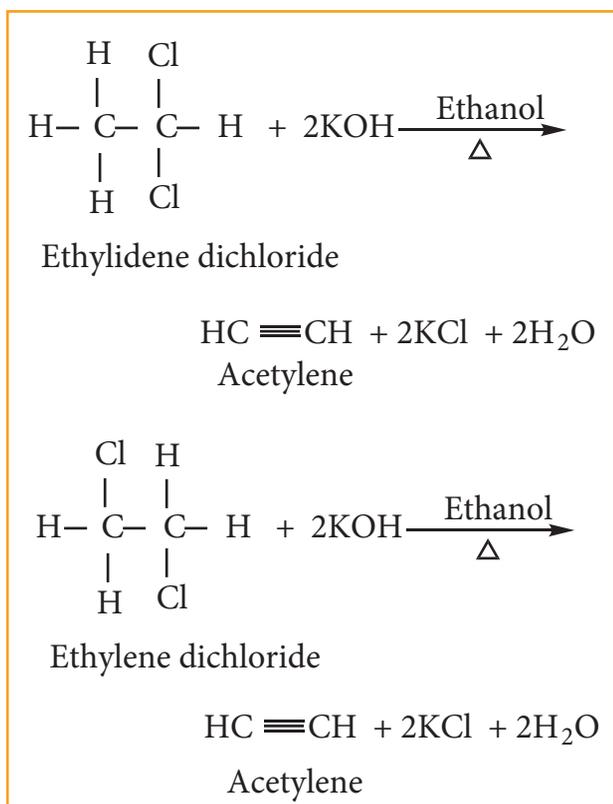
2) Reaction with Zinc (Dehalogenation)

Gem- Dihalides and vic- Dihalides on treatment with zinc dust in methanol give alkenes.



3) Reaction with Alcoholic KOH (Dehydrohalogenation)

gem- Dihalides and vic- Dihalides on treatment with alcoholic KOH give alkynes.



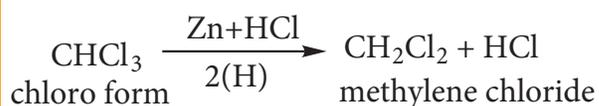
Methylene chloride (Di chloromethane)

Preparation

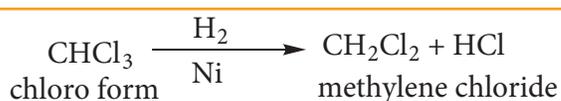
Methylene chloride is prepared by the following methods

1) Reduction of chloroform

a) Reduction of chloroform in the presence of Zn + HCl gives methylene chloride.

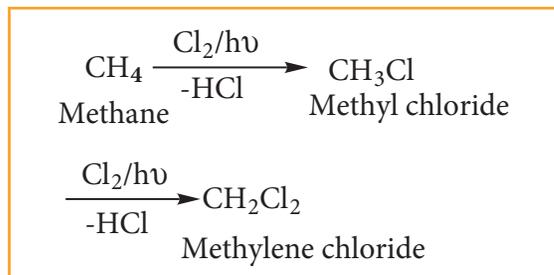


b) Reduction of chloroform using H₂/Ni



2) Chlorination of methane

Chlorination of methane gives methylene chloride



Uses of methylene chloride

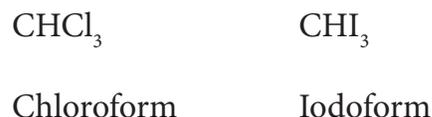
Methylene chloride is used as

- 1) aerosol spray propellant
- 2) solvent in paint remover
- 3) process solvent in the manufacture of drugs
- 4) a metal cleaning solvent

14.6.2 Trihaloalkane

Trihaloalkanes are compounds obtained by replacing three hydrogen atoms of a hydrocarbon by three halogen atoms.

Example



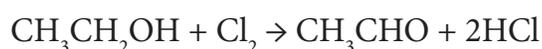
1) Chloroform

Chloroform is an important trihaloalkane. Dumas named CHCl_3 as chloroform as it gives formic acid on hydrolysis.

Preparation:

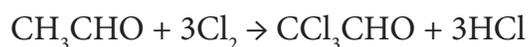
Chloroform is prepared in the laboratory by the reaction between ethyl alcohol with bleaching powder followed by the distillation of the product chloroform. Bleaching powder act as a source of chlorine and calcium hydroxide. This reaction is called haloform reaction. The reaction proceeds in three steps as shown below.

Step – 1: Oxidation



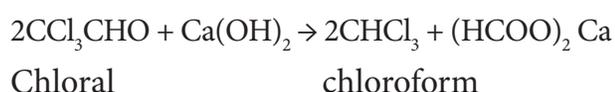
Ethyl alcohol Acetaldehyde

Step – 2: Chlorination



Acetaldehyde Trichloro acetaldehyde

Step – 3: Hydrolysis



Properties

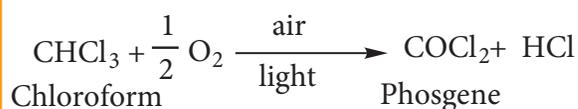
Physical properties

- (i) Chloroform is a colourless liquid with peculiar sickly smell and a burning taste
- (ii) The vapours of chloroform when inhaled it causes unconsciousness (depress the central nervous system) and hence it is used as an anaesthetic.

Chemical properties

1) Oxidation

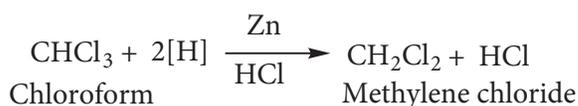
Chloroform undergoes oxidation in the presence of light and air to form phosgene (carbonyl chloride)



Since phosgene is very poisonous, its presence makes chloroform unfit for use as anaesthetic.

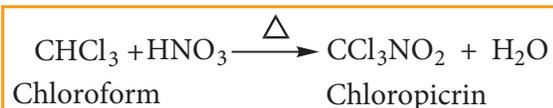
2) Reduction

Chloroform undergoes reduction with zinc and HCl in the presence of ethyl alcohol to form methylene chloride.



3) Nitration

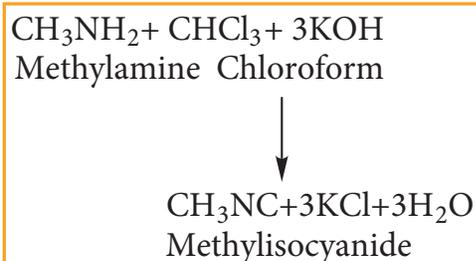
Chloroform reacts with nitric acid to form chloropicrin. (Trichloro nitro methane)



It used as an insecticide and soil sterilising agent.

4) Carbylamine reaction

Chloroform reacts with aliphatic or aromatic primary amine and alcoholic caustic potash, to give foul smelling alkyl isocyanide (carbylamines)



This reaction is used to test primary amine.

Evaluate Yourself



- 7) Chloroform is kept with a little ethyl alcohol in a dark coloured bottle why?

14.6.3 Tetra haloalkane

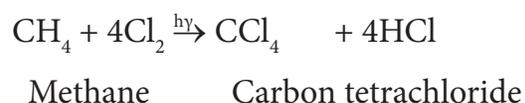
Carbon tetrachloride is a good example for tetra haloalkane

Carbon tetrachloride

Preparation

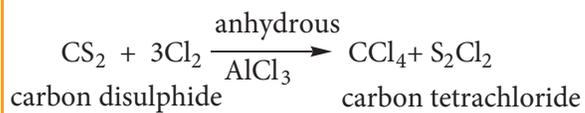
1. Chlorination of methane

The reaction of methane with excess of chlorine in the presence of sunlight will give carbon tetrachloride as the major product.



2. Action of carbon disulphide with chlorine gas

Carbon disulphide reacts with chlorine gas in the presence of anhydrous AlCl_3 as catalyst giving carbon tetrachloride



Physical properties

- (i) Carbon tetrachloride is a colourless liquid with its specific smell
- (ii) It is insoluble in water and soluble in organic solvents

Chemical properties

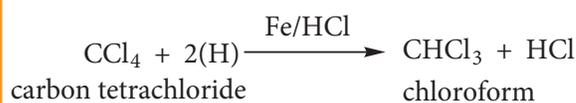
(i) Hydrolysis

Carbon tetrachloride reacts with hot water or with hot water vapour producing the poisonous gas, phosgene.



(ii) Reduction

Carbon tetrachloride is reduced by iron powder in dilute HCl medium to form chloroform



14.6.4 Freons (CFC)

The chloro fluoro derivatives of methane and ethane are called freons.

Nomenclature

Freon is represented as Freon-cba

Where c = number of carbon atoms - 1

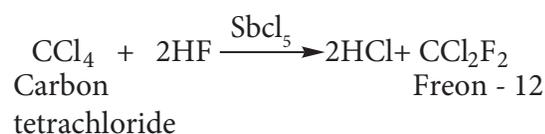
b = number of hydrogen atoms + 1

a = total number of fluorine atoms

Example

Formula	C-1	H+1	F	Name
CFCl_3	1-1=0	0+1=1	1	Freon-11
CF_2Cl_2	1-1=0	0+1=1	2	Freon-12
$\text{C}_2\text{F}_2\text{Cl}_4$	2-1=1	0+1=1	2	Freon-112
$\text{C}_2\text{F}_3\text{Cl}_3$	2-1=1	0+1=1	3	Freon-113

Freon - 12 is prepared by the action of hydrogen fluoride on carbon tetrachloride in the presence of catalytic amount of antimony pentachloride. This is called swartz reaction.



Physical properties

Freons are highly stable, unreactive, non corrosive, non toxic, easily liquefiable gases.

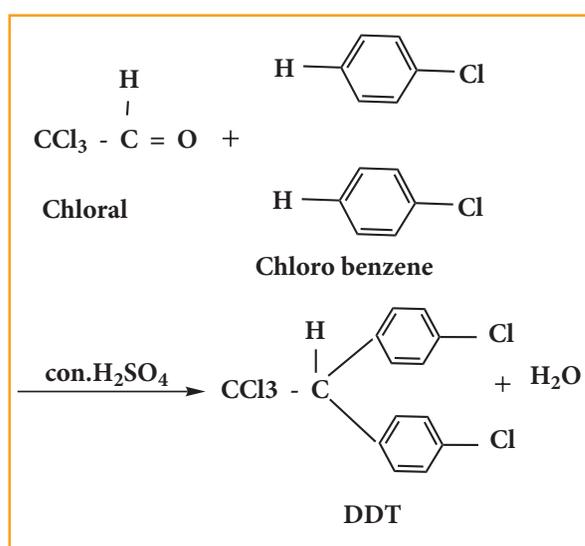
Uses:

- (i) Freons are used as refrigerants in refrigerators and air conditioners.
- (ii) It is used as a propellant for aerosols and foams
- (iii) It is used as propellant for foams to spray out deodorants, shaving creams, and insecticides.

14.6.5 DDT (p,p'-dichloro diphenyl tri-chloro ethane)

DDT, the first chlorinated organic pesticide was prepared in 1873, and in 1939 Paul Muller discovered the effectiveness of DDT as an insecticide. He was awarded Noble prize in medicine and physiology in 1948 for this discovery.

DDT can be prepared by heating a mixture of chlorobenzene with chloral (Trichloro acetaldehyde) in the presence of $\text{Conc. H}_2\text{SO}_4$.



Evaluate Yourself

8) What is the IUPAC name of the insecticide DDT? Why is their use banned in most of the countries?

Uses:

- DDT is used to control certain insects which carries diseases like malaria and yellow fever
- It is used in farms to control some agricultural pests
- It is used in building construction as pest control
- It is used to kill various insects like housefly and mosquitoes due to its high and specific toxicity.

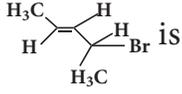
SUMMARY

- The compounds obtained by the substitution of hydrogen atom of alkanes by halogen atom are called haloalkane, while the compounds obtained by the substitution of hydrogen atoms of arenes by halogen atom are called haloarenes.
- Modern classification of halo compounds is based on the halogen with carbon possessing sp^3 hybridisation. In these compounds the electronegativity of halogen is more than that of carbon, hence $\text{C}^{\delta+} - \text{X}^{\delta-}$ bond becomes polar.
- Haloalkane
- Haloalkanes are prepared from alkanes, alkenes or alcohols. The boiling points of haloalkane are higher than that of corresponding hydrocarbons.
- Haloalkane undergoes nucleophilic substitution and elimination reactions. Primary alkyl halides undergo $\text{S}_{\text{N}}2$ mechanism. If the reactant is chiral, the product formed exhibits inversion of stereo chemical configuration. Tertiary alkyl halide undergoes $\text{S}_{\text{N}}1$ mechanism, via carbonium ion formation. If the reactant is chiral, the product formed is optically inactive due to racemisation.
- Organo metallic compound
- Haloalkane reacts with metal to form organometallic compounds like Grignard reagent. It is represented as $\text{R}^{\delta-} - \text{Mg}^{\delta+} \text{X}$. Grignard reagent reacts with variety of substances to give almost all class of organic compounds like alcohols, aldehydes, ketones, acids etc.
- Haloarenes

- Haloarenes are prepared from arenes or by decomposition of benzene diazonium chloride. Haloarenes are more stable than haloalkane. C - X bond in halo arenes is short and strong.
- Under normal conditions halo arenes do not undergo nucleophilic substitution but takes part in electrophilic substitution. Electron withdrawing inductive effect of halogen atom deactivates the benzene ring whereas resonating structure control o, p directing nature of halo arenes.
- Poly halogen compounds
- Organic compounds having two or more halogen atoms are called poly halogen compounds. These compounds are useful in our day to day life but pose environmental threat.
- Chloroform is used as an anesthetic, but because of its toxic nature it has been replaced by less toxic and safer anaesthetic like ethers.
- Iodoform is used as an antiseptic, due to the liberation of free iodine. But it has been replaced by other formulation containing iodine, due to its objectional smell.
- Carbon tetrachloride is used in fire extinguishers. Freons are used as refrigerant. But both these compounds lead to adverse environmental effect.
- DDT is used an effective insecticide. Now a days it is banned because of it's long term toxic effect.

Evaluation

I. Choose the best answer.

- The IUPAC name of  is
 - 2-Bromo pent - 3 - ene
 - 4-Bromo pent - 2 - ene
 - 2-Bromo pent - 4 - ene
 - 4-Bromo pent - 1 - ene
- Of the following compounds, which has the highest boiling point?
 - n-Butyl chloride
 - Isobutyl chloride
 - t-Butyl chloride
 - n-propyl chloride
- Arrange the following compounds in increasing order of their density

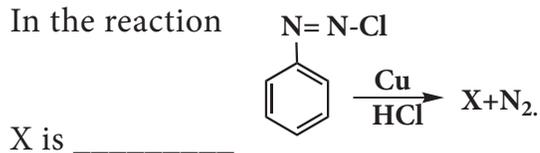
A) CCl ₄	B) CHCl ₃
C) CH ₂ Cl ₂	D) CH ₃ Cl

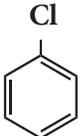
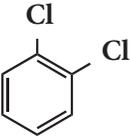
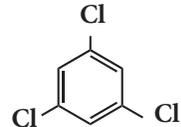
 - D < C < B < A
 - C > B > A > D
 - A < B < C < D
 - C > A > B > D
- With respect to the position of - Cl in the compound CH₃ - CH = CH - CH₂ - Cl, it is classified as
 - Vinyl
 - Allyl
 - Secondary
 - Aralkyl
- What should be the correct IUPAC name of diethyl chloromethane?
 - 3 - Chloro pentane
 - 1-Chloropentane
 - 1-Chloro-1, 1, diethyl methane
 - 1 -Chloro-1-ethyl propane

6. C - X bond is strongest in

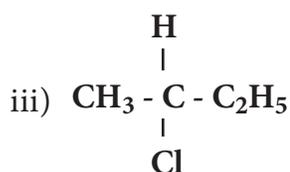
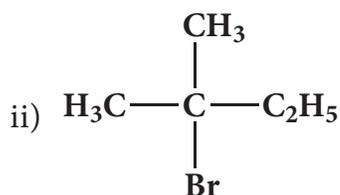
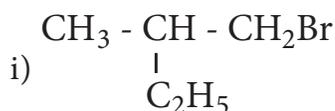
- Chloromethane
- Iodomethane
- Bromomethane
- Fluoromethane

7. In the reaction



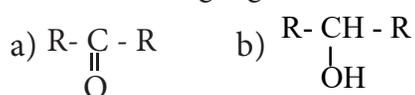
- 
- 
- 
- 

8. Which of the following compounds will give racemic mixture on nucleophilic substitution by OH⁻ ion?



- (i)
- (ii) and (iii)
- (iii)
- (i) and (ii)

9. The treatment of ethyl formate with excess of RMgX gives



c) R-CHO d) R-O-R

10. Benzene reacts with Cl₂ in the presence of FeCl₃ and in absence of sunlight to form

- Chlorobenzene
- Benzyl chloride
- Benzal chloride
- Benzene hexachloride

11. The name of C₂F₄Cl₂ is _____

- Freon - 112
- Freon - 113
- Freon - 114
- Freon - 115

12. Which of the following reagent is helpful to differentiate ethylene dichloride and ethylidene chloride?

- Zn / methanol
- KOH / ethanol
- aqueous KOH
- ZnCl₂ / Con HCl

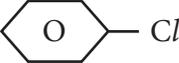
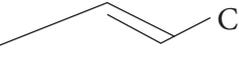
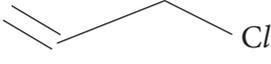
13. Match the compounds given in Column I with suitable items given in Column II

	Column I (Compound)		Column II (Uses)
A	Iodoform	1	Fire extinguisher
B	Carbon tetra chloride	2	Insecticide
C	CFC	3	Antiseptic
D	DDT	4	Refrigerants



Code

- a) A → 2 B → 4 C → 1 D → 3
b) A → 3 B → 2 C → 4 D → 1
c) A → 1 B → 2 C → 3 D → 4
d) A → 3 B → 1 C → 4 D → 2
14. **Assertion:** In mono haloarenes, electrophilic substitution occurs at ortho and para positions.
Reason: Halogen atom is a ring deactivator
- (i) If both assertion and reason are true and reason is the correct explanation of assertion.
(ii) If both assertion and reason are true but reason is not the correct explanation of assertion.
(iii) If assertion is true but reason is false.
(iv) If both assertion and reason are false.
15. Consider the reaction,
$$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + \text{NaCN} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CN} + \text{NaBr}$$

This reaction will be the fastest in
a) ethanol b) methanol
c) DMF (N, N' – dimethyl formamide)
d) water
16. Freon-12 is manufactured from tetrachloro methane by
a) Wurtz reaction
b) Swarts reaction
c) Haloform reaction
d) Gattermann reaction
17. The most easily hydrolysed molecule under SN^1 condition is
a) allyl chloride
b) ethyl chloride
c) isopropylchloride
d) benzyl chloride
18. The carbo cation formed in SN^1 reaction of alkyl halide in the slow step is
a) sp^3 hybridised b) sp^2 hybridised
c) sp hybridised d) none of these
19. The major products obtained when chlorobenzene is nitrated with HNO_3 and $\text{con H}_2\text{SO}_4$
a) 1-chloro-4-nitrobenzene
b) 1-chloro-2-nitrobenzene
c) 1-chloro-3-nitrobenzene
d) 1-chloro-1-nitrobenzene
20. Which one of the following is most reactive towards nucleophilic substitution reaction ?
a) 
b) 
c) 
d) 
21. Ethylidene chloride on treatment with aqueous KOH gives
a) acetaldehyde
b) ethyleneglycol
c) formaldehyde
d) glyoxal
22. The raw material for Rasching process
a) chloro benzene b) phenol
c) benzene d) anisole





23. Chloroform reacts with nitric acid to produce

- a) nitro toluene
- b) nitro glycerine
- c) chloropicrin
- d) chloropicric acid

24. acetone $\xrightarrow[\text{ii) H}_2\text{O} / \text{H}^{-1}]{\text{i) CH}_3\text{MgI}}$ X, X is

- a) 2-propanol
 - b) 2-methyl-2-propanol
 - c) 1-propanol
 - d) acetanol
25. Silverpropionate when refluxed with Bromine in carbontetrachloride gives

- a) propionic acid
- b) chloro ethane
- c) bromo ethane
- d) chloro propane

26. Classify the following compounds in the form of alkyl, allylic, vinyl, benzylic halides

a) $\text{CH}_3 - \text{CH} = \text{CH} - \text{Cl}$

(ii) $\text{C}_6\text{H}_5\text{CH}_2\text{I}$

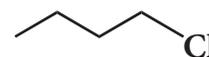
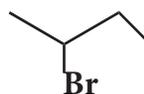
(iii) $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ | \\ \text{Br} \end{array}$

(iv) $\text{CH}_2 = \text{CH} - \text{Cl}$

II. Write brief answer to the following questions.

- 27. Why chlorination of methane is not possible in dark?
- 28. How will you prepare n propyl iodide from n-propyl bromide?

29. Which alkyl halide from the following pair is i) chiral ii) undergoes faster $\text{S}_\text{N}2$ reaction?



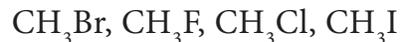
30. How does chlorobenzene react with sodium in the presence of ether? What is the name of the reaction?

31. Give reasons for polarity of C-X bond in halo alkane.

32. Why is it necessary to avoid even traces of moisture during the use of Grignard reagent?

33. What happens when acetyl chloride is treated with excess of CH_3MgI ?

34. Arrange the following alkyl halide in increasing order of bond enthalpy of RX



35. What happens when chloroform reacts with oxygen in the presence of sunlight?

36. Write down the possible isomers of $\text{C}_5\text{H}_{11}\text{Br}$ and give their IUPAC and common names.

37. Mention any three methods of preparation of haloalkanes from alcohols.

38. Compare $\text{S}_\text{N}1$ and $\text{S}_\text{N}2$ reaction mechanisms.

39. Reagents and the conditions used in the reactions are given below. Complete the table by writing down the product and the name of the reaction.



Reaction	Product	Name of the reaction
$\text{CH}_3\text{CH}_2\text{OH} + \text{SOCl}_2 \xrightarrow{\text{pyridine}} ?$	-----	-----
$\text{CH}_3\text{CH}_2\text{Br} + \text{AgF} \longrightarrow ?$	-----	-----
$\text{C}_6\text{H}_5\text{Cl} + \text{Na} \xrightarrow{\text{ether}} ?$	-----	-----

40. Discuss the aromatic nucleophilic substitutions reaction of chlorobenzene.
41. Account for the following
- (i) t-butyl chloride reacts with aqueous KOH by S_N1 mechanism while n-butyl chloride reacts with S_N2 mechanism.
- (ii) p-dichloro benzene has higher melting point than those of o-and m-dichloro benzene.
42. In an experiment ethyliodide in ether is allowed to stand over magnesium pieces. Magnesium dissolves and product is formed
- a) Name the product and write the equation for the reaction.
- b) Why all the reagents used in the reaction should be dry? Explain
- c) How is acetone prepared from the product obtained in the experiment.
43. Write a chemical reaction useful to prepare the following:
- i) Freon-12 from Carbon tetrachloride
- ii) Carbon tetrachloride from carbon disulphide
44. What are Freons? Discuss their uses

and environmental effects

45. Predict the products when bromoethane is treated with the following
- i) KNO_2
- ii) AgNO_2
46. Explain the mechanism of S_N1 reaction by highlighting the stereochemistry behind it
47. Write short notes on the the following
- i) Raschig process
- ii) Dows Process
- iii) Darzens process
48. Starting from CH_3MgI , How will you prepare the following?
- i) Acetic acid
- ii) Acetone
- iii) Ethyl acetate
- iv) Iso propyl alcohol
- v) Methyl cyanide
49. Complete the following reactions
- i) $\text{CH}_3 - \text{CH} = \text{CH}_2 + \text{HBr} \xrightarrow{\text{Peroxide}}$
- ii) $\text{CH}_3 - \text{CH}_2 - \text{Br} + \text{NaSH} \xrightarrow[\text{H}_2\text{O}]{\text{alcohol}}$
- iii) $\text{C}_6\text{H}_5\text{Cl} + \text{Mg} \xrightarrow{\text{THF}}$
- iv) $\text{CHCl}_3 + \text{HNO}_3 \xrightarrow{\Delta}$
- v) $\text{CCl}_4 + \text{H}_2\text{O} \xrightarrow{\Delta}$
50. Explain the preparation of the following compounds
- i) DDT ii) Chloroform



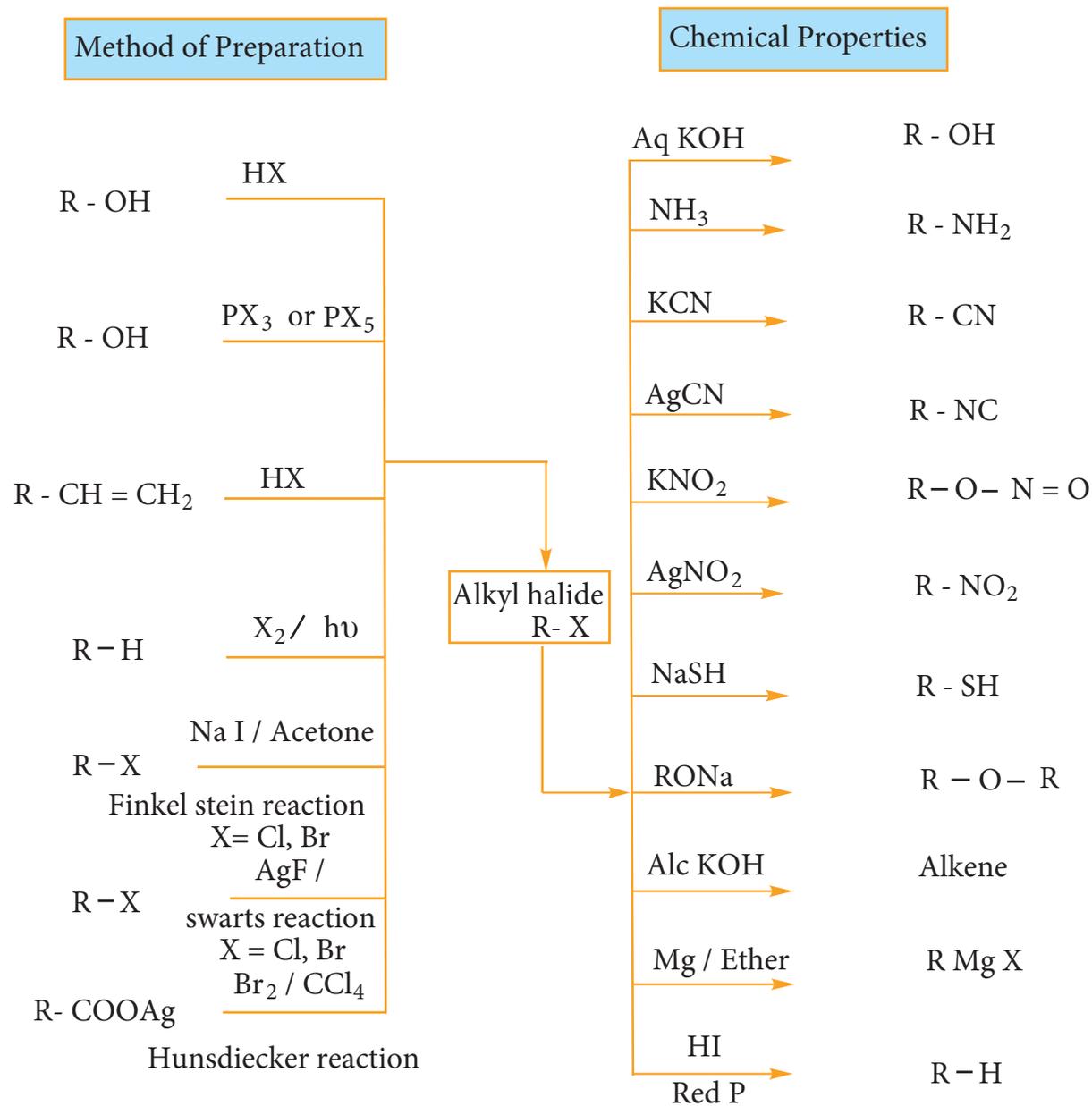


- iii) Biphenyl
iv) Chloropicrin
v) Freon-12
51. An organic compound (A) with molecular formula C_2H_5Cl reacts with KOH gives compounds (B) and with alcoholic KOH gives compound (C). Identify (A), (B), and (C)
52. Simplest alkene (A) reacts with HCl to form compound (B). Compound (B) reacts with ammonia to form compound (C) of molecular formula C_2H_7N . Compound (C) undergoes carbylamine test. Identify (A), (B), and (C).
53. A hydrocarbon C_3H_6 (A) reacts with HBr to form compound (B). Compound (B) reacts with aqueous potassium hydroxide to give (C) of molecular formula C_3H_8O . What are (A) (B) and (C). Explain the reactions.
54. Two isomers (A) and (B) have the same molecular formula $C_2H_4Cl_2$. Compound (A) reacts with aqueous KOH gives compound (C) of molecular formula C_2H_4O . Compound (B) reacts with aqueous KOH gives compound (D) of molecular formula $C_2H_6O_2$. Identify (A), (B), (C) and (D).



FLOW CHART

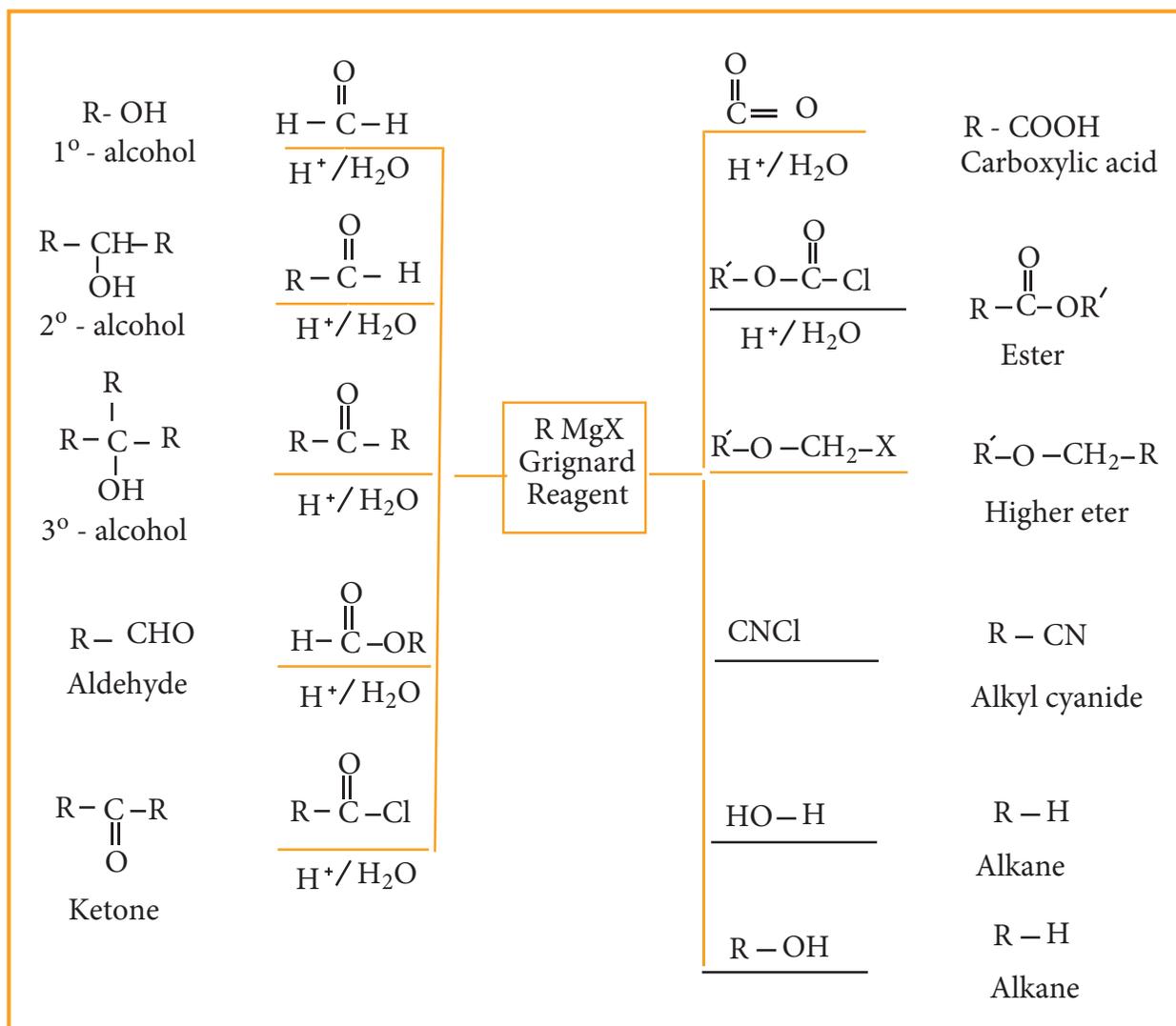
Haloalkane

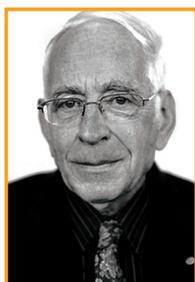




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Synthetic uses of Grignard reagent





The Nobel Prize in chemistry 2005 was awarded jointly to **Yves Chauvin**, **Robert H. Grubbs** and **Richard R. Schrock** for the development of new chemicals based on Green chemistry.

In 1971 Yves Chauvin explained the types of metal compound that act as catalysts in the reactions. Richard Schrock was the first to produce efficient metal compound catalysts for metathesis in 1990. Two years later Robert Grubbs developed better catalysts, stable in air that was highlighted in many applications.

Learning Objectives

After studying this unit, students will be able to

- Know the various concepts of environmental chemistry
- classify the various types of environmental pollutions.
- recognize the particulate pollutants and their effects.
- explain the cause and hazardous effects of acid rain, greenhouse effect, ozone depletion and global warming.
- know the reason for water pollution and recognize the prescribed standard for drinking water.
- highlight the strategies to control various types of pollution
- appreciate the meaning of green chemistry and comprehend the importance of green chemistry in day today life.

15. INTRODUCTION

We are very familiar with the word environment. It includes the air we breathe, the water that covers most of the earth's surface, the plants and animals around us and much more. These days, when we hear people talk about “the environment”, they are often referring to the overall condition of our planet, or how healthy it is.

Environmental chemistry is a branch of chemistry which deals with the study of chemicals and chemical processes occurring in the environment by direct human activities. It also deals with sources, causes and methods of controlling air, water and soil pollution.

15.1 Environmental Pollution

Any undesirable change in our environment that has harmful effects on plants, animals and human beings is called environmental pollution.

Environmental pollution is usually caused by the addition of waste products of human activity to the environment. The substances which cause pollution of environment are called pollutants. The pollutants may be solids, liquids or gaseous substances present in significant concentration in the environment. Our environment becomes polluted day by day, by the increased addition of industrial and domestic wastes to it. The air we breathe, the water we drink and the place where we live in, are highly contaminated.

The pollutants are classified as bio-degradable and non-biodegradable pollutants.

i. Bio-degradable pollutants :

The pollutants which can be easily decomposed by the natural biological processes are called bio-degradable pollutants. Examples: plant wastes, animal wastes etc.

ii. Non bio-degradable pollutants :

The pollutants which cannot be decomposed by the natural biological processes are called Non bio-degradable pollutants. Examples: metal wastes (mainly Hg and Pb), D.D.T, plastics, nuclear wastes etc., These pollutants are harmful to living organisms even in low concentration. As they are not degraded naturally, it is difficult to eliminate them from our environment.

15.2. Atmospheric Pollution

Earth's atmosphere is a layer of gases retained by the earth's gravity. It contains roughly 78% nitrogen, 21% oxygen, 0.93% argon, 0.04% carbon dioxide, trace amounts of other gases and little amount of water vapour. This mixture is commonly known as air.

Earth's atmosphere can be divided into different layers with characteristic altitude and temperature. The various regions of atmosphere are given in table 15.1.

Table 15.1 Regions of atmosphere

Region	Altitude from earth's surface	Temperature range	Gases/ species present
Troposphere	0-10 km	15°C to -56°C	N ₂ , O ₂ CO ₂ H ₂ O (vap)

Region	Altitude from earth's surface	Temperature range	Gases/ species present
Stratosphere (ozonosphere)	10-50 km	-56°C to -2°C	N ₂ O ₂ O ₃ O atoms
Mesosphere	50-85 km	-2°C to -92°C	N ₂ O ₂ ⁺ NO ⁺
Thermosphere	85-500 km	-92°C to 1200°C	O ₂ ⁺ O ⁺ NO ⁺ e ⁻

Troposphere :

The lowest layer of the atmosphere is called the troposphere and it extends from 0 – 10 km from the earth surface. About 80% of the mass of the atmosphere is in this layer. This troposphere is further divided as follows.

i) Hydrosphere:

Hydrosphere includes all types of water sources like oceans, seas, rivers, lakes, streams, underground water, polar icecaps, clouds etc. It covers about 75% of the earth's surface. Hence the earth is called as a blue planet.

ii) Lithosphere:

Lithosphere includes soil, rocks and mountains which are solid components of earth.

iii) Biosphere:

It includes the lithosphere hydrosphere and atmosphere intergrating

the living organism present in the lithosphere, hydrosphere and atmosphere.



The Bhopal Tragedy

The world's worst chemical disaster happened in the Indian city of Bhopal in the early morning hours of December 3, 1984. An explosion at the Union Carbide pesticide plant released a cloud of toxic gas (methyl isocyanate) CH₃NCO into the air. Since the gas was twice as heavy as air, it did not drift away but formed a 'blanket' over the surrounding area. It attacked people's lungs and affected their breathing. Thousands of people died and the lives of many were ruined. The lungs, brain, eyes, muscles as well as gastrointestinal, neurological and immune systems of those who survived were severely affected.

15.3. Types of environmental pollution

Atmospheric pollution is generally studied as tropospheric pollution. Different types of atmospheric pollutions are

- (1) Air pollution
- (2) Water pollution
- (3) Soil pollution.

15.3.1 Air pollution

Any undesirable change in air which adversely affects living organisms is called air pollution. Air pollution is limited to troposphere and stratosphere. Air pollution is mainly due to the excessive discharge of undesirable foreign matter in to the atmospheric air.



Fig 15.1 Air Pollution

types of air pollutants

Air pollutants may exist in two major forms namely, gases and particulates.

15.3.1.1 Gaseous air pollutants

Oxides of sulphur, oxides of nitrogen, oxides of carbon, and hydrocarbons are the gaseous air pollutants.

a. Oxides of Sulphur

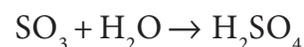
Sulphur dioxide and sulphur trioxide are produced by burning sulphur containing fossil fuels and roasting sulphide ores. Sulphur dioxide is a poisonous gas to both animals and plants. Sulphur dioxide causes eye irritation, coughing and respiratory diseases like asthma, bronchitis, etc.

Sulphur dioxide is oxidised into more harmful sulphur trioxide in the presence of particulate matter present in polluted air .



SO_3 combines with atmospheric water vapour to form H_2SO_4 , which comes

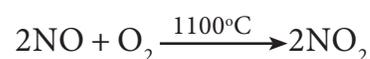
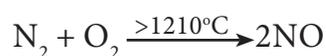
down in the form of acid rain.



Some harmful effects of acid rain will be discussed in section 15.3

b. Oxides of nitrogen

Oxides of nitrogen are produced during high temperature combustion processes, oxidation of nitrogen in air and from the combustion of fuels (coal, diesel, petrol etc.).



The oxides of nitrogen are converted into nitric acid which comes down in the form of acid rain. They also form reddish brown haze in heavy traffic. Nitrogen dioxide potentially damages plant leaves and retards photosynthesis. NO_2 is a respiratory irritant and it can cause asthma and lung injury. Nitrogen dioxide is also harmful to various textile fibres and metals.

c. Oxides of carbon

The major pollutants of oxides of carbon are carbon monoxide and carbon dioxide.

(i) Carbon Monoxide

Carbon monoxide is a poisonous gas produced as a result of incomplete combustion of coal or firewood. It is released into the air mainly by automobile exhaust. It binds with haemoglobin



and forms carboxy haemoglobin which impairs normal oxygen transport by blood and hence the oxygen carrying capacity of blood is reduced. This oxygen deficiency results in headache, dizziness, tension, Loss of consciousness, blurring of eye sight and cardiac arrest.

(ii) Carbon dioxide

Carbon dioxide is released into the atmosphere mainly by the process of respiration, burning of fossil fuels, forest fire, decomposition of limestone in cement industry etc.

Green plants can convert CO_2 gas in the atmosphere into carbohydrate and oxygen through a process called photosynthesis. The increased CO_2 level in the atmosphere is responsible for global warming. It causes headache and nausea.

(d) Hydrocarbon

The compounds composed of carbon and hydrogen only are called hydrocarbons. They are mainly produced naturally (marsh gas) and also by incomplete combustion of automobile fuel.

They are potential cancer causing (carcinogenic) agents. For example, polynuclear aromatic hydrocarbons (PAH) are carcinogenic, they cause irritation in eyes and mucous membranes.

15.3.1.2 Greenhouse effect and Global warming:

In 1987, Jean Baptiste Fourier a French mathematician and scientist

coined the term “Greenhouse Effect” for trapping of heat in the atmosphere by certain gases.

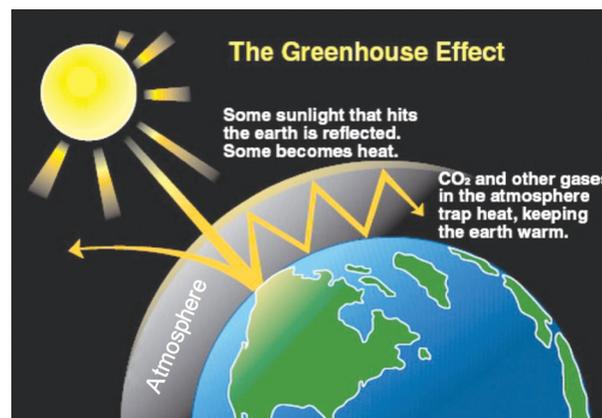


Fig 15.2 Greenhouse effect

The earth’s atmosphere allows most of the visible light from the Sun to pass through and reach Earth’s surface. As Earth’s surface is heated by sunlight, it radiates part of this energy back toward space as longer wavelengths (IR).

Some of the heat is trapped by CH_4 , CO_2 , CFCs and water vapour present in the atmosphere. They absorb IR radiation and effectively block a large portion of earth’s emitted radiation. The radiation thus absorbed is partly reemitted to earth’s surface. Therefore, the earth’s surface gets heated up by a phenomenon called greenhouse effect.

Thus Greenhouse effect may be defined as the heating up of the earth surface due to trapping of infrared radiations reflected by earth’s surface by CO_2 layer in the atmosphere”. The heating up of earth through the greenhouse effect is called global warming.

Without the heating caused by the greenhouse effect, Earth’s average surface



temperature would be only about $-18\text{ }^{\circ}\text{C}$ ($0\text{ }^{\circ}\text{F}$). Although the greenhouse effect is a naturally occurring phenomenon, it is intensified by the continuous emission of greenhouse gases into the atmosphere.

During the past 100 years, the amount of carbon dioxide in the atmosphere increased by roughly 30 percent and the amount of methane more than doubled. If these trends continue, the average global temperature will increase which can lead to melting of polar ice caps and flooding of low lying areas. This will increase incidence of infectious diseases like dengue, malaria etc.

15.3.1.3 Acid Rain

Rain water normally has a pH of 5.6 due to dissolution of atmospheric CO_2 into it. Oxides of sulphur and nitrogen in the atmosphere may be absorbed by droplets of water that make up clouds and get chemically converted into sulphuric acid and nitric acid respectively. As a result, pH of rain water drops below the level 5.6, hence it is called acid rain.

Acid rain is a by-product of a variety of sulphur and nitrogen oxides in the atmosphere. Burning of fossil fuels (coal and oil) in power stations, furnaces and petrol, diesel in motor engines produce sulphur dioxide and nitrogen oxides. The main contributors of acid rain are SO_2 and NO_2 . They are converted into sulphuric acid and nitric acid respectively by the reaction with oxygen and water.



Harmful effects of acid rain:

Some harmful effects are discussed below.

(i) Acid rain causes extensive damage to buildings and structural materials of marbles. This attack on marble is termed as Stone leprosy.



(ii) Acid rain affects plants and animal life in aquatic ecosystem.

(iii) It is harmful for agriculture, trees and plants as it dissolves and removes the nutrients needed for their growth.

(iv) It corrodes water pipes resulting in the leaching of heavy metals such as iron, lead and copper into drinking water which have toxic effects.

(v) It causes respiratory ailment in humans and animals.



Fig 15. 3. Effect Of Acid Rain On Tajmahal

15.3.2 Particulate matter (Particulate pollutants)

Particulate pollutants are small solid particles and liquid droplets suspended in air. Many of particulate pollutants are hazardous. Examples: dust, pollen, smoke, soot and liquid droplets (aerosols) etc.,

They are blown into the atmosphere by volcanic eruption, blowing of dust, incomplete combustion of fossil fuels induces soot. Combustion of high ash fossil fuels creates fly ash and finishing of metals throws metallic particles into the atmosphere.

15.3.2.1. Types of Particulates:

Particulate in the atmosphere may be of two types, viable or non-viable.

a. Viable particulates

The viable particulates are the small size living organisms such as bacteria, fungi, moulds, algae, etc. which are dispersed in air. Some of the fungi cause allergy in human beings and diseases in plants.

b. Non-viable particulates

The non-viable particulates are small solid particles and liquid droplets suspended in air. They help in the transportation of viable particles. There are four types of non-viable particulates in the atmosphere. They are classified according to their nature and size as follows

(i) Smoke

Smoke particulate consists of solid particles (or) mixture of solid and liquid

particles formed by combustion of organic matter.

For example, cigarette smoke, oil smoke, smokes from burning of fossil fuel, garbage and dry leaves.

(ii) Dust:

Dust composed of fine solid particles produced during crushing and grinding of solid materials.

For example, sand from sand blasting, saw dust from wood works, cement dust from cement factories and fly ash from power generating units.

(iii) Mists

They are formed by particles of spray liquids and condensation of vapours in air.

For example, sulphuric acid mist, herbicides and insecticides sprays can form mists.

(iv) Fumes

Fumes are obtained by condensation of vapours released during sublimation, distillation, boiling and calcination and by several other chemical reactions.

For example, organic solvents, metals and metallic oxides form fume particles.

15.3.2.2. Health effects of particulate pollutants:

- i. Dust, mist, fumes, etc., are air borne particles which are dangerous for human health. Particulate pollutants



bigger than 5 microns are likely to settle in the nasal passage whereas particles of about 10 micron enters the lungs easily and causes scarring or fibrosis of lung lining. They irritate the lungs and causes cancer and asthma. This disease is also called pneumoconiosis. Coal miners may suffer from black lung disease. Textile workers may suffer from white lung disease.

- ii. Lead particulates affect children's brain, interferes maturation of RBCs and even cause cancer.
- iii. Particulates in the atmosphere reduce visibility by scattering and absorption of sunlight. It is dangerous for aircraft and motor vehicles
- iv. Particulates provide nuclei for cloud formation and increase fog and rain.
- v. Particulates deposit on plant leaves and hinder the intake of CO_2 from the air and affect photosynthesis.

15.3.2.3. Techniques to reduce particulate pollutants

The particulates from air can be removed by using electrostatic precipitators, gravity settling chambers, and wet scrubbers or by cyclone collectors. These techniques are based on washing away or settling of the particulates.

15.3.3 Smog

Smog is a combination of smoke and fog which forms droplets that remain suspended in the air.



Fig 15.4 classical smog

Smog is a chemical mixture of gases that forms a brownish yellow haze over urban cities. Smog mainly consists of ground level ozone, oxides of nitrogen, volatile organic compounds, SO_2 , acidic aerosols and gases, and particulate matter.

There are two types of smog. One is Classical smog caused by coal smoke and fog, second one is photo chemical smog caused by photo chemical oxidants. They are discussed below in detail.

(i) Classical smog or London smog

Classical smog was first observed in London in December 1952 and hence it is also known as London smog. It consists of coal smoke and fog.

It occurs in cool humid climate. This atmospheric smog found in many large cities. The chemical composition is the mixture of SO_2 , SO_3 and humidity. It generally occurs in the morning and becomes worse when the sun rises.

This is mainly due to the induced oxidation of SO_2 to SO_3 , which reacts with water yielding sulphuric acid aerosol.

Chemically it is reducing in nature because of high concentration of SO_2 and so it is also called as reducing smog.

Effects of classical smog:

- Smog is primarily responsible for acid rain.
- Smog results in poor visibility and it affects air and road transport.
- It also causes bronchial irritation.

Great London Smog



The great smog of London, or great smog of 1952, was a severe air-pollution event that affected the British capital of London in early December 1952. It lasted from Friday, 5 December to Tuesday, 9 December 1952 and then dispersed quickly when the weather changed. It caused major disruption by reducing visibility and even penetrating indoor areas. Government medical reports in the following weeks, however, estimated that until 8 December, 4,000 people had died as a direct result of the smog and 100,000 more were made ill by the smog's effects on the human respiratory tract.

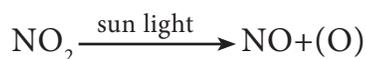
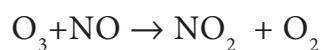
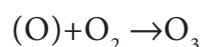
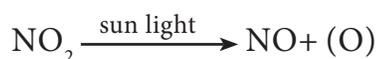
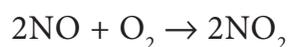
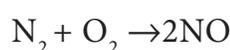
ii) Photo chemical smog or Los Angel Smog

Photo Chemical smog was first observed in Los Angels in 1950. It occurs in warm, dry and sunny climate. This type

of smog is formed by the combination of smoke, dust and fog with air pollutants like oxides of nitrogen and hydrocarbons in the presence of sunlight.

It forms when the sun shines and becomes worse in the afternoon. Chemically it is oxidizing in nature because of high concentration of oxidizing agents NO_2 and O_3 , so it is also called as oxidizing smog.

Photo chemical smog is formed through sequence of following reactions.



NO and O_3 are strong oxidizing agent and can react with unburnt hydrocarbons in polluted air to form formaldehyde, acrolein and peroxy acetyl nitrate (PAN).

Effects of photo chemical smog

The three main components of photo chemical smog are nitrogen oxide, ozone and oxidised hydro carbon like formaldehyde (HCHO), Acrolein ($\text{CH}_2=\text{CH}-\text{CHO}$), peroxy acetyl nitrate (PAN).

Photochemical smog causes irritation to eyes, skin and lungs, increase in chances of asthma.



High concentrations of ozone and NO can cause nose and throat irritation, chest pain, uncomfortable in breathing, etc.

PAN is toxic to plants, attacks younger leaves and cause bronzing and glazing of their surfaces

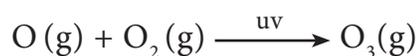
It causes corrosion of metals stones, building materials and painted surfaces.

Control of Photo chemical smog

The formation of photochemical smog can be suppressed by preventing the release of nitrogen oxides and hydrocarbons into the atmosphere from the motor vehicles by using catalytic convertors in engines. Plantation of certain trees like Pinus, Pyrus, Querus Vitus and juniparus can metabolise nitrogen oxide.

15.4. Stratospheric pollution

At high altitudes to the atmosphere consists of a layer of ozone (O₃) which acts as an umbrella or shield for harmful UV radiations. It protects us from harmful effect such as skin cancer. UV radiation can convert molecular oxygen into ozone as shown in the following reaction.



Ozone gas is thermodynamically unstable and readily decomposes to molecular oxygen.

15.4.1 Depletion of Ozone Layer (Ozone hole)

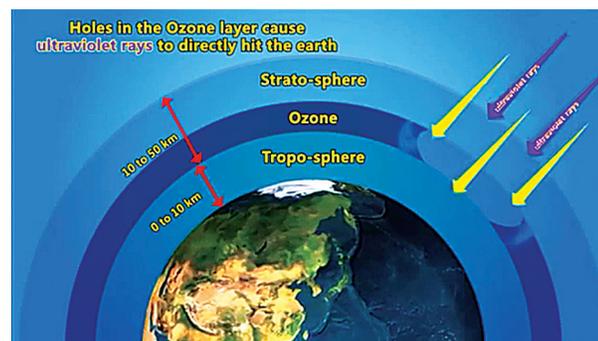


Fig 15.5 Ozone Depletion

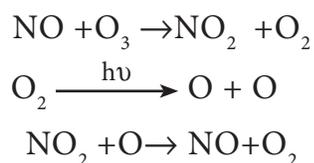
In recent years, a gradual depletion of this protective ozone layer has been reported. Nitric oxide and CFC are found to be most responsible for depletion of ozone layer.

Generally substances that cause depletion of ozone or make it thinner are called Ozone Depletion Substances abbreviated as ODS. The loss of ozone molecules in the upper atmosphere is termed as depletion of stratospheric ozone.

Oxides of Nitrogen:

Nitrogen oxides introduced directly into the stratosphere by the supersonic jet aircraft engines in the form of exhaust gases.

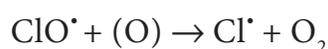
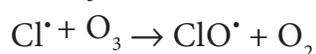
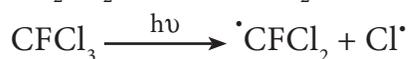
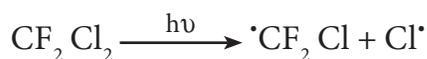
These oxides are also released by combustion of fossil fuels and nitrogen fertilizers. Inert nitrous oxide in the stratosphere is photochemically converted into more reactive nitric oxide. Oxides of nitrogen catalyse the decomposition of ozone and are themselves regenerated. Ozone gets depleted as shown below.



Thus NO is regenerated in the chain reaction.

Chloro Fluoro Carbons (CFC) Freons

The chloro fluoro derivatives of methane and ethane are referred by trade name Freons. These Chloro Fluoro Carbon compounds are stable, non-toxic, noncorrosive and non-inflammable, easily liquefiable and are used in refrigerators, air-conditioners and in the production of plastic foams. CFC's are the exhaust of supersonic air craft's and jumbo jets flying in the upper atmosphere. They slowly pass from troposphere to stratosphere. They stay for very longer period of 50 - 100 years. In the presence of uv radiation, CFC's break up into chlorine free radical



Chlorine radical is regenerated in the course of reaction. Due to this continuous attack of $\text{Cl}\cdot$ thinning of ozone layer takes place which leads to formation of ozone hole.

It is estimated that for every reactive chlorine atom generated in the stratosphere 1,00,000 molecules of ozone are depleted.

15.4.2 Environmental Impact of Ozone Depletion

The formation and destruction of ozone is a regular natural process, which never disturbs the equilibrium level of ozone

in the stratosphere. Any change in the equilibrium level of the ozone in the atmosphere will adversely affect life in the biosphere in the following ways.

Depletion of ozone layer will allow more UV rays to reach the earth surface and layer would cause skin cancer and also decrease the immunity level in human beings.

UV radiation affects plant proteins which leads to harmful mutation of cells.

UV radiation affects the growth of phytoplankton, as a result ocean food chain is disturbed and even damages the fish productivity.

15.5 Water Pollution

Water is essential for life. Without water life would have been impossible. The slogan, 'Save Water, Water will save you' tell us the importance of water. Such slogans tell us to save water. Apart from saving water, maintaining its quality is also equally important.



Fig 15.6 water pollution

Now a days water is getting polluted due to human activities and the availability of potable water in nature is becoming rare day by day. Water pollution is defined as "The addition of foreign substances or factors like heat which degrades the

quality of water, so that it becomes health hazard or unfit to use.”

The water pollutants originate from both natural and human activities. The source of water pollution is classified as Point and Non-point source.

Easily identified source of place of pollution is called as point source. Example: municipal and industrial discharge pipes.

Non-point source cannot be identified easily, example: agricultural runoff, mining wastes, acid rain, and storm-water drainage and construction sediments.

Table 15.2: List of major water pollutants and their sources.

No	Pollutant	Sources
1	Microorganisms	Domestic sewage, domestic waste water, dung heap
2	Organic wastes	Domestic sewage, animal excreta, food processing factory waste, detergents and decayed animals and plants,
3	Plant nutrients	Chemical fertilisers
4	Heavy metals	Heavy metal producing factories
5	Sediments	Soil erosion by agriculture and strip-mining
6	Pesticides	Chemicals used for killing insects, fungi and weeds
7	Radioactive substances	Mining of uranium containing minerals
8	Heat	Water used for cooling in industries

15.6 Causes of water pollution

(i) Microbiological (Pathogens)

Disease causing microorganisms like bacteria, viruses and protozoa are most serious water pollutants.

They come from domestic sewage and animal excreta. Fish and shellfish can become contaminated and people who eat them can become ill. Some serious diseases like polio and cholera are water borne diseases. Human excreta contain bacteria such as *Escherichia coli* and *Streptococcus faecalis* which cause gastrointestinal diseases



(ii) Organic wastes:

Organic matter such as leaves, grass, trash etc can also pollute water. Water pollution is caused by excessive phytoplankton growth within water.

Microorganisms present in water decompose these organic matter and consume dissolved oxygen in water.

Eutrophication:

Eutrophication is a process by which water bodies receive excess nutrients that stimulates excessive plant growth (algae, other plant weeds). This enhanced plant growth in water bodies is called as algae bloom.

The growth of algae in extreme abundance covers the water surface and reduces the oxygen concentration in water. Thus, bloom-infested water inhibits the growth of other living organisms in the water body. This process in which the nutrient rich water bodies support a dense plant population, kills animal life by depriving it of oxygen and results in loss of biodiversity is known as eutrophication.

Biochemical oxygen demand(BOD)

The total amount of oxygen in milligrams consumed by microorganisms in decomposing the waste in one litre of water at 20°C for a period of 5 days is called biochemical oxygen demand (BOD) and its value is expressed in ppm.

BOD is used as a measure of degree of water pollution. Clean water would have BOD value less than 5 ppm whereas

highly polluted water has BOD value of 17 ppm or more.

Chemical Oxygen Demand (COD)

BOD measurement takes 5 days so another parameter called the Chemical Oxygen Demand (COD) is measured.

Chemical oxygen demand (COD) is defined as the amount of oxygen required by the organic matter in a sample of water for its oxidation by a strong oxidising agent like $K_2Cr_2O_7$ in acid medium for a period of 2 hrs.

(iii) Chemical wastes:

A whole variety of chemicals from industries, such as metals and solvents are poisonous to fish and other aquatic life.

Some toxic pesticides can accumulate in fish and shell fish and poison the people who eat them. Detergents and oils float and spoil the water bodies. Acids from mine drainage and salts from various sources can also contaminate water sources.

Harmful effects of chemical water pollutants:

1. Cadmium and mercury can cause kidney damage.
2. Lead poisoning can leads to the severe damage of kidneys, liver, brain etc. it also affects central nervous system
3. Polychlorinated biphenyls (PCBs) causes skin diseases and are carcinogenic in nature.

15.7 Quality of drinking water:

Now a days most of us hesitate to use natural water directly for drinking, because biological, physical or chemical impurities from different sources mix with surface water or ground water.

Institutions like WHO (World Health Organisation) at world level and BIS (Bureau of Indian Standards) and ICMR (ICMR: Indian Council of Medical Research) at national level have prescribed standards for quality of drinking water. Standard characteristics prescribed for deciding the quality of drinking water by BIS, in 1991 are shown in Table.15.3

Table 15.3 Standard characteristics of drinking water

S.No	Characteristics	Desirable limit
I	Physico-chemical Characteristics	
i)	pH	6.5 to 8.5
ii)	Total Dissolved Solids (TDS)	500 ppm
iii)	Total Hardness (as CaCO ₃)	300 ppm
iv)	Nitrate	45 ppm
v)	Chloride	250 ppm
vi)	Sulphate	200 ppm
vii)	Fluoride	1 ppm
II	Biological Characteristics	
i)	Escherichia Coli (E.Coli)	Not at all
ii)	Coliforms	Not to exceed 10 (In 100 ml water sample)

Fluoride:

Fluoride ion deficiency in drinking water causes tooth decay. Water soluble fluorides are added to increase the fluoride ion concentration upto 1 ppm.

The Fluoride ions make the enamel on teeth much harder by converting hydroxyapatite, $[3(\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2)]$, the enamel on the surface of the teeth, into much harder fluorapatite, $[3(\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2)]$.

However, Fluoride ion concentration above 2 ppm causes brown mottling of teeth. Excess fluoride causes damage to bone and teeth.

Lead :

Drinking water containing lead contamination above 50ppb can cause damage to

liver, kidney and reproductive systems.

Sulphate:

Moderate level of sulphate is harmless. Excessive concentration (>500ppm) of sulphates in drinking water causes laxative effect.

Nitrate:

Use of drinking water having concentration of nitrate higher than 45 ppm may causes methemoglobinemia (blue baby syndrome) disease in children.

Total dissolved solids (TDS):

Most of the salts are soluble in water. It includes cations like calcium, magnesium, sodium, potassium, iron and anions like carbonate, bicarbonate, chloride, sulphate, phosphate and nitrate. Use of drinking water having total dissolved solids concentration higher than 500 ppm causes possibilities of irritation in stomach and intestine.

15.8 Soil Pollution



Fig 15.7 soil pollution

Soil is a thin layer of organic and inorganic material that covers the earth's rocky surface. Soil constitutes the upper crust of the earth, which supports land, plants and animals.

Soil pollution is defined as the buildup of persistent toxic compounds, radioactive materials, chemical salts and disease causing agents in soils which have harmful effects on plant growth and animal health.

Soil pollution affects the structure and fertility of soil, groundwater quality and food chain in biological ecosystem.

15.8.1 Sources of soil pollution

The major sources of which pollute the soil are discussed below

1) Artificial fertilizers:

Soil nutrients are useful for growth of plants. Plants obtains carbon, hydrogen and oxygen from air or water, whereas other essential nutrients like nitrogen, phosphorous, potassium, calcium, magnesium, sulphur are being absorbed from soil. To remove the deficiency of nutrients in soil, farmers add artificial fertilizers. Increased use of phosphate fertilizers or excess use of artificial fertilizers like NPK in soil, results in reduced yield in that soil.

2) Pesticides:

Pesticides are the chemicals that are used to kill or stop the growth of unwanted organisms. But these pesticides can affect the health of human beings.

These are further classified as

a. Insecticides:

Insecticides like DDT, BHC, aldrin etc. can stay in soil for long period of time and are absorbed by soil. They contaminate root crops like carrot, raddish, etc.

b. Fungicide:

Organo mercury compounds are used as most common fungicide. They dissociate in soil to produce mercury which is highly toxic.

c. Herbicides:

Herbicides are the chemical compounds used to control unwanted plants. They are otherwise known as weed killers. Example sodium chlorate (NaClO_3) and sodium arsenite (Na_3AsO_3). Most of the herbicides are toxic to mammals.

3) Industrial wastes

Industrial activities have been the biggest contributor to the soil pollution especially the mining and manufacturing activities.

Large number of toxic wastes are released from industries. Industrial wastes include cyanides, chromates, acids, alkalis, and metals like mercury, copper, zinc, cadmium and lead etc. These industrial wastes in the soil surface lie for a long time and make it unsuitable for use.

15.9 Strategies to control environmental pollution

After studying air, water and soil pollution, as responsible individuals we must take responsibility to protect our environment. Think of steps which you would like to undertake for controlling environmental pollution not only in your locality but also in national and international level. We must realize about our environmental threat, focus strongly on this issues and be an eye opener to save our environment. We can think about following strategies to control environmental pollution.

1. Waste management: Environmental pollution can be controlled by proper disposal of wastes.
2. Recycling: a large amount of disposed waste material can be reused by recycling the waste, thus it reduces the land fill and converts waste into useful forms.
3. Substitution of less toxic solvents for highly toxic ones used in certain industrial processes.
4. Use of fuels with lower sulphur content (e.g., washed coal)
5. Growing more trees.
6. Control measures in vehicle emissions are adequate.

Efforts to control environmental pollution have resulted in development of science for synthesis of chemical favorable to environment and it is called green chemistry.

15.10 Green Chemistry

Green chemistry is a chemical philosophy encouraging the design of products and processes that reduce or eliminate the use and generation of hazardous substances.

For this, scientist are trying to develop methods to produce eco-friendly compounds. This can be best understood by considering the following example in which styrene is produced both by traditional and greener routes.

Traditional route

This method involves two steps. Carcinogenic benzene reacts with ethylene to form ethyl benzene. Then ethyl benzene on dehydrogenation using $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ gives styrene.

Greener route

To avoid carcinogenic benzene, greener route is to start with cheaper and environmentally safer xylenes.

15.10.1. Green chemistry in day-to-day life

A few contribution of green chemistry in our day to day life is given below

(1) Dry cleaning of clothes

Solvents like tetrachloroethylene used in dry cleaning of clothes, pollute the ground water and are carcinogenic. In the place of tetrachloroethylene, liquefied CO_2 with suitable detergent, is an alternate solvent used. Liquefied CO_2 is not harmful

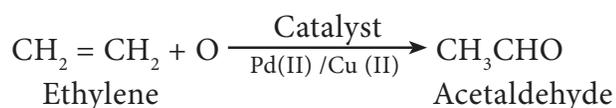
to the ground water. Now a days H_2O_2 used for bleaching clothes in laundry, gives better results and utilises less water.

(2) Bleaching of paper

Conventional method of bleaching was done with chlorine. Now a days H_2O_2 can be used for bleaching paper in presence of catalyst.

(3) Synthesis of chemicals

Acetaldehyde is now commercially prepared by one step oxidation of ethene in the presence of ionic catalyst in aqueous medium with 90% yield.



(4) Instead of petrol, methanol is used as a fuel in automobiles.

(5) Neem based pesticides have been synthesised, which are safer than the chlorinated hydrocarbons.

Every individual has an important role for preventing pollution and improving our environment. We are responsible for environmental protection. Let us begin to save our environment and provide a clean earth for our future generations.

SUMMARY

Environmental chemistry plays a vital role in environment. Environmental chemistry means scientific study of chemical and bio chemical process occurring in environment. World



Environmental Day is celebrated on fifth of June of every year.

Environmental Pollution:

Environmental pollution is the effect of undesirable changes in the surrounding that have harmful effects on living things.

Pollutants are generally classified as rapidly degradable (e.g. discarded vegetables), slowly degradable (e.g. Agriculture waste) and non-bio degradable pollutants (e.g. DDT, plastic materials).

Atmospheric pollution

Atmospheric pollutions include tropospheric and stratospheric pollution. Troposphere and stratosphere greatly affect the biosphere of the earth due to which the study of pollutions in these regions is most important.

Tropospheric pollution:

Troposphere is the lowest region of atmosphere in which man, animal and plants exist. Gaseous pollutants like SO_x , NO_x , CO , CO_2 , O_3 hydrocarbons and particulate pollutants like dust, mist, fumes, smog cause pollutions in troposphere

Acid rain:

When the PH of rain water becomes lower than 5.6 it is called acid rain. Acid rain is a byproduct of various human activities that emit sulphuroxides and nitrogen oxides in atmosphere. It damages buildings, statues and other monuments..

The acid rain in water reservoir like rivers, ponds adversely affects microbes, aquatic plants and fishes.

Greenhouse effect:

The process of warming up of earth is known as greenhouse effect or global warming. CO_2 , CH_4 , O_3 , CFC, N_2 and water vapour present in atmosphere act as a greenhouse gases. Heat retaining capacity of greenhouse gases are called Global Warming Potential (GWP). The GWP based sequence of greenhouse gases is as $CFC > N_2O > CH_4 > CO_2$.

Stratospheric pollution:

Stratosphere extends above troposphere up to 50Km above.

Depletion of ozone layer:

Ozone layer present in stratosphere protect the living species against harmful UV rays from space but Ozone Depletion Substance (ODS) used by humans deplete ozone layer. To create awareness in the Whole world, United Nations decided to celebrate 16th September of every year as "Ozone Layer Protection Day".

Water pollution

Water is the elixir of life, but it is polluted by point and nonpoint sources. Institutions like World Health Organization (WHO) and Bureau of Indian standards (BIS) and Indian Council of Medical Research (ICMR) have prescribed standards for quality of drinking water.

Soil pollution

Lithosphere with humus cover is known as soil. The topsoil provides water and all nutrients required by plants for their growth. Industrial waste, artificial fertilisers and pesticides result in soil pollution.

Waste management

The strategies for controlling environmental pollution are called waste management. Waste management involves reduction and proper disposal of waste. Wastes are produced in three forms, solid, liquid and gas. Solid waste can be disposed by segregation, dumping, incineration and composting.

Green chemistry

Efforts to control environmental pollution resulted in development of science for synthesis of chemicals favorable to environment which is called green chemistry. Green chemistry means science of environmentally favorable chemical synthesis.

Evaluation



I. Choose the best answer.

- The gaseous envelope around the earth is known as atmosphere. The region lying between an altitudes of 11-50 km is _____
 - Troposphere
 - Mesosphere
 - Thermosphere
 - stratosphere
- Which of the following is natural and human disturbance in ecology?
 - Forest fire
 - Floods
 - Acid rain
 - Green house effect
- Bhopal Gas Tragedy is a case of _____
 - thermal pollution
 - air pollution
 - nuclear pollution
 - land pollution
- Haemoglobin of the blood forms carboxy haemoglobin with
 - Carbon dioxide
 - Carbon tetra chloride
 - Carbon monoxide
 - Carbonic acid
- Which sequence for green house gases is based on GWP?
 - $\text{CFC} > \text{N}_2\text{O} > \text{CO}_2 > \text{CH}_4$
 - $\text{CFC} > \text{CO}_2 > \text{N}_2\text{O} > \text{CH}_4$
 - $\text{CFC} > \text{N}_2\text{O} > \text{CH}_4 > \text{CO}_2$
 - $\text{CFC} > \text{CH}_4 > \text{N}_2\text{O} > \text{CO}_2$
- Photo chemical smog formed in congested metropolitan cities mainly consists of
 - Ozone, SO_2 and hydrocarbons
 - Ozone, PAN and NO_2
 - PAN, smoke and SO_2
 - Hydrocarbons, SO_2 and CO_2
- The pH of normal rain water is
 - 6.5
 - 7.5
 - 5.6
 - 4.6



8. Ozone depletion will cause
- forest fires
 - eutrophication
 - bio magnification
 - global warming
9. Identify the wrong statement in the following
- The clean water would have a BOD value of more than 5 ppm
 - Greenhouse effect is also called as Global warming
 - Minute solid particles in air is known as particulate pollutants
 - Biosphere is the protective blanket of gases surrounding the earth
10. Living in the atmosphere of CO is dangerous because it
- Combines with O_2 present inside to form CO_2
 - Reduces organic matter of tissues
 - Combines with haemoglobin and makes it incapable to absorb oxygen
 - Diluted the blood
11. Release of oxides of nitrogen and hydrocarbons into the atmosphere by motor vehicles is prevented by using _____
- grit chamber
 - scrubbers
 - trickling filters
 - catalytic convertors

12. Biochemical oxygen Demand value less than 5 ppm indicates a water sample to be
- highly polluted
 - poor in dissolved oxygen
 - rich in dissolved oxygen
 - low COD
13. Match the List I with List II and select the correct answer using the code given below the lists

List I		List II	
A	Depletion of ozone layer	1	CO_2
B	Acid rain	2	NO
C	Photochemical smog	3	SO_2
D	Green house effect	4	CFC

Code:

	A	B	C	D
a	3	4	1	2
b	2	1	4	3
c	4	3	2	1
d	2	4	1	3

14.

List I		List II	
A	Stone leprosy	1	CO
B	Biological magnification	2	Green house gases
C	Global warming	3	Acid rain
D	Combination with haemoglobin	4	DDT



Code:

	A	B	C	D
a	1	2	3	4
b	3	4	2	1
c	2	3	4	1
d	4	2	1	3

The questions gives below consists of an assertion the reason. Choose the correct option out of the choices given below each question

- i) Both (A) and R are correct and (R) is the correct explanation of (A)
 - ii) Both (A) and R are correct and (R) is not the correct explanation of (A)
 - iii) Both (A) and R are not correct
 - iv) (A) is correct but (R) is not correct
15. **Assertion (A):** If BOD level of water in a reservoir is more than 5 ppm it is highly polluted
- Reason(R) :** High biological oxygen demand means high activity of bacteria in water
- a) i b) ii
c) iii d) iv
16. **Assertion (A):** Excessive use of chlorinated pesticide causes soil and water pollution.
- Reason (R) :** Such pesticides are non-biodegradable.
- a) i b) ii
c) iii d) iv

17. **Assertion (A):** Oxygen plays a key role in the troposphere

Reason (R): Troposphere is not responsible for all biological activities

- a) i b) ii
c) iii d) iv

II. Write brief answer to the following questions.

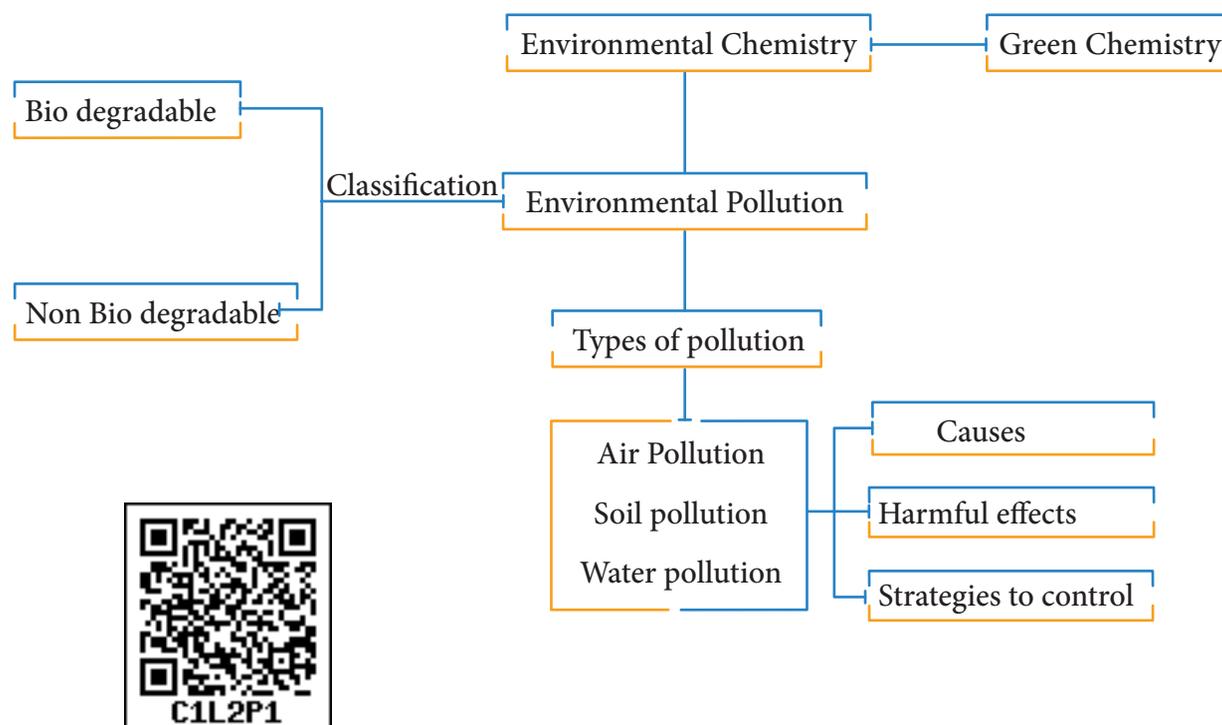
18. Dissolved oxygen in water is responsible for aquatic life. What processes are responsible for the reduction in dissolved oxygen in water?
19. What would happen, if the greenhouse gases were totally missing in the earth's atmosphere?
20. Define smog.
21. Which is considered to be earth's protective umbrella? Why?
22. What are degradable and non-degradable pollutants?
23. From where does ozone come in the photo chemical smog?
24. A person was using water supplied by corporation. Due to shortage of water he started using underground water. He felt laxative effect. What could be the cause?
25. What is green chemistry?
26. Explain how does greenhouse effect cause global warming
27. Mention the standards prescribed by BIS for quality of drinking water
28. How does classical smog differ from photochemical smog?



29. What are particulate pollutants? Explain any three.
30. Even though the use of pesticides increases the crop production, they adversely affect the living organisms. Explain the function and the adverse effects of the pesticides.
31. Ethane burns completely in air to give CO₂, while in a limited supply of air gives CO. The same gases are found in automobile exhaust. Both CO and CO₂ are atmospheric pollutants
- What is the danger associated with these gases
 - How do the pollutants affect the human body?
32. On the basis of chemical reactions
- involved, explain how do CFC's cause depletion of ozone layer in stratosphere?
33. How is acid rain formed? Explain its effect
34. Differentiate the following
- BOD and COD
 - Viable and non-viable particulate pollutants
35. Explain how oxygen deficiency is caused by carbon monoxide in our blood? Give its effect
36. What are the various methods you suggest to protect our environment from pollution?



CONCEPT MAP



PRACTICALS

Inorganic Qualitative Analysis

Instructions to the students:

- The students are required to have an observation and a record note book
- The students are advised to use overcoat and safety glass in laboratory.
- They are not permitted to taste or touch any reagent. If any reagent falls on skin, it must be immediately washed with water.
- The students should not inhale any gas or vapour directly.
- To transfer any solutions use droppers and for salts use spatula. During heating of a test tube, the open end should not face any student.
- For any accident in lab, immediately report to the teacher - incharge.
- Follow the systematic procedure carefully during analysis.
- Try to understand the chemistry in each test clearly. In the inference column there may be wording such as "Presence of or May be". Presence of means it is confirmed either the cation or anion, and May be means doubtful, further analysis is required.

List of salts

1. Lead Nitrate
2. Copper Sulphate
3. Copper Carbonate
4. Ferric Chloride
5. Zinc Sulphate
6. Zinc Sulphide
7. Aluminium Sulphate
8. Aluminium Nitrate
9. Calcium Carbonate
10. Barium Chloride
11. Ammonium Chloride
12. Ammonium Bromide
13. Magnesium Sulphate
14. Magnesium Carbonate
15. Magnesium Phosphate



Systematic analysis of a simple salt

Analysis of anions

Salt NO:

Date:

Serial NO:	Experiment	Observation	Inference
1	Note the colour of the salt	Blue (or) Green	May be copper salt
		Brown	May be an iron salt
2	Action of heat: A small amount of a salt is strongly heated in a dry test tube.	A colourless gas with the pungent smell, forming a dense white fumes when a glass rod dipped in Conc. HCl is brought close to its mouth	Presence of an ammonium salt
		A reddish brown gas is evolved	Presence of a nitrate salt
		Salt is yellow when hot and white when cold	May be a zinc salt
3.	Flame test: Take a small amount of salt in a watch glass. Add a drop of Conc. HCl to it and form a paste. Take the paste at the charred end of the splinter and introduce it near the Bunsen flame	Bluish green flame	Presence of a copper salt
		Apple green	Presence of a barium salt
		Brick red	Presence of a calcium salt
4.	Action of dil. HCl: Take a small amount of salt in a test tube and add about 1mL of dil. HCl to it. Gently heat it in the Bunsen flame	Brisk effervescence is noted. A colourless, odourless gas turning lime water milky evolves	Presence of carbonate
		A colourless gas with a rotten egg smell turning a paper dipped in lead acetate shining black evolves	Presence of sulphide



5	<p>Action of Conc. H_2SO_4:</p> <p>Take a small amount of a salt in a dry test tube, add about 0.5mL of Conc. H_2SO_4 and gently heat it in the Bunsen flame</p>	<p>A colourless gas evolves. It gives a dense white fumes when a glass rod dipped in liquid ammonia is brought close to its mouth</p>	Presence of chloride
		<p>A reddish brown gas turning moist fluorescein paper green evolves</p>	Presence of bromide
		<p>Reddish brown gas turning acidified ferrous sulphate paper green evolves.</p>	Presence of nitrate
6	<p>Action of MnO_2 and Conc. H_2SO_4:</p> <p>Take a small amount of salt in a test tube, add pinch of MnO_2 and about 0.5mL of Conc. H_2SO_4 and gently heat it in the Bunsen flame</p>	<p>A greenish yellow gas turning starch iodide paper blue evolves</p>	Presence of chloride
		<p>A reddish brown gas turning moist fluorescein paper red evolves</p>	Presence of bromide
7.	<p>Action of Conc. H_2SO_4 and copper turning:</p> <p>Take a small quantity of salt in a dry test tube and add few copper turnings and about 1mL of Conc. H_2SO_4. Gently heat it</p>	<p>A reddish brown gas with fishy odour turning a moist ferrous sulphate paper brown evolves</p>	Presence of nitrate.
8.	<p>Action of dil. NaOH solution:</p> <p>To a small quantity of a salt add about 1mL of dil. NaOH solution and gently heat it.</p>	<p>A colourless gas with the pungent smell giving dense white fumes with a glass rod dipped in con. HCl evolves</p>	Presence of ammonium salt
9.	<p>Chromyl chloride test:</p> <p>Take a small quantity of salt in a test tube, add a pinch of potassium dichromate and three drops Conc. H_2SO_4. Gently heat it. Pass the vapours to enter another test tube containing about 0.5mL of sodium hydroxide. If a yellow solution is obtained, add about 1mL each of dil. acetic acid and lead acetate</p>	<p>A yellow ppt is obtained</p>	Presence of chloride.



Analysis with sodium carbonate extract

Preparation of sodium carbonate extract:

Take 1g of the given salt and 3g of solid sodium carbonate in a 100mL beaker. Add 20g of distilled water to it. Heat the beaker with its contents on a hot plate or Bunsen burner. After boiling the solution for few mins, filter it through a filter paper in a funnel and collect the filtrate in another beaker. The filtrate is called sodium carbonate extract.

10.	Test for halides: To about one mL of the sodium carbonate extract add dil. HNO_3 in drops with shaking until the effervescence ceases, and then add about 1mL of AgNO_3 , and shake it well.	A curdy white precipitate (ppt) insoluble in about 1mL of dil. ammonia is formed	Presence of chloride
		A pale yellow ppt sparingly soluble in ammonia is formed	Presence of bromide
		A black ppt is formed	Presence of sulphide
11	Test with barium chloride: To about one mL of the sodium carbonate extract, add dil. acetic acid in drops with shaking until the effervescence ceases, then add 1mL of barium chloride solution and shake it.	A white ppt is formed insoluble in dil H_2SO_4	Presence of sulphate
12	Test with lead acetate: To about 1mL of the sodium carbonate extract, add 1mL of dil acetic acid and heat it, until the effervescence ceases, and then add 1mL of lead acetate	A white ppt soluble in excess of ammonium acetate is formed	Presence of sulphate
13	Brown ring test: To about 1mL of the sodium carbonate extract add dil. H_2SO_4 in drops with shaking until the effervescence ceases and about 0.5mL of freshly prepared ferrous sulphate solution. Then keeping the test tube in a slanting position add Conc. H_2SO_4 along the sides of the test tube.	A brown ring is formed	Presence of nitrate



14	Ammonium molybdate test: To one portion of the extract , add dil HNO_3 until the effervescence ceases, then add about 1mL each of ammonium molybdate and Conc. HNO_3	A canary yellow ppt is formed.	Presence of phosphate
15	Test with sodium nitro bruside: To about 1mL of the sodium carbonate extract add 1mL of dil .ammonia. Then add about few drops of sodium nitro prusside.	A purple or violet colouration appears	Presence of sulphide.

Reasoning

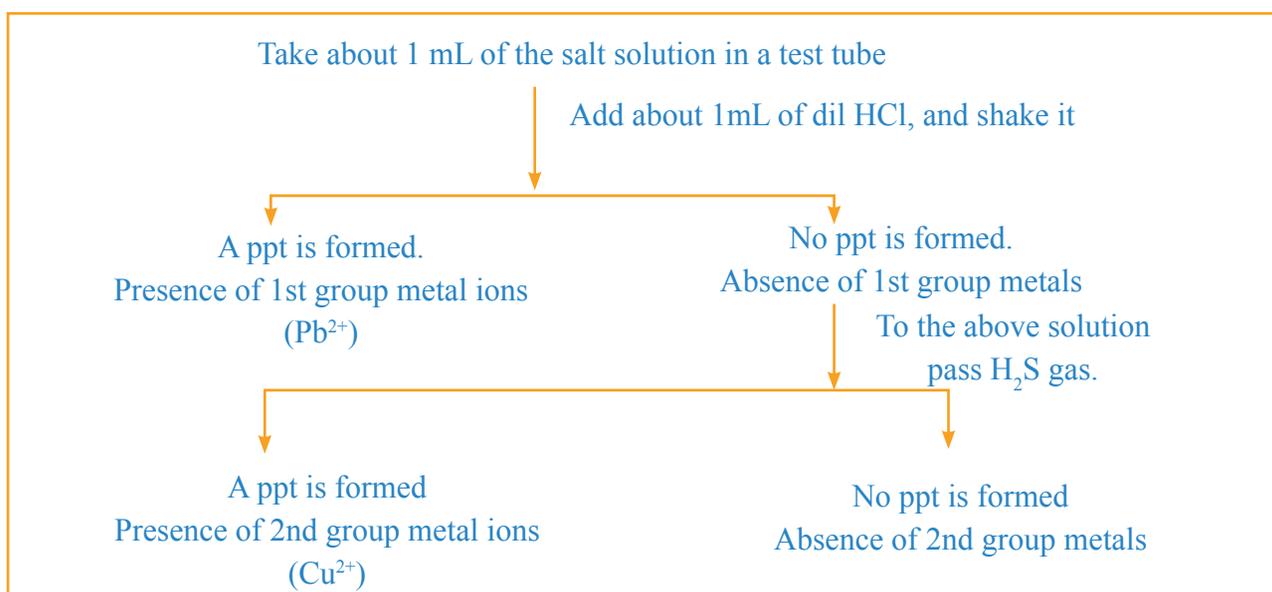
1	Action of heat: The reddish brown gas is NO_2 and N_2O_4 The zinc sulphate salts are yellow when hot and white when cold due to formation of semiconducting ZnO . At high temp there is bandgap excitation of electrons. When the excited electrons fall back from valence band to conduction band, light is emitted.
2	Flame test: To convert metallic salts into chlorides Conc.HCl is used. Generally chloride salts are more volatile than sulphate salts, so sulphuric acid is not used. When the metallic chlorides are introduced into flame, they are vapourised. In the middle of the flame, Cl^- reduces metal ions into metal atoms. The metal atoms are then excited by the flame photons, and when the excited electrons fall back, they emit light of characteristic colour.
3	Copper turning test: When copper turning dissolves in sulphuric acid, electrons and copper ions are formed. The electrons are then used to reduce nitrate in the presence of H^+ to NO_2
4	Chromyl chloride test: When a chloride salt is heated in the presence of sulphuric acid, CrO_2Cl_2 chromyl chloride is formed. With NaOH it forms Na_2CrO_4 .With lead acetate it forms yellow PbCrO_4 ppt
5	Test for halides: If any halide ion is present in sodium carbonate extract, it reacts with silver nitrate to form , to form the silver halide ppt. chloride forms AgCl ppt, bromide forms AgBr ppt,and iodide forms AgI ppt. AgCl dissolves in ammonia by forming $\text{Ag}(\text{NH}_3)_2^+$ complex. AgBr forms little amount of complex



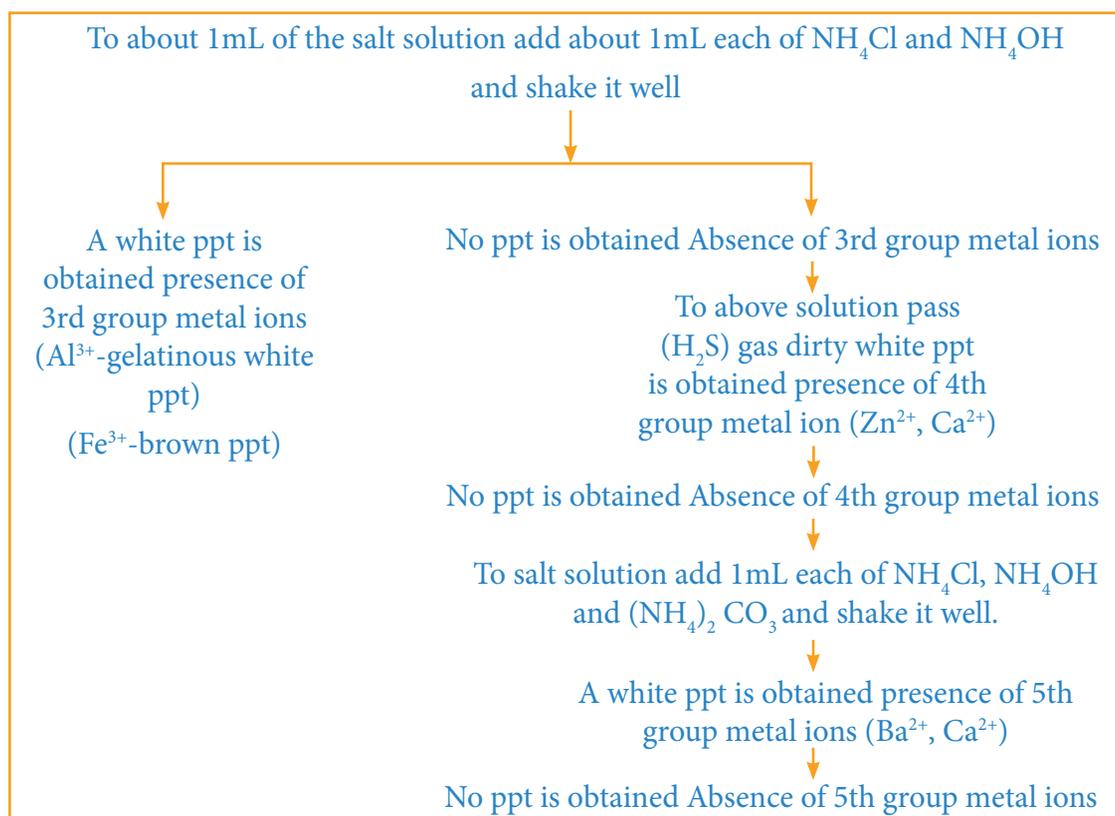
6	Test with barium chloride: Barium forms insoluble ppt with oxalate(BaC_2O_4) and sulphate(BaSO_4) BaC_2O_4 dissolves in dil. H_2SO_4 and decolourises KMnO_4 when gently heated. BaSO_4 is insoluble.
7	Test with lead acetate: Lead acetate forms lead sulphate (PbSO_4) ppt
8	Brown ring test: The brown ring is due to nitroso ferrous sulphate $[\text{Fe}(\text{NO})]\text{SO}_4$
9	Ammonium molybdate test: The canary yellow ppt is due to formation of ammonium phospho molybdate $(\text{NH}_4)_3[\text{P}(\text{Mo}_3\text{O}_{10})_4]$
10	Sodium nitro prusside test: The purple colour is due to the complex $\text{Na}_4[\text{Fe}(\text{CN}_5)\text{NOS}]$

Preparation of solution of the simple salt for the analysis of cations:

To a small amount of salt in a test tube add 2 to 3mL of water, shake it and gently heat it. If a clear solution is obtained, directly use it for the analysis of cations. If the salt is insoluble, take a small amount of salt in another test tube, add 3mL of dil. HCl or dil. HNO_3 , shake it and gently heat it. If the salt dissolves, use the clear solution for the analysis of cations. This solution is called “original solution”.



The 3rd group metal ions form metal hydroxide ppt. The 4th group metal ions form metal sulphide ppt.



Analysis of 6 group metal ions

To about 1mL of the original salt solution add about 1mL each of NH_4Cl , NH_4OH and $\text{NH}_4\text{H}_2\text{PO}_4$, and scratch the sides of the test tube.

A white ppt is obtained. Presence of magnesium

To about 1mL of the original salt solution add dil. NaOH in drops with shaking. A white ppt insoluble in excess of NaOH is formed.

Presence of Magnesium

To about 1mL of the original salt solution add about 1mL of Magneson reagent. A blue ppt is formed. Presence of magnesium.

To about 1mL of the original salt solution add about 1mL each of Nessler's reagent and NaOH . A chocolate brown ppt is obtained. Presence of ammonium

Reasoning:

Magnesium forms MgNH_4PO_4 ppt.

Maneson reagent is p-nitro azobenzene resorcinol. The blue ppt is due to precipitation of magneson by $\text{Mg}(\text{OH})_2$

Nessler's reagent is prepared by slowly adding potassium iodide to mercury chloride. Initially a white ppt of HgI_2 is obtained. The ppt dissolves in excess forming a clear solution. This clear solution is called the "Nessler's reagent". It is $\text{K}_2[\text{HgI}_4]$

The brown ppt is due to $\text{HgO} \cdot \text{Hg}(\text{NH}_2)\text{I}$. It is a basic mercury (ii) amido amine.

Analysis of group ppt:

Analysis of the 1st group ppt:

Experiment	Observation	Inference
To the ppt add about 1mL of water and boil it	The ppt dissolves	Presence of lead
Test for Lead: i.) To one portion of the hot solution add about 1mL of K_2CrO_4 ii.) To an another portion of the hot solution add about 1mL of KI. To the yellow ppt add about 1mL of water, boil and cool.	A yellow ppt is obtained A yellow ppt is obtained. The yellow ppt dissolves on boiling , and on cooling golden spangles appear	Presence of lead

Reasoning:

Lead forms $PbCrO_4$ and PbI_2 ppt - Recrystallisation of lead iodide crystals appeared as golden yellow spangles.

Analysis of the 2nd group ppt:

To the ppt add about 1mL of dil HNO_3 and boil it. The ppt dissolves. Cool it.

i) To one portion of the solution add ammonium hydroxide	No ppt is obtained, but the solution is blue	Presence of copper
iii) Test for copper: To the blue coloured solution add about 1mL each of acetic acid and potassium ferrocyanide	A red brown ppt is obtained	Presence of copper

Reasoning

Prepare sodium stannite solution by mixing equal volume of about 1mL each of stannous chloride and sodium hydroxide.

With NH_4OH copper forms soluble $[Cu(NH_3)_4]^{2+}$ complex,
Copper forms a brown ppt of $K_2Cu[Fe(CN)_6]$

Analysis of the 3rd group ppt:

To the ppt add a pinch of sodium peroxide and boil it	A red or brown ppt is obtained A colourless solution is obtained	Presence of iron Presence of aluminium
i.) Test for iron: To one portion of the red ppt add about 1mL of dil HCl and boil it and then add about 1mL of potassium ferrocyanide	A blue ppt is obtained	Presence of iron
ii.) To an another portion of the ppt add about 1mL of dil. HNO_3 boil it and then add about 1ml of KCNS	A blood red colouration is seen	Presence of iron
iii.) Test for aluminium: To the colourless solution add dil. HCl and shake it	A gelatinous white ppt is obtained	Presence of aluminium



Reasoning:

Obtain sodium peroxide by mixing equal volume of about 1mL each of NaOH and H₂O₂

Iron forms a blue ppt(prussian blue) of Fe₄[Fe(CN)₆]₃

Iron forms [Fe (CN)₆]³⁻ complex which is blood red coloured.

Aluminium forms a gelatinous white ppt of Al(OH)₃

Analysis of the 4th group ppt

To the ppt add dil HCl and boil it	The ppt dissolves	Presence of zinc
i.)Test for zinc To the solution add about 1.5mL of dil. NaOH and boil it	A clear solution is obtained	Presence of zinc

Reasoning:

Zinc initially forms Zn (OH)₂ ppt, and it dissolves in excess to form sodium zincate (Na₂ZnO₂)

Zinc forms white ppt of ZnS

Analysis of the 5th group ppt:

To the ppt add about 1mL of dil. acetic acid and gently heat it. The ppt dissolves. Divide the solution into two portions. i).To one portion add about 1mL of potassium chromate	A yellow ppt is obtained. Filter the ppt using a funnel and filter paper, and transfer the residue to a watch glass. Add a drop of Conc. HCl. Take a portion of the paste at the charred end of a splinter and introduce near the Bunsen flame. A transient green is imparted to the flame	Presence of barium.
ii). To an another portion add about 1mL of ammonium sulphate	A white ppt is obtained. Filter the ppt using a filter paper and funnel. Transfer the residue to a watch glass. Add a drop of Conc. HCl. Take the residue at the charred end of the splinter and introduce near the Bunsen flame. A crimson red colour is seen If no ppt is obtained, to the solution add about 1mL of potassium ferrocyanide and shake it. A pale yellow ppt appears.	Presence of calcium

Reasoning:

Barium forms a yellow BaCrO₄ ppt

The pale yellow ppt of calcium is due to Ca₂[Fe(CN)₆]

KEY ANSWERS

UNIT-8 CHEMICAL EQUILIBRIUM EVALUATE YOURSELF

1.

	Fe ³⁺	SCN ⁻	[Fe(SCN) ²⁺]
Initial Concentration(M)	1 × 10 ⁻³ (10 × 10 ⁻⁴)	8 × 10 ⁻⁴	–
Reacted	2 × 10 ⁻⁴	2 × 10 ⁻⁴	–
Equilibrium Concentration	8 × 10 ⁻⁴	6 × 10 ⁻⁴	2 × 10 ⁻⁴

$$K_{eq} = \frac{[\text{Fe(SCN)}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^{-}]}$$

$$= \frac{2 \times 10^{-4} \text{ M}}{8 \times 10^{-4} \text{ M} \times 6 \times 10^{-4} \text{ M}}$$

$$= 0.0416 \times 10^4$$

$$K_{eq} = 4.16 \times 10^2 \text{ M}^{-1}$$

2. $2 \text{NO(g)} + \text{O}_2 \text{(g)} \rightleftharpoons 2\text{NO}_2 \text{(g)}$

	NO ₂	O ₂	NO ₂
Initial Partial Pressure	1	1	–
Reacted	0.96	0.48	–
Equilibrium Partial Pressure	0.04	0.52	0.96

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 \cdot P_{\text{O}_2}}$$

$$= \frac{0.96 \times 0.96}{0.04 \times 0.04 \times 0.52}$$

$$= 11.07 \times 10^2 \text{ (atm)}^{-1}$$

3. $\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2 \text{(g)} + \text{H}_2 \text{(g)}$

Given $K_p = 2.7$

$$[\text{CO}] = 0.13, [\text{H}_2\text{O}] = 0.56$$

$$[\text{CO}_2] = 0.78; [\text{H}_2] = 0.28$$

$$V = 2\text{L}$$

$$K_p = K_c \text{ (RT)}$$

$$2.7 = K_c \text{ (RT)}^0$$

$$K_c = 2.7$$

$$Q_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]}$$

$$= \left(\frac{0.78}{2}\right)\left(\frac{0.28}{2}\right)$$

$$= \left(\frac{0.13}{2}\right)\left(\frac{0.56}{2}\right)$$

$$Q = 3$$

$Q > K_c$, Hence the reaction proceed in the reverse direction.

4. $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$

Given that $[\text{PCl}_5]_{\text{initial}} = 1 \text{ mol}$; $V = 1 \text{ dm}^3$; $K_c = 2$

	PCl ₅	PCl ₃	Cl ₂
Initial no. of moles	1	–	–
No. of moles	x	–	–
No. of moles at equilibrium	1-x	x	x
Equilibrium concentration	$\frac{1-x}{1}$	$\frac{x}{1}$	$\frac{x}{1}$

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

$$2 = \frac{x \times x}{(1-x)}$$

$$2 - 2x = x^2$$

$$x^2 + 2x - 2 = 0$$

solution for a quadratic equation

$$ax^2 + bx + c = 0 \text{ are,}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$a = 1 \quad b = 2 \quad c = -2$$

$$x = \frac{-2 \pm \sqrt{4 - 4 \times 1 \times -2}}{2 \times 1}$$

$$= \frac{-2 \pm \sqrt{12}}{2} = \frac{-2 \pm \sqrt{4 \times 3}}{2}$$

$$x = \frac{-2 \pm 2\sqrt{3}}{2}$$

$$= \frac{-2 + 2\sqrt{3}}{2}, \frac{-2 - 2\sqrt{3}}{2}$$

$$x = -1 + \sqrt{3}; -1 - \sqrt{3}$$

Since X is +ve

$$= -1 + 1.732$$

$-1 - \sqrt{3}$ not possible

$$= 0.732$$

∴ Equilibrium concentration of

$$[\text{PCl}_5]_{\text{eq}} = \frac{1-x}{1} = 1 - 0.732 = 0.268 \text{ M}$$

$$[\text{PCl}_3]_{\text{eq}} = \frac{x}{1} = \frac{0.732}{1} = 0.732$$

$$[\text{Cl}_2]_{\text{eq}} = \frac{x}{1} = \frac{0.732}{1} = 0.732$$

5. $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
 $T_1 = 298 \text{ K} \quad K_p = 0.15$
 $T_2 = 100^\circ \text{C} = 100 + 273 = 373 \text{ K};$
 $K_{p_2} = ?$

$$\log \left(\frac{K_2}{K_1} \right) = \frac{\Delta H^\circ}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$K_2 > K_1 \text{ and } T_2 > T_1$$

$$\log \left(\frac{K_{p_2}}{0.15} \right) = \frac{57.2 \text{ KJ mol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \left[\frac{373 - 298}{373 \times 298} \right]$$

$$\log \left(\frac{K_{p_2}}{0.15} \right) = \frac{57.2 \times 10^3 \times 75}{2.303 \times 8.314 \times 373 \times 298}$$

$$\log \left(\frac{K_{p_2}}{0.15} \right) = 2.02$$

$$\frac{K_{p_2}}{0.15} = 104.7$$

$$K_{p_2} = 104.7 \times 0.15$$

$$K_{p_2} = 15.705$$

KEY FOR MCQs

1. $K_b = 0.8 \times 10^{-5}$

$$K_f = 1.6 \times 10^{-4}$$

$$K_{\text{eq}} = \frac{K_f}{K_b} = \frac{1.6 \times 10^{-4}}{0.8 \times 10^{-5}} = 20 \text{ (Option(a))}$$

2. $K_1 = \frac{[\text{A}_3\text{BC}]^2}{[\text{A}_2]^3 [\text{B}_2][\text{C}]^2} \dots\dots\dots (1)$

$$K_2 = \frac{[\text{A}_2]^{3/2} [\text{B}_2]^{1/2} [\text{C}]}{[\text{A}_3\text{BC}]}$$

$$\Rightarrow K_2^2 = \frac{[\text{A}_2]^3 [\text{B}_2][\text{C}]^2}{[\text{A}_3\text{BC}]^2} \dots\dots\dots (2)$$

Comparing (1) & (2)

$$K_2^2 = \frac{1}{K_1}$$

$$\Rightarrow K_2 = K_1^{-1/2} \text{ (Option(b))}$$

3. $T_1 = 25 + 273 = 298 \text{ K}$

$$T_2 = 700 \text{ K}$$

$$\log \left(\frac{K_2}{K_1} \right) = \frac{\Delta H^\circ}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

In this case, $T_2 > T_1$ and $K_1 > K_2$

$$\Rightarrow \frac{2.303 R \log \left(\frac{K_2}{K_1} \right)}{\left(\frac{T_2 - T_1}{T_1 T_2} \right)} = \Delta H^\circ$$

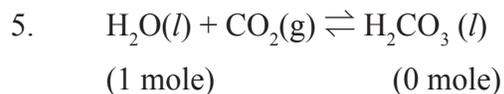
$$\Rightarrow \frac{-\text{ve}}{+\text{ve}} = \Delta H^\circ$$

ΔH° is -ve ie., forward reaction is exothermic (option a)

4. Increase in temperature, favours the endothermic reaction,

Given that formation of NH_3 is exothermic i.e., the reverse reaction is endothermic.

\therefore increase in temperature, shift the equilibrium to left option (c)



increase in pressure, favours the forward reaction.

option (a)

6. option (a) : wrong statement

Correct statement is, for a system at equilibrium, $Q = K_{\text{eq}}$

$$7. K_1 = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} K_2 = \frac{[\text{NO}]^2}{[\text{NO}]^2[\text{O}_2]} K = \frac{[\text{N}_2]^{1/2}[\text{O}_2]}{[\text{NO}_2]}$$

$$\sqrt{K_1} = \frac{[\text{NO}]}{[\text{N}_2]^{1/2}[\text{O}_2]^{1/2}} \quad \sqrt{K_2} = \frac{[\text{NO}_2]}{[\text{NO}][\text{O}_2]^{1/2}}$$

$$\sqrt{K_1 \cdot K_2} = \frac{[\text{NO}_2]}{[\text{N}_2]^{1/2}[\text{O}_2]}$$

$$\therefore K = \frac{1}{\sqrt{K_1 K_2}} \text{ (Option(a))}$$

8. $[\text{A}] = 1 \times 10^{-4} \text{ M} ; [\text{B}] = 2 \times 10^{-3} \text{ M}$
 $[\text{C}] = 1.5 \times 10^{-4} \text{ M}$



$$K = \frac{[\text{B}]^2 [\text{C}_2]}{[\text{A}]^2} = \frac{(2 \times 10^{-3})^2 (1.5 \times 10^{-4})}{(1 \times 10^{-4})^2}$$

$$= 6.0 \times 10^{-2} = 0.06 \text{ (Option(a))}$$

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

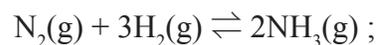
$$3.2 \times 10^{-6} = \frac{[\text{Products}]}{[\text{Reactants}]}$$

$K_c < 10^{-3}$; indicates

that $[\text{Reactants}] \gg [\text{Products}]$

option (b) is correct, largely towards reverse direction.

10. for the reaction,



$\Delta n_g = 2 - 4 = -2$

$\therefore K_p = K_c (RT)^{-2}$

$\Rightarrow \frac{K_c}{K_p} = (RT)^2 \text{ (Option(d))}$

11.

	AB	A	B
Initial no. of moles	100	-	-
No. of moles dissociated and formed	20	20	20
No. of moles at equilibrium	80	20	20

Total no. of moles at equilibrium = $80 + 20 + 20 = 120$

$$K_p = \frac{P_A \cdot P_B}{P_{AB}} = \frac{\left(\frac{20}{120} \times P\right) \left(\frac{20}{120} \times P\right)}{\left(\frac{80}{120} \times P\right)} = \frac{P}{24}$$

$24K_p = P$ (option (a))

12. For reaction given in option (a), (b) & (c) $\Delta n_g = 0$

For option (d) $\Delta n_g = 2 - 1 = 1$

$\therefore K_p = K_c (RT)$

option (d)

13.

	PCl_5	PCl_3	Cl_2
Initial no. of moles	0.5	-	-
No. of moles dissociated	x	-	-
No. of moles at equilibrium	$0.5 - x$	x	x

Total no. of moles at equilibrium = $0.5 - x + x + x = 0.5 + x$

option (b)

14.

	$x \rightleftharpoons y + z$			$A \rightleftharpoons 2B$	
	x	y	z	A	B
Initial no. of moles	a	-	-	a	-
Number of moles dissociated	x	-	-	x	-
No. of moles at equilibrium	a - x	x	x	a - x	2x
Total no. of moles at equilibrium	a - x + x + x = a + x			a - x + 2x = a + x	

$$\frac{K_{P_1}}{K_{P_2}} = \frac{P_y P_z}{P_x} \times \frac{P_A}{P_B^2}$$

$$\frac{K_{P_1}}{K_{P_2}} = \left[\frac{\left(\frac{x}{a+x}\right) P_1 \left(\frac{x}{a+x}\right) P_1}{\left(\frac{a-x}{a+x}\right) \times P_1} \right] \times \left[\frac{\left(\frac{a-x}{a+x}\right) P_2}{\frac{4x^2 P_2^2}{(a+x)^2}} \right]$$

$$\frac{K_{P_1}}{K_{P_2}} = \frac{P_1}{4P_2}$$

Given that $\frac{K_{P_1}}{K_{P_2}} = \frac{9}{1}$

$$\therefore \frac{9}{1} = \frac{P_1}{4P_2} \Rightarrow \frac{P_1}{P_2} = \frac{36}{1}$$

option (a) is correct

$$15. \quad K_C = \frac{[\text{Fe}^{3+}][\text{OH}^-]^3}{[\text{Fe}(\text{OH})_3(\text{s})]}$$

$$K_C = [\text{Fe}^{3+}] \times \frac{1}{64} [\text{OH}^-]^3$$

To maintain K_C as constant, concentration of Fe^{3+} will increase by 64 times.

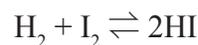
option (d)

$$16. \quad K_p = 0.5$$

$$Q = \frac{P_{\text{PCl}_3} \cdot P_{\text{Cl}_2}}{P_{\text{PCl}_5}}$$

$$Q = \frac{1 \times 1}{1}$$

$Q > K_p$ \therefore Reverse reaction is favoured ; i.e. more PCl_5 will be produced. option (c)

17. $V = 1\text{L}$ 

$$[\text{H}_2]_{\text{initial}} = [\text{I}_2]_{\text{initial}} = a$$

$$[\text{H}_2]_{\text{eq}} = [\text{I}_2]_{\text{eq}} = (a - x)$$

$$\text{and } [\text{HI}]_{\text{eq}} = 2x$$

$$K_C = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

$$\therefore K_C = \frac{4x^2}{(a-x)^2}$$

$$\text{Given that } K_C = \frac{K_f}{K_r} = 1$$

$$\therefore 4x^2 = (a-x)^2$$

$$4x^2 = a^2 + x^2 - 2ax$$

$$3x^2 + 2ax - a^2 = 0$$

$$x = -a \text{ \& } x = \frac{a}{3}$$

$$\text{degree of dissociation} = \frac{a}{3} \times 100$$

$$= 33.33 \%$$

option (a)

$$18. \quad K_f = 2.5 \times 10^2$$

$$K_C = 50$$

$$K_r = ?$$

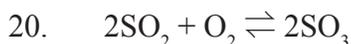
$$K_C = \frac{K_f}{K_r}$$

$$50 = \frac{2.5 \times 10^2}{K_r}$$

$$K_r = 5 \text{ (Option (b))}$$

19. correct statement : Physical processes occurs at the same rate at equilibrium

\therefore option (c) is incorrect statement



$$K_1 = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$$

dissociation of 1 mole of SO_3



$$K_2 = \frac{[\text{SO}_2][\text{O}_2]^{1/2}}{[\text{SO}_3]} \quad \therefore K_2 = \frac{1}{\sqrt{K_1}}$$

option (c) is correct

21. option (b)

22. $\text{A} + \text{B} \rightleftharpoons \text{C}$

$$K_c = \frac{[\text{C}]}{[\text{A}][\text{B}]}$$

if [A] and [B] are doubled, [C] increases 4 times to maintain K_c as constant.

\therefore equilibrium constant will remain the same – option (d)

23. on cooling, reverse reaction predominates and the solution is pink in colour.

\therefore decrease in temperature, favours the reverse reaction ie reverse reaction is exothermic and for the forward reaction is endothermic ($\Delta H > 0$)

option (a)

$$24. \quad K_1 = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$K_2 = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

$$K_3 = \frac{[\text{H}_2\text{O}]}{[\text{H}_2][\text{O}_2]^{1/2}}$$

$$K = \frac{[\text{NO}]^2 [\text{H}_2\text{O}]^3}{[\text{NH}_3]^2 [\text{O}_2]^{5/2}}$$

$$K = \frac{(K_2)(K_3)^3}{(K_1)} = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \times \frac{[\text{H}_2\text{O}]^3}{[\text{H}_2]^3 [\text{O}_2]^{3/2}} \times \frac{[\text{N}_2] [\text{H}_2]^3}{[\text{NH}_3]^2}$$

$$= \frac{[\text{NO}]^2 [\text{H}_2\text{O}]^3}{[\text{NH}_3]^2 [\text{O}_2]^{5/2}}$$

option (c)

25. Given that $K_p = 1.6 \text{ atm}$

$$V_1 = 20 \text{ L} \quad V_2 = ?$$

$$T_1 = 400 \text{ K} \quad T_2 = 400 \text{ K}$$

$$K_p = P_{\text{CO}_2}$$

$$\therefore P_{\text{CO}_2} = 1.6 \text{ atm}$$

$$P_1 = 0.4 \text{ atm.} \quad P_2 = 1.6 \text{ atm}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\therefore V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2} = \frac{0.4 \text{ atm} \times 20 \text{ L}}{400 \text{ K}} \times \frac{400 \text{ K}}{1.6 \text{ atm}}$$

$$= 5 \text{ L} \quad (\text{option b})$$

$$31. \quad K_c = \frac{[\text{AB}]^2}{[\text{A}_2][\text{B}_2]} \quad \begin{array}{l} \text{A – green} \\ \text{B – blue} \end{array}$$

Given that 'V' is constant (closed system)

At equilibrium

$$K_c = \frac{\left(\frac{4}{V}\right)^2}{\left(\frac{2}{V}\right)\left(\frac{2}{V}\right)} = \frac{16}{4} = 4$$

$$K_p = K_c (RT)^{\Delta n}$$

$$K_p = 4(RT)^0 = 4$$

At Stage 'x'

$$Q = \frac{\left(\frac{6}{V}\right)^2}{\left(\frac{2}{V}\right)\left(\frac{1}{V}\right)} = \frac{36}{2} = 18$$

$Q > K_c$ ie., reverse reaction is favoured

At Stage 'y'

$$Q = \frac{\left(\frac{3}{V}\right)^2}{\left(\frac{3}{V}\right)\left(\frac{3}{V}\right)} = \frac{9}{3 \times 3} = 1$$

$K_c > Q$ ie., forward reaction is favoured.

$$37. \quad K_c = \frac{[\text{NH}_3]^4 [\text{O}_2]^5}{[\text{NO}]^4 [\text{H}_2\text{O}]^6}$$

Chemical equation is,



$$40. \quad \text{Given that} \quad [\text{PCl}_5]_{\text{initial}} = \frac{1 \text{ mole}}{1 \text{ dm}^3}$$

$$[\text{Cl}_2]_{\text{eq}} = 0.6 \text{ mole dm}^{-3}$$

$$\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$$

$$[\text{PCl}_3]_{\text{eq}} = 0.6 \text{ mole dm}^{-3}$$

$$[\text{PCl}_5]_{\text{eq}} = 0.4 \text{ mole dm}^{-3}$$

$$\therefore K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{0.6 \times 0.6}{0.4}$$

$$K_c = 0.9$$

41. for the reaction,



$$\Delta n_g = 1 - 0 = 1$$

$$\therefore K_p = K_c (\text{RT})$$

$$2.2 \times 10^{-4} = K_c (0.0821) (1002)$$

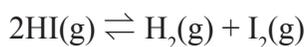
$$K_c = \frac{2.2 \times 10^{-4}}{0.0821 \times 1002}$$

$$= 2.674 \times 10^{-6}$$

42. $V = 3\text{L}$

$$[\text{HI}]_{\text{initial}} = \frac{0.3 \text{ mol}}{3\text{L}} = 0.1 \text{ M}$$

$$[\text{HI}]_{\text{eq}} = 0.05 \text{ M}$$



	HI(g)	H ₂ (g)	I ₂ (g)
Initial Con- centration	0.1	–	–
Reacted	0.05	–	–
Equilibri- um concen- tration	0.05	0.025	0.025

$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$$

$$= \frac{0.025 \times 0.025}{0.05 \times 0.05}$$

$$K_c = 0.25$$

$$K_p = K_c (\text{RT})^{\Delta n_g}$$

$$\Delta n_g = 2 - 2 = 0$$

$$K_p = 0.25 (\text{RT})^0$$

$$K_p = 0.25$$



$$K_c = 4 \times 10^{-2} \text{ mol lit}^{-2}$$

$$\text{Volume} = 500 \text{ ml} = \frac{1}{2} \text{ L}$$

$$[\text{CH}_4]_{\text{in}} = \frac{1 \text{ mol}}{\frac{1}{2} \text{ L}} \quad [\text{CS}_2]_{\text{in}} = \frac{1 \text{ mol}}{\frac{1}{2} \text{ L}}$$

$$= 2 \text{ mol L}^{-1} \quad = 2 \text{ mol L}^{-1}$$

$$[\text{H}_2\text{S}]_{\text{in}} = \frac{2 \text{ mol}}{\frac{1}{2} \text{ L}} = 4 \text{ mol L}^{-1} \quad [\text{H}_2] = \frac{2 \text{ mol}}{\frac{1}{2} \text{ L}} = 4 \text{ mol L}^{-1}$$

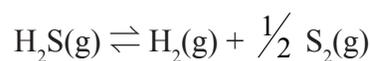
$$Q = \frac{[\text{CS}_2][\text{H}_2]^4}{[\text{CH}_4][\text{H}_2\text{S}]^2}$$

$$\therefore Q = \frac{2 \times (4)^4}{(2) \times (4)^2} = 16$$

$$Q > K_c$$

\therefore The reaction will proceed in the reverse direction to reach the equilibrium.

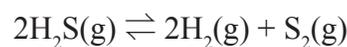
44. $K_c = 4 \times 10^{-2}$ for the reaction,



$$K_c = \frac{[\text{H}_2][\text{S}_2]^{1/2}}{[\text{H}_2\text{S}]}$$

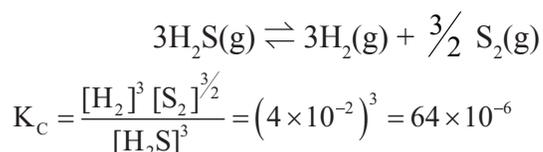
$$\Rightarrow 4 \times 10^{-2} = \frac{[\text{H}_2][\text{S}_2]^{1/2}}{[\text{H}_2\text{S}]}$$

For the reaction,



$$K_C = \frac{[H_2]^2 [S_2]}{[H_2S]^2} = (4 \times 10^{-2})^2 = 16 \times 10^{-4}$$

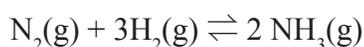
For the reaction,



45. Given $m_{N_2} = 28 \text{ g}$ $m_{H_2} = 6 \text{ g}$
 $V = 1 \text{ L}$

$$(n_{N_2})_{\text{initial}} = \frac{28}{28} = 1 \text{ mol}$$

$$(n_{H_2})_{\text{initial}} = \frac{6}{2} = 3 \text{ mol}$$

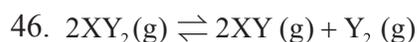


	$N_2(g)$	$H_2(g)$	$NH_3(g)$
Initial concentration	1	3	—
Reacted	0.5	1.5	—
Equilibrium concentration	0.5	1.5	1

$$[NH_3] = \left(\frac{17}{17}\right) = 1 \text{ mol} = 1 \text{ mol}$$

Weight of $N_2 = (\text{no. of moles of } N_2) \times$
molar mass of N_2
 $= 0.5 \times 28 = 14 \text{ g}$

Weight of $H_2 = (\text{no. of moles of } H_2) \times$
molar mass of H_2
 $= 1.5 \times 2 = 3 \text{ g}$



	XY_2	XY	Y_2
Initial no. of moles	1	—	—
No. of moles dissociated	x	—	—
No. of moles at equilibrium	$(1-x) \cong 1$	x	$\frac{x}{2}$

$$\text{Total No. of moles} = 1 - x + x + \frac{x}{2}$$

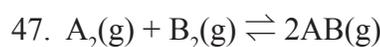
$$= 1 + \frac{x}{2} \cong 1$$

[\because Given that $x \ll 1$; $1 - x \cong 1$ and
 $1 + \frac{x}{2} \cong 1$]

$$K_P = \frac{(P_{XY})^2 (P_{Y_2})}{(P_{XY_2})^2} = \frac{\left(\frac{x}{1} \times P\right)^2 \left(\frac{\frac{x}{2}}{1} \times P\right)}{\left(\frac{1}{1} \times P\right)^2}$$

$$K_P = \frac{x^2 P^{\cancel{2}} \times P}{2 P^{\cancel{2}}}$$

$$\Rightarrow \boxed{2K_P = x^3 P}$$



	A_2	B_2	AB
Initial Concentration	1	1	—
No. of moles reacted	x	x	—
No. of moles at equilibrium	$1 - x$	$1 - x$	$2x$

Total no. of moles = $1 - x + 1 - x + 2x$
 $= 2$

$$K_P = \frac{(P_{AB})^2}{(P_{A_2})(P_{B_2})} = \frac{\left(\frac{2x}{2} \times P\right)^2}{\left(\frac{(1-x)}{2} \times P\right) \left(\frac{(1-x)}{2} \times P\right)}$$

$$K_P = \frac{4x^2}{(1-x)^2}$$

Given that $K_P = 1$; $\frac{4x^2}{(1-x)^2} = 1$

$$\Rightarrow 4x^2 = (1-x)^2$$

$$\Rightarrow 4x^2 = 1 + x^2 - 2x$$

$$3x^2 + 2x - 1 = 0$$

$$x = \frac{-2 \pm \sqrt{4 - 4 \times 3 \times -1}}{2(3)}$$

$$x = \frac{-2 \pm \sqrt{4 + 12}}{6}$$

$$= \frac{-2 \pm \sqrt{16}}{6}$$

$$= \frac{-2+4}{6}; \frac{-2-4}{6}$$

$$= \frac{2}{6}; \frac{-6}{6}$$

$$x = 0.33; -1 \text{ (not possible)}$$

$$\therefore [A_2]_{\text{eq}} = 1 - x = 1 - 0.33 = 0.67$$

$$[B_2]_{\text{eq}} = 1 - x = 1 - 0.33 = 0.67$$

$$[AB]_{\text{eq}} = 2x = 2 \times 0.33 = 0.66$$

49. $K_{p_1} = 8.19 \times 10^2$ $T_1 = 298$ K

$$K_{p_2} = 4.6 \times 10^{-1}$$
 $T_2 = 498$ K

$$\log \left(\frac{K_{p_2}}{K_{p_1}} \right) = \frac{\Delta H^\circ}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log \left(\frac{4.6 \times 10^{-1}}{8.19 \times 10^2} \right) = \frac{\Delta H^\circ}{2.303 \times 8.314} \left(\frac{498 - 298}{498 \times 298} \right)$$

$$\frac{-3.2505 \times 2.303 \times 8.314 \times 498 \times 298}{200} = \Delta H^\circ$$

$$\Delta H^\circ = -46181 \text{ J mol}^{-1}$$

$$\Delta H^\circ = -46.18 \text{ KJ mol}^{-1}$$

50. $P_{\text{CO}_2} = 1.017 \times 10^{-3}$ atm $T = 500^\circ$ C

$$K_p = P_{\text{CO}_2}$$

$$\therefore K_{p_1} = 1.017 \times 10^{-3}$$
 $T = 500 + 273 = 773$ K

$$K_{p_2} = ?$$
 $T = 600 + 273 = 873$ K

$$\Delta H^\circ = 181 \text{ KJ mol}^{-1}$$

$$\log \left(\frac{K_{p_2}}{K_{p_1}} \right) = \frac{\Delta H^\circ}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log \left(\frac{K_{p_2}}{1.017 \times 10^{-3}} \right) = \frac{181 \times 10^3}{2.303 \times 8.314} \left(\frac{873 - 773}{873 \times 773} \right)$$

$$\log \left(\frac{K_{p_2}}{1.017 \times 10^{-3}} \right) = \frac{181 \times 10^3 \times 100}{2.303 \times 8.314 \times 873 \times 773}$$

$$\frac{K_{p_2}}{1.017 \times 10^{-3}} = \text{anti log of (1.40)}$$

$$\frac{K_{p_2}}{1.017 \times 10^{-3}} = 25.12$$

$$\Rightarrow K_{p_2} = 25.12 \times 1.017 \times 10^{-3}$$

$$K_{p_2} = 25.54 \times 10^{-3}$$

Unit - 9

Evaluate yourself :

1) mass of KOH = 5.6 g

$$\text{no. of moles} = \frac{5.6}{56} = 0.1 \text{ mol}$$

i) Volume of the solution = 500 ml = 0.5 L

ii) Volume of the solution = 1 L

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{volume of solution (in L)}}$$

$$= \frac{0.1}{0.5} = 0.2 \text{ M}$$

ii) Volume of the solution = 1 L

$$\text{molarity} = \frac{0.1}{1} = 0.1 \text{ M}$$

2. mass of glucose = 2.82 g

$$\text{no. of moles of glucose} = \frac{2.82}{180} = 0.016$$

mass of water = 30 g

$$= \frac{30}{18} = 1.67$$

$$x_{\text{H}_2\text{O}} = \frac{1.67}{1.67 + 0.016} = \frac{1.67}{1.686} = 0.99$$

$$\therefore x_{\text{H}_2\text{O}} + x_{\text{glucose}} = 1$$

$$0.99 + x_{\text{glucose}} = 1$$

$$x_{\text{glucose}} = 1 - 0.99$$

$$= 0.01$$

3.10% $\frac{W}{V}$ means that 10g

of solute in 100ml solution

$$\therefore \text{amount of iodopovidone in } 1.5 \text{ ml} = \frac{10 \text{ g}}{100 \text{ ml}} \times 1.5 \text{ ml} \\ = 0.15 \text{ g}$$

$$4. \frac{\text{mass of dissolved solid}}{\text{mass of water}} \times 10^6$$

$$\frac{5 \times 10^{-3} \text{ g}}{1.05 \times 10^3 \text{ g}} \times 10^6 = 4.76 \text{ ppm}$$

$$5. \text{ (a) mass of 1.5 moles of } \text{CoCl}_2 = 1.5 \times 129.9$$

$$= 194.85 \text{ g}$$

194.85 g anhydrous cobalt chloride is dissolved in water and the solution is made up to one litre in a standard flask.

6. 6% $\frac{V}{V}$ aqueous solution contains 6g of methanol in 100 ml solution.

\therefore To prepare 500 ml of 6% $\frac{V}{V}$ solution of methanol 30g methanol is taken in a 500 ml standard flask and required quantity of water is added to make up the solution to 500 ml.

$$6. C_1 V_1 = C_2 V_2$$

$$6 \text{ M } (V_1) = 0.25 \text{ M} \times 500 \text{ ml}$$

$$V_1 = \frac{0.25 \times 500}{6}$$

$$V_1 = 20.83 \text{ mL}$$

$$7. \text{ Total pressure} = 1 \text{ atm}$$

$$P_{\text{N}_2} = \left(\frac{80}{100}\right) \times \text{total pressure} = \frac{80}{100} \times 1 \text{ atm} = 0.8 \text{ atm}$$

$$P_{\text{O}_2} = \left(\frac{20}{100}\right) \times 1 = 0.2 \text{ atm}$$

According to Henry's Law

$$P_{\text{solute}} = K_{\text{H}} x_{\text{solute in solution}}$$

$$\therefore P_{\text{N}_2} = (K_{\text{H}})_{\text{Nitrogen}} \times \text{mole fraction of } \text{N}_2 \text{ in solution}$$

$$\frac{0.8}{8.5 \times 10^4} = x_{\text{N}_2}$$

$$x_{\text{N}_2} = 9.4 \times 10^{-6}$$

Similarly,

$$x_{\text{O}_2} = \frac{0.2}{4.6 \times 10^4}$$

$$= 4.3 \times 10^{-6}$$

$$9. P_{\text{pure benzene}}^{\circ} = 50.71 \text{ mm Hg}$$

$$P_{\text{naphthalene}}^{\circ} = 32.06 \text{ mm Hg}$$

$$\text{Number of moles of benzene} = \frac{39}{78} = 0.5 \text{ mol}$$

$$\text{Number of moles of naphthalene} = \frac{128}{128} = 1 \text{ mol}$$

$$\text{mole fraction of benzene} = \frac{0.5}{1.5} = 0.33$$

$$\text{mole fraction of naphthalene} = 1 - 0.33 = 0.67$$

Partial vapour pressure of benzene

$$= P_{\text{benzene}}^{\circ} \times \text{mole fraction of benzene}$$

$$= 50.71 \times 0.33$$

$$= 16.73 \text{ mm Hg}$$

Partial vapour pressure of naphthalene

$$= 32.06 \times 0.67$$

$$= 21.48 \text{ mm Hg}$$

Mole fraction of benzene in vapour

$$\text{phase} = \frac{16.73}{16.73 + 21.48} = \frac{16.73}{38.21} = 0.44$$

Mole fraction of naphthalene in vapour

$$\text{phase} = 1 - 0.44 = 0.56$$

$$10. P_A^\circ = 10 \text{ torr}, P_{\text{solution}} = 9 \text{ torr}$$

$$W_A = 20 \text{ g} \quad W_B = 1 \text{ g}$$

$$M_A = 200 \text{ g mol}^{-1} \quad M_B = ?$$

$$\frac{\Delta P}{P_A^\circ} = \frac{W_B \times M_A}{M_B \times W_A}$$

$$\frac{10-9}{10} = \frac{1 \times 200}{M_B \times 20}$$

$$M_B = \frac{200}{20} \times 10 = 100 \text{ g mol}^{-1}$$

$$11. W_2 = 2.56 \text{ g}$$

$$W_1 = 100 \text{ g}$$

$$T = 319.692 \text{ K}$$

$$K_b = 2.42 \text{ K Kg mol}^{-1}$$

$$\Delta T_b = (319.692 - 319.450) \text{ K}$$

$$= 0.242 \text{ K}$$

$$M_2 = \frac{K_b \times W_2 \times 100}{\Delta T_b \times W_1}$$

$$= \frac{2.42 \times 2.56 \times 1000}{0.242 \times 100}$$

$$M_2 = 256 \text{ g mol}^{-1}$$

Molecular mass of sulphur in solution

$$= 256 \text{ g mol}^{-1}$$

atomic mass of one mole of sulphur atom = 32

No. of atoms in a molecule of sulphur

$$= \frac{256}{32} = 8$$

Hence molecular formula of sulphur is S_8 .

$$12. W_2 = 2 \text{ g} \quad W_1 = 75 \text{ g}$$

$$\Delta T_f = 0.2 \text{ K} \quad K_f = 5.12 \text{ K Kg mol}^{-1}$$

$$M_2 = ?$$

$$M_2 = \frac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1} = \frac{5.12 \times 2 \times 1000}{0.2 \times 75}$$

$$= 682.66 \text{ g mol}^{-1}$$

13. Osmotic pressure of urea solution $(\pi_1) = CRT$

$$= \frac{W_2}{M_2 V} RT$$

$$= \frac{6}{60 \times 1} \times RT$$

Osmotic pressure of glucose solution

$$(\pi_2) = \frac{W_2}{180 \times 1} \times RT$$

For isotonic solution,

$$\pi_1 = \pi_2$$

$$\frac{6}{60} RT = \frac{W_2}{180} RT$$

$$\Rightarrow W_2 = \frac{6}{60} \times 180$$

$$W_2 = 18 \text{ g}$$

$$14. i = \frac{\text{Observed property}}{\text{Theoretical property (calculated)}}$$

Given $\Delta T_f = 0.680 \text{ K}$

$$m = 0.2 \text{ m}$$

$$\Delta T_f (\text{observed}) = 0.680 \text{ K}$$

$$\Delta T_f (\text{calculated}) = K_f \cdot m$$

$$= 1.86 \text{ K Kg mol}^{-1} \times 0.2 \text{ mol Kg}^{-1}$$

$$= 0.372 \text{ K}$$

$$i = \frac{(\Delta T_f) \text{ Observed}}{(\Delta T_f) \text{ Calculated}} = \frac{0.680 \text{ K}}{0.372 \text{ K}} = 1.82$$

MCQ

$$1. \text{ molality} = \frac{\text{number of moles of solute}}{\text{weight of solvent (in kg)}}$$

$$= \frac{\left(\frac{1.8}{180}\right)}{0.25} = \frac{0.01}{0.25} = 0.04 \text{ M}$$

option (d) is correct.

2. option (d) is correct. Molality and mole fraction are independent of temperature.

$$3. M_1 \times V_1 = M_2 \times V_2 \quad [\because 0.1 \text{ M Al(OH)}_3 \text{ gives } 3 \times 0.1 = 0.3 \text{ M OH}^- \text{ ions}]$$

$$0.3 \times V_1 = 0.1 \times 21$$

$$V_1 = \frac{0.1 \times 21}{0.3} = 7 \text{ ml}$$

option (b)

$$4. \quad P_{N_2} = 0.76 \text{ atm}$$

$$K_H = 7.6 \times 10^4$$

$$x = ?$$

$$P_{N_2} = K_H \cdot x$$

$$0.76 = 7.6 \times 10^4 \times x$$

$$\therefore x = \frac{0.76}{7.6 \times 10^4} = 1 \times 10^{-5} \text{ (option d)}$$

$$5. \quad K_H = 8 \times 10^4$$

$$(x_{N_2})_{\text{in air}} = 0.5$$

Total pressure = 4 atm

pressure Partial pressure of nitrogen
= mole fraction \times total pressure

$$0.5 \times 4 = 2$$

$$(P_{N_2}) = K_H \times \text{mole fraction of } N_2 \text{ in solution}$$

$$2 = 8 \times 10^4 \times \frac{\text{number of moles of nitrogen}}{\text{Total number of moles}}$$

$$\frac{10 + \text{number of moles } N_2}{\text{number of moles } N_2} = \frac{8 \times 10^4}{2}$$

$$\frac{10}{\text{number of moles } N_2} + 1 = 4 \times 10^4$$

$$\frac{10}{\text{number of moles } N_2} = 40000 - 1$$

$$\therefore \text{number of moles } N_2 = \frac{10}{39999}$$

$$= 2.5 \times 10^{-4} \text{ (option d)}$$

6 for an ideal solution,

$$\Delta S_{\text{mix}} \neq 0 ; \text{ Hence } \Delta G_{\text{mix}} \neq 0$$

\therefore incorrect is $\Delta G_{\text{mix}} = 0$ (option d)

7. Carbon dioxide ; most stable gas and has lowest value of Henrys Law constant.

$$8. \quad P_{\text{total}} = P_1 + P_2$$

$$= P_1 x_1 + P_2 x_2 \quad x_1 + x_2 = 1$$

$$= P_1 (1 - x_2) + P_2 x_2 \quad x_1 = 1 - x_2$$

$$= P_1 - P_1 x_2 + P_2 x_2$$

$$= P_1 - x_2 (P_1 - P_2)$$

option (c)

$$9. \quad \pi = CRT$$

$$\pi = \frac{n}{V} RT$$

$\pi V = nRT$ option (b)

10. Ethanol and water
option (d)

$$11. \quad \text{Given, } (K_H)_A = x$$

$$(K_H)_B = y$$

$$\frac{x_A}{x_B} = 0.2$$

$$\left(\frac{x_B}{x_A} \right)_{\text{in solution}} = ?$$

$$P_A = x (x_A)_{\text{in solution}} \text{ --- (1)}$$

$$P_B = y (x_B)_{\text{in solution}} \text{ --- (2)}$$

$$\left(\frac{x_B}{x_A} \right)_{\text{in solution}} = \frac{P_B}{P_A} \times \frac{x}{y}$$

$$= \frac{x_B}{x_A} \times \frac{x}{y}$$

$$= \frac{1}{0.2} \times \frac{x}{y} = \frac{5x}{y} \text{ (option d)}$$

$$12. \quad \frac{\Delta P}{P^\circ} = \frac{n_2}{n_1}$$

$$W_2 = 6.5 \text{ g}$$

$$W_1 = 100 \text{ g}$$

$$K_b = 0.52$$

$$\frac{\Delta P}{P^\circ} = \frac{W_2 M_1}{M_2 W_1}$$

$$\frac{760 - 732}{760} = \frac{6.5 \times 18}{M_2 \times 100}$$

$$\therefore M_2 = 31.75$$

$$\Delta T_b = K_b \cdot m$$

$$= \frac{0.52 \times 6.5 \times 1000}{31.75 \times 100} = 1.06$$

$$T_b - 100 = 1.06$$

$$T_b = 100 + 1.06$$

$$= 101.06 \approx 101^\circ \text{C}$$

13. $\frac{\Delta P}{P^\circ} = x_2$ (mole fraction of the solute)

option (b)

14. option (d) 0.1×3 ion $[\text{Ba}^{2+}, 2\text{NO}_3^-]$
 0.1×3 ion $[2\text{Na}^+, \text{SO}_4^{2-}]$

15. $(\pi_1)_{\text{non electrolyte}} = (\pi_2)_{\text{glucose}}$

$$C_1 RT = C_2 RT$$

$$\frac{W_1}{M_1} = \frac{W_2}{M_2} \quad \text{CH}_2\text{O}$$

$$12 + 2 + 16 = 30$$

$$\frac{6}{n(30)} = 0.025$$

$$\therefore n = \frac{6}{0.025 \times 30} = 8$$

\therefore molecular formula = $\text{C}_8\text{H}_{16}\text{O}_8$ (option b)

16. $K_H = 4 \times 10^4$ atm

$$(P_{\text{O}_2})_{\text{air}} = 0.4 \text{ atm}$$

$$(x_{\text{O}_2})_{\text{in solution}} = ?$$

$$(P_{\text{O}_2})_{\text{air}} = K_H (x_{\text{O}_2})_{\text{in solution}}$$

$$0.4 = 4 \times 10^4 (x_{\text{O}_2})_{\text{in solution}}$$

$$\Rightarrow (x_{\text{O}_2})_{\text{in solution}} = \frac{0.4}{4 \times 10^4} = 1 \times 10^{-5} \quad (\text{Option c})$$

17. Normality of $\text{H}_2\text{SO}_4 = (\text{no. of replacable H}^+) \times M$

$$= 2 \times 1.25$$

$$= 2.5 \text{ N}$$

18. ΔH_{mix} is negative and show negative deviation from Raoult's law.

option (d)

19. $\frac{\Delta P}{P^\circ} = x_{\text{sugar}}$

$$3.5 \times 10^{-3} = x_{\text{sugar}}$$

$$x_{\text{sugar}} + x_{\text{H}_2\text{O}} = 1$$

$$\therefore x_{\text{H}_2\text{O}} = 1 - 0.0035 = 0.9965 \quad (\text{Option d})$$

20. $\frac{\Delta P}{P^\circ} = x_2$

$$\frac{100 - 90}{100} = \frac{n_2}{n_2 + n_1}$$

$$\Rightarrow \frac{n_2 + n_1}{n_2} = \frac{100}{10} \quad \left[n_1 = \frac{92}{92} = 1 \right]$$

$$1 + \frac{1}{n_2} = 10$$

$$\frac{1}{n_2} = 9$$

$$\Rightarrow n_2 = \frac{1}{9}$$

$$\Rightarrow \frac{W_2}{M_2} = \frac{1}{9}$$

$$\Rightarrow W_2 = \frac{M_2}{9}$$

$$W_2 = \frac{80}{9} = 8.89 \text{ g}$$

21. $\pi = CRT$

$$y = x (m)$$

$$m = RT$$

$$310 \text{ R} = RT$$

$$\therefore T = 310 \text{ K}$$

$$= 37^\circ \text{C}$$

option (c)

22. $\pi = CRT$

$$\pi = \frac{W}{M \times V} \times RT$$

$$\therefore M = \frac{WRT}{\pi V}$$

$$= \frac{1.26 \times 0.083 \times 300}{2.52 \times 10^{-3} \times 0.2}$$

$$= 62.22 \text{ Kg mol}^{-1}$$

23. $\text{Ba}(\text{OH})_2$ dissociates to form

Ba^{2+} and 2OH^- ion

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

$$i = \alpha(n-1) + 1$$

$$\therefore n = i = 3 \text{ (for } \text{Ba}(\text{OH})_2, \alpha = 1)$$

24. 10% $\frac{W}{W}$ aqueous NaOH solution means that 10 g of sodium hydroxide in 100g solution

$$\text{molality} = \frac{\text{no. of moles of solute}}{\text{weight of solvent (in kg)}}$$

$$= \frac{\left(\frac{10}{40}\right)}{0.1} = \frac{0.25}{0.1} = 2.5 \text{ M}$$

$$25. \alpha = \frac{(1-i)n}{(n-1)} \text{ (or)} \frac{n(i-1)}{(1-n)}$$

option (c) is correct

26. Elevation of boiling point is more in the case of Na_3PO_4 (no. of ions 4 ; 3Na^+ , PO_4^{3-})

$$27. \Delta T_f = i \times K_f \times m \quad K_f = 1.86$$
$$i = \frac{\Delta T_f \times M_2 \times W_1}{K_f \times W_2 \times 1000} \quad W_2 = 5\text{g}$$
$$= \frac{3.64 \times 142 \times 45}{1.86 \times 5 \times 1000} \quad W_1 = 45\text{g}$$
$$\Delta T_f = 3.64$$
$$M_2 = 142$$
$$i = 2.5$$

28. Equimolal aqueous solution of KCl also shows 2°C depression in freezing point.

option (a) is correct.

$$29. i = 0.54$$

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

$$= \frac{(1-0.54)2}{(2-1)}$$

$$= 0.46 \times 2$$

$$\alpha = 0.92$$

30. a) both assertion and reason are correct and reason is the correct explanation of assertion.

40.

Given

Molarity = 12 M HCl

density of the solution = 1.2 g L^{-1}

In 12M HCl solution, there are 12 moles of HCl in 1 litre of the solution.

$$\text{molality} = \frac{\text{no. of moles of solute.}}{\text{mass of solvent (in kg)}}$$

calculate mass of water (solvent)

mass of 1 litre HCl solution

$$= \text{density} \times \text{volume}$$

$$= 1.2 \text{ gmL}^{-1} \times 1000 \text{ mL}$$

$$= 1200 \text{ g}$$

mass of HCl = no. of moles of

HCl \times molar mass of HCl

$$= 12 \text{ mol} \times 36.5 \text{ g mol}^{-1}$$

$$= 438 \text{ g}$$

mass of water = mass of HCl solution – mass of HCl

$$\text{mass of water} = 1200 - 438 = 762 \text{ g}$$

$$\text{molality} = \frac{12}{0.762}$$
$$= 15.75 \text{ m}$$

$$41. C = 0.25 \text{ M}$$

$$T = 370.28 \text{ K}$$

$$(\pi)_{\text{glucose}} = CRT$$

$$(\pi) = 0.25 \text{ molL}^{-1} \times 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 370.28 \text{ K}$$
$$= 7.59 \text{ atm}$$

42.

$$\text{molality} = \frac{\text{no. of moles of solute}}{\text{mass of solvent (in kg)}}$$

$$\text{no. of moles of glycine} = \frac{\text{mass of glycine}}{\text{molar mass of glycine}}$$

$$= \frac{7.5}{75} = 0.1$$

$$\text{molality} = \frac{0.1}{0.5 \text{ Kg}}$$
$$= 0.2 \text{ m}$$

$$43. \Delta T_f = K_f \cdot m$$

$$\text{ie } \Delta T_f \propto m$$

$$m_{\text{CH}_3\text{-OH}} = \frac{\left(\frac{10}{32}\right)}{0.1} = 3.125m$$

$$m_{\text{C}_2\text{H}_5\text{-OH}} = \frac{\left(\frac{20}{46}\right)}{0.2} = 2.174m$$

\therefore depression in freezing point is more in methanol solution and it will have lower freezing point.

44. In 10^{-4}M K_2SO_4 solution, there are 10^{-4} moles of potassium sulphate.

K_2SO_4 molecule contains 3 ions (2K^+ and 1SO_4^{2-})

1 mole of K_2SO_4 contains $3 \times 6.023 \times 10^{23}$ ions

10^{-4} mole of K_2SO_4 contains $3 \times 6.023 \times 10^{23} \times 10^{-4}$ ions
 $= 18.069 \times 10^{19}$

$$45. (k_H)_{\text{benzene}} = 4.2 \times 10^{-5} \text{ mm Hg}$$

Solubility of methane = ?

$$P = 750 \text{ mm Hg}$$

$$P = 840 \text{ mm Hg}$$

According to Henrys Law,

$$P = K_H \cdot x_{\text{in solution}}$$

$$750 \text{ mm Hg} = 4.2 \times 10^{-5} \text{ mm Hg} \cdot x_{\text{in solution}}$$

$$\Rightarrow x_{\text{in solution}} = \frac{750}{4.2 \times 10^{-5}}$$

i.e, solubility = 178.5×10^5

similarly at $P = 840 \text{ mm Hg}$

$$\text{solubility} = \frac{840}{4.2 \times 10^{-5}} \\ = 200 \times 10^{-5}$$

$$46. \Delta T_f = 0.093^\circ\text{C} = 0.093\text{K}$$

$$m = ?$$

$$K_f = 1.86\text{K Kg mol}^{-1}$$

$$\Delta T_f = K_f \cdot m$$

$$\therefore m = \frac{\Delta T_f}{K_f} \\ = \frac{0.093\text{K}}{1.86 \text{ K Kg mol}^{-1}} \\ = 0.05 \text{ mol Kg}^{-1} \\ = 0.05m$$

$$47. P_{\text{C}_6\text{H}_6}^0 = 640 \text{ mm Hg}$$

$$W_2 = 2.2 \text{ g (non volabile solute)}$$

$$W_1 = 40 \text{ g (benzene)}$$

$$P_{\text{solution}} = 600 \text{ mm Hg}$$

$$M_2 = ?$$

$$\frac{P^0 - P}{P^0} = x_2$$

$$\frac{640 - 600}{640} = \frac{n_2}{n_1 + n_2} \quad [\because n_1 \gg n_2 ; n_1 + n_2 \approx n_1]$$

$$\frac{40}{640} = \frac{n_2}{n_1}$$

$$0.0625 = \frac{W_2 \times M_1}{M_2 \times W_1}$$

$$M_2 = \frac{2.2 \times 78}{0.0625 \times 40} \\ = 68.64 \text{ g mol}^{-1}$$

UNIT -10

CHEMICAL BONDING

KEY FOR MCQs

1. Compound	No. of valance electron on the central atom
XeF ₂	10
AlCl ₃	6
SF ₆	12
SCl ₂	8
(option d)	



$$\text{formal charge of } O_A / O_B = N_V - \left(N_e + \frac{N_b}{2} \right)$$

$$= 6 - \left(4 + \frac{4}{2} \right)$$

$$= 6 - 6 = 0$$

$$\text{formal charge of C} = 4 - \left(0 + \frac{8}{2} \right)$$

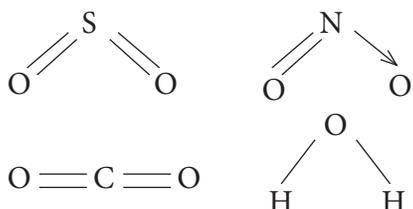
$$= 4 - 4 = 0$$

∴ Option (d) – (0, 0, 0)

3. $\ddot{\text{N}}\text{H}_3$, $\ddot{\text{P}}\text{H}_3$ – electron rich,
 $\text{CH}_3 - \text{CH}_3$ – Covalent neutral molecule.
 BH_3 – electron deficient

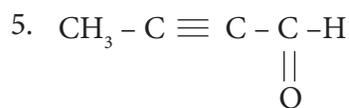
option (c)

4.



water contain only σ bonds and no π bonds

option (d) is correct



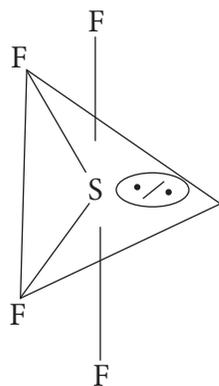
2 – butynal

no. of σ bonds = 8 [4C-H; 3C-C; 1C-O]

no. of π bonds = 3 [2C-C; 1C-O]

$$\therefore \text{ratio} = \frac{8}{3}$$

6.



Normal bond angle in regular trigonal bipyramidal are 90° and 120°

due to *l.p* - *b.p* repulsion, bond angle reduced 89° , 117°

option (d)

Correct Statement :

7. Oxygen molecule is paramagnetic

Correct Reason

It has two unpaired electron in its antibonding molecular orbital.

Option (c) assertion true and reason false.

8. Option (b) - two half filled orbitals overlap.

9. ClF_3 – Sp^3d hybridisation

NF_3 - Sp^3 hybridisation

BF_3 - Sp^2 hybridisation

Option (d) is correct.

10. Option (b) is correct Sp^3 hybridisation.

Orbital geometry tetrahedron, bond angle $109^\circ 28'$

11. bond order = $\frac{1}{2} (n_b - n_a)$

$$\text{bond order of } \text{O}_2^{2-} = \frac{1}{2} (8 - 6) = 1$$

$$\text{bond order of } \text{C}_2^+ = \frac{1}{2} (5 - 2) = 1.5$$

$$\text{bond order of } \text{O}_2 = \frac{1}{2} (8 - 4) = 2$$

$$\text{bond order of } \text{C}_2^{2-} = \frac{1}{2} (8 - 2) = 3$$

12. PCl_5 – Sp^3d hybridisation

S, P_x , P_y , P_z and $d_{x^2-y^2}$

option (c) is correct.

13. Option (b) $\text{O}_2 > \text{O}_3 > \text{H}_2\text{O}_2$

$$2 > 1.5 > 1$$

14. O_2^{2-} is diamagnetic. Additional two electrons paired in antibonding molecular orbital $\pi_{2p_y}^*$ and $\pi_{2p_z}^*$ (option (b))

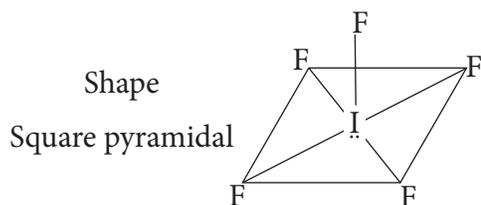
15. Bond order = $\frac{1}{2} (n_b - n_a)$

$$2.5 = \frac{1}{2} (8 - n_a)$$

$$\Rightarrow 5 = 8 - n_a$$

$$\Rightarrow n_a = 8 - 5 = 3 \text{ (option a)}$$

16. IF_5 - 5 bond pair + 1 lone pair
hybridisation Sp^3d^2



17. Correct statement :

All five Sp^3d hybrid orbitals are equivalent
 \therefore incorrect statement : Option (c)

18. SeF_4 , XeO_2F_2 - Sp^3d hybridisation,
option (a) T-shaped, one lone pair on central atom.

19. H_2O - Central atom Sp^3 hybridised
 NO_2^- - Central atom Sp^2 hybridised
 BF_3 - Central atom Sp^2 hybridised
 NH_2^- - Central atom Sp^3 hybridised
option (c) is correct.

20. NO_3^- - Sp^2 hybridisation, planar
 H_3O^+ - Sp^3 hybridisation, pyramidal
option (a) is correct.

21. $CH_3 - \overset{Sp^2}{CH} = \overset{Sp}{C} = \overset{Sp^3}{CH} - \overset{Sp^3}{CH_3}$ (option a)

22. XeF_2 is isostructural with ICl_2^-

23. CH_4 , $CH_3 - \overset{Sp^3}{CH_3}$, $CH_2 = \overset{Sp^2}{CH_2}$, $CH \equiv \overset{Sp}{CH}$

25, 25, 33.3, 50

option (a) is correct.

24. Co_2 - Linear

C_2H_2 - Linear

option (c) is correct.

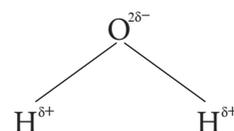
25. $l.p - l.p > l.p - b.p > b.p - b.p$

option (c) is correct

26. ClF_3 - Sp^3d hybridisation, 'T' shaped

option (c) is correct.

27.



option (d)

28. Correct statement is - the resonance hybrid should have lower energy than any of the contributing structure

Hence is correct statement is option (c)

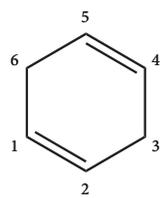
29. NH_4Cl (option (a))

30. 4U

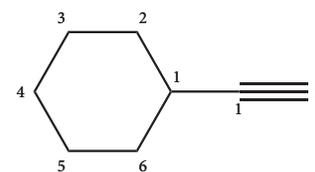
UNIT - 11

EVALUATE YOURSELF - KEY

2.

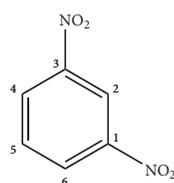


cyclohexa- 1,4-diene

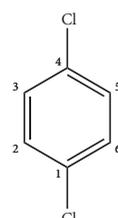


ethynyl cyclohexane

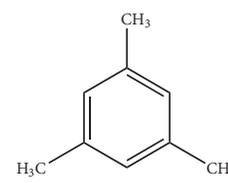
3.



1,3- dinitrobenzene

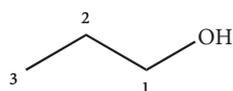


p-dichlorobenzene

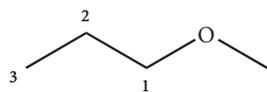


1, 3, 5 trimethylbenzene

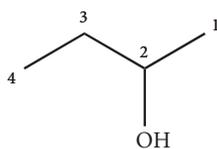
4.

 $C_4H_{10}O$ isomers

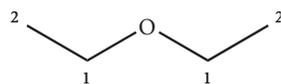
propan-1-ol



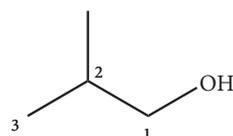
1-methoxypropane



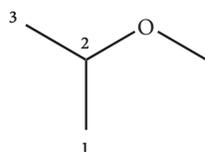
butan-2-ol



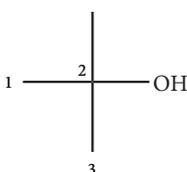
ethoxyethane



2-methylpropan-1-ol



2-methoxypropane



2-methylpropan-2-ol

5. Weight of organic substance $w = 0.2346$ g

Weight of water (x) = 0.2754 g

Weight of CO_2 (y) = 0.4488 g

$$\begin{aligned} \text{Percentage of carbon} &= \frac{12}{44} \times \frac{y}{w} \times 100 \\ &= \frac{12}{44} \times \frac{0.4488}{0.2346} \times 100 \\ &= 52.17\% \end{aligned}$$

$$\begin{aligned} \text{Percentage of hydrogen} &= \frac{2}{18} \times \frac{x}{w} \times 100 \\ &= \frac{2}{18} \times \frac{0.2754}{0.2346} \times 100 \\ &= 13.04\% \end{aligned}$$

$$\begin{aligned} \text{Percentage of oxygen} &= [100 - (52.17 + 13.04)] \\ &= 100 - 65.21 = 34.79\% \end{aligned}$$

6. Weight of organic substance (w) = 0.16 g

Weight of Barium sulphate (x) = 0.35 g

$$\begin{aligned} \text{Percentage of Sulphur} &= \frac{32}{233} \times \frac{x}{w} \times 100 \\ &= \frac{32}{233} \times \frac{0.35}{0.16} \times 100 \\ &= 30.04\% \end{aligned}$$

7. Weight of organic substance

(w) = 0.185 g

Weight of silver bromide (x) = 0.320 g

$$\begin{aligned} \text{Percentage of bromine} &= \frac{80}{188} \times \frac{x}{w} \times 100 \\ &= \frac{80}{188} \times \frac{0.32}{0.185} \times 100 \\ &= 73.6\% \end{aligned}$$

Weight of organic substance (w) = 0.40 g

Weight of silver iodide (x) = 0.235 g

$$\begin{aligned} \text{Percentage of iodine} &= \frac{127}{235} \times \frac{x}{w} \times 100 \\ &= \frac{127}{235} \times \frac{0.235}{0.40} \times 100 \\ &= 31.75\% \end{aligned}$$

8. Weight of organic substance (w) = 0.33 g

Weight of $Mg_2P_2O_7$ (x) = 0.397 g

$$\begin{aligned} \text{Percentage of phosphorous} &= \frac{62}{222} \times \frac{x}{w} \times 100 \\ &= \frac{62}{222} \times \frac{0.397}{0.33} \times 100 \\ &= 33.59\% \end{aligned}$$

9. Weight of organic compound (w) = 0.3 g

Strength of sulphuric acid used (N) = 0.1 N

Volume of sulphuric acid used (V) = 30 mL

30 ml of 0.1 N sulphuric acid = 30 ml of 0.1 N ammonia

$$\begin{aligned}\text{Percentage of nitrogen} &= \left(\frac{14 \times NV}{1000 \times w} \right) \times 100 \\ &= \left(\frac{14 \times 0.1 \times 30}{1000 \times 0.3} \right) \times 100 \\ &= 14\%\end{aligned}$$

UNIT -11

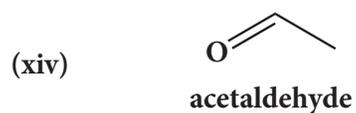
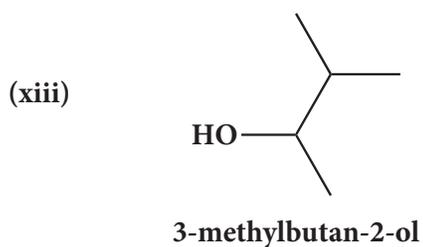
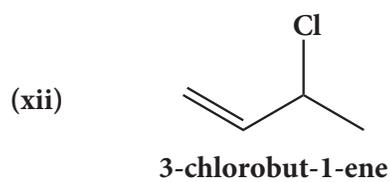
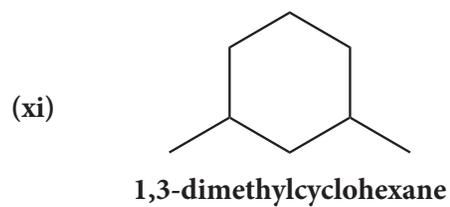
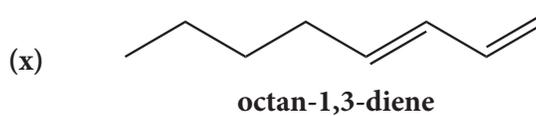
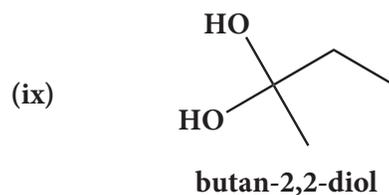
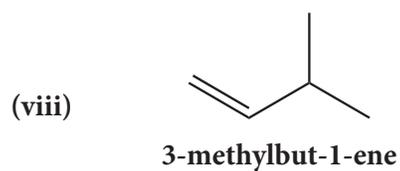
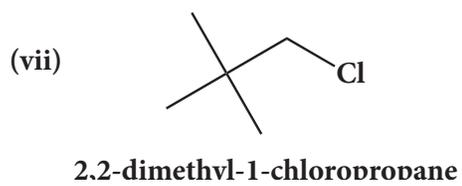
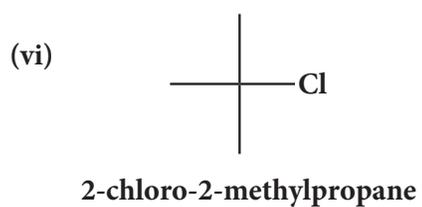
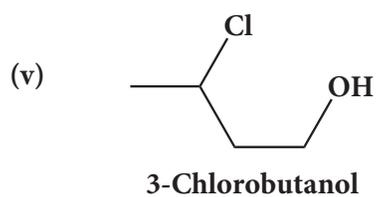
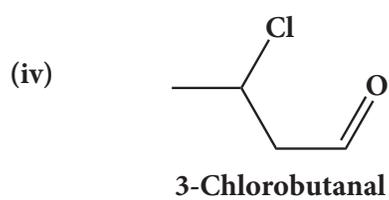
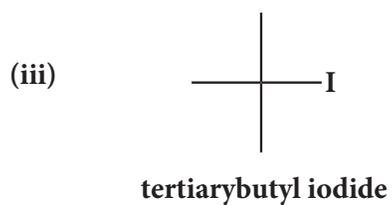
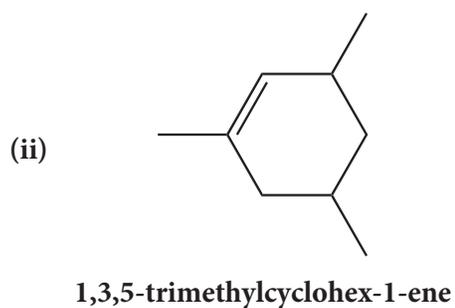
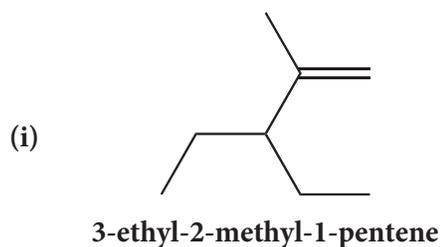
MCQs

- | | | | | | |
|---------|---------|---------|---------|---------|---------|
| 1. (a) | 2. (a) | 3. (c) | 4. (a) | 5. (d) | 6. (a) |
| 7. (b) | 8. (c) | 9. (a) | 10. (a) | 11. (b) | 12. (c) |
| 13. (c) | 14. (c) | 15. (d) | 16. (b) | 17. (c) | 18. (c) |
| 19. (b) | 20. (b) | 21. (c) | 22. (d) | 23. (c) | 24. (b) |
| 25. (b) | 26. (a) | 27. (c) | 28. (d) | 29. (b) | 30. (a) |

Question No : 38

- | | |
|-----------------------------|--|
| (i) 2,3,5-trimethylhexane | (viii) 5-oxohexanoic acid |
| (ii) 2-bromo-3-methylbutane | (ix) 3-ethyl-4-ethenylheptane |
| (iii) methoxymethane | (x) 2,4,4-trimethylpent-2-ene |
| (iv) 2-hydroxybutanal | (xi) 2-methyl-1-phenylpropan-1-amine |
| (v) buta-1,3-diene | (xii) 2,2-dimethyl-4-oxopentanenitrile |
| (vi) 4-chloropent-2-yne | (xiii) 2-ethoxypropane |
| (vii) 1-bromobut-2-ene | (xiv) 1-fluoro-4-methyl-2-nitrobenzene |
| | (xv) 3-bromo-2-methylpentanal |

Question No : 39





UNIT -12

MCQs

- | | | | | | |
|---------|---------|---------|---------|---------|---------|
| 1.(d) | 2.(a) | 3. (b) | 4. (c) | 5. (d) | 6. (c) |
| 7. (d) | 8. (d) | 9. (c) | 10. (a) | 11. (a) | 12. (d) |
| 13. (c) | 14. (d) | 15. (c) | | | |

UNIT -13

MCQs

- | | | | | | |
|---------|---------|---------|---------|---------|---------|
| 1.(b) | 2.(b) | 3. (d) | 4. (a) | 5. (c) | 6. (d) |
| 7. (c) | 8. (b) | 9. (a) | 10. (c) | 11. (d) | 12. (a) |
| 13. (a) | 14. (a) | 15. (c) | 16. (a) | 17. (c) | 18. (d) |
| 19. (d) | 20. (a) | 21. (d) | 22. (d) | 23. (a) | 24. (b) |
| 25. (d) | 26. (b) | 27. (a) | 28. (a) | 29. (c) | 30. (d) |

UNIT -14

MCQs

- | | | | | | |
|---------|----------|---------|---------|---------|---------|
| 1.(b) | 2.(a) | 3. (a) | 4. (b) | 5. (a) | 6. (d) |
| 7. (b) | 8. (c) | 9. (b) | 10. (a) | 11. (c) | 12. (c) |
| 13. (d) | 14. (b) | 15. (c) | 16. (b) | 17. (d) | 18. (b) |
| 19. (a) | 20. (d) | 21. (a) | 22. (c) | 23. (c) | 24. (b) |
| 25. (c) | | | | | |

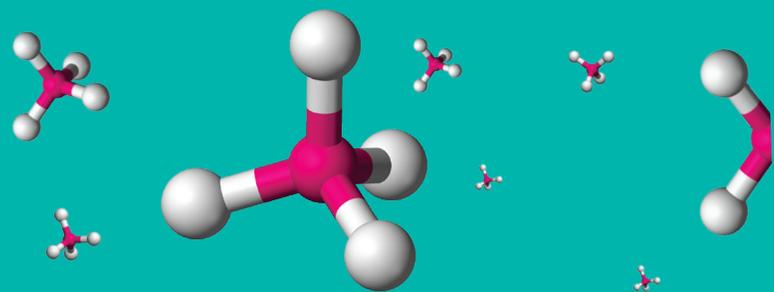
UNIT -15

MCQs

- | | | | | | |
|---------|---------|---------|---------|---------|---------|
| 1.(d) | 2.(a) | 3. (b) | 4. (c) | 5. (c) | 6. (b) |
| 7. (C) | 8. (c) | 9. (a) | 10. (c) | 11. (d) | 12. (c) |
| 13. (c) | 14. (b) | 15. (d) | 16. (a) | 17. (d) | |

GLOSSARY

A-Z



Acid rain	அமில மழை	
Addition reaction	சேர்க்கை வினை	
Algae bloom	பாசி படர்வு	
Aromatization	அரோமேடிக் சேர்மமாக்கல்	
Atmosphere	வளிமண்டலம்	
Azeotropic mixture	கொதிநிலைமாறாக்கலவை	
Bio degradable	உயிரிசிதைவுறும்	
Biosphere	உயிர்க்கோளம்	
Boiling point	கொதிநிலை	
Bond angle	பிணைப்புக் கோணம்	
Bond length	பிணைப்பு நீளம்	
Carbanion	கார்பன் எதிரயணி	
Chromatography	வண்ணப்பிரிகை முறை	
Colligative properties	தொகைசார் பண்புகள்	
Conformers	வச அமைப்புகள்	
Coordinate or dative bond	ஈதல் சகப்பிணைப்பு	
Coupling reaction	இணைப்பு வினை	
Covalent bond	சகப்பிணைப்பு	
Crystallisation	படிகமாக்கல்	
Delocalization	உள்ளடங்கா	
Depletion of ozone layer	ஓசோன்படல சிதைவு	
Depression of freezing point	உறைநிலைத் தாழ்வு	

Dipole moment	இருமுனை திருப்புத்திறன்
Dissociation constant	சிதைவு மாறிலி
Distillation	காய்ச்சி வடித்தல்
Dry cleaning	உலர் சலவை
Eco-friendly	சூழலுக்கு சாதகமான
Electrophiles	எலக்ட்ரான்கவர் காரணி
Elevation of boiling point	கொதிநிலை ஏற்றம்
Elimination reactions	நீக்கல் வினைகள்
Equilibrium	சமநிலை
Equilibrium constant	சமநிலை மாறிலி
Eutrophication	தூர்ந்துபோதல்
Fertilizer	உரம்
Free radicals	தனிஉறுப்புகள்
Freezing point	உறைநிலை
Functional groups	வினைசெயல் தொகுதிகள்
Geometrical isomerism	வடிவ மாற்றியம்
Global warming	உலக வெப்பமயமாதல்
Greenhouse effect	பசுமைஇல்லவிளைவு
Green chemistry	பசுமை வேதியியல்
Haze	பனிமூட்டம்
Heterocyclic	பல்லணு வளைய
Heterolytic cleavage	சீரற்ற பிளத்தல்
Homolytic cleavage	சீரான பிளத்தல்
Hybridisation	இனக்கலப்பு
Inductive effect	தூண்டல் விளைவு
Ionic bond	அயனிப் பிணைப்பு



Irreversible reaction	மீளா வினை
Isomerisation	ஐசோமராக்கல்
Isomerism	மாற்றியம்
Law of mass action	நிறைத் தாக்க விதி
Lithosphere	கற்கோளம்
LPG	திரவமாக்கப்பட்ட பெட்ரோலியம் வாயு
Mechanism	வினைவழி முறை
Miscible liquids	கலக்கும் திரவங்கள்
Mole fraction	மோல் பின்னம்
Molecular orbitals	மூலக்கூறு ஆர்பிட்டால்கள்
Microorganism	நுண்ணுயிரிகள்
Non-polar	முனைவற்ற
Non-biodegradable	உயிரிசிதைவுறாத
Nucleophiles	கருக்கவர்காரணி
Nucleophilic attack	கருகவர் தாக்குதல்
Octet rule	எண்ம விதி
Odd electron bonding	ஒற்றை எலக்ட்ரான் பிணைப்பு
Optical isomerism	ஒளியியல் மாற்றியம்
Osmosis	சவ்வூடுபரவல்
Osmotic pressure	சவ்வூடுபரவல் அழுத்தம்
Overlapping of orbitals	ஆர்பிட்டால்கள் மேற்பொருந்துதல்
Ozonolysis	ஓசோனேற்றம்
Particulate pollutant	துகள் பொருள் மாசுபடுத்திகள்
Polar	முனைவுள்ள
Pollutant	மாசுபடுத்திகள்
Prefix	முன்னொட்டு





Primary	ஓரிணைய
Pyrolysis	வெப்பத்தால் பகுத்தல்
Reaction quotient	வினை குணகம்
Recycle	மறுசுழற்சி
Reverse osmosis	எதிர் சவ்வூடுபரவல்
Reversible reaction	மீள் வினை
Secondary	ஈரிணைய
Sediment	படிவு
Side chain	பக்கச் சங்கிலி
Smog	பனிப்புக்கை
Solute	கரைபொருள்
Solvent extraction	கரைப்பான் கொண்டு சாறு இறக்குதல்
Stone leprosy	கல் சிதைவுறுதல்
Stratosphere	அடுக்கு மண்டலம்
Sublimation	பதங்கமாதல்
Substituent	பதிலிடும் தொகுதி
Substitution reactions	பதிலீட்டு வினைகள்
Suffix	பின்னொட்டு
Tertiary	மூவிணைய
Thermal cracking	வெப்ப சிதைத்தல்
Toxic	நச்சுத்தன்மை
Troposphere	அடிவெளி மண்டலம்
Valence electrons	இணைதிற எலக்ட்ரான்கள்
Vapour pressure	ஆவி அழுத்தம்



Chemistry – Class XI, VOL - 2

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