CHEMISTRY

HIGHER SECONDARY - SECOND YEAR

VOLUME - I

Untouchability is a sin
Untouchability is a crime
Untouchability is inhuman

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PREFACE

Chemistry, a branch of science concerned with the properties, structures and composition of substances and their reactions with one another. Inorganic Chemistry studies the preparation, properties and reactions of all chemical elements and their compounds, except those of carbon. Organic Chemistry studies the reactions of carbon compounds, which are 100 times more numerous than nonorganic ones. It also studies an immense variety of molecules, including those of industrial compounds such as plastics, rubber, dyes, drugs and solvents. Physical Chemistry deals with the Physical properties of substances, such as their boiling and melting points.

The present book is included for the students of higher secondary second year. For convenience sake this text book of chemistry is published in two volumes. This text book is written after following the revised syllabus, keeping in view the expectations of the National Council of Educational Research & Training (NCERT). This book will provide an "inverted pyramid" model to gain knowledge in all branches of chemistry. The topics such as Atomic Structure - II, Periodic Classification - II, Solid State - II, Thermodynamics - II, Chemical equilibrium - II, Chemical Kinetics - II, Electrochemistry - I and II are designed in such a way that students should have a continuous access to these topics. Hence, the knowledge gained in higher secondary first year will help the students to have a continuous access to these topics. The knowledge gained in +1 will help the students to achieve excellence in the path of quest for chemical knowledge. Many problems are introduced in inorganic, physical and organic chemistry to enhance the quantitative aptitude of students. The quantitative aptitude will enable the students to understand the concepts well.

The importance of chemistry is well known. A knowledge of chemistry will help anybody to understand biology, natural processes, geochemical concepts, pharmaceutical and biochemical concepts. Hence this text book will enhance the image of the students in such a way that they can face any competitive examination in future. The problems in all branches of chemistry and many more mechanisms of organic chemical reactions will help the students to understand the chemical principles.

Much informations about nobel laureates are given. These informations is not part of the syllabus. However, such information will help the students to know a lot about the scientists.

The questions that are given at the end of every chapter can be taken only as model questions. A lot of self evaluation questions, like, choose the best answer, one or two sentence answer type and short answer types questions are given in all chapters. While preparing the examination, students should not restrict themselves, only to the questions and problems given in the self evaluation. They must be prepared to answer the questions and problems from the entire text.

Learning objectives may create an awareness to understand each chapter.

Sufficient reference books are suggested so as to enable the students to acquire more informations about the concept of chemistry.

Dr. V. BALASUBRAMANIAN

Chairperson
Syllabus Revision Committee (Chemistry)
& Higher Secondary Second Year Chemistry
Text Book Writing Committee

Syllabus : Higher Secondary - Second Year Chemistry   Volume - I
INORGANIC CHEMISTRY

Unit 1 - Atomic Structure -II

Dual properties of electrons - de-Broglie relation - Heisenberg's uncertainty principle - Wave nature of an electron - Schrodinger wave equation (only equation, no derivation) - Eigen values and Eigen function- significance only - molecular orbital method. Application to Homo diatomic and Hetero diatomic molecules - Metallic Bond - Hybridization of atomic orbitals Hybridization involving s, p and d Orbitals - Types of forces between molecules.

Unit 2 - Periodic classification-II

Review of periodic properties - Calculation of atomic radii - Calculation of ionic radii - Method of determination of Ionisation potential - Factors affecting ionisation potential - Method to determine the electron affinity - Factors affecting EA - Various scales on electro negativity values.

Unit 3 - p - Block Elements - II

Group -13 General trends - Potash alum- Preparation, Properties and uses - Group 14 General trends - Silicates - Types and structure - Silicones - Structure and uses - Extraction of lead - Group - 15. General trends - Phosphorous - Allotropes and extraction - Compounds of phosphorous - Group - 16. General trends - H_2SO_4 - Manufacture and properties. - Group - 17 General characteristics. Physical and Chemical properties - Isolation of fluorine and its properties - Interhalogen compounds Group-18 Inert gases - Isolation, properties and uses.

Unit 4 d - BLOCK ELEMENTS

General characteristics of d-block elements - First transition series - Occurrence and principles of extraction - chromium, copper and zinc - Alloys - Second transition series - Occurrence and principles of extraction of silver - Third transition series - Compounds - $K_2Cr_2O_7$, $CuSO_45H_2O$, $AgNO_3$, Hg_2Cl_2, $ZnCO_3$, Purple of cassius.

Unit 5 - f-block elements

General characteristics of f - block elements and extraction - Comparison of Lanthanides and Actinides - Uses of lanthanides and actinides.

Unit 6 - Coordination Compounds and Bio-coordination Compounds

An introduction - Terminology in coordination chemistry - IUPAC nomenclature of mononuclear coordination compounds - Isomerism in coordination compounds - Structural isomerism - Geometrical isomerism in 4 - coordinate, 6 – coordinate complexes - Theories on coordination compounds - Werner's theory (brief) - Valence Bond theory - Crystal field theory - Uses of coordination compounds - Biocoordination compounds. Haemoglobin and chlorophyll.

Unit 7 - Nuclear chemistry

Nuclear energy nuclear fission and fusion - Radio carbon dating - Nuclear reaction in sun - Uses of radioactive isotopes.

PHYSICAL CHEMISTRY

Unit 8 - Solid state II

Types of packing in crystals - X-Ray crystal structure - Types of ionic crystals - Imperfections in solids - Properties of crystalline solids - Amorphous solid.

Unit 9 - Thermodynamics - II

Review of I law - Need for the II law of thermodynamics - Spontaneous and non spontaneous processes - Entropy - Gibb's free energy - Free energy change and chemical equilibrium - Third law of thermodynamics.

Unit 10 - Chemical equilibrium II

Applications of law of mass action - Le Chatlier's principle.

Unit 11 - Chemical Kinetics -II

First order reaction and pseudo first order reaction - Experimental determination of first order reaction - method of determining order of reaction - temperature dependence of rate constant - Simple and complex reactions.

Unit 12 – Surface Chemistry

Adsorption - Catalysis - Theory of catalysis - Colloids - Preparation of colloids - Properties of colloids - Emulsions.

Unit 13 – Electrochemistry – I

Conductors, insulators and semi conductors - Theory of electrical conductance - Theory of strong electrolytes - Faraday's laws of electrolysis - Specific resistance, specific conductance, equivalent and molar conductance - Variation of conductance with dilution - Kohlraush's law - Ionic product of water, pH and pOH - Buffer solutions - Use of pH values.

Unit 14 – Electrochemistry - II

Cells - Electrodes and electrode potentials - Construction of cell and EMF - Corrosion and its preventions - commercial production of chemicals - Fuel cells.

Unit 15 – Isomerism in Organic Chemistry

Geometrical isomerism - Conformations of cyclic compounds - Optical isomerism - Optical activity - Chirality - Compounds containing chiral centres - D-L and R-S notation - Isomerism in benzene.

Unit 16 – Hydroxy Derivatives

Nomenclature of alcohols - Classification of alcohols - General methods of preparation of primary alcohols - Properties Methods of distinction between three classes of alcohols 1°, 2° and 3°) - Methods of preparation of dihydric alcohols. (glycol) - Properties - Uses - Methods of preparation of trihydric alcohols - Properties - Uses - Aromatic alcohols - Methods of preparation of benzyl alcohol - Properties - Uses - Phenols - Manufacture of phenols - Properties - Chemical properties - Uses of Phenols.

Unit 17 - Ethers

Ethers - General methods of preparation of aliphatic ethers - Properties - Uses - Aromatic ethers - Preparation of anisole - Reactions of anisole - Uses.

Unit – 18 Carbonyl Compounds

Nomenclature of carbonyl compounds - Comparison of aldehydes and ketones - General methods of preparation of aldehydes - Properties - Uses Aromatic aldehydes - Preparation of benzaldehyde - Properties - Uses - Ketones - general methods of preparation of aliphatic ketones (acetone) - Properties - Uses - Aromatic ketones - preparation of acetophenone- Properties - Uses - preparation of benzophenone - Properties.

Unit 19 – Carboxylic Acids

Nomenclature - Preparation of aliphatic monocarboxyli c acids – formic acid - Properties - Uses - Tests for carboxylic acid - Monohydroxy mono carboxylic acids - Lactic acid – Sources - Synthesis of lactic acid - Aliphatic dicarboxylic acids - preparation of dicarboxylic acids – oxalic and succinic acids - Properties - Strengths of carboxylic acids - Aromatic acids - Preparation of benzoic acid - Properties - Uses - Preparation of salicylic acid - Properties - Uses - Derivatives of carboxylic acids - Preparation of acid chloride – acetyl chloride (CH_3COCl) - Preparation - Properties - Uses - Preparation of acetamide - Properties - Preparation of acetic anhydride - Properties - Preparation of esters- methyl acetate - Properties.

Unit - 20 Organic Nitrogen Compounds

Aliphatic nitro compounds - Preparation of aliphatic nitroalkanes - Properties - Uses - Aromatic nitro compounds - Preparation - Properties - Uses - Distinction between aliphatic and aromatic nitro compounds - Amines - Aliphatic amines - General methods of preparation - Properties - Distinction between 1°, 2°, and 3° amines - Aromatic amines - Synthesis of benzylamine - Properties - Aniline–preparation - Properties - Uses - Distinction between aliphatic and aromatic amines - Aliphatic nitriles - Preparation - properties - Uses - Diazonium salts - Preparation of benzene diazoniumchloride - Properties.

Unit 21 - Biomolecules

Carbohydrates – structural elucidation - Disaccharides and polysaccharides - Proteins - Amino acids - structure of proteins - Nucleic acids - Lipids.

Unit 22 - Chemistry in Action

Medicinal chemistry - Drug abuse - Dyes – classification and uses - Cosmetics – creams, perfumes, talcum powder and deodorants - chemicals in food - Preservatives artificial sweetening agents, antioxidants and edible colours - Insect repellant – pheromones and sex attractants - Rocket fuels - Types of polymers, preparation and uses.

CHEMISTRY PRACTICALS FOR STD XII

I. **Detection of Nitrogen, Halogen and Sulphur in organic compounds.**

II. **Detection of Functional groups present in organic compounds.**
   a) Saturation and Unsaturation
   b) Aromatic and aliphatic
   c) Aldehydes, carboxylic acids, diamides, phenolic groups-(Nature of any one functional group is identified)

III. **Qualitative analysis**
Determination of two cations and two anions in a given mixture.
Cations: Pb^{++}, Cu^{++}, Al^{3+}, Fe^{3+}, Zn^{2+}, Mn^{2+}, Ca^{++}, Ba^{2+}, Mg^{2+}, NH^{4+}
Anions: Borate, Sulphide, Sulphate, Carbonate, Nitrate, Chloride, Bromide.
(Insoluble and interfering ions are to be excluded. Also, two cations of the same group and anions of the following)
Combinations such as (Cl^- + Br^-) and (CO_3^{2-} + $C_2O_4^{2-}$) Should be avoided.

IV. **Volumetric analysis**
   a) Permanganometry
      1. Titration of Oxalic acid Vs $KMnO_4$
      2. Titration of ferrous ammonium sulphate against $KMnO_4$ solution.
   b) Dichrometry
      1. Standardization of $K_2Cr_2O_7$ solution.
      2. Any one estimation using $K_2Cr_2O_7$ as one of the oxidant.
Report should contain two acid radicals and two basic radicals, without mentioning the name of the salt.
Confirmatory tests should be exhibited.

CONTENTS

THE PERIODIC TABLE

Period	1	2	3	4	5	6	7	8	9	10	11	12	13/III	14	15	16	17	18
1	1 H 1.0079																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95.
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.68	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pdt 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
6	55 Cs 132.91	56 Ba 137.33	La-Lu	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	Ac-Lr	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Uun	111 Uuu	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uah	117 Uus	118 Uuo

Lanthanides

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97

Actinides

89 Ac (227)	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

S block   d block   p block   f block

(xi)

INORGANIC CHEMISTRY

In 1869, Russian Chemist Dmitry Mendeleyev develops the periodic table of the element. As Newlands did before him in 1863, Mendeleyev classifies the elements, according to their atomic weights and notices that they exhibit recurring patterns or periods of properties.

1. ATOMIC STRUCTURE - II

Learning Objectives

- *To study the dual property of electron and understand the property through experiments.*

- *To derive the de-broglie relation and learn its significance.*

- *To learn Heisenberg's uncertainty principle.*

- *To study Molecular Orbital Theory and its application to Homodiatomic and Heterodiatomic molecules.*

- *To understand the concept of Hybridisation and Hybridisation of s, p and d orbitals.*

CHRONOLOGY OF ATOMIC STRUCTURE

1. Dalton(1808)   : Discovery of atom

2. Julius Plucker (1859)   : First discoverer of cathode rays

3. Goldstein(1886)   : Discovered anode rays and proton

4. Sir.J.J.Thomson(1897)   : Discovered electron and determined charge/mass(e/m) ratio for electron

5. Rutherford(1891)   : Discovered nucleus and proposed atomic model

6. MaxPlanck(1901)   : Proposed quantum theory of radiation

7. RobertMillikan(1909)   : Determined charge of an electron

8. H.G.J.Mosely(1913)   : Discovered atomic number

9. Niels Bohr(1913)   : Proposed a new model of atom

10. Clark Maxwell(1921)   : Electromagnetic wave theory

11. de-Broglie(1923)   : Established wave nature of particles

12. Pauli(1927)   : Discovery of neutrino

13. Werner Heisenberg(1927)   : Uncertainty Principle

14. James Chadwick(1932)   : Discovery of neutron

15. Anderson(1932)   : Discovery of positron

16. Fermi(1934)   : Discovered antineutrino

17. Hideki Yukawa(1935)   : Discovered mesons

18. Segre(1955)   : Discovered antiproton

19. Cork and Association(1956)   : Discovered antineutron

Progress of Atomic Models

➢ In 1803, John Dalton, proposed his atomic theory. He suggested that atoms were indivisible solid spheres.

➢ J.J.Thomson proposed that an atom was a solid sphere of positively charged material and negatively charged particles, electrons were embedded in it like the seeds in a guava fruit. But later this concept was proved wrong.

➢ Rutherford suggested the planetary model, but this model was rejected.

➢ In 1913, Neils Bohr proposed that electrons revolve around the nucleus in a definite orbit with a particular energy. Based on the facts obtained from spectra of hydrogen atom, he introduced the concept of energy levels of atom.

➢ In 1916 Sommerfeld modified Bohr's model by introducing elliptical orbits for electron path. He defined sub energy levels for every major energy level predicted by Bohr.

➢ The concept of Quantum numbers was introduced to distinguish the orbital on the basis of their size, shape and orientation in space by using principal, azimuthal, magnetic and spin quantum numbers.

➢ From the study of quantum numbers, various rules are put forward for filling of electrons in various orbitals by following

* Aufbau principle

* Pauli exclusion principle and

* Hunds rule of maximum multiplicity.

➢ In 1921 Burry and Bohr gave a scheme for the arrangement of electrons in an atom. Further the nature of electron (s) is studied.

1.1 DUAL PROPERTY OF AN ELECTRON

In case of light, some phenomena like interference, diffraction etc., can be explained if light is supposed to have wave character. However certain other phenomena such as black body radiation and photo electric effect can be explained only if it is believed to be a stream of photons i.e., has particle character. Thus light is said to have a dual character. Such studies on light were made by Einstein in 1905.

Louis de Broglie, a French Physicist, in 1924, advanced the idea that like photons, all material particles such as electron, proton, atom, molecule, a piece of chalk, a piece of stone or iron ball possessed both wave character as well as particle character. The wave associated with a particle is called a matter wave.

1.1.1   Difference between a particle and a wave

The concept of a particle and a wave can be understood by the different points of distinction between them.

	PARTICLE		WAVE
1.	A particle occupies a well-defined position in space i.e a particle is **localized** in space e.g. a grain of sand, a cricket ball etc.	1.	a wave is spread out in space e.g. on throwing a stone in a pond of water, the waves start moving out in the form of concentric circles. Similarly, the sound of the speaker reaches everybody in the audience. Thus a wave is **delocalized** in space.
2.	When a particular space is occupied by one particle, the same space cannot be occupied simultaneously by any other particle. In other words, particles do **not interfere**.	2.	Two or more waves can coexist in the same region of space and hence **interfere**.
3.	When a number of particles are present in a given region of space, their **total value is equal to their sum** i.e it is neither less nor more.	3.	When a number of waves are present in a given region of space, due to interference, the **resultant wave can be larger or smaller** than the individual waves i.e. interference may be constructive or destructive.

1.1.2 Experiments to prove particle and wave property of Electrons

a) Verification of Wave character

i) Davisson and Germer's Experiment

In 1927 Davisson and Germer observed that, a beam of electrons obtained from a heated tungsten filament is accelerated by using a high positive potential. When this fine beam of accelerated electron is allowed to fall on a large single crystal of nickel, the electrons are scattered from the crystal in different directions. The diffraction pattern so obtained is similar to the diffraction pattern obtained by Bragg's experiment on diffraction of X-rays from a target in the same way (Fig. 1.1).
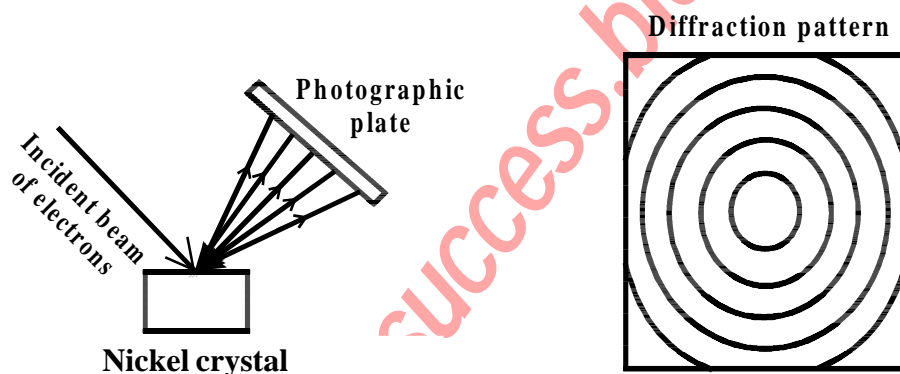

Fig.1.1 Electron diffraction experiment by Davisson and Germer

Since X-rays have wave character, therefore, the electrons must also have wave character associated with them. Moreover, the wave length of the electrons as determined by the diffraction experiments were found to be in agreement with the values calculated from de-Broglie equation.

From the above discussion, it is clear that an electron behaves as a wave.

ii) Thomson's experiment

G.P. Thomson in 1928 performed experiments with thin foil of gold in place of nickel crystal. He observed that if the beam of electrons after passing through the thin foil of gold is received on the photographic plate placed perpendicular to the direction of the beam, a diffraction pattern is observed as before (Fig. 1.2). This again confirmed the wave nature of electrons.
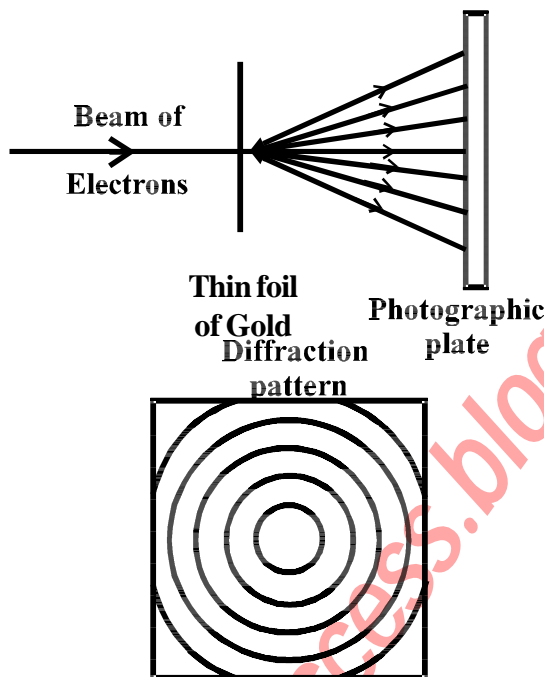
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Fig. 1.2 Diffraction of electron beam by thin foil of gold (G.P. Thomson experiment)

b) Verification of the particle character

The particle character of the electron is proved by the following different experiments:-

i) When an electron strikes a zinc sulphide screen, a spot of light known as scintillation is produced. A scintillation is localized on the zinc sulphide screen. Therefore the striking electron which produces it, also must be localized and is not spread out on the screen. But the localized character is possessed by particles. Hence electron has particle character.

ii) Experiments such as J.J.Thomson's experiment for determination of the ratio of charge to mass (i.e. e/m) and Milliken oil drop experiment for determination of charge on electron also show that electron has particle character.

iii) The phenomenon of Black body radiation and Photoelectric effect also prove the particle nature of radiation.

1.2 de-Broglie Relation

The wavelength of the wave associated with any material particle was calculated by analogy with photon as follows :-

In case of a photon, if it is assumed to have wave character, its energy is given by

$$E = h\nu \quad \text{(according to the Planck's quantum theory)} \quad \text{...(i)}$$

where ν is the frequency of the wave and h is Planck's constant.

If the photon is supposed to have particle character, its energy is given by

$$E = mc^2 \text{(according to Einstein equation)} \quad \text{...(ii)}$$

where m is the mass of photon and c is the velocity of light.

From equations (i) and (ii), we get

$$h\nu = mc^2$$

But $\nu = c / \lambda$

$\therefore \quad h \cdot c / \lambda = mc^2$

or $\lambda = h / mc$

de Broglie pointed out that the above equation is applicable to any material particle. The mass of the photon is replaced by the mass of the material particle and the velocity "c" of the photon is replaced by the velocity v of the material particle. Thus, for any material particle like electron, we may write

$$\boxed{\lambda = h / mv \text{ or } \lambda = h / p}$$

where $mv = p$ is the momentum of the particle.

The above equation is called **de Broglie equation** and 'λ' is called *de Broglie wavelength.*

Thus the significance of de Broglie equation lies in the fact that it relates the particle character with the wave character of matter.

Louis de-Broglie's concept of dual nature of matter finds application in the construction of electron microscope and in the study of surface structure of solids by electron diffraction. The de-Broglie's concept can be applied not only to electrons but also to other small particles like neutrons, protons, atoms, molecules etc.,

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Significance of de-Broglie waves

The wave nature of matter, however, has no significance for objects of ordinary size because wavelength of the wave associated with them is too small to be detected. This can be illustrated by the following examples.

i) Suppose we consider an electron of mass 9.1×10^{-31} kg and moving with a velocity of 10^7 ms^{-1}. Its de-Broglie wavelength will be;

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ kg m}^2\text{s}^{-1}}{9.1 \times 10^{-31} \text{ kg} \times 10^7 \text{ ms}^{-1}} = 0.727 \times 10^{-10}\text{m} = 7.27 \times 10^{-11}\text{m}$$

This value of λ can be measured by the method similar to that for the determination of wave length of X-rays.

ii) Let us now consider a ball of mass 10^{-2} kg moving with a velocity of 10^2 ms^{-1}. Its de-Broglie wave length will be;

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ kg m}^2\text{s}^{-1}}{10^{-2} \text{ kg} \times 10^2 \text{ ms}^{-1}} = 6.62 \times 10^{-34}\text{m}$$

This wavelength is too small to be measured, and hence de-Broglie relation has no significance for such a large object.

Thus, de-Broglie concept is significant only for sub-microscopic objects in the range of atoms, molecules or smaller sub-atomic particles.

Problem 1

The kinetic energy of sub-atomic particle is 5.85×10^{-25}J. Calculate the frequency of the particle wave. (Planck's constant, $h = 6.626 \times 10^{-34}$ Js)

Solution

K.E. $= \frac{1}{2} mv^2 = 5.85 \times 10^{-25}$J

By de-Broglie equation, $\lambda = \dfrac{h}{mv}$

But $\lambda = \dfrac{v}{\upsilon}$

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$$\therefore \qquad \frac{v}{\nu} = \frac{h}{mv}$$

$$\text{or} \quad \nu = \frac{mv^2}{h} = \frac{2 \times 5.85 \times 10^{-25}\,J}{6.626 \times 10^{-34}\,JS}$$

$$= 1.77 \times 10^9\ s^{-1}$$

Problem 2

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

Solution

Energy acquired by the electron (as kinetic energy) after being accelerated by a potential difference of 1 kV (i.e 1000 volts)

$$= 1000\ eV$$

$$= 1000 \times 1.609 \times 10^{-19}\,J,\ (1\,eV) = 1.609 \times 10^{-19}\ J)$$

(Energy in joules = Charge on the electron in coulombs × Pot. diff. in volts)

$$= 1.609 \times 10^{-16}\ J$$

i.e. Kinetic energy

$$\left(\frac{1}{2}mv^2\right) = 1.609 \times 10^{-16}\,J$$

$$\text{or} \quad \frac{1}{2} \times 9.1 \times 10^{-31}\,v^2 = 1.609 \times 10^{-16}\,J$$

$$\text{or} \qquad v^2 = 3.536 \times 10^{14}$$

$$\text{or} \qquad v = 1.88 \times 10^7\,ms^{-1}$$

$$\therefore \quad \lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{9.1 \times 10^{-31} \times 1.88 \times 10^7}$$

$$= 3.87 \times 10^{-11}\ m$$

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Problem 3

Calculate the wavelength associated with an electron (mass 9.1×10^{-31} kg) moving with a velocity of 10^3 m sec^{-1} (h=6.626×10^{-34} kg m^2 sec^{-1}).

Solution

Here we are given

$$m = 9.1 \times 10^{-31} \text{ kg}$$

$$v = 10^3 \text{ m sec}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$$

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{(9.1 \times 10^{-31}) \times 10^3}$$

$$= 7.25 \times 10^{-7} \text{ m}$$

Problem 4

A moving electron has 4.55×10^{-25} joules of kinetic energy. Calculate its wavelength (mass = 9.1×10^{-31} kg and h = 6.626×10^{-34} kg m^2 s^{-1}).

Solution

Here we are given

Kinetic energy i.e. $\dfrac{1}{2} mv^2 = 4.55 \times 10^{-25}$ J

$$m = 9.1 \times 10^{-31} \text{ kg}$$

$$h = 6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$$

$$\therefore \quad \frac{1}{2} \times (9.1 \times 10^{-31}) v^2 = 4.55 \times 10^{-25}$$

or $\quad v^2 = \dfrac{4.55 \times 10^{-25} \times 2}{9.1 \times 10^{-31}} = 10^6$

or $\quad v = 10^3$ m sec^{-1}

$$\therefore \qquad \lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{(9.1 \times 10^{-31}) \times 10^3}$$

$$= 7.25 \times 10^{-7} \text{ m.}$$

Problem 5

Calculate the kinetic energy of a moving electron which has a wavelength of 4.8 pm. [mass of electron $= 9.11 \times 10^{-31}$ kg, h $= 6.626 \times 10^{-34}$ Kg m^2 s^{-1}].

Solution

According to de-Broglie equation,

$$\lambda = \frac{h}{mv} \quad \text{or} \quad v = \frac{h}{m\lambda}$$

$$\therefore \qquad v = \frac{h}{m\lambda} = \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{9.11 \times 10^{-31} \text{ kg} \times 4.8 \times 10^{-12} \text{ m}} = 1.516 \times 10^8 \text{ ms}^{-1}$$

$$\text{Kinetic energy} = \frac{1}{2} mv^2 = \frac{1}{2} \times 9.11 \times 10^{-31} \text{ kg} \times (1.516 \times 10^8 \text{ ms}^{-1})^2$$

$$= 10.47 \times 10^{-15} \text{ kg m}^2 \text{ s}^{-2} = \mathbf{1.047 \times 10^{-14} \text{ J}}$$

Problem 6

Two particles A and B are in motion. If the wavelength associated with the particle A is 5×10^{-8} m, calculate the wavelength of particle B, if its momentum is half of A.

Solution

According to de-Broglie relation,

$$\lambda = \frac{h}{p} \quad \text{or} \quad p = \frac{h}{\lambda}$$

For particle A, $p_A = \dfrac{h}{\lambda_A}$

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Here, p_A and λ_A are the momentum and wavelength of particle A.

For particle B, $p_B = \dfrac{h}{\lambda_B}$

Here p_B and λ_B are the momentum and wavelength of particle B.

But, $\qquad p_B = \dfrac{1}{2} p_A$

$\therefore \qquad \dfrac{h}{\lambda_B} = \dfrac{1}{2} \dfrac{h}{\lambda_A}$

$\qquad \dfrac{\lambda_A}{\lambda_B} = \dfrac{1}{2} \quad$ or $\quad \lambda_B = 2\lambda_A$

But $\qquad \lambda_A = 5 \times 10^{-8}\,m$

$\qquad \lambda_B = 2\lambda_A = 2 \times 5 \times 10^{-8}\,m = 10 \times 10^{-8}\,m = \mathbf{10^{-7}\,m.}$

Problem for practice

1. Calculate the momentum of a particle which has a de-Broglie wavelength of $1A°$. [$h = 6.626 \times 10^{-34}\,kg\,m^2\,s^{-1}$]

    [**Ans. :** $6.63 \times 10^{-24}\,kg\,ms^{-1}$]

2. What is the mass of a photon of sodium light with a wavelength of $5890\,Å$? [$h = 6.626 \times 10^{-34}\,Js$]

    [**Ans. :** $3.75 \times 10^{-36}\,kg$]

3. Calculate the wavelength of $1000\,kg$ rocket moving with a velocity of 300 km per hour.

    [**Ans.:** $7.92 \times 10^{-39}\,m$]

4. What must be the velocity of a beam of electrons if they are to display a de-Broglie wavelength of $100Å$?

    [**Ans. :** $7.25 \times 10^{4}\,ms^{-1}$]

5. The wavelength of a moving body of mass $0.1\,mg$ is $3.31 \times 10^{-29}\,m$. Calculate its kinetic energy ($h = 6.626 \times 10^{-34}\,Js$).

    [**Ans :** $2 \times 10^{-3}\,J$]

6. Calculate the wavelength of a particle of mass m = 6.62×10^{-27} kg moving with kinetic energy 7.425×10^{-13} J (h = 6.626×10^{-34} kg m² sec⁻¹).

   [**Ans. :** 6.657×10^{-15} m]

7. Calculate the wavelength of an electron in a 10 MeV particle accelerator (1 MeV = 10^6eV).

   [**Ans. :** 0.39 pm]

8. What will be the wavelength of oxygen molecule in picometers moving with a velocity of 660 ms⁻¹ (h = 6.626×10^{-34} kg m² s⁻¹).

   [**Ans. :** 18.8 pm]

9. A moving electron has 4.9×10^{-25} joules of kinetic energy. Find out its de - Broglie wavelength (Given h = 6.626×10^{-34} Js; $m_e = 9.1 \times 10^{-31}$ kg).

   [**Ans. :** 7×10^{-7} m]

1.3 THE UNCERTAINTY PRINCIPLE

The position and the velocity of the bodies which we come across in our daily life can be determined accurately at a particular instant of time. Hence the path or trajectories of such bodies can be predicted. However, Werner Heisenberg in 1927 pointed out that we can never measure simultaneously and accurately both the position and velocity (or momentum) of a microscopic particle as small as an electron. Thus, it is not possible to talk of trajectory of an electron. This principle, which is a direct consequence of the dual nature of matter and radiation, states that, **"it is impossible to measure simultaneously both the position and velocity (or momentum) of a microscopic particle with absolute accuracy or certainty."**

Mathematically, uncertainty principle can be put as follows.

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

where, Δx = uncertainity in the position of the particle and
Δp = uncertainity in the momentum of the particle.

The sign $\geq$ means that the product of Δx and Δp can be either greater than or equal to h/4π but can never be less than h/4π.

Example 1

Calculate the uncertainty in the velocity of a wagon of mass 3000kg whose position is known to an accuracy of $\pm$ 10 pm (Planck's constant = 6.626×10^{-34} Kg m^2 s^{-1}.

Solution : Here we are given

m = 3000 kg

Δx = 10 pm

   = 10×10^{-12} m = 10^{-11} m

$\therefore$ By uncertainty principle,

$$\Delta v = \frac{h}{4\pi \times m \times \Delta x}$$

$$= \frac{6.626 \times 10^{-34}}{4 \times \frac{22}{7} \times 3000 \times 10^{-11}}$$

$$= \quad \mathbf{1.76 \times 10^{-27} ms^{-1}}$$

Example 2

Calculate the uncertainty in the position of an electron if the uncertainty in its velocity is 5.7×10^5 m/sec ($h = 6.626 \times 10^{-34}$ kg m^2 s^{-1}, mass of the electron $= 9.1 \times 10^{-31}$ kg).

Solution: Here we are given

$\Delta v = 5.7 \times 10^5$ ms^{-1}

m = 9.1×10^{-31} kg

h   = 6.626×10^{-34} kg m^2 s^{-1}

Substituting these values in the equation for uncertainty principle

i.e. $\Delta x \times (m \times \Delta v) = \dfrac{h}{4\pi}$

we have $\Delta x = \dfrac{h}{4\pi \times m \times \Delta v}$

$$= \frac{6.626 \times 10^{-34}}{4 \times \frac{22}{7} \times 9.1 \times 10^{-31} \times 5.7 \times 10^{5}}$$

$$= 1.0 \times 10^{-10} \text{ m}$$

i.e Uncertainty in position $= \pm 10^{-10}$ m.

PROBLEMS FOR PRACTICE

1. The approximate mass of an electron is 10^{-27} g. Calculate the uncertainty in its velocity if the uncertainty in its position were of the order of 10^{-11} m .

   [**Ans:** 5.25 x 10^{6} m sec^{-1}]

2. Calculate the product of uncertainity in position and velocity for an electron of mass 9.1 x 10^{-31} kg according to Heisenberg uncertainty principle.

   [**Ans:** 5.77 x 10^{-5} m^{2} sec^{-1}]

3. Calculate the uncertainty in velocity (Δv) of a cricket ball (mass = 0.15 kg) if the uncertainty position (Δx) is of the order of 1 Å (i.e. 10^{-10} m).

   [**Ans:** 3.5x10^{-24} m sec^{-1}]

4. Using uncertainity principle,calculate the uncertainty in velocity of an electron if the uncertainty in position is 10^{-4} m.

   [**Ans:** 0.577 m sec^{-1}]

5. The uncertainty in the position of a moving bullet of mass 10 g is 10^{-5} m.Calculate the uncertainty in its velocity .

   [**Ans:** 5.25 x 10^{-28} m sec^{-1}]

1.4 THE WAVE NATURE OF ELECTRONS

It has been made clear that, if a substance is divided into finer and finer pieces, we reach molecules and atoms, then we realize that the atoms consist of electrons and nuclei. It has been clarified that matter is a collection of ultra microscopic particles. Upto the 19th century, these particles were considered to move obeying Newtonian mechanics and Maxwellian electromagnetism. However, this view point has became doubtful after the proposal of **the Bohr model** of the atomic structure (Bohr's quantum theory).

On the other hand, **light** had been considered to be electromagnetic waves. However, after **the discovery of light quanta (photons),** it was clarified that

the light has wave nature at one time and particle nature at another time. Therefore, light has a kind of **duality.**

The idea of deBroglie wave nature waves or deBroglie matter waves is based on the fact that light has both wave and particle nature. Hence particle like electron or proton can also be considered to be **'particle'** with **'wave nature'.**

Einstein's relations which connect the particle and wave aspects in light quanta

$$E = h\nu, \qquad p = \frac{h}{\lambda} \tag{1}$$

would be satisfied for de Broglie matter waves as well. Therefore the relations, Eq.(1), are often called **Einstein-de Broglie's relations.**

If we apply these relations to the case of the Bohr model of the hydrogen atom, we can well understand its possibility as follows. If we consider that the electron in a hydrogen atom moves at constant speed along a circular orbit around the nucleus (proton), the **quantum condition** in Bohr's quantum theory is written as Eq(2). By using Einstein's relation $p = h/\lambda$ in this equation, the quantum condition is written

$$2\pi a = n\lambda, \qquad (n = 1, 2, 3, ...) \tag{2}$$

This equation means that the circumference of the circular orbit of the electron must be a integral multiple of the wavelength of de Broglie wave. In other word, de-Broglie wave accompanying the motion of the electron should be continuous. Therefore, we can easily understand the quantum condition that determines the stationary states by considering the continuity of de Broglie waves (See the following figure).
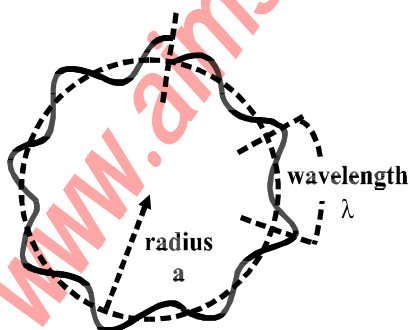
Bohr's quantum condition. The condition for stationary states

The circumference of the circular orbit of the electron should be an integral multiple of the wavelength of de Broglie wave, otherwise the wave cannot be smoothly continuous.

Energy of electron in an atom. By applying Schrodinger wave equation to hydrogen atom, the energy of electron (E_n) was found as :

$$E_n = -\frac{2\pi^2 m e^4}{n^2 h^2} \tag{1}$$

where n is the principal quantum number. This expression is same as Bohr's equation for energy of electron in a hydrogen atom.

Substituting the values of m, e and h in relation (1), we get

$$E_n = -\frac{1312}{n^2} \, \text{kJ mol}^{-1} \tag{2}$$

Significance of negative electronic energy

The energy of an electron at infinity is arbitrarily assumed to be zero. This state is called zero-energy state. When an electron moves and comes under the influence of nucleus, it does some work and spends its energy in this process. Thus, the energy of the electron decreases and it becomes less than zero ie., it acquires a negative value.

Example 1

The ionization energy of hydrogen atom in the ground state is $1312 \, \text{kJ mol}^{-1}$. Calculate the wavelength of radiation emitted when the electron in hydrogen atom makes a transition from n = 2 state to n = 1 state (Planck's constant, $h = 6.626 \times 10^{-34}$ Js; velocity of light, $c = 3 \times 10^8$ m s^{-1}; Avogadro's constant, $N_A = 6.0237 \times 10^{23}$ mol^{-1}).

Solution

I.E. of hydrogen atom in the ground state $= 1312 \, \text{kJ mol}^{-1}$

Energy of hydrogen atom in the first orbit (E_1) = -I.E = -1312 kJ mol^{-1}

Energy of hydrogen atom in the nth orbit (E_n) = $\dfrac{-1312}{n^2}$ kJ mol^{-1}

Energy of hydrogen atom in the second orbit (E_2) = $-\dfrac{1312}{2^2}$ = -328 kJ mol^{-1}

$\Delta E = E_2 - E_1 = [-328 - (-1312)] \text{kJ} = 984 \, \text{kJ mol}^{-1}$

Energy released per atom = $\dfrac{\Delta E}{N}$ = $\dfrac{984 \times 10^3 \, \text{J/atom}}{6.0237 \times 10^{23}}$

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$$\frac{\Delta E}{N} = h\nu = h\frac{c}{\lambda}; \qquad \therefore \lambda = \frac{Nh_1c}{\Delta E}$$

$$\therefore \lambda = \frac{6.626\times10^{-34}\,\text{Js}\times3\times10^{8}\,\text{ms}^{-1}\times6.0237\times10^{23}}{984\times10^{3}\,\text{J}} = 1.2\times10^{-7}\,\text{m}$$

Example 2

The electron energy of hydrogen atom in the ground state works out to be -2.18×10^{-18} J per atom. Calculate what will happen to the position of the electron in this atom if an energy of 1.938×10^{-18} J is supplied to the each hydrogen atom.

Solution

Energy of H atom in the ground state = -2.18×10^{-18} J atom^{-1}
Energy added = 1.938×10^{-18} J atom^{-1}
Energy of electron in the excited state = $(-2.18 + 1.938)\times10^{-18}$ J atom^{-1}
$$= -0.242\times10^{-18}\,\text{J atom}^{-1}$$

$$\therefore \qquad -0.242\times10^{-18}\,\text{J atom}^{-1} = \frac{-2.18\times10^{-18}\,\text{J atom}^{-1}}{n^2}$$

$$n^2 = \frac{-2.18\times10^{-18}\,\text{J atom}^{-1}}{-0.242\times10^{-18}\,\text{J atom}^{-1}} = 9, \quad n = 3$$

Hence electron will get excited to third shell.

Example 3

Calculate the ionisation energy of hydrogen atom as well as energy needed to promote its electron from first energy level to third energy level.

Solution

The energy of electron in hydrogen atom is given by the expression,

i) Ionisation energy is the amount of energy required to remove an electron from neutral gaseous atom i.e. to shift the electron from $n = 1$ to $n = \infty$

When $n = 1, E_1 = -1312$ kJ mol^{-1}; $\qquad n = \infty, \qquad E_\infty = 0$

$\therefore$ Ionisation energy = $E_\infty - E_1 = 0 - (-1312$ kJ mol$^{-1}) = +1312$ kJ mol^{-1}

ii)   Energies of electron when present in n = 1 and n = 3 are :

$$E_1 = \frac{-1312}{1^2} = -1312 \, \text{kJ mol}^{-1} \qquad : \qquad E_3 = \frac{-1312}{3^2} = -146 \, \text{kJ mol}^{-1}$$

∴ Energy needed to promote an electron from

n = 1 to n = 3 is, ΔE where $\Delta E = E_3 - E_1 = [-146 - (-1312)] \, \text{kJ mol}^{-1}$

= 1166 kJ mol^{-1}

Shapes of orbitals

An orbital is the region of space around the nucleus within which the probability of finding an electron of given energy is maximum .The shape of this region (electron cloud) gives the shape of the orbital. The plot of angular wave functions or square of angular wave functions (probability functions) give us the shapes of orbitals.These two plots differ only slightly. Let us consider the individual shapes.

Shape of s-orbitals

For s-orbitals, when $l = 0$, the value of m is 0 i.e., there is only one possible orientation. This means that the probability of finding an electron is the same in all directions at a given distance from the nucleus. It should, therefore, be spherical in shape. Hence all s- orbitals are non- directional and spherically symmetrical about the nucleus.

The size of an s-orbital depends upon value of the principal quantum number n. Greater the value of 'n' larger is the size of the orbital.
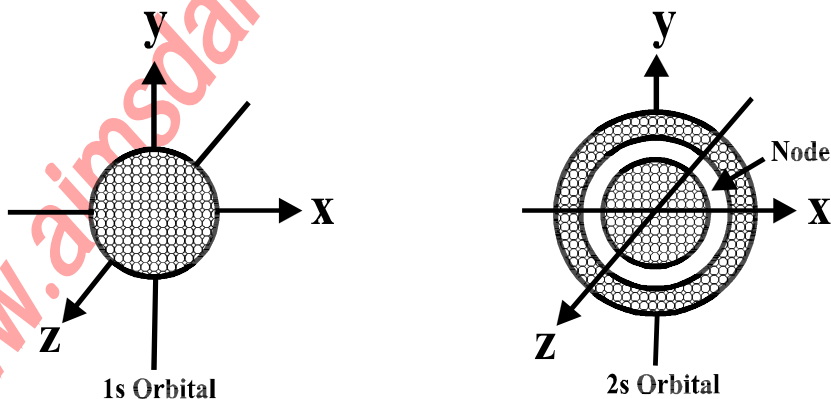

1s Orbital   2s Orbital

Fig. 1.3 Shapes of 1s and 2s-orbitals

An important feature of the 2s-orbital is that there is a spherical shell within this orbital where the probability of finding the electron is zero (nearly). This is called a node or nodal surface. In 2s orbital there is one spherical node. The number of nodal surfaces or nodes in s-orbital of any energy level is equal to (n-1), where n is the principal quantum number.

Shape of p-orbitals

For p-subshell $l = 1$, there are three values of m namely -1, 0, +1. It means that p orbitals can have three possible orientations. These three p-orbitals are equal in energy (degenerate state) but differ in their orientations. Each p-orbital consists of two lobes symmetrical about a particular axis. Depending upon the orientation of the lobes, these are denoted as $2p_x$, $2p_y$ and $2p_z$ accordingly as they are symmetrical about X, Y and Z - axis respectively.

The lines in the figure represents the cross-section of the three dimensional boundary surface of p-orbitals. The boundary surface means the surface which encloses 90 percent of the dots representing the electrons. Two lobes of each p-orbital are separated by a nodal plane (a plane having zero electron density). For example, for $2p_x$ orbital, YZ plane is the nodal plane x .
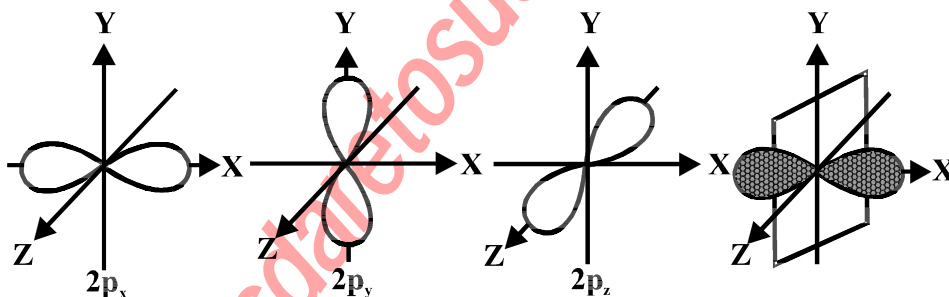

Fig.1.4 Shapes of $2p_x$, $2p_y$ and $2p_z$ orbitals

Fig. 1.5 Nodal plane for $2p_x$ orbital

Thus, p-orbitals have dumb-bell shape and have directional character. The probability of finding the electron is equal in both the lobes. The p-orbitals of higher energy levels have similar shapes although their size are bigger.

Shape of d-orbitals

For d-subshell, $l = 2$, there are five values of m namely -2, -1, 0, 1, 2. It

means d- orbitals can have five orientations. These are represented by d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$ and d_{z^2}; for example, $3d_{xy}$, $3d_{yz}$, $3d_{zx}$, $3d_{x^2-y^2}$ and $3d_{z^2}$. The d_{xy}, d_{yz} and d_{zx} orbitals have same shape i.e., clover leaf shape but they lie in XY, YZ and ZX-planes respectively. The d_{z^2} orbital is symmetrical about Z-axis and has a dumb - bell shape with a doughnut shaped electron cloud in the centre. The $d_{x^2-y^2}$ orbital is also clovar leaf shaped but its leaves are directed along the X and Y- axis.

The reason for the presence of four lobes in any nd orbital lies in the fact that the d - orbitals have two nodes, and hence two changes in algebraic sign of ψ, which lead to four lobes.
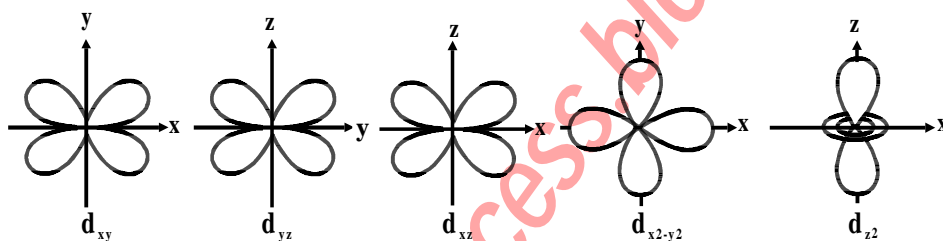
Fig. 1.6 Shapes of d-orbitals

1.5 MOLECULAR ORBITAL THEORY

Molecular orbital theory was put forward by Hund and Mullikan in 1932. This theory is modern and more rational. This theory assume that in molecules, atomic orbitals lose their identity and the electrons in molecules are present in new orbitals called molecular orbitals. A brief outline of this theory is given below:

(i) In a molecule, electrons are present in new orbitals called **molecular orbitals**.

(ii) Molecular orbitals are formed by combination of atomic orbitals of equal energies (in case of homonuclear molecules) or of comparable energies (in case of heteronuclear molecules).

(iii) The number of molecular orbitals formed is equal to the number of atomic orbitals undergoing combination.

(iv) Two atomic orbitals can combine to form two molecular orbitals. One of these two molecular orbitals one has a lower energy and the other has a higher energy. The molecular orbital with lower energy is called **bonding molecular orbita**l and the other with higher energy is called **anti bonding molecular orbital.**

(v) The shapes of molecular orbitals depend upon the shapes of combining atomic orbitals.

(vi) The bonding molecular orbitals are represented by σ (sigma), π (pi), δ (delta) and the antibonding molecular orbitals are represented by σ*, π*, δ*.

(vii) The molecular orbitals are filled in the increasing order of their energies, starting with orbital of least energy. **(Aufbau principle).**

(viii) A molecular orbital can accommodate only two electrons and these two electrons must have opposite spins. **(Paul's exclusion principle).**

(ix) While filling molecular orbitals of equal energy, pairing of electrons does not take place until all such molecular orbitals are singly filled with electrons having parallel spins. **(Hund's rule).**

1.5.1 Energy level diagram for molecular orbitals

In case of homonuclear diatomic molecules, combination of two 1s atomic orbitals of participating atoms give rise to two new molecular orbitals designated as σ_{1s} and σ^{*}_{1s}. In the same manner the 2s and three 2p-orbitals of each atom i.e., eight atomic orbitals can give rise to eight new molecular orbitals viz.,

$$\sigma_{2s}, \sigma^{*}_{2s}, \pi_{2p_x}, \pi^{*}_{2p_x}, \pi_{2p_y}, \pi^{*}_{2p_y}, \sigma_{2p_z}, \sigma^{*}_{2p_z}.$$

Atomic Structure and Chemical Bonding

Energy levels of these molecular orbitals have been determined experimentally by spectroscopic studies. The order of increasing energy in case of the diatomic homonuclear molecules of first and second period of the periodic table is as given below:

$$\sigma_{1s} < \sigma^{*}_{1s} < \sigma_{2s} < \sigma^{*}_{2s} < \pi_{2p_x} = \pi_{2p_y} < \sigma_{2p_z} < \pi^{*}_{2p_x} = \pi^{*}_{2p_y} < \sigma^{*}_{2p_z}$$

This order of energies of various molecular orbitals is valid for molecules or ions like, H_2, H_2^+, He_2^+, He_2 (hypothetical), Li_2, Be_2 (hypothetical), B_2, C_2 and N_2 molecules. This energy diagram for the molecular orbitals is shown in Fig.1.7a. However, experimental evidence for oxygen and heavier diatomic molecules have shown that above sequence of energy levels of MOs is not correct. In case of these elements, the order of energy levels of σ_{2p_z}, π_{2p_x} and π_{2p_y} is reversed i.e., σ_{2p_z} has lesser energy than π_{2p_x} or π_{2p_y}. Thus, the order of increasing energy of MOs for these molecules is as follows.

$$\sigma_{1s} < \sigma^{*}_{1s} < \sigma_{2s} < \sigma^{*}_{2s} < \sigma_{2p_z} < \pi_{2p_x} = \pi_{2p_y} < \pi^{*}_{2p_x} = \pi^{*}_{2p_y} < \sigma^{*}_{2p_z}$$

This order of energies of various MOs is valid for molecules or ions like O_2, O_2^- (super oxide ion), O_2^{2-} (peroxide ion), F_2 and Ne_2 (hypothetical). This energy level diagram for MOs is shown in Fig.1.7(b).
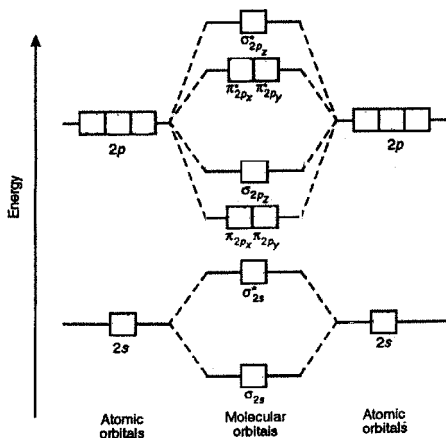

Fig. 1.7a Molecular orbital energy level diagram for diatomic homonuclear molecules of first and second period (except O_2, F_2 etc.)
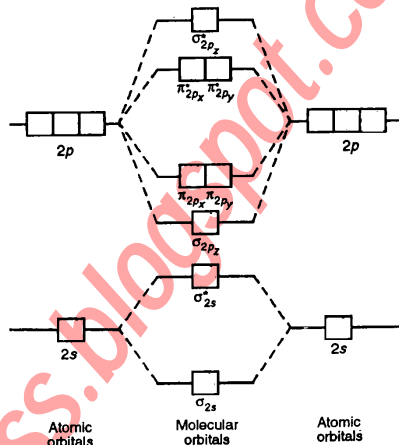
Fig. 1.7b.Molecular orbital energy level diagram for homonuclear diatomic molecules of O_2 and other heavier elements

1.5.2 Electronic configuration of a molecule and its correlation with molecular behaviour

The distribution of electrons among various molecular orbitals is called electronic configuration of a molecule. It can give us very important information about the molecules as explained below.

1. Stability of a molecule in terms of a number of electrons in bonding and antibonding molecular orbitals. From the electronic configuration it is possible to find out the number of electrons in bonding molecular orbitals(N_b) and number of electrons in antibonding molecular orbitals (N_a).

(a)   If $N_b > N_a$, the molecule is stable : This is evident because in this case the influence of bonding electrons will be more than the influence of antibonding electrons, resulting in a net force of attraction.

(b)   If $N_b < N_a$, the molecule is unstable : This is again obvious because in this case the influence of antibonding electrons will be more than the influence

of bonding electrons, resulting in a net force of repulsion.

(c)   *If $N_b = N_a$, the molecule is unstable :* This is because in this case the influence of bonding electrons will be equal to the influence of antibonding electrons resulting in no net force of attraction.

2. Bond order and stability of a molecule or an ion. The stability of a molecule or an ion can also be determined from another parameter called bond order. **Bond order** may be defined as half the difference between the number of electrons in bonding molecular orbitals (N_b) and the number of electrons in antibonding molecular orbitals (N_a) i.e,

$$\textbf{Bond Order} = \frac{1}{2}(N_b - N_a)$$

The resulting molecule or ion will be stable if $N_b > N_a$ i.e., if bond order is positive. The resulting molecule or ion will be unstable if $N_b \leq N_a$ i.e, if bond order is negative or zero.

3. Relative stability of molecules or ions in terms of bond order : The stability of a molecule or an ion is directly proportional to bond order. Thus, a molecule with bond order 3 (e.g., N_2) is more stable (i.e., has a higher bond dissociation energy) than a molecule with bond order 2 (e.g., O_2) or 1 (e.g., Li_2).

4. Nature of bond in terms of bond order : A chemical bond can be single, double or triple but cannot be a fraction, on the otherhand bond order can be a fraction.

5. Bond length in terms of bond order : Bond length is found to be inversely proportional to bond order. Greater the bond order, shorter the bond length and vice versa.

For example, the bond length in nitrogen molecule (bond order = 3) is shorter than in oxygen molecule (bond order = 2), which in turn is shorter than in hydrogen molecule (bond order = 1).

Table 1.   **Bond order, Bond dissociation energy and bond length in N_2, O_2 and Li_2 molecules**

Molecule	Bond order	Bond dissociation energy	Bond length
Nitrogen	3	945 kJ mol^{-1}	110 pm
Oxygen	2	495 kJ mol^{-1}	121 pm
Lithium	1	110 kJ mol^{-1}	267 pm

6. Diamagnetic and paramagnetic nature of the molecule : If all the electrons in the molecule are paired then the substance is diamagnetic in nature. On the other hand, if the molecule has unpaired electron(s) it is paramagnetic in nature.

1.5.3   Molecular orbital energy level diagrams of certain diatomic homonuclear molecules and molecular ions

The filling of molecular orbitals is governed by the following principles. (i) Aufbau principle (ii) Pauli's exclusion principle and (iii) Hund's rule of maximum multiplicity. Now, let us consider some examples of homonuclear diatomic molecules.

1. Hydrogen molecule, H_2. It is formed by the combination of two hydrogen atoms. Each hydrogen atom in the ground state has one electron in 1s orbital. Therefore, in all there are two electrons in hydrogen molecule which are present in lower most σ_{1s} molecular orbital. According to Pauli's exclusion principle, these two electrons should have opposite spins.

The molecular orbital electronic configuration of hydrogen molecule is $(\sigma_{1s})^2$. The molecular orbital energy level diagram of H_2 molecule is given in Fig. 1.8.
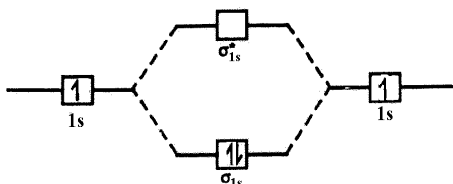

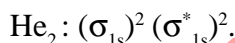**Fig. 1.8 Molecular orbital energy level diagram of H_2 molecule**

The bond order of H_2 molecule can be calculated as follows.

Here, $N_b = 2$ and $N_a = 0$

$$\therefore \quad \text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1.$$

i)   *Nature of bond* : This means that the two hydrogen atoms in a molecule of hydrogen are bonded by a single covalent bond.

ii) *Diamagnetic character* : Since no unpaired electron is present in hydrogen molecule, it is diamagnetic in nature.

2. Diatomic helium molecule, He$_2$ (Hypothetical). The electronic configuration of helium ($Z = 2$) in the ground state is $1s^2$. As each helium atom contains two electrons, there will be four electrons in He$_2$ molecule. Keeping in view the Aufbau principle and Pauli's exclusion principle its electronic configuration would be as follows.

$$\text{He}_2 : (\sigma_{1s})^2 \, (\sigma^*_{1s})^2.$$

The molecular orbital energy level diagram of He$_2$ (hypothetical) is given in Fig. 1.9.
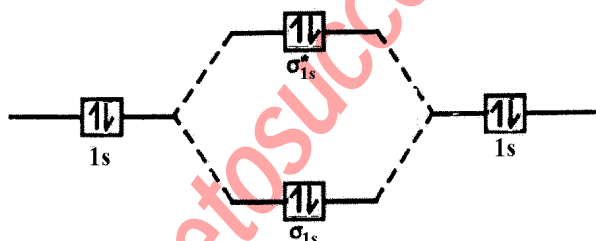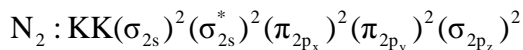

Fig. 1.9   Molecular orbital energy level diagram of He$_2$ (hypothetical) molecule

Here, $N_b = 2$ and $N_a = 2$

$$\therefore \quad \text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-2}{2} = 0.$$

As the bond order for He$_2$ comes out to be zero, this molecule does not exist.

3. Nitrogen molecule (N$_2$). The electronic configuration of nitrogen ($Z = 7$) in the ground state is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$. Therefore, the total number of electrons present in nitrogen molecule (N$_2$) is 14. These 14 electrons can be accommodated in the various molecular orbitals in order of increasing energy.

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$$N_2 : KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_x})^2(\pi_{2p_y})^2(\sigma_{2p_z})^2$$

Here $(\sigma_{1s})^2(\sigma_{1s}^*)^2$ part of the configuration is abbreviated as KK, which denotes the K shells of the two atoms. In calculating bond order, we can ignore KK, as it includes two bonding and two antibonding electrons.

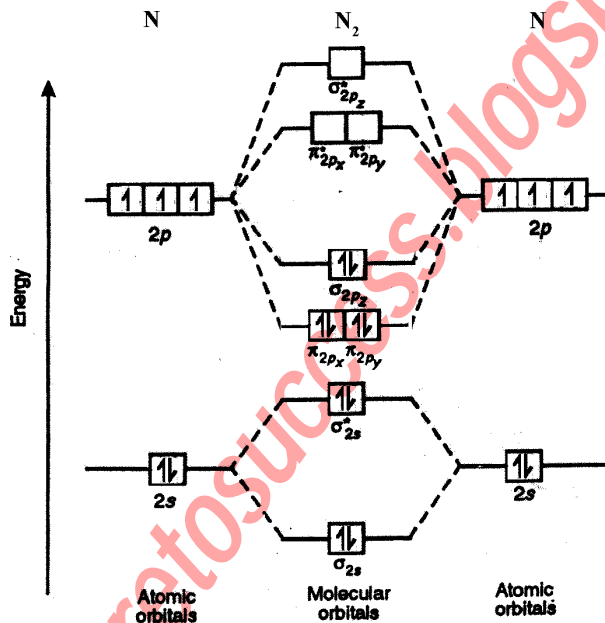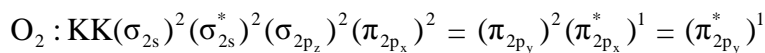The molecular orbital energy level diagram of N_2 is given in Fig. 1.10.

Fig. 1.10 Molecular orbital energy level diagram of N_2

The bond order of N_2 can be calculated as follows.

Here, $N_b = 8$ and $N_a = 2$

$\therefore$ Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{8 - 2}{2} = 3.$

i) *Nature of bond :* A bond order of 3 means that a triple bond is present in a molecule of nitrogen.

ii) *Diamagnetic nature :* Since all the electrons in nitrogen are paired, it is diamagnetic in nature.

4. Oxygen molecule, O_2. The electronic configuration of oxygen $(Z = 8)$ in the ground state is $1s^2 2s^2 2p^4$. Each oxygen atom has 8 electrons, hence, in O_2

molecule there are 16 electrons. Therefore, the electronic configuration of O_2 is as follows.

$$O_2 : KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p_x})^2 = (\pi_{2p_y})^2(\pi_{2p_x}^*)^1 = (\pi_{2p_y}^*)^1$$

Here $(\sigma_{1s})^2(\sigma_{1s}^*)^2$ part of the configuration is abbreviated as KK.

The molecular orbital energy level diagram of O_2 molecule is given in Fig.1.11.
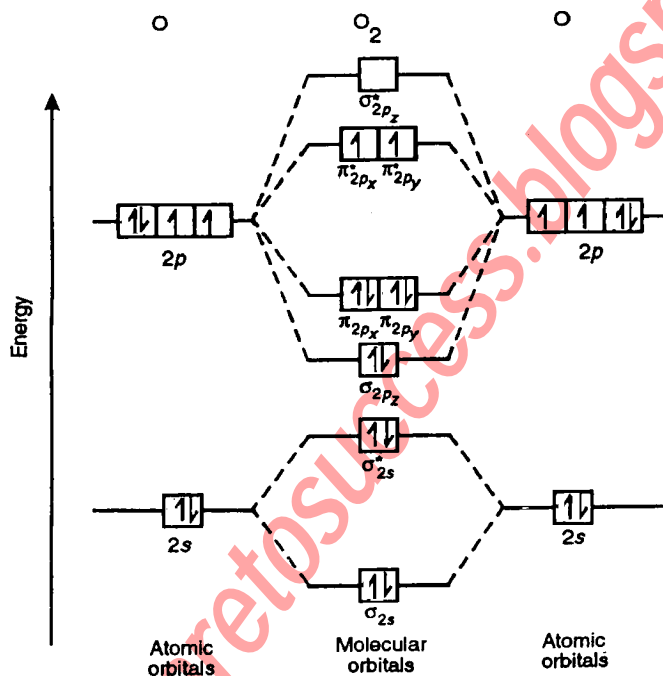

Fig. 1.11 Molecular orbital energy level diagram of O_2 molecule

$$\therefore \qquad \text{Bond order} = \frac{N_b - N_a}{2} = \frac{8-4}{2} = 2.$$

1.6   HYBRIDISATION

Hybridization is the concept of intermixing of the orbitals of an atom having nearly the same energy to give exactly equivalent orbitals with same energy, identical shapes and symmetrical orientations in space.

The new equivalent orbitals formed are known as the **hybrid orbitals** or hybridized orbitals. Hybrid orbitals have properties entirely different from the properties of the original orbitals from which they have been obtained.

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Salient Features regarding Hybridisation

i)   Orbitals involved in hybridization should have nearly the same energy.
ii) The orbitals of one and the same atom participate in hybridization.
iii) The number of hybrid orbitals formed is equal to the number of hybridizing orbitals.
iv) The hybrid orbitals are all equivalent in shape and energy.
v)   A hybrid orbital which is taking part in bond formation must contain one electron in it.
vi) Due to the electronic repulsions between the hybrid orbitals, they tend to remain at the maximum distance apart.
vii) The head on overlap of atomic orbitals give sigma (σ) bonds.
viii) The sidewise or lateral overlap of atomic orbitals give pi (π) bonds.

1.6.1 Tips to Predict the Type of Hybridisation in a Molecule or Ion (Other than Complex Ions)

Step 1 : Add the number of valence electrons of all the atoms present in the given molecule/ion.

Step 2 : In case of a cation, subtract the number of electrons equal to the charge on the cation and in case of an anion, add number of electrons equal to the charge on the anion.

Step 3 : (i) If the result obtained in step 2 is less than 8, divide it by 2 and find the sum of the quotient and remainder.

(ii) If the result obtained in step 2 lies between 9 and 56, divide it by 8 and find the first quotient (Q_1). Divide the remainder R_1 (if any) by 2 and find the second quotient (Q_2). Add all the quotients and the final remainder (R_2).

Let the final result obtained in (i) or (ii) be X. The type of hybridisation is decided by the value of X as follows :

Value of X	2	3	4	5	6	7
Type of hybridisation	sp	sp^2	sp^3	sp^3d	sp^3d^2	sp^3d^3

Example

i)   **$BeCl_2$**
Total valence electrons $= 2 + 7 \times 2 = 16$

$$\frac{16}{8} = 2(Q_1) + zero(R_1) \quad ; \qquad X = 2$$

$\therefore$ Hybridisation = **sp**

ii) **BF_3**

Total valence electrons $= 3 + 7 \times 3 = 24$

$$\frac{24}{8} = 3(Q_1) + zero(R_1) \quad ; \qquad X = 3$$

$\therefore$ Hybridisation = **sp^2**

iii) **NH_3**

Total valence electrons $= 5 + 3 = 8 \quad ; \quad X = \frac{8}{2} = 4$

$\therefore$ Hybridisation = **sp^3**

iv) **H_2O**

Total valence electrons $= 2 + 6 = 8 \quad ; \quad X = \frac{8}{2} = 4$

$\therefore$ Hybridisation = **sp^3**

v) **PCl_5**

Total valence electrons $= 5 + 7 \times 5 = 40$

$$\frac{40}{8} = 5(Q_1) + zero(R_1) \quad ; \qquad X = 5$$

$\therefore$ Hybridisation = **sp^3d**

vi) **SF_6**

Total valence electrons $= 6 + 7 \times 6 = 48$

$$\frac{48}{8} = 6(Q_1) + 0(R_1) \quad ; \quad X = 6$$

$\therefore$ Hybridisation = **sp^3d^2**

vii) **IF_7**

Total valence electrons $= 7 + 7 \times 7 = 56$

$$\frac{56}{8} = 7(Q_1) + 0(R_1) \quad ; \qquad X = 7$$

$\therefore$ Hybridisation = **sp^3d^3**

viii) **NO_2^- ion**

Total valence electrons $= 5 + 2 \times 6 = 17$

Charge $= -1$. Total electrons $= 17 + 1 = 18$

$$\frac{18}{8} = 2(Q_1) + 2(R_1) \; ; \; \frac{2}{2} = 1(Q_2) + 0(R_2) \; ; \quad X = 2+1+0=3$$

$\therefore$ Hybridisation $=$ **sp^2**

ix) **NO_3^- ion**

Total valence electrons $= 5 + 3 \times 6 = 23$; Charge $= -1$

$\therefore$ Total electrons $= 23 + 1 = 24$

$$\frac{24}{8} = 3(Q_1) + 0(R_1) \quad ; \quad X = 3$$

$\therefore$ Hybridisation $=$ **sp^2**

x) **CO_3^{2-}**

Total valence electrons $= 4 + 3 \times 6 = 22$; Charge $= -2$

$\therefore$ Total electrons $= 22 + 2 = 24$

$$\frac{24}{8} = 3(Q_1) + 0(R_1) \quad ; \quad X = 3$$

$\therefore$ Hybridisation $=$ **sp^2**

xi) **SO_4^{2-}**

Total valence electrons $= 6 + 4 \times 6 = 30$; Charge $= -2$

$\therefore$ Total electrons $= 30 + 2 = 32$

$$\frac{32}{8} = 4(Q_1) + 0(R_1) \quad ; \quad X = 4$$

$\therefore$ Hybridisation $=$ **sp^3**

xii) **ICl_4^-**

Total valence electrons $= 7 + 7 \times 4 = 35$; Charge $= -1$

$\therefore$ Total electrons $= 35 + 1 = 36$

$$\frac{36}{8} = 4(Q_1) + 4(R_1) \; ; \; \frac{4}{2} = 2(Q_2) + 0(R_2) \; ; \; X = 4 + 2 + 0 = 6$$

$\therefore$ Hybridisation = **sp³d²**

xiii) **NH$_4$⁺**

Total valence electrons $= 5 + 4 = 9$; Charge $= +1$

$\therefore$ Total electrons in NH$_4$⁺ $= 9 - 1 = 8$

$$\frac{8}{2} = 4(Q_1) + 0(R_1) \quad ; \quad X = 4$$

$\therefore$ Hybridisation is **sp³**

Hybridisation in some Typical Molecules and Ions

Hybridisation	Examples
sp	Be F$_2$, BeCl$_2$, C$_2$H$_2$, CO$_2$
sp²	SO$_2$, BH$_3$, BF$_3$, NO$_2$⁻, NO$_3$⁻, CO$_3$²⁻
sp³	NH$_3$, H$_2$O, CH$_4$, CCl$_4$, SiCl$_4$, H$_3$O⁺, NH$_4$⁺, ClO$_2$⁻, ClO$_3$⁻, ClO$_4$⁻, NF$_3$
sp³d	PCl$_5$, ClF$_3$, SF$_4$, XeF$_2$
sp³d²	SF$_6$, XeF$_4$, XeOF$_4$, BrF$_5$
sp³d³	IF$_7$, XeF$_6$

1.7 INTERMOLECULAR FORCES

The ionic, covalent and coordinate bond arises due to attractive forces between atoms. Vander Waal (Dutch physicist, 1873) was the first to propose the existence of attractive forces between the atoms of inert gases with fully filled orbitals. These forces also exist between non-polar molecules as well as polar molecules. The attractive interactions between the molecules are responsible for bringing the molecules close together. The attractive interactions between the different molecule of a substance are called intermolecular forces. The magnitude of these forces is maximum in the solids and decreases on passing from solid to liquids and from liquid to gaseous state. Vander Waal successfully explained the liquefaction of gases on the basis of inter molecular forces. These forces are purely electrostatic and thus physical in nature.

Hydrogen bonding. Hydrogen bonding comes into existence as a result of dipole-dipole interactions between the molecule in which hydrogen atom is covalently bonded to a highly electronegative atom. Therefore, the conditions for the effective hydrogen bonding are :

i) high electronegativity of the atom bonded to hydrogen atom so that bond is sufficiently polar.

ii) small size of the atom bonded to hydrogen so that it is able to attract the bonding electron pair effectively.

If the atom bonded to hydrogen has low value of electronegativity and/or large atomic size, dipole-dipole interactions are not strong enough to allow effective hydrogen bonding.

Only nitrogen, oxygen and fluorine form strong hydrogen bonds because they have high value of electronegativity and small atomic size.

Strength of H-bonds. It is a weak bond because it is merely an electrostatic force and not a chemical bond. Its strength depends upon the electronegativity of atom to which H atom is covalently bonded. Since electronegativity of $F > O >$ N, the strength of H- bond is in the order H - F .... H > H-O.....H > H-N.....H. Hydrogen bonds are much weaker than covalent bonds. The bond strength of different bonds is in the order : Ionic bond > Covalent bond > Hydrogen bond > dipole-dipole interactions, Vander Waal's (London forces).

Types of Hydrogen bonds

There are two different types of hydrogen bonds as :

i) Intermolecular hydrogen bonding. This type of bond is formed between the two molecules of the same or different compounds. Some examples of the compounds exhibiting intermolecular hydrogen bonds are :

$$\delta+ \quad \delta-$$

1. Hydrogen fluoride, H - F. In the solid state, hydrogen fluoride consists of long zig-zag chains of molecules associated by hydrogen bonds as shown below :
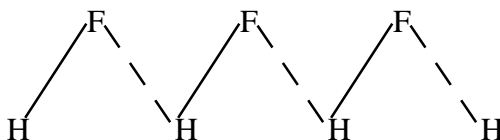
Therefore, hydrogen fluoride is represented as $(HF)_n$.

2. Water
$$\overset{\delta^{2-}}{O} - \overset{\delta^+}{H}$$
$$\underset{\underset{\delta^+}{H}}{|}$$
. In water molecule, the electronegative oxygen atom
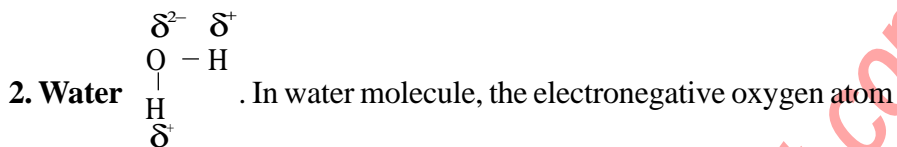
forms two polar covalent bonds with two hydrogen atoms. The oxygen atom due to its higher electronegativity acquires partial negative charge and the two hydrogen atoms acquire partial positive charge. The negatively charged oxygen forms two hydrogen bonds with two positively charged hydrogen atoms of two neighbouring molecules. Each oxygen atom is tetrahedrally surrounded by four hydrogen atoms as shown below :
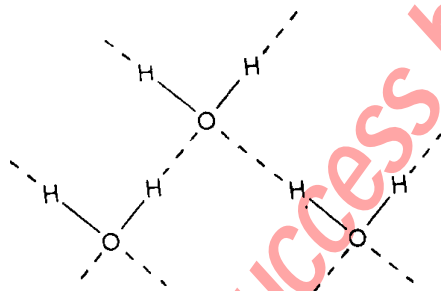
Hydrogen bonding in water results in a hydrogen bridge (H-O-H) network extending in three dimensions and the associated water molecule may be expressed as $(H_2O)_n$.

ii) Intramolecular hydrogen bonding. This type of bond is formed between hydrogen atom and N, O or F atom of the same molecule. This type of hydrogen bonding is commonly called chelation and is more frequently found in organic compounds. Intramolecular hydrogen bonding is possible when a six or five membered rings can be formed.
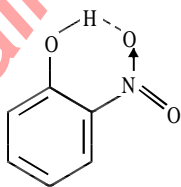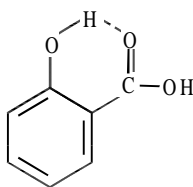
O-Nitrophenol   **Salicylic Acid**   **Salicylaldehyde**

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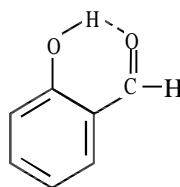
Intramolecular hydrogen bonding (chelation) decreases the boiling point of the compound and also its solubility in water by restricting the possibility of inter-molecular hydrogen bonding.

Importance of H-bonding

i)   Life would have been impossible without liquid water which is the result of intermolecular H-bonding in it.

ii)   Hydrogen bonding increase the rigidity and strength of wood fibres and thus makes it an article of great utility to meet requirements of housing, furniture, etc.

iii) The cotton, silk or synthetic fibres also own their rigidity and tensile strength to hydrogen bonding.

iv)   Most of our food materials such as carbohydrates and proteins also consist of hydrogen bonding.

v)   Hydrogen bonding also exists in various tissues, organs, skin, blood and bones.

SELF EVALUATION

A.   Choose the correct answer

1. $En = -\dfrac{313.6}{n^2}$, If the value of Ei = -34.84 to which value 'n' corresponds

      a)   4   b)   3   c)   2   d)   1

2.   Dual character of an electron was explained by

      a) Bohr   b) Heisenberg   c) de-Broglie   d) Pauli

3.   de-Broglie equation is

      a) $\lambda = \dfrac{mv}{h}$ b) $\lambda = hmv$ c) $\lambda = \dfrac{hv}{m}$ d) $\lambda = \dfrac{h}{mv}$

4.   The value of Bohr radius for hydrogen atom is

      a) 0.529×10^{-8} cm   b) 0.529×10^{-10} cm
      c) 0.529×10^{-6} cm   d) 0.529×10^{-12} cm

5. Which of the following particle having same kinetic energy, would have the maximum de-Broglie wave length

   a) α-particle   b) proton   c) β-particle   d) neutron

6. If the energy of an electron in the second Bohr orbit of H-atom is -E, what is the energy of the electron in the Bohr's first orbit?

   a) 2E   b) -4E   c) -2E   d) 4E

7. The energy of electron in an atom is given by $E_n =$

   a) $-\dfrac{4\pi^2 me^4}{n^2 h^2}$ b) $-\dfrac{2\pi^2 me^2}{n^2 h^2}$ c) $-\dfrac{2\pi^2 me^4}{n^2 h^2}$ d) $-\dfrac{2\pi\, me^4}{n^2 h^2}$

8. The bond order of oxygen molecule is

   a) 2.5   b) 1   c) 3   d) 2

9. The hybridisation in SF_6 molecule is

   a) sp^3 b) $sp^3 d^2$ c) $sp^3 d$ d) $sp^3 d^3$

10. The intramolecular hydrogen bonding is present in

    a) o-nitrophenol   b) m-nitro phenol   c) p-nitrophenol   d) None

B.   Answer in one or two sentences

11. What do you understand by the dual character of matter?

12. State Heisenberg's uncertainty principle.

13. What is the significance of negative electronic energy?

14. Define an orbital.

15. What are molecular orbitals?

16. Why He_2 is not formed?

17. What is bond order?

18. Define hybridisation.

C.   Answer not exceeding 60 words

19. Discuss the Davisson and Germer experiment.

20. Derive de-Broglie's equation. What is its significance?

21. Discuss the shapes of s, p and d orbitals.

22. Briefly explain Molecular Orbital Theory.

23. Explain the formation of O_2 molecule by molecular orbital theory.

Summary

This chapter explains the dual nature of matter. de-Broglie equation is derived and its significance is discussed. Heisenberg uncertainty principle is explained. Schrodinger's wave equation and wave functions are explained.

Molecular orbital theory and its application to certain homo diatomic and hetero diatomic molecules are discussed. The concept of hybridisation of atomic orbitals and its applications are discussed. Different types of forces exist between molecules are explained.

References

1) Theoretical principles of Inorganic Chemistry-G.S.Yanker, 9th Edn-1993.

2) Selected topics in Inorganic Chemistry - V.Mallik, G.D.Tuli and R.D.Madan, 6th Ed. - 2002.

3) Concise Inorganic Chemistry - J.D.Lec, 3rd Ed. - 1977 and 5th Ed. 2002.

2. PERIODIC CLASSIFICATION - II

Learning Objectives

- *To recall the periodic properties Atomic/Ionic radii, Ionisation Energy, Electron affinity and electronegativity.*

- *To learn the calculation of atomic and ionic radii using different parameters.*

- *To study the methods of determination of ionisation potential and differentiate I, II and III ionisation potential.*

- *To know how to explain the factors affecting ionisation potential with specific examples.*

- *To understand the methods to determine the electron affinity and factors affecting electron affinity.*

- *To analyse the various scales of electronegativity values using simple relations.*

2.1 REVIEW OF PERIODIC PROPERTIES

Repetition of properties of elements at regular intervals in the periodic table is called periodicity in properties. The periodicity is mostly due to similar outermost electronic configuration of the elements. Some of the properties are briefly reviewed.

2.1.1 Atomic and Ionic radii

Atomic or Ionic radius is generally defined as the distance between the centre of the nucleus and the outermost shell of electrons in an atom or ion.

As we move from left to right across a period, there is regular decrease in atomic and ionic radii of the elements. This is due to the increase in the nuclear charge and the additive electrons are added to the same electronic level. On moving down a group both atomic and ionic radii increase with increasing atomic number. The increase in size is due to introduction of extra energy shells which outweigh the effect of increased nuclear charge.

2.1.2 Ionisation Energy (Ionisation Potential)

The energy required to remove the most loosely bound electron from an isolated atom in the gaseous state in known as Ionisation Energy.

$$\text{Atom}_{(g)} \xrightarrow{\text{Energy}} \text{Positive Ion}_{(g)} + \text{Electron}$$
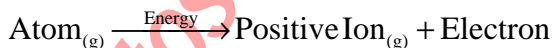
The ionisation energy of an atom depends on the following factors (i) size of the atom (ii) charge on the nucleus (iii) screening effect of inner electrons (iv) penetration effect of electrons (v) effect of half-filled and completely filled sublevels.

In a period, the value of ionisation potential increases from left to right with breaks where the atoms have somewhat stable configurations. In a group, the ionisation potential decreases from top to bottom.

2.1.3 Electron affinity

Electron affinity or electron gain enthalpy is the amount of energy released when an isolated gaseous atom accepts an electron to form a monovalent gaseous anion.

$$\text{Atom}_{(g)} + \text{Electron} \rightarrow \text{Anion}_{(g)} + \text{Energy}$$
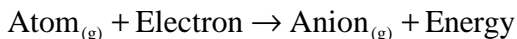
Electron gain enthalpies generally increase on moving from left to right in a period. Electron gain enthalpies generally decrease on moving down the group.

2.1.4   Electronegativity

Electronegativity may be defined as the relative tendency of an atom in a molecule to attract the shared pair of electrons towards itself.

In a period, electronegativity increases on moving from left to right. This is due to the reason that the nuclear charge increases whereas atomic radius decreases. In a group, electronegativity decreases on moving down the group. This is due to the effect of the increased atomic radius.

2.1.5   Anomalous periodic properties

A few irregularities that are seen in the increasing values of ionisation potential along a period can be explained on the basis of the concept of half-filled and completely filled orbitals.

2.2   CALCULATION OF ATOMIC RADIUS (COVALENT RADIUS)

Atomic radius is the distance from the centre of the nucleus to the point where the electron density is effectively zero.

a.   Homonuclear diatomic molecules

In case of homonuclear diatomic molecules of A_2 type (e.g. F_2, Cl_2, Br_2, I_2 ... etc.) the bond length, $d(A-A)$ is given by

$$d(A - A) = r(A) + r(A)$$

$$d(A - A) = 2 \times r(A)$$

$$r(A) = \frac{d(A-A)}{2}$$

The above equation shows that in the case of homonuclear diatomic molecule of A_2 type, the covalent radius of an atom A, $r(A)$ is equal to one half of the inter-nuclear distance, $d(A-A)$. Therefore, the covalent radius of an atom in a homonuclear diatomic molecule can be obtained by dividing the internuclear distance by two.

Example

1. Cl_2 molecule

The value of Cl–Cl bond distance as found experimentally is 1.98Å. Thus

$$r(Cl) = \frac{d(Cl-Cl)}{2} = \frac{1.98}{2} = 0.99\text{Å}$$

2. Diamond

The value of d(C–C) distance as found experimentally in a variety of saturated hydrocarbons is 1.54Å.

Thus $$r(C) = \frac{d(C-C)}{2} = \frac{1.54}{2} = 0.77\text{Å}$$

b. Heteronuclear diatomic molecule

In case of heteronuclear diatomic molecule of AB type, bond length d(A – B) is given by

$$d(A - B) = r(A) + r(B)$$

r(A) and r(B) are the covalent radii of A and B atoms.

Example

i) CCl_4 molecule

The experimental value of d(C – Cl) is 1.76 Å

Thus $$d(C–Cl) = r(C) + r(Cl)$$
$$r(C) = d(C – Cl) – r(Cl)$$
$$= 1.76 – r(Cl)$$

Thus the covalent radius of carbon atom can be calculated by subtracting the covalent radius of Cl atom from d(C–Cl) bond length. The covalent radius of Cl atom can also be obtained, provided that covalent radius of C atom is known.

ii) SiC

The experimental value of d(Si-C) is 1.93 Å. Thus,

$$d(Si – C) = r(Si) + r(C)$$

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$$r(Si) \quad = \quad d(Si - C) - r(C)$$
$$= \quad 1.93 - r(C)$$
$$= \quad 1.93 - 0.77 \quad [\because r(C) = 0.77 \text{ Å}]$$
$$= \quad 1.16 \text{ Å}$$

The experimental values of covalent bond length for some common homonuclear diatomic molecules are given below.

	Molecule	Bond	Bond length (Å)
i)	H_2	H–H	0.74
ii)	F_2	F–F	1.44
iii)	Cl_2	Cl–Cl	1.98
iv)	Br_2	Br–Br	2.28
v)	$H_3C\text{-}CH_3$	C–C	1.54

2.2.1 Calculation of ionic radii

Pauling's Method

Pauling has calculated the radii of the ions on the basis of the observed internuclear distances in four crystals namely NaF, KCl, RbBr and CsI. In each ionic crystal the cations and anions are isoelectronic with inert gas configuration.

NaF crystal   : Na^+ - 2, 8 ⎫
                         F^- - 2, 8 ⎬   Ne type configuration

KCl crystal   : K^+ - 2, 8, 8 ⎫
                        Cl^- - 2, 8, 8 ⎬   Ar type configuration
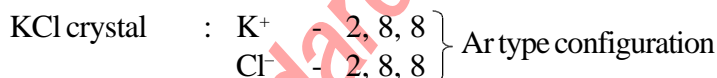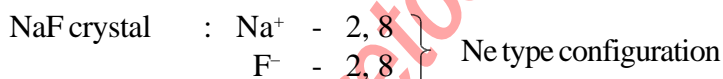
Further the following two assumptions are made to assign the ionic radii.

i) The cations and anions of an ionic crystal are assumed to be in contact with each other and hence the sum of their radii will be equal to the inter nuclear distance between them.

$$r(C^+) + r(A^-) = d(C^+ - A^-) \tag{1}$$

where

$r(C^+)$ -   radius of cation, C^+

$r(A^-)$ -   radius of anion, A^-

d(C^+–A^-) - internuclear distance between C^+ and A^- ions in C^+A^- ionic crystal

ii) For a given noble gas configuration, the radius of an ion is inversely proportional to its effective nuclear charge. i.e.

$$r(C^+) \quad \alpha \quad \frac{1}{Z^*(C^+)} \tag{2}$$

$$r(A^-) \quad \alpha \quad \frac{1}{Z^*(A^-)} \tag{3}$$

where,

$Z^*(C^+)$ & $Z^*(A^-)$ are the effective nuclear charges of cation (C^+) and anion (A^-) respectively. On combining (2) & (3)

$$\frac{r(C^+)}{r(A^-)} \quad = \quad \frac{Z^*(A^-)}{Z^*(C^+)} \tag{4}$$

Hence the above two equations (1) & (4) can be used to evaluate the values of r(C^+) and r(A^-) provided that the values of d(C^+–A^-), $Z^*(C^+)$ and $Z^*(A^-)$ are known.

Slater rules

The value of screening constant (S) and effective nuclear charge (Z^*) can be calculated by using Slater's rules. According to these rules the value of "S" for a given electron is estimated as follows.

i) Write down the complete electronic configuration of the element and divide the electrons into the following orbital groups starting from the inside of the atom.

(1s) : (2s, 2p) : (3s, 3p) : (3d) : (4s, 4p) :

(4d) : (4f) : (5s, 5p) : (6s, 6p) ....etc.

ii) Select the electron for which the value of S is to be calculated. For this calculation add up the contributions to S for the other electrons according to the following rules.

Type of electron	Contribution to S for each electron of this type
i) All electrons in groups outside the electron chosen	0
ii) All other electrons in the same group as the chosen one (n)	0.35 (or 0.30 for 1s electron)
iii) All electrons in shell immediately inside (n–1)	0.85
iv) All electrons further inside	1.00

Calculation of effective nuclear charge (Z*)

Example 1

Calculate the effective nuclear charge experienced by the 4s electron in potassium atom.

Solution

The electronic configuration of K atom is

$K_{19} = (1s^2) (2s^2 2p^6) (3s^2 3p^6) 4s^1$
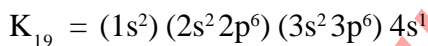
Effective nuclear charge $(Z^*) = Z - S$

$Z^* = 19 - [(0.85 \times$ No. of electrons in $(n-1)^{th}$ shell) $+ (1.00$ total number of electrons in the inner shells)]

$= 19 - [0.85 \times (8) + (1.00 \times 10)]$

$Z^* = 2.20$

Example 2

Calculate the effective nuclear charge of the last electron in an atom whose configuration is $1s^2 2s^2 2p^6 3s^2 3p^5$

$Z = 17$

$Z^* = Z - S$

$= 17 - [(0.35 \times$ No. of other electrons in n^{th} shell)
$+ (0.85 \times$ No. of electrons in $(n-1)^{th}$ shell)
$+ (1.00 \times$ total number of electrons in the inner shells)]

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$$= 17 - [(0.35 \times 6) + (0.85 \times 8) + (1 \times 2)]$$
$$= 17 - 10.9 = 6.1$$

Calculation of ionic radii

Example

Calculate the ionic radii of K^+ and Cl^- ions in KCl crystal. The internuclear distance between K^+ an Cl^- ions are found to be 3.14Å.

Solution

$$r(K^+) + r(Cl^-) = d(K^+–Cl^-) = 3.14 \text{ Å} \qquad (1)$$

K^+ and Cl^- ions have Ar (Z=18) type configuration. The effective nuclear charge for K^+ and Cl^- can be calculated as follows.

$$
\begin{array}{lll}
K^+ \quad = & (1s^2) & (2s^2\,2p^6) \qquad (3s^2\,3p^6) \\
& \text{innershell} & (n-1)^{th} \text{ shell} \qquad n^{th} \text{ shell}
\end{array}
$$

$$
\begin{aligned}
Z^*(K^+) \quad &= \quad Z - S \\
&= \quad 19 - [(0.35 \times 7) + (0.85 \times 8) + (1 \times 2)] \\
&= \quad 19 - 11.25 = 7.75
\end{aligned}
$$

$$
\begin{aligned}
Z^*(Cl^-) \quad &= \quad 17 - [(0.35 \times 7) + (0.85 \times 8) + (1 \times 2)] \\
&= \quad 17 - 11.25 = 5.75
\end{aligned}
$$

$$\therefore \quad \frac{r(K^+)}{r(Cl^-)} = \frac{Z^*(Cl^-)}{Z^*(K^+)} = \frac{5.75}{7.75} = 0.74$$

$$\therefore \quad r(K^+) = 0.74\, r(Cl^-) \qquad (2)$$

Substitute (2) in (1)

$$0.74\, r(Cl^-) + r(Cl^-) = 3.14 \text{ Å} \qquad (3)$$
$$1.74\, r(Cl^-) = 3.14 \text{ Å}$$

$$r(Cl^-) = \frac{3.14\text{Å}}{1.74} = 1.81\text{Å}$$

From (2)

$$r(K^+) = 0.74\, r(Cl^-)$$
$$= 0.74 \times 1.81\ \text{Å}$$
$$= 1.33\ \text{Å}$$
$$r(K^+) = 1.33\ \text{Å}$$
$$r(Cl^-) = 1.81\ \text{Å}$$

Ionisation potential

Ionisation energy of an element is defined as the amount of energy required to remove the most loosely bound electron from isolated neutral gaseous atom in its lowest energy state. The process is represented as

$$M_{(g)} + \text{Energy supplied} \xrightarrow{\ I_1\ } M^+_{(g)} + e^-$$
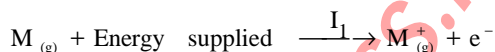
Ionisation energy is measured in electron volts per atom (eV/atom), kilo calories per mole (kcal/mole) or kilo joules per mole (kJ/mole).

Successive ionisation potentials

In addition to first ionisation potential (I_1) defined above, second, third. etc. ionisation potentials are also known. Second ionisation potential (I_2) is the energy required to remove one more electron from the gaseous cation, $M^+_{(g)}$ to get the doubly positively charged gaseous cation, $M^{2+}(g)$, i.e.,

$$M^+_{(g)} + I_2 \rightarrow M^{2+}_{(g)} + e^-$$
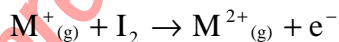
Similarly, third ionisation potential (I_3) is the energy required to remove still one more electron from $M^{2+}_{(g)}$ cation to get $M^{3+}_{(g)}$ cation, i.e.

$$M^{2+}_{(g)} + I_3 \rightarrow M^{3+}_{(g)} + e^-$$
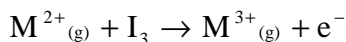
Similarly ionisation potentials of higher and higher grades are also known.

Each successive ionization potential or energy is greater than the previous one, since the electron must be removed against the net positive charge on the ion.

Factors governing ionization energy. The ionization energy depends upon the following factors:

(a) Size of atom or ion. The ionization energy decreases with the increasing size of atom. The larger the size of atom, lesser is the ionization energy. This is due to the fact that electrons are tightly held in smaller atoms whereas in large atoms, electrons are held quite loose, i.e., lesser energy is required for removal of electrons from larger atoms than the smaller one. Hence ionization energy is lower for larger atoms and higher for smaller atoms.

Example 1

The I.E of Be (At. No.4) is greater than that of Li (At. No.3) because the nuclear charge of Be (Z=4) is greater than Li(Z=3). Higher the nuclear charge, greater would be the force of attraction between nucleus and outermost electron. Hence, the first I.E. of Be is than that of Li.

Example 2

The I.E. of Be is more than that of B though the nuclear charge of boron atom (Z=5) is greater than that of beryllium atom (Z = 4). This can be explained as follows:

Boron atom (Z = 5; $1s^2 \, 2s^2 \, 2p_x^{\,1} \, 2p_y^{\,0} \, 2p_z^{\,0}$) is having one unpaired electron in the 2p-subshell. Be-atom ($Z = 4$; $1s^2 \, 2s^2$) is having paired electrons in the 2s-subshell.

As the fully filled 2s-subshell in Be-atom is more stable than B-atom due to symmetry, more energy would be needed to remove an electron from Be-atom. Hence, Be has high I. E.

3. The I.E. of carbon (At. No.6) more than that of boron (At. No.5)

Reason: Carbon (Z = 6; $1s^2 \, 2s^2 \, 2p_x^{\,1} \, 2p_y^{\,1} 2p_z^{\,0}$) is having more nuclear charge than boron (Z = 5; $1s^2 \, 2s^2 \, 2p_x^{\,1} \, 2p_y^{\,0} 2p_z^{\,0}$). In both the cases, one has to remove electron from same 2p-subshell. Carbon is having more nuclear charge than boron. Therefore the nucleus of carbon, attracts the outer 2p-electron more firmly than does boron. Thus, first I.E. of carbon would be more than that of boron.

(b) Magnitude of nuclear charge. The higher the nuclear charge of protons in the nucleus, the higher is the ionization energy. Because of the higher

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nuclear charge, the electrons are bound with more force and hence higher energy will be required for their removal. For instance, magnesium has higher nuclear charge (12 protons) as compared to sodium (11 protons). Hence ionization energy in case of magnesium is higher as compared to sodium.

Similarly the I.E. of fluorine is more than that of oxygen. It can be explained as follows.

(i) F (Z = 9; $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$) is having more nuclear charge than oxygen (Z = 8; $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$). In both the cases, the electron has to be removed from the same 2p-subshell. As fluorine is having more nuclear charge than oxygen, it means that the nucleus of fluorine will attract the outer 2p-electrons more firmly than oxygen. Hence, first I.E. of fluorine would be more than that of oxygen.

(c) Effect of number of electrons in the inner shells. (Screening or shielding effect). The attractive force exerted by the nucleus on the most loosely bound electron is atleast partially counterbalanced by the repulsive forces exerted by the electrons present in the inner shells. The electron to be removed is thus shielded from the nucleus by the electrons in the inner shell. Thus, the electron in the valence shell experiences less attraction from the nucleus. Hence the ionisation energy will be low. This is another reason why ionization energy decreases in moving down a group.

(d) Effect of shape of orbital. The shape of orbital also influences the ionization potential. As s-electrons remain closer to the nucleus than p-,d-, and f-electrons of the same valence shell, the ionization energy decreases in the order given below:

$$s > p > d > f$$

For instance, the first ionization energy of aluminium is lower than that of magnesium. The electronic configuration of magnesium is [Ne]$3s^2$ and that of aluminium is [Ne] $3s^2 3p^1$. Thus, one has to remove 3p-electron in case of aluminium and 3s electron in the case of magnesium. But it is easier to remove the p electron than the s-electron. Thus, the first ionization energy of aluminium is lower than that of magnesium.

(e) Effect of arrangement of electrons. The more stable the electronic arrangement, the greater is the ionization energy. As the noble gases have the stablest electronic arrangements, they show maximum ionization energy.

Example

The I.E of Ne is greater than that of F. It can be explained as follows:

The nuclear charge of Ne $(Z = 10)$ is more than that of F $(Z = 9)$. Greater the nuclear charge, greater would be the force of attraction between nucleus and outermost electron. Hence, the first I.E. of neon would be greater than that of fluorine.

Electron Affinity or Electron gain enthalpy (E.A.)

The electron affinity of an element may be defined as amount of energy which is released when an extra electron enters the valence orbital of an isolated neutral atom to form a negative ion.

$$\text{Atom}_{(g)} + \text{Electron}_{(g)} \rightarrow \text{Negative ion}_{(g)} + \text{Energy}$$
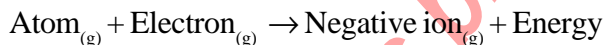
The greater the energy released in the process of taking up the extra electron, the greater will be the electron affinity. Thus, ionisation potential measures the tendency of an atom to change into a cation $(M \rightarrow M^+ + 1e^-)$ whereas the electron affinity measures the tendency of an atom to change into anion $(X + e^- \rightarrow X^-)$.

Successive Electron Affinities. As more than one electron can be introduced in an atom, it is called second electron affinity for the addition of two electrons and so on. The first E. A. of active non metals is positive (exothermic) while the second E. A. even for the formation of oxide or sulphide ion is negative (endothermic). For example, the overall E.A. for the formation of oxide or sulphide ions has been found to be endothermic to the extent of 640 and 390 kJ mol^{-1} respectively.

$$X^-_{(g)} + e^- + \text{energy} \rightarrow X^{2-}_{(g)}$$
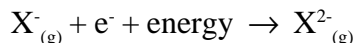
It is interesting to note that the electron affinity of elements having a $d^{10} s^2$ configuration has been found to be negative. This is so due to the accommodation of the electron in the higher p-orbital (Zn = -87 kJ mol^{-1}, Cd = -56 kJ mol^{-1}).

Elements of group 17 possess high electron affinity. The reason for this is that by picking up an electron halogens attain the stable noble gas electronic configuration.

The electron affinity is expressed in kJ mol^{-1}.

Change of Electron Affinity along a Group. On moving down a group, the size of atom increases significantly and hence, the effective nuclear attraction for the electron decreases. Consequently the atom will possess less tendency to attract additional electrons towards itself. It means that electron affinity would decrease as we move down a group. In case of halogens the decrease in electron affinity from chlorine to iodine is due to steady increase in atomic radii from chlorine to iodine.

On moving down a group the electron affinity decreases. Thus, the electron affinity of Cl should be less than F. But actually the electron affinity of F $(320 \text{ kJ mol}^{-1})$ is less than Cl $(348 \text{ kJ mol}^{-1})$. The reason for this is probably due to small size of fluorine atom. The addition of an extra electron produces high electron density which increases strong electron-electron repulsion. The repulsive forces between electrons results in low electron affinity.

Electron affinities of noble gases are zero. As these atoms possess ns^2np^6 configuration in their valence shells, these are stablest atoms and there are no chances for the addition of an extra electron. Thus, the electron affinities of noble gases are zero.

Electron affinities of beryllium and nitrogen are almost zero. This may be due to the extra stability of the completed 2s-orbital in beryllium and of the exactly half-filled p-orbital in nitrogen. As these are stable electronic configurations, they do not have tendency to accept electrons and therefore, the electron affinities for beryllium and nitrogen are zero.

Change of Electron Affinity along a Period. On moving across a period, the size of atoms decreases and nuclear charge increases. Both these factors favour an increase in force of attraction exerted by the nucleus on the electrons. Consequently, the atom will possess a greater tendency to attract the additional electron, i.e., its electronic affinity would increase as we move from left to right. Due to this reason electron affinities of non-metals are high whereas those of metals are low.

Of all the metals, the E.A. of gold is comparatively high $(222.7 \text{ kJ mol}^{-1})$. This value may be attributed to the higher effective nuclear charge and poor shielding of the nucleus by d electrons.

Factors affecting electron affinity

(1) Atomic size

$$\text{Electron affinity } \alpha \frac{1}{\text{Size of atom}}$$

Smaller the size of an atom, greater is its electron affinity. As the size of atom increases, the effective nuclear charge decreases or the nuclear attraction for adding electron decreases. Consequently, atom will have less tendency to attract additional electron towards itself. Therefore.

Electron affinity α Effective nuclear charge.

In general, electron affinity decreases in going down the group and increases in going from left to right across the period. On moving down the group atomic size increases and on going from left to right in a period atomic size decreases.

(2) Shielding or Screening Effect

$$\text{Electron affinity } \alpha \frac{1}{\text{Shielding effect}}$$

Electronic energy state, lying between nucleus and outermost state hinder the nuclear attraction for incoming electron. Therefore, greater the number of inner lying state, less will be the electron affinity.

(3) Electronic Configuration - The electronic configurations of elements influence their electron affinities to a considerable extent.

Electron affinities of inert gases are zero. This is because their atoms have stable $ns^2 np^6$ configuration in their valence shell and there is no possibility for addition of an extra electron.

Electron affinity of beryllium, magnesium and calcium is practically zero. This is attributed to extra stability of the fully completed s-orbitals in them. Thus, if an atom has fully filled or half filled orbitals, its electron affinity will be low.

Example 1

The electron affinities of Be, Mg and N are almost zero because both Be $(Z = 4; 1s^2 2s^2)$ and Mg $(Z = 12; 1s^2 2s^2 2p^6 3s^2)$ are having s orbital fully

filled in their valence shell. Fully filled orbitals are most stable due to symmetry. Therefore, these elements would be having least tendency to accept electron. Hence, Be and Mg would be having zero electron affinity.

N (Z = 7 ; $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$) is having half filled 2p-subshell. Half filled sub shells are most stable due to symmetry (Hund's rule). Thus, nitrogen is having least tendency to accept electron. Hence, nitrogen is having almost zero electron affinity.

Example 2

Electron affinity of fluorine is less than that of chlorine. Although the electron affinity of elements decreases down the group, yet fluorine is having less electron affinity than chlorine because the size of F-atom (0.71 Å) is very small and has only two shells, i.e., n = 1, 2 ($_9F = 1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$).

i) Because of small size of fluorine atom the 2p-subshell becomes compact. There occurs repulsion among electrons of the valence shell and also with electron to be added. This repulsion is responsible for less tendency of F-atom to accept electron.

ii) Because of small size of fluorine there occurs large crowding of electrons around the nucleus. This crowding is able to screen the nucleus. Because of this, effective nuclear charge gets decreased. Thus, the electron is having less attraction during addition. Hence electron affinity gets decreased.

2.5 ELECTRONEGATIVITY SCALES

Electronegativity scale is an arbitary scale. They are based on various types of experimental data like bond energy, dipole moment, ionisation potential and electron affinity. Most commonly used scales are

1. Pauling's scale
2. Mulliken's scale
3. Sanderson's scale
4. Alfred and Rochow's scale

Pauling's scale (1932)

This scale is based on an empirical relation between the energy of a bond and the electronegativities of bonded atoms.

Consider a bond A-B between two dissimilar atoms A and B of a molecule AB. Let the bond energies of A-A, B-B and A-B bonds be represented as E_{A-A}, E_{B-B} and E_{A-B} respectively. It may be seen that the bond dissociation energy of A-B is almost higher than the geometric mean of the bond dissociation energies of A-A and B-B bonds i.e.,

$$E_{A-B} > \sqrt{E_{A-A} \times E_{B-B}}$$

Their difference (Δ) is related to the difference in the electronegativities of A and B according to the following equation

$$\Delta = E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}$$
$$= (X_A - X_B)^2$$
(or)
$$0.208 \sqrt{\Delta} = X_A - X_B$$

Here, X_A and X_B are the electronegativities of A and B respectively.

The factor 0.208 arises from the conversion of Kcals to electron volt.

Considering arbitarily the electronegativity of hydrogen to be 2.1, Pauling calculated electronegativities of other elements with the help of this equation.

Disadvantage of Pauling scale

The disadvantage of Pauling's scale is that bond energies are not known with any degree of accuracy for many solid elements.

Problem

Calculate the electronegativity of chlorine from the following data

$E_{H-H} = 104$ K cal mol^{-1} ; $E_{Cl-Cl} = 36$ K cal mol^{-1}

$E_{H-Cl} = 134$ K cal mol^{-1}

According to Pauling's equation

$$\Delta = E_{HCl} - \sqrt{E_{H-H} \times E_{Cl-Cl}}$$
$$\Delta = 134 - \sqrt{104 \times 36}$$
$$= 134 - 61.18 = 72.82$$

$$0.208\sqrt{\Delta} \quad = \quad X_{Cl} - X_H$$

$$\Rightarrow \quad X_{Cl} - X_H \quad = \quad 0.208\sqrt{72.82}$$

$$= \quad 1.77$$

$$X_{Cl} - 2.1 \quad = \quad 1.77 \qquad [\because X_H = 2.1]$$

$$X_{Cl} \quad = \quad 1.77 + 2.1$$

$$= \quad 3.87$$

2. Mulliken's Scale

In 1934, Mulliken suggested an alternative approach to electronegativity based on ionization energy and electron affinity of an atom. According to this method electronegativity could be regarded as the average of the ionization energy and electron affinity of an atom

$$\text{Electronegativity} = \frac{I.E. + E.A}{2}$$

Mulliken used ionisation energy and electron affinity values measured in electron volts and values were found to be 2.8 times higher than Pauling values.

The values of ionisation energy and electron affinity are measured in kJ mol^{-1} and 1eV =96.48 kJ mol^{-1}.

Therefore the commonly accepted Pauling values are more nearly obtained by

$$\text{Electronegativity} = \frac{I.E. + E.A}{2 \times 2.8 \times 96.48} = \frac{I.E. + E.A}{540}$$

This method has an ordinary theoretical basis and also has advantage that different values can be obtained for different oxidation states of the same element.

Disadvantage

Although Mulliken's scale is less empirical than Pauling Scale, yet it suffers from a serious disadvantage that electron affinities with the exception of a few elements are not reliably known.

Problem

Calculate the electronegativity values of fluorine and chlorine on Mulliken's scale, given that (Ionisation potential) F = 17.4 eV/atom (Electron affinity) F = 3.62 ev/atom, $(IP)_{Cl}$ = 13.0 ev/atom and $(EA)_{Cl}$ = 4.0 ev

Electronegativity of fluorine $= \dfrac{(IP)_F + (EA)_F}{2 \times 2.8}$

$= \dfrac{17.4 + 3.62}{5.6} = \dfrac{21.02}{5.6} = 3.75$

Electronegativity of chlorine $= \dfrac{(IP)_{Cl} + (EA)_{Cl}}{2 \times 2.8}$

$= \dfrac{13.0 + 4.0}{5.6} = \dfrac{17}{5.6} = 3.03$

Applications of electronegativity

1) Nature of bond

The concept of electronegativity can be used to predict whether the bond between similar or dissimilar atoms is non-polar covalent bond, polar covalent bond (or) ionic bond.

i) When $X_A = X_B$, i.e. $X_A - X_B = 0$, then A-B bond is non polar covalent bond or simply covalent bond and is represented as A-B. eg. H-H bond in H_2 molecule is a covalent bond and is represented as H-H bond.

ii) When X_A is slightly greater than X_B, i.e. $X_A - X_B$ is small, the A-B bond is polar covalent bond and is represented as $A^{\delta-}-B^{\delta+}$. e.g. The O-H bonds in H_2O molecule are polar covalent bonds and are represented as $O^{\delta-}-H^{\delta+}$, since $X_O > X_H$ and $X_O - X_H$ is small.

iii) When $X_A \gg X_B$, i.e., $X_A - X_B$ is very large, A-B bond is more ionic or polar bond and is represented as A^--B^+, Since $X_A \gg X_B$. For example Na-Cl bond in Na Cl molecule is an ionic bond and is represented as Na^+Cl^- (Here Cl = A and Na = B).

2. Percentage of ionic character in a polar covalent bond

Pauling estimated the percentage of ionic character in various $A^{\delta-}$–$B^{\delta+}$ polar covalent bonds from known $(X_A - X_B)$ values and has derived the following conclusions :

(i)   When $(X_A - X_B) = 1.7$, the amount of ionic character in $A^{\delta-}$–$B^{\delta+}$ bond is 50% and that of covalent character is also 50%. Thus A-B bond is 50% ionic and 50% covalent.

(ii)   When $(X_A - X_B) < 1.7$, the amount of ionic character in $A^{\delta-}$–$B^{\delta+}$ bond is less than 50% and that of covalent character is more than 50%. Thus $A^{\delta-}$–$B^{\delta+}$ bond is predominantly covalent and hence is represented as A–B.

(iii) When $(X_A - X_B) > 1.7$, the amount of ionic character in $A^{\delta-}$–$B^{\delta+}$ bond is more than 50% and that of covalent character is less than 50%. Hence $A^{\delta-}$–$B^{\delta+}$ bond is predominantly ionic and hence is represented as A^-B^+.

SELF EVALUATION

A. Choose the correct answer

1. The value of C-C distance found experimentally in a saturated hydrocarbon is

    a) 1.34Å   b) 1.36Å   c) 1.54Å   d) 1.56Å

2. On moving down the group, the radius of an ion

    a) Decreases   b) Increases   c) No change   d)None of these

3. Effective nuclear charge (Z^*) can be calculated by using the formula

    a) $Z^* = Z - S$ b) $Z^* = Z + S$ c) $Z^* = S - Z$ d) $Z = Z^* - S$

4. Pick the correct statement

    a) Carbon having more nuclear charge than boron

    b) The size of carbon atoms is larger than boron

    c) Carbon forms electron deficient compounds

    d) Carbon forms ionic compounds

5. Comparing the ionisation energy of fluorine with carbon, fluorine has

    a) higher ionisation energy   b) lower ionisation energy

    c) same ionisation energy   c) none of these

6. Among the following which has the maximum ionisation energy

    a) Alkali elements   b) Alkaline elements

    c) Halogens   c) Noble gases

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7. The electron affinity of an atom
   a) directly proportional to its size   b) inversely proportional to its size
   c) is independent of its size   d) none of these
8. Among the following which has higher electron affinity value
   a) Fluorine   b) Chlorine   c) Bromine   d) Iodine
9. The scale which is based on an empirical relation between the energy of a
   bond and the electronegativities of bonded atoms is
   a) Pauling scale   b) Mulliken's scale
   c) Sanderson's scale   d) Alfred and Rochow's scale
10. Electron affinity is expressed in
    a) kJ   b) J   c) kJ mol   d) kJ mol^{-1}
11. The bond length of Cl_2 molecule is
    a) 0.74   b) 1.44   c) 1.98   d) 2.28
12. The order of ionization energy
    a) s < p < d < f   b) s > p > d > f   c) s > d > p > f   d) s<d<p<f
13. Across the period, electron affinity
    a) decreases   b) increases
    c) decrease and the increases   d) increase and then decreases
14. Noble gases have _____ electron affinity
    a) High   b) Low   c) Zero   d) Very low
15. When $X_A >> X_B$, A–B bond is
    a) polar covalent   b) non-polar covalent   c) Ionic   d) metallic

B.   Answer in one or two sentences

16. Arrange the following species in the increasing order of size
    a) O^{2-}, F^-, Mg^{2+}, Na^+
    b)   F, F^-
    c)   N, O
    d) Fe^{2+}, Fe, Fe^{3+}
    e) Na^+, Cl^-, Na, Cl
    f)   I, I^+, I^-
17. Arrange the following elements in the increasing order of their first ionisation
    potentials, give proper explanation for your answer.
    a)   Li, Be, B   b) N, O, F   c) C, N, O, F

18. Which element of the following has the highest ionisation potential?
    Na, Cl, Si and Ar.
19. Describe with reasons which atom in each of the following pairs has higher ionisation energy?
    a)   Mg and Al   b) B and Al   c) Al and Si
20. Which element of the following pairs of elements has higher ionisation energy? Justify your answer
    a)   K or Ca   b) Be or B   c)   I or Ba   d) F or Cl   e) N or O
21. Which element of the following groups of elements has smallest ionisation energy. Justify your answer.
    a) Ca or Be   b) Ca or K   c) Cl or I   d) Be, B, C
22. Answer the following questions
    a) Which element has the most positive value of electron affinity?
    b) Which element has low electronegativity?
23. Mention the disadvantage of Pauling and Mulliken scale.
24. Why EA of fluorine is less than that of chlorine?
C.   Answer not exceeding 60 words
25. How is atomic radii calculated from covalent bond length?
26. Explain Pauling method to determine ionic radii.
27. Explain the variation of IE along the group and period.
28. Explain the various factors that affect electron affinity.
29. How electronegativity values help to find out the nature of bonding between atoms?

Summary

    The periodicity in properties of elements are reviewed briefly. Atomic and ionic radii of molecules are calculated by using simple examples. The factors governing ionisation potential are explained with specific examples. The factors affecting electron affinity are discussed briefly. The different scales of electronegativity values are explained in detail.

References

1)   Concise Inorganic Chemistry, J.D. Lee, 3rd Edition, 1977.
2)   Selected Topics in Inorganic Chemistry, Wakid V.Malik, G.D.Tuli, R.D.Madan 7th edition, 2001.

3. p - BLOCK ELEMENTS

Learning Objectives

- ✎ *Understand the general trends in the chemistry of elements of groups 13,14,15,16,17 and 18.*

- ✎ *Understands the preparation, properties and the uses of potash alum.*

- ✎ *Knowledge about know about silicones.*

- ✎ *Understand the extraction of lead, properties and the uses of lead.*

- ✎ *Understands the preparation, properties, uses and the structure of halides, oxides, oxyacids and hydrides of phosphorus.*

- ✎ *Recognize the anomalous behavior of Fluorine.*

- ✎ *Understand about interhalogen compounds.*

- ✎ *Know about the isolation of noble gases.*

- ✎ *Recognises the preparation, properties and the structure of xenon compounds.*

- ✎ *Appreciates the application of noble gases.*

PERIODIC TABLE

	13	14	15	16	17	18	
			ns^2np^{1-5}				
						He	①
d	B	C	N	O	F	Ne	②
12	Al	Si	P	S	Cl	Ar	③
	Ga	Ge	As	Se	Br	Kr	④
	In	Sn	Sb	Te	I	Xe	⑤
	Tl	Pb	Bi	Po	At	Rn	⑥
							⑦
	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6	

13 ⟶ Boron group
14 ⟶ Carbon group
15 ⟶ Nitrogen group
16 ⟶ Oxygen group
17 ⟶ Halogen family
18 ⟶ Noble gases

p-block elements grouped with s-block elements are called as main group elements or representative elements. There are 44 main group elements. p–block elements occupy groups 13-18 of the periodic table including inert gases. p-block elements play dominant part in all natural processes. Aluminium plays vital role in aircraft and as conductors. Carbon is the backbone of all organic compounds. Silicon chips play a vital part in computers. Nitrogen acts as a building block of life. Molecular oxygen is a cell fuel.

General characteristics of p-block elements

1. The general electronic configuration of p-block elements is $ns^2 np^{1-6}$.

2. These elements include metals and non-metals with a few semi metals (Metalloids)

3. Most of them form covalent compounds.

4. These elements possess relatively higher ionisation energy and the value tends to increase along the period but decrease down the group.

5. Most of the elements show negative (except some metals) as well as positive oxidation states (except Fluorine).

6. One of the familiar characteristic of p-block elements is to show inert pair effect i.e. the tendency of being less availability for ns electron in bonding. The inert pair effect increases down the group with the increase in atomic number.

Group 13 elements – The Boron family

The group 13(IIIA) elements are Boron, aluminium, gallium, indium and thallium.

➢ Boron is a relatively rare element, accounting for only about 0.001% of the earth's crust by mass.

➢ Aluminium is the most important of 13th group elements.

➢ Gallium is remarkable for its unusually low melting point (29.7°C) and therefore generally exist as a liquid at room temperature. Its most important use is in making gallium arsenide. This is a semi conductor material employed in the manufacture of diode lasers for laser printers, compact – disc players and fibre optic communication devices.

➢ Indium is also used in making semi conductor devices, such as transistors and electrical resistance thermometers called thermistors.

➢ Thallium is extremely toxic and has no commercial use.

3.1 GENERAL TRENDS

Electronic configurations: The general electronic configuration of the various elements of this family is $ns^2\, np^1$.

Table 3.1 Electronic configuration of group 13 elements

Element	Atomic Number	Electronic Configuration	Group Number	Period Number
Boron	5	[He] $2s^2\, 2p^1$	13	2
Aluminium	13	[Ne] $3s^2\, 3p^1$	13	3
Gallium	31	[Ar] $3d^{10}\, 4s^2\, 4p^1$	13	4
Indium	49	[Kr] $4d^{10}\, 5s^2\, 5p^1$	13	5
Thallium	81	[Xe] $4f^{14}\, 5d^{10}\, 6s^2\, 6p^1$	13	6

3.1.1 Potash Alum, $K_2 SO_4 . Al_2 (SO_4)_3 . 24 H_2O$

Potash Alum is manufactured from alunite or alum stone.

From Alunite: Alunite or alum stone is $K_2SO_4 . Al_2(SO_4)_3 . 4Al(OH)_3$. It is finely powdered and boiled with dilute sulphuric acid, the aluminium hydroxide part changes into aluminium sulphate. When a little more potassium sulphate in calculated amount is added, the alum is crystallised.

Properties

1. Potash alum is a white crystalline solid.
2. It is soluble in water but insoluble in alcohol.
3. The aqueous solution is acidic due to the hydrolysis of $Al_2 (SO_4)_3$.
4. When heated, it melts at 365K and on further heating loses the whole of its water of crystallisation and swells up. The swollen mass so produced is called **burnt alum**.

Uses

1. It is used in purification of water, water proofing of textiles and in dyeing and paper industry.
2. It is also employed to arrest bleeding.

3.2 GROUP - 14 ELEMENTS - THE CARBON FAMILY

The group 14 (IVA) elements – carbon, silicon, germanium, tin and lead are especially important both in industry and in living organisms.

➢ Carbon is an essential constituent of the molecules on which life is based.

➢ Silicon is the second most abundant element in the earth's crust.

➢ Both silicon and germanium are used in making modern solid – state electronic devices.

➢ Tin and lead have been known and used since ancient times.

General Trends

Electronic configuration: The elements of this group possess $ns^2 np^2$ electronic configuration.

Element	Atomic Number	Electronic Configuration	Group Number	Period Number
Carbon	6	[He] $2s^2 2p^2$	14	2
Silicon	14	[Ne] $3s^2 3p^2$	14	3
Germanium	32	[Ar] $3d^{10} 4s^2 4p^2$	14	4
Tin	50	[Kr] $4d^{10} 5s^2 5p^2$	14	5
Lead	82	[Xe] $4f^{14} 5d^{10} 6s^2 6p^2$	14	6

Table 3.2 Electronic Configuration of Group 14 elements

3.2.1 Silicones – structure and uses

The silicones are a group of organosilicon polymers. They have a wide variety of commercial uses.

The complete hydrolysis of $SiCl_4$ yields silica SiO_2, which has a very stable three-dimensional structure. The fundamental research of F.S. Kipping on the hydrolysis of alkyl-substituted chlorosilanes led, not to the expected silicon compound analogous to a ketone, but to long-chain polymers called silicones.
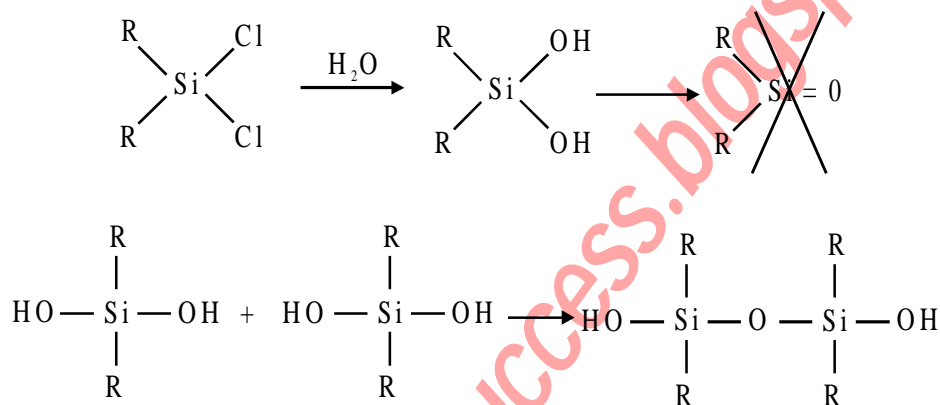
The starting materials for the manufacture of silicones are alkyl-substituted chlorosilanes. Thus the hydrolysis of trialkylmonochlorosilane R_3SiCl yields hexa-alkylsiloxane.
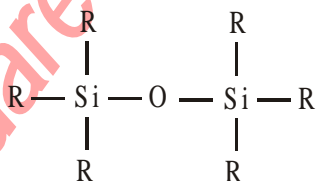
The dialkyldichlorosilane R_2SiCl_2 on hydrolysis gives rise to straight chain polymers and, since an active OH group is left at each end of the chain, polymerisation continues and the chain increases in length.
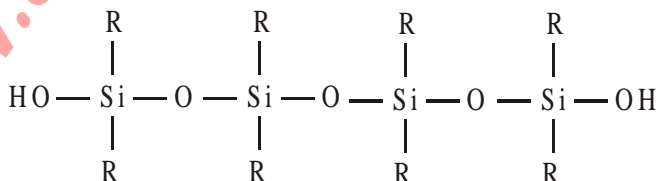
The hydrolysis of alkyl tricholorosilane $RSiCl_3$ gives a very complex cross-linked polymer.

$$
\begin{array}{ccc}
| & & | \\
O & & O \\
| & & | \\
R - Si - O - Si - R \\
| & & | \\
O & & O \\
| & & | \\
R - Si - O - Si - R \\
| & & | \\
O & & O \\
| & & |
\end{array}
$$
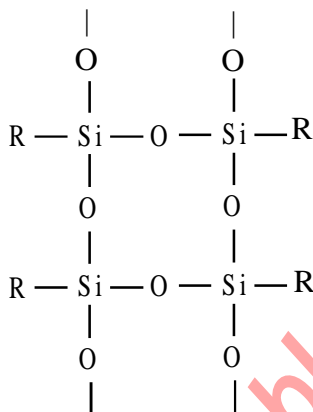
Uses

1) Silicones act as excellent insulators for electric motors and other appliances as they can withstand high temperatures.

2) Straight chain polymers of 20 to 500 units are used as silicone fluids. They are water repellent because of the organic side group. These polymers are used in waterproofing textiles, as lubricants and as polish.

3) Silicone rubber retain their elasticity even at low temperatures and resist chemical attack. They are mixed with paints to make them damp-resistant.

4) Silicone resins, a cross-linked polymer used as non-stick coating for pans and are used in paints and varnish.

5) Silicone oils are highly stable and non-volatile even on heating. Hence used for high temperature oil bath, high vacuum pump etc.

3.2.2 Metallurgy of Lead

Ores

1. Galena   PbS
2. Cerrusite $PbCO_3$
3. Anglesite $PbSO_4$
4. Lead ochre PbO

Extraction: Lead is mainly extracted from the sulphide ore galena. Galena contains lead sulphide and small quantities of silver.

1.   Concentration: The ore is concentrated by froth floatation process.

2.   Smelting in a Reverberatory furnace: The concentrated ore is roasted in a reverberatory furnace at a moderate temperature. The temperature of furnace is controlled by regulating the air supply. During roasting, galena is partly oxidized to lead monoxide and partly to lead sulphate.

Fig. 3.1 A reverberatory furnace

$$2PbS + 3O_2 \rightarrow 2\ PbO + 2SO_2$$
$$PbS + 2O_2 \rightarrow PbSO_4$$
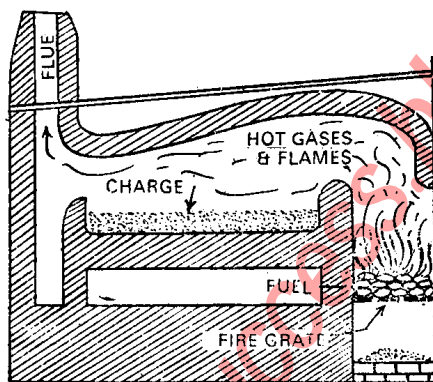
More of galena is then added. The temperature is raised and simultaneously the air supply is reduced. Lead sulphide reacts with the two oxidised products giving lead.

$$PbS + 2PbO \rightarrow 3Pb + SO_2$$
$$PbS + PbSO_4 \rightarrow 2Pb + 2SO_2$$
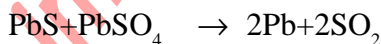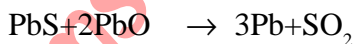
Thus in this process roasting and smelting are carried out in the same furnace, at two different temperatures.

About 90% of lead is obtained as metal, the rest passes into slag. Lead is recovered from the slag by heating with lime and powdered coke.

```
┌─────────────────┐   Concentration    ┌─────────────────┐
│  Powdered ore   │ ─────────────────► │  ore rich in PbS │
└─────────────────┘                    └─────────────────┘
                                                │ roasting
                                                ▼
                                    ┌──────────────────────────┐
┌─────────────────┐                 │ ore rich in PbO, PbSO₄, PbS │
│ Pure lead metal │                 └──────────────────────────┘
└─────────────────┘                             │ smelting
        ▲        Electrolytic                    ▼
        │        refining               ┌──────────────┐
        │                               │ Impure Metal │
        │                               └──────────────┘
        │                                       │
        │                                       │ Liquation
        │                                       ▼
┌─────────────────┐  Desilverisation   ┌─────────────────┐
│ Pb metal +Au, Sn│ ◄───────────────── │  Pb +Sn, Ag, Au │
└─────────────────┘                    └─────────────────┘
```
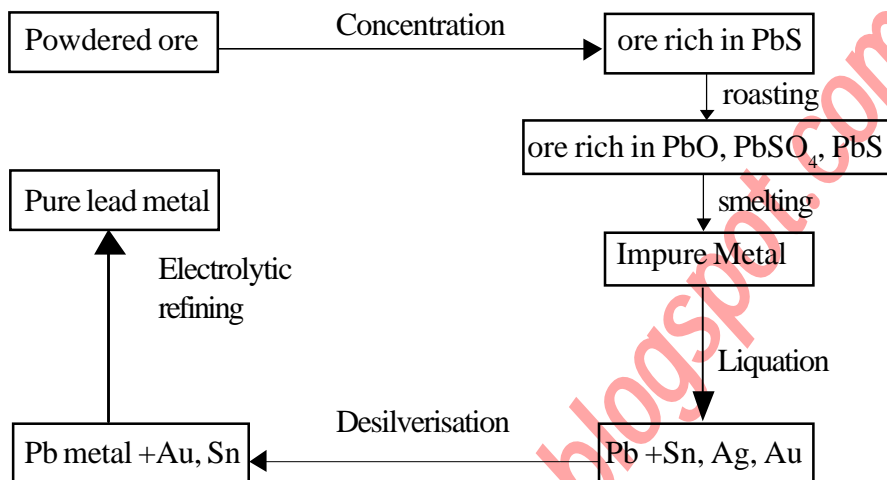
Purification of Lead

Lead extracted by the above method contains impurities such as silver, copper, tin, bismuth, gold and iron. It is refined by the following processes.

a. Liquation

The impure metal is heated on a sloping hearth. Lead melts and flows down the slope. The infusible impurities remain on the hearth.

b. Desilverisation

Silver is removed by either Pattinson's process or Park's process.

c. Electrolytic refining

Very pure lead is obtained by this process.

Anode – Impure lead

Cathode – Very pure lead

Electrolyte – Lead fluosilicate + Hydrofluosilicic Acid

$\qquad\qquad$ ($PbSiF_6$) $\qquad$ (H_2SiF_6)

The metallic impurities which are more electropositive than lead, such as iron and tin, go into the solution while the rest of the impurities are thrown down as anode mud.

Physical properties

1. Lead is a bluish grey metal with a bright luster.
2. It is soft and can be cut with a knife and drawn into a wire and rolled into a sheet.
3. It is not a good conductor of heat and electricity.
4. It marks paper.

Chemical properties

1.   Action of air

i)   It is unaffected by dry air but in moist air a layer of lead carbonate or lead hydroxide is deposited on its surface which protects it from further action of air.

ii)   When heated in air or oxygen, lead is oxidized to litharge (PbO) and red lead (Pb_3O_4)

$$2Pb + O_2 \ \rightarrow \ 2PbO$$

$$3Pb + 2O_2 \rightarrow Pb_3O_4$$
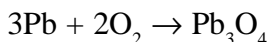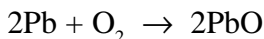
2.   Action of water

Lead is not attacked by pure water in the absence of air, but water containing dissolved air has a solvent action on it due to the formation of lead hydroxide (a poisonous substance). This phenomenon is called **Plumbo solvency**.

$$2Pb + O_2 + 2H_2O \ \rightarrow \ 2Pb(OH)_2$$

3.   Action of acids

i)   Dilute H_2SO_4 and HCl have no action on lead.

ii)   Hot Conc. H_2SO_4 liberates SO_2 but the reaction is retarded by the formation of an insoluble layer of lead sulphate.

$$Pb + 2H_2SO_4 \rightarrow PbSO_4 + 2H_2O + SO_2 \uparrow$$

iii) Concentrated HCl evolves hydrogen and also forms Chloroplumbic acid

$$Pb + 2HCl \qquad \rightarrow \quad PbCl_2 + H_2 \uparrow$$

$$PbCl_2 + 2HCl \quad \rightleftharpoons \quad H_2PbCl_4$$
$$\qquad\qquad\qquad\qquad \text{chloroplumbic acid}$$

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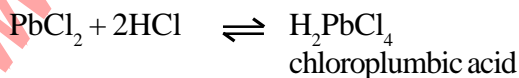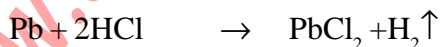
Uses: Lead is used

1. For making lead pipes,
2. For making telegraph and telephone wires,
3. In making bullets and lead accumulators,
4. In lead chambers, for the manufacture of sulphuric acid,
5. For making alloys like solder, pewter and type metal,
6. For preparing tetraethyl lead ($Pb(C_2H_5)_4$) which is used as an additive to petrol to prevent knocking.

Problem

An element **A** belongs to 14th group and occupies period number 6. **A** reacts with conc. HCl. to give **B** an acid. **A** is used to prepare **C** which is used as an antiknock in automobiles. Identify the element **A** and the compounds **B** and **C** Write the reactions.

Solution

1. As per the position in the periodic table, the element A is lead.

2. Lead with Conc. HCl gives **B**

$$Pb + 4\ HCl \quad \rightarrow \quad H_2PbCl_4 \ + \ H_2$$

∴ Compound **B** is chloroplumbic acid.

3. Compound **C** is tetraethyl lead.

3.3 GROUP – 15 ELEMENTS – THE NITROGEN FAMILY

The group 15 (VA) elements are nitrogen, phosphorus, arsenic, antimony and bismuth.

➢ Nitrogen is a gas. It makes up 78% of the earth's atmosphere by volume.

➢ Phosphorus is the most abundant element of 15th group, accounting for 0.10% of the mass of the earth's crust.

➢ Arsenic is also used to make pesticides and semi conductors, such as GeAs.

➢ Bismuth is a silvery solid. Bismuth compounds are present in some pharmaceuticals such as Pepto–bismol.

➢ The natural abundance of As, Sb and Bi in the earth's crust is relatively low.

General trends

Electronic configuration: All these elements have general electronic configuration of $ns^2\,np^3$.

Table 3.3 Electronic configuration of group 15 elements

Element	Atomic Number	Electronic Configuration	Group Number	Period Number
Nitrogen	7	[He] $2s^2\,2p^3$	15	2
Phosphorus	15	[Ne] $3s^2\,3p^3$	15	3
Arsenic	33	[Ar] $3d^{10}\,4s^2\,4p^3$	15	4
Antimony	51	[Kr] $4d^{10}\,5s^2\,5p^3$	15	5
Bismuth	83	[Xe] $4f^{14}\,5d^{10}\,6s^2\,6p^3$	15	6

3.3.1   Compounds of Phosphorus

a)   Halides of Phosphorus

Phosphorus combines with all the halogens forming phosphorus halides which are all covalent compounds. Phosphorus chlorides are more important. Tri and pentachlorides of phosphorus are most common.

I.   Phosphorus Trichloride, PCl_3

Preparation: PCl_3 is prepared by heating white phosphorus in a current of dry chlorine.

$$P_4 + 6Cl_2 \rightarrow 4PCl_3$$
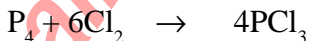
Dry white phosphorus is placed in the retort and gently heated on a water bath. A current of pure, dry chlorine is led over the phosphorus. The phosphorus trichloride formed being volatile distils over and is collected in a water cooled receiver.
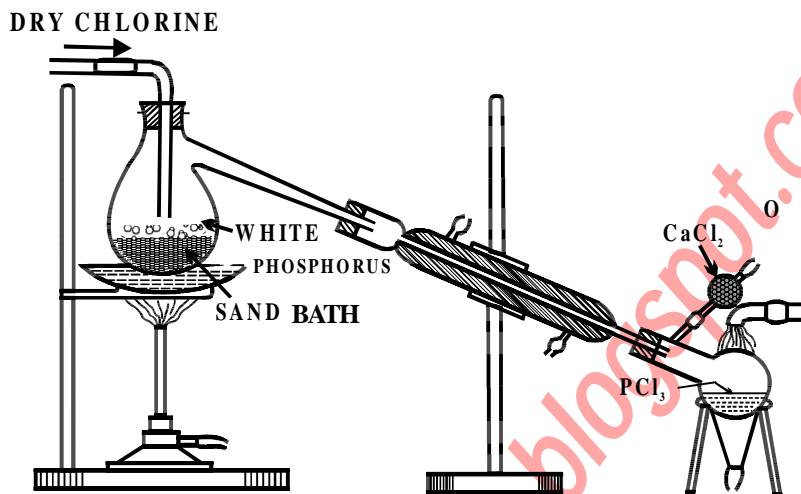
Fig. 3.2 Laboratory Preparation of PCl$_3$

The phosphorus trichloride obtained as above contains some PCl$_5$ as impurity. This is removed by distilling the PCl$_3$ over white phosphorus.

Physical properties

1. Colourless low boiling liquid
2. It fumes in moist air
3. It has pungent odour.

Chemical Properties

1. It is violently hydrolysed by water giving phosphorus acid and hydrochloric acid gas.

$$PCl_3 + 3 H_2O \rightarrow 3HCl + H_3PO_3$$
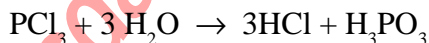
In a similar manner it reacts with organic compounds containing hydroxyl (OH) group, such as acids and alcohols.

$$PCl_3 + 3CH_3COOH \rightarrow 3CH_3COCl + H_3PO_3$$
$$\text{Acetic Acid} \qquad \text{Acetyl Chloride}$$

$$PCl_3 + 3C_2H_5OH \rightarrow 3 C_2H_5Cl + H_3PO_3$$
$$\text{Ethyl alcohol} \qquad \text{Ethyl Chloride}$$
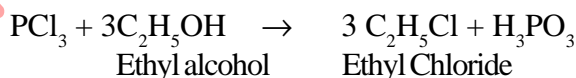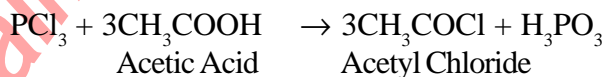
2. It reacts with chlorine or sulphuryl chloride forming phosphorus pentachloride.

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$$PCl_3 + Cl_2 \rightarrow \quad PCl_5$$

$$PCl_3 + SO_2Cl_2 \rightarrow \quad PCl_5 + SO_2$$
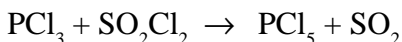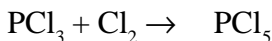
3. It readily combines with oxygen forming phosphorus oxychloride

$$2PCl_3 + O_2 \rightarrow 2POCl_3$$
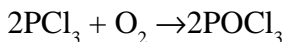
4. It reacts with SO_3 to form phosphorus oxychloride and SO_2

$$SO_3 + PCl_3 \rightarrow POCl_3 + SO_2$$
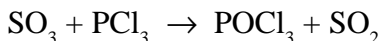
Structure: PCl_3 molecule has a pyramidal shape, which arises from sp^3 hybridisation of phosphorus atom. One of the tetrahedral positions is occupied by a lone pair of electrons.

x - Electron of p

• - Electron of Cl
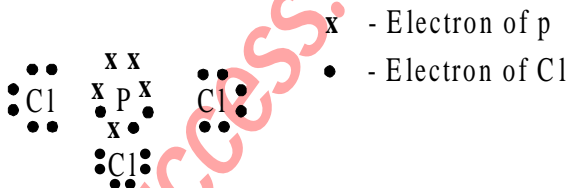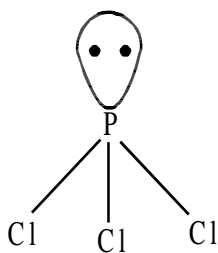
II. Phosphorus pentachloride, PCl_5

Preparation: Phosphorus pentachloride is usually prepared by the action of an excess of chlorine on phosphorus trichloride.

$$PCl_3 + Cl_2 \rightarrow PCl_5$$
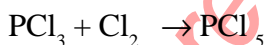
Physical properties

1. Phosphorus pentachloride is a yellowish white crystalline solid.
2. It sublimes on heating at 473 K and melts at 318 K under pressure.

Chemical properties

1. Phosphorus pentachloride dissociates on heating into phosphorus trichloride and chlorine.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$
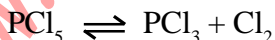
2. It is violently hydrolysed by water giving phosphorus oxychloride or phosphoric acid depending upon the quantity of water.

$$PCl_5 + H_2O \xrightarrow{\text{insufficient water}} POCl_3 + 2HCl$$

$$PCl_5 + 4H_2O \xrightarrow{\text{Excess of water}} H_3PO_4 + 5HCl$$
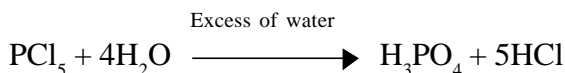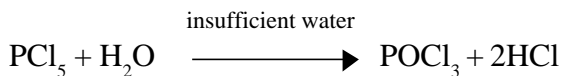
3. It reacts with compounds containing hydroxyl groups forming chloro derivatives. In all these cases, the hydroxyl group is replaced by chlorine.

$$\underset{\text{Ethyl Alcohol}}{C_2H_5OH} + PCl_5 \rightarrow \underset{\text{Ethyl Chloride}}{C_2H_5Cl} + POCl_3 + HCl$$
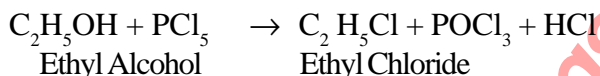
4. It reacts with metals on heating to give corresponding chlorides.

$$2Ag + PCl_5 \rightarrow 2\,AgCl + PCl_3$$
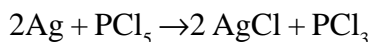
Structure

PCl_5 molecule has trigonal bipyramidal shape in vapour state which arises from sp^3d hybridisation of phosphorus atom.

x - Electron of p

• - Electron of Cl
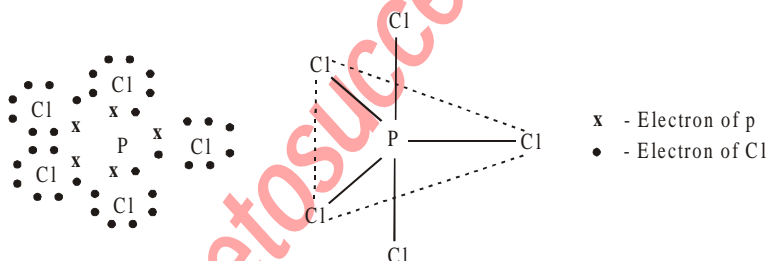
b) Oxides of phosphorus

I. Phosphorus trioxide P_2O_3 or P_4O_6

It is obtained by the combustion of phosphorus in a limited supply of air.

$$4P + 3O_2 \rightarrow 2P_2O_3$$
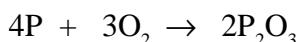
Physical properties

1. It is a white waxy substance
2. It has a garlic odour.

Chemical properties

1. It reacts with cold water, gives phosphorus acid.

$$P_2O_3 + 3H_2O \rightarrow 2H_3PO_3$$

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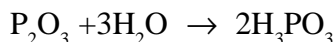
2.   It reacts with hot water vigorously to form inflammable phosphine.

$$2P_2O_3 + 6H_2O \rightarrow PH_3 \uparrow + 3H_3PO_4$$
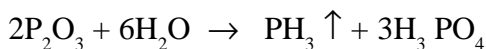
II.   Phosphorus pentoxide P_2O_5 or P_4O_{10}

Phosphorus pentoxide can be prepared by burning phosphorus with sufficient supply of air.

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$
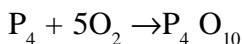
Physical properties

It is a white solid and an acidic oxide.

Chemical properties

1.   It reacts with moisture to form metaphosphoric acid.

$$P_4O_{10} + 2H_2O \rightarrow 4HPO_3$$
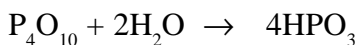
When the solution is boiled, the metaphosphoric acid is changed to orthophosphoric acid.

$$HPO_3 + H_2O \rightarrow H_3PO_4$$
$$\text{or}$$
$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$
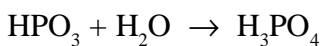
2.   Phosphorus pentoxide extracts water from many inorganic compound including sulphuric acid, nitric acid and several organic compounds. It is therefore, used as a powerful dehydrating agent.

$$H_2SO_4 \xrightarrow[- H_2O]{P_4O_{10}} SO_3$$

$$2HNO_3 \xrightarrow[- H_2O]{P_4O_{10}} N_2O_5$$

$$\underset{\text{Amide}}{RCONH_2} \xrightarrow[-H_2O]{P_4O_{10}} \underset{\text{Nitrile}}{RCN}$$
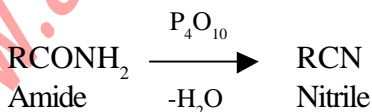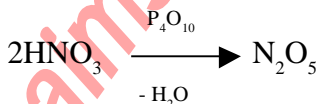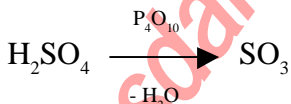
Use: It is used as a dehydrating agent.

c)   **Oxy-Acids of Phosphorus**

I.   **Phosphorus acid - H_3PO_3**

It is prepared by the action of cold water on phosphorus (III) oxide or phosphorus (III) chloride.

$$P_2O_3 + 3H_2O \rightarrow 2H_3PO_3$$
$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$
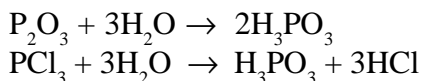
Physical properties

It is a white crystalline solid with garlic taste.

Chemical Properties

1.   **Acidic nature:** It is a dibasic acid and gives salts of two types.

$$H_3PO_3 + NaOH \rightarrow NaH_2PO_3 + H_2O$$
Sodium dihydrogen Phosphite

$$H_3PO_3 + 2NaOH \rightarrow Na_2HPO_3 + 2H_2O$$
Disodium hydrogen Phosphite
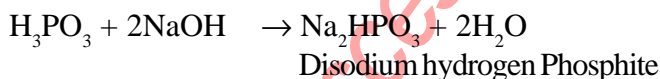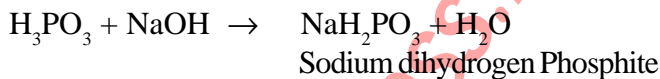
2.   When it is heated it undergoes auto-oxidation and reduction to form phosphoric acid and phosphine.

$$4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$$
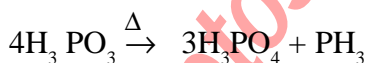
3.   It is a powerful reducing agent because it has P-H bond. It reduces silver nitrate solution into silver.

$$2AgNO_3 + H_3PO_3 + H_2O \rightarrow 2Ag + H_3PO_4 + 2HNO_3$$
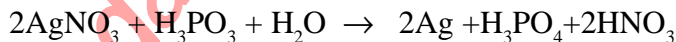
Electronic structure
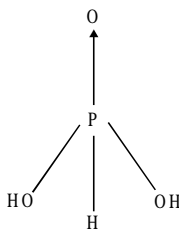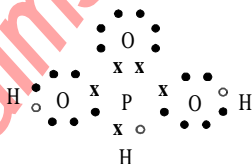
x - Electron of P
• - Electron of Cl
○ - Electron of H

Use: It is used as a reducing agent

II. Ortho phosphoric Acid, H_3PO_4

Preparation

1.   It is prepared by dissolving phosphorus pentoxide in water and boiling the solution.

$$P_2O_5 + 3H_2O \quad \rightarrow \quad 2H_3PO_4$$

2.   **Laboratory preparation:** In the laboratory orthophosphoric acid can be prepared by boiling a mixture of red phosphorus with 50% nitric acid in a flask fitted with a reflux condenser on a water bath till no more oxides of nitrogen are liberated.

Iodine acts as a catalyst. The product is evaporated below 453 K and then cooled in a vaccum desiccator surrounded by freezing mixture when crystals of orthophosphoric acid are deposited.

$$P + 5HNO_3 \quad \rightarrow \quad H_3PO_4 + 5NO_2 + H_2O$$

Physical properties

1.   It is a deliquescent crystalline solid.
2.   It is soluble in water.

Chemical properties

1.   It is a tribasic acid. It combines with alkalies like NaOH to form three series of salts.

$$H_3PO_4 + NaOH \quad \rightarrow \quad NaH_2PO_4 \quad + \quad H_2O$$
Sodium Di hydrogen Phosphate

$$H_3PO_4 + 2NaOH \quad \rightarrow \quad Na_2HPO_4 \quad + \quad 2H_2O$$
Disodium hydrogen Phosphate

$$H_3PO_4 + 3NaOH \quad \rightarrow \quad Na_3PO_4 \quad + \quad 3H_2O$$
Sodium Phosphate

2.   On heating it gives pyrophosphoric acid at 523 K and at 589 K gives metaphosphoric acid

$$H_3PO_4 \xrightarrow{\text{523K}} H_4P_2O_7 \xrightarrow{\text{589K}} 2HPO_3 + H_2O$$

3.   On reaction with silver nitrate, it gives yellow precipitate of silver phosphate.

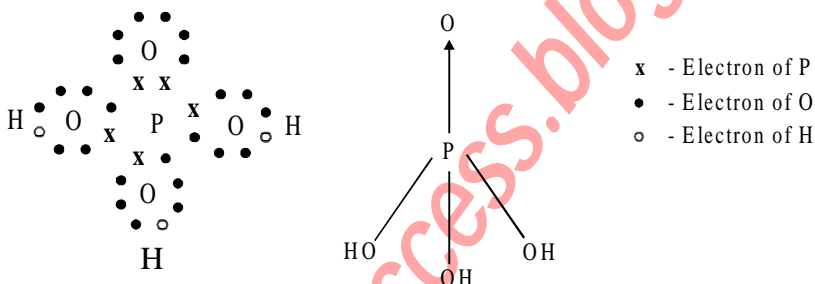$$H_3PO_4 + 3AgNO_3 \rightarrow Ag_3PO_4 + 3HNO_3$$

76

Uses

1.   It is used in the preparation of HBr and HI as a substitute for sulphuric acid.
2.   It is used as souring agent in the preparation of soft drinks.
3.   It is used in the preparation of phosphate salts of sodium, potassium and ammonium.
4.   It is used in the manufacture of phosphatic fertilisers.

Structure

Being a tribasic acid, the structure of phosphoric acid is represented as

x - Electron of P
• - Electron of O
○ - Electron of H

III. B. Pyrophosphoric acid, $H_4P_2O_7$

Preparation: Pyrophosphoric acid is prepared by heating orthophosphoric acid to 523 K – 533 K.

$$2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O$$

Physical Properties

It is a colourless crystalline solid.

Chemical Properties

1.   It is reconverted to orthophosphoric acid on boiling with water

$$H_4P_2O_7 + H_2O \rightarrow 2H_3PO_4$$

2.   When heated strongly, it yields metaphosphoric acid

$$H_4P_2O_7 \longrightarrow 2HPO_3 + H_2O$$

Structure: The Structure of pyrophosphoric acid is represented as:
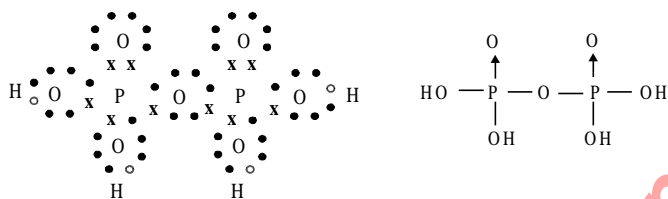
d) Phosphine - PH_3

Phosphine is the best known hydride of phosphorus.

Laboratory preparation: It is usually obtained by boiling white phosphorus with 30-40% solution of caustic soda in an inert atmosphere of CO_2.

$$4P \ + \ 3NaOH \ + \ 3H_2O \ \rightarrow PH_3 \ + \ 3NaH_2PO_2$$
$$\text{Sodium hypophosphite}$$
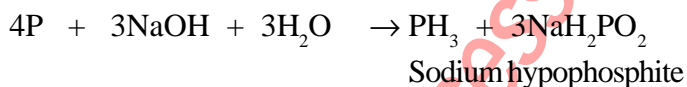
Phosphine so obtained is impure. It is passed into an aqueous solution of hydrogen iodide, PH_4I is formed. PH_4I is heated with KOH or NaOH, pure phosphine is obtained.

$$PH_3 \ + \ HI \ \rightarrow \ PH_4I$$

$$PH_4I \ + \ NaOH \ \rightarrow PH_3 \ + \ NaI \ + \ H_2O$$
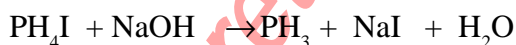
Physical properties

Phosphine is colourless gas with rotten fish odour.

Chemical properties

**1. Dissociation:** Phosphine dissociates at about 723 K and gives red phosphorus.

$$4PH_3 \ \xrightarrow{723\,K} \ P_4 \ + \ 6H_2$$
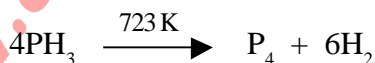
2. Action of air: It burns with oxygen and produces phosphorus pentoxide.

$$4PH_3 \ + \ 8O_2 \ \rightarrow \ P_4O_{10} \ + \ 6H_2O$$

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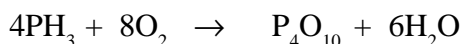
3. **Action of chlorine:** Phosphine burns in chlorine spontaneously forming PCl_3 and PCl_5.

$$PH_3 \ + \ 3Cl_2 \qquad \rightarrow \qquad PCl_3 \ + \ 3HCl$$

$$PH_3 \ + \ 4Cl_2 \qquad \rightarrow \qquad PCl_5 \ + \ 3HCl$$
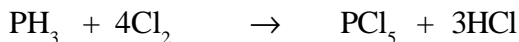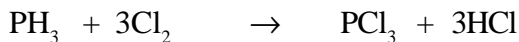
4. **Reducing properties:** PH_3 is a powerful reducing agent. When it is passed through the salt solutions, corresponding metal is formed.

$$PH_3 + \ 6AgNO_3 + \ 3H_2O \rightarrow 6Ag + 6HNO_3 \ + \ H_3PO_3$$
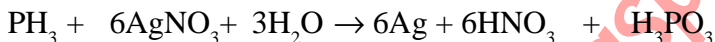
Uses

1. **Smoke screens**

When PH_3 burns it produces smoke which is dense enough to serve as smoke screens.

2. **Holme's signal :** Containers which have a perforated bottom and a hole at the top are filled with calcium phosphide and calcium carbide. These are thrown into the sea. Water enters the container through the bottom and reacts with calcium carbide and calcium phosphide to give acetylene and phosphine. Phosphine gets ignited spontaneously as it comes in contact with air and also ignites acetylene. Thus a bright red flame is produced which is accompanied by huge smoke due to the burning of phosphine. This serves as a signal to the approaching ships.

$$Ca_3P_2 \ + \ 6H_2O \rightarrow \ 2\,PH_3\uparrow \quad + \ 3Ca(OH)_2$$

$$CaC_2 \quad + \ 2H_2O \rightarrow \ C_2H_2 \uparrow + \ Ca(OH)_2$$

Problem

An element 'A' occupies group number 15 and period number 3 reacts with chlorine to give **B** which further reacts with chlorine to give **C** at 273 K. Both B and C are chlorinating agent for organic compounds. **C** is a better chlorinating agent because it chlorinates metals also. **B** reacts with SO_3 and reduces it to SO_2. **B** has a pyramidal shape. **C** has trigonal bipyramidal shape by sp^3d hybridisation. Identify the element A and the compounds B and C. Write the reactions.

1. The element which occupies group number 15 and period number 3 is phosphorus. Therefore A is phosphorus. Phosphorus reacts with chlorine
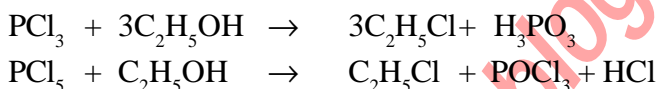
to give PCl_3. Therefore compound B is phosphorus trichloride and it has a pyramidal shape.

$$P_4 + 6Cl_2 \quad \rightarrow \quad 4PCl_3$$
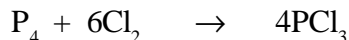
2. PCl_3 further reacts with Cl_2 to give PCl_5. Therefore, the compound C is phosphorus pentachloride and it has a trigonal bipyramidal shape.
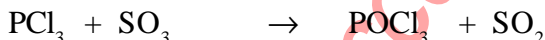
$$PCl_3 + Cl_2 \quad \rightarrow \quad PCl_5$$

3. PCl_3 and PCl_5 are chlorinating agents for organic compounds. So, both reacts with C_2H_5OH gives C_2H_5Cl.

$$PCl_3 + 3C_2H_5OH \rightarrow \quad 3C_2H_5Cl + H_3PO_3$$
$$PCl_5 + C_2H_5OH \quad \rightarrow \quad C_2H_5Cl + POCl_3 + HCl$$

4. PCl_5 is a better chlorinating agent. So it chlorinates copper.

$$PCl_5 + 2Cu \quad \rightarrow \quad 2CuCl + PCl_3$$
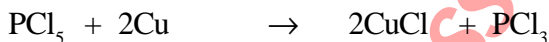
5. PCl_3 reacts with SO_3 and reduces it to SO_2.

$$PCl_3 + SO_3 \quad \rightarrow \quad POCl_3 + SO_2$$

3.4 Group 16 THE 'OXYGEN' FAMILY

The group 16 (VI A) elements are oxygen, sulphur, selenium, tellurium and polonium. The first four elements are collectively called CHALCOGENS or ore forming elements, because many metal ores occur as oxides and sulphides.

➢ Oxygen the most abundant element, is an important constituent of atmosphere and ocean. It constitutes 46.6% earth's crust.

➢ Sulphur is less abundant and occurs in free and combined states. Sulphur is also known as Brim stone.

➢ Polonium, a radioactive element that occurs in trace amounts in uranium ores. Its name from Poland, the home country of Marie Curie who discovered the element in 1898.

General Trends

Electronic configuration

All of these elements have ns^2np^4 configuration, just two electrons short of an octet configuration.

Table 3.4 Electronic configuration of Group 16 elements

Element	Atomic Number	Electronic Configuration	Group Number	Period Number
Oxygen	8	[He] $2s^2 2p^4$	16	2
Sulphur	16	[Ne] $3s^2 3p^4$	16	3
Selenium	34	[Ar] $3d^{10}\ 4s^2\ 4p^4$	16	4
Tellurium	52	[Kr] $4d^{10}\ 5s^2\ 5p^4$	16	5
Polonium	84	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$	16	6

3.5 GROUP 17 - THE HALOGEN FAMILY

Group 17 of the periodic table contains the elements fluorine, chlorine, bromine, iodine and astatine. These are collectively known as HALOGENS. It is derived from two Greek words Halo and Gens meaning "Salt producer". Because most of them exist in Sea water.

General Trends

Electronic Configuration: All these elements possess ns^2np^5 configuration.

Table 3.5 Electronic Configuration of group 17 elements

| Element	Atomic Number	Electronic Configuration	Group Number	Period Number
Fluorine	9	[He] $2s^2 2p^5$	17	2
Chlorine	17	[Ne] $3s^2 3p^5$	17	3
Bromine	35	[Ar] $3d^{10}\ 4s^2\ 4p^5$	17	4
Iodine	53	[Kr] $4d^{10}\ 5s^2\ 5p^5$	17	5
Astatine	85	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^5$	17	6

Chemical Properties

1.   Oxidising power: An important feature of the halogen is their oxidising property which is due to high electron affinity of halogen atoms. The oxidising power decreases from fluorine to iodine. Fluorine is the strongest oxidising agent. It oxidises other halide ions to halogens in solution or when dry.

$$F_2 + 2\,X^- \rightarrow 2F^- + X_2 \quad (X^- = Cl^-, Br^-, I^-)$$
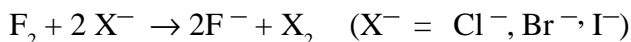
Halogen of low atomic number oxidises the halide ion of higher atomic number.

2.   Solubility: Halogens, being non-polar molecules, do not dissolve to a considerable extent in a polar solvent like water. However, fluorine reacts with water readily forming a mixture of O_2 and O_3.

$$2F_2 + 2H_2O \rightarrow 4HF + O_2$$

$$3F_2 + 3H_2O \rightarrow 6HF + O_3$$
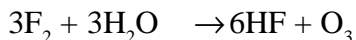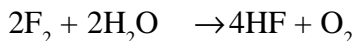
Chlorine, bromine and Iodine are more soluble in organic solvents such as CCl_4, $CHCl_3$ and produce yellow, brown and violet colour.

3.   Hydrides of the Halogens (Hydrogen halides):

i)   All halogens react with hydrogen to form volatile covalent hydrides of formula HX.

ii)   These hydrides are called hydracids.

iii)   The activity of halogens towards hydrogen decreases from fluorine to iodine. Hydrogen combines explosively with fluorine even in dark. It combines with chlorine in the presence of sunlight and with bromine on heating. Hydrogen combines with iodine on heating and in presence of a catalyst.

iv)   Hydracids are the reducing agents.

v)   Except HF, all hydrogen halides are gases. HF is a liquid because of inter molecular hydrogen bonding.

H –F .... H –F .... H–F .... H–F

vi)   The acidic character of HX are in the following order.

HF < HCl < HBr < HI.
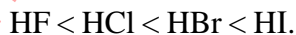
Anamalous Nature of Fluorine

1. Fluorine is the most reactive element among halogen. This is due to the minimum value of F–F bond dissociation energy.

2. Fluorine decomposes cold dilute alkalies liberating OF_2 and with conc. alkali, O_2 is liberated. Under similar conditions, the other halogens will give rise to the hypohalites and halates respectively.

3. It has the greatest affinity for hydrogen, forming HF which is associated due to the hydrogen bonding. Hydrofluoric acid is a weak acid whereas the other hydrohalic acids are strong acids.

    ...... H– F...... H– F..... H–F.
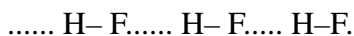
4. It differs markedly from the other halogens in that it can form two types of salts with metals. NaF and $NaHF_2$.

5. The salts of HF differ from the corresponding salts of other hydracids. AgF is soluble in water while the other AgX are insoluble.

6. Being strongly electronegative it can have only a negative oxidation state while the other halogens can have negative as well as positive oxidation state.

7. HF attacks glass while others do not.

8. Fluorine, because of the absence of d-orbitals in its valence shell does not form any polyhalides. Thus we have I_3^-, Br_3^-, Cl_3^- ions but no F_3^- ion.

ETCHING ON GLASS

Etching glass

Industrially, hydrogen fluoride is obtained by heating fluorspar (CaF_2) with concentrated H_2SO_4 in a lead vessel.

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF.$$
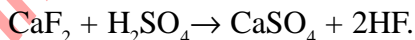
HF distils over and the vapours are condensed in water in a lead receiver. Aqueous HF thus obtained is stored in wax bottles. It cannot be stored in glass or silica bottles as it attacks silicates and silica.

$$Na_2 SiO_3 + 6HF \rightarrow Na_2SiF_6 + 3H_2O$$

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$
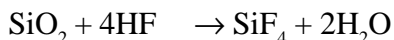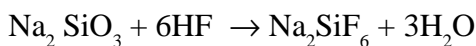
The action of hydrofluoric acid on silica and silicates is used for etching glass. The glass article is first covered with a film on wax. The design to be etched is now drawn on the waxed surface and is then exposed to the action of hydrofluoric acid. Now the glass can be very soon etched. The wax is finally washed off with turpentine.

3.5.1 ISOLATION OF FLUORINE

Symbol - F   Atomic number -9   Period Number   :   2

Valency –1   Atomic mass–19   Group Number   :   17

Fluorine does not occur free in nature. It occurs in the combined form.

Dennis' Method: This was devised by Dennis, Veeder and Rochow in 1931. In this fluorine is prepared by the electrolysis of fused sodium or potassium hydrogen fluoride (perfectly dry) Electrolysis is carried out between graphite electrodes in a V-shaped electrically heated copper tube. The ends of the tube are covered with copper caps into which the graphite electrodes are fixed with bakelite cement. The copper tube is thickly lagged to prevent loss of heat.
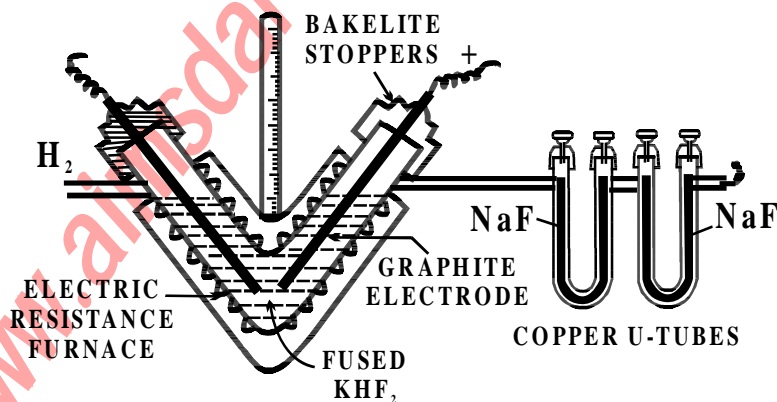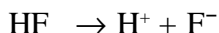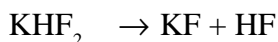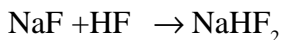
$$KHF_2 \rightarrow KF + HF$$
$$HF \rightarrow H^+ + F^-$$
$$2H^+ + 2e^- \rightarrow H_2 \quad \text{(At cathode)}$$
$$2F^- - 2e^- \rightarrow F_2 \quad \text{(At anode)}$$

Fig. 3.3 Preparation of fluorine

Fluorine liberated at the anode is passed through the U-tube containing sodium fluoride. This removes the hydrogen fluoride vapours coming with fluorine.

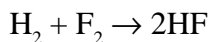$$NaF + HF \rightarrow NaHF_2$$

Physical Properties

1. Fluorine is a gas and has pale greenish yellow colour.
2. It has extremely pungent and penetrating odour.
3. It is heavier than air.

Chemical Properties

Fluorine is the most active member of halogen family.

**1. Action with Hydrogen:** Hydrogen explodes violently in fluorine even in the dark.

$$H_2 + F_2 \rightarrow 2HF$$

2. Action with non-metals: Non-metals like carbon, silicon and phosphorus burn in fluorine forming fluorides.

$$C + 2F_2 \rightarrow CF_4$$
Tetra fluoromethane

$$Si + 2F_2 \rightarrow SiF_4$$
Silicon tetrafluoride

$$2P + 5F_2 \rightarrow 2PF_5$$
Phosphorus pentafluoride

3. Action with metals: It reacts with metals forming corresponding fluorides.

$$2Ag + F_2 \rightarrow 2AgF$$
$$2Al + 3F_2 \rightarrow 2AlF_3$$
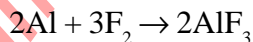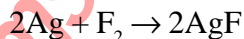
4. Formation of Interhalogen compounds: It forms a variety of inter halogen compounds with other halogens.

$$Br_2 + 3F_2 \rightarrow 2Br\,F_3$$
$$I_2 + 5F_2 \rightarrow 2\,IF_5$$
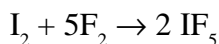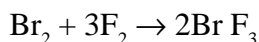
Uses

1. Fluorine is used in the manufacture of a series of compounds known as freons. These non-toxic, non-combustible and volatile liquids are used as refrigerants in refrigerators, deep freezers and air conditioners. The most common, freon is known as dichlorodifluoro methane $CF_2 Cl_2$.

2. CaF_2 is used as flux in metallurgy.

3. NaF is used as a preservative to prevent fermentation and also for preventing dental cavities.

4. SF_6 is used as an insulating material in high voltage equipment.

5. Teflon is used as container to store hydrofluoric acid.
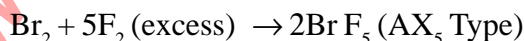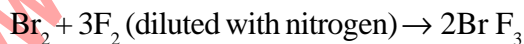
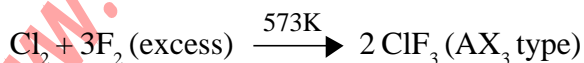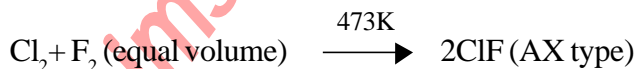6. UF_6 is used in the separation of U^{235} from U^{238}.

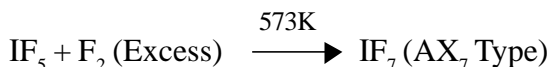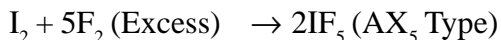## INTERHALOGEN COMPOUNDS OR INTERHALOGENS

Each halogen combines with another halogen to form several compounds known as interhalogen compounds. The less electronegative element is written first. In naming also, the less electronegative element is mentioned first.

They are divided into four types.

AX	AX$_3$	AX$_5$	AX$_7$
ClF BrF BrCl ICl IBr	ClF$_3$ BrF$_3$ ICl$_3$	BrF$_5$ IF$_5$	IF$_7$

They can all be prepared by direct combination or by the action of a halogen on a lower interhalogen, the product formed depends on the conditions.

$$Cl_2 + F_2 \text{ (equal volume)} \xrightarrow{473K} 2ClF \text{ (AX type)}$$

$$I_2 + Cl_2 \text{ liquid (equi molar)} \rightarrow 2ICl \text{ (AX type)}$$

$$Cl_2 + 3F_2 \text{ (excess)} \xrightarrow{573K} 2 ClF_3 \text{ (AX}_3 \text{ type)}$$

$$Br_2 + 3F_2 \text{ (diluted with nitrogen)} \rightarrow 2Br F_3$$

$$Br_2 + 5F_2 \text{ (excess)} \rightarrow 2Br F_5 \text{ (AX}_5 \text{ Type)}$$

$$I_2 + 5F_2 \text{ (Excess)} \rightarrow 2IF_5 \text{ (AX}_5 \text{ Type)}$$

$$IF_5 + F_2 \text{ (Excess)} \xrightarrow{573K} IF_7 \text{ (AX}_7 \text{ Type)}$$

The bonds are essentially covalent because of the small electronegativity difference, and the melting and boiling points increase as the difference in electronegativity increases.

The interhalogens are generally more reactive than the halogens (except F) because the A-X bond is weaker than the X–X bond in the halogens. The reactions are similar to those of the halogens. Hydrolysis gives halide and oxyhalide ions, the oxyhalide ion being formed from the larger halogen present.

$$BrF_5 + 3 \text{ OH}^- \longrightarrow 5F^- + BrO_3^- + 3 H^+$$
$$\text{Bromate}$$

$$ICl + OH^- \longrightarrow Cl^- + OI^- + H^+$$
$$\text{hypoiodite}$$
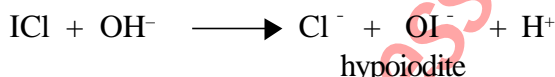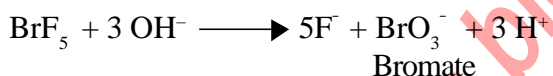
Structures of interhalogen compounds

Interhalogen compounds are generally covalent compounds in which the larger halogen forms the central atom.

1.   Type AX. As excepted, the compounds of the type AX are linear. Thus ClF, BrF, BrCl, IBr and ICl are all **linear** in structure.

Electronic structure of Chlorine atom, in the ground state and hybridised state is represented as in Fig. 3.4.
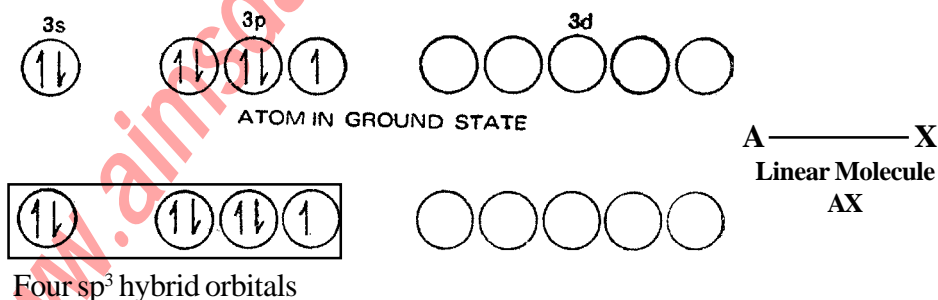

Four sp³ hybrid orbitals

Figure 3.4 Linear structure of the interhalogen compounds
of the type AX

Although the spatial arrangement of the four electron pairs (bp = 1 and lps = 3) round the central chlorine atom is tetrahedral, due to the presence of three lone pairs of electrons in three hybrid orbitals, the shape of AX molecule gets distorted and become linear.

2.   Type AX$_3$ Compounds of the type AX$_3$ have trigonal bipyramidal structure, Fig. 3.5 for the ClF$_3$ molecule.

Bipyramidal structure arises out of sp^3d hybridisation involved in the formation of this compound, as illustrated in the Fig.3.6. The three dotted arrows indicate electrons contributed by the three fluorine atoms (without lone pair it is T-shaped).

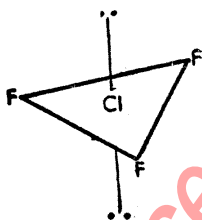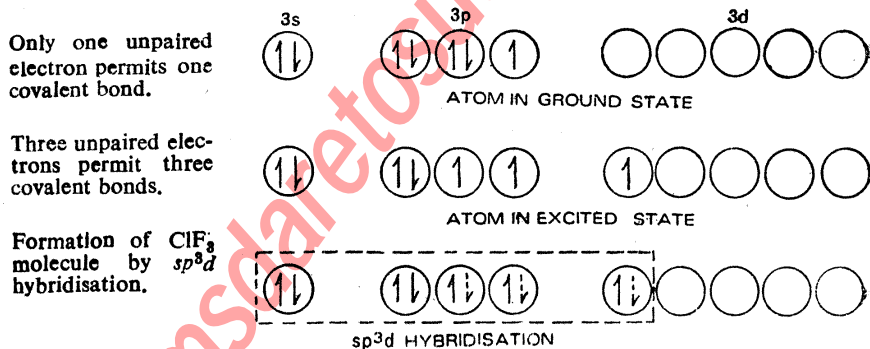**Fig. 3.5 Bi pyramidal structure of ClF$_3$ molecule**

Fig. 3.6 sp^3d hybridisation involved in the formation of Cl F$_3$ molecule

3.   Type AX$_5$ (IF$_5$, BrF$_5$, etc.) These compounds are formed by sp^3d^2 hybridisation and hence have an **octahedral** structure, as shown in Fig. 3.7 for the formation of IF$_5$ molecule (without lone pair it is square pyramidal).
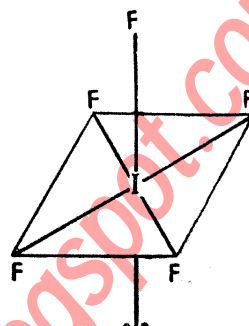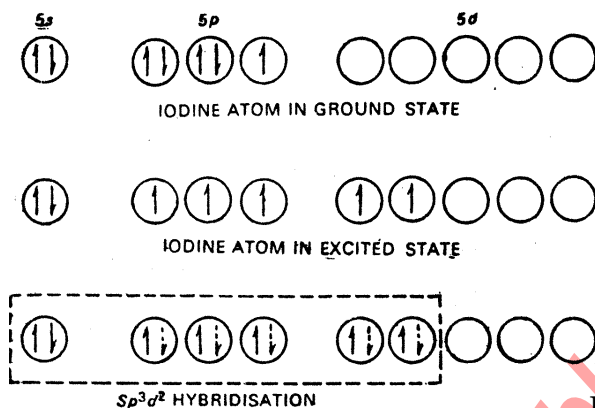
Fig. 3.7 Structure of IF$_5$

4.   Type AX$_7$ (IF$_7$). This compound has a pentagonalbipyramidal structure since this is formed by sp^3d^3 hybridisation.
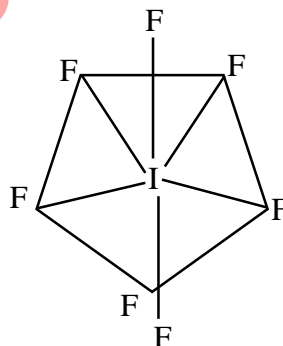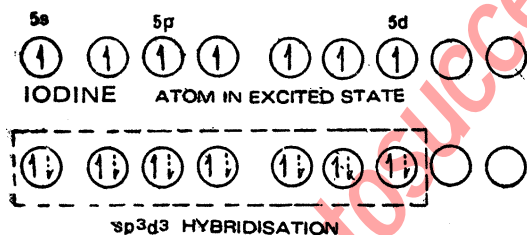
Fig. 3.8 Structure of IF$_7$

Problem

An element **A** occupies group number 17 and period number 2, shows anomalous behaviour. **A** reacts with water forms a mixture of **B, C** and acid **D**. **B** and **C** are allotropes. **A** also reacts with hydrogen violently even in dark to give an acid **D.** Identify **A,B,C** and **D.** write the reactions.

Solution

i)   The element **A** that occupies group number 17 and period number 2 is fluorine.

ii)   Fluorine reacts with water and forms a mixture of **B** and **C**

$$2F_2 + 2H_2O   \rightarrow   4HF + O_2$$

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$$3F_2 + 3H_2O \quad \rightarrow \quad 6HF + O_3$$
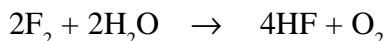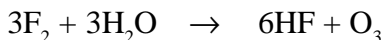
Therefore, **B** is Oxygen and **C** is Ozone.

iii) Fluorine reacts with hydrogen to give **D.**

$$F_2 + H_2 \quad \rightarrow \quad 2HF$$

D is Hydrofluoric acid.

3.6 GROUP 18 NOBLE GASES OR INERT GASES

Group 18 of the periodic table consists of helium, neon, argon, krypton, xenon and radon. All these are gases under ordinary conditions of temperature and pressure. All of them (except Rn) are present in air in traces. Rn is obtained from radio active distintegration of radium.

On account of their very minute quantities in atmosphere, they were named as **rare gases.** Due to their chemical inactivity these were named as **inert gases.** A number of xenon compounds and two krypton fluorides were prepared and thus they were named as **noble gases.**

Electronic Configuration

All these elements possess $ns^2 np^6$ configuration. The differentiating electron enters into p-sub shell and thus are included in p-block elements.

Table 3.6 Electronic Configuration of Group 18 elements

| Element	Atomic Number	Electronic Configuration	Group Number	Period Number
Helium	2	$1s^2$	18	1
Neon	10	$1s^2 2s^2 2p^6$	18	2
Argon	18	$1s^2 2s^2 2p^6 3s^2\ 3p^6$	18	3
Krypton	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2\ 4p^6$	18	4
Xenon	54	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$ $4p^6 4d^{10} 5s^2\ 5p^6$	18	5
Radon	86	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2\ 4p^6$ $4d^{10} 4f^{14} 5s^2\ 5p^6 5d^{10} 6s^2\ 6p^6$	18	6

ISOLATION OF NOBLE GASES

The noble gases are isolated from air by removing oxygen and nitrogen from air free from carbon-di-oxide, water vapour, dust particles, etc., This can be accomplished by either chemical methods or physical methods. In the chemical method, the unwanted gases are removed by means of compound formation while in the physical method, these are removed by the fractional evaporation of liquid air.

CHEMICAL METHOD

The first step in this method is to isolate the noble gases mixed together, from the atmosphere by passing repeated electric sparks in air so as to remove nitrogen and oxygen as nitrogen dioxide $(N_2 + 2O_2 \rightarrow 2NO_2)$. The second step is to separate the various constituents from one another taking advantage of the fact that they can be adsorbed on activated charcoal at different temperatures.

Step 1 Removal of oxygen and nitrogen of the atmosphere as Nitrogen dioxide

Ramsay - Raleigh's method:- A mixture of air and oxygen is constantly admitted into a glass globe of about 50 litres capacity. Two platinum electrodes are introduced and a discharge from a transformer of about 6000 - 8000 volts is passed by the action of which nitrogen and oxygen rapidly combine to form oxides of nitrogen. The oxides are dissolved out in a solution of sodium hydroxide continuously circulated through the flask.

$$N_2 + O_2 \rightarrow 2\ NO$$
$$2\ NO + O_2 \rightarrow 2NO_2$$
$$2NO_2 + 2NaOH \rightarrow NaNO_3 + NaNO_2 + H_2O$$
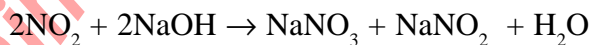
Oxygen if any is removed by introducing alkaline pyrogallol in the globe. The supply of air and electric discharge is shut after some time and the remaining mixture of noble gases is pumped out.
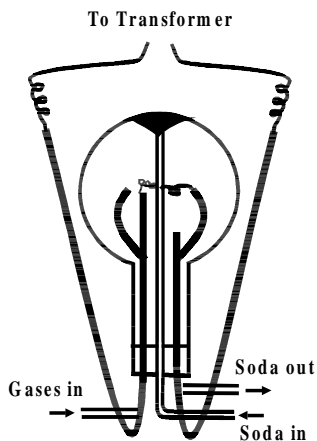
Fig. 3.9 Chemical method for isolation of noble gases

Step 2 Separation of noble gases (DEWAR'S METHOD)

The mixture of noble gases obtained by the above method is separated into individual constituents by the use of coconut charcoal which adsorbs different gases at different temperatures.
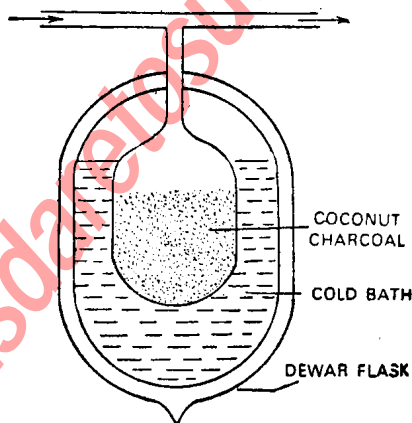
Fig. 3.10 Separation of noble gases (Dewar's method)

The mixture of noble gases is passed into a double-walled bulb containing coconut charcoal and placed in a low temperature bath at 173K. It is allowed to remain in contact with the charcoal for about half an hour. At 173K, only argon,

krypton and xenon are adsorbed by the charcoal while helium and neon remain unadsorbed. These are pumped out and collected.

The mixture of helium and neon is kept in contact with coconut charcoal at 93K which completely adsorbs neon leaving free helium.

The charcoal at 173K containing argon, krypton and xenon is placed in contact with another charcoal at the temperature of the liquid air when argon diffuse into the other charcoal.

The temperature of the first charcoal (temp.173K) still containing krypton and xenon is raised to 183K when krypton is set free while xenon remain adsorbed in the charcoal. When it is heated, xenon is recovered.

XENON FLUORIDE COMPOUNDS

Xenon forms three binary Fluorides XeF_2, XeF_4, and XeF_6 by the direct union of elements under appropriate experimental conditions.

$$Xe + F_2 \xrightarrow{\text{673K}} XeF_2$$

$$Xe + 2 F_2 \xrightarrow{\text{673K}} XeF_4$$

$$Xe + 3 F_2 \xrightarrow{\text{573K}} XeF_6$$
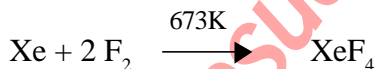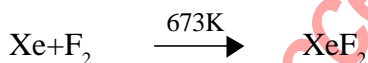
PROPERTIES: XeF_2, XeF_4 and XeF_6 are colourless crystalline solids subliming readily at 298K. They are powerful fluorinating agents. They are readily hydrolysed by even traces of water. For example.

$$2XeF_2 + 2 H_2O \rightarrow 2Xe + 4HF + O_2$$
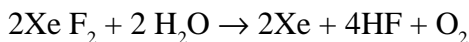
Structure: The structure of the three xenon fluorides can be deduced from VSEPR theory. XeF_2 and XeF_4 have the linear and square planar structure respectively. XeF_6, has 7 electron pairs (6 bonding and one lone pair) and thus have a distorted octahedral structure in the gas phase.

USES OF NOBLE GAS

(A) HELIUM

1. Because of its lightness and non-inflammability helium is used to filling balloons for meteorological observations.
2. Because of its lightness it is used in inflating aeroplane tyres.
3. Helium oxygen mixture is used by deep-sea divers in preference to nitrogen oxygen mixtures. It is much less soluble in blood than N_2. This prevents "**bends**" which is the pain caused by formation of nitrogen bubbles in blood veins when a diver comes to the surface.
4. A mixture of oxygen and helium is used in the treatment of asthma.
5. Liquid helium (b.pt 4.2K) is used as cryogenic agent for carrying out various experiments at low temperatures.
6. It is used to produce and sustain powerful super conducting magnets which form essential part of modern NMR Spectrometers and Magnetic Resonance Imaging system (MRI) for clinical diagnosis.

(B) NEON

1. Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes.
2. Mixed with helium it is used to protect electrical instruments from high Voltages.
3. It is also used in beacon lights for safety of air navigation as the light possesses fog and storm-penetrating power.
4. Neon light is used in botanical gardens as it stimulates growth and helps the formation of chlorophyll.

(C) ARGON

1. Mixed with 26% percent nitrogen it is used in gas filled electric lamps.
2. It is also used in radio valves and tubes.

(D) KRYPTON AND XENON

1. Krypton and xenon are also used in filling incandescent metal filament electric bulbs.
2. They are also used to a small extent in discharge tubes.

(E) RADON

1. It is used in radioactive research and in radiotherapy for treatment of cancer.

SELF EVALUATION

A. Choose the correct answer

1 Which of the following does not belong to group 13?

   a) B   b) Al   c) Ge   d) In

2. Which of the following is most abundant in earth's crust?

   a) C   b) Si   c) Ge   d) Sn

3. An element which was burnt in limited supply of air to give oxide **A** which on treatment with water gives an acid. **B**. Acid **B** on heating gives acid **C** which gives yellow precipitate with $AgNO_3$ solution **A** is

   a) SO_2 b) NO_2 c) P_2O_3 d) SO_3

4. The compound with garlic odour is

   a) P_2O_3 b) P_2O_5 c) H_3PO_3 d) H_3PO_4

5. The shape of PCl_5 is

   a) pyramidal   b) trigonal bipyramidal

   c) linear   d) tetrahedral

6. The compound used as smoke screen

   a) PCl_3 b) PCl_5 c) PH_3 d) H_3PO_3

7. Which shows only -1 oxidation state?

   a) fluorine   b) bromine   c) chlorine   d) iodine

8. One can draw the map of building on a glass plate by

   a) HI   b) HF   c) HBr   d) HCl

9. Among the halogen acid, the weakest acid is

   a) HF   b) HCl   c) HBr   d) HI

10. Halogens belong to the group number

   a) 14   b) 15   c) 17   d) 18

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11. The noble gases are unreactive because they

    a) have same number of electrons   b) have an atomicity of one
    c) are gases with low densities   d) have stable electronic configuration.

12. The shape of XeF_4 is

    a) tetrahedral   b) octahedral   c) square planar   d) pyramidal

13. Which is not known?

    a) XeF_6 b) XeF_4 c) XeO_3 d) ArF_6

14. The lightest gas which is non-inflammable is

    a) He   b) H_2 c) N_2 d) Ar

15. Which of the following has highest first ionisation energy?

    a) He   b) Ne   c) Ar   d) Kr.

B.   Answer in one or two sentences

16. Write a note on plumbo solvency.

17. H_3PO_3 is diprotic. Why?

18. Draw the structure of   a) PCl_5 b) H_3PO_3

19. Prove that P_2O_5 a powerful dehydrating agent.

20. Why H_2O is a liquid while H_2S is a gas?

21. Why the compounds of fluorine with oxygen are called fluorides of oxygen and not oxides of fluorine?

22. Fluorine atom is more electronegative than iodine atom yet, HF has lower acid strength than HI. Explain?

23. What are interhalogen compounds? How are they formed?

24. Discuss the oxidising power of fluorine.

25. How is XeF_6 prepared?

26. Why do noble gases form compounds with fluorine and oxygen only?

27. Write the uses of Neon?

C. Answer not exceeding 60 words

28. What are silicones? How are they prepared? Mention its uses?

29. Give an account of manufacture of lead. Describe its important properties and uses.

30. How are the following compounds prepared from phosphorus?

    a) P_2O_3 b) P_2O_5 c) PCl_3 d) PCl_5 e) PH_3

31. How fluorine is isolated from their fluorides? Describe its important properties and uses.

32. Give a detailed account of the interhalogen compounds with special reference to the compounds involving iodine. Draw their structures.

33. Describe in detail how noble gases are isolated from air?

34. Give an account of various types of compounds which are formed by xenon?

D. Practice Problems

1. An element **A** belongs to 14th group is a metal, which can be cut with a knife. It is not a good conductor of heat and electricity. **A** in pure state does not react with water but air dissolved water forms hydroxide. Identify **A.**

2. An element **A** occupies group number 15 and period number 3, exhibits allotropy and it is tetra atomic. **A** reacts with caustic soda a to give **B** which is having rotten fish odour. **A** reacts with chlorine to give **C** which has a smell of garlic. Identity **A**, **B** and **C**. Write the reactions.

3. An element **A** occupies group number 15 and period number 3, reacts with chlorine to give compound **B**. The compound **B** on hydrolysis gives a dibasic acid **C**. The compound **C** on heating undergoes auto oxidation and reduction to give a tribasic acid **D**. Identify the element **A**, compound **B**, **C** and **D**. Write the reactions.

4. An element **A** occupies group number 17 and period number 2, is the most electronegative element. Element **A** reacts with another element **B**, Which occupies group number 17 and period number 4, to give a compound **C**.

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Compound **C** undergoes sp^3d^2 hybridisation and has octahedral structure. Identify the elements **A** and **B** and the compound **C**. Write the reactions.

SUMMARY

➢ Groups 13-18 of the periodic table are known as p-block elements.

➢ Group 13 is known as boron family. Potash alum is manufactured from alunite.

➢ Group 14 is known as carbon family. Silicones are organo silicon polymers. Lead is extracted from galena.

➢ Group 15 is known as nitrogen family. Phosphorus form oxides, halides, oxyacids and hydrides.

➢ Group 16 is known as oxygen family.

➢ Group 17 is known as halogen family. Fluorine has different behaviour than other halogens. Halogens are extremely reactive and as such they are found in the combined state only. Fluorine is the most electronegative of all elements. F_2 is obtained by electrolysis of their halide salts.

➢ Group 18 is known as rare gases or inert gases, with closed valence shell electronic configuration exhibit low chemical reactivity. Xenon can form compounds with fluorine.

References

1. Inorganic Chemistry by P.L.Soni.

2. Inorganic Chemistry by Puri and Sharma.

3. Concise Inorganic Chemistry by J.D.Lee.

4. Chemistry fourth edition by McMurry Fay.

4. *d* - BLOCK ELEMENTS

Learning Objectives

❧ *To study the nature of four transition series and their general characteristic properties of d-block elements.*

❧ *To learn the general methods of extraction of metals.*

❧ *To have an idea about the composition, properties and uses of alloys.*

❧ *To study about the methods of preparation of compounds, their properties and uses.*

"There will come a time, when the world will be filled with one science, one truth, one industry, one brotherhood, one friendship with nature... this is my belief, it progresses, it grows stronger, this is worth living for, this is worth waiting for."

Dimitry Mendeleyev, Russian Chemist in YA Urmantsev.

	3	4	5	6	7	8	9	10	11	12	
	21 Sc 3d	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	
	39 Y 4d	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	13-17 p-BLOCK
	57 La 5d	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	
	89 Ac 6d	104 Rf	105 Ha	106 Dh	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub	

1-2 s-BLOCK

18 inert gases

The d-block elements are located in the middle of the periodic table and consists of metals only. It consists of four series, each series consists of 10 elements.

In these elements, the last electron enters the d orbital of the penultimate shell i.e. the last electron goes to $(n-1)$ d orbital. Hence these elements are named as d-block elements. These elements have partly filled d-subshells in their elementary form or in their simple ions. The d-block elements are called transition elements because these represent a transition from highly electropositive elements (metals) of s-block to least electropositive elements (non-metals) of p-block.

Classification of d-block Elements

Based on whether the last electron goes to 3d,4d,5d or 6d orbital, d-block elements are classified into four series. They are

i)   3d series or First transition series ($_{21}$Sc to $_{30}$Zn)

ii) 4d series or Second transition series ($_{39}$Y to $_{48}$Cd)

iii) 5d series or Third transition series ($_{57}$La and $_{72}$Hf to $_{80}$Hg)

iv) 6d series or Fourth transition series ($_{89}$Ac and $_{104}$Rf to 112) or Incomplete series.

Electronic configuration of d-block Elements

In the transition elements, d-orbitals of penultimate shell are successively filled. The first transition series involves the filling of 3d orbitals. It starts from scandium (Z=21) and goes up to zinc (Z=30).

The second transition series involves the filling of 4d-orbitals and includes 10 elements from yttrium (Z=39) to cadmium (Z=48).

The third transition series involves filling of 5d-orbitals. The first element of this series is lanthanum (Z=57). It is followed by fourteen elements called lanthanides which involve the filling of 4f-orbitals. The next nine elements from hafnium (Z=72) to mercury (Z=80) belong to third transition series.

The general electronic configuration of transition elements is $(n-1)d^{1-10} ns^{1-2}$.

4.1 General characteristics of d-block elements

4.1.1 Atomic and Ionic Radii

The atomic and ionic radii of transition elements are smaller than those of p-block elements and larger than those of s-block elements. The atomic and ionic radii of first transition elements are given in the Table 4.1.

Table 4.1 Atomic radii of elements of first transition series

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic (pm) radii	144	132	122	118	117	117	116	115	117	125

The atomic radii of first transition series decreases from Sc to Cr and remains almost constant till Cu and then increases towards the end. This can be explained based on two effects namely screening and the nuclear charge effect. These two effects oppose each other resulting in increase in nuclear charge. Hence very slight variation in the atomic radii from Cr to Cu is observed.

It has been observed that Zirconium and Hafnium have almost equal atomic radii. This is because of lanthanide contraction.

4.1.2 Metallic character

All the transition elements are metals, since the number of electrons in the outermost shell is very small, being equal to 2. They are hard, malleable and

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ductile. The presence of partially d-orbitals favours covalent bonding. These metals are good conductors of heat and electricity.

4.1.3 Formation of coloured ions

Most of the transition metal compounds are coloured in their solid or solution form. The colour of transition metal ions is due to the presence of unpaired electrons in it and the energy gap between two energy levels in the same d-subshell being small. Hence very small amount of energy is required for excitation of electrons from one energy level to the other. The energy can be easily provided by the visible light. The colour observed corresponds to the complementary colour of the light absorbed.

The colour of some transition metal ions are given in the Table 4.2.

Ion	Outer Configuration	Colour
Sc^{3+}, Ti^{4+}	$3d^0$	Colourless
Ti^{3+}	$3d^1$	Purple
V^{3+}	$3d^2$	Green
V^{2+}, Cr^{3+}	$3d^3$	Violet
Mn^{3+}	$3d^4$	Violet
Mn^{2+}	$3d^5$	Pink
Fe^{3+}	$3d^5$	Brown
Fe^{2+}	$3d^6$	Green
Co^{2+}	$3d^7$	Pink
Ni^{2+}	$3d^8$	Green
Cu^{2+}	$3d^9$	Blue
Cu^+	$3d^{10}$	Colourless
Zn^{2+}	$3d^{10}$	Colourless

It may be noted that Zinc, Cadmium and Mercury salts do not form any coloured compounds because of the absence of vacant d orbitals to which electrons can be excited. Sc^{3+} ions are also colourless because of the absence of d-electrons.

4.1.4 Catalytic Properties

Most of the transition metals and their compounds are used as catalyst. The catalytic activity of transition metals is due to the following reasons.

i) They show a variety of oxidation states and thereby can form intermediate products with various reactants.

ii) They are also capable of forming interstitial compounds which can adsorb and activate the reacting species.

Some examples of catalyst are

i) Iron / molybdenum act as catalyst in the synthesis of ammonia by Haber's Process.

ii) Vanadium pentoxide (V_2O_5) is used for catalytic oxidation of SO_2 to SO_3

iii) $TiCl_4$ is employed as a catalyst in the manufacture of polythene.

4.1.5 Variable oxidation states

All transition elements exhibit variety of oxidation states (or) variable valencies in their compounds. This property is due to the following reasons.

i) These elements have several $(n-1)$ d and ns electrons.

ii) The energies of $(n-1)$d and ns orbitals are fairly close to each other.

Salient features of oxidation states of transition elements

1. The elements which exhibit the maximum number of oxidation states occur either in or near the middle of the series. For example , in the first transition series manganese exhibits maximum number of oxidation states $(+2$ to $+7)$.

2. The elements in the beginning of the series exhibit fewer oxidation states because they have less number of d-electrons which they can lose or contribute for sharing. The elements at the end of the series exhibit fewer oxidation states, because they have too many d electrons and hence fewer vacant d-orbitals can be involved in bonding.

3.	The transition elements in lower oxidation states (+2 and +3) generally form ionic bonds and in higher oxidation state form covalent bonds.

4.	The highest oxidation state shown by any transition metal is +8. For example, ruthenium and osmium show highest oxidation states of +8 in some of their compounds.

5.	Some transition metals show oxidation state of zero in their compounds. $Ni(CO)_4$ and $Fe(CO)_5$ are common examples.

### 4.1.6	Magnetic Properties

The magnetic properties of a substance are determined by the number of unpaired electrons in it. There are two main type of substances.

### i)	Paramagnetic substances

The paramagnetic character arises because of the presence of unpaired electrons. Paramagnetic substances are the substances which are attracted by magnetic field.

### ii)	Diamagnetic Substances

Diamagnetic character arises because of the absence of unpaired electrons. Diamagnetic substance are the substances which are repelled by the magnetic field.

Most of the transition elements and their compounds are paramagnetic and are attracted by magnetic field. Greater the number of unpaired electrons in the substance greater is the paramagnetic character, The magnetic character of a substance is expressed in terms of magnetic moments. The magnetic moment can be calculated using the relation

$$\mu = \sqrt{n(n+2)}\, BM \text{ (Bohr Magneton)}$$

n = number of unpaired electrons

Example

Ti^{3+} - The number of unpaired electrons is 1. Hence

$$\mu = \sqrt{1(1+2)}\, BM \ = \ \sqrt{3} \ = 1.732 \text{ B.M}$$

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Larger the value of magnetic moment, the greater is the paramagnetic character.

In addition to paramagnetic and diamagnetic substance, there are a few substances such as iron which are highly magnetic as compared to ordinary metals. These substances are called ferromagnetic substances

4.1.7 Complex formation

The cations of d-block elements have strong tendency to form complexes with certain molecules (e.g. CO, NO, NH_3....etc) or ions (e.g. F^-, Cl^-, CN^- ....etc) called ligands. Their tendency to form complexes is due to two reasons.

i)   Small size and high positive charge density.

ii)   Presence of vacant (n-1)d orbitals which are of appropriate energy to accept lone pair and unshared pair of electrons from the ligands for bonding with them.

Examples of some complex compounds are,

$[Cu(NH_3)_4]^{2+}$, $[Ag(NH_3)_2]^+$, $[Fe(CN)_6]^{4-}$,....etc.
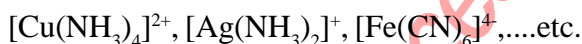
4.1.8 Formation of alloys

Transition metals form alloys with each other. This is because they have almost similar size and the atoms of one metal can easily take up positions in the crystal lattice of the other.

Eg. Alloys of Cr-Ni, Cr-Ni-Fe, Cr-V-Fe, Mn-Fe......etc.

4.2 FIRST TRANSITION SERIES

4.2.1 Occurrence and principles of extraction of copper

Atomic mass   : 63.54   Valency :   1 and 2
Atomic number : 29   Symbol :   Cu
Position in the periodic table : Period Number -4, Group Number -11.

Occurrence

Copper was known to the earliest races of mankind. It was named as cuprum by the Romans because they used to get it from the island of Cyprus. Copper is found in the native state as well as in the combined state. Native copper is found in large quantities in Michigan (USA). In India, copper is mainly found in Singhbhum (Bihar), Khetri and Darbia (Rajasthan) and in Tamilnadu.

Ores

i) Copper pyrite, $CuFeS_2$.
ii) Cuprite or Ruby copper, Cu_2O.
iii) Copper glance, Cu_2S.

The chief ore of copper is copper pyrite. It yields nearly 76% of the world production of copper.

Extraction from copper pyrites

Extraction of copper from copper pyrites involves the following steps.

1. Crushing and concentration

The ore is crushed and then concentrated by froth-floatation process.

2. Roasting

The concentrated ore is heated strongly in the reverberatory furnace, in excess of air. During roasting,

i) Moisture is removed.
ii) The volatile impurities are removed.
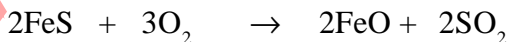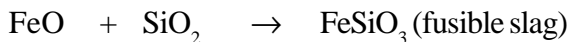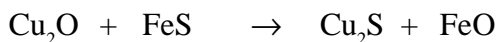iii) Sulphur, phosphorus, arsenic and antimony which are present as impurity are removed as volatile oxides.
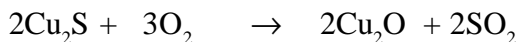
$$S + O_2 \rightarrow SO_2$$
$$P_4 + 5O_2 \rightarrow 2P_2O_5$$
$$4As + 3O_2 \rightarrow 2As_2O_3$$
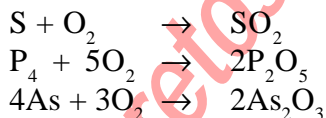
iv) The copper pyrite is partly converted into sulphides of copper and iron.

$$2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$$
$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$
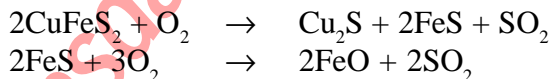
3. Smelting

The roasted ore is mixed with powdered coke and sand and is heated in a blast furnace. It is made of steel plates lined inside with fire clay bricks. Hot air at 800°C is introduced from the tuyers near the base of the furnace. As a result, the following changes occur.

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$

$$FeO \ + \ SiO_2 \quad \rightarrow \quad FeSiO_3 \text{(fusible slag)}$$
$$2Cu_2S + \ 3O_2 \quad \rightarrow \quad 2Cu_2O \ + 2SO_2$$
$$Cu_2O \ + \ FeS \quad \rightarrow \quad Cu_2S \ + \ FeO$$
$$FeO \ + \ SiO_2 \quad \rightarrow \quad FeSiO_3 \text{(fusible slag)}$$
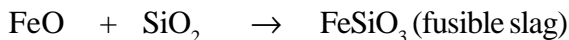
As a result of smelting, two separate molten layers are formed at the bottom of the furnace. The upper layer consists of slag and is removed as a waste while the lower layer is called matte. It chiefly consists of cuprous sulphide and some unchanged ferrous sulphide.

4.   Bessemerisation

The molten matte is transfered to a Bessemer converter as shown in the Fig. 4.2. The Bessemer is mounted on a horizontal axis and is fitted with small pipes called tuyeres through which a blast of hot air and fine sand is admitted.

Any sulphur, arsenic and antimony still present escape as their respective oxides. Ferrous sulphide present in matte is oxidised to ferrous oxide which combines with silica to form slag

$$2FeS \ + \ 3O_2 \quad \rightarrow \quad 2FeO \ + \ 2SO_2$$
$$FeO \ + \ SiO_2 \quad \rightarrow \quad FeSiO_3 \text{(slag)}$$
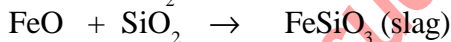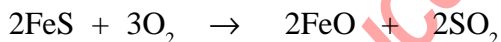
Some of the cuprous sulphide undergoes oxidation to form cuprous oxide which then reacts with more cuprous sulphide to give copper metal. The impure metal thus obtained is called blister copper and is about 98% pure.

$$2Cu_2S \ + \ 3O_2 \quad \rightarrow \quad 2Cu_2O \ + \ 2SO_2$$
$$2Cu_2O \ + \ Cu_2S \rightarrow \quad 6Cu \quad + \ SO_2$$

5.   Refining

Blister copper contains about 2% of impurities and it is purified by electrolytic refining.

Electrolytic Refining

This method is used to get metal of high degree of purity. For electrolytic refining of copper,

i)   A block of impure copper metal acts as anode

ii)   A thin plate of pure copper metal acts as cathode

iii)   Copper sulphate solution acidified with sulphuric acid is taken as electrolyte.

When electric current is passed through the electrolytic solution pure copper get deposited on the cathode ,impurities settle near the anode in the form of sludge called anode mud.

Properties

Physical properties

Copper is a reddish brown metal, with high lustre, high density and high melting point 1356°C.

Chemical Properties

i)   Action of air and moisture

Copper gets covered with a green layer of basic copper carbonate, in the presence of CO_2 and moisture

$$2Cu + O_2 + CO_2 + H_2O \rightarrow Cu(OH)_2 . CuCO_3$$
$$\text{(Green) Copper Carbonate}$$

ii)   Action of Heat

Copper when heated to redness (below 1370K) in the presence of oxygen or air, first it gets converted to black cupric oxide and further heating to above 1370K, it gets converted into red cuprous oxide.

$$2Cu + O_2 \xrightarrow{\text{Below } 1370\,K} 2CuO$$
$$4Cu + O_2 \xrightarrow{\text{Above } 1370\,K} 2Cu_2O$$
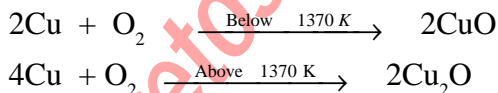
iii)   Action of acids

a)   With dil.HCl and H_2SO_4

Dilute acids such as HCl and H_2SO_4 have no action on these metals in the absence of air or an oxidising agent. Copper dissolves in these acids in the presence of air

$$2Cu + 4HCl + O_2 \text{ (air)} \rightarrow 2CuCl_2 + 2H_2O$$
$$2Cu + 2H_2SO_4 + O_2 \text{ (air)} \rightarrow 2CuSO_4 + 2H_2O$$
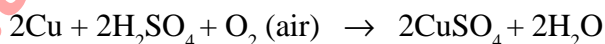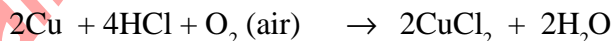
b)   With dil. HNO_3

Copper reacts with dil.HNO_3 with the liberation of NO gas.

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

c) With con.HNO_3 and con. H_2SO_4

Copper reacts with con.HNO_3 and con.H_2SO_4 with the liberation of NO_2 and SO_2 respectively.

$$Cu + 4HNO_3 \text{ (con)} \quad \rightarrow \quad Cu(NO_3)_2 + 2NO_2\uparrow + 2H_2O$$

$$Cu + 2H_2SO_4 \text{ (con)} \quad \rightarrow \quad CuSO_4 + SO_2\uparrow + 2H_2O$$
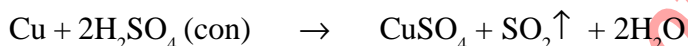
iv) Action of chlorine

Chlorine reacts with copper, resulting in the formation of copper chloride.

$$Cu + Cl_2 \quad \rightarrow \quad CuCl_2$$
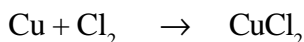
v) Action of alkalis

Copper is not attacked by alkalies.

Uses

1. It is extensively used for making electric cables and other electric appliances.
2. It is used for making utensils, containers, calorimeters, coins, ... etc.
3. It is used in electroplating.
4. It is alloyed with gold and silver for making coins and jewellery.

Alloys of Copper

	Alloy	% composition	Uses
i)	Brass	Cu = 60-80, Zn = 20-40	For making utensils, condenser tubes, wires, ...etc.
ii)	Bronze	Cu = 75-90, Sn = 10-25	For making cooking utensils, statues, coins ...etc.
iii)	Gun metal	Cu = 87, Sn = 10, Zn = 3	For making gun barrels, gears, castings etc.

4.2.2 Occurrence and principles of extraction of chromium

Chromium

Atomic mass   :   51.99   Valency :   0,1,2,3,4,5,6

Atomic number :   24   Symbol :   Cr

Position in the periodic table : Period Number -4, Group Number -6.

L.N. Vanquelin, a french chemist discovered a new element in 1797, while examining a mineral found in Siberia. It was named chromium because it forms coloured compounds [Greek word - chroma - colour]

Occurrence

Metallic chromium does not occur in the native state. In India chromite ore occurs in Bihar, Mysore, Chennai and Bombay.

Ores

The important ore of chromium is

Chromite or chrome ore, $FeO\ Cr_2O_3$

The chief ore of chromium is chromite ore.

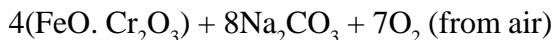### Extraction of chromium metal from chromite ore

The extraction of chromium metal from chromite ore consists of the following steps.

1. Concentration

The crushed ore is concentrated by gravity separation method.
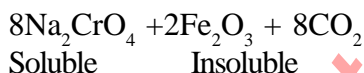
2. Conversion of the concentrated chromite ore into Na_2CrO_4

The concentrated ore is mixed with excess of Na_2CO_3 and a small amount of lime and roasted in a reverberatory furnace at 900-1000°C in the presence of free supply of air. During this process, chromite ore is converted into soluble sodium chromate.
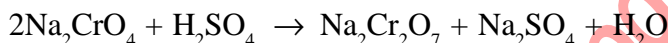
4(FeO. Cr_2O_3) + 8Na_2CO_3 + 7O_2 (from air)

Chromite ore   ↓ 900-1000°C

$$8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$
Soluble   Insoluble

## Conversion of Na_2CrO_4 into $Na_2Cr_2O_7$

The solution containing Na_2CrO_4 is treated with a calculated quantity of H_2SO_4, Na_2CrO_4 is converted into $Na_2Cr_2O_7$.

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

Conversion of $Na_2Cr_2O_7$ into Cr_2O_3

$Na_2Cr_2O_7$ is heated with carbon to get sodium chromite, $Na_2Cr_2O_4$ which on treatment with H_2O, gives Cr_2O_3 precipitate.

$$Na_2Cr_2O_7 + 3C \rightarrow Na_2Cr_2O_4 + 3CO\uparrow$$

$$Na_2Cr_2O_4 + H_2O \rightarrow Cr_2O_3\downarrow + 2\ NaOH$$
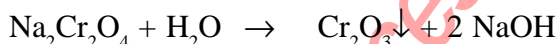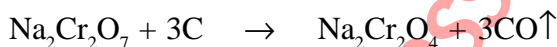
Reduction of Cr_2O_3 to chromium metal
Aluminothermic process

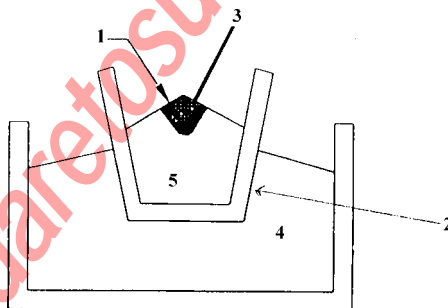**Fig. 4.1 Aluminothermic process**

1. BaO_2 + Mg Powder   2. Fireclay crucible   3. Magnesium ribbon,

4. Sand   5. Cr_2O_3 + Al

Chromic oxide is mixed with powdered Aluminium in the ratio 3:1 and is placed in a large fire clay crucible. A mixture of barium peroxide and Mg powder is placed over this. The crucible is surrounded by sand which prevents loss of heat by radiation. The mixture is ignited by a piece of Mg ribbon. During this process a large amount of heat is liberated, in which Cr_2O_3 is reduced to chromium.

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The molten chromium is collected in the crucible and aluminium oxide is removed as slag.

$$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3 + 468.6 \text{ kJ}$$
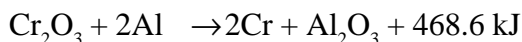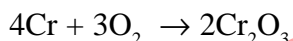
Properties of Cr

Physical Properties

1. The metal is silvery white and crystalline.

2. It is very hard and brittle

3. It melts at 2113K.

Chemical Properties

1. **Action of air** : It is unaffected by air at ordinary temperatures.

   When heated to very high temperature at about 2000°C it is oxidised to chromic oxide.

   $$4Cr + 3O_2 \rightarrow 2Cr_2O_3$$

2. **Action of Water** : There is no action at ordinary temperatures. However it decomposes steam at red heat to give chromic oxide and hydrogen.

   $$2Cr + 3H_2O \rightarrow Cr_2O_3 + 3H_2$$

3. **Action of Acids** : It dissolves in dilute hydrochloric acid and sulphuric acid to liberate hydrogen and forms chromous salts.

   $$Cr + 2HCl \rightarrow CrCl_2 + H_2\uparrow$$
   $$Cr + H_2SO_4 \rightarrow CrSO_4 + H_2\uparrow$$
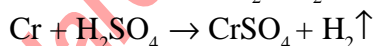
4. With hot concentrated sulphuric acid it gives chromic sulphate and liberates sulphur dioxide.

   $$2Cr + 6H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3SO_2 + 6H_2O$$
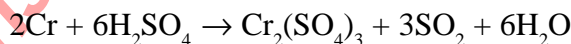
5. Dilute nitric acid does not attack the pure metal while concentrated acid renders it inactive or passive i.e., it does not show its usual reactions.

6. **Action with Halogens** : Chromium combines directly with fluorine and dry chlorine to give chromium (III) halides.

   $$2Cr + 3F_2 \rightarrow 2CrF_3$$
   $$2Cr + 3Cl_2 \rightarrow 2CrCl_3$$

112
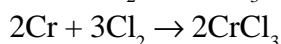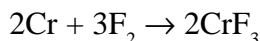
Use : In chrome - plating.

1. The articles to be plated with chromium are made the cathode in an electrolytic bath consisting of chromic acid and sulphuric acid while the anode is made of a plate of lead. During electrolysis chromium deposits on the article (cathode). Generally the articles are first plated with nickel and then subjected to chromium plating.

2. In the manufacture of alloy steels (e.g.) chrome steel, chrome vanadium steel, stainless steel and tungsten steel.

3. Chrome nickel steel is used for armour plates.

4. Chromium salts are used as mordants and in the manufacture of coloured glass and pottery.

5. Chromium compounds are used in dyeing as pigments and in tanning of leather.

Alloys of chromium

	Alloy	% composition	Uses
i)	Ferrochrome	Cr = 65% Fe = 35%	It is used in manufacture of chrome steel, burglar proof safe
ii)	Stainless steel	Cr = 11-13% C = 0.1 - 0.4% Fe = 73% Ni = 8%	It is used for cutlery and house hold wares.
iii)	Nichrome	Cr = 15%, Ni = 60% Fe = 25%	It is used in resistance wires for electrical heating
iv)	Stellite	Cr = 20-35% Co = 40-80% Ni = 0.25% C = 0.75 - 2.5%	It is used in cutlery, surgical instruments,.....etc.

4.2.3 Occurrence and principles of extraction of zinc

Zinc

Atomic mass	:	65.37	Valence :	2

Atomic number : 30   Symbol : Zn

Position in the periodic table : Period Number -4, Group Number -12.

The ancient used an alloy of Zn and Cu not very different from brass without knowing its actual composition. Zinc has been known in our country for a long time and has been mentioned in Ayurvedic treatises as yashda. It is commonly called jast.

Occurrence

Zinc does not occur in the native form since it is a reactive metal. However, in the combined state, zinc is widely distributed.

Ores

The important ores of zinc are

i)   Zinc blende, ZnS

ii)   Calamine, $ZnCO_3$

iii)   Zincite, ZnO

The chief ore of Zinc is Zinc blende. In India large deposits of zinc blende occur in Zawar mines near Udaipur in Rajasthan.
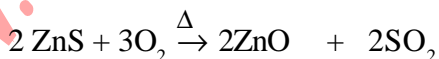
Extraction of Zinc from Zinc blende

The extraction of Zinc from Zinc blende involves the following steps.

1. Concentration

The ore is crushed and then concentrated by froth-floatation process.

2. Roasting

The concentrated ore is then roasted in the presence of excess of air at about 1200 K.

$$2 \, ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO \quad + \quad 2SO_2$$

3. Reduction

Zinc oxide is mixed with powdered coke and heated to 1673 K in a fire clay retort, in which ZnO is reduced to zinc metal.

$$ZnO + C \quad \xrightarrow{1673\ K} \quad Zn + CO$$
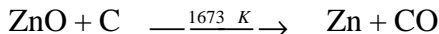
Purification

Zinc is purified by electrolytic refining. In this process, Impure Zinc is anode and cathode is of pure thin sheet of Zinc. The electrolyte is $ZnSO_4$ solution containing a little of dil.H_2SO_4. On passing electric current, pure zinc get deposited at the cathode.
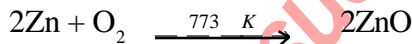
Properties

Physical properties

i)   Zinc is a bluish white metal

ii)   It is good conductor of heat and electricity.

iii) It is malleable and ductile.
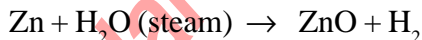
Chemical properties

i)   Action of air

When heated in air at 773 K, it burns to form a white cloud of Zinc oxide which settles to form a wooly flock called philosopher's wool.

$$2Zn + O_2 \quad \xrightarrow{773\ K} \quad 2ZnO$$

ii)   Action of water

Pure zinc does not react with water but impure zinc (Zn-Cu couple) decomposes steam quite readily evolving H_2 gas.

$$Zn + H_2O \text{ (steam)} \rightarrow ZnO + H_2$$

iii) Action of dilute acids

Pure zinc is not attacked by dilute acids. However, impure zinc reacts with dilute acids with the liberation of H_2.

$$Zn + 2HCl \quad \rightarrow \quad ZnCl_2 + H_2\uparrow$$
$$Zn + H_2SO_4 \quad \rightarrow \quad ZnSO_4 + H_2\uparrow$$
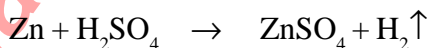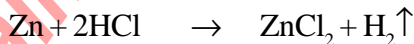
iv) Action of con.H_2SO_4

Zinc reacts with hot con.H_2SO_4 forming $ZnSO_4$.

$$Zn + 2H_2SO_4 \quad \rightarrow ZnSO_4 + SO_2\uparrow + 2H_2O$$

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v) Action of HNO₃

Zinc reacts with HNO_3 at various concentrations and it gives different products.

$$4 Zn + 10 HNO_3 (dil) \rightarrow 4 Zn (NO_3)_2 + N_2O + 5 H_2O$$
$$\text{Nitrous oxide}$$

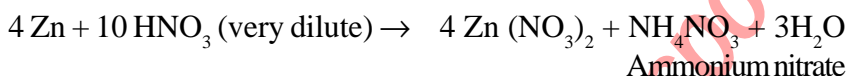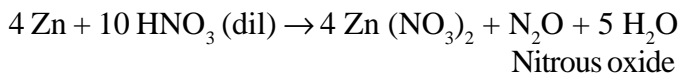$$4 Zn + 10 HNO_3 (very\ dilute) \rightarrow 4 Zn (NO_3)_2 + NH_4NO_3 + 3H_2O$$
$$\text{Ammonium nitrate}$$

vi) Action of alkalies

Zinc dissolves in hot NaOH solution forming soluble zincate ion.

$$Zn + 2NaOH + 2H_2O \rightarrow Na_2ZnO_2 + H_2O$$
$$\text{Sodium zincate}$$
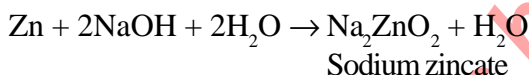
Uses of zinc

1. It is widely used for galvanizing iron sheets.
2. It is used in the extraction of gold and silver by the cyanide process.
3. Zinc plates and rods are used in batteries and dry cells.
4. Zinc dust and granulated zinc are used in laboratory as reducing agents.

4.3 SECOND TRANSITION SERIES

4.3.1 Occurrence and principles of extraction of silver

Silver

Atomic mass : 108   Valency : 1

Atomic number : 47   Symbol : Ag

Position in the periodic table : Period Number -5, Group Number -11.

Occurrence

Silver occurs both in the native as well as in the combined state.

Ores

The important ores of silver are

i) Argentite or silverglance, Ag_2S

ii) Horn silver or chlorargyrite, AgCl

iii) Pyrargyrite or Ruby silver, $Ag_2S . Sb_2 S_3$

The chief ore of silver is Argentite. The silver content in these ores is very small

(about 1%). Silver is obtained to a small extent from the gold ores in the kolar fields in Karnataka and in the Anantapur mines.

## Extraction of silver from the Argentite ore

Silver is extracted from the argentite ore by the Mac-Arthur and Forrest's cyanide process. The various steps involved in this process are as follows.

1. Concentration

The crushed ore is concentrated by froth-floatation process.

2. Treatment of the ore with NaCN

The concentrated ore is treated with 0.4-0.6% solution of sodium cyanide for several hours. The mixture is continuously agitated by a current of air, so that Ag present in the ore is converted into soluble sodium argento complex.

$$Ag_2S + 4NaCN \rightleftharpoons 2Na\,[Ag(CN)_2] + Na_2S$$
$$\text{Sodium argento cyanide (soluble)}$$
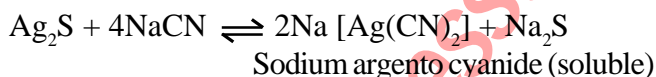
3. Precipitation of silver

The solution containing sodium argento cyanide is filtered to remove insoluble impurities and filtrate is treated with zinc dust, silver gets precipitated.

$$2Na\,[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$

4. Electrolytic refining

The impure silver is further purified by electrolytic refining. The impure silver is made the anode while a thin sheet of pure silver act as the cathode. The electrolyte is silvernitrate acidified with 1% nitric acid. On passing electricity pure silver gets deposited at the cathode.

5. Extraction of silver from silver coins

Silver coins are Ag-Cu alloys. Ag can be obtained from such an allloy by dissolving the alloy in concentrated HNO_3, a solution containing mixture of $AgNO_3$ and $Cu(NO_3)_2$ is obtained. The solution is boiled to expel excess of nitric acid, then the solution is treated with con.HCl, silver is precipitated as AgCl. AgCl is separated and converted to silver by fusing with excess Na_2CO_3.

$$4AgCl + 2Na_2CO_3 \rightarrow 4Ag\downarrow + 4NaCl + 2CO_2 + O_2$$

The silver thus obtained, is purified by fusion with borax and followed by electrolytic purification.

Properties

Physical properties

i)   It is a white lustrous metal.

ii) It melts at 1233°C and boils at 2485°C.

iii) Molten silver absorbs about twenty times its volume of oxygen which it again expels on cooling. Globules of molten silver are thrown off. This is called "spitting of silver". This can be prevented by covering the molten metal with a layer of charcoal.
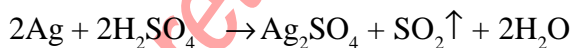
Chemical properties

i)   With dilute HNO_3

Dilute HNO_3 reacts with silver liberating nitric oxide.

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO\uparrow + 2H_2O$$

ii) With con.HNO_3 or con.H_2SO_4

Hot con.HNO_3 or con.H_2SO_4 react with silver liberating NO_2 and SO_2 respectively.

$$Ag + 2\ HNO_3 \rightarrow AgNO_3 + NO_2\uparrow + H_2O$$

$$2Ag + 2H_2SO_4 \rightarrow Ag_2SO_4 + SO_2\uparrow + 2H_2O$$

iii) Action with chlorine

Chlorine attacks silver, forming silver chloride.

$$2Ag + Cl_2 \rightarrow 2AgCl$$
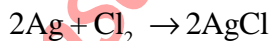
iv) Action of alkalies

Silver is not attacked by alkalies.

Uses of silver

i)   Silver salts are used in silvering of mirrors

ii) AgBr is used in photography

iii) Silver salts are used in silver plating.

iv)   Silver is used in making electrodes.

v)   Silver leaf is used in medicine, while silver amalgam is employed in dental filling.

4.4   THIRD TRANSITION SERIES

4.4.1   Occurrence and principles of extraction of gold

Gold

Atomic mass   :   196.97   Valency : 1 and 3

Atomic number :   79   Symbol :   Au

Position in the periodic table : Period Number -6, Group Number -11.

Occurrence

Gold is mainly found in the native state either mixed with quartz in ancient rocks (vein gold) or scattered in sand and gravel (placer gold) or in the alluvial sand (alluvial gold).

Ores

The important ore of gold is

Alluvial sand or gravel

Nearly half of the total world production of gold comes from the mines in South Africa. India occupies 8th position among the gold producing countries of the world and account for about 2% of the total world production. The Kolar mines in Karnataka produce about 99.97% of our gold output.

Extraction from Gold Ores - Mac Arthur Forrest Cyanide Process. The extraction of gold from the sulphide or telluride ore involves the following steps :

### i)   Crushing, grinding and concentration

The gold ore is crushed and powdered, and then concentrated by froth-floatation process.

ii)   Roasting

The concentrated ore is roasted in excess of air or oxygen when impurities of sulphur, arsenic and tellurium are oxidised and escape as their volatile oxides.

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iii) Treatment with KCN

The finely powdered roasted ore is taken in large vats made up of cement or iron and having false wooden bottoms with holes. It is then treated with a dilute (0.5%) solution of KCN in presence of excess of air for 24 hours. As a result, gold dissolves in KCN to form a soluble complex called potassium aurocyanide.

$$4Au + 8KCN + 2H_2O + O_2 \rightarrow 4K[Au(CN)_2] + 4KOH$$
$$\text{Pot. aurocyanide}$$
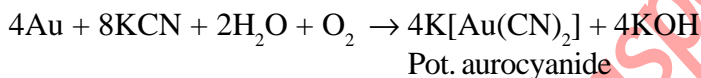
iv) Precipitation of gold

The above solution containing potassium aurocyanide is filtered to remove insoluble impurities and then treated with zinc dust. Gold being less electropositive than zinc, it gets precipitated.

$$2K[Au(CN_2] + Zn \rightarrow K_2[Zn(CN)_4] + 2\ Au\downarrow$$
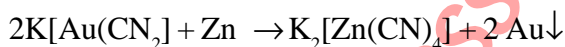
The precipitated gold is recovered by filtration .It is further purified by electro-refining.

iv) Electrolytic refining

This method is used when very pure gold is required. The impure gold is made the anode while a thin sheet of pure gold acts as the cathode. The electrolyte consists of a solution of auric chloride ($AuCl_3$) acidified with 10-12% HCl. On passing current pure gold gets deposited on the cathode.

Properties

Physical properties

i) Gold is a lustrous yellow metal which melts at 1063°C to a green liquid and boils at 2610°C.

ii) It is the most malleable and ductile of all metals.

iii) It is a good conductor of heat and electricity.

Chemical properties

i) Gold is unaffected by dry or moist air or oxygen.
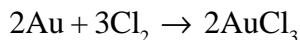
ii) Alkalies have no action on gold.

iii) With Aquaregia

Gold dissolves in aquaregia (3 parts of con.HCl + 1 part of con.HNO_3) to form auric chloride.

$$2Au + 9\ HCl + 3HNO_3 \rightarrow 2AuCl_3 + 6H_2O + 3NOCl$$

$$\text{Auric chloride} \qquad \text{Nitrosyl chloride}$$
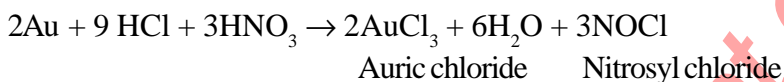
iv) With chlorine

At 200°C, gold is readily attacked by chlorine forming auric chloride.

$$2Au + 3Cl_2 \rightarrow 2AuCl_3$$

Uses

i) It is used in coinage, jewellery and ornamental vessels.
ii) Gold leaf is used for decorations, lettering and in medicine as tonic.
iii) "Purple of cassius" which is a combination of gold with colloidal stannic hydroxide is used for making ruby red glass and high class pottery.

Fineness of gold

Gold content of an alloy of gold is termed its fineness and is generally expressed in carats. Pure gold is 24 carats. Ornaments available these days are made of 18 carat gold, which is an alloy containing 18 parts by weight of gold alloyed with 6 parts by weight of another metal generally copper.

4.5 COMPOUNDS
4.5.1 Potassium dichromate ($K_2Cr_2O_7$)
Preparation of potassium dichromate from chrome iron ore

The preparation of $K_2Cr_2O_7$ from its ore involves the following steps

i) Conversion of chrome iron ore to sodium chromate

The powdered ore is mixed with Na_2CO_3 and quick lime, then roasted in a reverberatory furnace with free expose to air.

$$4FeO.Cr_2O_3 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2\uparrow$$
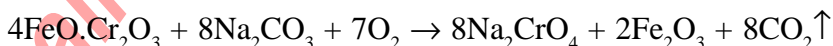
ii) Conversion of Na_2CrO_4 to $Na_2Cr_2O_7$

Sodium chromate solution so obtained is filtered and treated with con.H_2SO_4, when sodium chromate is converted to sodium dichromate.

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$
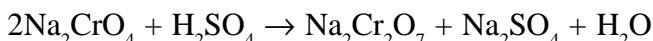
iii) Conversion of sodium dichromate into potassium dichromate

Hot concentrated solution of sodium dichromate is treated with KCl, when potassium dichromate, being much less soluble than sodium salt, crystallizes out on cooling.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$
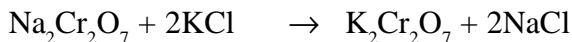
Properties

Physical properties

1. It forms orange red crystals which melt at 396°C.
2. It is moderately soluble in cold water but freely soluble in hot water.
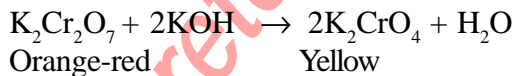
Chemical properties

1. Action of Heat

On heating, $K_2Cr_2O_7$ decomposes to give potassium chromate with evolution of O_2 gas.

$$4K_2Cr_2O_7 \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3\,O_2$$

2. With Alkalies

When an alkali is added to an orange-red solution of $K_2Cr_2O_7$, a yellow solution results due to formation of potassium chromate.

$$K_2Cr_2O_7 + 2KOH \rightarrow 2K_2CrO_4 + H_2O$$
Orange-red   Yellow

on acidifying the yellow colour of K_2CrO_4 again changes to orange red due to reformation of $K_2Cr_2O_7$.

$$2K_2CrO_4 + H_2SO_4 \rightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$
                       Orange red

The inter conversion is explained on the basis of the fact that in $K_2Cr_2O_7$ solution, orange red $Cr_2O_7^{2-}$ ions are in equilibrium with yellow CrO_4^{2-} ions.

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$$
Orange red   Yellow

3. Oxidising properties

$K_2Cr_2O_7$ is a powerful oxidising agent. In presence of dil.H_2SO_4, one mole

of this compound gives three atoms of oxygen as shown below.

$$K_2Cr_2O_7 + 4 \text{ dil.}H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3(O)$$

Some other examples of oxidising property of $K_2Cr_2O_7$ are given below.

i) It liberates I_2 from KI

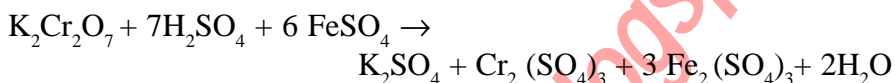$$K_2Cr_2O_7 + 7H_2SO_4 + 6KI \rightarrow 4 K_2SO_4 + Cr_2(SO_4)_3 + 3 I_2 + 7H_2O$$

ii) It oxidises ferrous to ferric salt

$$K_2Cr_2O_7 + 7H_2SO_4 + 6 FeSO_4 \rightarrow$$
$$K_2SO_4 + Cr_2(SO_4)_3 + 3 Fe_2(SO_4)_3 + 2H_2O$$

iii) It oxidises H_2S to sulphur

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$

4. Chromyl chloride test

When salt containing chloride is treated with $K_2Cr_2O_7$ and con. H_2SO_4 reddish brown vapours of chromyl chloride are obtained.
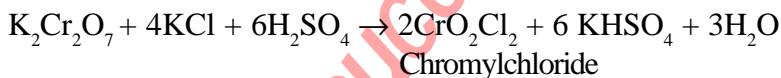
$$K_2Cr_2O_7 + 4KCl + 6H_2SO_4 \rightarrow 2CrO_2Cl_2 + 6 KHSO_4 + 3H_2O$$
$$\text{Chromylchloride}$$

This reaction is used in the detection of chloride ions in qualitative analysis.

Uses

i) It is used in volumetric analysis
ii) In chrome tanning in leather industry
iii) In calico printing and dyeing
iv) In photography and in hardening gelatin film.

4.5.2 Copper Sulphate ($CuSO_4.5H_2O$); Blue vitriol

Preparation

In laboratory it is prepared by dissolving cupric oxide (or) cupric hydroxide (or) cupric carbonate in dilute H_2SO_4

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$$
$$Cu(OH)_2 + H_2SO_4 \rightarrow CuSO_4 + 2H_2O$$
$$CuCO_3 + H_2SO_4 \rightarrow CuSO_4 + H_2O + CO_2\uparrow$$
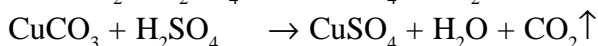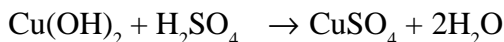
Properties

Physical properties

1. The anhydrous salt is colourless but the hydrated salt is blue in colour.
2. It readily dissolves in water but is insoluble in alcohol.

Chemical Properties

1. Action of Heat

On heating $CuSO_4.5H_2O$ loses its water of crystallization and decomposes at 720°C to give cupric oxide and sulphur trioxide.

$$CuSO_4.5H_2O \quad \xrightarrow[\substack{-4H_2O}]{100°C} \quad CuSO_4.H_2O$$

$$\Big\downarrow{\scriptstyle -H_2O} \;\; 230°C$$

$$SO_3 + CuO \quad \xleftarrow{720°C} \quad CuSO_4$$

(Blue) — (White)
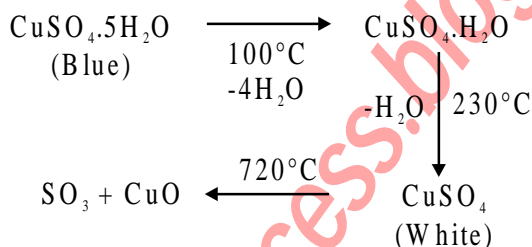
2. Action of ammonia

Copper sulphate gives deep blue colour with NH_4OH forming complex compound.

$$CuSO_4 + 4NH_4OH \rightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$$

3. Action of KI

When KI is added to a solution of $CuSO_4$, a white precipitate of cuprous iodide is produced.

$$CuSO_4 + 2KI \rightarrow CuI_2 + K_2SO_4$$
$$\text{(unstable)}$$

$$2CuI_2 \rightarrow Cu_2I_2 + I_2$$
$$\text{(white ppt)}$$
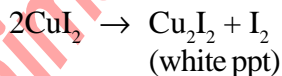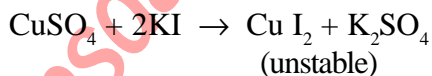
4. Action with KCN

A yellow precipitate of cupric cyanide is first formed with KCN and it decomposes to give cyanogen gas.

$$CuSO_4 + 2KCN \rightarrow Cu(CN)_2 + K_2SO_4$$

$$2Cu(CN)_2 \rightarrow Cu_2(CN)_2 + (CN)_2$$
$$\text{cyanogen}$$
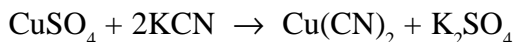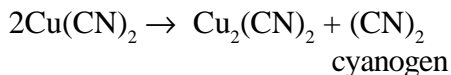
5. Action of alkalies

With alkalies, a pale blue precipitate of copper hydroxide is formed.

$$CuSO_4 + 2NaOH \rightarrow Cu(OH)_2 + Na_2SO_4$$
$$\text{Pale blue precipitate}$$
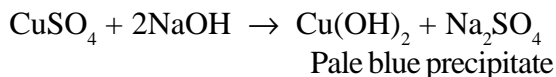
6. Action with H_2S

With H_2S it gives a black precipitate of copper sulphide.

$$CuSO_4 + H_2S \rightarrow CuS + H_2SO_4$$
$$\text{(Black ppt)}$$
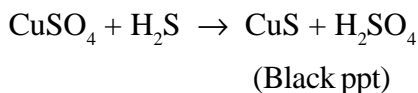
Uses

1. It is used as a germicide and insecticide in agriculture.

2. A mixture of copper sulphate and lime, commonly known as Bordeaux mixture, is used as fungicide.

3. It is used in electroplating, calicoprinting and in electrical batteries.

4.5.3 Silver nitrate or Lunar caustic ($AgNO_3$)

Preparation

Silver nitrate is prepared by dissolving silver in dilute nitric acid.

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + 2H_2O + NO\uparrow$$

Properties

Physical

1. It is soluble in water.
2. Its aqueous solution may decompose on exposure to light.

Chemical Properties

1. Action of Heat

On heating $AgNO_3$ decomposes in two stages

$$2AgNO_3 \xrightarrow{723\ K} 2AgNO_2 + O_2$$
$$\text{Silver nitrite}$$

$$AgNO_2 \xrightarrow{980\ K} Ag + NO_2$$
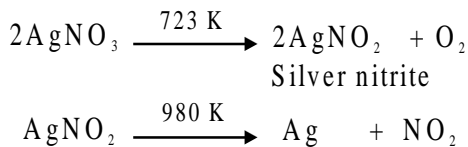
2. With NaCl

$AgNO_3$ gives white precipitate of AgCl with soluble ionic chlorides.

$$AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$$
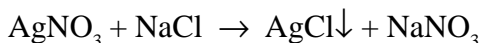
3. Silver nitrate is strongly caustic and oxidizing in nature.

4. With KBr & KI

$AgNO_3$ gives pale yellow precipitate of AgBr with bromides and yellow AgI with iodides.

$$AgNO_3 + KBr \rightarrow AgBr + KNO_3$$
$$\text{Yellow ppt}$$

$$AgNO_3 + KI \rightarrow AgI + KNO_3$$
$$\text{Yellow ppt}$$
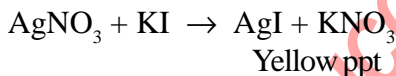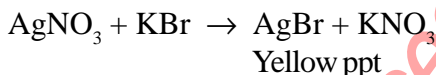
5. Action with organic compounds

Ammoniacal silver nitrate (Tollen's reagent) is reduced to silver mirror by compounds like formic acid, formaldehyde or glucose

$$2AgNO_3 + 2NH_4OH \rightarrow Ag_2O + 2NH_4NO_3 + H_2O$$
$$Ag_2O + HCOOH \rightarrow 2Ag\downarrow + H_2O + CO_2$$
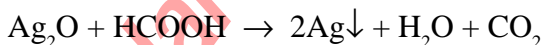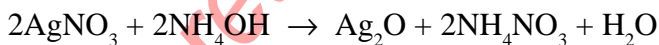
Uses

1. It is used in the preparation of silver halides which are extensively used in photography.
2. It is used in silvering mirrors.
3. It is used in preparation of marking inks and hair dyes.
4. It is used for silver plating.
5. It is used as laboratory reagent.

4.5.4 Zinc carbonate ($ZnCO_3$)

Zinc carbonate occurs in nature as calamine.

Preparation

When $NaHCO_3$ is added to Zinc sulphate solution, $ZnCO_3$ is obtained.

$$ZnSO_4 + 2NaHCO_3 \rightarrow ZnCO_3 + Na_2SO_4 + H_2O + CO_2\uparrow$$

Properties

Physical properties

It is a white powder, insoluble in water.

Chemical properties

i) Action of Heat

On heating at $300°C$, Zinc carbonate decomposes into Zinc oxide and carbon dioxide

$$ZnCO_3 \xrightarrow{300°C} ZnO + CO_2$$
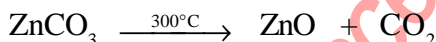
Uses

i)   It is used in making ointment for curing skin diseases.

ii) It is used in the preparation of cosmetics.

iii) It is used a pigment for rubber.

4.5.5 Purple of cassius

Purple of cassius is only a form of colloidal gold. It is purple or red in colour and after the name of Cassius who discovered it.

Preparation

It is prepared by mixing very dilute solution of gold chloride with stannous chloride solution.

$$2AuCl_3 + 3\,SnCl_2 \rightarrow 2Au\downarrow + 3SnCl_4$$

The gold thus precipitated is adsorbed by stannic hydroxide formed by the hydrolysis of $SnCl_4$.

$$SnCl_4 + 4H_2O \rightarrow Sn(OH)_4 + 4HCl$$

Uses

It is used in making ruby-red glass and high class pottery.

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SELF EVALUATION

A. Choose the correct answer

1. The general electronic configuration of d-block elements is
   a) $(n-1)d^{1-10} ns^{0-2}$ b) $(n-1) d^{1-5} ns^2$
   c) $(n-1)d^0 ns^1$ d) None of these

2. Formation of coloured ions is possible when compounds contains
   a) paired electrons   b) unpaired electrons
   c) lone pairs of electrons   d) none of the above

3. Paramagnetism is common in
   a) p-block elements   b) d-block elements
   c) s-block elements   d) f-block elements

4. The colour of $Ti(H_2O)_6^{3+}$ ion is due
   a) d-d transistion
   b) Presence of water molecules
   c) Inter atomic transfer of electrons
   d) None of the above

5. The electronic configuration of chromium is
   a) $3d^6 4s^0$ b) $3d^5 4s^1$
   b) $3d^4 4s^2$ d) $3d^3 4s^2 4p^1$

6. Paramagnetism is the property of
   a) paired electrons   b) completely filled electronic subshells
   c) unpaired electrons   d) completely vacant electronic subshells

7. d-block elements form coloured ions because
   a) They absorb some energy for d-s transition
   b) They absorb some energy for p-d transition
   c) They absorb some energy for d-d transition
   d) They do not absorb any energy

8. The correct electronic configuration of copper atom is
   a) $3d^{10} 4s^1$ b) $3d^{10} 4s^2$ c) $3d^9 4s^2$ d) $3d^5 4s^2 4p^4$

9. Copper is extracted from
   a) cuprite   b) copper glance
   c) malachite   d) copper pyrites

10. Silver salt used in photography is
    a) $AgCl$ b) $AgNO_3$ c) AgF d) $AgBr$

11. Sodiumthiosulphate is used in photography because of its
    a) Oxidizing behaviour   b) Reducing behaviour
    c) Complexing behaviour   d) Photochemical behaviour

12. Excess of sodium hydroxide reacts with zinc to form
    a) $Zn\,H_2$ b) $Na_2\,ZnO_2$ c) ZnO d) $Zn(OH)_2$

13. Which of the following compounds will not give positive chromyl chloride test?
    a) $CuCl_2$ b) $HgCl_2$ c) $ZnCl_2$ d) C_6H_5Cl

14. Which of the ions will give colourless aqueous solution?
    a) Ni^{2+} b) Fe^{2+} c) Cu^{2+} d) Cu^+

15. Which of the following compounds is not coloured?
    a) Na_2CuCl_4 b) Na_2CdI_4 c) $K_4[Fe(CN)_6]$ d) $K_3[Fe(CN)_6]$

16. In the extraction of Cu, the reaction which does not take place in the Bessemer converter is
    a) $2CuFeS_2 + O_2 \rightarrow Cu_2S + FeS + SO_2$
    b) $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$
    c) $2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$
    d) $2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$

17. Select the wrong statement
    a) All cuprous salts are blue in colour
    b) Transition metals are highly reactive
    c) All cuprous salts are white in colour
    d) Mercury is a liquid metal

18. Choose the wrong statement regarding $K_2Cr_2O_7$
    a) It is a powerful oxidizing agent
    b) It is used in tanning industry
    c) It is soluble in water
    d) It reduces ferric sulphate to ferrous sulphate

19. For a transistion metal ion, the effective magnetic moment in BM is given by the formula

a) $\sqrt{n(n-1)}$ b) $\sqrt{n(n+1)}$ c) $\sqrt{n(n+2)}$ d) $\sqrt{n(n+1)(n+2)}$

20. The correct statement in respect of d-block elements is
    a) They are all metals.
    b) They show variable valency.
    c) They form coloured ions and complex salts.
    d) All above statement are correct.

21. Which compound is formed when excess of KCN is added to an aqueous solution of copper sulphate
    a) $Cu_2(CN)_2$ b) $K_2[Cu(CN)_6]$
    c) $K[Cu(CN)_2]$ d) $Cu_2(CN)_2 + (CN)_2$

22. Which of the following has the maximum number of unpaired electrons?
    a) Mn^{2+} b) Ti^{3+} c) V^{3+} d) Fe^{2+}

23. Among the following statement, the incorrect one is
    a) Calamine and siderite are carbonates.
    b) Argentite and cuprite are oxides.
    c) Zinc blende and pyrites are sulphides.
    d) Malachite and azurite are ores of copper.

24. The chemical composition of slag formed during the smelting process in the extraction of copper is
    a) $Cu_2O + FeS$ b) $FeSiO_3$ c) $CuFeS_2$ d) $Cu_2S + FeO$

25. The transition element with the lowest atomic number is
    a) Scandium   b) Titanium   c) Zinc   d) Lanthanum

26. Which transition element show highest oxidation state
    a) Sc   b) Ti   c) Os   d) Zn

B. Answer in one or two sentences

27. What are "d"-block elements?
28. How d-block elements are classified?
29. Explain why d-block elements exhibit variable oxidation states?
30. Why transistion elements form complexes?
31. Why does Mn(II) show maximum paramagnetic character among the bivalent ions of the first transition series?
32. Why Zn^{2+} salts are white while Ni^{2+} salts are coloured?

33. $[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless. Explain.

34. A substance is found to have a magnetic moment of 3.9 BM. How many unpaired electrons does it contain?

35. Explain why the melting and boiling points of Zn,Cd,Hg are low?

36. Explain why Mn^{2+} is more stable than Mn^{3+}?

37. Write two alloys of copper and their uses.

38. Write short notes on alumino thermic process?

39. Name the first and last element in the second transition series.

40. Name the lightest and the heaviest elements (in terms of density) among the transition elements.

41. Which of the following ions would form colourless complexes?
    Cu^{2+}, Zn^{2+}, Ti^{3+}, Ti^{4+}, Cd^{2+}

42. What happens when KI solution is added to an aqueous solution of copper sulphate?

43. What is the action of heat on copper sulphate crystals?

C. Answer not exceeding 60 words

44. Explain briefly the extraction of copper from its chief ore.

45. Name the ores of gold. Explain how it is extracted from its alluvial gavel.

46. List the ores of silver. How silver is extracted from Argentite?

47. Briefly explain the extraction of zinc from zinc blende.

48. Explain how dichromate is extracted from its chromite are. Write the balanced chemical equation for the reaction between an acidified solution of $K_2Cr_2O_7$ and KI.

D. Exercise Problems

49. The chief ore of Zinc, on roasting gave a compound A, which on reduction by carbon, gives B. Identity A and B, give the chemical reactions.

50. A sulphate compound of group 11. This compound is also called as Blue vitriol.The compound undergoes decomposition at various temperature

$$A \xrightarrow{305K} B \xrightarrow{373K} C \xrightarrow{423K} D$$
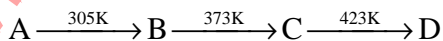
Identify the compounds A, B, C and D.

51. A compound of chromium, in which chromium exists in +6 oxidation state. Its chief ore (A) on roasting with molten alkali gives compound (B).This compound on acidification gave compound C. Compound C on treatment with KCl gave compound D. Identify the compounds A,B,C and D. Explain with proper chemical reactions.

Summary

The general characteristic properties of d- block elements are briefly explained. General methods of extraction of metals, purification and properties are thoroughly discussed .The methods of preparation of compounds, properties and their uses are explained in detail.

References

1. New concise Inorganic Chemistry by J.D.Lee, 3rd Edition, ELBS.

2. Advanced Inorganic Chemistry, P.L.Soni.

d-Block
TRANSITION ELEMENTS

1-2 s-BLOCK

| 3	4	5	6	7	8	9	10	11	12
21 Sc 3d	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y 4d	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
57 La 5d	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
89 Ac 6d	104 Rf	105 Ha	106 Dh	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub

13-17 p-BLOCK

18 inert gases

5. *f* - BLOCK ELEMENTS

Learning Objectives

❧ *To learn the general characteristics of f-block elements and extraction.*

❧ *To study the comparison of properties of Lanthanides and Actinides*

❧ *To know the general method of extraction of Lanthanides.*

❧ *To recognise the uses of Lanthanides and Actinides.*

Sweedish chemist Carl mosander discovered the metallic element Lanthanum in 1839.

In 1951 Nobel prize was shared between Edwin Mcmillan (USA) and Glenn Seaborg (USA) for discovery and work in chemistry of transuranic elements. Glean seaborg (University of California) discovered Californium.
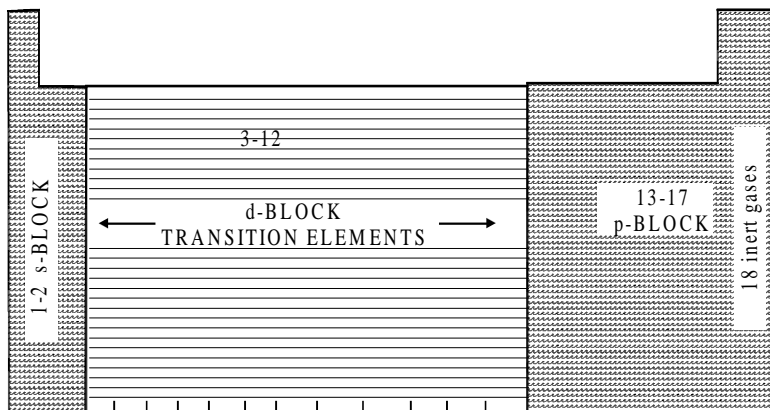
f- Block

INNER TRANSITION ELEMENTS

Lanthanide series	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinide series	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

The position of f block elements in the periodic table, is explained above.

The elements in which the extra electron enters (n- 2)f orbitals are called f- block elements. These elements are also called as inner transition elements because they form a transition series within the transition elements. The f-block elements are also known as rare earth elements. These are divided into two series.

i) The Lanthanide series (4f-block elements)
ii) The Actinide series (5f- block elements)

5.1 General Characteristics of f-block elements and extraction
5.1.1 The Lanthanide Series

The Lanthanide series include fifteen elements i.e. lanthanum ($_{57}$ La) to lutetium ($_{71}$ Lu). Lanthanum and Lutetium have no partly filled 4f- subshell but have electrons in 5d-subshell. Thus these elements should not be included in this series. However, all these elements closely resemble lanthanum and hence are considered together.

General properties of Lanthanides

1. Electronic configuration

The electronic configuration of Lanthanides are listed in the table 5.1. The fourteen electrons are filled in Ce to Lu with configuration $[_{54}Xe]4f^{1-14}5d^1 6s^2$

2. Oxidation states

The common oxidation state exhibited by all the lanthanides is $+3$ (Ln^{3+}) in aqueous solutions and in their solid compounds. Some elements exhibit $+2$ and $+4$ states as uncommon oxidation states.

La	-	+3
Ce	-	+3, +4, +2
Pr	-	+3, +4
Nd	-	+3, +4, +2

3. Radii of tripositive lanthanide ions

The size of M^{3+} ions decreases as we move through the lanthanides from lanthanum to lutetium. This steady decrease in ionic radii of M^{3+} cations in the lanthanide series is called Lanthanide contraction.

Cause of lanthanide contraction

The lanthanide contraction is due to the imperfect shielding of one 4f electron by another in the same sub shell. As we move along the lanthanide series, the nuclear charge and the number of 4f electrons increase by one unit at each step. However, due to imperfect shielding, the effective nuclear charge increases causing a contraction in electron cloud of 4f-subshell.

Consequences of lanthanide contraction

Important consequences of lanthanide contraction are given below.

i) Basicity of ions

Due to lanthanide contraction, the size of Ln^{3+} ions decreases regularly with increase in atomic number. According to Fajan's rule, decrease in size of Ln^{3+} ions increase the covalent character and decreases the basic character between Ln^{3+} and OH^- ion in $Ln(OH)_3$. Since the order of size of Ln^{3+} ions are

$$La^{3+} > Ce^{3+} \ldots\ldots\ldots\ldots\ldots > Lu^{3+}$$

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ii)   There is regular decrease in their ionic radii.

iii) Regular decrease in their tendency to act as reducing agent, with increase in atomic number.

iv)   Due to lanthanide contraction, second and third rows of d-block transistion elements are quite close in properties.

v)   Due to lanthanide contraction, these elements occur together in natural minerals and are difficult to separate.

5.1.2   The Actinide Series (5f block elements)

In 1923 Neils Bohr postulated the existence of an actinide series analogous to the lanthanide series.

The fifteen elements from actinium to lawrencium constitute the actinide series of the periodic table.

General Properties of Actinide Series

The general electronic configuration of actinides is [Rn] $5f^{0,1-14}$ $6d^{0,1-2}$ $7s^2$ where Rn stands for radon core.

2.   Oxidation states

These elements shows the oxidation states of +2, +3, +4, +5 and +6. Out of these, +4 oxidation state is most common state.

3.   Radii of M^{3+} and M^{4+} ions

The ionic radii of actinide elements decrease gradually as we move along the actinide series. The steady decrease in the ionic radii with increase in nuclear charge is called actinide contraction and is analogous to lanthanide contraction.
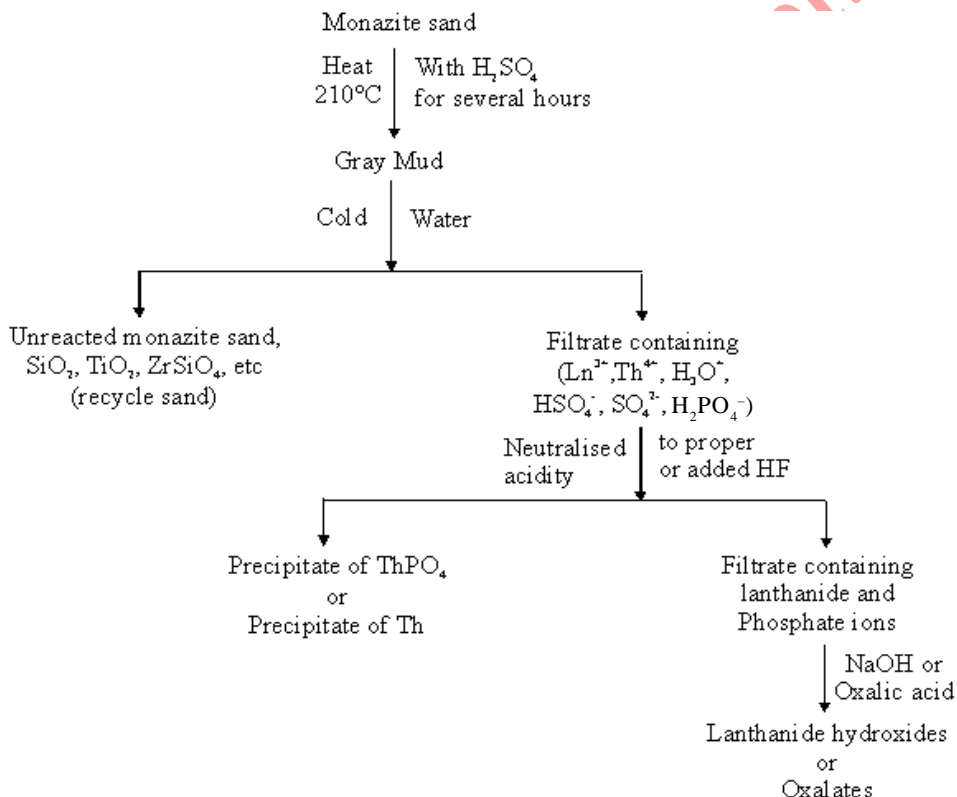
Cause of actinide contraction

Cause of actinide contraction is the imperfect shielding by 5f-electrons. As we proceed from one element to the next one in actinide series, the nuclear charge increases by +1 at each next element which is not compensated due to poor shielding effect of 5f orbitals due to their more diffuse shape. Hence as the atomic number increases, the inward pull experienced by 5f-electrons increase. Consequently steady decrease in size occurs in the actinide series.

5.1.3 Extraction of Lanthanides from Monazite sand

The method used for extraction of lanthanides from monazite sand consists of the steps which have been shown in flowsheet.

Flow sheet : Extraction of lanthanide from monazite sand

Monazite sand

Heat 210°C | With H_2SO_4 for several hours

Gray Mud

Cold | Water

Unreacted monazite sand, SiO_2, TiO_2, $ZrSiO_4$, etc (recycle sand)

Filtrate containing (Ln^{3+}, Th^{4+}, H_3O^+, HSO_4^-, SO_4^{2-}, $H_2PO_4^-$)

Neutralised acidity | to proper or added HF

Precipitate of $ThPO_4$ or Precipitate of Th

Filtrate containing lanthanide and Phosphate ions

| NaOH or Oxalic acid

Lanthanide hydroxides or Oxalates

Individual lanthanides are separated by a suitable physical method. The anhydrous fluorides and chlorides are heated under argon atmosphere in presence of calcium at 1270 K to get the individual metal. The pure metal is obtained by heating the trifluorides of lanthanides in the presence of calcium and lithium.

5.2 Comparison of Lanthanides and Actinides

Points of Similarities and difference. Both show close resemblance because these involve filling of f-subshells. Both have coloured ions, low

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electronegativity, high reactivity and show magnetic properties. However, these also differ from each other as shown in the following table.

	Lanthanides		Actinides
i)	Binding energies of 4f electrons are higher.	i)	Binding energies of 5f electrons are lower.
ii)	Maximum oxidation satate exhibited by lanthanides is +4 e.g. Ce^{4+}	ii)	Due to lower binding energies they show higher oxidation states such as +4, +5 and +6. Uranium exhibits +6 oxidation state in UF_6 and UO_2Cl_2
iii)	4f electrons have greater shielding effect.	iii)	5f electrons have poor shielding effect.
iv)	Most of their ions are colourless.	iv)	Most of their ions are coloured U^{3+} (red), U^{4+} (green) and UO_2^{2+} (yellow)
v)	They are paramagnetic but magnetic properties can be easily explained.	v)	They are also paramagnetic but their magnetic properties are very difficult to interpret.
vi)	They do not form complexes easily.	vi)	They have much greater tendency to form complexes.
vii)	Except promethium, they are non-radioactive.	vii)	All of them are radioactive.
viii)	Their compounds are less basic.	viii)	Their compounds are more basic.
ix)	They do not form oxocations.	ix)	They form oxocations such as UO_2^{2+}, UO^+, NpO_2^+, PuO_2^+.

5.3 Uses of Lanthanides and actinides

Use of lanthanides

1. A pyrophoric alloy which contains cerium, lanthanum and Neodymium; iron; aluminium; calcium, carbon and silicon is used in cigarette lighters, toys, flame throwing tanks and tracer bullets.

2. Ceria (CeO_2) and thoria (ThO_2) are used in gas lamp materials.

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3. Cerium salts are used in dyeing cotton, lead storage batteries and as catalyst.

4. Lanthanides are used in metallothermic reactions due to their extraordinary reducing property. Lanthanido - thermic processes can yield sufficiently pure Nb, Zr, Fe, Co, Ni, Mn, Y, W, U, B and Si.

5. Alloys of Lanthanides are known as mish - metals .The major constituents of mish-metals are Ce(45-50%), La(25%), Nd(5%) and small quantities of other lanthanide metals and Fe and Ca impurities. Mish-metals are used for the production of brands of steel like heat resistant, stainless and instrumental steels. Mg- alloys containing 30% mishmetal and 1% Zr are useful in making parts of jet engines.

Uses of Actinides

1. U-235 is fissionable, it is used as fuel in nuclear power plants and as a component in nuclear weapons.

2. Plutonium - 238 is used as a power source in long mission space probes.

SELF EVALUATION

A. Choose the correct answer

1. The electronic configuration of Lanthanides is

   a) $[Xe]4f^0 5d^0 6s^0$ b) $[Xe] 4f^{1-7} 5d^1 6s^1$
   c) $[Xe]4f^{1-14} 5d^1 6s^2$ c) $[Xe]4f^{1-14} 5d^{1-10} 6s^2$

2. The electronic configuration of Actinides is

   a) $[Rn]5f^{0-14} 6d^0 7s^0$ b) $[Rn]5f^{0-14} 6d^{0-2} 7s^0$
   c) $[Rn]5f^{0-14} 6d^{0-2} 7s^1$ d) $[Rn]5f^{0-14} 6d^{0-2} 7s^2$

3. The lanthanide contraction is responsible for the fact that

   a) Zn and Y have about the same radius
   b) Zr and Nb have similar oxidation state
   c) Zr and Hf have about the same radius
   d) Zr and Zn have the same oxidation state

4. The most common oxidation state of lanthanides is

   a) +2   b) +1   c) +3   d) +4

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5. Lanthanides are extracted from

a) Limonite   b) Monazite   c) Magnetite   d) Cassiterite

6. The elements in which the extra electron enters (n-2)f orbitals are called

    a)   s block elements   b)   p block elements
    c)   d block elements   d)   f block elements

7. The Lanthanides contraction is due to

a) Perfect shielding of 4f electron   b) Imperfect shielding of 4f electron
c) Perfect shielding of 3d electron   d) Imperfect shielding of 3d electron

8. Ceria is used in

a) toys   b) tracer bullets   c) gas lamp materials   d) none of the above

9. _____is used in gas lamp material

a) MnO_2 b) CeO_2 c) N_2O_5 d) Fe_2O_3

10. Alloys of Lanthanides are called as

a) Mish-metals   b) Metalloids   c) Plate metals   d) Actinides

11. Metallothermic processes involving Lanthanides are called as

a) Aluminothermic process   b) Lanthanido-thermic process
c) Reduction process   d) Oxidation process

12. _____form oxocations

a) Lanthanides   b) Actinides   c) Noble gases   d) Alkalimetals
13. Maximum oxidation state exhibited by Lanthanides is

    a) +1   b) +2   c) +3   d) +4

14. Lanthanides are separated by

a) Fractional distillation   b) Steam distillation
c) Fractional Crystallisation   d) Sublimation

B. Answer in one or two sentences

15. What are inner transition (f-block) elements? Give two examples.

16. What is the difference in the electronic configuration of transition and inner-transition elements?

17. What are lanthanides? Give the various oxidation states of lanthanides.

18. What are mish metals? Give their uses.

19. Write the uses of Lanthanides and Actinides.

C. Answer not exceeding 60 words

20. What is lanthanide contraction? Discuss its causes and consequences.

21. Account for the following.
    i) +3 oxidation state of lanthanides is the most stable.
    ii) A few 4f elements show +2 or +4 oxidation states in addition to the characteristic oxidation state of +3.
    iii) Lanthanides are grouped together.

22. Comparing $La(OH)_3$ and $Lu(OH)_3$, which is more basic and explain why?

23. Discuss the position of lanthanides in the periodic table.

24. Describe the extraction of Lanthanides from monozite sand.

Summary

The elements in which the extra electron enters (n-2) f orbitals are called f-block elements. These elements are also called as inner transition elements. The two series of f-block elements are lanthanide series and Actinide series. The general properties of lanthanides and electronic configuration, oxidation states radii of tripositive ions are discussed. Cause and consequences of lanthanide contraction are discussed. General properties of actinide elements are given. A flow chart is given for extraction of lanthanides from monazite sand. Similarities and differences between lanthanides and actinides are tabulated.

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2) Advanced Inorganic Chemistry Vol.I Gurdeep Raj, Goel Publishing House, 2002.

6. COORDINATION COMPOUNDS AND BIO-COORDINATION COMPOUNDS

Learning Objectives

@ *To understand the nature of simple salts, double salts and complex salts.*

@ *To know the meaning of ligand, central metal ion, coordination number, charge on complex ion, oxidation state of central metal ion and chelates.*

@ *To learn the latest nomenclature of coordination compounds as per IUPAC rules.*

@ *To understand the types of isomerisms present in coordination compounds.*

@ *To learn briefly about, Werner's theory and valence bond theory.*

@ *To appreciate the importance and applications of coordination and bio-coordination compounds.*

6.1 INTRODUCTION

A salt is formed by the neutralisation of an acid by a base. There are different types of salts. They are:-

    a)   Simple salt

    b)   Molecular (or) addition compounds

a)   Simple salt

A simple salt is formed by the neutralisation of an acid by a base.

$$KOH \; + \; HCl \quad \rightarrow \quad KCl \; + \; H_2O$$

Normally, a simple salt ionises in water and produces ions in solution. The solution of the simple salt exhibits the properties of its component ions.

b)   Molecular (or) addition compounds

i)   Double salts

These are molecular compounds which are formed by the evaporation of solution containing two (or) more salts in stoichiometric proportions. Hence the molecular compounds which dissociate in solution into its constituent ions are known as double salt. Double salts retain their properties only in solid state.

They are also called as lattice compounds.

Example

$K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$ -   Potash alum

$FeSO_4 . (NH_4)_2 SO_4. 6H_2O$ -   Mohr's salt

$K_2SO_4 . Al_2(SO_4)_3 . 24H_2O \rightarrow 2K^+ + 2Al^{3+} + 4SO_4^{2-} + 24H_2O$
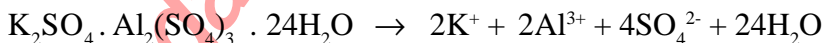
The double salts give the test of all their constituent ions in solution.

ii)   Coordination (or complex) compounds

Coordination compound is 'a compound formed from a Lewis acid and a Lewis base'. The molecular compounds, do not dissociate into its constituent ions in solution are called coordination compounds.

Example

$$Fe(CN)_2 + 4KCN \quad \rightarrow \quad Fe(CN)_2 . 4KCN \;\; (or) \; K_4[Fe(CN)_6]$$

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Ferrous cyanide

$$Fe(CN)_2 \cdot 4KCN \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$
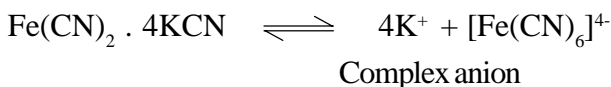
Complex anion

In $K_4[Fe(CN)_6]$ the individual components lose their identity. The metal of the complex ion is not free in solution unlike metal in double salt in solution.

Nature of coordination (or) complex compounds

i) An anionic complex compound contains a complex anion and simple cation.

$$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$

simple cation   complex anion
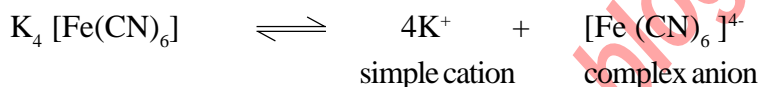
ii) A cationic complex contains complex cation and simple anion

$$[Co(NH_3)_6]Cl_3 \rightleftharpoons [Co(NH_3)_6]^{3+} + 3Cl^-$$

complex cation   simple anion
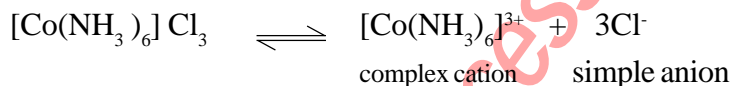
iii) In the case of a complex compound, $[Cr(NH_3)_6][Co(CN)_6]$, it gives both complex cation and complex anion

$$[Cr(NH_3)_6][Co(CN)_6] \rightleftharpoons [Cr(NH_3)_6]^{3+} + [Co(CN)_6]^{3-}$$

complex cation   complex anion

6.2 TERMINOLOGY USED IN COORDINATION CHEMISTRY

(a) Lewis Acid

All electron acceptors are lewis acids.

(b) Lewis Base

All electron donors are lewis base.

(c) Central metal ion

In the complex ion an acceptor accepts a pair of electrons from the donor atoms. The acceptor is usually a metal / metal ion to which one (or) more of neutral molecules (or) anions are attached. The acceptor metal cation is referred to as central metal cation. Hence, central metal cation in a complex serves as a lewis acid.

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(d) Oxidation state

This number denotes the charge, explaining the number of electrons it has lost to form the cation. It is oxidation number that denotes the charge, if the central metal atom would have if all the ligand in the complex were removed along with their electron pairs that were shared with the central atom. It is usually represented by Roman Numeral.

(e) Ligand (Latin word meaning to bind)

A ligand is an ion (or) a molecule capable of functioning as an electron donor. Therefore the neutral molecules or ions which are directly attached to the central metal ion are called as ligand (or) coordination groups. These coordination groups or ligands can donate a pair of electrons to the central metal ion (or) atom. Hence, in a complex compound ligands act as Lewisbases.

Types of ligands

When a ligand is bound to a metal ion through a single donor atom, as with Cl^-, H_2O or NH_3, the ligand is said to be unidentate. Whenever a single coordinating group (or) ligand occupies two (or) more coordination position on the same central metal ions, a complex possessing a closed ring is formed. Such ligands are called polydentate ligands. When a single ligand has two coordinating positions, it is called bidentate ligand and when there are three coordinating positions available, it is called a tridentate ligand and so on. For example, ethylenediamine is a bidentate ligand because it has two amino groups each of which can donate a pair of electrons.

$$NH_2 - CH_2 - CH_2 - NH_2$$
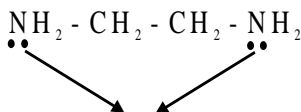
Name of the ligands

Positive ligands

The positive ligands are named with an ending -ium.

$$NH_2 - NH_3^+ \text{ hydrazinium}$$
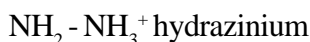
This ligand, though positive can bind through the uncharged nitrogen.

Neutral ligands

The neutral ligands are named as such without any special name. But water is written as 'aqua : Ammonia is written as ammine. Note that two m's to distinguish from organic amine

CO-Carbonyl, NO-Nitrosyl, $NH_2 - CH_2 - CH_2 - NH_2$-ethylenediamine (en), Pyridine C_5H_5N.

Negative Ligands

Negative ligands end in suffix 'O'.

Example

F^--Fluoro, Cl^--Chloro, $C_2O_4^{2-}$-Oxalato, CN^--Cyano, NO_2^--Nitro, Br^--Bromo, SO_4^{2-}-Sulphato, CH_3COO^--acetato CNS^--thiocyanato, NCS^--isothiocyanato, $S_2O_3^{2-}$-thiosulphato.

Chelates

If a ligand is capable of forming more than one bond with the central metal atom (or) ion then the ring structures are produced which are known as metal chelates. Hence the ring forming group are described as chelating agents (or) polydentate ligands.
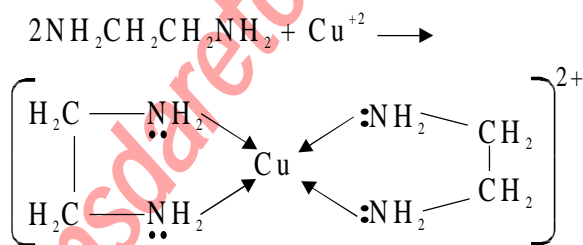
Coordination sphere

In a complex compound, it usually, central metal ion and the ligands are enclosed with in square bracket is called as coordination sphere. This represents a single constituent unit. The ionisable species are placed outside the square bracket.

$$[M(L)_n]^{(n-) \text{ (or) } (n+)}$$

$$[Fe(CN)_6]^{4-}, \quad [Cu(NH_3)_4]^{2+}$$
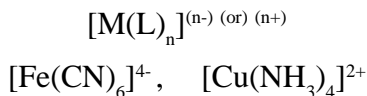
These ions do not ionise to give the test for constituent ions.

Coordination number

The coordination number of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded. Numerically coordination number represents the total number of the chemical bonds formed between the central metal ion and the donor atoms of the ligands. For example in $K_4[Fe(CN)_6]$ the coordination number of Fe(II) is 6 and in $[Cu(NH_3)_4]SO_4$ the coordination number of Cu(II) is 4.

Charge on the complex ion

Charge on the complex ion is equal to the sum of the charges on the metal ion and their ligands.

Example

1. $[Cu(NH_3)_4]^{2+}$ can be written as $[Cu^{2+}(NH_3)_4]^{2+}$ since NH_3 ligand is neutral.

    The sum of the charges on the metal ion and the ligands $= +2$.

    This can be determined as shown below

    Charge on the metal ion $(Cu^{2+}) = +2$

    Charge on the ligand $(NH_3) = 4 \times 0 = 0$

    $\therefore$ Net charge on the complex ion $= +2 + 0 = +2$

2. Similarly for $[Fe(CN)_6]^{4-}$ (or) $[Fe^{2+}(CN)_6]^{4-}$

    The sum of the charge on the metal ion and the ligand $= -4$.

    Charge on the metal ion $(Fe^{2+}) \quad = \quad +2$

    Charge on the ligand $(CN^-) \qquad = \quad 6 \times (-1) = -6$

    $\therefore$ Net charge on the complex $\quad = \quad +2 - 6 \quad = \quad -4$

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6.3 IUPAC NOMENCLATURE OF MONONUCLEAR COORDINATION COMPOUNDS

The rules are outlined below

1. In naming the entire complex, the name of the cation is given first and the anion second (just as for sodium chloride), no matter whether the cation or the anion is the complex species.

2. In the complex ion, the name of the ligand or ligands precedes that of the central metal atom (This procedure is reversed for writing formulae).

3. Ligand names generally end with 'O' if the ligand is negative ('chloro' for Cl^-, 'cyano' for CN^-, 'hydrido' for H^-) and unmodified if the ligand is neutral ('methylamine' for $MeNH_2$).

    Special ligand names are 'aqua' for water, 'ammine' for ammonia, 'carbonyl' for CO, nitrosyl' for NO.

4. A Greek prefix (mono, di, tri, tetra, penta, hexa, etc.) indicates the number of each ligand (mono is usually omitted for a single ligand of a given type). If the name of the ligand itself contains the terms mono, di, tri, like triphenylphosphine, ligand name is enclosed in parentheses and its number is given with the alternate prefixes bis, tris, tetrakis instead.

    For example, $[Ni(PPh_3)_2Cl_2]$ is named dichlorobis(triphenylphosphine) nickel(II).

5. A Roman numeral or a zero in parentheses is used to indicate the oxidation state of the central metal atom.

6. If the complex ion is negative, the name of the metal ends in 'ate' for example, ferrate, cuprate, nickelate, cobaltate etc.

7. If more than one ligand is present in the species, then the ligands are named in alphabetical order regardless of the number of each. For example, NH_3 (ammine) would be considered as 'a' ligand and come before Cl^- (chloro).

Some additional notes

i) Some metals in anions have special names

B	Borate	Au	Aurate	Ag	Argentate	Fe	Ferrate
Pb	Plumbate	Sn	Stannate	Cu	Cuprate	Ni	Nickelate

ii)   Use of brackets or enclosing marks.

Square brackets are used to enclose a complex ion or neutral coordination species.

Examples

$[Co(en)_3]Cl_3$ tris(ethylenediamine)cobalt(III) chloride

$[Co(NH_3)_3(NO_2)_3]$ triamminetrinitrocobalt (III)

$K_2[CoCl_4]$ potassiumtetrachlorocobaltate(II)

note that it is not necessary to enclose the halogens in brackets.

A systematic approach to drawing and naming coordination complexes

For the complex $K_3[Cr(C_2O_4)_3].3H_2O$

Q1) What is the central metal ion?   A1) Central metal is Chromium

Q2) What is its oxidation state?   A2) O.S. is III

Q3) What is its electronic configuration? A3) electronic configuration is d^3

Q4) What is its coordination number?   A4) C.N. is 6(3 bidentate ligands present)

Q5) What is the shape of the ion?   A5) structure is octahedral

Q6) Can the structure have isomers?   A6) Yes, optical isomers are possible

Q7) What is the IUPAC name of the   A7) Potassiumtris(oxalato) complex?   chromate(III) trihydrate

IUPAC Nomenclature of mono nuclear coordination compounds

$[Co^{III}(NH_3)_5Cl]^{2+}$ -   pentaamminechlorocobalt(III) ion

$[Co^{III}(NH_3)_6]Cl_3$ -   Hexaamminecobalt(III) chloride

$[Cr^{III}(en)_3]Cl_3$ -   Tris (ethylenediamine)chromium(III) chloride

$K_4[Fe^{II}(CN)_6]$ -   Potassium hexacyanoferrate(II)

$[Ni^{II}(CN)_4]^{2-}$ -   Tetracyanonickelate(II) ion

$[Cu^{II}(NH_3)_4]^{2+}$ -   Tetraamminecopper(II) ion

$[Pt^{II}Cl_2(NH_3)_2]$ -   Diamminedichloroplatinum(II)

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6.4 ISOMERISM

Compounds having the same chemical formula but different physical and chemical properties due to the different structural arrangements are called isomers. This phenomenon is known as isomerism.

Coordination compounds exhibit two major types of isomerism, namely (A) structural isomerism and (B) stereoisomerism (space isomerism). Each of these is further classified as shown below.

A) Structural isomerism

    a) Coordination isomerism   b) Ionisation isomerism

    c) Hydrate or Solvate isomerism   d) Linkage isomerism

    e) Ligand Isomerism

B) Stereoisomerism

    a) Geometrical isomerism   b) Optical isomerism

6.4.1   A)   Structural isomerism

a)   Coordination isomerism

In a bimetallic complex, both complex cation and complex anion may be present. In such a case the distribution of ligands between the two coordination spheres can vary, giving rise to isomers called the coordination isomers. This phenomenon is called coordination isomerism. This isomerism is illustrated by the following pairs of complexes where the complex cation and anion contain different metal centres.

1. $[Co^{III}(NH_3)_6] [Cr(CN)_6]$ and $[Cr^{III}(NH_3)_6] [Co^{III}(CN)_6]$
     Hexammine hexacyano   Hexamine   hexacyano
     cobalt(III)   chromate(III)   chromium (III) cobaltate (III)

2. $[Pt^{II}(NH_3)_4] [CuCl_4]$ and $[Cu(NH_3)_4] [PtCl_4]$
     Tetraammine Tetrachloro   Tetraammine Tetrachloro
     platinum (II) cuparate (II)   copper (II) platinate (II)

b)   Ionisation isomerism

Coordination compounds having the same molecular formula but forming different ions in solution are called ionisation isomers. This property is known as ionisation isomerism.

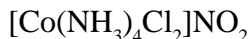An example of this type of isomerism is furnished by the red-violet,
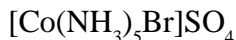
$[Co(NH_3)_5Br]SO_4$ $[Co(NH_3)_5SO_4]Br$
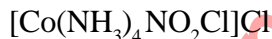pentaamminebromocobalt(III) sulphate   pentaamminesulphatocobalt (III) bromide
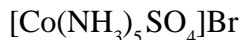
The red-violet isomer yields sulphate ion and the red isomer furnishes bromide ion in solution.
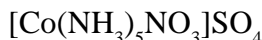
$[Co(NH_3)_4Cl_2]NO_2$ and $[Co(NH_3)_4NO_2Cl]Cl$
Tetraamminedichlorocobalt(III) nitrite   Tetraamminechloronitrocobalt(III) chloride

$[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$
pentaamminenitratocobalt(III) sulphate   pentaamminesulphatocobalt(III) nitrate
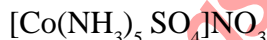
c) Hydrate isomerism or Solvate isomerism

The best known examples of this type of isomerism occurs for chromium chloride "$CrCl_3.6H_2O$" which may contain 4, 5, (or) 6 coordinated water molecules.

1. $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ - Bright green
     Tetraaquadichlorochromium(III) chloride dihydrate

2. $[Cr(H_2O)_5Cl]Cl_2.H_2O$ - grey-green
     Pentaaquachlorochromium(III) chloride monohydrate

3. $[Cr(H_2O)_6]Cl_3$ - Violet
     Hexaaquachromium(III) chloride

These isomers have very different chemical properties and on reaction with $AgNO_3$ to test for Cl^- ions, would find 1,2, and 3 Cl^- ions in solution respectively.

d) Linkage isomerism

Linkage isomerism occurs with ambidentate ligands. These ligands are capable of coordinating in more than one way. The best known cases involve the monodentate ligands SCN^-/NCS^- and NO_2^-/ONO^-

For example
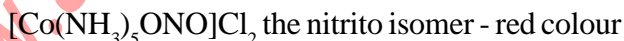
$[Co(NH_3)_5ONO]Cl_2$ the nitrito isomer - red colour
pentaamminenitritocobalt(III) chloride - O attached

$[Co(NH_3)_5NO_2]Cl_2$ the nitro isomer - yellow colour
pentaamminenitrocobalt(III) chloride - N attached

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e) Ligand isomerism

Ligand isomerism arises from the presence of ligands which can adopt different isomeric forms. An example is provided by diaminopropane, which may have the amine groups in the terminal (1,3-) positions or in the 1,2-positions.

$$H_2N - CH_2 - CH_2 - CH_2 - NH_2 \quad \text{or} \quad H_2N - CH_2 - \underset{\overset{|}{NH_2}}{CH} - CH_3$$
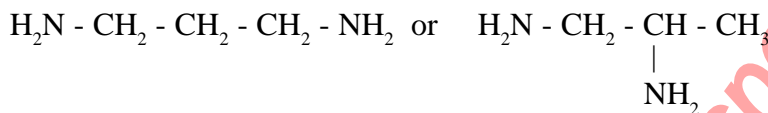
6.4.2 Stereoisomerism (space isomerism)

Consider two compounds containing the same ligands attached to the same central metal ion, but the arrangement of ligands in space about the central metal ion are different, then these two compounds are said to be stereoisomers and this phenomenon is known as stereoisomerism. There are two different types of stereoisomerism. a) Geometrical isomerism or b) Optical isomerism.

### a) Geometrical (or) cis-trans isomerism

Geometric isomers are possible for both square planar and octahedral complexes, but not tetrahedral. In a cis-isomer two identical (or) similar groups are adjacent to each other whereas in a trans-isomer they are diametrically opposite to each other.

Square planar complexes of the type $[Ma_2b_2]n^{\pm}$ where a and b are monodentate ligands, exist as cis and trans-isomers as shown below. Example of this type of complexes are $[Pt(NH_3)_2 Cl_2]$ and $[Pd(NH_3)_2 (NO_2)_2]$. The cis-trans isomers of these compounds are represented as

cis-isomer

trans-isomer

cis-isomer

trans-isomer
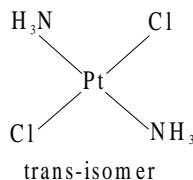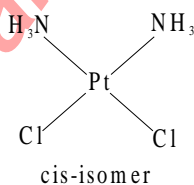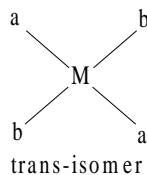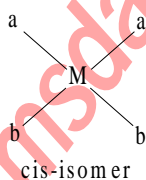
cis-diamminedichloroplatinum (II)

trans - diamminedichloroplatinum (II)

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cis-isomer

cis-diamminedinitropalladium(II)


trans-isomer

trans-diamminedinitropalladium(II)
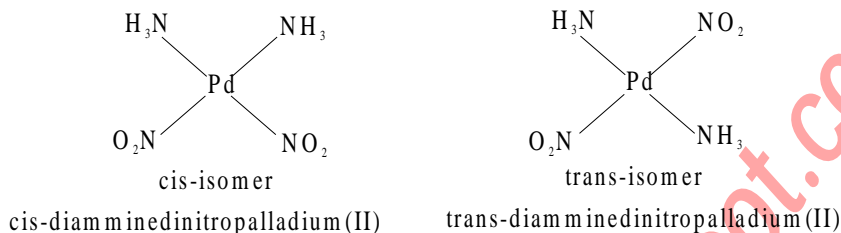
In the octahedral complex, the different coordination positions are numbered as shown below
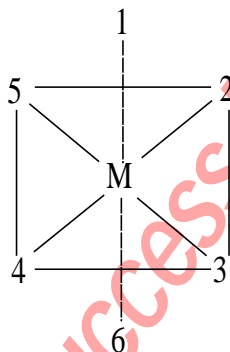
Along the twelve edges of the octahedron, there are twelve cis positions. They are (1,2) (1,3) (1,4) (1,5) (2,6) (3,6) (4,6) (5,6) (3,4) (4,5) (2,5) and (2,3). In order to avoid confusion, generally it is assumed that the 1,2 positions are cis-positions. There are three trans positions; they are (1,6) (2,4) and (3,5). Normally it is taken that 1,6 positions are trans-positions in order to avoid confusion.

An octahedral complex of the type $[Ma_4b_2]$ where a and b are monodentate ligands, exists as two geometrical Isomers:
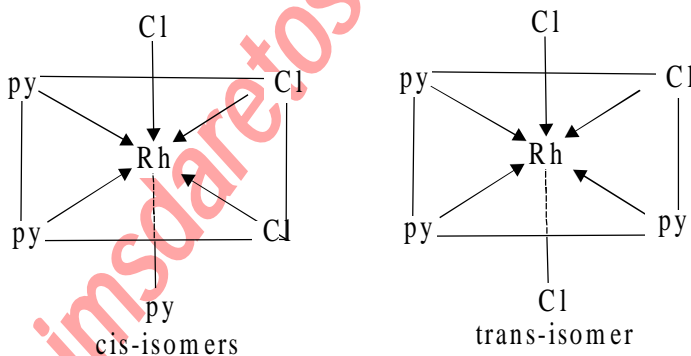

cis-isomer

trans-isomer

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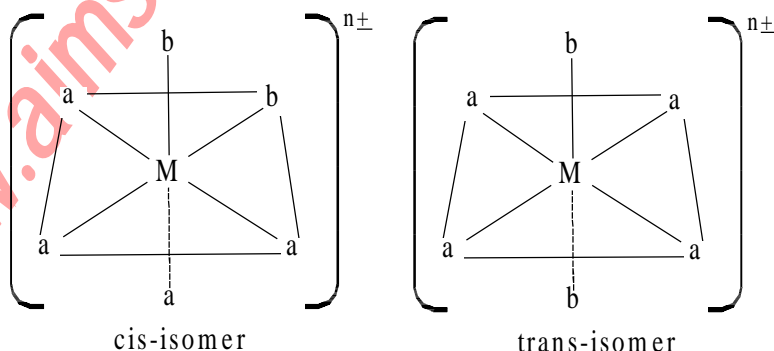
A specific example for such Isomerism is $[Co(NH_3)_4Cl_2]^+$ which exists as two geometrical isomers.

The octahedral complex are of the type $[M(AA)_2a_2]^{n\pm}$ where (AA) is a symmetrical bidentate ligand such as ethylenediamine $H_2N-CH_2-CH_2-NH_2$ and 'a' is a monodentate ligand. A specific example for this is $[Co(H_2N-CH_2-CH_2-NH_2)_2Cl_2]^+$

cis-isomer   trans-isomer
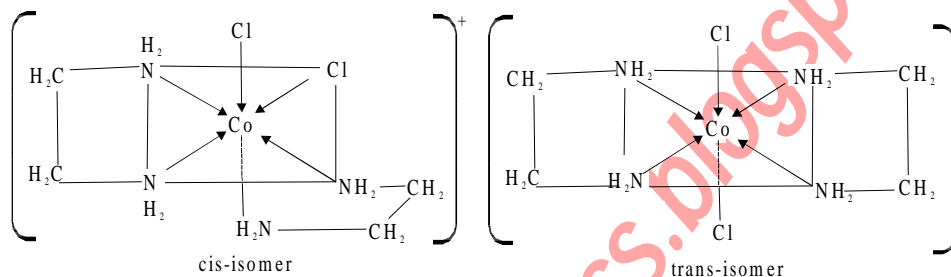
The octahedral complex of the type, $[Ma_3b_3]^{n\pm}$, where a and b are monodentate ligands also exist as geometrical isomers, For example, $[Rh(py)_3Cl_3]$ exist as cis-(1,2,3 trichlorocomplex) and trans-(1,2,6-trichloro complex) isomers as represented below

cis-isomers   trans-isomer

b)   Optical Isomerism

This is a phenomenon in which certain organic or inorganic compounds have the property of rotating plane polarised light. The compounds which exhibit this property are called optical isomers. The optical isomers of a compound have identical physical and chemical properties. The only distinguishing property is

that the isomers rotate the plane of polarised light either to the left or right. In a coordination compound of type $[PtCl_2(en)_2]_1^{2+}$, two geometrical isomers are possible. They are cis and trans. Among these two isomers, cis isomer shows optical activity because the whole molecule is asymmetric.
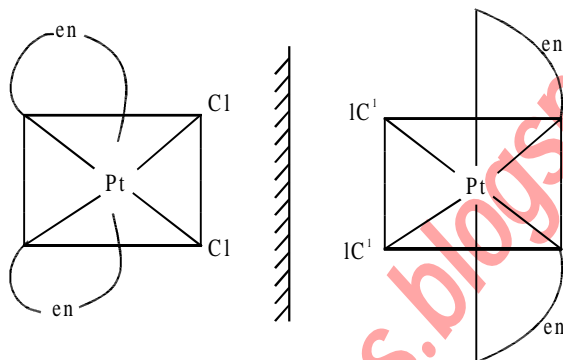
Optical isomers of cis $(PtCl_2(en)_2]^{2+}$

6.5 THEORIES OF COORDINATION COMPOUNDS

6.5.1 Werner's Theory

Alfred Werner (1866-1919) French born Swiss chemist founded the modern theory on coordination compounds. His theory and pioneering experimental work on metal complexes won for him the Nobel Prize for chemistry in 1913. Werner was the first inorganic chemist to be awarded the nobel prize in chemistry. He is considered at **"Father of coordination chemistry"**.

Brief concepts of Werner's theory of coordination compounds

Alfred Werner studied the structure of coordination complexes and put forward his ideas in the year 1893 which were known as 'Werner's coordination theory.
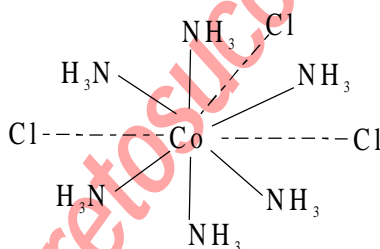
Postulates of Werner's theory

1)   Every metal atom has two types of valencies
      i) Primary valency or ionisable valency
      ii) Secondary valency or non ionisable valency

2)   The primary valency corresponds to the oxidation state of the metal ion. The primary valency of the metal ion is always satisfied by negative ions.

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3) Secondary valency corresponds to the coordination number of the metal ion or atom. The secondary valencies may be satisfied by either negative ions or neutral molecules.

4) The molecules or ion that satisfy secondary valencies are called ligands.

5) The ligands which satisfy secondary valencies must project in definite directions in space. So the secondary valencies are directional in nature whereas the primary valencies are non-directional in nature.

6) The ligands have unshared pair of electrons. These unshared pair of electrons are donated to central metal ion or atom in a compound. Such compounds are called coordination compounds.

Werner's representation

Werner represented the first member of the series $[Co(NH_3)_6]Cl_3$ as follows. In this representation, the primary valency (dotted lines) are satisfied by the three chloride ions. The six secondary valencies (solid lines) are satisfied by the six ammonia molecules.

Defects of Werner's theory

Werner's theory describes the structures of many coordination compounds successfully. However, it does not explain the magnetic and spectral properties.

6.5.2   Valence bond theory (VB Theory)

Valence bond theory, primarily the work of Linus Pauling regarded bonding as characterized by the overlap of atomic or hybrid orbitals of individual atoms.

The postulates of valence bond theory

1)   The central metal atom/ion makes available a number of vacant orbitals equal to its coordination number.

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2) These vacant orbitals form covalent bonds with the ligand orbitals.

3) A covalent bond is formed by the overlap of a vacant metal orbital and filled ligand orbitals. This complete overlap leads to the formation of a metal ligand, σ (sigma) bond.

4) A strong covalent bond is formed only when the orbitals overlap to the maximum extent. This maximum overlapping is possible only when the metal vacant orbitals undergo a process called 'hybridisation'. A hybridised orbital has a better directional characteristics than an unhybridised one.

The following table gives the coordination number, orbital hybridisation and spatial geometry of the more important geometrics.

Coordination number	Types of hybridisation	Geometry
2	sp	linear
4	sp^3	tetrahedral
4	dsp^2	square planar
6	d^2sp^3	octahedral
6	sp^3d^2	octahedral

Magnetic moment

A species having atleast one unpaired electron, is said to be paramagnetic. It is attracted by an external field. The paramagnetic moment is given by the following spin-only formula.

$$\mu_s = \sqrt{n(n+2)} \ \ BM$$

μ_s = spin-only magnetic moment

n = number of unpaired electrons

BM = Bohr magneton, the unit which expresses the magnetic moment. When the species does not contain any unpaired electron, it is diamagnetic.
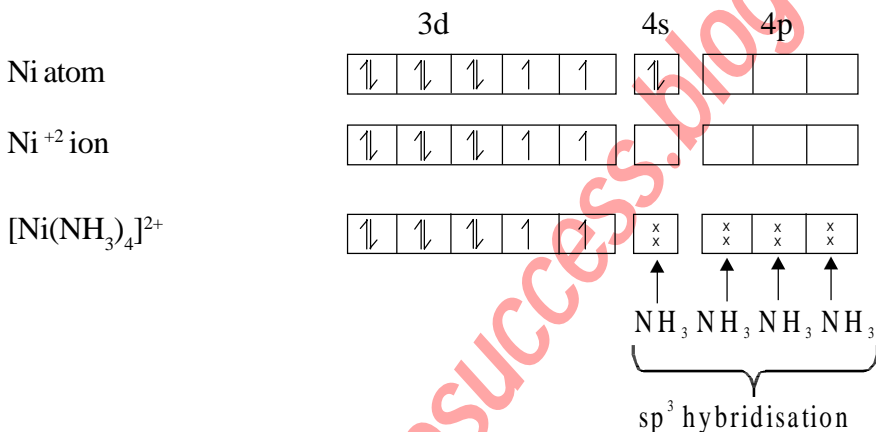
Number of unpaired electrons	Spin-only moment (BM)
1	$\sqrt{1(1+2)} = \sqrt{3} = 1.73$
2	$\sqrt{2(2+2)} = \sqrt{8} = 2.83$

$$3 \qquad \sqrt{3(3+2)} = \sqrt{15} = 3.87$$

$$4 \qquad \sqrt{4(4+2)} = \sqrt{24} = 4.90$$

$$5 \qquad \sqrt{5(5+2)} = \sqrt{35} = 5.92$$

Applications of valence bond theory

1) Nickel atom

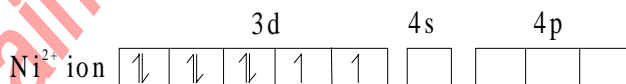Outer electronic configuration $\quad 3d^8 \quad 4s^2$

Number of unpaired electrons = 2

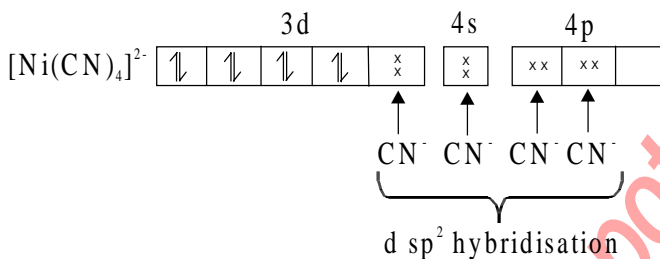$$\therefore \quad \mu_s = \sqrt{2(2+2)} = 2.83 \, \text{BM}$$

Since the hybridisation is sp^3, the geometry of the molecule is tetrahedral.

2) $[Ni(CN)_4]^{2-}$

Another possible geometry for the 4 coordinated complex is the square planar configuration involving dsp^2 hybridisation.

The ligand CN^- is a powerful ligand. Hence it forces the unpaired electrons to pair up in d orbitals. Hence this complex ion does not contain unpaired electrons. It is diamagnetic.
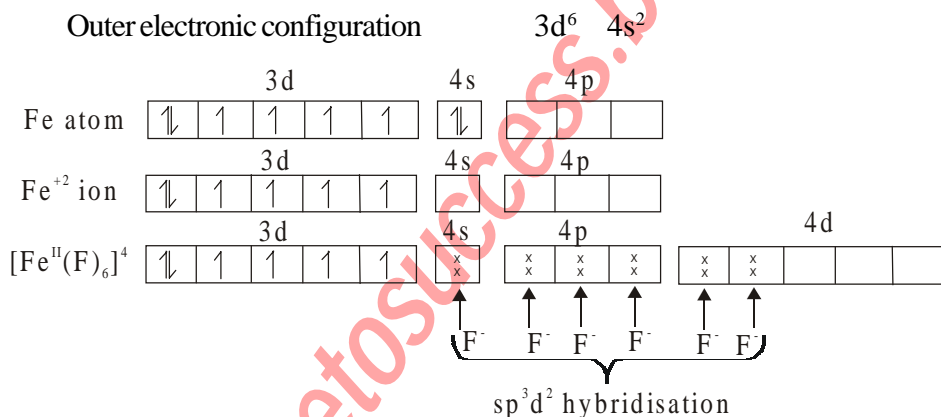
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$$3d \qquad 4s \qquad 4p$$

$[Ni(CN)_4]^{2-}$ | ⇅ | ⇅ | ⇅ | ⇅ | xx | | xx | | xx | xx | |

$$\uparrow \qquad \uparrow \qquad \uparrow \qquad \uparrow$$
$$CN^- \quad CN^- \quad CN^- \quad CN^-$$

$d\,sp^2\,hybridisation$

The geometry of the molecule is square planar.

Octahedral complexes

1) Fe atom

Outer electronic configuration $\qquad 3d^6 \quad 4s^2$

$$3d \qquad\qquad 4s \qquad 4p$$

Fe atom | ⇅ | ↑ | ↑ | ↑ | ↑ | | ⇅ | | | |

$$3d \qquad\qquad 4s \qquad 4p$$

Fe^{+2} ion | ⇅ | ↑ | ↑ | ↑ | ↑ | | | | | |

$$3d \qquad\qquad 4s \qquad 4p \qquad\qquad 4d$$

$[Fe^{II}(F)_6]^4$ | ⇅ | ↑ | ↑ | ↑ | ↑ | | xx | | xx | xx | xx | | xx | xx | | | |

$$\uparrow \quad \uparrow \quad \uparrow \quad \uparrow \qquad \uparrow \quad \uparrow$$
$$F^- \quad F^- \quad F^- \quad F^- \qquad F^- \quad F^-$$
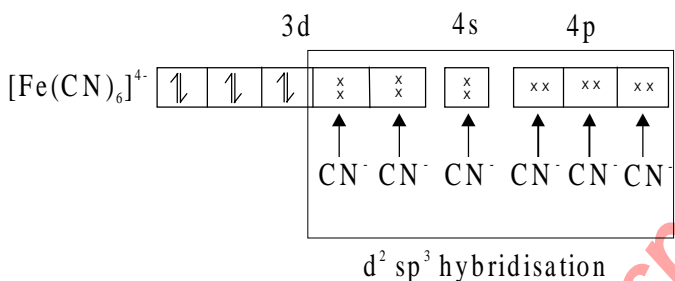
$sp^3d^2\,hybridisation$

Number of unpaired electron $= 4$

$$\therefore \quad \mu_s \sqrt{4(4+2)} = \sqrt{24} = 4.90\,BM$$

The molecule is paramagnetic. The geometry of the molecule is octahedral.

2) Fe^{+2} ion

$$3d \qquad\qquad 4s \qquad 4p$$

| ⇅ | ↑ | ↑ | ↑ | ↑ | | | | | |

In $[Fe(CN)_6]^{4-}$ complex the CN^- ligand is a powerful ligand, it forces the unpaired electrons in 3d level to pair up inside. Hence the species has no unpaired electron. The molecule is diamagnetic.

$$d^2 sp^3 \text{ hybridisation}$$

The molecular geometry is octahedral.

Defects of Valence bond theory

Although VB theory was the principal way in which chemist visualized coordination compounds until the 1950s, it has fallen into disfavour due to its inability to account for various magnetic, electronic and spectroscopic properties of these compounds.

6.6 Uses of coordination compounds

1. Dyes and Pigments

Coordination compounds have been used from the earliest times as dyes and pigments, for example madder dye which is red, was used by the ancient Greeks and others. It is a complex of hydroxyanthraquinone. A more modern example is the pigment copper phthalocyanine, which is blue.

2. Analytical Chemistry

The coordination compounds used for various purpose, in the laboratary are as follows.

a) Colour Tests : Since many complexes are highly coloured they can be used as colourimetric reagents e.g. formation of red 2,2'-bipyridyl and 1,10-phenanthroline complexes as a test for Fe^{2+}

b) Gravimetric Analysis : Here chelating ligands are often used to form insoluble complexes e.g. $Ni(DMG)_2$ and $Al(oxine)_3$.

c) Complexometric Titrations and Masking Agents : An example of this is the use of EDTA in the volumetric determination of a wide variety of metal ions in solution, e.g. Zn^{2+}, Pb^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, etc. By careful adjustment of

the pH and using suitable indicators, mixtures of metals can be analysed, e.g. Bi^{3+} in the presence of Pb^{2+}. Alternatively, EDTA may be used as a masking agent to remove a metal ion which would interfere with the analysis of a second metal ion present.

3. Extraction of Metals

Sometimes certain metals can be leached from their ores by formation of stable complexes e.g. Ag and Au as complexes of cyanide ion.

4. Bio-Inorganic Chemistry

Naturally occurring complexes include haemoglobin, chlorophyll, vitamin B_{12} etc.

Therapeutic chelating agents are used as antidotes for heavy metal poisoning.

EDTA and other complexing agents have been used to speed the elimination of harmful radioactive and other toxic elements from the body. (e.g. Pb^{2+}). In these cases a soluble metal chelate is formed.

5. Chemotherapy

An example here is the use of cis-$Pt(NH_3)_2Cl_2$ as an anti-tumour drug.

6. Synthetic detergents

Synthetic detergents containing chelating agents such as tripolyphosphate. The chelating agent sequesters hard-water cations, rendering them incapable of interfering with the surfactant.

6.7 BIO COORDINATION COMPOUNDS

Coordination compounds play an important role in many biological processes in plants and animals.

The following table gives some of the important bio coordination compounds.

Name	Function
1. Haemoglobin	Transport and storage of oxygen
2. Chlorophyll	Photosynthesis
3. Ferredoxins Rubredoxins	Electron Transfer

Among the Bio-coordination compounds function and nature of haemoglobin and chlorophyll play dominant role in natural process.

6.7.1 Haemoglobin

Haemoglobin in the red blood cells carries oxygen from the lungs to the tissues. It delivers the oxygen molecule to myoglobin in the tissues. When the oxygen has been released for cell respiration, haemoglobin loses its bright red colour and becomes purple. It then combines with the waste carbon dioxide produced by the cells and deposits in the lungs so that the gas can be exhaled.

Nature of haemoglobin and myoglobin

Both are having the same structure excepting the fact that myoglobin is a monomer and haemoglobin is a tetramer. Both are iron-porphyrin complex.

These are biocoordination complexes formed between porphyrin and iron in its +2 oxidation state (Fe^{2+}). The iron-porphyrin complex is called the heme group, which is a part of haemoglobin. Each haemoglobin molecule consists of four subunits, each unit is being a folded chain.

The working part of haemoglobin is a hemegroup containing an Fe^{2+} cation coordinated to four nitrogen atoms of porphyrin group and one nitrogen atom of histidine group. The sixth octahedral site is available to bind oxygen molecule.

6.7.2 Chlorophyll

Chlorophyll is a magnesium - porphyrin complex. The magnesium is at the centre of the modified porphyrin ring septeon (corrin). The oxidation state of magnesium is +2 (Mg^{2+}). The modified porphyrin acts as the ligand.

There are several kinds of chlorophyll that vary slightly in their molecular structure.

In plants, chlorophyll 'a' is the pigment directly responsible for the transformation of light energy to chemical energy. Hence in plants, the green pigment chlorophyll helps photosynthesis. The conversion of atmospheric carbondioxide and atmospheric moisture into carbohydrate and molecular oxygen in the presence of sunlight, by the plant is called as photosynthesis. Chlorophyll acts as a light sensitiser in this important process.

$$xCO_2 + yH_2O \xrightarrow[\text{sunlight}]{\text{chlorophyll}} Cx(H_2O)y + O_2$$
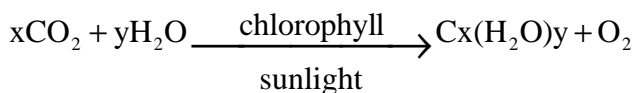
Photosynthesis requires, in addition to chlorophyll, the help of four other metal complexes, a manganese complexes, two iron complexes and a copper complex.

All oxygenated animals take molecular oxygen through haemoglobin and release CO_2. But chlorophyll helps in the conversion of atmosphere CO_2 into molecular oxygen which act as a fuel for human cell.

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SELF EVALUATION

</div>

A. Choose the correct answer

1.   Which a double salt

      a) $K_2SO_4.Al_2(SO_4)_3.24H_2O$ b) NaCl   c) $K_4[Fe(CN)_6]$ d) KCl

2.   An example of a complex compound having coordination number 4.

      a) $K_4[Fe(CN)_6]$ b) $[Co(en)_3]Cl_3$

      c) $[Fe(H_2O)_6]Cl_3$ d) $[Cu(NH_3)_4]Cl_2$

3.   The geometry of $[Cu(NH_3)_4]^{2+}$ complex ion

      a) Linear   b) Tetrahedral   c) Square planar   d) Angular

4.   An example of a chelating ligand is

      a) NO_2^- b) Chloro   c) Bromo   d) en

5.   The geometry of complex ion $[Fe(CN)_6]^{4-}$ is

      a) tetrahedral   b) square planar   c) Octahedral   d) triangular

6.   The oxidation number of Nickel in the complex ion, $[NiCl_4]^{2-}$ is

      a) +1   b) -1   c) +2   d) -2

7.   Which is not an anionic complex?

      a) $[Cu(NH_3)_4]Cl_2$ b) $K_4[Fe(CN)_6]$
      c) $K_3[Fe(CN)_6]$ d) $[NiCl_4]^{2-}$

8.   The geometry of $[Ni(CN)_4]^{2-}$ is

      a) . Tetrahedral   b)   Square planar
      c)   Triangular   d)   Octahedral

9.   An example of an ambidentate ligand is

      a) CN^- b) Cl^- c) NO_2^- d) I^-

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</div>

10. $[FeF_6]^{4-}$ is paramagnetic because

   a) F^- is a weaker ligand   b) F^- is a strong ligand

   b) F^- is a flexidentate ligand   d) F^- is a chelating ligand

11. In $[Fe^{II}(CN)_6]^{4-}$, the central metal ion is

   a) Fe   b) Fe^{+2} c) Fe^{+3} d) CN^-

12. The coordination number of Ni(II) in $[Ni(CN)_4]^{2-}$ is

   a) 2   b) 4   c) 5   d) 6

13. The name of $[Pt^{IV}(NH_3)_2Cl_2]^{2+}$ is

   a) Diamminedichloroplatinum(IV) ion

   b) Diamminedichloroplanitate(IV)

   c) Diamminedichloroplatinum

   d) Dichlorodiammineplatinum(IV) ion

14. For a compound $K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$, the complex ion is

   a) K^+ b) CN^- c) Fe^{II} d) $[Fe(CN)_6]^{4-}$

15. A metal ion from the first transition series forms an octahedral complex with magnetic moment of 4.9 BM and another octahedral complex which is diamagnetic. The metal ion is

   a) Fe^{2+} b) Co^{2+} c) Mn^{2+} d) Ni^{2+}

16. Paramagnetic moment is expressed in

   a) Debye unit   b) K Joules   c) BM   d) ergs

17. The type of isomerism found in the complexes $[Co(NO_2)(NH_3)_5]SO_4$ and $[Co(SO_4)(NH_3)_5] NO_2$

   a) Hydrate isomerism   b) Coordination isomerism

   c) Linkage isomerism   d) Ionisation

18. Valence bond theory does not explain the property of complex compound

   a) geometry   b) magnetic   c) nature of ligand   d) colour

B. Answer in one or two sentences

19. What are simple salts? Give one example.

20. What are double salts? Give one example.

21. In what way complex salt differs from double salt?

22. What are ligands and coordination number?

23. Give one example for a monodentate ligand, a bidentate ligand and a chelating ligand.

24. Calculate the charge on the central metal ion present in the following complexes.

   a) $[Fe(NH_3)_4Cl_2] NO_3$ b) $Na[B(NO_3)_4]$

25. Name the following complexes

   a) $[Co(NH_3)_5(H_2O)]Cl_3$ b) $Na[B(NO_3)_4]$

26. Write the formula structure of the following

   a) tris(ethylenediamine)cobalt(III) ion
   b) pentaamminesulphatocobalt(III) chloride

27. Draw the structure of cis and trans-$[Pt(NH_3)_2Cl_2]$

28. What are chelates? Give one example.

C. Answer not exceeding 60 words

29. Explain coordination and ionisation isomerism with suitable examples.

30. Mention the type of hybridisation and magnetic property of the following complexes using VB theory

   a) $[FeF_6]^{4-}$ b) $[Fe(CN)_6]^{4-}$

31. For the complexes $K_4[Fe(CN)_6]$, $[Cu(NH_3)_4] SO_4$ mention

   a) Name   b) Central metal ion   c) Ligands   d) Coordination number

32. How is the paramagnetic moment related to the number of unpaired electrons in?

   a) $K_4[Fe(CN)_6]$ b) $K_3[Fe(CN)_6]$

33. In what way $[FeF_6]^{4-}$ differs from $[Fe(CN)_6]^{4-}$.

34. $[Ni(CN)_4]^{2-}$ diamagnetic, whereas $[NiCl_4]^{2-}$ is paramagnetic. Explain.

35. $[Cu(NH_3)_4]^{2+}$ is square planar, where as $[NiCl_4]^{2-}$ is tetrahedral. Explain.

36. Explain the limitations of VB theory.

37. Taking $[FeF_6]^{4-}$ as an example, discuss geometry, nature of d-orbital splitting and magnetic property using VB theory.

38. Mention the function of haemoglobin in natural process.

39. How chlorophyll is important in environmental chemistry? Mention its function.

Summary

The nature of coordination compounds are discussed in detail. The terminology used in coordination chemistry and types of isomerism found in coordination compounds are explained with specific examples. The development of the nature of bonding is discussed using Werner's theory and valence bond theory. The scope and limitations of these theories are also compared. A brief discussion on applications of coordination compounds is presented. The function and role of haemoglobin and chlorophyll are explained.

Reference

1. Coordination Chemistry, S.F.A.Kettle, The English language book society and Nelson, 1969.

2. Concise Inorganic Chemistry, J.D.Lee, Chapman and Hall, London, 1992.

7. NUCLEAR CHEMISTRY

Learning Objectives

❒   *Review of basic nuclear chemistry.*

❒   *Know about the nuclear reactions and chemical reactions.*

❒   *Learn about nuclear energy and nature of nuclear fission and nuclear fusion reactions.*

❒   *Learn about principle of nuclear reactors.*

❒   *Know about the nuclear reactions in sun.*

❒   Learn about the application of radioactive isotopes including tracer technique adopted in understanding reaction mechanisms.

Henry Becquerel (France) was awarded nobel prize for his discovery of spontaneous radioactivity in 1903.

In the same year Pierre Curie (France) and Mary Curie (France) were awarded for their research on radiation phenomenon. In 1911, Marie Curie (France) was awarded nobel prize for the discovery of radium and polonium, and the isolation of radium. In 1938, Enrico Fermi (Italy) was awarded Nobel Prize for the discovery of nuclear reactions induced by slow neutrons.

Nuclear Chemistry

* Radioactivity : The phenomenon of spontaneous disintegration of certain atomic nuclei resulting in the emission of radioactive rays is called radioactivity. Radioactivity is a nuclear phenomenon and it is not affected by external factors such as temperature, pressure etc. This phenomenon was discovered by Henry Becqurel.

* To explain the spontaneous decay of radioactive elements, Rutherford and Soddy put forward the theory of radioactive disintegration. According to this theory the quantity of a radioactive element which disappears in unit time is directly proportional to the amount (atoms) of radioactive substance present at that time.

  Based on the above theory, the following equation is derived which confirms that all radioactive reactions follow I order

$$t = \frac{2.303}{\lambda} \log \frac{N_0}{N}$$

λ = decay constant N_0 = Number of radioactive atoms present initially

                                              N = Number of radioactive atoms at time 't'

* **Half life period** : The time required to disintegrate one half of any radioactive substance is called half life period ($t^{1/2}$). The half life period ($t^{1/2}$) of a radioactive substance is independent of initial concentration. It depends only on the disintegration constant (λ) of the radioactive element. $t^{1/2}$ is used to indicate the relative stability of radioactive substance. If $t^{1/2}$ is the shorter, faster is the rate of decay and hence the substance is more unstable and viceversa.

$$\left(t^{1/2} = \frac{0.693}{\lambda} \right)$$

Average life, τ (Tau) $= \dfrac{1}{\lambda} = \dfrac{t^{1/2}}{0.693} = 1.44 \, t^{1/2}$

* Since radioactivity is a nuclear phenomenon, it must be connected with the instability of the nucleus.

* An α - particle is equal to the bundle of two protons and two neutrons and hence it is equal to the Helium nucleus ($_2He^4$).

* β-particle is a fast moving electron.

* γ-radiation is a waver of very short wavelength with very high energy.

* Radioactive decay series : Radioactive heavy nuclei decay by a series of α - emission or β emissions, finally resulting in the formation of a stable isotope of lead. There are about 4 decay series.

  4n   - Thorium series

  4n+1 - Neptunium series

  4n+2 - Uranium series

  4n+3 - Actinium series

* **Binding energy of Nucleus**

  Whenever a nucleus is formed, certain mass is converted into energy. Hence for atom, the atomic mass is lower than the sum of masses of protons, neutrons and electrons present. The difference in mass is termed as "mass defect". This is the measure of the binding energy of proton and neutron in the nucleus. The relationship between mass - energy is explained by Einstein equation $\Delta E = \Delta m\, C^2$.

7.1 Difference between chemical reactions and nuclear reactions

In ordinary chemical reactions, the nuclei of the atoms taking part in a chemical reaction remain unaffected. Only the electrons in the extranuclear part of atoms take part in the chemical process.

However, during disintegration of atoms (naturally or artificially), the nuclei of atoms are affected resulting in the formation of new nuclei. Such reactions in which the nuclei of the atoms interact with other nuclei or lighter particles or photons resulting in the formation of new nuclei and one or more lighter particles are called nuclear reactions.

	Chemical reactions		Nuclear reactions
1.	These reaction involve some loss, gain or overlap of outer orbital electrons of the reactant atoms.	1.	Nuclear reactions involve emission of alpha, beta and gamma particles from the nucleus.
2.	A chemical reaction is balanced in terms of mass only	2.	Nuclear reaction is balanced in terms of both mass and energy.
3.	The energy changes in any chemical reaction is very much less when compared with nuclear reaction.	3.	The energy changes are far exceed than the energy changes in chemical reactions.
4.	In chemical reactions, the energy is expressed in terms of kilojoules per mole.	4.	In nuclear reactions, the energy involved is expressed in MeV (Million electron volts) per individual nucleus.
5.	No new element is produced since nucleus is unaffected.	5.	New element / isotope may be produced during the nuclear reaction.

The following facts are taken into account while expressing a nuclear reaction:

i) Reactions are written like a chemical equation. Reactants are written on the left hand side and products on the right hand side with an arrow in between.

ii) Mass number is written as super script on the symbol of the element. For example $_7N^{14}$ stands for an atom of nitrogen with mass number 14 and atomic number 7.

iii) In a chemical reaction the total number of atoms of various elements are balanced on the two sides. Similarly in nuclear reaction , the total mass number and atomic number are balanced on the two sides.

iv) Symbols used for projectiles:

The bombarding particles are called projectiles. These projectiles are represented by the following symbols.

$_0n^1$ - neutron
$_1H^1$ or p - proton
$_2He^4$ or α - α particle
$_1H^2$ or $_1D^2$ - deuteron
$_{-1}e^0$ or e - electron or β-particle
$_{+1}e^0$ - positron

The nucleus to be attacked is called as target nucleus or parent. The new nuclide is called as recoil nucleus or daughter. The particle ejected during a nuclear reaction is called as ejected particle.
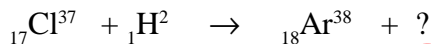
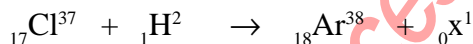Representation of nuclear reaction:

$$_7N^{14} \quad + \quad _2He^4 \quad \rightarrow \quad _8O^{17} \quad + \quad _1H^1$$

$\qquad$ projectile $\qquad\qquad\qquad$ ejected particle
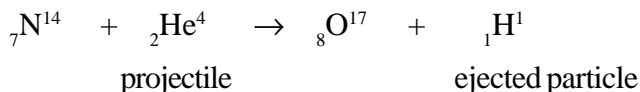
This reaction can be represented as (α, p) type reaction. Hence the above reaction is represented as $_7N^{14} (\alpha,p) {}_8O^{17}$.

Balancing of nuclear reaction

Example

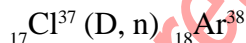$$_{17}Cl^{37} \quad + \quad _1H^2 \quad \rightarrow \quad _{18}Ar^{38} \quad + \quad ?$$

Solution

$$_{17}Cl^{37} \quad + \quad _1H^2 \quad \rightarrow \quad _{18}Ar^{38} \quad + \quad _0x^1$$

$\therefore$ x is neutron

Hence

$$_{17}Cl^{37} \quad + \quad _1H^2 \quad \rightarrow \quad _{18}Ar^{38} \quad + \quad _0n^1$$
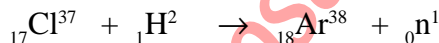
This reaction is represented as

$$_{17}Cl^{37} (D, n) \ _{18}Ar^{38}$$

Q value of a nuclear reaction

The amount of energy absorbed or released during nuclear reaction is called Q-value of nuclear reaction.

$$Q_{value} \quad = \quad (m_p - m_r) \, 931 \text{ MeV}$$

where $\quad m_r \quad$ - Sum of the masses of reactants
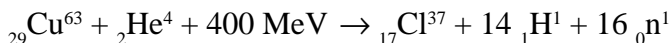$\qquad\quad m_p \quad$ - Sum of the masses of products

In the case of energy absorbed then $m_p > m_r$, then Q value will be positive.

Q value of a nuclear reaction in the case of energy released $= (m_p - m_r)$ 931 MeV. In the case of energy released, $m_r > m_p$, and hence Q value will be negative.

7.2 TYPE OF NUCLEAR REACTION

1. Spallation reaction

These are the reactions in which high speed projectiles may chip a heavy nucleus into several fragments.

$$_{29}Cu^{63} + _{2}He^{4} + 400 \text{ MeV} \rightarrow _{17}Cl^{37} + 14 \, _{1}H^{1} + 16 \, _{0}n^{1}$$
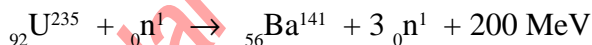
2. Nuclear fission reaction

Nuclear fission is the process in which a heavy nucleus breaks up into two lighter nuclei of almost equal size with the release of an enormous amount of energy. This type of nuclear fission reaction was first observed by German Chemists Otto Hahn, F.Strassman and Meitner by bombarding $_{92}U^{235}$ with slow moving neutrons. The process is usually accompanied by emission of neutrons. The nuclear fission has been produced in heavy nuclei such as $^{235}U, ^{238}U, ^{232}Th$ by neutrons, protons, deuterons.
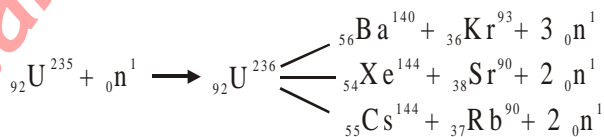
Mechanism of fission

In the fission process, the heavy nucleus absorbs a neutron and forms an unstable compound nucleus. The compound nucleus then breaks up more or less in the middle to give fission product.

Example

A typical example of the fission process in the fission of uranium by neutrons is explained by the following equation.

$$_{92}U^{235} + _{0}n^{1} \rightarrow _{56}Ba^{141} + 3 \, _{0}n^{1} + 200 \text{ MeV}$$

Further, the neutrons released (say three) from the fission of first uranium atoms can hit three other uranium atoms. In this way a chain reaction is set up resulting into the liberation of an enormous amount of energy. In the case of nuclear fission, $_{92}U^{236}$ formed breaks up in several ways.

$$_{92}U^{235} + _{0}n^{1} \longrightarrow _{92}U^{236} \begin{cases} _{56}Ba^{140} + _{36}Kr^{93} + 3 \, _{0}n^{1} \\ _{54}Xe^{144} + _{38}Sr^{90} + 2 \, _{0}n^{1} \\ _{55}Cs^{144} + _{37}Rb^{90} + 2 \, _{0}n^{1} \end{cases}$$

This fission process is self multiplying process and hence a tremendous amount of energy is released in a very short interval of time. Therefore, explosion takes place. Atom bomb is based on nuclear fission process.

Energy released in nuclear fission reaction

$$_{92}U^{235} + _{0}n^{1} \rightarrow _{42}Mo^{95} + _{57}La^{139} + 2_{0}n^{1} + 7_{-1}e^{0}$$
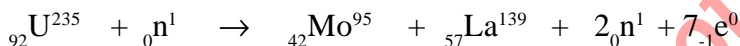
The isotopic mass of U^{235} = 235.118 amu
The isotopic mass of $_{42}Mo^{95}$ = 94.936 amu
The isotopic mass of $_{57}La^{139}$ = 138.95 amu
The isotopic mass of $_{0}n^{1}$ = 1.009 amu
$\therefore 235.118 + 1.009 \rightarrow 94.936 + 138.95 + 2 \times 1.009$
    236.127 amu $\rightarrow$ 235.906 amu
$\therefore$ The mass converted into energy is
    = (236.127 – 235.906) amu
    = 0.213 amu

Since 1amu (atomic mass unit) = 931 MeV, for one ^{235}U fission energy released = $0.213 \times 931.48 = 200$ MeV

The first atom bomb used in Hiroshima (Japan) utilised $_{92}U^{235}$ isotope as the main reacting substance and second bomb in Nagasaki made use of Plutonium (239) (August 1945). The fission in both the cases is similar and uncontrolled. Enormous amount of energy equal to that produced by 20000 tons of TNT is produced accompanied by heat, light and radioactive radiations.

Nuclear Power Generator

A nuclear reactor or nuclear power generator is a kind of furnace for carrying out the controlled fission of a radioactive material like U^{235} for producing power.
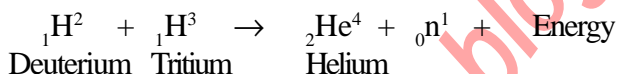
The core of the nuclear reactor produces heat through nuclear fission. Heavy water at high pressure takes heat away from the core. In the heat exchanger, the heavy water inside the reactor gives up its heat to water outside the reactor, which boils to form steam. The steam is taken away to drive turbines that make electricity. In Tamilnadu atomic power stations generating electricity are situated at Kalpakkam and another one is being constructed at Koodamkulam.

3) Nuclear Fusion

When lighter nuclei moving at a high speed are fused together to form a heavy nucleus, the process is called nuclear fusion.

In fusion reaction, the mass of heavier nucleus formed is less than the total mass of two lighter nuclei. Thus, just like a fission reaction, the source of energy in a fusion reaction is also the disappearance of mass, which gets converted into energy.

Nuclear fusion reaction takes place at very high temperature of about 10^8K. Therefore, this reaction is called thermonuclear reaction.

$$_1H^2 \ + \ _1H^3 \quad \rightarrow \quad _2He^4 \ + \ _0n^1 \ + \quad \text{Energy}$$
$$\text{Deuterium} \quad \text{Tritium} \qquad \text{Helium}$$

The Mass loss is equal to 0.018 amu and the corresponding energy released is 1.79×10^9 KJmol^{-1}.

Hydrogen Bomb

The highly destructive hydrogen bomb is also based on the fusion reactions of hydrogen to form helium producing large amount of energy. Hydrogen bomb consists of an arrangement for nuclear fission in the centre surrounded by a mixture of deuterium ($_1H^2$) and lithium isotope ($_3Li^6$). Fission reaction provides the high temperature necessary to start the fusion.

Fusion reactions take place in hydrogen bomb.

i) Fission $\rightarrow$ heat + neutrons
ii) $_3Li^6 \ + \ _0n^1 \quad \rightarrow \quad _1H^3 \ + \ _2He^4 \ + \ 4.78 \, \text{MeV}$
$\quad _1H^2 \ + \ _1H^3 \quad \rightarrow \quad _2He^4 \ + \ _0n^1 \quad + \ 17.6 \, \text{MeV}$

7.3 RADIOCARBON DATING

This method was developed by Willard and Libby to determine the age of wood or animal fossils. This method is based on the fact that $_6C^{14}$, radioactive isotope of carbon is formed in the upper atmosphere by reaction with neutrons (from cosmic rays).

$$_7N^{14} \ + \ _0n^1 \qquad \rightarrow \qquad _6C^{14} \ + \ _1H^1$$
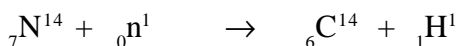
The C^{14} atoms thus produced are rapidly oxidised to $^{14}CO_2$ which in turn is incorporated in plants as result of photosynthesis. Animals too consume C^{14} by

eating plants. On death, organisms cease to take in fresh carbonations. Carbon-14 begins to decay.

$$_6C^{14} \quad \rightarrow \quad _7N^{14} \ + \ _{-1}e^0$$
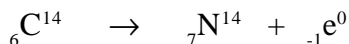
5700 years a fossil (plant or animal) will lose half the amount of carbon-14 present in its living state. Therefore by knowing either the amount of C^{14} or the number of β-particles emitted per minute per gram of carbon at the initial and final stages, the age of carbon material can be determined by the following equation.

$$t = \frac{2.303 \times t^{1/2}}{0.693} \quad \log \ \frac{\text{Amount of } C^{14} \text{ in fresh wood}}{\text{Amount of } C^{14} \text{ in dead wood}}$$
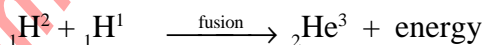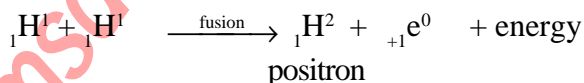
Uses

1) Carbon dating has proved to be a great tool for correlating facts of historical importance.

2) It is very useful in understanding the evolution of life, and rise and fall of civilizations.

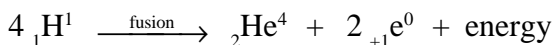## 7.4 NUCLEAR REACTIONS TAKING PLACE IN SUN (STARS)

It has been estimated that the sun is giving out energy equally in all possible directions at the rate of 3.7×10^{33} ergs/sec. The energy of the sun is supposed to arise from the fusion of hydrogen nuclei into helium nuclei which in going on inside it all the time.

The various fusion reactions taking place in the sun are as follows:

a) Proton - proton chain reaction:

$$_1H^1 + _1H^1 \quad \xrightarrow{\text{fusion}} \quad _1H^2 + \ _{+1}e^0 \quad + \text{ energy}$$
$$\text{positron}$$

$$_1H^2 + _1H^1 \quad \xrightarrow{\text{fusion}} \quad _2He^3 + \text{ energy}$$

$$_2He^3 + _1H^1 \quad \xrightarrow{\text{fusion}} \quad _2He^4 + \ _{+1}e^0 + \text{ energy}$$
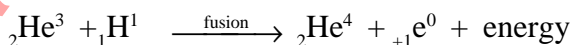
The overall reaction, therefore, may be written as:

$$4 _1H^1 \quad \xrightarrow{\text{fusion}} \quad _2He^4 + \ 2 _{+1}e^0 + \text{ energy}$$

7.5 USES OF RADIOACTIVE ISOTOPES
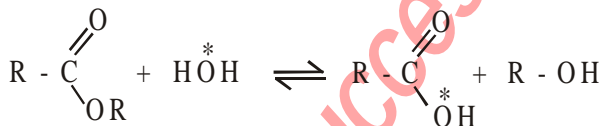
a) Study of reaction mechanism

i) Mechanism of photosynthesis in plants

A small quantity of Radioactive $C\overset{*}{O}_2$ containing radioactive oxygen O^{18} is mixed with ordinary carbondioxide and the process is carried out. It has been found that oxygen gas evolved along with sugar formation is non-radioactive. Therefore O_2 produced comes from water and not from carbondioxide. So the correct mechanism is as follows.

$$6C\overset{*}{O}_2 \ + \ 6H_2O \ \rightarrow \ C_6H_{12}O_6 \ + 6\overset{*}{O}_2$$
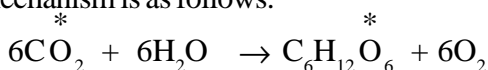
ii) Study of hydrolysis of ester

By labelling oxygen, the mechanism of ester hydrolysis can be studied by using water labelled with O^{18}. The hydrolysis of an ester by water enriched with radioactive oxygen is indicated as :

$$R - \overset{\displaystyle O}{\underset{\displaystyle OR}{C}} \ + \ H\overset{*}{O}H \ \rightleftharpoons \ R - \overset{\displaystyle O}{\underset{\displaystyle \overset{*}{O}H}{C}} \ + \ R - OH$$

Therefore it is the acid and not alcohol produced which is radioactive confirming the above mechanism.

Radioactive isotopes which are useful in medicine

Isotope		Use
$_1H^3$	Tritium	Measure water content of the body
$_6C^{11}$	Carbon - 11	Brain scan
$_6C^{14}$	Carbon - 14	Radio immunology
$_{53}I^{131}$	Iodine - 131	Diagnosis of damaged heart muscles and hyper thyroidism
$_{80}Hg^{197}$	Mercury - 197	Kidney scan
$_{15}P^{32}$	Phosphorous-32	Detection of eye tumours
$_{26}Fe^{59}$	Iron - 59	Diagnosis of anemia
$_{27}Co^{60}$	Cobalt - 60	Treatment of cancer

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| $_{11}Na^{24}$ | Sodium - 24 | Location of blood clots and circularity disorders |
| $_{79}Au^{198}$ | Gold - 198 | Curing of cancers |

Radio isotopes which are useful in industry and in agriculture

$_{38}Sr^{90}$ Strontium - 90 Thickness of coatings or levels of liquids in tanks
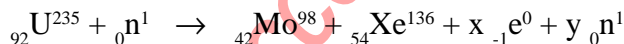
Practice Problems

1) On neutron bombardment fragmentation of U-235 occurs according to the equation

$$_{92}U^{235} + _0n^1 \rightarrow _{42}Mo^{95} + _{57}La^{139} + x _{-1}e^0 + y _0n^1$$
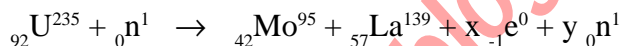
Calculate the values of x and y.

[**Ans** : x = 7, y = 2]

2) On neutron bombardment fragmentation of U-235 occurs according to the equation.

$$_{92}U^{235} + _0n^1 \rightarrow _{42}Mo^{98} + _{54}Xe^{136} + x _{-1}e^0 + y _0n^1$$

Calculate the values of x and y.

[**Ans** : x = 4, y = 2]

Solved Problems

1. After 24 hours, only 0.125 g out of the initial quantity of 1g of a radioisotope remains behind. what is half-life period?

Solution

$N_0 = 1g$ $N = 0.125$ g,   t = 24 hours

$$\therefore \lambda = \frac{2.303}{t} \log \frac{N_0}{N}$$

$$= \frac{2.303}{24} \log \frac{1}{0.125}$$

$$= 0.0866 \text{ hour}^{-1}$$

$$\therefore t\frac{1}{2} = \frac{0.693}{\lambda} = \frac{0.693}{0.0866} = 7.99 \text{ hours}$$

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2. Half-life period of a radioactive element is 100 seconds. Calculate the disintegration constant and average life period. How much time will it take for 90% decay?

Solution

$$t\frac{1}{2} \;=\; 100 \text{ sec}$$

$$\therefore \;\; \lambda = \frac{0.693}{t\frac{1}{2}} \;\; = \;\; \frac{0.693}{100} \;=\; 0.00693 \text{ sec}^{-1}$$

Average life period, $\tau = \dfrac{1}{\lambda} = \dfrac{1}{0.00693} = 144.3$ sec

For 90% decay, $N_0 = 100$; $N = (100 - 90) = 10$

$$t \;=\; \frac{2.303}{\lambda} \log \frac{N_0}{N}$$

$$= \frac{2.303}{0.00693} \;\; \log \frac{100}{10}$$

$$= \frac{2.303}{0.00693} \;\; \log 10 \;=\; 332.3 \text{ sec}$$

3. The half-life of cobalt - 60 is 5.26 years. Calculate the % activity remaining after 4 years.

Solution

$$t\frac{1}{2} \;=\; 5.26 \text{ years}$$

$$\lambda \;\; = \;\; \frac{0.693}{5.26} \text{ year}^{-1}$$

$$t \;\; = \;\; 4 \text{ years}$$

Here to find the % of activity (i.e) to find $\dfrac{N}{N_0}$

$$\lambda \;\; = \;\; \frac{2.303}{t} \; \log \frac{N_0}{N}$$

$$\log \frac{N_0}{N} = \frac{\lambda \times t}{2.303}$$

$$= \frac{0.693}{5.26} \times \frac{4}{2.303}$$

$$= 0.2288$$

$$\frac{N_0}{N} = \text{Antilog}\,(0.2288)$$

$$= 1.693$$

$$\frac{N}{N_0} = \frac{1}{1.693} = 0.59$$

% of activity $= 0.59 \times 100$

$= 59\%$

4. Wooden artifact and freshly cut tree are having 7.6 and 15.2 counts min^{-1}g^{-1} of carbon (t½ = 5700 years) respectively. Calculate the age of the artifact.

Age of the artifact $\dfrac{2.303}{\lambda} \log \left[\dfrac{\text{Amount of fresh wood}}{\text{Amount of old wood}} \right]$

But $\quad$ t½ $= \dfrac{0.693}{\lambda}$

$\therefore \lambda = \dfrac{0.693}{\text{t½}}$

$\therefore$ Age of the artifact $= \dfrac{2.303 \times \text{t½}}{0.693} \log \left[\dfrac{\text{Amount of fresh wood}}{\text{Amount of old wood}} \right]$

$$= \frac{2.303 \times 5700}{0.693} \log \frac{15.2}{7.6}$$

$= 5700$ years

5. Half life period of a radio active element is 1500 years. Find the value of disintegration constant interms of second.

$$\lambda = \frac{0.693}{t^{1/2}} = \frac{0.693}{1500 \text{ yrs}}$$

$$= \frac{0.693}{1500 \times 365 \times 24 \times 60 \times 60 \text{ sec}}$$

$$= \frac{0.693}{4730 \times 4 \times 10^4} \text{ sec}^{-1}$$

$$= 0.1465 \times 10^{-10} \text{ sec}^{-1}$$

6. Calculate the number of α and β particles emitted in the conversion of $_{90}Th^{232}$ to $_{82}pb^{208}$.

Let 'a' and 'b' be the number of α β particles emitted during the change

$$_{90}Th^{232} \rightarrow {}_{82}pb^{208} + a\ {}_{2}He^4 + b\ {}_{-1}e^0$$
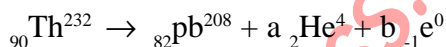
Comparing the mass numbers,

$$232 = 208 + 4a + b \times 0$$
$$4a = 232 - 208$$
$$= 24$$
$$a = 6$$

Comparing the atomic numbers

$$90 = 82 + 2 \times a + (-1)b$$
$$= 82 + 2a - b$$
$$2a - b = 90 - 82 = 8$$
$$2(6) - b = 8$$
$$b = 12 - 8 = 4$$

Number of α - particle emitted = 6
Number of β - particles emitted = 4

7. The atomic masses of Li, He and proton are 7.01823 amu, 4.00387 amu and 1.00715 amu respectively. Calculate the energy evolved in the reaction, $_{3}Li^7 + {}_{1}H^1 \rightarrow 2\ {}_{2}He^4 + \Delta E$ Given 1 amu = 931 MeV.

Solution

Mass of reactants = mass of Li + mass of H
$$= 7.01823 + 1.00715$$
$$= 8.02538 \text{ amu}$$

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Mass of products $= 2 \times$ mass of He
                    $= 2 \times 4.00\,387$
                    $= 8.00\,774$ amu

Mass loss during change $= (8.02538 - 8.00774)$ amu
                        $= 0.01764$ amu

$\therefore$ Energy evolved during reaction
                    $= 0.0176 \times 931$ MeV
                    $= 16.423$ MeV

8. Calculate the number of neutrons in the remaining atom after emission of an α particle from $_{92}X^{238}$ atom. also report the mass number and atomic number of the product atom.

Solution $_{92}X^{238} \rightarrow {}_{A}X^{m} + {}_{2}He^{4}$
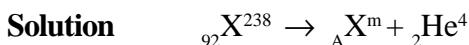
Comparing mass number of both sides,
    $238 = m + 4$
    $m = 238 - 4 = 234$
Comparing atomic number on both sides,
    $92 = A + 2$
    $A = 92 - 2 = 90$
X has atomic number $= 90$
and mass number $= 234$
Number of neutrons $= 234 - 90 = 144$.

9. Determine the average life of U^{238} having $t\frac{1}{2} = 140$ days.

Solution

$t\frac{1}{2} = \dfrac{0.693}{\lambda}$ ($\therefore$ Average life, $\tau = \dfrac{1}{\lambda}$)

$\quad = 0.693\ \tau$

$\tau = \dfrac{t\frac{1}{2}}{0.693}$

$\quad = \dfrac{140}{0.693}$ days

$\quad = 202.02$ days

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10. The activity of a radioactive isotope falls to 12.5% in 90 days. Calculate the half life and decay constant.

Solution

$N_0 = 100$ $N = 12.5$ $t = 90$ days

decay constant $\lambda = \dfrac{2.303}{t} \log \dfrac{N_0}{N}$

$$= \dfrac{2.303}{90} \ \log \dfrac{100}{12.5}$$

$$= 0.02558 \log 8$$

$$= 2.311 \times 10^{-2} \ \text{days}^{-1}$$

$t\frac{1}{2} = \dfrac{0.693}{\lambda} = \dfrac{0.693}{2.311 \times 10^{-2}} = 29.99 \, \text{days}$

11. Calculate Q value of the following nuclear reaction $_{13}Al^{27} + _{2}He^{4} \rightarrow _{14}Si^{30} + _{1}H^{1} + Q$. The exact mass of $_{13}Al^{27}$ is 26.9815 amu, $_{14}Si^{30}$ is 29.9738, $_{2}He^{4}$ is 4.0026 amu and $_{1}H^{1}$ is 1.0078 amu.

$\Delta m \ = \ (29.9738 + 1.0078) - (26.9815 + 4.0026)$

$\ \ \ \ \ \ = \ -0.0025 \ \text{amu}$

$Q \ \ \ = \ 0.0025 \times 931 \ \text{MeV}$

$\ \ \ \ \ \ = \ 2.329 \ \text{MeV}$

SELF EVALUATION

A.   Choose the correct answer

1. The phenomenon of radioactivity was discovered by
   a) Madam curie   b) Pierre curie   c) Henry Becquerrel   d) Rutherford

2. The most penetrating radiations are
   a) α rays   b) β rays   c) γ rays   d) all are equally penetrating

3. In the nuclear reaction, $_{92}U^{238} \rightarrow _{82}Pb^{206}$, the number of α and β particles emitted are

   a) $7\alpha, 5\beta$ b) $6\alpha, 4\beta$ c) $4\alpha, 3\beta$ d) $8\alpha, 6\beta$

4. Which one of the following particles is used to bombard $_{13}Al^{27}$ to give $_{15}p^{30}$ and a neutron

   a) α particle   b) deuteron   c) proton   d) neutron

5. The reaction $_5B^8 \rightarrow {}_4Be^8$ takes place due to

   a) α decay   b) β decay   c) electron capture   d) positron decay

6. Radioactivity is due to

   a) Stable electronic configuration   b) Stable nucleus
   c) Unstable nucleus   d) Unstable electronic configuration

7. In the following radioactive decay, $_{92}x^{232} \rightarrow {}_{89}y^{220}$, how many α and β particles are ejected.

   a) 3α and 3β b) 5α and 3β c) 3α and 5β d) 5α and 5β

8. $_{92}U^{235}$ nucleus absorbs a neutron and disintegrates into $_{54}Xe^{139}$, $_{38}Sr^{94}$ and x. What will be the product x?

   a) 3 neutrons   b) 2 neutrons   c) α particle   d) β particle

9. Loss of a β-particle is equivalent to

   a) Increase of one proton only   b) Decrease of one neutron only
   c) Both (a) and (b)   d) None of these

10. Which of the following is used as neutron absorber in the nuclear reactor?

    a) Water   b) Deuterium   c) Some compound of uranium   d) Cadmium

B.   Answer in one or two sentences

11. Define radio activity.

12. What is half life period.

13. Write two difference between chemical reaction and nuclear reaction.

14. What is Q value of a nuclear reaction?

15. What are the types of nuclear reaction. Give example for each type.

16. Explain the principle behind the Hydrogen bomb.

17. What is Radio carbon dating?

18. State two uses of radio carbon dating.

19. What is binding energy of Nucleus?

20. Complete the following nuclear reactions

   i) $_{42}Mo^{96}$ (....., n) $_{43}Tc^{97}$

   ii) ....$(\alpha, 2n)$ $_{85}At^{211}$

   iii) $_{96}Cm^{246} + _{6}C^{12} \rightarrow$ .....$+4(_{0}n^{1})$

   iv) $_{7}N^{15}$ (p, α) ....

   v) $_{11}Na^{23}$ (n, β) ....

   vi) $_{19}K^{39}$ (p, d) ....

   vii) $_{27}Co^{59}$ (d, p) ....

   viii) $_{13}Al^{27}$ (α, n) ....

   ix) $_{11}Na^{23} +$ .... $\rightarrow _{12}Mg^{23} + _{0}n^{1}$

C. Answer not exceeding 60 words

21. What is radioactivity? How was the phenomenon discovered?

22. What is nuclear fission? What are controlled and uncontrolled fission reactions? How can the energy released in such reactions be used for practical purposes?

23. What is nuclear fusion? How do nuclear fusion reactions differ from fission reactions?

24. Differentiate chemical reactions from nuclear reactions.

25. Explain the use of radioactive isotopes with specified examples.

D. Problems

26. How many α and β particles will be emitted by an element $_{84}A^{218}$ is changing to a stable isotope of $_{82}B^{206}$?

27. Calculate the decay constant for Ag^{108} if its half life is 2.31 minutes.

28. The half life of Th^{233} is 1.4×10^{10} years. Calculate its disintegration constant.

29. Complete the following nuclear reactions

   i) $_{18}Ar^{40} + $ _____? _____ $\rightarrow _{19}K^{40} + _{0}n^{1}$

   ii) _____?_____ $+ _{1}H^{1} \rightarrow _{2}He^{4} + _{2}He^{4}$

   iii) $_{88}Ra^{236} \rightarrow$ _____?_____ $+ _{2}He^{4}$

   iv) $_{92}U^{238} \rightarrow _{56}Ba^{143} +$ _____$+_{0}n^{1}$

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30. $_{92}U^{238}$ undergoes a series of changes by emitting α and β particles and finally $_{82}pb^{206}$ is formed. Calculate the number of and particles emitted during the change.

31. The atomic mass of Th is 232 and its atomic number is 90. In terms of its radioactivity six α and four β particles are emitted. What is the mass number and atomic number of the product.

32. Calculate the average life of $_{79}Au^{198}$ leaving $t\frac{1}{2} = 150$ days.

33. Complete the following

    i) $_7N^{14} + _2He^4 \rightarrow _8O^{17} + \underline{\quad?\quad}$.

    ii) $_{92}U^{235} + _0n^1 \rightarrow _{56}Ba^{137} + _{36}Kr^{93} + \underline{\quad?\quad}$.

    iii) $_{29}Cu^{53} \rightarrow _{28}Ni^{58} + \underline{\quad?\quad}$.

    iv) $2_1H^3 \rightarrow _2He^4 + \underline{\quad?\quad}$.

34. Predict the bombarding projectile in the following nuclear reactions

    i) $_{13}Al^{27} + ? \rightarrow _{11}Na^{24} + _2He^4$

    ii) $_{34}Se^{83} + ? \rightarrow _{34}Se^{84} + \gamma$ rays

    iii) $_7N^{14} + ? \rightarrow _8O^{17} + _1H^1$

35. The decay constant for $_6C^{14}$ is 2.31×10^{-4} year^{-1} calculate the half life period.

Summary

*   This chapter explains the basic concept of nuclear chemistry.

*   Difference about nuclear reaction and chemical reactions.

*   Nature of nuclear fission and nuclear fusion reactions are briefly explained.

*   Principle of nuclear reactors, nuclear reactions in sun and applications of radioactive isotopes are thoroughly discussed.

Reference

1.   Inorganic Chemistry by Puri and Sharma.

2.   Inorganic Chemistry by P.L.Soni.

PHYSICAL CHEMISTRY

"Physical Chemistry lies at the mathematical end of the spectrum that constitutes modern chemistry."

MATHEMATICAL RELATION

Logarithms and exponentials

$\ln x + \ln y + \ldots = \ln xy \ldots$

$\ln x - \ln y = \ln (x/y)$

$a \ln x = \ln x^a$

Derivatives

$d (f = g) = df + dg$

$d (fg) = fdg + gdf$

$d(f/g) = 1/g \, df - f/g^2 \, dg$

$dx^n/dx = nx^{n-1}$

$de^{ax}/dx = ae^{ax}$

$d \ln x /dx = 1/x$

Integrals

$\int x^n dx = x^{n+1}/ n+1$

$\int (1/x) \, dx = \ln x + \text{constant}$

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PHYSICAL CHEMISTRY

8. SOLID STATE - II

Learning Objectives

☇ *To study the analysis of crystal structure using X-rays.*

☇ *To recognise the properties and types of ionic crystals.*

☇ *To know the elementary idea about the conducting and superconducting properties of crystals.*

☇ *To learn the nature of Amorphous solids.*

REVIEW

Solids are characterised by incompressibility, rigidity and mechanical strength. Solids are usually classified as either crystalline or amorphous. Crystalline solids have definite and ordered arrangement of the constituents extended over a long distance and is called a long-range order. They possess a sharp melting point. Amorphous solids like glass, rubber etc., although possessing many characteristics of crystalline solids such as definite shape, rigidity and hardness, but are devoid of a regular internal structure and melt gradually over a range of temperature. For this reason they are not considered as true solids but rather highly supercooled liquids.

Crystallography : A study of internal structure of crystals. 1913 - English physicists, Father and Son, William and Lawrence Bragg developed X-ray crystallography further by establishing laws that govern the orderly arrangement of atoms in crystal interference and diffraction patterns. They also demonstrated the wave nature of X-rays. In 1915 William Bragg and Lawrence Bragg were awarded Nobel prize for physics for X-ray analysis of crystal structure.

UNIT CELL

Unit cell is the smallest fundamental repeating portion of a crystal lattice from which the crystal is built by repetition in three dimension.
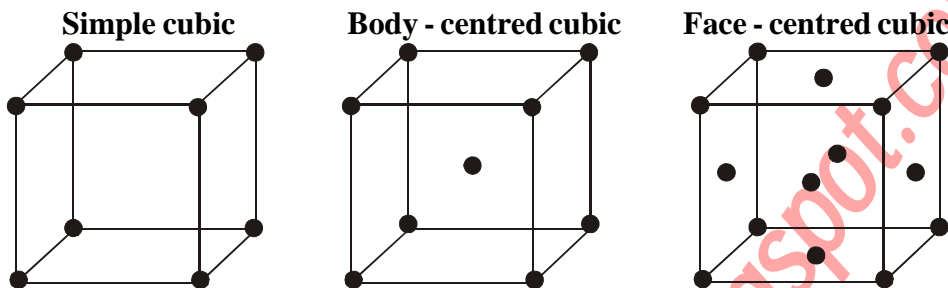
Characteristic parameters of a unit cell
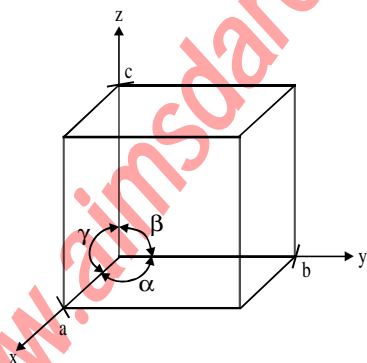
Crystallographic axes : ox, oy, oz

Interfacial angles : α, β, γ

Primitives (Intercepts) : a, b, c

Types of Cubic System

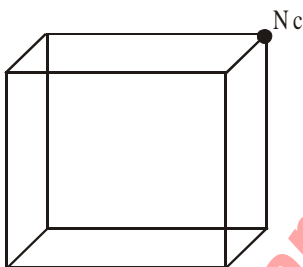| Simple cubic	Body - centred cubic	Face - centred cubic

Assignment of Atoms per unit cell in a cubic lattice

Simple Cubic

In a simple cubic where atoms are present at the corners only, each atom at the corner is shared equally by eight other unit cells. Hence the contribution of each atom to the unit cell is $\dfrac{1}{8}$.

The total number of atoms per unit cell

$$= \frac{Nc}{8} = 8 \times \frac{1}{8} = 1$$
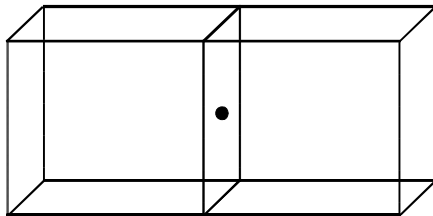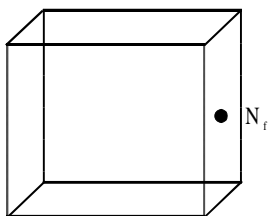
Nc is the number of atoms at the corners.

fcc

A face atom is shared equally between two unit cells and therefore a face atom contributes only $\left(\dfrac{N_f}{2} \right)$ to the unit cell.

The number of atoms per unit cell in fcc $= \dfrac{N_c}{8} + \dfrac{N_f}{2} = \dfrac{8}{8} + \dfrac{6}{2} = 1 + 3 = 4$
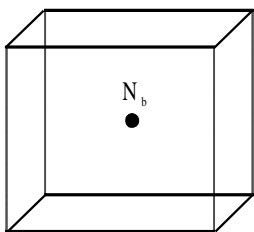
N_f = Number of atoms at the faces.

N_f = Number of atoms at the faces

BCC

In a bcc lattice, the body centred atom belongs exclusively to the unit cell. The total number of atoms per unit cell in bcc

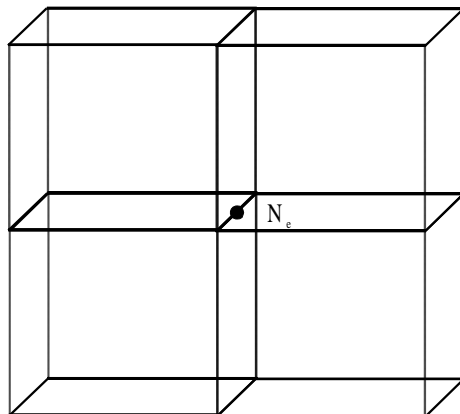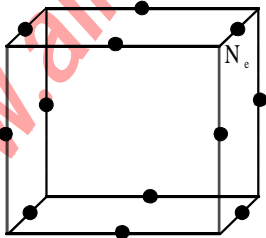$$= \frac{N_c}{8} + \frac{N_b}{1} = \frac{8}{8} + \frac{1}{1} = 1 + 1 = 2$$

N_b = Number of atoms inside the body

N_b

An Edge atom (or) Edge centred

An edge atom and edge centred is common to four unit cells and there are twelve edges of the unit cell. The contribution from each edge atom is therefore 1/4. The number of atoms per cell in edge centre.

$$= \frac{N_c}{8} + \frac{N_e}{4} \qquad N_e = \text{Number of atoms at the edge centre}$$

$$= \frac{8}{8} + \frac{12}{4} = 1 + 3 = 4$$

N_e

N_e

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8.1 X-RAYS AND CRYSTAL STRUCTURE

X-rays are electromagnetic waves of very short wavelength. The wave nature of X-rays is not confirmed by diffraction experiment, because a grating of about 40 million ruling per cm is required for diffraction experiment. The preparation of such a grating is highly impossible. At the same time, crystallographers believed that atoms in crystals are regularly arranged with an interatomic distance of about 10^{-8} cm. The wavelength of X-rays is, also, in the order of 10^{-8} cm. Based on this, Laue suggested that crystal can be used as a three dimensional diffraction grating for X-rays. This suggestion is carried out successfully by Laue in his experiment using zinc sulphide crystal. The photograph obtained is known as Laue diffraction pattern.

The Laue experiment confirmed the wave nature of X-rays and also established the fact that atoms or ions in crystals are arranged in regular three dimensional lattice. Though Laue diffraction pattern gives more information about the symmetry of crystals, the interpretation of the pattern seems to be difficult.

8.1.1 Bragg's Equation

W.L.Bragg and W.H.Bragg derived a mathematical relation to determine interatomic distances from X-ray diffraction patterns. The scattering of X-rays by crystals could be considered as reflection from successive planes of atoms in the crystals. However, unlike reflection of ordinary light, the reflection of X-rays can take place only at certain angles which are determined by the wavelength of the X-rays and the distance between the planes in the crystal. The fundamental equation which gives a simple relation between the wavelength of the X-rays, the interplanar distance in the crystal and the angle of reflection, is known as Bragg's equation.

Bragg's equation is $\boxed{n\lambda = 2d \sin\theta}$

where n is the order of reflection
   λ is the wavelength of X-rays
   d is the interplanar distance in the crystal
   θ is the angle of reflection

8.1.2 Significance of Bragg's equation

1) If we use X-rays of known wavelength (λ), then the interatomic distance (d) in an unknown crystal can be calculated. On the other hand, if we use a

crystal whose interatomic distance 'd' is known, then the wavelength of X-rays can be calculated.

2) The Bragg's equation gives the essential condition for diffraction to occur.

3) When the experiment is done, there will be a maximum reflection at a particular angle θ. That angle is noted. It corresponds to first order reflection (n=1). If the angle 'θ' is increased, maximum reflection at some other higher angle. It corresponds to second order reflection (n=2). Similarly, third, fourth and higher order of reflection occur at certain specific angles. The values of angles obtained are in accordance with the Bragg's equation. Hence Bragg's equation is experimentally verified.

8.1.3   Bragg's spectrometer method

This method is one of the important method for studying crystals using X-rays. The apparatus consists of a X-ray tube from which a narrow beam of X-rays is allowed to fall on the crystal mounted on a rotating table.The rotating table is provided with scale and vernier, from which the angle of incidence, θ can be measured.
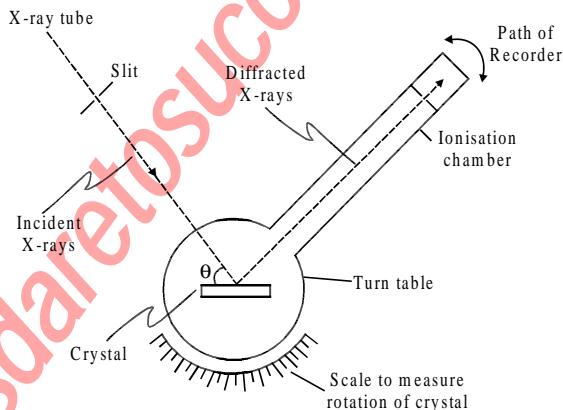

Fig. 8.1 X-ray spectrometer

An arm which is rotating about the same axis as the crystal table, carries an ionisation chamber. The rays reflected from the crystal enter into the ionisation chamber and ionise the gas present inside. Due to the ionisation, current is produced which is measured by electrometer. The current of ionisation is a direct measure of intensity of reflected beam from the crystal. For different angles of incidence, the corresponding ionisation current is measured from the electrometer. These values are plotted in the form of graph.

For sodium chloride, the maximum reflection or peaks for 100 plane occurred at $\theta = 5.9°$, $11.85°$ and $18.15°$. The sines of these angles are 0.103, 0.205 and 0.312 which are in the ratio 1:2:3. These peaks represent the first,second and third order reflections. The ratio confirms the correctness of Bragg's equation.

8.2 TYPES OF CRYSTALS

Crystals are classified into the following four types depending upon the nature of the units which occupy the lattice points.

1. Molecular Crystals   2. Covalent Crystals
3. Metallic Crystals   4. Ionic Crystals

8.2.1 Molecular Crystals

The lattice points in molecular crystals consist of molecules which do not carry any charge. The forces binding the molecules together are of two types (i) Dipole-dipole interaction and (ii) Vanderwaal's forces. Dipole-dipole forces occur in solids which consists of polar molecules e.g., ice. The Vanderwaal's forces are more general and occur in all kinds of molecular solids.

8.2.2 Covalent Crystals

The lattice in covalent crystals consists of atoms linked together by a continuous system of covalent bonds. Diamond is a good example for this type.

8.2.3 Metallic Crystals

Metallic crystal consists of an assemblage of positive ions immersed in a sea of mobile electrons. Thus, each electron belongs to a number of positive ions and each positive ion belong to a number of electrons. The force that binds a metal ion to a number of electrons within its sphere of influence is known as metallic bond. This force of attraction is strong and is thus responsible for a compact solid structure of metals.

8.2.4 Ionic Crystals

In ionic crystals, the units occupying lattice points are positive and negative ions. Each ion of a given sign is held by coulombic forces of attraction to all ions of opposite sign. The forces are very strong. The ionic crystals have the following characteristics.

1.   The heats of vapourisation of ionic crystals are high.
2.   The vapour pressure of ionic crystals at ordinary temperature are very low.
3.   The melting and boiling points of ionic crystals are very high.
4.   Ionic crystals are hard and brittle.
5.   Ionic crystals are insulators in the solid state.
6.   Ionic crystals are soluble in water and also in other polar solvents.
7.   Ionic solids are good conductors when dissolved in water.

8.2.5 Types of Ionic Crystals

The structure of ionic crystals is determined by the ratio of the numbers, the ratio of the sizes and the structural units. In general, ionic crystals are classified into AB and AB_2 type.

Substance of the general formula AB mostly crystallise in one of the following six forms.

	AB	AB	AB	AB	AB	AB
Lattice type :	CsCl	NaCl	FeS	ZnO	ZnS	BN
Coordination number :	8	6	6	4	4	3

Let us discuss the structure of CsCl for AB type. It is body centered cubic system. The chloride ions are at the corners of a cube where as Cs^+ ion is at the centre of the cube or vice versa. Each Cs^+ ion is connected with eight Cl^- ion and Cl^- is connected with eight Cs^+ ions.
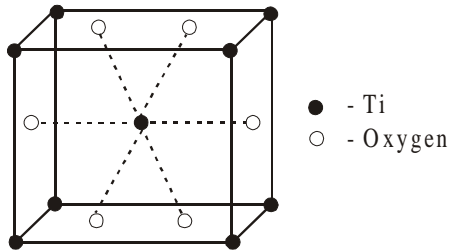

$\circ$ Cs^+
$\bullet$ Cl^-
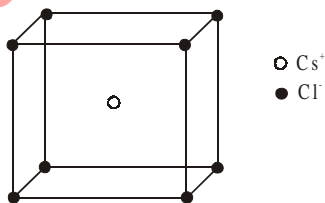
Number of chloride ions per unit $= \dfrac{N_c}{8} = \dfrac{8}{8} = 1$

Number of cesium ion per unit $= \dfrac{N_b}{1} = \dfrac{1}{1} = 1$

Thus number of CsCl units per unit cell is one.

Compounds having the general formula AB_2 generally crystallise in forms based on the following eight typical lattices like CO_2, SiO_2, TiO_2, CaF_2, Cu_2O, FeS_2, CdI_2 and MoS_2. For example Rutile (TiO_2) has the following structure.

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● - Ti
○ - Oxygen

8.3 IMPERFECTIONS IN SOLIDS

Almost all the crystals encountered in practice suffer from imperfections or defects of various kinds. An ideally perfect crystal is one which has the same unit cell and contains the same lattice points throughout the crystal. The term imperfection or defect is generally used to describe any deviation of the ideally perfect crystal from the periodic arrangement of its constituents.

8.3.1 Point Defects

If the deviation occurs due to missing atoms, displaced atoms or extra atoms, the imperfection is named as a point defect. Such defects arise due to imperfect packing during the original crystallisation or they may arise from thermal vibrations of atoms at elevated temperatures. The most common point defects are the Schottky defect and Frenkel defect. Comparatively less common point defects are the metal excess defect and the metal deficiency defect.

Schottky defects

This defect is caused if some of the lattice points are unoccupied. The points which are unoccupied are called lattice vacancies. The number of missing positive and negative ions is the same in this case and thus, the crystal remains neutral. The existence of two vacancies, one due to a missing Na^+ ion and the other due to a missing Cl^- ion in a crystal of NaCl is shown in Fig. 8.2.
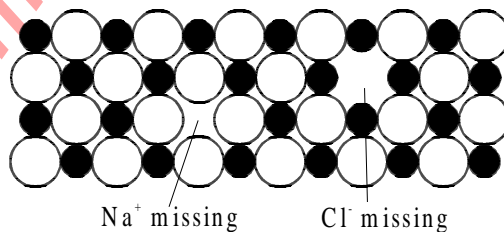

Na^+ missing Cl^- missing

Fig. 8.2 Schottky Defects in a Crystal

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Schottky defects appears generally in ionic crystals in which the positive and negative ions do not differ much in size.

Frenkel defects

This defect arise when an ion occupies an interstitial position between the lattice points. This defect occurs generally in ionic crystals in which the anion is much larger in size than the cation. AgBr is an example for this type of defect. One of the Ag^+ ion occupies a position in the interstitial space rather than its own appropriate site in the lattice is shown in Fig. 8.4.
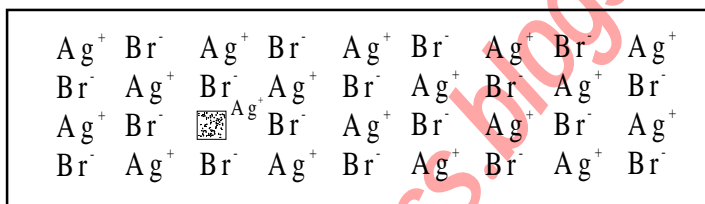
Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+
Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-
Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+
Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-

Fig. 8.3 Frenkel Defects in a Crystal

The crystal remains neutral since the number of positive ions is the same as the number of negative ions.

Metal excess defects

If a crystal of NaCl is heated in sodium vapour, it acquires a yellow colour. This yellow colour is due to the formation of a non-stoichiometric compound of NaCl in which there is a slight excess of sodium ions. This defect is called the metal excess defect.

Metal deficiency defects

In certain cases, one of the positive ions is missing from its lattice site and the extra negative charge is balanced by some nearby metal ion acquiring additional charges instead of original charge. This type of defect is generally found in compounds of transition metals which can exhibit variable valency. FeO and FeS show this type of defects.

8.4 PROPERTIES OF CRYSTALLINE SOLIDS

Crystalline solids exhibit an important property called conductivity. Conductivity is the property of a material by which it allows the flow of electric current. Conducting materials are generally classified into three types namely conductors, semi conductors and super conductors.

Typical metals are good conductors of electricity while elements like silicon and germanium are non conductors at ordinary temperature. However, they exhibit appreciable conductivity upon addition of impurities as Arsenic and Boron. The resulting materials are called semiconductors. Semi conductors which exhibit conductivity due to the flow of excess negative electrons are called n-type semiconductors. The conductivity due to the positive holes are called p-type semiconductors. Semiconductors find application in modern devices as recitifiers, transitors and solar cells.

8.4.1 Super conductors

The ability of certain ultra cold substances to conduct electricity without resistance is called super conductivity. This superconductivity state is a state in which a material has virtually zero electrical resistance. Substances having this property are called super conductors.
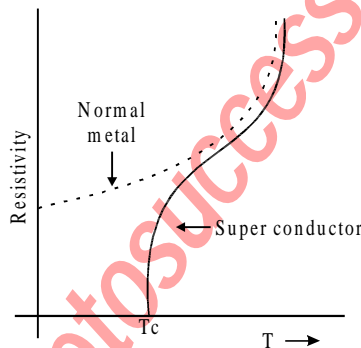
The super conducting transition temperature 'Tc' of a material is defined as a critical temperature at which the resistivity of the material is suddenly changed to zero. Thus at that temperature a material is changed from normal material to superconductor.

At the extremely low temperatures, vibration of the nuclei of certain atoms slow down so much and they synchronise with the passing waves of electrons in a flow of electric current. When this happens, resistance to electric current disappears.

8.4.2 Application of superconductors

1) It is a basis of new generation of energy saving power systems. Super conducting generators are smaller in size and weight when we compare with conventional generators. These generators consume very low energy and so we can save more energy.

2) High efficiency ore separating machines may be built using superconducting magnets.

3) Superconducting solenoids are used in Nuclear Magnetic Resonance Imaging equipment which is a whole body scan equipment.

8.5 AMORPHOUS SOLIDS

Amorphous solids possess properties of incompressibility and rigidity to a certain extent but they do not have definite geometrical forms.

8.5.1 Glasses

When certain liquids are cooled rapidly there is no formation of crystals at a definite temperature, such as occurring on slow cooling. The viscosity of the liquid increases steadily and finally a glassy substance is formed.

The chief characteristics of a glass are hardness, rigidity and ability to withstand shearing stresses which are all properties of the solid state. On the other hand glasses are optically isotropic and on heating without any sharp transition passes into a mobile liquid. At a high temperature glasses undergo phase transition when crystals separate first as they do form supercooled liquid. Therefore, glasses are regarded as amorphous solids or super cooled liquids as well. Thus, glassy or vitreous state is a condition in which certain substance can exist, lying between the solid and liquid states.

Solved Problems

1) Determine the number of formula units of NaCl in one unit cell. NaCl is face centred cubic.

Solution

In the fcc arrangement, there are Eight corners $8 \times \dfrac{1}{8} = Cl^-$ ion

At the six faces $\qquad 6 \times \dfrac{1}{2} = 3Cl^-$ ions

Along the 12 edges $12 \times \dfrac{1}{4} = 3Na^+$ ions

At the cube centre $\dfrac{1\times1=1Na^{+}\ \text{ion}}{\text{Total 4 Cl}^{-}\ \text{and 4Na}^{+}\ \text{ions}}$

Hence, the unit cell contains four NaCl units.

2) The diffraction of crystal of Barium with X-ray of wavelength 2.29A° gives a first order reflection at 27°8′. What is the distance between the diffracted planes?

Bragg's equation is $n\lambda = 2d \sin\theta$

$n = 1,\qquad \lambda = 2.29\ A°\qquad d = ?\qquad \theta = 27°8′$

on substitution, $1 \times 2.29A° = 2d \sin 27°8′$

$2.29A° = 2d\ (0.456)$

$$d = \dfrac{2.29A°}{2\times0.456}\quad = \quad 2.51\ A°$$

3) In a fcc arrangement, the corner atoms are A type and those at face centres are B type. What is the simplest formula of the compound ?

Solution

Number of A type atoms in the unit cell, $8\times\dfrac{1}{8}=1$

Number of B type atoms in the unit cell, $6\times\dfrac{1}{2}=3$

Hence the formula is AB_3

4) In a fcc lattice of A and B type atoms are present. A atoms are present at the corners while B type are at face centres. If in each unit cell, one of the A type atom is missing from the corner, what is the simplest formula of the compound?

Number of atoms of A type in the unit cell $= 7\times\dfrac{1}{8}=\dfrac{7}{8}$

Number of atoms of B type in the unit cell $= 6\times\dfrac{1}{2}=3$

Hence the formula is $A_{7/8}\,B_3$ or A_7B_{24}

Problems for practice

1. The diffraction of a crystal with X-ray of wavelength 2.31A° gives a first order reflection at 28°.9′. What is the distance between the diffracted planes.

   [**Ans** : 2.447 A°]

2. Diffraction angle 2θ equal to 14.8° for a crystal having interplanar distance in the crystal is 0.400 nm when second order diffraction was observed. Calculate the wavelength of X-ray used. [**Ans** : 0.0515 nm]

3. Find the interplanar distance in a crystal in which a series of planes produce a first order reflection from a copper X-ray tube ($\lambda = 1.542$ A°) at an angle of 23.2°. [**Ans** : 1.9573 A°]

4. The X-ray of wavelength 1.5A° are incident on a crystal having an interatomic distance of 1.6A°. Find out the angles at which the first and second order reflection take place. [**Ans** : 27°57′; 69°38′]

5. Calculate the angle at which (a) first order reflection and (b) second order reflection will occur in an X-ray spectrometer when X-ray of wavelength 1.54A° are diffracted by the atoms of a crystal, given that the interplanar distance is 4.04A°. [**Ans** : 10°59′ ; 22°24′]

SELF EVALUATION

A. Choose the correct answer

1. The number of chloride ions that surrounds the central Na^+ ion in NaCl crystal is_____.

   (a) 12 (b) 8 (c) 6 (d) 4

2. The Bragg's equation is

   (a) $\lambda = 2d \sin\theta$ (b) $nd = 2\lambda \sin\theta$ (c) $2\lambda = nd \sin\theta$ (d) $n\lambda = 2d \sin\theta$

3. A regular three dimensional arrangement of identical points in space is called

   (a) Unit cell (b) Space lattice (c) Primitive (d) Crystallography

4. The smallest repeating unit in space lattice which when repeated over and again results in the crystal of the given substance is called

   (a) Space lattice (b) Crystal lattice (c) Unit cell (d) Isomorphism

5. The crystal structure of CsCl is

(a) Simple cubic   (b) face-centred cubic
(c) Tetragonal   (d) Body centred cubic

6. An example for Frenkel defect is
(a) NaCl   (b) AgBr   (c) CsCl   (d) FeS

7. Semiconductors which exhibit conductivity due to the flow of excess negative electrons are called

(a) Super conductors   (b) n-type semiconductors
(c) p-type semiconductors   (d) Insulators

8. In the Bragg's equation for diffraction of X-rays,'n' represents

(a) The number of moles   (b) Avogadro number
(c) A quantum number   (d) Order of reflection

9. The number of close neighbours in a body centred cubic lattice of identical spheres is

(a) 6   (b) 4   (c) 12   (d) 8

10. The crystals which are good conductors of electricity and heat are

(a) Ionic crystals   (b) Molecular crystals
(c) Metallic crystals   (d) Covalent crystals

11. In a simple cubic cell, each point on a corner is shared by

(a) One unit cell   (b) Two unit cell   (c) 8 unit cell   (d) 4 unit cell

12. The ability of certain ultra cold substances to conduct electricity without resistance is called

(a) Semiconductor   (b) Conductor   (c) Superconductor   (d) Insulator

13. The total number of atoms per unit cell is bcc is

(a) 1   (b) 2   (c) 3   (d) 4

14. Rutile is

(a) TiO_2 (b) Cu_2O (c) MoS_2 (d) Ru

15. Semiconductors are used as

(a) rectifiers   (b) transistors   (c) solar cells   (d) all the above

16. An example of metal deficiency defect

    (a) NaCl   (b) AgCl   (c) CsCl   (d) FeS

B. Answer in one or two sentences

17. Define the terms; space lattice and unit cell.

18. State Bragg's law.

19. What are superconductors?

20. Sketch the (a) simple cubic (b) face-centred cubic and (c) body centred cubic lattices.

21. How crystals are classified?

22. Give example for molecular and ionic crystals.

23. What is a vitreous state?

24. Give two example for AB and AB_2 type ionic crystals.

25. What is imperfection in solids?

26. What is coordination number?

27. Write a note on the assignment of atoms per unit cell in fcc.

28. Write a short note on metallic crystals.

29. How are glasses formed?

C. Answer not exceeding 60 words

30. What is Bragg's equation? Give its significance.

31. Write the properties of ionic crystals.

32. Explain Schottky and Frenkel defects.

33. What is super conductivity? Give its uses.

34. Explain AB and AB_2 type ionic crystals with one example for each.

35. How Bragg's equation is used for determining crystal structure.

36. Explain Bragg's spectrometer method.

37. Explain the nature of glass.

Summary

The study of crystals by X-rays are discussed.Types of ionic crystals AB and AB_2 type are explained with examples. An elementary idea about imperfections in solids. The properties of ionic crystals and nature and properties of glasses are discussed. Bragg's equation and its significance are discussed.

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9. THERMODYNAMICS II

Learning Objectives

- ❧ *To review first law of thermodynamics and to know its limitations.*

- ❧ *To learn the definition of second law of thermodynamics and the mathematical statements.*

- ❧ *To study the differences of spontaneous and non spontaneous reactions with examples. Also to learn the mathematical representation of entropy 'S'.*

- ❧ *To learn about Gibbs free energy change and to know the relation $\Delta G = \Delta H - T\Delta S$.*

- ❧ *To study the significance of ΔG*

9.1 LIMITATIONS OF FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics tells us that energy can be changed from one form to another but can be neither created nor destroyed in any process. The mathematical expression which is used to represent the first law of thermodynamics is $\Delta E = q-w$, where ΔE refers to the internal energy change of the system when 'w' amount of work is done by the system when it absorbs 'q' amount of heat and carries out 'w' amount of work. However, this law possesses many limitations such as given below.

1. The first law of thermodynamics merely indicates that in any process there is a transformation between the various forms of energy involved in the process but provides no information regarding the feasibility of such transformation.

2. First law does not provide any information regarding the direction a processes will take whether it is a spontaneous or a non spontaneous process.

9.2 SECOND LAW OF THERMODYNAMICS

Second law of thermodynamics can be stated in many ways:

i) "It is impossible to construct an engine which operated in a complete cycle will absorb heat from a single body and convert it completely to work without leaving some changes in the working system".

This is called as the Kelvin – Planck statement of II law of thermodynamics.

ii) "It is impossible to transfer heat from a cold body to a hot body by a machine without doing some work".

This is called as the clausius statement of II law of thermodynamics.

iii) 'A process accompanied by increase in entropy tends to be spontaneous". This statement is called as the entropy statement of II law of thermodynamics. Entropy is a measure of randomness or disorder of the molecules of a system and it is a thermodynamic state function. A system always spontaneously changes from ordered to a disordered state. Therefore entropy of a spontaneous process is constantly increasing.

iv) "Efficiency of a machine can never be cent percent".

v) The heat Efficiency of any machine is given by the value of ratio of output to input energies. Output can be in the form of any measurable energy or temperature change while input can be in the form of heat energy or fuel amount which can be converted to heat energy.

thus % efficiency $= \dfrac{\text{output}}{\text{input}} \times 100$

The machine can be a heat engine also. Consider a heat engine which has an initial temperature T_1 and final temperature as T_2, then if $T_1 > T_2$ then when some amount of heat is being converted into work, T_2 is the lowered temperature.

The efficiency 'η' is given by,

$$\text{\% efficiency} = \left(\frac{T_1 - T_2}{T_1}\right) \times 100$$

According to II law of thermodynamics it is impossible to have a machine or heat engine which converts the input energy completely into output energy or output work without any amount of heat or energy being absorbed by the machine.

Hence, % efficiency can never be achieved as cent percent.

$$\therefore \text{\% efficiency} = \left(1 - \frac{T_2}{T_1}\right) \times 100$$

By II law, $T_2 < T_1$ % efficiency less than 100.

9.3 ENTROPY AND ENTROPY CHANGE

The entropy function 'S' introduced in the second law of thermodynamics is explained as below.

Entropy function 'S' represents the ratio of the heat involved (q) to the temperature (T) of the process. That is $S = \dfrac{q}{T}$. This relation is valid only for reversible processes. If a system is changed from state 1 to state 2 at constant temperature and if δq_{rev} is the heat involved in the process, then entropy change of the process (ΔS) is given by,

$$S_2 - S_1 = \Delta S \quad = = \int_1^2 \frac{\delta q_{rev}}{T}$$

where the process is a reversible one. Entropy (S) and the change in entropy of

the process (ΔS) are each state functions even though q and δq path functions. In a reversible process, entropy of universe remains a constant.

$$S_{universe} = S_{system} + S_{surroundings} = Constant$$

Entropy change (ΔS) can be derived for various thermodynamic processes as below:

Isothermal process (T = constant)

$$\Delta S = \frac{1}{T}\int_1^2 \delta q_{rev} = \frac{q_2 - q_1}{T}$$

Isothermal and isobaric process (T and P = Constant)

$$\Delta S = \frac{1}{T}\int_1^2 \delta q_{p,rev}$$

Isothermal, and isochoric process (T and V - Constant)

$$\Delta S = \frac{1}{T}\int_1^2 \delta q_{v,rev}$$

The term 'natural process means that the process is spontaneous and does not need to be induced. In order to find out whether a process is spontaneous or not, the entropy changes of the system and the surroundings for the stipulated process is considered. If this change is positive i.e. if the entropy of the universe increases, the process will take place spontaneously and irreversibly.

If the entropy change of the universe is zero or negative ($\Delta S < 0$) the system will behave as non spontaneous.

When the external pressure is less than the internal pressure of a gaseous system, the gas expands spontaneously. When volume increases in expansion, the disorder in the movement of gaseous molecules increases. Thus, spontaneous processes are associated with increase in disorder. When disorder in a process is favoured it occurs spontaneously and we say, the entropy change is positive. Entropy is a measure of microscopic disorder in the system and also represents spontaneity.

For a reversible process,

$$\Delta S_{system} = - \Delta S_{surroundings}$$

$$\therefore \Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = 0.$$

For an irreversible (spontaneous) process.

$$\Delta S_{univ} > 0 \text{ (positive value)}$$

Entopy change in a physical (phase) transformation can be determined particularly for evaporation of liquids at the boiling points, using Trouton's rule. According to this rule, the heat of vaporisation (ΔH_{vap}) in calories per mole divided by the boiling point of the liquid in Kelvin is a constant equal to 21 cal deg^{-1} mole^{-1} and is known as the entropy of vapourisaiton.

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} = 21 \text{cal.deg}^{-1}.\text{mole}^{-1}$$

ΔH_{vap} = Enthalpy change of vapourisation = Latent heat of vapourisation. This equation is useful for estimating the molar heat of vaporization of a liquid of known boiling point. Substances that deviate from this rule are as follows:

i)   Low boiling liquids such as hydrogen and Helium which boil only a little above 0K.

ii) Polar substances like water, alcohol which form hydrogen bonded liquids and exhibit very high boiling points as well as high ΔH_{vap}.

iii) Liquids such as acetic acid whose molecules are partially associated in the vapor phase and possess very low entropy vaporization which is very much less than 21 cals/ mol/deg.

Those liquids that obey Troutons rule are said to behave ideally.

Example 1

The normal boiling point CCl_4, $CHCl_3$ and H_2S are 76.7°C, 61.5°C and –59.6°C respectively. Calculate the molar heat of vapourisation of each liquid, assuming ideal behaviour.

Since the liquids behave ideally, Trouton's rule is obeyed.

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b^4} = 21 \text{cal.deg}^{-1}.\text{mole}^{-1}$$

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$$\therefore \Delta H_{vap} \text{ of } CCl_4 \quad = (21 \text{ cal. mole}^{-1}. \text{ deg}^{-1} \times 4.184 J)\ (273 + 76.7)K$$
$$= 30.71 \text{ kJ mol.}^{-1}$$

$$\Delta H_{vap} \text{ of } CHCl_3 \quad = (21 \text{ cal. mole}^{-1}. \text{deg}^{-1} \times 4.184\ J)\ (273 + 61.5)K$$
$$= 29.376 \text{ kJ mol}^{-1}$$

$$\Delta H_{vap} \text{ of } H_2S \quad = (21 \text{ cal mol}^{-1}. \text{deg}^{-1} \times 4.184\ J) \times (273 - 59.6)K$$
$$= 18.74 \text{ kJ.mol}^{-1}$$

Characteristics of entropy 'S'

i) The term 'S' entropy is evolved from the formulation of II law of thermodynamics as a thermodynamic state function.

ii) Entropy change 'ΔS' of a system under a process is defined as the constant equal to the ratio of the heat change accompanying a process at constant temperature to the temperature of the system under process. The process should be reversible at that temperature.

$$\Delta S_{rev} = \frac{\Delta q_{rev}}{T(K)}$$

Heat, q is not a state function, But for a reversible process $\Delta q = (q_2 - q_1)$ divided by temperature (T) of the process is a state function.

iii) A spontaneous process is accompanied by increase in the 'disorder' (or) 'randomness' of the molecules constituting the system. Entropy increases in all spontaneous processes. Hence entropy may be regarded as a measure of disorder (or) randomness of the molecules of the system.

iv) When a system undergoes a physical (or) a chemical process, there occurs a change in the entropy of the system and also in its surroundings. This total change in the entropy of the system and its surroundings is termed as the entropy change of the universe brought about by the process. For an isothermal process (T=constant), the entropy change of the universe during a reversible process is Zero.

The entropy of the universe increases in an irreversible process.

v) The energy of the universe remains constant although the entropy of the universe tends to a maximum.

vi)   For a spontaneous process, at constant T, ΔS is positive ($\Delta S > 0$).

    ΔS is positive ($\Delta S > 0$).   For an equilibrium process, ΔS is zero.

    For a non spontaneous process,

    ΔS is negative or ($\Delta S < 0$).

vii)   **Units of entropy:** The dimension of entropy are energy in terms of heat X temperature^{-1}. The entropy is expressed as calories per degree which is referred to as the entropy units (eu). Since entropy also depends on the quantity of the substance, unit of entropy is calories per degree per mole (or) eu. per mole.

    cgs units of entropy is cal.K^{-1} denoted as eu. The SI unit is JK^{-1} and denoted EU. 1 eu = 4.184 EU.

viii)   Entropy change is related to enthalpy change as follows:

    For a reversible and isothermal process,

    $\Delta S = \dfrac{\Delta q_{rev}}{T}$. Since ΔH is the heat absorbed (or) evolved in the process at constant T and pressure P. ΔS is also calculated from ΔH as $\Delta S = \dfrac{\Delta H}{T}$ where T is the temperature of the process involving ΔH, amount of enthalpy change, at constant pressure.

Example 2

    Calculate the entropy change involved in the conversion of 1 mole of ice at $0^{o}C$ and 1 atm to liquid at $0^{o}C$ and 1 atm. The enthalpy of fusion per mole of ice is 6008 J mol^{-1}.

$$H_2O \ (s) \xrightarrow{\ 0^{o}C\ } H_2O \ (l)$$

Ice   273 K   Water liquid
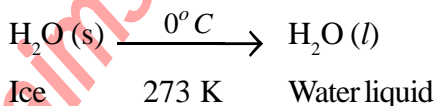
$$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{Tm(K)} = \frac{6008 \ J.mol^{-1}}{(0+273) \ K}$$

$$\therefore \Delta S_{fusion} = 22.007 \ J \ mol^{-1} \ K^{-1}.$$

Example 3
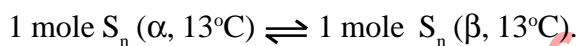
Calculate the change of entropy for the process, water (liq) to water (vapor, 373K) involving $\Delta H_{vap} = 40850$ J mol^{-1} at 373K.

$$\Delta S_{vap} \;=\; \frac{\Delta H_{vab}}{Tb\,(K)} = \frac{40850\,J/mol}{373K} = 109.517 \,J.K.^{-1}mol^{-1}$$

$$\Delta S_{vap} \;=\; 109.52 \text{ J mole}^{-1} \text{ K}^{-1}$$

Example 4

Evaluate the entropy change for the following process possessing ΔH transition $= 2090$ J.mol^{-1}

1 mole S_n (α, 13°C) $\rightleftharpoons$ 1 mole S_n (β, 13°C).

$$T_{transition} = 13+273 = 286 \text{ K.}$$

$$\Delta S_{trans} = \frac{\Delta H_{trans}}{T_{trans}\,(K)} = \frac{2090\,J.mol^{-1}}{286\,K}$$

$$\Delta S_{trans} = 7.307 \text{ J.K}^{-1} \text{ mol.}^{-1}$$

Example 5

When does entropy increase in a process?.

a)   In a chemical reaction, when number of molecules of products are more than the number of molecules of reactant entropy increases.

b)   In physical process, when a solid changes to liquid, when a liquid changes to vapour and when a solid changes to vapour, entropy increase in all these processes.

Example 6

Calculate the entropy changes in the system, and in the surroundings and the total entropy change in the universe when during a process 75 J of heat flow out of the system at 55°C to the surroundings at 20°C.

$$T_{system} \;=\; 273+55 = 328 \text{ K.}$$

$$T_{surroundings} \;=\; 20+273 = 293 \text{ K.}$$

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$$\Delta S_{univ} = \Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

$$\Delta S_{system} = \frac{q_{system}}{T_{system}} = \frac{-75J}{328K} = -0.2287 Jk^{-1}$$

$$\Delta S_{Surroundings} = \frac{q_{surroundings}}{T_{surroundings}} = \frac{+75J}{293K} = +0.260\ JK^{-1}$$

$$\therefore \Delta S_{univ} = \Delta S_{total} = (-0.2287 + 0.26)$$
$$= +0.0313\ JK^{-1}$$

Example 7

1 mole of an ideal gas maintained at 4.1 atm and at a certain temperature absorbs 3710J heat and expands to 2 litres. Calculate the entropy change in expansion process.

For 1 mole of an ideal gas,

$$PV = RT, \qquad P = 4.1\ atm \qquad V = 2\ lit$$

$$\therefore\ Temperature = \frac{4.1\,atm \times 2lit \times 1\,mole}{0.082\,lit\,atm\,K^{-1}\,mol^{-1}} = 100\ K.$$

$$\Delta S = \frac{q}{T} = \frac{3710\ J}{100\ K} = 37.1\ J\ K^{-1}mol^{-1.}$$

ΔS of expansion = 37.1 J K^{-1}mol$^{-1.}$

Standard Entropy

The absolute entropy of a pure substance at 25°C (298 K) and 1 atm pressure is called the standard entropy, S°. The standard entropies of all substances either elements or compounds at any temperature above 0°K always have positive values.

When the standard entropies, S° of various substances are known, the standard entropy change of a chemical process or reaction is written as

$$\Delta S° = \Sigma S°_{products} - \Sigma S°_{reactants}$$

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This ΔS° is the standard entropy change of the reaction.

Standard entropy change of formation, $\Delta S°_f$ is defined as the entropy of formation of 1 mole of compound from the elements present in the standard conditions. $\Delta S°_f$ can be calculated for chemical compounds using the $S°$ values of elements from which the compound is formed.

$$\Delta S°_{f\ compound} = \Sigma S°_{compound} - \Sigma S°_{elements}$$

Example 8

Calculate the standard entropy of formation $\Delta S°_f$ of $CO_2(g)$. Given the standard entropies of $CO_2(g)$, $C(s)$, $O_2(g)$ as 213.6, 5.740 and 205.0 JK^{-1} respectively.

$$\begin{aligned}
\Delta S°_{f\ compound} &= \Sigma S°_{compound} - \Sigma S°_{elements} \\
&= S°CO_2(g) - [S°_{C_{(s)}} + S°O_2(g)]\ JK^{-1} \\
&= 213.6 - 5.74 - 205.0 \\
\Delta S°_{f, CO_2(g)} &= 2.86\ JK^{-1}
\end{aligned}$$

When standard entropy of formation of compounds are known, the standard entropy change for a stoichiometrically balanced chemical reaction can be written as,

$$\Delta S°_{reaction} = \Sigma \Delta S°_{f\ products} - \Sigma \Delta S°_{f\ reactants}$$

Example 9

Urea hydrolysis in presence of water to produce ammonia and carbondioxide. The standard entropies of reactants and products are given, for urea, $H_2O(l)$, $CO_2(g)$, $NH_3(g)$ are 41.55, 16.72, 51.06 and 46.01 cals. mol^{-1}. K^{-1} respectively. What is the standard entropy change for this reaction. Predict the spontaneity of the reaction.

$$\Delta S°_{reaction} = \Sigma S°_{(product)} - \Sigma S°_{(reactants)}$$

The reaction is,

$$CO(NH_2)_{2(aq)} + H_2O_{(l)} \rightarrow CO_{2(g)} + 2NH_{3(g)}$$
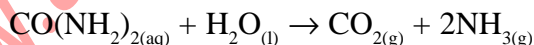
$$\begin{aligned}
\Delta S°_{reaction} &= (S°_{CO_2(g)} + 2S°NH_{3(g)}) - (S°_{urea(aq)} + S°_{H2O(l)}) \\
&= (51.06 + 2 \times 46.01 - 41.55 - 16.72)\ cal.K^{-1} \\
&= 84.81\ cal.\ K^{-1}.
\end{aligned}$$

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$\Delta S^{\circ}_{reaction}$ is a positive value. that is $\Delta S^{\circ}_{reaction}$ increases. Hence urea hydrolysis in water is a spontaneous reaction.

9.4 Gibbs free energy 'G'

According to II law of thermodynamics, inorder to predict the spontaneity of a process entropy of universe is considered. $\Delta S_{universe}$ is the sum of ΔS_{system} and $\Delta S_{surroundings}$. It is difficult to determine $\Delta S_{surroundings}$ in most of the physical and chemical processes. Therefore a thermodynamic function which reformulates the spontaneity criterion considering only the system under study is required.

For this purpose, "a free energy function" has been introduced by II law of thermodynamics. The free energy function, called the Gibbs free energy function, denoted by the symbol 'G' is mathematically defined as,

$$G = H - TS$$

where H = enthalpy or heat content of the system, T = Temperature in Kelvin and S = entropy

This expression is valid for constant temperature and pressure processes. In an isothermal process, if ΔH and ΔS are the changes in enthalpy and entropy of the system, then free energy change ΔG is given by,

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

If 1 and 2 refer to the initial and final states of the system during the isothermal process, then

$$\Delta G = (G_2 - G_1) = (H_2 - H_1) - T(S_2 - S_1)$$

from I law of thermodynamics

$$\Delta H = \Delta E + P\Delta V$$

Therefore $\Delta G = \Delta E + P\Delta V - T\Delta S$.

For a spontaneous process, the enthalpy change at constant pressure will be negative. This is because in an exothermic process, the enthalpy of the final state (H_2) is lower than the enthalpy of the initial state (H_1) so that ($H_2 - H_1$) is negative and the process take place spontaneously to attain the lower enthalpy state. Similarly, the entropy change (ΔS) increases in a spontaneous process since entropy of the final state S_2 will be greater than the initial state S_1 so that ($S_2 - S_1$) = ΔS, is positive. Combining negative ΔH and positive ΔS, in the

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expression for free energy change ΔG, at constant temperature, the overall magnitude of ΔG becomes negative for a spontaneous process. Here, ΔH and ΔS terms refer only to the system.

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

Hence, criterion for the prediction of feasibility of a reaction (or) the prediction of thermodynamic spontaneity of a process based on the free energy change (ΔG) of the process is given as : when at constant temperature and pressure of the system, if,

ΔG < 0,   ΔG is –ve, the process is spontaneous and feasible

i.e.   ΔG = 0,   the process is in equilibrium

i.e.   ΔG < 0,   ΔG is +ve, the process is non spontaneous and non feasible.

In chemical thermodynamics, spontaneous processes are also known as irreversible (or) feasible processes while non spontaneous processes are known as non feasible processes since time factor of the process is not considered here.

All reversible processes are considered as equilibrium processes.

Thermodynamic conditions for spontaneity and equilibrium		
Spontaneous (irreversible) at constant P and T	Equilibrium (reversible)	Non spontaneous (nonfeasible)
ΔG < 0 ΔH < 0 ΔS > 0	ΔG = 0 ΔH = 0 ΔS = 0	ΔG > 0 ΔH > 0 ΔS < 0

Characteristics of Free energy 'G'

i)   G is defined as (H-TS) where H and S are the enthalpy and entropy of the system respectively. T = temperature. Since H and S are state functions, G is a state function.

ii)   G is an extensive property while $\Delta G = (G_2 - G_1)$ which is the free energy change between the initial (1) and final (2) states of the system becomes the intensive property when mass remains constant between initial and final states (or) when the system is a closed system.

iii)   G has a single value for the thermodynamic state of the system.

iv)   G and ΔG values correspond to the system only. There are three cases of ΔG in predicting the nature of the process. When, $\Delta G < 0$ (negative), the process is spontaneous and feasible; $\Delta G = 0$. The process is in equilibrium and $\Delta G > 0$ (positive), the process is nonspontaneous and not feasible.

v) $\Delta G = \Delta H - T\Delta S$. But according to I law of thermodynamics, $\Delta H = \Delta E + P\Delta V$ and $\Delta E = q - w$.

$\therefore \quad \Delta G = q - w + P\Delta V - T\Delta S$

But $\Delta S = \dfrac{q}{T}$ and $T\Delta S = q = $ heat involved in the process.

$\therefore \quad \Delta G = q - w + P\Delta V - q = -w + P\Delta V$

(or) $-\Delta G = w - P\Delta V = $ network.

The decrease in free energy $-\Delta G$, accompanying a process taking place at constant temperature and pressure is equal to the maximum obtainable work from the system other than work of expansion.

This quantity is called as the "net work" of the system and it is equal to $(w - P\Delta V)$.

$\therefore \quad$ Net work $= -\Delta G = w - P\Delta V$.

$-\Delta G$ represents all others forms of work obtainable from the system such as electrical, chemical or surface work etc other than P-V work.

Standard free energy ($G°$)

Like standard enthalpy of formation of substances, standard enthalpy change of a reaction, standard free energy of formation of substances and standard free energy change of reactions are considered. The standard free energy value ($G°$) of all substances either elements or compounds may be calculated from $H°$ and $S°$ values at standard conditions of temperature (298 K) and pressure (1 atm) and the substance being present in the standard state.

i.e $\qquad G° = H° - TS°$

Standard free energies of formation of elements are taken as zero. Hence, standard free energy change of a reaction which is stoichiometrically balanced, is

equal to the difference between the total sum of the standard free energies of products and the total sum of the standard free energies of reactants, at standard conditions.

$$\Delta G^\circ_{reaction} = \Sigma G^\circ_{product} - \Sigma G^\circ_{reactants}$$

$\Delta G^\circ_{reaction}$ can also be calculated from $\Delta H^\circ_{reaction}$ and $\Delta S^\circ_{reaction}$ values. $\Delta H^\circ_{reaction}$ and $\Delta S^\circ_{reaction}$ can be calculated from H°_f and S° values of respective product and reactant molecules at the constant temperature and pressure.

Example 10

For a chemical reaction the values of ΔH and ΔS at 300 K are –10 k cal mol^{-1} and 20 cal. deg^{-1} mol^{-1} respectively. What is the value of ΔG of the reaction? Calculate the ΔG of reaction at 400 K assuming ΔH and ΔS values are constant. Predict the nature of the reaction.
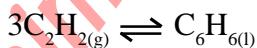
$$\Delta G = \Delta H - T\Delta S$$

at 300 K; ΔG = –10,000 – 20 × 300
= –16,000 cals. mole^{-1}

at 400 K; ΔG = –10,000 – 20 × 400
= –18,000 cals. mole^{-1}

At 300 K and 400 K, the values of ΔG reaction are negative (<0). Therefore the reaction is spontaneous (feasible) at both temperatures.

Example 11

ΔH° for the reaction $3C_2H_{2(g)} \rightleftharpoons C_6H_{6(l)}$ is -631 kJ. mol^{-1} at 25°C. Calculate ΔG° reaction and predict the direction in which the reaction is spontaneous at 1 atm pressure. Given $S^\circ C_2H_2 = 200.8$ JK^{-1}mol^{-1} and $S^\circ C_6H_6 = 172.8$ JK^{-1} mol^{-1}.

$$3C_2H_{2(g)} \rightleftharpoons C_6H_{6(l)}$$

$$\Delta S^\circ = \Sigma S^\circ_{products} - \Sigma S^\circ_{reactants}$$

$$= S^\circ_{C_6H_{6(l)}} - 3 \times S^\circ_{C_2H_2}$$

$$= 172.8 - 3 \times 200.8 = -429.8 \text{ JK}^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ; \quad T = 298°K$$

$$\Delta H^\circ = -631 \text{ KJ. mol}^{-1}$$

$\therefore \Delta G = -631000 + (298 \times 429.8)$

$\qquad = -502.979$ kJ.

Since $\Delta G°$ is a –ve value, the reaction is spontaneous.

Example 12

Show that the reaction $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$ at 300 K is spontaneous and exothermic, where the standard entropy change is -0.094 kJ $mol^{-1}K^{-1}$. The standard Gibbs free energies of formation for CO_2 and CO are -394.4 and -137.2 kJ.mol^{-1} respectively.

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \quad \rightarrow \quad CO_{2(g)}$$

$\Delta G°_{reaction} = \Sigma G°_{f\ products} - \Sigma G°_{f\ reactants}$

$\qquad = G°_{fCO_2} - G°_{fCO} - \frac{1}{2}G°_{f}O_2$

$\qquad = -394.4 + 137.2 - 0$

$\qquad = -257.2$ kJ mol^{-1}

$\Delta G°_{reaction} = -257.2 = \Delta H°_{reaction} - 300 \times \Delta S°_{reaction}$

$\therefore \Delta H°_{reaction} = -257.2 - 300\ (-0.094)$

$\quad \Delta H°_{reaction} = -285.4$ kJ. mol^{-1}

$\Delta G°_{reaction}$ has –ve value. Therefore the reaction is spontaneous.

Also $\Delta H°_{reaction}$ has –ve value. Therefore the reaction is exothermic.

SELF EVALUATION

A. Choose the correct answer

1. The amount of heat exchanged with the surrounding at constant temperature and pressure is called

   a) ΔE b) ΔH c) ΔS d) ΔG

2. All the naturally occuring processes proceed spontaneously in a direction which leads to

   a) decrease of entropy   b) increase in enthalpy

   c) increase in free energy   d) decrease of free energy

3. In an adiabatic process which of the following is true?

   a) $q = w$ b) $q = 0$ c) $\Delta E = q$ d) $P\Delta V = 0$

4. When a liquid boils, there is

   a) an increase in entropy   b) a decrease in entropy
   c) an increase in heat of vapourisation   d) an increase in free energy

5. If ΔG for a reaction is negative, the change is

   a)   Spontaneous   b)   Non-spontaneous
   c)   Reversible   d)   Equilibrium

6. Which of the following does not result in an increase in the entropy?

   a) crystallisation of sucrose from solution   b) rusting of iron
   c) conversion of ice to water   d) vaporisation of camphor

7. In which of the following process, the process is always non-feasible?

   a) $\Delta H > 0, \Delta S > 0$ b) $\Delta H < 0, \Delta S > 0$
   c) $\Delta H > 0, \Delta S < 0$ d) $\Delta H < 0, \Delta S < 0$

8. Change in Gibb's free energy is given by

   a) $\Delta G = \Delta H + T\Delta S$ a) $\Delta G = \Delta H - T\Delta S$
   c) $\Delta G = \Delta H \times T\Delta S$ d)   None of the above

9. For the reaction $2Cl_{(g)} \rightarrow Cl_{2(g)}$, the signs of ΔH and ΔS respectively are

   a) $+, -$ b) $+, +$ c) $-, -$ d) $-, +$

B. Answer in one or two sentences

10. What is entropy? What are the units of entropy?

11. Predict the feasibility of a reaction when

    i) both ΔH and ΔS increase
    ii) both ΔH and ΔS decrease
    iii) ΔH decreases but ΔS increases

12. What is Gibb's free energy?

13. Give Kelvin statement of second law of thermodynamics.

14. How ΔG is related to ΔH and ΔS? What is the meaning of $\Delta G = 0$?

15. Mention the essential condition for spontaneity in a chemical reaction.

C. Answer not exceeding 60 words

16. State the various statements of second law of thermodynamics.

17. What are spontaneous reactions? What are the conditions for the spontaneity of a process?

Exercises

18. Calculate the maximum efficiency % possible from a thermal engine operating between 110°C and 25°C. **[Ans : 22.2%]**

19. What is the entropy change of an engine that operates at 100°C when 453.6 k.cal of heat is supplied to it? **[Ans : ΔS= 1216.1 cals K^{-1}]**

20. Calculate the entropy increase in the evaporation of 1 mole of a liquid when it boils at 100°C having heat of vaporisation at 100°C as 540 cals\gm.

    [Ans : ΔS = 26.06 cal K^{-1} mol^{-1}]

21. In the reaction $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$, $\Delta H°$ reaction is + 179.9 kJmol^{-1} and $\Delta S°_{reaction} = 66.09$ JK^{-1}mol^{-1}. calculate $\Delta G°$ reaction at 300K.

    [Ans : $\Delta G°_r$ = 160.07 kJ. mol^{-1}]

22. Calculate the standard free energy change ($\Delta G°$) of the following reaction and say whether it is feasible at 373 K or not $\frac{1}{2}H_{2(g)} + \frac{1}{2}I_{2(g)} \rightarrow HI_{(g)}$; $\Delta H°_r$ is +25.95 kJ mole^{-1}. Standard entropies of $HI_{(g)}$, $H_{2(g)}$ and $I_{2(g)}$ are 206.3, 130.6 and 116.7 JK^{-1} mole^{-1}. **[Ans : Spontaneous]**

23. Calculate standard free energy of formation of $H_2O_{(l)}$. The standard enthalpy of formation of $H_2O_{(l)}$ is 285.85 kJ and standard entropies of $H_{2(g)}$, $O_{2(g)}$ and $H_2O_{(l)}$ are 130.5, 205.0 and 70.3 J.K^{-1} mole^{-1} respectively.

    [Ans : -237.36 kJ mole^{-1}]

24. In the reaction $\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightarrow NH_{3(g)}$. The standard entropies of $N_{2(g)}$, $H_{2(g)}$ and $NH_{3(g)}$ are 191.6, 130.5 and 192.5 JK^{-1} mol^{-1} respectively. If free energy change of the reaction is –16.67 kJ. Calculate the $\Delta H°_{reaction}$ for the formation of NH_3 at 298K. **[Ans : – 46.19 kJ]**

25. Predict whether the reaction $CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)}$ is spontaneous or not. The standard free energies of formation of $CO_{(g)}$, $H_2O_{(g)}$ and $CO_{2(g)}$ are -137.27, -228.6 and -394.38 kJ mole^{-1} respectively.

[**Ans** : $\Delta G^\circ_r = -28.51$ kJ]

26. Calculate the standard free energy change of the reaction : $4NH_{3(g)} + 5O_2 \rightarrow 4NO_{(g)} + 6H_2O_{(l)}$ and predict on the feasibility of the reaction. Standard free energies of formation of $NH_{3(g)}$, $NO_{(g)}$ and $H_2O_{(l)}$ are 16.65, 86.61, -237.20 kJ. mole^{-1} respectively.

[**Ans** : -1010.02 kJ mole^{-1}]

27. The standard heat of formation of $H_2O_{(l)}$ from its elements is -285.83 kJ. mole^{-1} and the standard entropy change for the same reaction is -327 JK^{-1} at 25°C. Will the reaction be spontaneous at 25°C?

[**Ans** : $\Delta G^\circ_r = -ve$; spontaneous]

28. The boiling point of benzene at 1 atm is 80.2°C. Calculate the enthalpy of vaporisation of benzene at its b. pt.   [**Ans** : 30.022 kJ.mol^{-1}]

29. The standard entropy change ΔS°_r for

$$CH_{4(g)} + 2O_{2(g)} \quad \rightarrow \quad CO_{2(g)} + 2H_2O_{(l)}$$
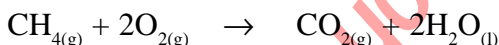
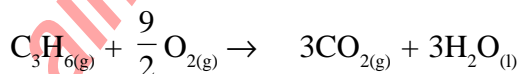is -242.98 JK^{-1} at 25°C. Calculate the standard reaction enthalpy for the above reaction if standard Gibbs energy of formation of $CH_{4(g)}$, $CO_{2(g)}$ and $H_2O_{(l)}$ are -50.72, -394.36 and - 237.13 kJ mol^{-1} respectively.

[**Ans** : $\Delta H^\circ_r = -890.31$ kJ.mol^{-1}]

30. Standard enthalpy change for combustion of methane is -890 kJ mol^{-1} and standard entropy change for the same combustive reaction is -242.98 J.K^{-1} at 25°C. Calculate ΔG° of the reaction.   [**Ans** : 817.6 kJ mole^{-1}]

31. The standard entropy change for the reaction

$$C_3H_{6(g)} + \frac{9}{2} O_{2(g)} \rightarrow \quad 3CO_{2(g)} + 3H_2O_{(l)}$$

is -339.23 JK^{-1} at 25°C. Calculate the standard reaction enthalpy change if the standard Gibbs energy of formation of $C_3H_{6(g)}$, $CO_{2(g)}$ and $H_2O_{(l)}$ are 62.78, -394.36 and -237.13 kJ.mol^{-1} respectively.

[**Ans** : -2058.2 kJ mole^{-1}]

Summary

* I law of thermodynamics possesses limitations on the directional, spontaneity and probability of occurrence characteristics of a process.

* II law of thermodynamics can be stated in many ways. Entropy function 'S' is a state function defined as q_{rev}/T. For a process with ΔS equals to positive (or) zero (or) negative value becomes spontaneous (or) equilibrium (or) non spontaneous respectively. Trouton rule is $\Delta S_{vap} = \dfrac{\Delta H_{vap}}{T_b}$.

$$\Delta S^{\circ}_{reaction} = \Sigma S^{\circ}_{products} - \Sigma S^{\circ}_{reactants}$$

* Entropy S, is a measure of 'randomness' or disorder of the process. S refers to spontaneity of a process.

* Gibbs free energy function $G = H - TS$ is a state function and for a system at constant T, the free energy change $\Delta G = \Delta H - T\Delta S$. ΔG value is characteristic of a system and feasibility of process can be predicted as follows : At constant temperature, if ΔG is > 0 (or $= 0$ or < 0 then the process becomes nonspontaneous (or a equilibrium (or) spontaneous process.

References

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2) Physical Chemistry by P.W.Alkins Oxford University Press.

10. CHEMICAL EQUILIBRIUM - II

Learning Objectives

❧ *To study the applications of law of mass action for equilibrium reactions with gaseous phase reactants and products.*

❧ *To relate K_p and K_c as $K_p = K_c (RT)^{\Delta n_g}$ and to study the equilibria with $\Delta n_g = 0$, +ve and -ve.*

❧ *To learn the statement of Le Chatlier's principle.*

❧ *To learn to apply Le Chatlier's principle to Haber's process and Contact process.*

10.1 ATTAINMENT OF EQUILIBRIUM IN CHEMICAL REACTIONS

A chemical reaction in equilibrium involves the opposing reactions. One of the reactions produces the products and is known as the forward reaction while the other produces the reactants from products and is known as the reverse reaction. Chemical equilibrium is dynamic in nature. At equilibrium, reactant and product molecules are both present in the reaction mixture in definite amounts. The equilibrium concentrations of the reactants and products do not change under constant temperature, pressure and catalysts etc.

Consider a general equilibrium reaction at constant temperature represented by

$$aA + bB \underset{k_r}{\overset{k_f}{\rightleftharpoons}} cC + dD$$
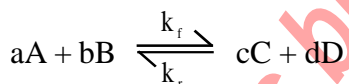
According to law of mass action, the rate of forward reaction is

$$R_f = k_f [A]^a [B]^b$$

and the rate of reverse reaction is

$$R_r = k_r [C]^c [D]^d$$

where k_f and k_r are the rate constants of the forward and reverse reactions respectively.

At equilibrium $R_f = R_r$

$$\therefore k_f [A]^a [B]^b = k_r [C]^c [D]^d$$

$$\frac{k_f}{k_r} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$\frac{k_f}{k_r} = K_c = \text{equilibrium constant}$$

$$\therefore K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

This equation of K_c is also known as equilibrium law equation. K_c is the equilibrium constant expressed in terms of molar concentrations of reactants and

products. For reactions involving gaseous reactants or products or both, it is more convenient to use partial pressures instead of molar concentrations. Thus K_c in equilibrium law equation becomes K_p which is the equilibrium constant expressed in terms of partial pressure.

10.1.1 Relationship between K_p and K_c

Consider a general chemical equilibrium reaction in which the reactants and products are in gaseous phases,
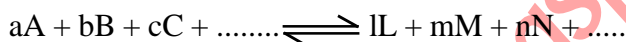
$$aA + bB + cC + ... \rightleftharpoons lL + mM + nN + ...$$

then

$$K_p = \frac{p_L^l p_M^m p_N^n .....}{p_A^a p_B^b p_C^e ......}$$

where p is the partial pressure of the respectivée gases. In terms of molar concentrations of reactants and products

$$K_c = \frac{[L]^l [M]^M [N]^n ....}{[A]^a [B]^b [C]^c ......}$$

For any gaseous component 'i' in a mixture, its partial pressure 'p_i' is related to its molar concentration 'C_i' as

$$C_i = \frac{p_i}{RT} \quad \text{since} \quad p_i = \frac{n_i}{V} RT$$

where $\dfrac{n_i}{V} = C_i$ = number of moles of i per litre. V = volume in litres.

Substituting, concentration terms by partial pressures,

$$K_c = \frac{(p_L/RT)^l (p_M/RT)^m (p_N/RT)^n ...}{(p_A/RT)^a (p_B/RT)^b (p_C/RT)^c ...}$$

$$= \frac{p_L^l p_M^m p_N^n .....}{p_A^a p_B^b p_C^e ......} \left(\frac{1}{RT} \right)^{(l+m+n+....)-(a+b+c+...)}$$

$$= \frac{K_p}{(RT)^{\Delta n_g}} \text{ and } \quad \therefore K_p = K_c(RT)^{\Delta n_g}$$

where Δn_g = total number of stoichiometric moles of gaseous products - total number of stoichiometric moles of gaseous reactants.

Usually, depending on the sign of Δn_g, K_p and K_c are related in three ways.

Case (i)

When $\Delta n_g = 0$, the total number of moles of gaseous products are equal to the total number of moles of gaseous reactants.

For example, in the formation equilibrium of HI,

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$
$$\Delta n_g = 2-(1+1) = 2-2 = 0$$
$$\therefore \quad K_p = K_c(RT)^O$$
$$K_p = K_c$$
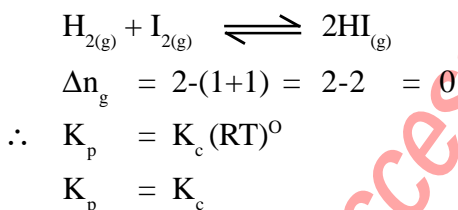
Case (ii)

When $\Delta n_g = +ve$, the total number of moles of gaseous products are greater than the total number of moles of gaseous reactants.

For example, $2H_2O_{(g)} + 2Cl_{2(g)} \rightleftharpoons 4HCl_{(g)} + O_{2(g)}$

$$\Delta n_g = (4+1) - (2+2)$$
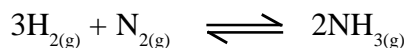$$= 5 - 4 = 1$$
$$\therefore K_p = K_c(RT)^1$$
$$K_p = K_c RT$$
$$\text{and } K_p > K_c$$

Case (iii)

When $\Delta n_g = -ve$, the total number of moles of gaseous products are lesser than the total number of moles of gaseous reactants.

For example, consider the formation equilibrium of ammonia,

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

$$\Delta n_g = 2 - (3+1)$$
$$= 2 - 4 = -2$$

$$\therefore K_p = K_c (RT)^{-2}$$

$$K_p = \frac{K_c}{(RT)^2}$$

and $K_p < K_c$

10.1.2 Dependance of dissociation constant with formation equilibrium constant

In a formation equilibrium reaction, the reactants and products are written at the LHS and RHS of the equilibrium sign respectively. For the same reaction, the dissociation equilibrium consists of the products in the place of reactants and reactants in the place of products being written at the LHS and RHS of the equilibrium sign respectively.
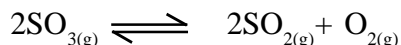
In such cases, the equilibrium constant of the dissociation equilibrium reaction which is also known as the dissociation constant, is found to be the reciprocal value of the equilibrium constant for the formation equilibrium reaction. For example, consider the formation equilibrium reaction of SO_3, from SO_2 and O_2 gases,

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

The equilibrium constant, K_c, is given by

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} \ dm^3/mole$$

In the dissociation equilibrium reaction of SO_3, the reactants become products and vice versa.

$$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$$

The equilibrium constant of the dissociation equilibrium is K_c', given by

$$K_c' = \frac{[SO_2]^2[O_2]}{[SO_3]^2} = \frac{1}{K_c} \ mole/dm^3$$

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K_c' is considered as the dissociation constant of SO_3 gas. Usually, the equilibrium constant of the dissociation equilibrium is the reciprocal of the equilibrium constant of the formation equilibrium reaction.

10.1.3 Applications of law of chemical equilibrium to homogeneous equilibria

Formation equilibrium of HI

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$
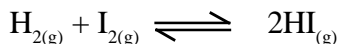
In this equilibrium reaction, the number of moles of the products is equal to the number of moles of the reactants ($\Delta_{ng} = 0$). Let us assume 'a' and 'b' moles of H_2 and I_2 gases being present in 'V' litres of the reaction vessel. At equilibrium, let x moles each of H_2 and I_2 react to form 2x moles of HI. Then, the equilibrium concentrations in moles litre of H_2, I_2 and HI in the reaction mixture will be (a-x)/V, (b-x)/V and 2x/V respectively. Since $\Delta n_g = 0$, Kc = Kp.
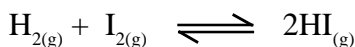
$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$= \frac{(2x/V)^2}{\frac{(a-x)}{V} \times \frac{(b-x)}{V}} \qquad = \frac{4x^2}{V^2} \times \frac{V^2}{(a-x)(b-x)}$$

$$= \frac{4x^2}{(a-x)(b-x)} = K_p$$

x is also known as the extent of reaction.

Problem

Calculate the K_c, when a mixture containing 8.07 moles of H_2 and 9.08 moles of I_2 are reacted at 448°C until 13.38 moles of HI was formed at the equilibrium.

The reaction equilibrium is

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$$K_c = \frac{(2x)^2}{(a-x)(b-x)}$$

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$$a = 8.07 \text{ moles} \qquad b = 9.08 \text{ moles} \qquad 2x = 13.38 \text{ moles}$$
$$\therefore x = 6.69 \text{ moles}$$

$$K_c = \frac{(13.38)^2}{(8.07 - 6.69)(9.08 - 6.69)}$$

$$= 54.29.$$

The equilibrium constant, K_c, value determines the direction and the extent of the reaction that may proceed for maximum yield of the product for constant conditions of temperature, pressure, initial concentrations of reactants or products as applied on the reaction equilibrium.

In order to find the direction in which a reaction equilibrium may proceed under different sets of initial concentrations of reactants and products which are not equal to the respective equilibrium concentrations, a term known as reaction quotient 'Q' is used. 'Q' is defined as the ratio of product of initial concentrations of products to the product of initial concentrations of reactants under non-equilibrium conditions. For example, in the equilibrium.

$$aA + bB \rightleftharpoons lL + mM$$

Let [A], [B], [L] and [M] be the actual concentrations present before the occurrence of equilibrium. These concentrations are considered as the non-equilibrium concentration conditions and the reaction quotient 'Q' is given as

$$Q = \frac{[L]^l [M]^m}{[A]^a [B]^b}$$

Let K_c be the equilibrium constant value of the equilibrium reaction in terms of molar concentrations of reactants and products and the values of K_c and Q can be compared.

When Q is greater than K_c ($Q > K_c$) the reaction will proceed so as to reduce Q. That is, more of reactants will be formed from the products which means the reverse reaction is favoured. When Q is lesser than K_c ($Q < K_c$) the reaction will proceed so as to increase the concentration of products which is the forward reaction. These aspects will hold good only when Q and K_c are under the same conditions of temperature and pressure.

Problem

Initially, 0.1 moles each of H_2 and I_2 gases and 0.02 moles of HI gas are mixed in a reaction vessel of constant volume at 300K. Predict the direction towards which the reaction proceeds [$K_c = 3.5 \times 10^{-2}$].

The formation equilibrium is

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$
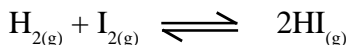
$$K_c = \frac{[HI]_e^2}{[H_2]_e[I_2]_e} = 3.5 \times 10^{-2} \text{ at 300 K}$$

Under non equilibrium conditions

$$Q = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2 \times 10^{-2})^2}{0.1 \times 0.1} = 4 \times 10^{-2}$$

Thus $Q > K_c$.

Therefore, the reaction will proceed initially before attaining the equilibrium in a direction such that Q value is reduced. That is, concentrations of H_2 and I_2 should be increases, which is a reverse reaction.

The reaction proceeds in the left side of formation equilibrium of HI and HI decomposes initially to H_2 and I_2 until $Q = K_c$.

Dissociation equilibrium of PCl$_5$

The dissociation equilibrium of PCl$_5$ in gaseous state is written as

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$
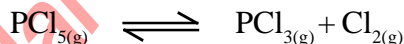
Let 'a' moles of PCl$_5$ vapour be present in 'V' litres initially. If x moles of PCl$_5$ dissociate to PCl$_3$ and Cl$_2$ gases at equilibrium at constant 'V' litres, then molar concentrations of PCl$_5$, PCl$_3$ and Cl$_2$ gases at equilibrium will be $\dfrac{a-x}{V}$, $\dfrac{x}{V}$ and $\dfrac{x}{V}$ respectively.

$$K_c = \frac{[PCl_3][Cl_2]_e}{[PCl_5]_e}$$

$$= \frac{x/V \times x/V}{(a-x)/V} = \frac{x^2}{V^2} \times \frac{V}{(a-x)}$$

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$$K_c = \frac{x^2}{(a-x)V}$$

x is also known as the degree of dissociation which represents the fraction of total moles of reactant dissociated.

$$x = \frac{\text{Number of moles dissociated}}{\text{Total number of moles present initially}}$$

If initially 1 mole of PCl_5 is present then

$$K_c = \frac{x^2}{(1-x)V} = \frac{x^2P}{(1-x)RT}$$

In terms of partial pressures of PCl_5, PCl_3 and PCl_2 then

$$K_p = \frac{p_{PCl_3} \cdot p_{Cl_2}}{p_{PCl_5}} \text{ atm}$$

and $K_p = \dfrac{x^2 P}{(1-x^2)} \text{ atm}$

If the degree of dissociation is small compared to unity, then $(1-x)$ is approximately equal to 1.0.

$$\therefore K_c = \frac{x^2}{V} \text{ (or)} \quad x^2 = K_c \times V$$

$$x \, \alpha \, \sqrt{V} \quad \text{But V} \, \alpha \, \frac{1}{P}$$

$$x \, \alpha \, \sqrt{\frac{1}{P}}$$

where x is small, degree of dissociation varies inversely as the square root of pressure (or) varies directly as the square root of volume of the system.

Problem

Degree of dissociation of PCl_5 at 1 atm and 25°C is 0.2. Calculate the pressure at which PCl_5 is half dissociated at 25°C.

For PCl_5 dissociation equilibrium,

$$K_p = \frac{x^2 P}{1 - x^2} \qquad \begin{aligned} P &= \text{total pressure} = 1 \text{ atm} \\ x &= 0.2 \end{aligned}$$

$$K_p = \frac{(0.2)^2 (1.0)}{1 - (0.2)^2} = \frac{0.04}{1 - 0.04} = \frac{0.04}{0.96} = 0.042 \text{ atm}$$

when $x = 0.5$, $P = ?$

$$P = \frac{K_p (1 - x^2)}{x^2} = \frac{0.042(1 - (0.5)^2)}{(0.5)^2} = \frac{0.042(1 - 0.25)}{0.25}$$

$$= \frac{0.042(0.75)}{0.25} = 0.126 \text{ atm}$$

10.2   Le Chatelier's Principle

There are three major factors that alter the state of equilibrium. They are concentration, temperature and pressure. The addition of a catalyst has no effect on the state of equilibrium. Its presence merely hastens the approach of the equilibrium.

Le Chatelier's Principle

According to this principle, if a system at equilibrium is subjected to a disturbance or stress, then the equilibrium shifts in the direction that tends to nullify the effect of the disturbance or stress. Let us consider the effects of changes in temperature, concentration and pressure, on the equilibrium reactions and the predictions of Le Chatelier's principle.

Effect of change of concentration

Consider the following equilibrium reaction

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

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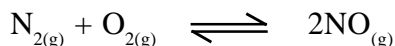
At the equilibrium conditions the reaction mixture contains both the reactant and product molecules, that is, N_2, O_2 and NO molecules. The concentrations of reactant and product molecules are constant and remain the same as long as the equilibrium conditions are maintained the same. If a change is imposed on the system by purposely adding NO into the reaction mixture then the product concentration is raised. Since the system possesses equilibrium concentrations of reactants and products, the excess amount of NO react in the reverse direction to produce back the reactants and this results in the increase in concentrations of N_2 and O_2. Similarly if the concentration of reactants such as N_2 and O_2 are purposely raised when the system is already in the state of equilibrium, the excess concentrations of N_2 and O_2 favour forward reaction. Concentration of NO is raised in the reaction mixture.

In general, in a chemical equilibrium increasing the concentrations of the reactants results in shifting the equilibrium in favour of the products while increasing the concentrations of the products results in shifting the equilibrium in favour of the reactants.

Effect of change of temperature

A chemical equilibrium actually involves two opposing reactions. One favouring the formation of products and the other favouring the formation of reactants. If the forward reaction in a chemical equilibrium is endothermic (accompanied by absorption of heat) then the reverse reaction is exothermic (accompanied by evolution of heat).

Let us consider the example

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} ; \quad \Delta H = +59.0 \text{ kJ/mole}$$
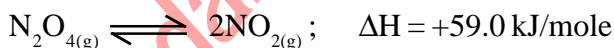
In this equilibrium, the reaction of the product formation (NO_2) is endothermic in nature and therefore, the reverse reaction of reactant formation (N_2O_4) should be exothermic. If the above equilibrium reaction mixture is heated then its temperature will be raised. According to Le Chatelier's principle, the equilibrium will shift in the direction which tends to undo the effect of heat. Therefore, the equilibrium will shift towards the formation of NO_2 and subsequently dissociation of N_2O_4 increases. Therefore, generally, when the temperature is raised in a chemical equilibrium, among the forward and reverse reactions, the more endothermic reaction will be favoured. Similarly, if the temperature of the

equilibrium is decreased i.e., cooled, then the exothermic reaction among the forward and reverse reaction of the equilibrium will be favoured.

Effect of change of pressure

If a system in equilibrium consists of reactants and products in gaseous state, then the concentrations of all components can be altered by changing the total pressure of the system. Consider the equilibrium in the gaseous state such as

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$
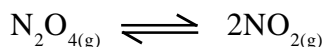
Increase in the total pressure of the system in equilibrium will decrease the volume proportionately. According to Le Chatlier's principle, the change can be counteracted by shifting the equilibrium towards decreasing the moles of products. Hence, the reaction of combination of NO_2 molecules to N_2O_4 formation will be favoured.

In case of a gas phase equilibrium which is accompanied by decrease in number of moles of products formed, the effect of pressure can be considered as follows,

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$
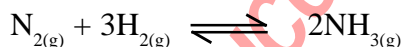
If the pressure is increased then the volume will decrease proportionately. Consequently, the equilibrium will shift in the direction in which there is a decrease in the total number of moles, ie., favours the formation reaction of NH_3. Here from four moles of reactants two moles of NH_3 are formed. Thus at higher pressures, the yield of ammonia will be more.

Haber's Process

Ammonia is mainly used as a source of nitrogen fertiliser, in nitric acid production and in nitrogen containing pharmaceuticals. Ammonia is commercially produced in industries from the gaseous elements nitrogen and hydrogen in air by means of Haber's process. Ammonia formation reaction is an equilibrium reaction.

$$N_{2(g)} + 3H_{2(g)} \overset{Fe}{\rightleftharpoons} 2NH_{3(g)} \qquad \Delta H^0_f = -22.0 \, \text{kcal/mole}$$
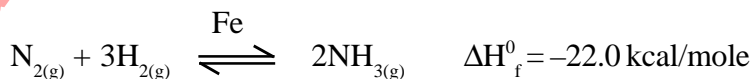
The forward reaction is accompanied by decrease in the number of moles of reactants and according to Le Chatlier's principle, an increase in pressure favours

such a reaction and shifts the equilibrium towards the product formation direction. Therefore, nearly 300-500 atm pressure is applied on 3:1 mole ratio of H_2:N_2 gas mixture in the reaction chamber for maximum yield of ammonia. The ammonia formation reaction is exothermic. By Le Chatlier's principle, increase in temperature favours decomposition reaction of ammonia. However, at low temperature the time to reach the equilibrium becomes very long. Hence an optimum temperature close to 500°C-550°C is maintained. Iron catalyst is chosen to speed up the attainment of the equilibrium concentration of ammonia. In order to maintain the equilibrium conditions, steam is passed to remove away the ammonia as and when it is formed so that the equilibrium remains shifted towards the product side. The maximum yield of ammonia is nearly 37%.

Contact Process

This process involves the equilibrium reaction of oxidation of SO_2 gas by gaseous oxygen in air to manufacture large quantities of SO_3 gas.

$$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{\text{v}_2\text{O}_5} 2SO_{3(g)} \qquad \Delta H^0_f = -47 \text{ kcal/mole}$$
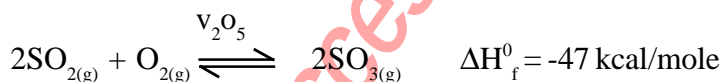
The formation reaction of SO_3 involves a decrease in the overall moles of the reactants. By Le Chatlier's principle, when large pressure is applied, forward reaction is favoured. 700 atm - 1200 atm pressure is maintained on the 2:1 mole ratio mixture of pure SO_2 and O_2 gases in the reaction chamber. SO_3 production is an exothermic reaction. Hence, increase in temperature favours SO_3 dissociation. However, lowering of temperature prolongs the time of attainment of equilibrium. Therefore, an optimum temperature at nearly 400°C to 450°C is maintained to favour the equilibrium.

The most widely used catalyst for SO_3 production is porous vanadium pentoxide (V_2O_5). Presence of moisture deactivates the catalyst. Only dry and pure SO_2 and O_2 gases are used over the catalyst. Since oxidation of SO_2 is a slow process, presence of V_2O_5 speeds up the equilibrium process and high yield of SO_3 is achieved in a short period. SO_3 is the anhydride of H_2SO_4. Therefore, SO_3 from contact process along with steam is used in oleum and H_2SO_4 manufacturing processes in contact process, the yield of SO_3 is nearly 97%.

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SELF EVALUATION

A. Choose the correct answer

1. State of chemical equilibrium is:
   a) dynamic   b) stationery   c) none   d) both

2. If the equilibrium constants of the following reactions are $2A \rightleftharpoons B$ is K_1 and $B \rightleftharpoons 2A$ is K_2, then

   a) $K_1 = 2K_2$ b) $K_1 = 1/K_2$ c) $K_2 = (K_1)^2$ d) $K_1 = 1/K_2^2$

3. In the reversible reaction $2HI \rightleftharpoons H_2 + I_2$, K_p is
   a) greater than K_c b) less than K_c c) Equal to K_c d) Zero

4. In the equilibrium $N_2 + 3H_2 \rightleftharpoons 2NH_3$, the maximum yield of ammonia will be obtained with the process having
   a)   low pressure and high temperature
   b)   low pressure and low temperature
   c)   high temperature and high pressure
   d)   high pressure and low temperature

5. For the homogeneous gas reaction at 600 K
   $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$
   the equilibrium constant K_c has the unit

   a) $(mol\,dm^{-3})^{-1}$ b) $(mol\,dm^{-3})$ c) $(mol\,dm^{-3})^{10}$ d) $(mol\,dm^{-3})^{-9}$

6. Two moles of ammonia gas are introduced into a previously evacuated 1.0 dm^3 vessel in which it partially dissociates at high temperature. At equilibrium 1.0 mole of ammonia remains. The equilibrium constant K_c for the dissociation is
   a) $27/16\,(mole\,dm^{-3})^2$ b) $27/8\,(mole\,dm^{-3})^2$
   c) $27/4\,(mole\,dm^{-3})^2$ c) None of these

7. An equilibrium reaction is endothermic if K_1 and K_2 are the equilibrium constants at T_1 and T_2 temperatures respectively and if T_2 is greater than T_1 then
   a) K_1 is less than K_2 b) K_1 is greater than K_2
   c) K_1 is equal to K_2 d) None

   [*Ans:* 1-a; 2-b; 3-c; 4-d, 5-b, 6-a and 7-a]

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B. Answer in one or two sentences

8. Dissociation of PCl_5 decreases in presence of increase in Cl_2 why?

9. Write the equilibrium constant for the following

   i) $H_2O_{2(g)} \rightleftharpoons H_2O_{(g)} + \frac{1}{2}O_{2(g)}$

   ii) $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$

   iii) $N_2O_{4(g)} \rightleftharpoons 2\ NO_{2(g)}$

10. State Le Chatelier's principle.

11. What is equilibrium constant?

12. Why do equilibrium reactions referred to as dynamic equilibrium?

13. What happens when $\Delta n_g = 0$, $\Delta n_g = -ve$, $\Delta n_g = +ve$ in a gaseous reaction.

14. Calculate Δn_g, for the following reactions

   i) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

   ii) $2H_2O_{(g)} + 2Cl_{2(g)} \rightleftharpoons 4HCl_{(g)} + O_{(g)}$

C. Answer not exceeding 60 words

15. Derive the relation $K_p = K_c\ (RT)^{\Delta n_g}$ for a general chemical equilibrium reaction.

16. State Le Chatelier's principle. Discuss the effect of pressure, concentration and temperature on the following reaction.

$$N_{2g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

17. Derive the expressions for K_c and K_p for decomposition of PCl_5.

D. Practice Problems

18. The equilibrium constant Kc for $A_{(g)} \rightleftharpoons B_{(g)}$ is 2.5×10^{-2}. The rate constant of the forward reaction is $0.05\ sec^{-1}$. Calculate the rate constant of the reverse reaction.   [**Ans** : $2.0\ sec^{-1}$]

19. In the equilibrium $H_2 + I_2 \rightleftharpoons 2\,HI$ the number of moles of H_2, I_2 and HI are 1,2,3 moles respectively. Total pressure of the reaction mixture is 60 atm. Calculate the partial pressures of H_2, I_2 and HI in the mixture.

           [*Ans:* 10 atm, 20 atm, 30 atm]

20. In 1 litre volume reaction vessel, the equilibrium constant K_c of the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ is $2 \times 10^{-4}\ lit^{-1}$. What will be the degree of dissociation assuming only a small extent of 1 mole of PCl_5 has dissociated?

   [*Ans:* x = 1.414×10^{-2}]

21. At temperature T_1, the equilibrium constant of reaction is K_1. At a higher temperature T_2, K_2 is 10% of K_1. Predict whether the equilibrium is endothermic or exothermic.   [***Ans***: Exothermic]

22. At 35°C, the value of K_p for the equilibrium reaction $N_2O_4 \rightleftharpoons 2NO_2$ is 0.3174, Calculate the degree of dissociation when P is 0.2382 atm.

[***Ans***: x = 0.5768]

23. For the equilibrium $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$ the value of the equilibrium constant K_c is 3.75×10^{-6} at 790°C. Calculate K_p for this equilibrium at the same temperature. Hint: $K_p = K_c(RT)^{\Delta ng}$ [***Ans:*** $K_p = 3.29 \times 10^{-4}$]

24. For the equilibrium $2SO_{3(g)} \rightleftharpoons SO_{2(g)} + O_{2(g)}$, the value of equilibrium constant is 4.8×10^{-3} at 700°C. At equilibrium, if the concentrations of SO_3 and SO_2 are 0.60M and 0.15M respectively. Calculate the concentration of O_2 in the equilibrium mixture.   [***Ans:*** 0.0768M]

25. Hydrogen iodide is injected into a container at 458°C. Certain amount of HI dissociates to H_2 and I_2. At equilibrium, concentration of HI is found to be 0.421M while $[H_2]$ and $[I_2]$ each equal to 6.04×10^{-2}M, at 458°C. Calculate the value of the equilibrium constant of the dissociation of HI at the same temperature.   [***Ans***: $K_c = 2.06 \times 10^{-2}$]

26. Dissociation equilibrium constant of HI is 2.06×10^{-2} at 458°C. At equilibrium, concentrations of HI and I_2 are 0.36M and 0.15M respectively. What is the equilibrium concentration of H_2 at 458°C.

[***Ans***: $[H_2] = 1.78 \times 10^{-2}$M]

27. The equilibrium constant for the reaction $2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$ is 0.15 at 900 K. Calculate the equilibrium constant for the reaction $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ at the same temperature.

[***Ans***: 6.67 mol^{-1} dm^3]

28. For the reaction $A + B \rightleftharpoons 3C$ at 25°C, a 3 litre volume reaction vessel contains 1,2 and 4 moles of A, B and C respectively at equilibrium, calculate the equilibrium constant K_c of the reaction at 25°C.[***Ans:*** 10.66 mol dm^{-3}]

29. How much PCl_5 must be added to one litre volume reaction vessel at 250°C in order to obtain a concentration of 0.1 mole of Cl_2, K_c for $PCl_5 \rightleftharpoons PCl_5 + Cl_2$ is 0.0414 mol dm^{-3} at 250°C.

[***Ans:*** 0.341 moles PCl_5]

30. At 540K, the equilibrium constant K_p for PCl_5 dissociation equilibrium at

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1.0 atm is 1.77 atm. Calculate equilibrium constant in molar concentration (K_c) at same temperature and pressure.

[**Ans**: $K_c = 4 \times 10^{-2}$ moles/litres]

Summary

- Law of mass action was applied to equilibrium reactions to determine the equilibrium constant.

$$aA + bB \rightleftharpoons lL + mM$$
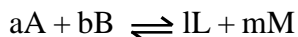
$$K = \frac{[L]^l[M]^m}{[A]^a[B]^b} = \frac{k_f}{k_r}$$

- Equilibrium constants in terms of molar concentration (K_c) and partial pressures (K_p) are related as $K_p = K_c(RT)^{\Delta n_g}$ for gaseous reactants and products in equilibrium.

When $\Delta n_g = 0$, $K_p = K_c$; $\Delta n_g = $ -ve, $K_p < K_c$ and $\Delta n_g = $ +ve, $K_p > K_c$.

- The reaction quotient (Q) of non equilibrium concentrations to equilibrium concentrations of reactants and products is related to equilibrium constant (K) of an equilibrium reaction as: when Q<K, more of product is formed; Q=K, equilibrium is attained; Q>K, more of reactant is formed.

- Degree of dissociation 'x'= $\dfrac{\text{no.of moles dissociated}}{\text{total no of moles present initially}}$

- Application of Le Chatelier's principle to explain effect of pressure, temperature and concentration on the equilibrium reactions. i) When the total number of moles are decreased in the equilibrium increase in pressure favour product formation. ii) For endothermic equilibrium, increase in temperature favours product formation. iii) Increase in reactant concentration (or) decrease in product concentration favours the product formation in equilibrium.
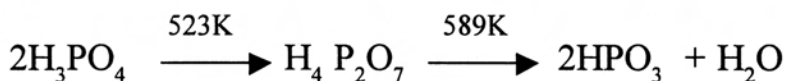
References

1. Text book of physical chemistry by S. Glasstone, Mac Millan, India Limited.

2. Physical chemistry by G.Castellan Narosa Publishing Company.
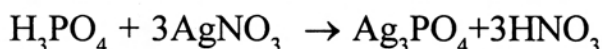
CORRECTED PAGES

(MAY 2016)

2. On heating it gives pyrophosphoric acid at 523 K and at 589 K gives metaphosphoric acid

$$2H_3PO_4 \xrightarrow{523K} H_4P_2O_7 \xrightarrow{589K} 2HPO_3 + H_2O$$

3. On reaction with silver nitrate, it gives yellow precipitate of silver phosphate.

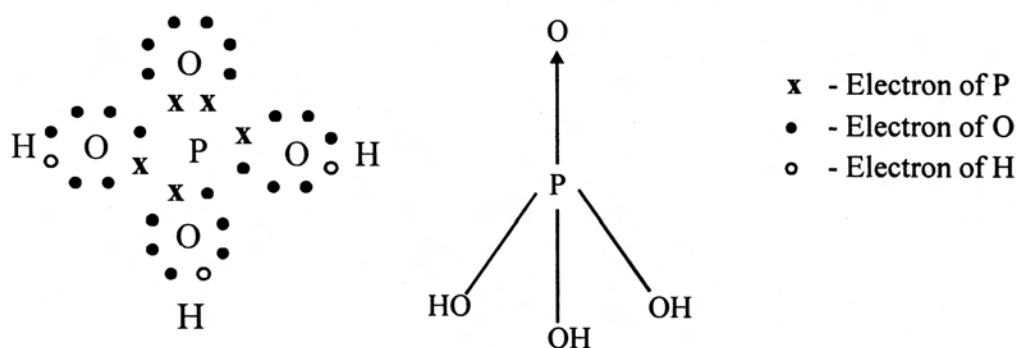$$H_3PO_4 + 3AgNO_3 \rightarrow Ag_3PO_4 + 3HNO_3$$

Uses

1. It is used in the preparation of HBr and HI as a substitute for sulphuric acid.
2. It is used as souring agent in the preparation of soft drinks.
3. It is used in the preparation of phosphate salts of sodium, potassium and ammonium.
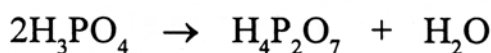4. It is used in the manufacture of phosphatic fertilisers.

Structure

Being a tribasic acid, the structure of phosphoric acid is represented as

x - Electron of P
• - Electron of O
o - Electron of H

III. B. Pyrophosphoric acid, $H_4P_2O_7$

Preparation: Pyrophosphoric acid is prepared by heating orthophosphoric acid to 523 K – 533 K.

$$2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O$$

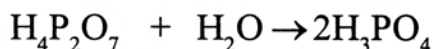## Physical Properties

It is a colourless crystalline solid.

Chemical Properties

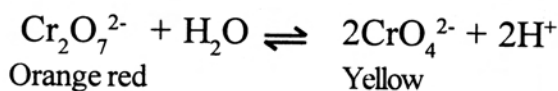1. It is reconverted to orthophosphoric acid on boiling with water

$$H_4P_2O_7 + H_2O \rightarrow 2H_3PO_4$$

2. When heated strongly, it yields metaphosphoric acid

$$H_4P_2O_7 \longrightarrow 2HPO_3 + H_2O$$

$$2K_2CrO_4 + H_2SO_4 \rightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$
<div align="center">Orange red</div>
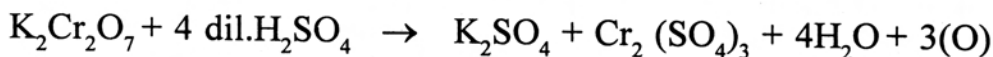
The inter conversion is explained on the basis of the fact that in $K_2Cr_2O_7$ solution, orange red $Cr_2O_7^{2-}$ ions are in equilibrium with yellow CrO_4^{2-} ions.
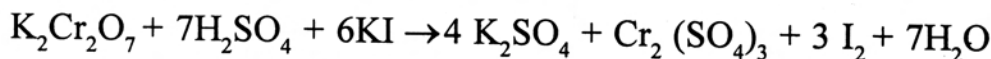
$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$$
<div align="center">Orange red   Yellow</div>

3. Oxidising properties

$K_2Cr_2O_7$ is a powerful oxidising agent. In presence of dil.H_2SO_4, one mole of this compound gives three atoms of oxygen as shown below.
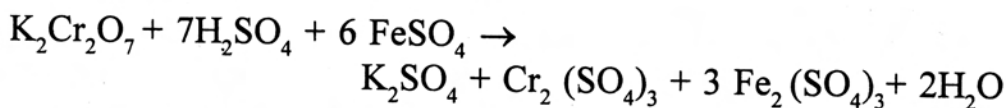
$$K_2Cr_2O_7 + 4 \text{ dil.}H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3(O)$$

Some other examples of oxidising property of $K_2Cr_2O_7$ are given below.

i) It liberates I_2 from KI

$$K_2Cr_2O_7 + 7H_2SO_4 + 6KI \rightarrow 4 K_2SO_4 + Cr_2(SO_4)_3 + 3 I_2 + 7H_2O$$

ii) It oxidises ferrous to ferric salt

$$K_2Cr_2O_7 + 7H_2SO_4 + 6 FeSO_4 \rightarrow$$
$$K_2SO_4 + Cr_2(SO_4)_3 + 3 Fe_2(SO_4)_3 + 2H_2O$$

iii) It oxidises H_2S to sulphur

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$

4. Chromyl chloride test

When salt containing chloride is treated with $K_2Cr_2O_7$ and con. H_2SO_4 orange red vapours of chromyl chloride are obtained.
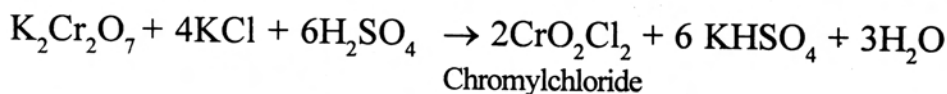
$$K_2Cr_2O_7 + 4KCl + 6H_2SO_4 \rightarrow 2CrO_2Cl_2 + 6 KHSO_4 + 3H_2O$$
<div align="center">Chromylchloride</div>

This reaction is used in the detection of chloride ions in qualitative analysis.

Uses

i)   It is used in volumetric analysis

ii) In chrome tanning in leather industry

iii) In calico printing and dyeing

iv) In photography and in hardening gelatin film.

4.5.2 Copper Sulphate ($CuSO_4.5H_2O$); Blue vitriol
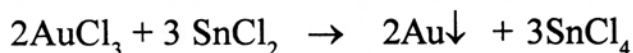
Preparation

In laboratory it is prepared by dissolving cupric oxide (or) cupric hydroxide (or) cupric carbonate in dilute H_2SO_4

4.5.5 Purple of cassius

Purple of cassius is only a form of colloidal gold. It is purple or red in colour and after the name of Cassius who discovered it.

Preparation

It is prepared by mixing very dilute solution of gold chloride with stannous chloride solution.

$$2AuCl_3 + 3\ SnCl_2 \rightarrow 2Au\downarrow + 3SnCl_4$$

The gold thus precipitated is adsorbed by stannic hydroxide formed by the hydrolysis of $SnCl_4$.

$$SnCl_4 + 4H_2O \rightarrow Sn(OH)_4 + 4HCl$$
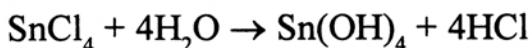
Uses

It is used in making ruby-red glass and high class pottery.

SELF EVALUATION

A. Choose the correct answer

1. The general electronic configuration of d-block elements is
   a) $(n-1)d^{1-10}\ ns^{1-2}$ b) $(n-1)\ d^{1-5}\ ns^2$
   c) $(n-1)d^0\ ns^1$ d) None of these

2. Formation of coloured ions is possible when compounds contains
   a) paired electrons   b) unpaired electrons
   c) lone pairs of electrons   d) none of the above

3. Paramagnetism is common in
   a) p-block elements   b) d-block elements
   c) s-block elements   d) f-block elements

4. The colour of $Ti(H_2O)_6^{3+}$ ion is due
   a) d-d transistion   b) Presence of water molecules
   c) Inter atomic transfer of electrons d) None of the above

5. The electronic configuration of chromium is
   a) $3d^6\ 4s^0$ b) $3d^5\ 4s^1$
   c) $3d^4\ 4s^2$ d) $3d^3\ 4s^2\ 4p^1$

6. Paramagnetism is the property of
   a) paired electrons   b) completely filled electronic subshells
   c) unpaired electrons   d) completely vacant electronic subshells

7. d-block elements form coloured ions because
   a)   They absorb some energy for d-s transition
   b)   They absorb some energy for p-d transition
   c)   They absorb some energy for d-d transition
   d)   They do not absorb any energy

ligand name is enclosed in parentheses and its number is given with the alternate prefixes bis, tris, tetrakis instead.

For example, $[Ni(PPh_3)_2Cl_2]$ is named dichlorobis(triphenylphosphine) nickel(II).

5.   A Roman numeral or a zero in parentheses is used to indicate the oxidation state of the central metal atom.

6.   If the complex ion is negative, the name of the metal ends in 'ate' for example, ferrate, cuprate, nickelate, cobaltate etc.

7.   If more than one ligand is present in the species, then the ligands are named in alphabetical order regardless of the number of each. For example, NH_3 (ammine) would be considered as 'a' ligand and come before Cl^- (chloro).

Some additional notes

i)   Some metals in anions have special names

B	Borate	Au	Aurate	Ag	Argentate	Fe	Ferrate
Pb	Plumbate	Sn	Stannate	Cu	Cuprate	Ni	Nickelate

ii) Use of brackets or enclosing marks.

Square brackets are used to enclose a complex ion or neutral coordination species.

Examples

$[Co(en)_3]Cl_3$	tris(ethylenediamine)cobalt(III) chloride
$[Co(NH_3)_3(NO_2)_3]$	triamminetrinitrocobalt (III)
$K_2[CoCl_4]$	potassiumtetrachlorocobaltate(II)

note that it is not necessary to enclose the halogens in brackets.

A systematic approach to drawing and naming coordination complexes

For the complex $K_3[Cr(C_2O_4)_3].3H_2O$

Q1) What is the central metal ion?	A1) Central metal is Chromium
Q2) What is its oxidation state?	A2) O.S. is III
Q3) What is its electronic configuration?	A3) electronic configuration is d^3
Q4) What is its coordination number?	A4) C.N. is 6(3 bidentate ligands present)
Q5) What is the shape of the ion?	A5) structure is octahedral
Q6) Can the structure have isomers?	A6) Yes, optical isomers are possible
Q7) What is the IUPAC name of the complex?	A7) Potassium tri (oxalato) chromate(III) trihydrate

$$Q_{value} = (m_p - m_r) \, 931 \text{ MeV}$$

where m_r - Sum of the masses of reactants
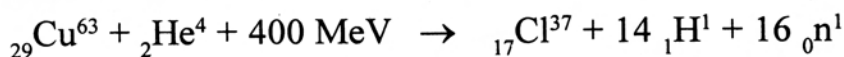
m_p - Sum of the masses of products

In the case of energy absorbed then $m_p > m_r$, then Q value will be positive.

Q value of a nuclear reaction in the case of energy released $= (m_p - m_r)$ 931 MeV. In the case of energy released, $m_r > m_p$, and hence Q value will be negative.

7.2 TYPE OF NUCLEAR REACTION

1. Spallation reaction

These are the reactions in which high speed projectiles may chip a heavy nucleus into several fragments.

$$_{29}Cu^{63} + {}_2He^4 + 400 \text{ MeV} \rightarrow {}_{17}Cl^{37} + 14 \, _1H^1 + 16 \, _0n^1$$

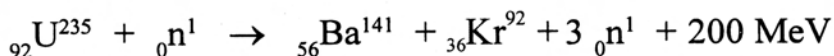### 2. Nuclear fission reaction

Nuclear fission is the process in which a heavy nucleus breaks up into two lighter nuclei of almost equal size with the release of an enormous amount of energy. This type of nuclear fission reaction was first observed by German Chemists Otto Hahn, F.Strassman and Meitner by bombarding $_{92}U^{235}$ with slow moving neutrons. The process is usually accompanied by emission of neutrons. The nuclear fission has been produced in heavy nuclei such as $^{235}U, ^{238}U, ^{232}Th$ by neutrons, protons, deuterons.

Mechanism of fission

In the fission process, the heavy nucleus absorbs a neutron and forms an unstable compound nucleus. The compound nucleus then breaks up more or less in the middle to give fission product.

Example

A typical example of the fission process in the fission of uranium by neutrons is explained by the following equation.

$$_{92}U^{235} + {}_0n^1 \rightarrow {}_{56}Ba^{141} + {}_{36}Kr^{92} + 3 \, _0n^1 + 200 \text{ MeV}$$

Further, the neutrons released (say three) from the fission of first uranium atoms can hit three other uranium atoms. In this way a chain reaction is set up resulting into the liberation of an enormous amount of energy. In the case of nuclear fission, $_{92}U^{236}$ formed breaks up in several ways.

$$_{92}U^{235} + {}_0n^1 \longrightarrow {}_{92}U^{236} \begin{cases} {}_{56}Ba^{140} + {}_{36}Kr^{93} + 3 \, _0n^1 \\ {}_{54}Xe^{144} + {}_{38}Sr^{90} + 2 \, _0n^1 \\ {}_{55}Cs^{144} + {}_{37}Rb^{90} + 2 \, _0n^1 \end{cases}$$