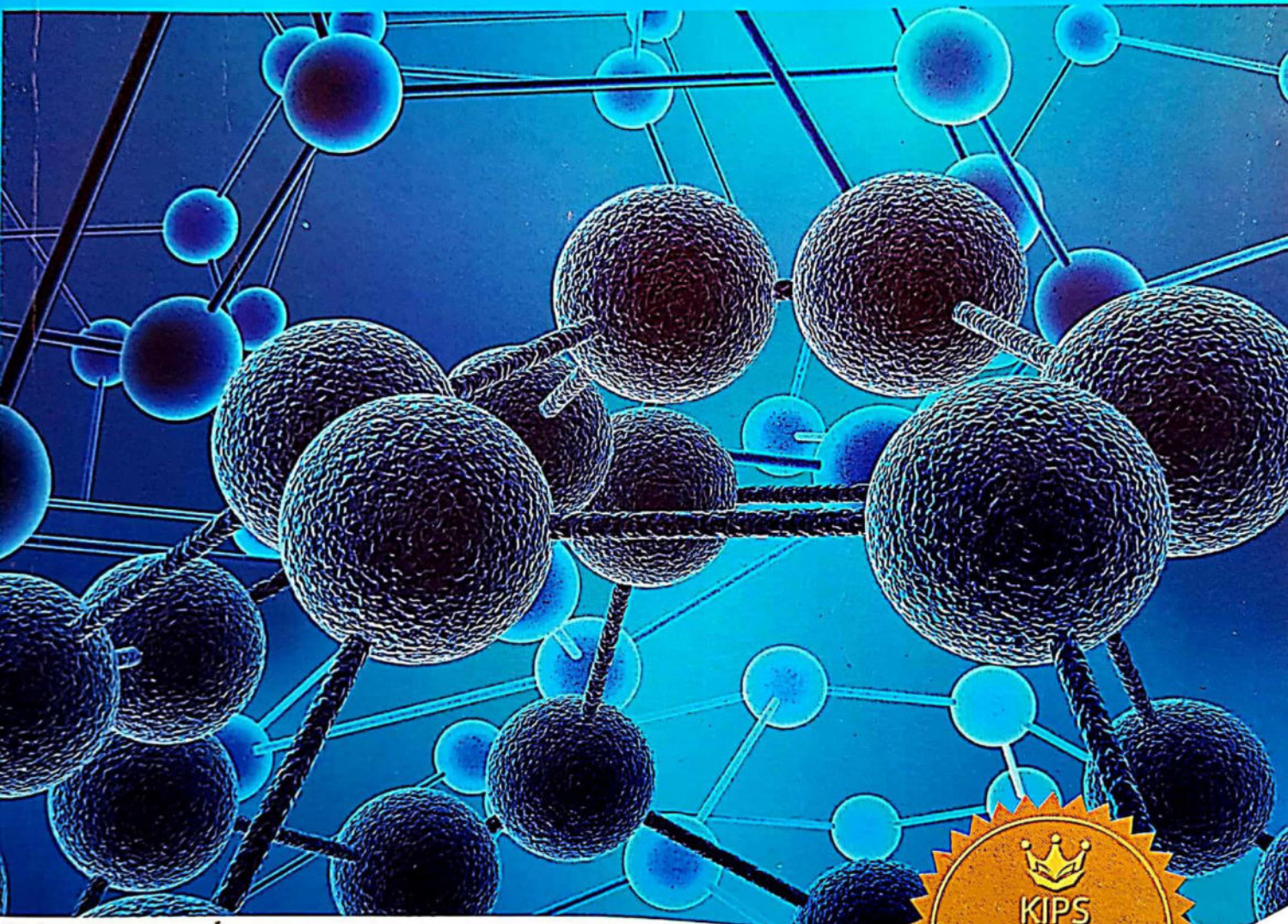
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- This diagnostic test is designed to help you to pinpoint the weak areas in your background Sit aside 1 hour to take this test. Check your answers with those at the end of the test. Then evaluate yourself.

ECAT

1. **Isotopes differ in**
   (a) arrangement of electrons in orbital (b) position in the periodic table
   (c) properties which depend upon mass (d) chemical properties
2. **The mass of one mole of electrons is**
   (a) 1.008 mg (b) 0.55 mg
   (c) 0.184 mg (d) 1.637 mg
3. **The volume occupied by 1.4g CO at S.T.P is**
   (a) 22.4 dm^3 (b) 2.24dm^3
   (c) 1.12 dm^3 (d) 112 cm^3
4. **The number of atoms in a molecule determines**
   (a) micromolecule (b) macromolecule
   (c) molecularity (d) atomicity
5. **Which of the following set has all species isoelectronic**
   (a) F^-, Cl^-, Br^- (b) Li^{+1}, Na^{+1}, k^{+1}
   (c) F^-, Ne, Na^+ (d) H^+, H^-, H
6. **Which element has same isotopes like palladium**
   (a) Nickel (b) Calcium
   (c) Cadmium (d) Tin
7. **Water absorber used in combustion analysis is**
   (a) 50% KOH (b) Lime water
   (c) $CaCl_2$ (d) $Mg(ClO_4)_2$
8. **A limiting reactant is one which**
   (a) is taken in lesser quantity in grams as compared to other reactants
   (b) is taken in lesser quantity in volume as compared to other reactants
   (c) gives the maximum amount of the product which is required
   (d) gives the minimum amount of the product under consideration
9. **The type of filtering media used for filtration depending upon.**
   (a) Nature of reactants (b) Nature of crucible
   (c) Nature of product (d) Nature of precipitate
10. **A safe and more reliable method for drying the crystal is through**
    (a) Hot air currents (b) Folds of filter paper
    (c) Oven (d) Vacuum desiccator
11. **A method of separation of components from its solution using Distribution law is**
    (a) Sublimation (b) Crystallisation
    (c) Solvent extraction (d) Distillation

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12. A real gas obeying Van der waal's equation will resemble the ideal gas if

(a) Both 'a' and 'b' are small
(b) Both 'a' and 'b' are large
(c) 'a' is small and 'b' is large
(d) 'a' is large and 'b' is small.

13. Equal masses of methane and oxygen are mixed in empty container at 150°C The fraction of total pressure exerted by oxygen is

(a) 8/9
(b) 16/17
(c) 1/3
(d) 1/9

14. Plasma is used in

(a) Fluorescent bulb
(b) Neon signs
(c) Lasers
(d) All of these

15. The molecules of CO_2 in dry ice form

(a) Ionic crystal
(b) Covalent crystal
(c) Molecular crystal
(d) Any type of crystal

16. Which of the following is pseudo solid

(a) CaF_2
(b) NaCl
(c) Glass
(d) Diamond

17. Only London dispersion forces are present among the

(a) Molecules of water in liquid state
(b) Atoms of helium in gaseous state at high temperature
(c) Molecules of hydrogen chloride gas
(d) Molecules of solid iodine

18. Bohr's model is contradicted by

(a) Planck's theory
(b) Pauli's exclusion principle
(c) Heisenberg's uncertainty principle
(d) All of these

19. Quantum number values for 3p orbitals are

(a) n=3 l=2
(b) n=3 l=0
(c) n=3 l=1
(d) n=3 l=3

20. When fast neutron strike the nucleus of nitrogen the particles ejected are

(a) α - particles
(b) β - particles
(c) γ - rays
(d) X – rays

21. Which specie has unpaired electrons in antibonding molecular orbitals

(a) O_2^{+2}
(b) N_2^{-2}
(c) B_2
(d) O_2^{-2}

22. Atomic radius can be determined by

(a) X – ray diffraction
(b) Spcetrophotometer
(c) Optical microscope
(d) Electron microscope

23. For a given process the heat changes at constant pressure (q_p) and at constant volume (q_v) are related to each other as

(a) $q_p = q_v$
(b) $q_p < q_v$
(c) $q_p > q_v$
(d) $q_p = q_v/2$

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24. **For which system does the equilibrium constant Kc has unit of (concentration)$^{-1}$**

(a) $N_2+3H_2 \rightleftharpoons 2NH_3$ (b) $H_2+I_2 \rightleftharpoons 2HI$

(c) $2NO_2 \rightleftharpoons N_2O_4$ (d) $2HF \rightleftharpoons H_2+F_2$

25. **Solubility product of AgCl is 2.0×10^{-10} mol^2 dm^{-6}. Maximum concentration of Ag^{+1} ions in the solution is**

(a) 2.0×10^{-10} mol dm^{-3} (b) 1.41×10^{-10} mol dm^{-3}

(c) 1.0×10^{-10} mol dm^{-3} (d) 1.0×10^{-20} mol dm^{-3}

26. **18g glucose is dissolved in 90g of water. The relative lowering in vapour pressure is equal to**

(a) $\frac{1}{5}$ (b) 5.1

(c) 6 (d) $\frac{1}{51}$

27. **Which of the following solution has the highest boiling point**

(a) 5.85 % NaCl Solution (b) 18.0 % glucose solution

(c) 6.0 % urea solution (d) All have same boiling point

28. **Stronger is the oxidizing agent, greater is the**

(a) Oxidation potential (b) Reduction potential

(c) E.M.F of cell (d) redox potential

29. **Which of the following can be used in laptops?**

(a) Silver oxide battery (b) Fuel cell

(c) Nickel cadmium cell (d) Lead accumulator

30. **Which is true about Zn-Cu galvanic cell?**

(a) Reduction occurs at anode

(b) K^+ ion transfer from salt bridge to left beaker of $ZnSO_4$

(c) Oxidation occurs at cathode

(d) Anode is negatively charged

31. **Which is the unit of (K) rate constant for zero order reaction**

(a) s^{-1} (b) mol dm^{-3} s^{-1}

(c) mol^{-1} dm^3 s^{-1} (d) mol^{-2} dm^6 s^{-1}

32. **Nitrates of which pair gives different products on thermal decomposition**

(a) Na, K (b) Mg, Ca

(c) Li, Na (d) Li, Ca

33. **Which is carnalite**

(a) KCl (b) NaCl

(c) KCl. $MgCl_2.6H_2O$ (d) Na_2CO_3. $10H_2O$

34. **Keeping in view the size of atom, which is in correct order**

(a) Mg > Sr (b) Ba > Mg

(c) Lu > Ce (d) Cl > 1

35. **Which one does not give borax bead test**

(a) Copper sulphate (b) Barium sulphate

(c) Cobalt sulphate (d) Nickel sulphate

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36. Which one is not the use of silicones

(a) Lubricant
(b) Water repellent film
(c) Rubber sheet
(d) Medicine

37. The most reactive allotropic form of phosphorus is

(a) White
(b) Red
(c) Black
(d) Violet

38. Chemical composition of cinnabar is

(a) FeS_2
(b) HgS
(c) PbS
(d) ZnS

39. Which molecule has the highest bond energy among the halogens

(a) Fluorine
(b) Chlorine
(c) Iodine
(d) Bromine

40. When chlorine is passed through hot solution of caustic soda the reaction is said as

(a) Displacement reaction
(b) Reduction reaction
(c) Disproportionation reaction
(d) Double displacement reaction

41. The most paramagnetic element is

(a) Iron
(b) Cobalt
(c) Chromium
(d) Manganese

42. In the complex $[Cr(OH)_3(H_2O)_3]$ the coordination number is

(a) 2
(b) 3
(c) 4
(d) 6

43. Which one of the following looks odd

(a) H_2SO_4
(b) $KMnO_4$
(c) H_2S
(d) K_2CrO_4

44. A great variety of the organic compounds is due to its property of carbon

(a) Show tetravalency
(b) Exhibit catenation
(c) Show isomerism
(d) Can form multiple bonds

45. In 1- pentene -4- yne the carbon exhibit hybridization

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

46. Vinyl acetylene combines with hydrochloric acid produces

(a) Divinyl acetylene
(b) Ethylidine dichloride
(c) Chloroprene
(d) 1,3,3-trichloro butane

47. When benzene is heated in air with V_2O_5 at 450°C yields

(a) Phenol
(b) Maleic anhydride
(c) Glyoxal
(d) Benzoic acid

48. When toluene reacts with chlorine in sunlight, the first major product is

(a) Benzyl chloride
(b) Benzal dichloride
(c) O-chlorotoluene
(d) O-chlorotoluene and P-chlorotoluene

49. Which one of the following will be sulphonated readily

(a) Chlorobenzene
(b) Toluene
(c) Nitrobenzene
(d) Benzene

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50. Which one of the following is not a good leaving group

(a) HSO_4^- (b) Cl^-

(c) OH^- (d) Br^-

51. When CO_2 is made to react with ethyl magnesium iodide in dry ether followed by acid hydrolysis yields

(a) Propane (b) Propanal

(c) Propanoic acid (d) Propanol

52. The process of fermentation involves all the enzymes except

(a) Diastase (b) Invertase

(c) Zymase (d) Sucrase

53. Ethyl chloride on reduction in the presence of Zn/HCl produces

(a) n-butane (b) Ethanol

(c) Ethane (d) Diethyl ether

54. Which one does not exhibit aldol condensation

(a) Ethanal (b) Acetone

(c) Benzaldehyde (d) Butanone

55. For industrial preparation of CH_3CHO catalytic promoter is

(a) $PdCl_2$ (b) Cu_2Cl_2

(c) $CuCl_2$ (d) $PbCl_2$

56. The common name of propane -1,3-dioic acid is

(a) Oxalic acid (b) Succinic acid

(c) Malonic acid (d) Fumaric acid

57. Which of the following is not a fatty acid

(a) Propanoic acid (b) Acetic acid

(c) Phthalic acid (d) Butanoic acid

58. Industrial materials, thermal power stations are coated with

(a) Polyester resins (b) Epoxy paints

(c) polyamide resins (d) Polyvinyl chloride

59. Which one of the following fertilizers provides the nitrogen and phosphorus to the plant

(a) Urea (b) Calcium superphosphate

(c) Diammonium phosphate (d) Potassium nitrate

60. Chlorination of water may be harmful if the water contains

(a) Ammonia (b) Dissolved oxygen

(c) Carbon dioxide (d) All of these

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Part - I

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Chapter 1

BASIC CONCEPTS

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ATOM

The smallest particle of an element which may or may not have an independent existence is called an atom.

May exist independently

Examples

Monoatomic gases

- Helium (He)
- Neon (Ne)
- Argon (Ar)

Atom is made up of more than 100 sub-atomic particles e.g.

Electron, Proton, Neutron → fundamental

Hypron, Neutrino → sub-atomic

May not exist independently

Examples

- Hydrogen (H_2)
- Oxygen (O_2)
- Nitrogen (N_2)

(a) HISTORICAL BACK GROUND

Scientist	Contribution
Democritus (Greek Philosopher)	He presented the concept of atom (atomos) means indivisible.
John Dalton (English School Teacher)	1- He recognized that law of conservation of mass and the law of definite proportion could be explained only by the existence of atoms. 2- He also presented his atomic theory
J.Berzelius (Swedish Scientist)	He determined the atomic masses of various elements and introduced the concept of their symbols

(b) EVIDENCE OF ATOM

Atom is very small particle and it is not possible to see an atom but evidence of its presence in an element can be seen by the following ways.

(i) Electron Microscopy

In electron microscope, the beam of electrons is used electron microscopic photograph of a piece of a graphite magnified about 15 millions times. The bright band in the figure are layers of carbon atoms.

(ii) By X-rays Diffraction Method

X rays diffraction pattern obtain from diffractometer has made us able to believe the existence of an atom.

(c) OTHER STRIKING INFORMATIONS RELATED TO ATOM

(i) Size of atom

According to x-rays study.

- The diameter of an atom is of the order 2×10^{-10}m (0.2nm)
- If atoms are joined together in a line, two million atoms will be required to cover a full stop

(ii) Mass of an atom

The mass of an atom ranges from $10^{-27} - 10^{-25}$kg or $10^{-24} - 10^{-22}$g).

(iii) Atomic Mass Unit

The unit used to express the relative atomic mass is called atomic mass unit (amu) and it is 1/12 of the mass of one atom of C-12.

1 a.m.u = 1.661×10^{-27}kg.

1 a.m.u = 1.661×10^{-24}g.

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MOLECULE

- The smallest particle of a pure substance which can exist independently is called molecule. It may contain one or more atoms of same element (homoatomic) or different elements (hetroatomic).

(a) Atomicity

The number of atoms present in a molecule is called its atomicity.

Homo-atomic		Hetero-atomic	
Atomicity	Examples	Atomicity	Examples
1 (monoatomic)	He, Ne, Ar	2 (diatomic)	NO, CO
2 (diatomic)	H_2, O_2, N_2	3 (polyatomic)	NO_2, H_2O, SO_2
3 (polyatomic)	O_3	4 (polyatomic)	NH_3, SO_3, H_2O_2
4 (polyatomic)	P_4	5 (polyatomic)	CH_4, HNO_3
8 (polyatomic)	S_8, Se_8, Po_8	7 (polyatomic)	H_2SO_4

- **Macromolecules**
  Haemoglobin, Starch, cellulose, diamond, silica proteins and lipids etc.

(c) Size of molecules

Size of molecules depends upon the following factors

- Number of atoms in a molecule (atomicity)
- Size of atom
- Shape of molecule

ION

The charged species which are formed by the loss or gain of one or more electrons are called ions.

- In case of mono-atomic ions cations are more abundant than anions
- In case of poly atomic ions anions are more abundant than cations.
- In case of molecular ions cations are more abundant than anions.

Types of Ions

Cations	Anions
Cation is formed by the loss of one or more electrons as a result of oxidations. e.g. $A \xrightarrow{\text{oxidation}} A^{\oplus} + e^-$	Anions is formed by the gain of one or more electrons as a result of reduction. $B + e^- \xrightarrow{\text{reduction}} B^-$
Formation of cation is always an endothermic process.	Formation of uni-negative ion is exothermic but formation of all other negative ions is endothermic
A cation may carry +1,+2,+3 etc.	A anion may carry –1,-2,-3 etc.
Size of cation is smaller than its parent atom.	Size of anion is greater than its parent atom.

MOLECULAR ION

The charged molecular species formed by the loss or gain of electron are called molecular ions.

Types of molecular ion

(a) Cationic molecular ion $(CH_4^{\oplus}, CO^{\oplus}, N_2^{\oplus})$

(b) Anionic molecular ion $(CH_3)_3C^-$

POINT TO BE REMEMBERED

- Number of cationic molecular ions is greater than the number of anionic molecular ions.

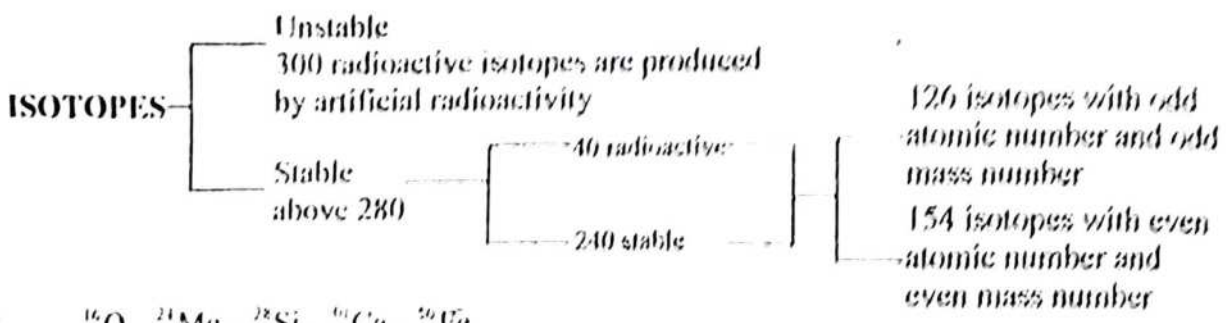
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ISOTOPES

Atoms of the same element having different mass number are called isotopes. The concept of isotopy was introduced by Soddy.

Occurrence

Elements occur in the nature in the form of isotopes. Occurrence of isotopes has been shown here.



- $^{16}_{8}O$, $^{24}_{12}Mg$, $^{28}_{14}Si$, $^{40}_{20}Ca$, $^{56}_{26}Fe$ form nearly 50% of the earth crust.

SIMILARITIES AND DISSIMILARITIES IN ISOTOPES OF ELEMENTS

Similarities	Dissimilarities
Same,	Different,
• Atomic number	• Mass number
• Number of Protons	• Number of Neutrons
• Electronic configuration	• Physical properties
• Position in periodic table	• Half life
• Chemical properties	• Rate of reaction

CLASSIFICATION OF ELEMENTS ON THE BASIS OF ISOTOPES

Basis	Examples
• Mono-isotopic elements	F, I, As, Au
• Di-isotopic elements	Cl, Br
• Tri-isotopic elements	H, O, N
• Tetra-isotopic elements	S
• Penta-isotopic elements	Ni
• Hexa isotopic elements	Cu, Pd
• Nano isotopic elements	Cd
• Undeca isotopic elements	Sn

TERMINOLOGY RELATED TO ISOTOPES

1. Mass number
2. Relative abundance

MASS SPECTROMETER

An instrument which is used to measure the exact masses of different isotopes of an element together with their relative abundances is called mass spectrometer.

Types of mass spectrometer

- Aston's mass spectrometer

It was designed to identify isotopes of an element on the basis of atomic masses.

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- Dempster's mass spectrometer
  It was designed to identify isotopes of an element which are in the solid state. It has five parts.

Parts of Spectroscope

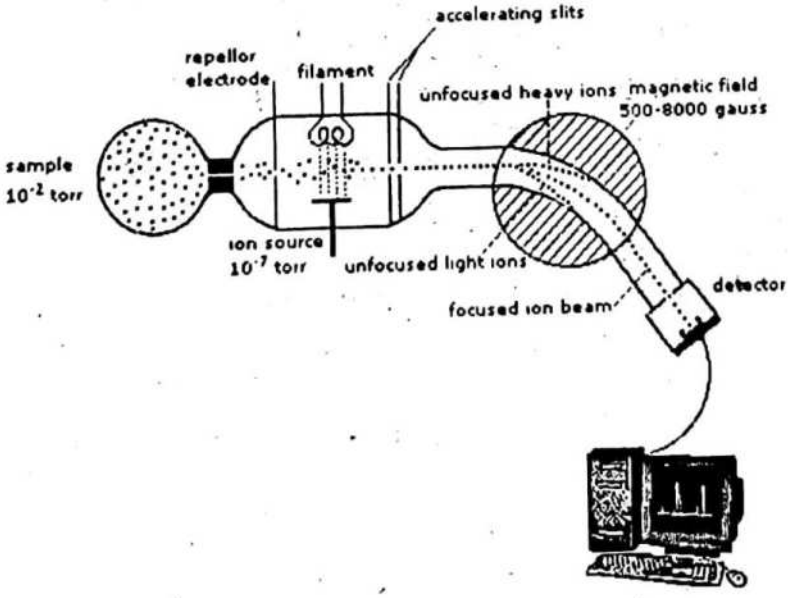
- Vaporization chamber
- Ionization chamber
- Electric field
- Magnetic field
- Ion collecter
- Recorder
- Amplifier

The first five parts are present in Dempster's Mass Spectrometer while last two parts are present in Modern Spectroscope.

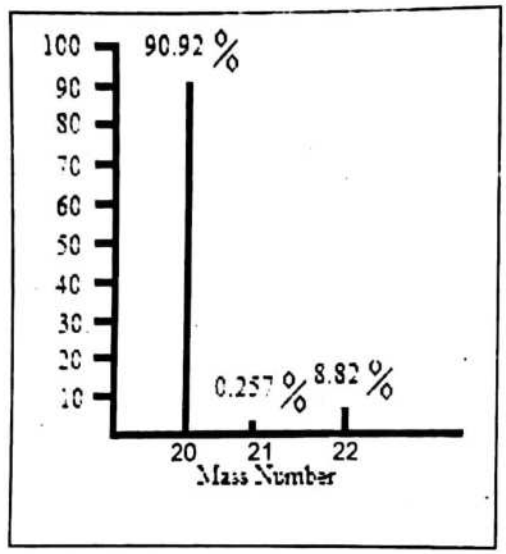
Instrumentation of Dempster's mass spectrometer

It has following five main parts.

Stages	Function
Vapourization chamber	In this chamber the sample of the element is vapourized. In this chamber the vapour pressure is reduced to 10^{-7}-10^{-6}torr
Ionization chamber	In this chamber sample of the element is ionized either by α-rays or by electron beam. $e^- + X \rightarrow X^{\oplus} + e^- + e^-$
Electric field	Electric field is applied to accelerate the positive ions. The applied potential difference is of 500-2000 volts.
Magnetic field	On passing through magnetic field, deflection of positive ions takes place according to their mass/charge ratio. $\frac{m}{e} = \frac{H^2r^2}{2E}$
Electrometer or ion collector	Ion collector receives positive ions according to their mass/charge ratio related to isotopes. 1- The strength of current measured by ion collector gives the relative abundance of ions of a definite m/e value. 2- The same experiment is performed with C-12 isotopes and the current strength is compared.



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Computer plotted graph for the isotopes of Neon (Ne)

OTHER TECHNIQUES FOR THE SEPARATION OF ISOTOPES

- Gaseous diffusion
- Thermal diffusion
- Distillation
- Ultra centrifuge
- Electromagnetic separation
- Laser separation

RELATIVE ATOMIC MASS

Relative atomic mass is the mass of an atom of an element as compared to the mass of an atom of carbon taken as 12.

Chlorine

Isotopes	$^{35}_{17}Cl$	$^{37}_{17}Cl$
Relative abundance	75%	25%

$$\text{Relative atomic mass of Cl} = \frac{35 \times 75 + 37 \times 25}{100}$$

Relative atomic mass = 26.25 + 9.25 = 35.5 amu

Neon

Isotopes	$^{20}_{10}Ne$	$^{21}_{10}Ne$	$^{22}_{10}Ne$
Relative abundance	90.92%	0.26%	8.82%

$$\text{Relative atomic mass of Neon} = \frac{20\times90.92+21\times0.26+22\times8.82}{100} = 20.18\,\text{amu}$$

ANALYSIS OF A COMPOUND

Qualitative analysis

Identification of types of elements present in a compound present in a compound.

Quantitative analysis

Determination of ratio between the masses of all the elements.

METHODS TO DETERMINE PERCENTAGE COMPOSITION

(a) Percentage composition

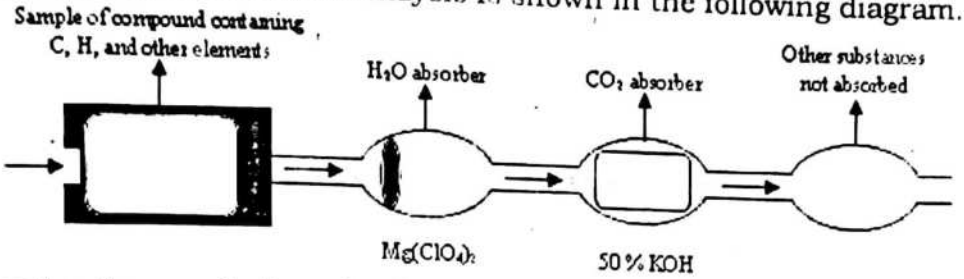
The percentage composition obtained from a given formula of a compound is called theoretical percentage composition.

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$$\%\text{age of an element} = \frac{\text{Number of atoms} \times \text{at.mass of element}}{\text{molecular formula of the compound}} \times 100$$

(b) Combustion analysis

The sequence of combustion analysis is shown in the following diagram.



- By combustion analysis only those organic compounds can be analyzed which simply contain carbon, hydrogen and oxygen.
- From the masses, percentages are calculated by using the following formulae:-

(a) $$\%\text{age of carbon} = \frac{\text{mass of } CO_2 \text{ obtained in experiment}}{\text{mass of organic compound}} \times \frac{12.01}{44.01} \times 100$$

(b) $$\%\text{age of hydrogen} = \frac{\text{mass of } H_2O \text{ obtained in experiment}}{\text{mass of organic compound}} \times \frac{2.0}{18.0} \times 100$$

(c) %age of oxygen = 100 – (% of carbon + % of Hydrogen)

DIFFERENCE BETWEEN EMPIRICAL AND MOLECULAR FORMULA

Empirical formula	Molecular formula
A formula which represents the simple whole number ratio of atoms of elements in a compound is called empirical formula.	A formula which represents actual number of atoms of each elements in a molecular compound is called molecular formula.
It is obtained from %age composition of elements i.e. chemical analysis	It is obtained by multiplying 'n' with empirical formula
This term is used for both molecular and ionic compounds	This term is used only for molecular compounds
Examples: NaCl, CH_2O, CH are empirical formulae of sodium chloride, glucose and benzene respectively.	Examples: $C_6H_{12}O_6$ and C_6H_6 are molecular formulae of glucose and benzene respectively.

Note:-

The term empirical formula is used for ionic compounds and giant covalent structures (sand SiO_2, graphite & diamond C). It is also used for covalent compounds as CH_2O for glucose and acetic acid.

RELATIONSHIP BETWEEN EMPIRICIAL AND MOLECULAR FORMULA

Molecular formula = n × empirical formula

MOLE

The atomic mass of an element, relative molecular mass of covalent compound or formula mass of ionic compound expressed in grams is called mole.

Examples

(i) Atomic mass of Na = 23.0 amu
1 mole of Na = 23.0g
(gram atom of Na)

(ii) Molecular mass of H_2O = 18.0 amu
1 mole of H_2O = 18.0g

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(gram molecule)

(iii) Formula mass of NaCl = 58.5 amu
1 mole of NaCl = 58.5g
(gram formula)

DETERMINATION OF MOLE

There are three main methods to determine number of moles of a substance.

1- When mass of substance is given in grams.

$$\text{No of moles of substance} = \frac{\text{mass in grams of given substance}}{\text{atomic mass/molecular mass/formula mass}} \quad = \frac{m}{M}$$

2- For a certain number of particles (atoms, ions or molecules)

$$\text{Number of moles of a substance} = \frac{\text{Number of particles of given substance}}{6.022\times10^{23}} \quad = \frac{N}{N_A}$$

3- For volume of a given gas in dm^3 at STP.

$$\text{Number of moles of gas} = \frac{\text{Volume of gas in } dm^3 \text{ at STP}}{22.4\times dm^3} \quad = \frac{V}{V_n}$$

One mole	**Particles**	6.022×10^{23} Atoms	6.022×10^{23} Molecules	6.022×10^{23} Formula Units	6.022×10^{23} Ions
	Mass	Gram Atomic Mass of Element	Gram molecular Mass of substance	Gram Formula Mass of formula unit	Gram Ionic Mass of ion
	Volume	At S.T.P (of gas) = 22.4 dm^3			

AVOGADRO'S NUMBER

It is the number of particles (atoms, ions or molecules) present in one mole of a substance. It is denoted by N_A. Its value is 6.022×10^{23}.

Examples

(i) Atomic mass of Na = 23.0 amu
1 mole (23.0g) of Na = 6.022×10^{23} atoms

(ii) Molecular mass of H_2O = 18.0 amu
1 mole (18.0g) of H_2O = 6.022×10^{23} molecules

(iii) Formula mass of NaCl = 58.5 amu
1 mole (58.5g) of NaCl = 6.022×10^{23} formula units

MOLAR VOLUME

One mole of an ideal gas at standard temperature and pressure (STP) occupies a volume of 22.414dm^3. This volume of 22.414dm^3 is called molar volume and its true only when the gas is ideal. With the help of this information, we can convert the mass of a gas at STP into its volume and vice versa.

Hence we can say that

(i) 2.016g of H_2 = 1 mole of H_2 = 6.02×10^{23} molecules of H_2 = 22.414dm^3 of H_2 at STP.

(ii) 16g of CH_4 = 6.02×10^{23} molecules of CH_4 = 22.414dm^3 of CH_4 at STP.

Point to be remembered: - It is very interesting to know from the above data that 22.414dm^3 of each gas has a different mass but the same number of molecules with few exceptions like N_2 and CO that have same masses, same number of atoms and same number of molecules in 22.414dm^3 at STP.

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Reason:- The masses and the sizes of the molecules don't affect the volume. Normally, it is known that in the gaseous state the distance between molecules is 300 times greater than their diameters.

STOICHIOMETRY

Stoichiometry is a branch of chemistry, which tells us the quantitative relationship between reactants and products in a balanced chemical equation.

LIMITATION OF CHEMICAL EQUATIONS

They do not tell about the

(i) Conditions (Temperature and pressure)
(ii) Rate of reaction
(iii) Physical state of reactants and products.
(iv) Mechanism of reaction

CONDITIONS FOR STOICHIOMETRIC CALCULATIONS

Stoichiometeric calculations are based on the following conditions:-

1- All the reactants must be completely converted into the products.
2- The side reaction must not occur.
3- The law of conservation of mass and the law of definite proportions must be obeyed while doing the calculations.

The following types of relationship can be studied with the help of a balanced chemical equation.

$$\underset{\text{2-moles}}{2H_{2(g)}} + \underset{\text{1-mole}}{O_{2(g)}} \longrightarrow \underset{\text{2-moles}}{2H_2O_{(g)}}$$

4g	32g	36g
$44.828dm^3$	$22.414dm^3$	$44.828dm^3$

(1) Mass-mass Relationship

If we are given the mass of one substance, we can calculate the mass of the other substance.

(2) Mass-mole Relationship or Mole-mass Relationship

If we are given the mass of one substance, we can calculate the moles of other substance and vice versa.

(3) Mass-volume Relationship

If we are given the mass of one substance, we can calculate the volume of the other substances and vice versa.

(4) Mole-mole Relationship

If we are given the mole of one substance, we can calculate the mole of the other substances and vice versa.

LIMITING REACTANT

Limiting reactant is a reactant that controls the amount of the products formed in a chemical reaction due to being less than the required amount. It can also be defined as follow: -

1- It is a reactant that produces least number of moles of product.
2- It is consumed earlier in the reaction.

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Identification of Limiting Reactant

To identify a limiting reactant, the following three steps are performed.

1- Calculate the number of moles from the given amount of reactants.

2- Calculate the number of moles of product formed from the given moles of each reactant.

3- Identify the reactant as limiting reactant which produces least moles of product.

YIELD

The amount of the product obtained as a result of the chemical reaction is called yield.

Types of Yield

(a) Theoretical Yield

The amount of the product calculated from the balanced chemical equation is called the theoretical yield.

(b) Actual Yield

The amount of the product obtained in a chemical reaction experimentally is called actual yield.

(c) Percentage Yield

$$\% \text{ yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

Point to be remembered: - Actual yield is always less than theoretical yield.

Reasons:-

(i) A practically inexperienced worker has many shortcomings and cannot get the expected yield.

(ii) The processes like filtration crystallization if not properly carried out, decrease the theoretical yield.

(iii) Some of the reactants might take part in a competing side reaction and reduce the amount of the desired product.

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PRACTICE EXERCISE

30 mins Time Yourself

1. **Diameter of an atom is in the order of**
   (a) 0.2m (b) 0.2mm
   (c) 0.2nm (d) 0.2pm
2. **Which of the following are isoelectronic species?**
   (a) H^+, H, H^- (b) Li^+, Na^+, K^+
   (c) Cl^-, Br^-, I^- (d) F^-, Ne, Na^+
3. **Mass spectrometer is used to determine Mass number of isotopes and**
   (a) Atomic number (b) Relative abundance
   (c) Electronic configuration (d) All of the above
4. **Molecular ions are formed by passing**
   (a) High energy electron beam (b) α-particle
   (c) X-rays (d) All of the above
5. **The number of peaks obtained in mass spectrometry shows**
   (a) Relative abundance (b) Average mass of element
   (c) Number of isotopes (d) Relative isotopic mass
6. **Empirical formula of chloroform is**
   (a) CH_2Cl_2 (b) CH_3Cl
   (c) CCl_4 (d) $CHCl_3$
7. **Which one is true about isotope?**
   (a) Same number of neutrons (b) Same mass number
   (c) Same physical properties (d) Same chemical properties
8. **Molecular mass of water (18g) means**
   (a) 1-mole molecules of water (b) 1-gram molecule of water
   (c) 3-gram atoms (d) All
9. **Which of the following ion formation is always exothermic?**
   (a) Uni-negative (b) Uni-positive
   (c) Di-negative (d) Di-positive
10. **Which of the following statements about isotopes is correct?**
    (a) Isotopes with odd atomic number are abundant
    (b) Isotopes with odd atomic number and even mass number are abundant
    (c) Isotopes with even atomic number and even mass number are abundant
    (d) Isotopes with even atomic number and odd mass no are abundant
11. **The sample of isotopes of an element which needs not to be vaporized in the vaporization chamber**
    (a) Gas (b) Liquid
    (c) Volatile solid (d) All
12. **One mole of CO_2 contains**
    (a) 6.022×10^{23} atoms of oxygen (b) 22-gram electrons
    (c) $6\ 022 \times 10^{23}$ atoms of carbon (d) Both 'B' and 'C'
13. **Avogadro's number may represent**
    (a) Volume of particles (b) Number of particles
    (c) Mass of particles (d) All of the above
14. **The number of isotopes of elements with even mass number and even atomic number are**
    (a) 280 (b) 300
    (c) 154 (d) 54
15. **Size of molecule depends upon**
    (a) Atomicity (b) Shape of molecule
    (c) Both a and b (d) Difficult to predict

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16. **Which of the following terms is not used for ionic compound?**
(a) formula unit (b) empirical formula
(c) molecular formula (d) formula mass

17. **0.36 moles of each aluminium and oxygen react with each other to produce aluminium oxide. The amount of product formed is**
(a) 0.18mole (b) 0.27mole
(c) 0.24mole (d) 0.09mole

18. **Which of the following terms is used for the mass of chlorine 35.5?**
(a) relative atomic mass (b) mass number
(c) atomic weight (d) relative isotopic mass

19. **Which one of the following has the maximum number of isotopes?**
(a) oxygen (b) carbon
(c) tin (d) chlorine

20. **Which one of the following is not the mono isotopic element?**
(a) arsenic (b) uranium
(c) iodine (d) Aurum

21. **The volume occupied by 2.8 g of N_2 at STP**
(a) 2.24 dm^3 (b) 22.4 dm^3
(c) 1.12 dm^3 (d) 112 cm^3

22. **The mass of decimole of electrons is**
(a) 1.008 mg (b) 0.184 mg
(c) 0.054 mg (d) 5.4 mg

23. **The number of moles of CO_2 which contains 16 g of oxygen is**
(a) 0.25 (b) 0.50
(c) 0.75 (d) 1.00

24. **Which of the following statements is wrong about isotopes?**
(a) they possess different mass number
(b) they possess different physical properties
(c) they possess same chemical properties
(d) they possess different position in the periodic table

25. **How many isotopes have odd atomic number?**
(a) 154 (b) 280
(c) 126 (d) 300

26. **Qualitative analysis is carried out for**
(a) Identification of elements (b) Estimation of amounts of elements
(c) Molar ratio of elements (d) Molar volume of elements

27. **Percentage of oxygen in calcium carbonate is**
(a) 80% (b) 64%
(c) 48% (d) 40%

28. **Combustion analysis is performed to determine**
(a) Empirical formula (b) Molecular mass
(c) Molecular formula (d) Formula mass

29. **Mostly elements have fractional atomic masses because of**
(a) mass of an atom itself is in fraction
(b) atomic masses are average masses of isobars
(c) atomic masses are average masses of isotopes proportional to their relative abundance
(d) atomic masses are average masses of isotopes

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30. **Isotopes differ in**
(a) properties which depend upon mass
(b) arrangement of electrons in orbitals
(c) chemical properties
(d) all of the above

31. **Which of the following is not a macromolecule?**
(a) sand
(b) haemoglobin
(c) diamond
(d) maltose

32. **Which of the following methods is used to estimate hydrogen in an organic compound?**
(a) Combustion method
(b) Duma's method
(c) Kjeldahl's method
(d) All of the above methods are for different purposes

33. **Isotopes of the same elements has**
(a) different number of protons
(b) same number of neutrons
(c) different number of neutrons
(d) same mass number (nucleon number)

34. **The nucleus of an atom of every element will always contain**
(a) neutrons
(b) protons and electrons
(c) protons
(d) protons and neutrons

35. **When cationic molecular ions are allowed to pass through strong magnetic field in mass spectrometer, which of the following ions is fallen first?**
(a) lighter
(b) intermediate
(c) heavier
(d) are collected at same time

36. **When 0.5 mole of phosphoric acid is dissolved in aqueous solution, how many moles of –ve and +ve ions are collected altogether?**
(a) 0.5
(b) 1.0
(c) 1.5
(d) 2.0

37. **For which of the following compounds the term empirical formula cannot be applied?**
(a) NaCl
(b) H_2O
(c) CCl_4
(d) It can be applied to all mentioned above

38. **Dempsters mass spectrometer has number of zones/parts**
(a) 5
(b) 4
(c) 3
(d) 2

39. **The properties of an element mostly corresponds to that isotope which has greater**
(a) Mass number
(b) Atomic mass
(c) Relative abundance
(d) All of the above

40. **1 a.m.u = _____**
(a) 1.6×10^{-27} Kg
(b) 1.6×10^{-24} Kg
(c) 1.6×10^{-26} Kg
(d) 1.6×10^{-28} Kg

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Chapter 2

EXPERIMENTAL TECHNIQUES IN CHEMISTRY

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ANALYTICAL CHEMISTRY

The branch of chemistry which gives a complete chemical characterization (both qualitative and quantitative analysis) of a compound is called analytical chemistry.

QUALITATIVE ANALYSIS

The analysis in which the detection or identification of the elements present in a compound is carried out is called qualitative analysis.

Examples

(i) Salt analysis
(ii) Detection of functional groups

QUANTITATIVE ANALYSIS

The analysis in which relative amounts of the elements are determined is called quantitative analysis.

Example:-

Volumetric analysis.

STEPS FOR QUANTITATIVE ANALYSIS

(i) Obtaining a sample for analysis.
(ii) Separation of desired constituents.
(iii) Measurement and calculation of results.
(iv) Drawing conclusion from the analysis.

Method of purification	Application
Filtration	Separation of soluble and insoluble solids
Evaporation	Separation of a soluble solid from the solution
Crystallization	Separation of a solid by cooling either its solution or molten liquid
Decanting and Centrifuging	Separation of suspension
Simple distillation	Separation of a liquid from a solution
Fractional distillation	Separation of a fraction from a mixture of miscible liquids
Separating funnel	Solvent extraction from the solution.
Sublimation	Separation of sublimant from mixture of solids
Chromatography	Separating colours, dyes, amino acid, etc

FILTRATION

This process is used to separate insoluble particles from liquids and it can be performed with several types of filter media.

METHODS OF FILTRATION

(i) Filtration through filter paper
(a) Ordinary filter paper
(b) Fluted filter paper

(ii) Filtration through filter crucibles
(a) Gooch crucible
(b) Sintered glass crucible

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Filtration through filter paper Slow process	Filtration through crucible Fast process
▪ Solvent passes through filter paper and insoluble particles remains on filter paper. ▪ Filter papers are classified on their size of pores. ▪ Filter paper should be filled with ppt. upto 1/4 - 1/2. ▪ Tip of stem should be in touch of beaker to avoid any splashing. ▪ Fluted filter paper is obtained by folding normal filter paper in such a way that a fan like with alternate elevations and depressions is obtained.	Two types of crucibles are available 1. Gooch crucible ▪ Made up of porcelain clay ▪ Perforated bottom is covered by paper pulp or filter paper ▪ Used for filtration of those ppts. which need to be ignited at high temperature. ▪ Asbestos is used instead of filter paper for those chemicals, which have a reaction with paper. 2. Sintered glass crucible ▪ Made up of glass ▪ Porous glass disc in bottom act as sieve. (filter medium)

DIFFERENCE BETWEEN GOOCH AND SINTERED GLASS CRUCIBLE

Gooch Crucible	Sintered Glass Crucible
• It is made up of porcelain. • It has a porous base. • Its base needs to be covered with a filter paper or an asbestos mat. • Reactive solutions like HCl, $KMnO_4$ can not be filtered if base is covered with filter paper. • To filter the reactive solutions, base is covered with asbestos mat. • There is contamination of filter paper with the crystals.	• It is made up of glass. • In its base sintered glass disc is sealed. • There is no need to cover the base with filter paper or asbestos mat. • Reactive solutions can safely be filtered. • There is no need of any alteration. • There is no contamination.

CRYSTALLIZATION

Separation of solid as crystals when hot saturated solution is cooled is called crystallization.

Choice of solvent

- Solvent is selected by hit and trial method.
- Suitable solvent dissolves excess of solute at high temperature and less amount of solute at room temperature.
- Solvent should not react with solute.
- Impurities should not be dissolved in solvent, if they get dissolved then should not be separated out as crystals along with solute.
- On cooling, it should deposit well formed crystals of pure compound.
- It should be cheaper.
- It should be safe and should be easily removable.

Solvents for Crystallization

Mostly used solvents are water, rectified spirit, ethanol, diethyl ether, acetone etc.

NOTE:-

If single solvent is not found suitable then combination of two or more solvents can be employed.

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Precaution

If solvent is inflammable then water bath is used for heating purposes so that it does not catch the fire.

PREPARATION OF SATURATED SOLUTION

The solute is dissolved in minimum amount of solvent at its boiling point to form a saturated solution.

Filtration

- Fluted filter paper or normal filter paper is used for the filtration of a hot solution.
- The filtration of a hot solution avoids premature crystals

Cooling

- Solution is cooled down at moderate rate crystals of pure compound will be produced.

Collection of crystals

- Gooch crucible is used for the separation of crystal.

Drying of crystallized substances

- Drying can be done by placing the crystals between the folds of filter paper.
- Drying can be done by heating the crystals in oven.
- Vacuum dessicator is used to dry the crystals
- $CaCl_2$, P_2O_5 and Silica gel are used in dessicator to absorb moisture.

Decolorization of undesirable colours.

- Crystals with deposition of coloring matter or resinous products are dissolved in solvent and boiled
- Solvent contains animal charcoal, which will adsorb colour.
- The solution is filtered in hot state.
- Moderate cooling is carried out.
- Crystals of pure substance will be separated out.

SUBLIMATION

The process in which, solid when heated, vapourizes directly without passing through the liquid phase is called sublimation.

Examples

(i) naphthalene	(ii) iodine	(iii) ammonium chloride
(iv) benzoic acid	(v) camphor	(vi) anthracene
(vii) anthraquinone	(viii) hexachloroethane	

SOLVENT EXTRACTION

Solvent extraction technique involves the separation of a solute from a solution by shaking the solution with an immiscible solvent in which the solute is more soluble. This technique is mostly applied to separate organic compounds from water.

Distribution Law or Partition Law

A solute distributes itself between two immiscible liquids in a constant ratio of concentrations irrespective of the amount of solute added.

Steps for Solvent Extraction

(i) Take a solution containing solute e.g. (I_2 dissolved in H_2O + KI system in the form of I_3^-) in a separating funnel.

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(ii) Add small amount of an immiscible solvent (e.g. CCl_4) in the separating funnel
(iii) Shake them well.
(iv) Separate the CCl_4 layer
(v) Evaporate the organic solvent to get dried crystals.
Repeat steps (ii) to (v) again and again for better extraction.

CHROMATOGRAPHY

The word chromatography originates from the Greek word "Khromatos" meaning colour writing.

A technique used for the separation of components of a mixture which involves the distribution of a solute between stationary phase and mobile phase is based on partition law or distribution law.

Stationary Phase

- It may be solid or liquid
- It may be packed in a column
- It may be spreaded as a layer or distributed as a film
- Examples:- Silica gel, alumina etc.

Mobile Phase

- It is also called eluent
- It competes with stationary phase for components of the mixture
- Examples:- Water, ethanol, acetic acid, acetone or a gas etc.

Principle of chromatography

The principle involved in chromatography depends upon the relative solubilities of the components between two phases. It is governed by distribution coefficient (K_D).

Classification of Chromatography

It can be classified in three ways:-

1- On the basis of shape
2- On the basis of phase
3- On the basis of mechanism

The Russian Botanist Mikhail Tswett was the first to understand the basis of chromatography and to apply it systematically as a method of separation.

Difference between adsorption and partition chromatography

Adsorption Chromatography	Partition Chromatography
1. The type of chromatography in which physical forces are involved in retentive ability of solute particles with stationary phase is called adsorption chromatography.	1. The type of chromatography in which separation involves distribution of the components is called partition chromatography.
2. In adsorption chromatography, a solid is used as stationary phase.	2. In partition chromatography, liquid or liquid supported on solid act as stationary phase.
3. Examples:- Column chromatography, thin layer chromatography (TLC).	3. Example:- Paper chromatography.

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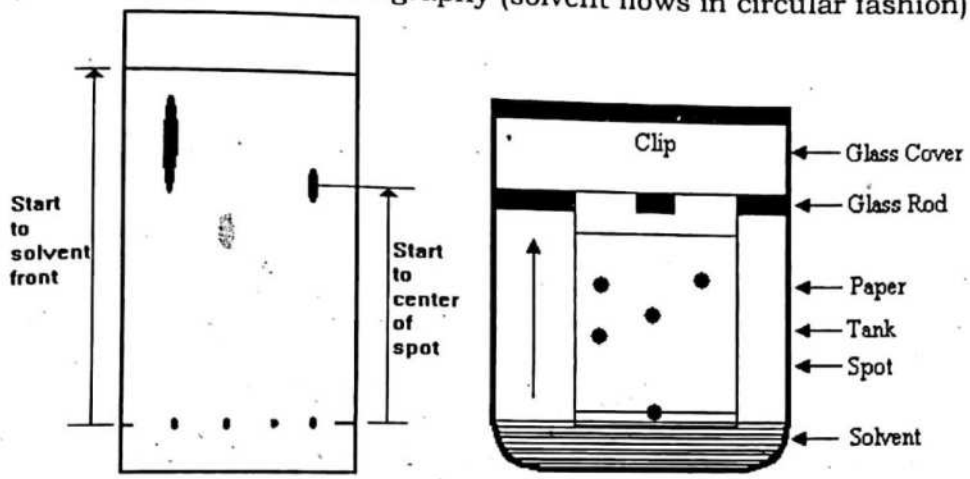
Paper Chromatography

In 1944, Consden Gordon and Martin introduced paper chromatography.

Different ways of paper chromatography

There are three common ways of carrying out this technique:-

1- Ascending paper chromatography (solvent rises up)
2- Descending paper chromatography (solvent flows down)
3- Radial/circular paper chromatography (solvent flows in circular fashion)



Uses of Chromatography

1- Separation and identification of coloured pigments.
2- Identification of medicines and proteins.
3- Analysis of urine.
4- Determination of purity of compounds.
5- Used in organic synthesis for separation, isolation and purification of the products.
6- Equally important in qualitative and quantitative analysis.

IMPORTANT DEFINITIONS AND TERMINOLOGIES

Soluble	A substance that is dissolved.
Insoluble	A substance that is not dissolved.
Solute	Normally a solid, which gets dissolves.
Solvent	Normally a liquid which dissolves solute
Solution	Solute + solvent (Homogeneous mixtures)
Residue	Insoluble solid which is left over the filter media.
Filtrate	A solution that passes through the filter paper.
Crystal	A solid that reappears from the solution on cooling
Mother liquor	A solution left after crystallization
Suspension	Fine particles that are held in a liquid and do not sink to the bottom.
Distillate	Fraction that condenses after distillation.
Miscible	Liquids that mix together
Immiscible	Liquids that do not mix and which can be separated by a separating funnel
Fraction	A distillate between a certain boiling point range separated by fractional distillation
Sublimate	Condensed solid formed during sublimation

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PRACTICE EXERCISE

30 mins Time Yourself

1. **Which of the following technique is used for the separation of insoluble particles from liquids?**
   (a) Filtration (b) Crystallization
   (c) Solvent extraction (d) Chromatography
2. **Which of the following way is used for classification of chromatography?**
   (a) Shape (b) Phase
   (c) Mechanism (d) All
3. **Fluted filter paper is used to**
   (a) Filter hot solution (b) Avoid premature crystallization
   (c) Increase the rate of filtration (d) Decrease the area
4. **Safe and the most reliable method of drying crystals is through**
   (a) Filter paper (b) Vacuum desiccators
   (c) Oven (d) None of these
5. **A substance having very high vapour pressure at its melting point , on heating will show**
   (a) Melting (b) Sublimation
   (c) Decomposition (d) Condensation
6. **A process controlled by Distributive law is**
   (a) Crystallization (b) Sublimation
   (c) Solvent extraction (d) Filtration
7. **A technique of partition chromatography in which the solvent is in a pool at the bottom of container**
   (a) Adsorption chromatography (b) Ascending chromatography
   (c) Radial chromatography (d) Descending chromatography
8. **Different components of a mixture have different R_f values due to**
   (a) Polar solvent used
   (b) Combination of solvents used
   (c) Their different distribution coefficients in the solvent
   (d) Distributive law
9. **Branch of chemistry that deals with the complete qualitative and quantitative analysis of a substance is**
   (a) Stoichio chemistry (b) Physical chemistry
   (c) Analytical chemistry (d) Quantum chemistry
10. **Identification of the components of a sample is**
    (a) Quantitative analysis (b) Qualitative analysis
    (c) Stoichiometry (d) Physical chemistry
11. **Estimation of amounts of different components in a sample is**
    (a) Quantitative analysis (b) Qualitative analysis
    (c) Stochiometery (d) Physical chemistry
12. **The technique used to separate components of mixture in solid phase.**
    (a) Crystallization (b) Filtration
    (c) Sublimation (d) Solvent extraction
13. **The solid which is left over the filter paper as a result of filtration**
    (a) Insoluble particles (b) Residue
    (c) Crystals (d) Mud

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14. Size of filter paper is selected according to the amount of
(a) Solution (b) Insoluble solute
(c) Soluble solute (d) Solvent

15. Gooch Crucibles are made up of
(a) Plastic (b) Fibre
(c) Porcelain (d) Steel

16. Rate of filtration can be increased by applying gentle suction
(a) Gooch crucible (b) Filter paper
(c) Sintered crucible (d) All of the above

17. Sintered crucible is made up of
(a) Plastic (b) Glass
(c) Porcetain (d) Fiber

18. The tip of funnel should touch the wall of the breaker in order to avoid
(a) Inconsistent flow of filtration (b) Splashing
(c) Premature crystallization (d) All of above

19. Separation of a solid from its hot saturated solution by cooling is called
(a) Vapourization (b) Solvent extraction
(c) Filtration (d) Crystallization

20. In crystallization, if the solvent is inflammable then direct heating is
(a) Needed (b) Avoided
(c) Depends on temperature (d) Crystallization does not involve heating

21. Which of the following technique is simple and efficient to purify a substance
(a) Filtration (b) Sublimation
(c) Crystallization (d) Solvent extraction

22. In solvent extraction, ether is used to separate products of organic synthesis from
(a) Water (b) Iodine
(c) Hydrochloric acid (d) Gases

23. 95% ethanol is called
(a) Methylated spirit (b) Wood spirit
(c) Rectified spirit (d) Absolute alcohol

24. The use of $CaCl_2$ and P_2O_5 in the process of crystallization is as a
(a) Oxidizing agent (b) Reducing agent
(c) Drying agent (d) Colouring agent

25. Ratio of the amount of solute in organic and aqueous solvent is
(a) Retardation factor (b) Distribution co-efficient
(c) Distribution in aqueous solution (d) All statements are wrong

26. Without suction pump, filtration is
(a) Fast process (b) Slow process
(c) Rapid process (d) All are possible

27. Animal charcoal adsorbs the coloured
(a) Impurities (b) Crystals
(c) Solvents (d) Both 'A' and 'B'

28. Direct conversion of solids into vapours is called
(a) Solvent extraction (b) Sublimation
(c) Crystallization (d) Vaporization

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29. **Crystallization does not involve**
(a) Heating (b) Sublimation
(c) Cooling (d) Vaporization

30. **In CCl_4, I_2 shows**
(a) Red colour (b) Purple colour
(c) Blue colour (d) Yellow colour

31. **Repeated extraction using small portions of solvents is more**
(a) Reliable (b) Efficient
(c) Rapid (d) slow

32. **Silica gel and alumina are used as**
(a) Mobile phase (b) Stationary phase
(c) Mixed phase (d) Single phase

33. **Shaking two immiscible liquids increases**
(a) Length of contact (b) Volume of contact
(c) Area of contact (d) All of above

34. **The solvent or mixture of solvents used for separation of compounds is called**
(a) Stationary phase (b) Mobile phase
(c) Dynamic phase (d) Static phase

35. **Which is not a sublime material**
(a) Iodine (b) Benzoic acid
(c) Ammonium chloride (d) Potash alum

36. **Sintered glass is a porous material used for**
(a) Absorption (b) Adsorption
(c) Filtration (d) Sublimation

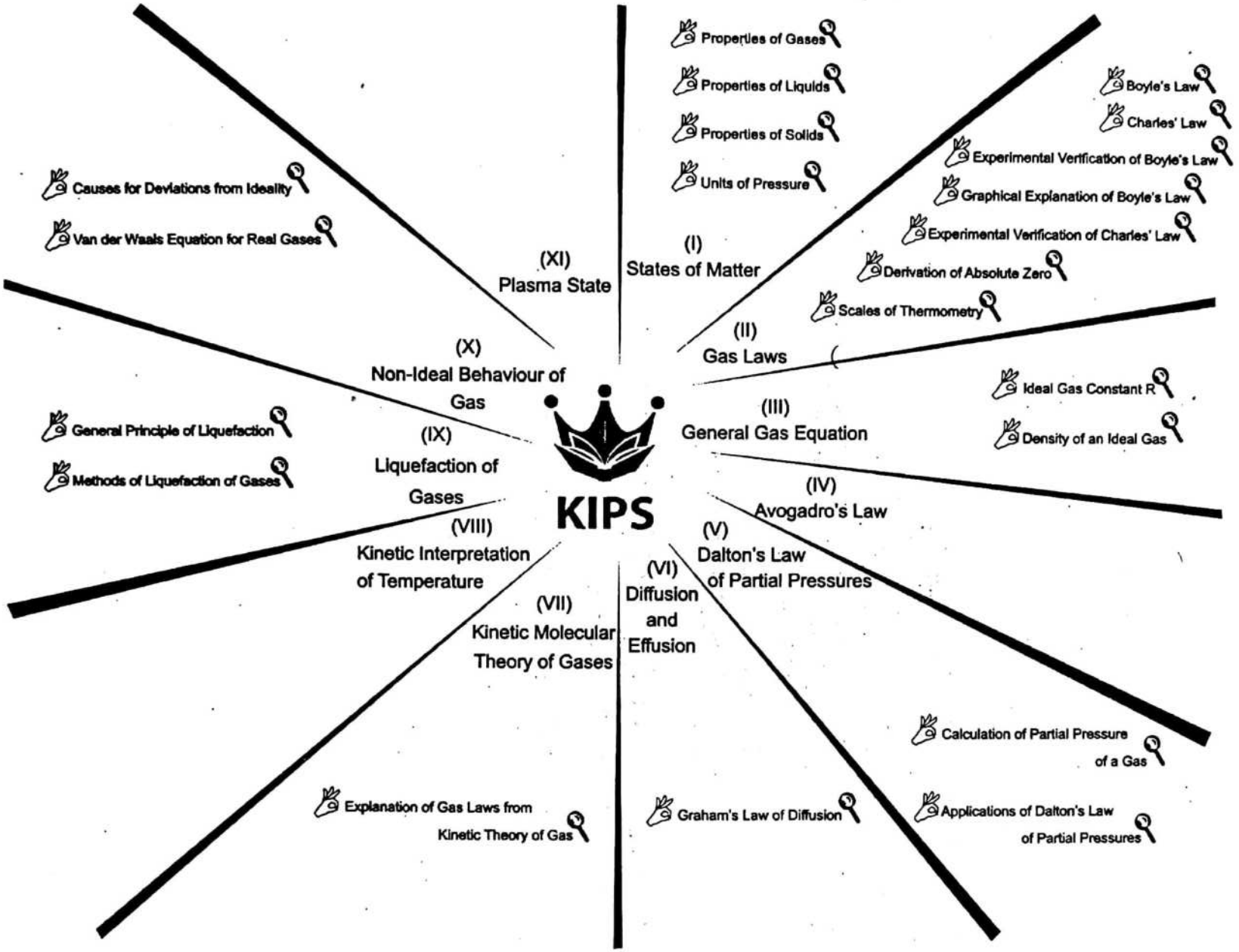
37. **Selection of filter paper depends on size of particles to be**
(a) Filtered (b) Dried
(c) Decolorized (d) Decanted

38. **The solution remaining after the formation of crystals is called**
(a) Mother liquor (b) Dilute solution
(c) Residue (d) both 'A' and 'B'

39. **Which is not related pair of term used in analytical techniques**
(a) Filtrate, residue (b) Sublimate, sublimation
(c) Drying, desiccator (d) Separating funnel, mother liquor

40. **The major steps involved in complete quantitative analysis are**
(a) 2 (b) 3
(c) 4 (d) 5

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MATTER

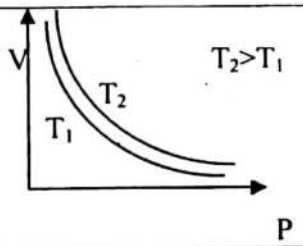
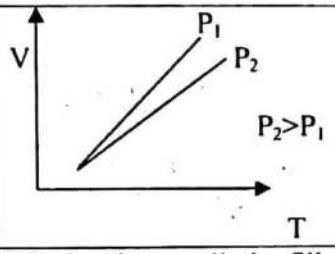
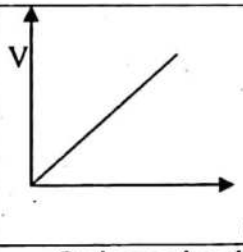
Anything which has mass and occupies space is called matter.

COMPARATIVE STUDY OF STATES OF MATTER

Gas	Liquid	Solid
Molecules are widely separated by large empty spaces.	Molecules are close to each other.	Molecules are very close to each other.
No intermolecular attractions.	Weak intermolecular attraction.	Strongest intermolecular attractions.
Molecules have very high kinetic energy.	Molecules have moderate K.E	Molecules have Very low K.E
Molecules move about easily. Hence no fixed shape and fixed volume.	Molecules slip over each other. Hence no fixed shape but fixed volume.	Molecules are closely packed. Hence fixed shape and fixed volume.
Occupy all the available space.	Volume is fixed.	Volume is fixed.
Molecules undertake translational, rotational and vibrational motion.	Molecules undertake restricted translational, rotational and vibrational motion.	Molecules undertake vibrational motion only.
The rate of diffusion and effusion is maximum.	The rate of diffusion is less than gas.	There is no diffusion and effusion in solids generally.
Particles are not arranged in a particular pattern.	Particles arrange themselves in row but do not give fixed arrangement.	Particles arrange themselves in a particular pattern in crystalline solids.
Joule's Thomson effect is shown	Absent	Absent
Effusion is present	Absent	Absent
Effective collisions are present.	Effective collisions are present.	Absent
Examples: Air, methane, ammonia	Examples: water, Alcohol. Oil	Examples: Diamond, Rock, Salt.

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GAS LAWS

Particulars	Boyle's law	Charles's law	Avogadro's law
Statement	The volume of a given mass of an ideal gas is inversely proportional to the applied pressure at constant temperature.	The volume of the given mass of an ideal gas is directly proportional to the absolute temperature at constant pressure	The volume of a given ideal gas is directly proportional to the number of moles at STP.
		The volume of given mass of a gas increases or decreases by 1/273 of its original volume at 0°C for every 1°C rise or fall in temperature at constant pressure	Equal volumes of all the ideal gases contain equal number of molecules at same temperature and pressure.
Mathematical representation	$PV=K$ or $P_1V_1=P_2V_2$	$V/T=K$ or $V_1/T_1=V_2/T_2$	$V/n=K$ or $V_1/n_1=V_2/n_2$
Graphical verification			
Experimental observation	By putting a weight on moveable piston of cylinder filled with gas. The volume of gas decreases.	On heating a cylinder filled with gases having a moveable piston. The volume of gases increases.	On increasing the number of moles of a gas in a closed cylinder. The volume increases.

GENERAL GAS EQUATION

On combining the Boyle's law, Charles's law and Avogadro's law,

$PV=K$

$V/T=K$

$V/n=K$

we get

$PV = nRT$ (R is called general gas constant)

This is called an ideal gas equation or general gas equation. This equation is completely obeyed by the ideal gases.

1-atm

The pressure of air which can support 760 mm of Hg column at sea level is called one atmospheric pressure.

1-atm
= 76 cm of Hg
= 760 mm of Hg
= 760 torr
= 14.7 psi
= 101325 Pa (Nm^{-2})
= 1:01325 Bar

Rearrangement of general gas equation

Boyle's law $PV=nRT = k$ (when "n" and "T" are constant)

Charles's law $\frac{V}{T}=\frac{nR}{P}=k$ (when "n" and "P" are constant)

Avogadro's law $\frac{V}{n}=\frac{RT}{P}=k$ (when "T" and "P" are constant)

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IDEAL GAS CONSTANT(R)

The value of R depends upon the units chosen for pressure, volume and temperature. It is independent of the nature of gas.

The value of "R" can be derived by using general gas equation.

$$PV = nRT$$
$$R = PV/nT$$

UNITS OF R

(a) When P is in atm and V in dm^3

$R = 0.0821\ dm^3\ atm\ K^{-1}\ mol^{-1}$

(b) When P is in mm Hg or torr and V in dm^3 or cm^3

$R = 62.4 dm^3\ mm\ Hg\ K^{-1}\ mol^{-1}$

$R = 62400\ cm^3\ torr\ K^{-1}\ mol^{-1}$

(c) When P is in Nm^{-2} and V in m^3 (SI units)

$R = 8.314 NmK^{-1}\ mol^{-1}$

$R = 8.314 JK^{-1}\ mol^{-1}$

$R = 1.987\ calK^{-1}\ mol^{-1}$

$1\ m^3 = 1000\ dm^3$
$1 dm^3 = 1000\ cm^3$
$1 dm^3 = 0.001\ m^3$
$1 cm^3 = 0.001 dm^3$
$1 cm^3 = 10^{-5}\ m^3$

$1 Nm = 1 J$
$1 cal. = 4.18 J$
$1 J = 0.239\ cal$
$1 J = 10^7\ ergs$

DALTON'S LAW OF PARTIAL PRESSURES

Statement

"The total pressure exerted by a mixture of non-reacting gases is equal to the sum of their individual partial pressures"

Mathematical Form

$P_{total} = P_1+P_2+P_3+$.....(At constant V and T)

Where P_1, P_2, P_3..... refer to the pressures of each individual gas.

$$P \propto n$$

RELATION WITH GENERAL GAS EQUATION

$$P_1 = n_1\left(\frac{RT}{V}\right), P_2 = n_2\left(\frac{RT}{V}\right), P_3 = n_3\left(\frac{RT}{V}\right).....$$

Since all the gases in the mixture have same temperature and pressure, So the total pressure depends only on the total moles of gases in mixture.

$$P_{Total} = (n_1+n_2+n_3+.....)\frac{RT}{V}$$

$$P_t = n_t \frac{RT}{V}$$

$$P_tV = n_t RT$$

$$P_t \propto n_t$$

The individual pressure of a gas in the mixture of gases is called its partial pressure

$$P_A = X_A P_t$$

PARTIAL PRESSURE OF A GAS

$$P_tV = n_t RT$$
$$p_AV = n_ART$$
$$p_BV = n_BRT$$
$$p_A = x_AP_t$$
$$p_A \propto X_A$$
$$p_B \propto X_B$$

Conclusion

Partial pressure of a gas is the mole fraction of that gas multiplied by the total pressure exerted by the mixture of gases.

Mole Fraction (X)

The number of moles of the component divided by the total number of moles in the mixture.

$$\text{Mole Fraction} = \frac{\text{Moles of component}}{\text{Total mole in mixture}}$$

- X of any gas in mixture is always less than unity.
- The sum of mole fractions is always equal to unity.

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Applications Of Dalton's Law

- In calculation of P_x of dry gas collected over water.
  $P_{dry} = p_{moist} - p_{w.vap}$(aqueous tension)
- In respiration (P_{O_2} in air=159torr, P_{O_2} in lung=116torr)
- In maintaining P_{O_2} in pilot cabin
- In respiratory cylinder of sea divers

Deep Sea divers use the mixture of helium 80% and oxygen 20%

GRAHAM'S LAW OF DIFFUSION

Statement

"The rate of diffusion or effusion of a gas is inversely proportional to the square root of its density or molecular mass at constant temperature and pressure."

Rate $\alpha \frac{1}{\sqrt{d}}$ (at constant temperature and pressure)

Comparing the two gases at same temperature and pressure,

The Graham's law will be

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

OR

$$(r_1/r_2 = (d_2/d_1)^{1/2}$$

Thomas Graham was Scottish chemist. He introduced this law in 1846

Diffusion
Diffusion is the mixing of different gas molecules by random motion under condition where molecular collisions occur.

Effusion
It is the escape of a gas through a pinhole without molecular collisions.

Application

The mixture of gases can be separated into their pure components by taking the advantage of the different rate of diffusion of the components.

KINETIC THEORY OF GASES (KMT)

Name of Scientist	Contribution
Bernoulli	Founder of KMT
Clausius	Derived Kinetic equation and deduced all the gas laws from KMT
Maxwell	Parented the law of distribution of velocities
Boltzman	Studied the distribution of energies among the molecules
Van der Waal	Corrected the pressure and volume factors in ideal gas equation to make it applicable to the real gases.

Postulates of kinetic molecular theory

- Every gas consists of large number of very small particles called molecules. Gases like He, Ne, Ar have mono-atomic molecules.
- The molecules of gas move haphazardly, colliding among themselves and with the walls of container changing their directions.
- The pressure exerted by the gas molecules is due to the collision of its molecules with the walls of container. The collisions among the molecules are perfectly elastic.

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- The molecules of the gases are widely separated from one another and there are sufficient empty spaces among them.
- The molecules of the gases have no forces of attraction for each other
- The actual volume of molecules of a gas is negligible as compared to the volume occupied by the gas.
- The motion imparted to the molecules by gravity is negligible as compared to the effect of the continued collisions between them
- The average kinetic energy of the gas molecules varies directly as the absolute temperature of the gas.

CLAUSIUS KINETIC ENERGY EQUATION

$$PV = \frac{1}{3}mN\overline{c^2}$$ ($\overline{c^2}$ is called mean square velocity)

RELATIONSHIP BETWEEN THE ABSOLUTE TEMPERATURE AND VELOCITIES OF GAS MOLECULES:

According to Maxwell distribution law of velocities.

- Root mean square velocity (C_{rms}) = $\sqrt{\frac{3RT}{M}}$
- Average velocity (V_{av}) = $\sqrt{\frac{8RT}{\pi M}}$
- Most probable velocity = $\sqrt{\frac{2RT}{M}}$

KIPS CREATION

Determine the average speed of a helium atom at room temp

$$C_{rms} = \sqrt{\frac{3RT}{M}}$$

$M = 4x10^{-3}Kg/mol$

CONCLUSIONS

- In gases and liquids, temperature is the measure of average translational kinetic energy of the molecules
- In solids, temperature is the measure of average vibrational kinetic energies of molecules.
- The average transnational kinetic energy of gas molecules is directly proportional to the Kelvin temperature of a gas i.e.

$$E_k \alpha T$$

- When heat flows from one body to another, the molecules in the hotter body give up some of their kinetic energy through collisions to the molecules in the colder body.

NOTE:-
Kinetic equation of gases can be employed to justify all the gas laws. In other words it proves the gas laws to get their explanation from kinetic theory of gases.

ABSOLUTE ZERO

The temperature at which motion of molecules ceases.

$0K = -273.16^{\circ}C = -459^{\circ}F$

The absolute temperature is unattainable and the current attempts resulted in temperature as low as $10^{-5}K$

LIQUEFACTION OF GASES

Liquefaction of gases is the process by which substances in their gaseous state are converted to the liquid state. When pressure on a gas is increased, its molecules come closer together, and its temperature is reduced to its critical temperature, at which P.E dominates over K.E to change it from gaseous to the liquid state.

Methods for Liquefaction of Gases

- Faraday's method (cooling is done through freezing mixture)
- Lind's method (sudden expansion of a gas to a region of low pressure)
- Claud's method (gas is allowed to do some mechanical work)

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IMPORTANT TERMS

Critical temperature	It is the highest at which a substance can exist as a liquid, is called its critical temperature (T_C).
Critical pressure	It is the pressure which is required to bring about liquefaction of a gas at its critical temperature (T_C)

Joule Thomson Effect

Sudden expansion of a gas into a region of low pressure causes cooling.

NOTE

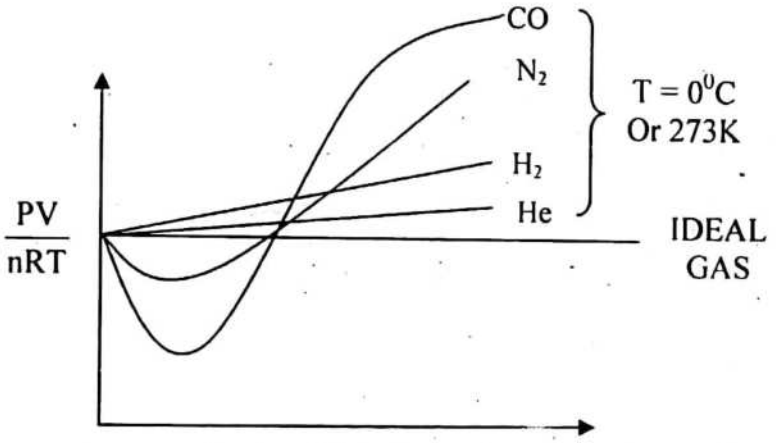
This effect is the basis of Lind's method of liquefaction.

Factors Affecting the Critical Temperature

- Size of the molecule.
- Shape of the molecule.
- Intermolecular forces among the molecules.

NON- IDEAL BEHAVIOR OF GASES

- If a graph is plotted between pressure on x-axis and the $\frac{PV}{nRT}$ (compressibility factor or Z) on y-axis for an ideal gas, a straight line parallel to the pressure axis is obtained.
- For real gases (non-ideal gases), the graph is no more parallel to the pressure axis.



- At high temperature under lo P(atm) e, the graph for real gases come closer to the expected straight line.
- If Z = 1 then line would be parallel to x-axis.
- If Z < 1 then the line obtained will be below the line of ideal gas which means that there is larger decrease in volume of the gas than predicted by general gas equation due to the appearance of attractive forces present among the molecules
- If Z > 1 then the line obtained will be above the line of an ideal gas which means that there is less decrease in the volume of the gas than predicted by the general gas equation due to appearance of repulsive forces present among the molecules

Conclusion

(i) Gases are ideal at low pressure and non-ideal at high pressure.
(ii) Gases are ideal at high temperature and non-ideal at low temperature.

VAN DER WAAL'S EQUATION FOR REAL GASES

The real gases deviate from ideal behavior due to two faulty assumptions of KMT of gases. These are;

(i) The volume of the gas molecules themselves is negligible as compared to the total gas volume.
(ii) There are no attractive forces among the molecules of a gas.

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Experimental Observation and Volume Correction

When a gas is highly compressed then the whole volume of the container is not available to molecules because of their actual volume together with their effective volume which is not negligible under this condition. So we have to exclude this volume.

Actual volume of one mole of gas molecule = V_m

Effective volume of one mole of gas molecules = b

$$b = 4V_m$$

so,

$$V_{free} = V_{vessel} - b$$

Microscopic Study of Gas and Pressure Correction

When pressure on the gas is increased and its temperature is decreased the molecules come close to each other which results in the appearance of attractive forces among gas molecules.

A molecule in the interior of a gas is attracted by the other molecules on all sides so these attractive forces are cancelled out. However, when a molecule strikes the wall of the container, it experiences a force of attraction towards the other molecules in the gas. This decreases the force of its impact on the wall. This results a decrease in pressure denoted by P'. so the observed pressure is less than the ideal pressure P_i by an amount P'.

$$P = P_i - P'$$
$$P_i = P + P'$$

For real gases, it is observed that molecules occupy only 0.05% of the total volume at STP, but at 500 atm and 0°C, the volume occupied by gas molecules is 20% of the total volume.

Molecules attract one another at distances up to about 10 molecular diameters.

Mathematical Representation

Both these corrections can be represented mathematically by the modification of the general gas equation called the van der Waal's equation.

- The increase in V caused by the effect of molecular volume is corrected by subtracting an amount nb from the observed volume. i.e.

$$V - nb$$

- The change in pressure caused by the effect of intermolecular attractions is best corrected by adding an amount an^2/v^2 to the pressure.

Correction for intermolecular attraction

Correction for molecular volume

Van der Waal's equation $\left(P+\frac{an^2}{V^2}\right)(V-nb) = nRT$

For n moles of gas $P = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$

For one mole of gs $P = (RT/V-b) - a/V^2$

Here "a" and "b" are called Van der Waal's constant.

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Units of (a)

(i) $Nm^{-4} mol^{-2}$ (S.I Units)

(ii) $atm\ dm^{6} mol^{-2}$ (other common units)

Units of (b)

(i) $m^3 mol^{-1}$ (S.I Units)

(ii) $dm^3 mol^{-1}$ (other common units)

COMPARATIVE STUDY OF REAL AND IDEAL GASES

Ideal Gases	Real Gases
Ideal gas obeys the gas laws strictly under all T and P.	They do not obey the gas laws under all condition of T and P.
Their actual volume is negligible as compared to the volume of container.	They do possess some volume that is not negligible under highly compressed state.
There are no intermolecular attractions or repulsions.	There exist negligible forces of attraction or repulsion under ordinary conditions.
The molecules of an ideal gas undergo elastic collisions.	The molecules of a real gas undergo inelastic collisions.
They can not be liquefied.	They can be liquefied at critical temperature by applying critical pressure.

PLASMA STATE

The most primitive state of matter which is ionized gas mixture consisting of ions, electrons and neutral atoms is called plasma state.

- Plasma was identified by an English scientist William Crooks in 1979.
- Plasma is estimated to constitute more than 99% of the visible universe.
- Artificial plasma can be created by using electrical charges on a gas.
- Natural plasma exist only at very high temperature or low temperatures Vacuums.
- It shows a collective response to electric and magnetic fields.
- It is macroscopically neutral.
- It has a lot of important technological applications.

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PRACTICE EXERCISE

30 mins Time Yourself

1. **What is the relative rate of effusion of CO and CO_2?**
   (a) CO is 1.25 times faster than CO_2 (b) CO is 3.75 times faster than CO_2
   (c) CO_2 is 1.25 times faster than CO (d) Both diffuse at the same rate
2. **Which of these gases diffuse more quickly than oxygen?**
   (a) H_2S (b) NO
   (c) Cl_2 (d) N_2O
3. **The molar volume of Co_2 is gas maximum at**
   (a) 273 k (b) 127°C and 1 atm
   (c) 0°C and 2 atm (d) 273°C and 2 atm
4. **The weakest (in strength) of the following intermolecular forces is**
   (a) Hydrogen bonding (b) Vander Waal's forces
   (c) Forces among the polar molecules (d) Ionic bond
5. **Ideal gasses have all the following characteristics except.**
   (a) Absence of intermolecular forces
   (b) Collisions among the molecules of an ideal gas are perfectly elastic
   (c) The molecules occupy no space
   (d) All of the above are correct
6. **Which of the following statements is true about plasma**
   (a) It may be the first state of matter. (b) It is not a phase transition.
   (c) It is a conductor of electricity. (d) All of the above
7. **Which statement is correct**
   (a) $PV_m \alpha T$ (b) $P \alpha CT$
   (c) $PM \alpha dT$ (d) All above
8. **Under what conditions the gases deviate from the ideal behavior?**
   (a) High temperature (b) Low temperature
   (c) High pressure (d) b and c
9. **Which one has the lowest density at room temperature?**
   (a) Ne (b) N_2
   (c) NH_3 (d) CO
10. **The introduction of Kelvin scale in thermometry is according to**
    (a) Boyle's law (b) Charles' law
    (c) Dalton's law (d) Graham's law
11. **0.5 mole of nitrogen gas and 0.5 mole of carbon monoxide gas at STP have same**
    (a) Value of "a" (b) Mass
    (c) Atoms (d) Both b and c
12. **At constant temperature the pressure of an ideal gas is doubled, its density becomes**
    (a) Half (b) Double
    (c) Same (d) None
13. **The diffusion of gases at absolute zero will be**
    (a) Unchanged (b) Slightly decreased
    (c) Slightly increased (d) Zero
14. **Which of the following option is incorrect about gases?**
    (a) All molecules move with same speed.
    (b) All molecules behave independently
    (c) PV/RT = n
    (d) All gases cannot be liquefied through Lind's Method

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15. **Critical temperature for different gases is different and depends upon**
(a) Size of molecule (b) Shape of molecule
(c) Intermolecular attractions (d) All of the above

16. **In how many forms do matter exists?**
(a) Three (b) Four
(c) Five (d) Two

17. **What is the simplest form of matter?**
(a) Gas (b) Liquid
(c) Solid (d) Semi solid

18. **What is the abundant form of matter on earth?**
(a) Gas (b) Liquid
(c) Solid (d) Plasma

19. **Which state of matter has the lowest density?**
(a) Gas (b) Liquid
(c) Solid (d) plasma

20. **What do we call to sudden expansion of gases?**
(a) Avogadro's law (b) Graham's law of diffusion
(c) Joule Thomson effect (d) Dalton's law of partial pressure

21. **The solid particles only posses**
(a) Translational motion (b) Vibrational motion
(c) Rotational motion (d) All of above motions

22. **For a gas where volume and pressures are 1dm³ and 2 atm respectively, what should be its new volume, when pressure is increased to 6 atm at constant temperature?**
(a) 1/2dm³ (b) 1/3dm³
(c) 1/4dm³ (d) 2/3 dm³

23. **If 1/V is plotted on X-axis and pressure on Y-axis at constant temperature, what should appear**
(a) Straight line parallel to x-axis (b) Straight line parallel to y-axis
(c) Straight line (d) Curve

24. **The general gas equation to know the volumes of the gas at various temperatures is**
(a) $V_o = \frac{273V_T}{273+T}$ (b) $V_o = V_T\left(1-\frac{T}{273}\right)$
(c) $V_T = V_0\left(1+\frac{T}{273}\right)$ (d) None of the above

25. **Which one is the right value for R?**
(a) 0.0821 atm dm³ k⁻¹ mol⁻ (b) 0.0821 atm m³ k⁻¹ mol⁻¹
(c) 2 cal k⁻¹ mol⁻¹ (d) 8.314 Nm² k⁻¹ mol⁻¹

26. **One mole of an ideal gas at 546.3 K under 2 atm pressure has a volume of**
(a) 22.414 m³ (b) 44.828 dm³
(c) 22.414 dm³ (d) 11.212 cm³

27. **The partial pressure exerted by the water vapours is called**
(a) Surface tension (b) Aqueous tension
(c) Vapour pressure (d) Hydraulic pressure

28. **Which one is not the partial pressure of oxygen in the lungs?**
(a) 0.1526 atm (b) 116 mm of Hg
(c) 116 torr (d) 1 atm

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29. **The spreading of fragrance or scent in air is due to**
(a) Diffusion (b) Effusion
(c) Attraction with air (d) Low density

30. **Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of total pressure exerted by oxygen is**
(a) $\frac{1}{3}$ (b) $\frac{8}{9}$
(c) $\frac{1}{9}$ (d) $\frac{16}{17}$

31. **The kinetic molecular theory of gases was put forward in 1738 by**
(a) Boltzman (b) Maxwell
(c) Clausius (d) Bernoulli

32. **The expression for root mean square velocity is**
(a) $C_{rms}=\sqrt{(3RT/M)^2}$ (b) $C_{rms}=\sqrt{3RT/M}$
(c) $C_{rms}=3RT/M$ (d) $C_{rms}=\sqrt{3/2RT/M}$

33. **The highest temperature at which a substance can exist as a liquid is called its**
(a) Critical temperature (b) Standard temperature
(c) Absolute temperature (d) Upper consulate temperature

34. **Hydrogen effuses four times more rapidly than volume of an unknown gas, molar mass of unknown gas should be**
(a) 16 $gmol^{-1}$ (b) 32 $gmol^{-1}$
(c) 48 $gmol^{-1}$ (d) 64 $gmol^{-1}$

35. **What will be the pressure of 1 mole of an ideal gas maintained at 300 K and 250cm³ volume?**
(a) 98.5 atm (b) 96.7 atm
(c) 95.8 atm (d) 97.1 atm

36. **The processes of effusion and diffusion are best understand by**
(a) Dalton's law (b) Avogadro's law
(c) Graham's law (d) Charles law

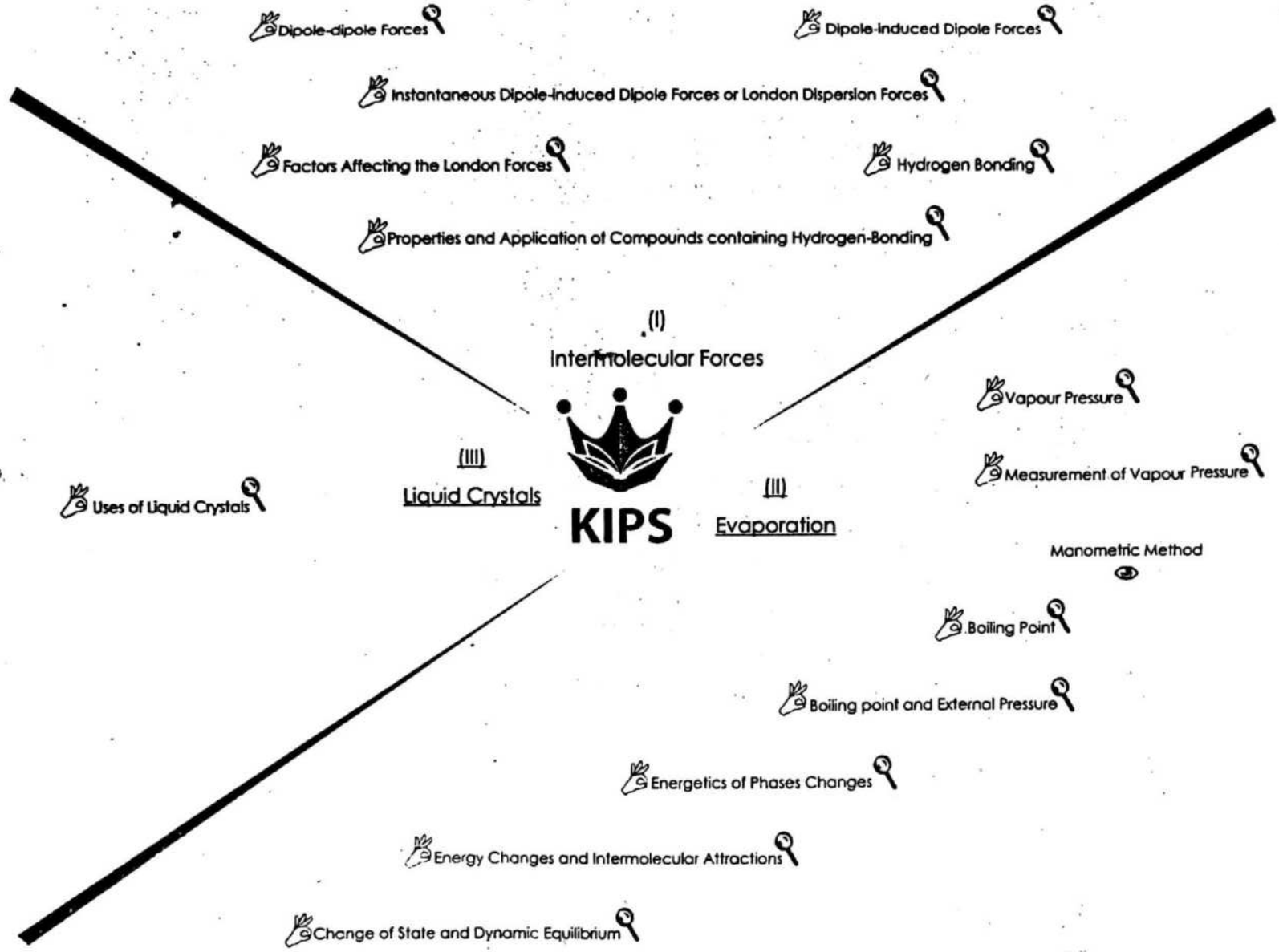
37. **Who made volume and pressure correction to explain deviation of gases from ideal behaviour?**
(a) Clausius (b) Boltzman
(c) Charles (d) Van der waal

38. **The non-ideal behaviour results chiefly from**
(a) Intermolecular attraction and infinite volume
(b) Elastic collisions and finite volume
(c) Intermolecular attractions and finite volume
(d) Intermolecular attraction only

39. **The gases become non-ideal at**
(a) High temperature and high pressure
(b) Low temperature and low pressure
(c) High temperature and low pressure
(d) Low temperature and high pressure

40. **Lind's method is employed for**
(a) Separation of gases (b) Expansion of gases
(c) Compression of gases (d) Liquefaction of gases

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INTRAMOLECULAR FORCES

The forces, which are present within the molecules, are called intramolecular forces e.g.

- Covalent bond
- Ionic bond
- Co-ordinate covalent bond etc.

"Intra" means "within" so attractive forces within molecules are called intramolecular forces.

These forces are stronger as compared to intermolecular forces related to the chemical properties only.

INTERMOLECULAR FORCES

The forces present among the molecules are called intermolecular forces.

1. Dipole-dipole forces
2. Ion-dipole forces
3. Dipole-induced dipole forces
4. Instantaneous dipole-induced dipole forces (London dispersion forces)
5. Hydrogen bonding

Significance

- All the intermolecular forces are electrical in origin and are resulted from the mutual attraction of unlike charges or the mutual repulsion of like charges.
- Many of the physical properties of liquids can be explained on the basis of intermolecular forces.

"Inter" means "between" so attractive forces between the molecules are called intermolecular forces.

DIPOLE-DIPOLE FORCES

The electrostatic forces of attraction produced when the positive end of one molecule attracts the negative end of neighbouring molecule are called dipole dipole forces.

Factors affecting the strength of dipole-dipole forces

- Electronegativity difference between the bonded atoms
- Intermolecular distance

Examples

- These are present in polar molecules. e.g. HCl and $CHCl_3$
- These forces are approximately one percent as effective as a covalent bond.
- In gaseous phase, the dipole dipole forces are least.
- Greater the strength of dipole dipole forces, greater the values of melting point boiling point, heat of vapourization and heat of sublimation.

Factors Affecting the Strength of Intermolecular Forces

Ion-dipole force	Dipole-induced dipole force	London dispersion forces	Dipole-dipole forces	Hydrogen bond
➢ Charge density of the ion ➢ polarity of the molecule ➢ size of the molecule	➢ Polarity of polar molecule ➢ Size of the molecules ➢ Collision frequency	➢ Size of the molecules ➢ Collision frequency	➢ Polarity of molecules ➢ Size of the molecules ➢ Collision frequency	➢ Polarity of molecules ➢ Number of utilizable lone pairs

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LONDON DISPERSION FORCES

The short range forces of attraction created between one end of instantaneous dipole and the opposite end of the induced dipole are called instantaneous dipole induced dipole interaction or London Dispersion forces.

Non-polar molecules

- Mono-atomic or homoatomic molecules are always non-polar e.g. H_2, O_2, F_2, Cl_2, N_2 etc.
- Binary compounds whose central atom is from group IIA, IIIA or IVA are non-polar. They have symmetrical shape. e.g. $BeCl_2$, BH_3, CCl_4 etc are also non-polar.

Polar molecules

- molecules that posses different atoms are usually polar. e.g CH_3Cl, HOCl, H_2SO_4 etc.
- Binary compounds whose central atom is from group VA, VIA or VIIA are dipolar e.g. H_2S, HCl, HF etc.

- A German physicist Fritz London explained these forces in 1930.
- These forces are present in all types of molecules whether polar or non-polar.

Variations

- London dispersion forces increase down the group due to increase in size hence the polarizibility e.g. boiling point of fluorine (gas) is –188.1°C while that of iodine (solid) is +184.4°C.
- In hydrocarbon with the increase of chain length the inter molecular forces increase e.g. the boiling point of ethane (C_2H_6) is -88.6°C and of hexane (C_6H_{14}) is 68.7°C.

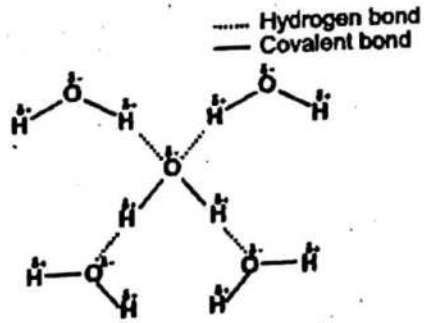
HYDROGEN BONDING

Hydrogen bonding is the electrostatic force of attraction between a highly electronegative atom and partial positively charged hydrogen atom.

Points to be Remembered

- Exceptionally low acidic strength of HF molecule as compared to HCl, HBr and HI is due to strong hydrogen bonding.
- Ammonia and hydrogen fluoride can form only one hydrogen bond due to presence of only one utilizable lone pair of electrons and one utilizable H-atom respectively.
- Water can form two hydrogen bonds as it has two utilizable hydrogen atoms and two utilizable lone pairs on oxygen atom.

The strength of hydrogen bond is generally twenty times less than that of a covalent bond.



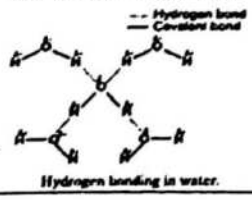
Hydrogen bonding in water.

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A COMPARISON OF INTER-MOLECULAR FORCES

Forces	Strength	Characteristics
Ion –dipole	Moderate (10-50kJ/mol)	Occurs between ions and polar solvents
Dipole-dipole	Weak (3-4KJ/mol)	Occurs between polar molecules
London dispersion	Weak (1-10KJ/mol)	Occurs between all molecules
Hydrogen bond	Moderate (10-40KJ/mol)	H and N or O or F usually

PROPERTIES OF COMPOUNDS CONTAINING HYDROGEN BOND

Property	Description
Thermodynamic properties of covalent hydrides	▪ Greater the E.N difference, stronger will be hydrogen bond. Compounds with such condition have higher B.P than those molecules, which does not have such property. ▪ In HF and H_2O, more E.N difference is between H and F than H and O, but water has high B.P than HF, it is due to greater number of H-bonds between water than in HF.
Application in biological compounds	**Fiber proteins** Fiber proteins consist of large chains of amino acids and these chains are coiled about one another into a spiral. This spiral is called helix. Such a helix may either be right handed or left handed (α-helix and β-helix). In both cases >NH and >CO adjacent to one another are linked together by H-bond. **DNA** Deoxyribonucleic acid (DNA) has two spiral chains. These are coiled about each other and are linked together by H-bond between the nitrogenous bases i.e. A=T and G≡C and give rise to double helical structure. **Food Material** The food materials like carbohydrates e.g. glucose, fructose and sucrose have –OH groups which are responsible for the H-bond in them.
Clothing	Hydrogen bonding is involved in thread.
Solubility	▪ Compound with hydrogen bond is soluble in compound having hydrogen bond e.g. H_2O and C_2H_5OH are soluble with each other.
Cleaning action	▪ Soaps and detergents perform the cleansing action because the polar part of their molecules are water soluble due to hydrogen-bonding and the non-polar parts remain outside water, because they are alkyl or benzyl portions and are insoluble in water.
Hydrogen bonds in paints and dyes	▪ The adhesive property of paints and other dyes like glue etc. is due to hydrogen bond.
Structure of ice  Hydrogen bonding in water.	▪ In ice, the oxygen atom of water molecule is surrounded by four H-atoms. The two H atoms are linked through covalent bond while the other two H-atoms are linked through H-bond. This is extended throughout creating the empty spaces in the structure. That is why when water freezes it occupies 9% more space and its density decreases. That's why ice floats on the surface of water.

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ENERGETICS OF PHASE CHANGE

Particulars	Description
Enthalpy change	At constant P, heat change during the process in which physical or chemical change occur is called enthalpy change (ΔH).
Molar heat of fusion	It is the amount of heat absorbed by one mole of a solid when it melts into liquid form at its melting point. The pressure, during the change is kept one atmosphere. P (1atm). It is denoted by ΔH_f.
Molar heat of vaporization	It is the amount of heat absorbed when one mole of a liquid is changed into vapours at its boiling point. The pressure, during the change is kept one atmosphere. It is denoted by ΔH_v.
Molar heat of sublimation	It is the amount of heat absorbed when one mole of a solid sublimes to give one mole of vapours at a particular temperature and one atmospheric pressure. It is denoted by ΔH_s.

FACTORS AFFECTING MOLAR HEATS	
Nature of material	Polar liquids have high ΔH_v molar heat of vaporization than non-polar. Polar solids have high ΔH_f molar heat of fusion than non-polar.
Size of molecule	Larger the size of molecules, greater will be ΔH_v

EVAPORATION

The spontaneous change of a liquid into its vapours is called evaporation and it continues at all temperatures.

Example:

$$H_2O_{(l)} \longrightarrow H_2O_{(g)} \qquad \Delta H_v = 40.7 kJ\ mol^{-1}$$

Characteristics

It is,

- A natural phenomenon
- a cooling process
- continued at all temperature
- an endothermic process
- a surface phenomenon

Factors affecting evaporation

- surface area of the liquid
- nature of the liquid
  - size of the molecules
  - shape of the molecules
  - inter molecular forces
- temperature
- external pressure

VAPOUR PRESSURE

The pressure exerted by the vapours of a liquid in equilibrium with its liquid at a given temperature is called vapour pressure.

Factors affecting vapour pressure

- nature of the liquid
  - size of the molecules
  - shape of the molecules
  - inter molecular forces

Barometer
A device for measuring the pressure of the atmosphere.
Manometer
A device for measuring pressure of a gas or a liquid in vessel.

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- Due to weaker intermolecular forces, at 20°C vapour pressure of isopentane is more (580 torr) than glycerol (0.00016 torr)

- external pressure

Point to be remembered

- Vapour pressure of water is 4.579 torr at 0°C.
- The rate of change of a vapour pressure with temperature can be calculated by Clausius Clapeyron equation.

Measuring vapour pressure

Measurement

- Manometer is used to measure V.P.
- Thermostat is a system whose temperature can be control by means of Knob.
- Vacuum is created by vacuum pump
- Liquid is frozen and then melted, so that air can be removed

$$P = Pa + \Delta h$$

Boiling point

The temperature at which the vapour pressure of the liquid becomes equal to external pressure is called boiling point.

Boiling point depends upon external pressure.

No.	External Pressure	Boiling Point of H_2O
(1)	1489 torr	120°C
(2)	700 torr	98°C (Muree Hills)
(3)	323 torr	69°C (Mount Averest)
(4)	23.7 torr	25°C

The boiling point and decomposition point of glycerine is 290°C

KINDS OF PHASE CHANGES

Phase transition	Name	Examples
Solid – liquid	Fusion, melting	Melting of snow and ice
Solid – gas	Sublimation	Sublimation of dry ice
Liquid – solid	Freezing (solidification)	Freezing of water
Liquid – gas	Vapourization	Evaporation of water
Gas – liquid	Condensation or liquification	Formation of dew
Gas – solid	Condensation or solidification (Deposition)	Formation of frost or snow

DYNAMIC EQUILIBRIUM

A situation when two opposing changes occur at equal rates is called dynamic equilibrium e.g.

$$\text{ice} \underset{}{\overset{0^\circ C}{\rightleftharpoons}} \text{water}$$

LIQUID CRYSTALS

A state that exists between two temperatures i.e. melting temperature and clearing temperature is called liquid crystals.

DISCOVERY

An Austrian botanist, Frederick Reinitzer discovered liquid crystals in 1888 while studying cholesteryl benzoate

$$\text{Crystal} \overset{145^\circ C}{\rightleftharpoons} \text{liquid crystal} \overset{179^\circ C}{\rightleftharpoons} \text{Clear liquid}$$

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Properties

- Fluidity like liquids
- Optical properties
- Isotropic

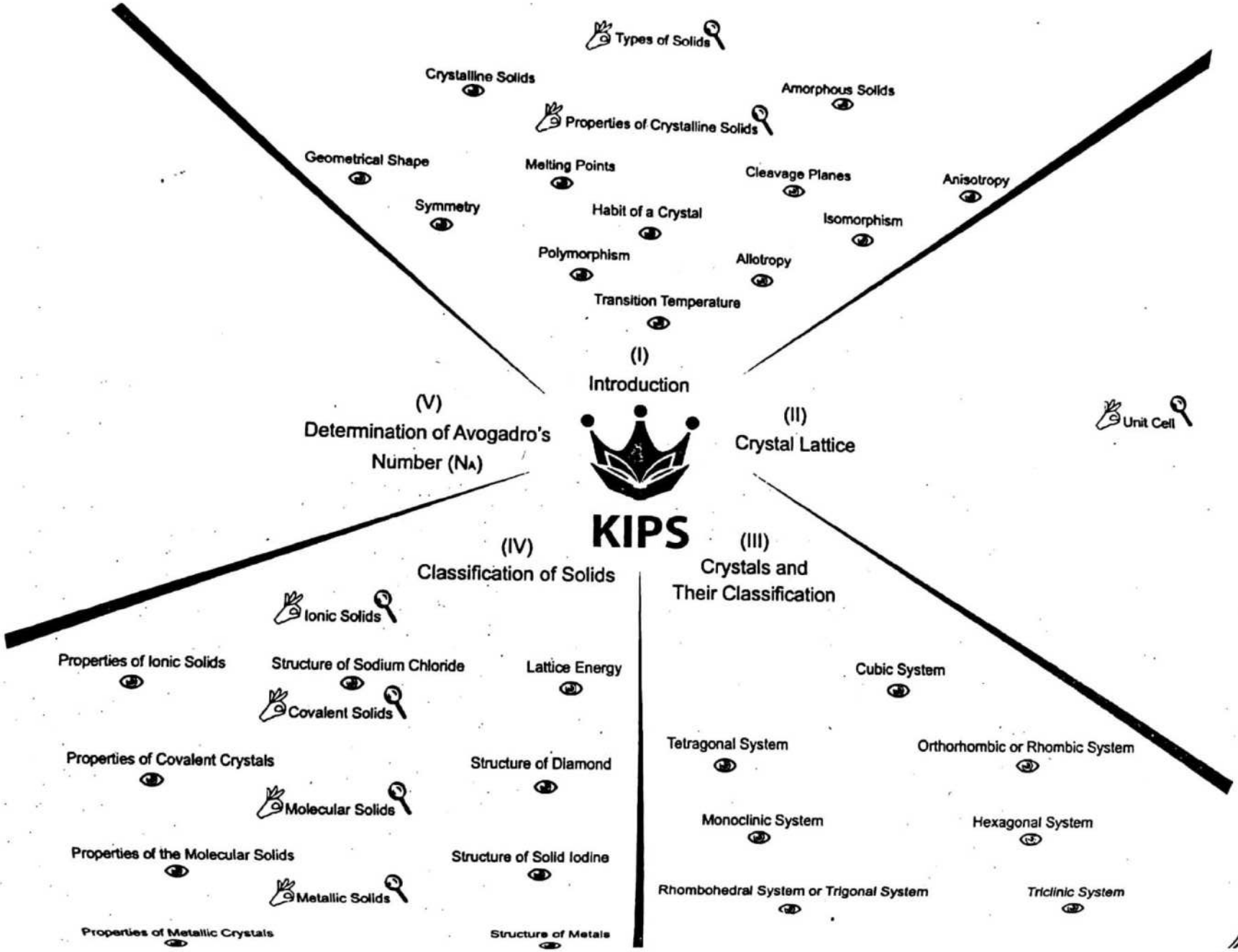
Types of liquid crystals

1. Nematic
2. Smectic
3. Cholesteric

USES OF LIQUID CRYSTALS

Usage	Description
Colour display	• Liquid crystals diffract light and imparts colour. • Colour changes with change in temperature.
Temperature sensor	• Used as temperature sensor.
Electrical circuit	• Used to detect potential failure in electric circuit.
Diagnosis	• Used to locate veins, arteries, infections and tumors. • Used in diagnosis of breast cancer.
Electrical devices	• Used in digital watches, computer and calculators
Chromatography	• Used as a solvent.
Others	• Oscillographic and TV displays use liquid crystal screen.

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SOLIDS

Those substances which are rigid, hard, having definite shape and definite volume are called solids.

TYPES OF SOLID

Name	Details
Crystalline solids	▪ Molecules, ions or atoms arranged in specific three-dimensional pattern e.g. NaCl, KCl, sucrose, I_2 and ice etc.
Amorphous solids (Pseudo solids)	▪ Molecules, ions or atoms do not have regular order of arrangement e.g. rubber, glue, glass etc.

PROPERTIES OF CRYSTALLINE SOLIDS

Property	Description
Geometric shape	Have definite geometry and shape.
Melting Point	Sharp melting points.
Cleavage planes	Whenever the crystalline solids are broken they do so along definite planes. These planes are called the cleavage planes.
Symmetry	▪ The repetition of faces, angles and edges when a solid is rotated by 360° along its axis is called symmetry. ▪ There are many types of symmetry elements: - ➢ Centre of symmetry ➢ Plane of symmetry ➢ Axis of symmetry
Habit of a crystal	▪ The shape of crystal in which it usually grows is called habit of a crystal.
Isomorphism	▪ The phenomenon in which two different compounds exist in the same crystalline form is called isomorphism. ▪ Many solids show isomorphism e.g. $NaNO_3$ and KNO_3 exhibit rhombohedral crystalline form.
Polymorphism	▪ The phenomenon in which one compound contains more than one crystalline forms is called polymorphism. ▪ e.g. $AgNO_3$ exists in Rhombohedral and orthorhombic from. ▪ Compounds exhibit this phenomenon.
Allotropy	▪ The phenomenon in which an element exists in more than one crystalline form is called allotropy. ▪ e.g. C exists as graphite and diamond. ▪ Elements exhibit this phenomenon.
Transition temperature	It is that temperature at which two crystalline forms of the same substance can co-exist in equilibrium with each other. ▪ Above and below this temperature only one form exists. Grey tin (cubic) $\underset{}{\overset{13.2^{\circ}C}{\rightleftharpoons}}$ White tin (tetragonal)

CRYSTAL LATTICE

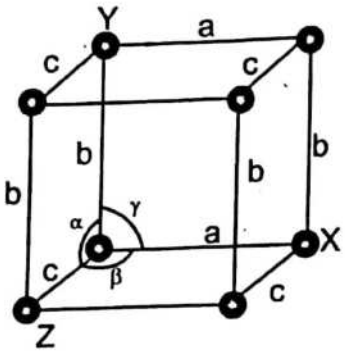
Array of points representing atoms, ions or molecules of crystal, arranged at different sites in three dimensional space called lattice.

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UNIT CELL

The smallest part of crystal lattice, that has all the characteristic features of crystal is called a unit cell.

- Unit cell contains three angles (α, β, γ) and three axis a,b,c. These six parameters are called unit cell dimensions or crystallographic elements.



Crystallography

The study of the structure and properties of crystals with the help of x-rays is called crystallography.

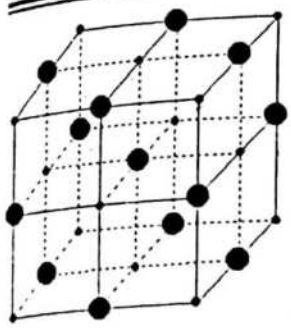
CRYSTAL AND THEIR CLASSIFICATION

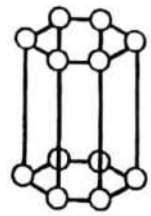
- There are 230 different forms of crystals on the basis of symmetry of geometrical structures of crystals.
- The cubic system consists of three separate types of structures.
  - Simple (primitive)
  - Face centered
  - Body centered
- The basic difference between Bravis lattice are
  - Angles between the faces
  - Relative proportions of the sides
- There are 14 types of Bravis lattices.
- There are 7 crystal systems.

CRYSTAL SYSTEM

Name	Length	Angles	Examples
Cubic	$a = b = c$ All sides equal	$\alpha = \beta = \gamma = 90^0$ All angles equal	NaCl, NaBr Diamond
Tetragonal	$a = b \neq c$ Two sides equal	$\alpha = \beta = \gamma = 90^0$ All angles equal	$BaSO_4 . 4H_2O$ SnO_2
Orthorhombic	$a \neq b \neq c$ All sides unequal	$\alpha = \beta = \gamma = 90^0$ All angles equal	$FeSO_4 . 7H_2O$ $ZnSO_4 . 7H_2O$
Trigonal or Rhombohedral	$a = b = c$ All sides equal	$\alpha = \beta = \gamma$ Each angle between 90^0 to 120^0	$NaNO_3$ KNO_3
Hexagonal	$a = b \neq c$ Two sides equal	$\alpha = \beta = 90^0$ $\gamma = 120^0$	Graphite ZnO, CdS
Monoclinic	$a \neq b \neq c$ All sides unequal	$\alpha = \gamma = 90^0$ $\beta > 90^0$	$CaSO_4$, Borax $Na_2CO_3 . 10H_2O$
Triclinic	$a \neq b \neq c$ All sides unequal	$\alpha \neq \beta \neq \gamma$ All angles unequal	$CuSO_4 . 5H_2O$ $K_2Cr_2O_7$

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Hexagonal crystal

Some important points are as follows:

NaCl

- In NaCl, each Na^+ is surrounded by six Cl^- ions.
- Distance between two consective Cl^- ions is 5.63 A°.
- In each unit cell there are four formula units = $\frac{8}{8}+\frac{6}{2}=4$ formula units

Lattice Energy

- Energy released to form one mole of ionic compound from its Gaseous ions is called lattice energy.
- With increase in the size of cation or anion, lattice energy decreases and vice versa.

Diamond

- In diamond, C atom is sp^3 hybridized and geometry is tetrahedral.
- Bond angle in diamond is 109.5°.

Type of Solid	Structural Particles	Intermolecular Forces	Typical Properties	Examples
metallic	cations plus delocalized electrons	metallic bonds	hardness varies from soft to very hard; melting point varies from low to very high; lustrous; ductile; malleable; very good conductors of heat and electricity	Na; Mg; Al; Fe; Zn; Cu; Ag; W
ionic	cations and anions	electrostatic attractions	hard; moderate to very high melting points; nonconductors of electricity (but good electrical conductors in the molten state)	NaCl; $NaNO_3$; MgO
molecular	molecules (atoms of noble gases)	London and/or dipole-dipole and/or hydrogen bonds covalent bonds	soft: low melting points; nonconductors of heat and electricity; sublime easily in many cases	Noble-gas elements; CH_4; CO_2; P_4; S_8;I_2;H_2O
network covalent	atoms	covalent bonds	very hard; very high melting points; nonconductors of electricity	C (diamond); SiC; SiO_2

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METALLIC SOLIDS

Theories of metallic bonding

(a) Electron pool or electron gas theory.

This theory was proposed by Drude and extended by Loren in 1923. According to this theory, each atom in a metal crystal loses all of its valence electrons. These valence electrons form a pool or a gas. The positively charged metal ions are believed to be held together by electron pool or gas.

(b) Valence bond theory

This theory was presented by L. Pauling.

According to his theory, the metallic bond is treated essentially as covalent in character.

(c) Molecular orbital theory Or band theory

According to this theory, it is assumed that the electrons in the completely filled orbitals are essentially localized, while atomic orbitals containing the valence electrons interact or overlap to form a set of delocalized orbitals. These delocalized orbitals are the molecular orbitals which extend over the entire crystal lattice. Such a combination of atomic orbitals produce a large number of closely spaced states. These states of energy are also known as bands of energy.

STRUCTURE OF METALS

In the metals the atoms are packed together in the form of layers to fill the spaces completely as much as possible. This packing is of two types based on the arrangement of the third layer of atoms.

- Hexagonal Close Packing
- Cubic Close Packing

Hexagonal Close Packing

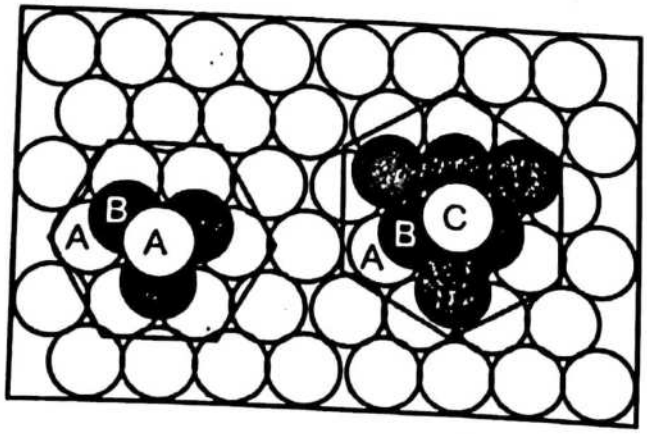
ABAB or 1212

Atom of third layer are over the atoms of second layer as arranged in the first layer.

Cubic Close Packing

ABCABC or 123123

Atoms of third layer are not lying over the atoms of first or second layer.



In ABCABC cubic close packing and ABAB hexagonal close packing the coordination number is 12.

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DETERMINATION OF AVOGADRO'S NUMBER (N_A)

Avigadro's number can be calculated in a number of different ways. One of the most accurate methods for determining this number is based on the study of crystalline solids. The following steps are carried while calculating this number by considering the lithium fluoride. The crystal of LiF is primitive cubic.

- **For N_A, we require**
  - Molar mass(GFM, GMM, GAM)
  - Density
  - Molar volume
  - Distance among the particles(ions, molecules, atoms)

- **Calculate**
  - Edge length of crystalline solid(primitive cubic crystal)
  - Number of particles along each edge length
  - Take the cube of the value calculated in the above step.

- **Result**
  - 6.022×10^{23} particles (ions of one type, molecules, atoms)

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PRACTICE EXERCISE

35 mins Time Yourself

1. **Which of the following has strongest intermolecular forces of attraction?**
   (a) Hydrogen(H_2)
   (b) Chlorine (Cl_2)
   (c) Iodine (I_2)
   (d) Methane (CH_4)
2. **Which has strongest bonding in the solid state?**
   (a) Hydrogen Chloride (HCl)
   (b) Chlorine (Cl_2)
   (c) Xenon(Xe)
   (d) Sodium Chloride (NaCl)
3. **When substance moves from a solid to a liquid state, all of the following changes occur except**
   (a) Molecules become more disordered.
   (b) K.E of the molecules decreases
   (c) Intermolecular forces become weaker
   (d) Molecule become further separated
4. **When the atoms of third layer are arranged in such a way that they directly lie above the atoms of first layer then this arrangement is called**
   (a) ABAB (hexagonal)
   (b) ABCABC (Cubic)
   (c) Orthorhombic
   (d) Rhombohedral
5. **In order to mention the boiling point of water at 110°C, the external pressure should be**
   (a) Between 760 torr and 1200 torr
   (b) Between 200 torr and 760 torr
   (c) 765 torr
   (d) any value of pressure
6. **Which one is false for evaporation?**
   (a) Surface phenomenon
   (b) Continuous
   (c) Exothermic
   (d) Cause cooling
7. **Vapour pressure of water at 100°C is**
   (a) 55 mm Hg
   (b) 760 mm Hg
   (c) 355 mm Hg
   (d) 1489 mm Hg
8. **Which one of the following does not show hydrogen bonding?**
   (a) Water
   (b) Ethyl alcohol
   (c) Phenol
   (d) Diethyl ether
9. **Liquid crystal is discovered by**
   (a) William Crooks
   (b) Fredrick Reinitzer
   (c) J.J Thomson
   (d) Bravis
10. **Which one is a conductor but is not malleable?**
    (a) Iron
    (b) Graphite
    (c) Silver
    (d) Platinum
11. **Hydrogen bonding is involved in**
    (a) Solubility
    (b) Cleansing action of detergents
    (c) Biological molecules
    (d) All
12. **Actually the vapour pressure on the surface of liquid in the flask is equal to**
    (a) Δh
    (b) $Pa - \Delta h$
    (c) $Pa + \Delta h$
    (d) $Pt = Pa - \Delta h$
13. **Forces of attraction, which may be present between all kinds of atoms and molecules are**
    (a) intramolecular
    (b) intermolecular
    (c) van der Waal
    (d) Dipole-induced dipole
14. **The density of water may be**
    (a) Equal to that of ice
    (b) Greater than that of ice
    (c) Less than that of ice
    (d) All are possible

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15. **The quantity of heat required to convert one mole of liquid into its vapours at its boiling point is called molar heat of**
(a) vapourization (b) evaporation
(c) crystallization (d) sublimation

16. **Steam causes more severe burn than the boiling water because it possesses.**
(a) Latent heat of fusion (b) Latent heat of vapourization
(c) Latent heat of sublimation (d) All of the above

17. **Water has maximum density at**
(a) 0°C (b) 2°C
(c) 4°C (d) 100°C

18. **The conversion of vapours back into their liquid state is called**
(a) crystallization (b) evaporization
(c) vapourization (d) condensation

19. **Formation of vapours from the surface of a liquid is called**
(a) vapourization (b) evaporation
(c) condensation (d) cracking

20. **When water freezes at 0°C its density decreases due to**
(a) Change of bond angles
(b) Cubic structure of ice
(c) Empty space present in the structure of ice
(d) Change of bond length

21. **The attractive forces between the partial positive end of one molecule and partial negative end of other molecule are called**
(a) Dipole-dipole forces (b) Ion dipole-dipole forces
(c) London dispersion forces (d) Debye forces

22. **The boiling point increases down the zero group element due to**
(a) Ion dipole forces (b) London forces
(c) Hydrogen bonding (d) Dipole-dipole forces

23. **Vapour pressure is not affected by**
(a) Surface area (b) temperature
(c) intermolecular forces (d) atmospheric pressure

24. **Rising of a wetting liquid in a capillary tube is due to**
(a) Surface tension (b) Cohesive forces
(c) Adhesive forces (d) viscosity

25. **Table salt crystallizes with a**
(a) Face centered cubic lattice (b) body centered cubic lattice
(c) simple cubic lattice (d) orthorhombic lattice

26. **The number of formula units in 29.25g of common salt**
(a) 6.022×10^{23} (b) 3.01×10^{23}
(c) $2 \times N_A$ (d) $4 \times 6.022 \times 10^{23}$

27. **During which process, empty spaces between particles become minimum?**
(a) ionization (b) condensation
(c) fusion (d) evaporation

28. **Liquid gets the shape of the container when it is poured into it. Which one of the following reason justifies it?**
(a) Liquid do not have definite shape (b) Liquid do not have definite volume
(c) Liquid is highly compressible (d) Liquid molecules can slide over each other

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29. **Which one of the follow[illegible] highest volatility**
(a) Diet[illegible]
(b) Ethyl alcohol
(c) [illegible]
(d) Ethylene glycol

30. **M[illegible] of water is**
(a) 40.7 kJ/mole
(b) 40.7 J/mole
(c) 40.7 cal/mole
(d) 40.7 kcal/mole

31. **If we provide very high amount of heat to a liquid its boiling point will**
(a) increase
(b) remains constant
(c) decrease
(d) there will be no boiling

32. **Crystallites are**
(a) crystalline so[illegible]
(b) amorphous solids
(c) liquid crys[illegible]
(d) all of the above

33. **A solid may [illegible]ade up of**
(a) Atoms
(b) Ions
(c) Molecules
(d) a, b and c

34. **A malleable solid is one which can be**
(a) Converted into wires
(b) Converted into thin sheets
(c) Melted easily
(d) All of above

35. **Amorphous substances possess**
(a) No definite geometry
(b) No definite heat of fusion
(c) No sharp melting points
(d) All of the above

36. **Crystalline solids can be identified easily from their**
(a) Sharp melting point
(b) Definite geometry
(c) Transition temperature
(d) Colour

37. **Boiling points of hydrocarbons increase with the increase in number of carbon atoms. It is mainly due to**
(a) More strength of H-bonding
(b) More strength of London forces
(c) Less polarizability
(d) All of the above

38. **Ice is _____ crystal**
(a) Metallic
(b) Molecular
(c) Covalent
(d) Ionic

39. **Select a pair of compounds, which are isomorphic in nature.**
(a) NaCl and KNO_3
(b) MgO and NaF
(c) KNO_3 and MgO
(d) NaF and $CaCO_3$

40. **The viscosity of solids is**
(a) Infinite
(b) Negligible
(c) Medium
(d) No concept of viscosity in solids

41. **$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$ is representation of crystal system**
(a) Monoclinic
(b) Triclinic
(c) Hexagonal
(d) Trigonal

42. **The phenomenon in which a compound exists in two or more crystalline forms is called**
(a) Isomorphism
(b) Polymorphism
(c) Anisotropy
(d) Allotropy

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43. **Which solids are called true solids?**
(a) Metallic (b) Amorphous
(c) Crystalline (d) Vitreous

44. **Bucky balls is an allotropic form of**
(a) Sulphur (b) Carbon
(c) Silica (d) Tin

45. **The number of amino acid units for each turn of helix, on average are**
(a) 21 (b) 23
(c) 25 (d) 27

46. **Isomorphic substances have**
(a) Same physical and chemical properties
(b) Same physical and different chemical properties
(c) Different physical and same chemical properties
(d) Different physical and chemical properties

47. **If a physical and chemical change takes place at a constant pressure, then the heat change during the process is called**
(a) Heat of transition (b) Heat of fusion
(c) Enthalpy change (d) All of above

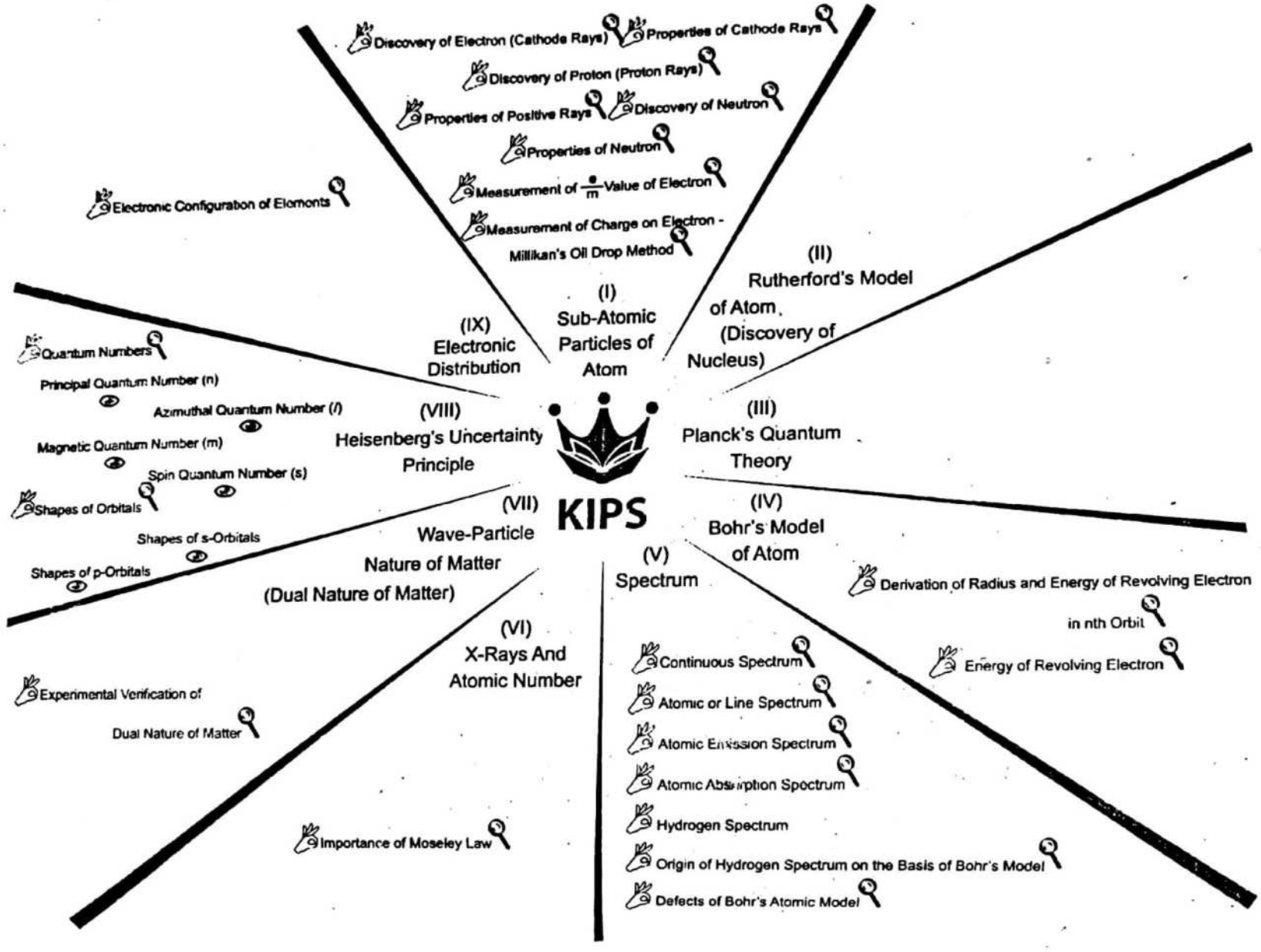
48. **The pressure during the molar heat of fusion is kept**
(a) 0 atmosphere (b) one atmosphere
(c) 2 atmosphere (d) 10 atmosphere

49. **The amount of heat absorbed when one mole of a liquid is changed into gas at its boiling point is**
(a) Molar heat of sublimation (b) Molar heat of fusion
(c) Molar heat of vapourization (d) Latent heat of that liquid

50. **All the enthalpy changes are**
(a) Negative (b) Positive
(c) May or may not be "a" or "b" (d) none

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Chapter 5

ATOMIC STRUCTURE

DISCOVERY OF ELECTRON

An English scientist, William Crooks performed discharge tube experiment for the discovery of electron.

Principle

Gases are non-conductor at ordinary pressure. They can be made conductor by decreasing pressure.

Experiment

- A gas is filled in discharge tube
- Strength of voltage depends upon the length of tube and pressure of gas filled.
- At pressure 0.01 torr, rays are produced in discharge tube on applying a potential difference of 5000-10,000 volts.
- Cathode rays are nothing but electrons.

PROPERTIES OF CATHODE RAYS

(a) **Charge**

- In 1895, J.Perrin observed the behavior of cathode rays under the influence of magnetic field.
- In 1897, J.J Thomson noted the negative charge on these rays when passed through electric field.

(b) **Mode of movement**

- These rays cast a sharp shadow of an opaque object placed in their path. They travel perpendicular to the surface of cathode.

(c) **Material particles**

These rays consist of material particles because they possess momentum.

(d) **e/m ratio**

Their e/m ratio is just equal to electrons.

(e) **Penetration power:**

Very low penetration power. However these rays can ionize gases.

(f) **Naming**

Stoney named these particles as electrons.

Do You Know

A television tube works through the deflection of a cathode rays beam by electromagnetic coil.

Do Not Mix

Particle	Symbol	Charges
Alpha	$^{4}_{2}He$	+ Ve
Beta	$^{0}_{-1}e$	– Ve
Neutron	$^{1}_{0}n$	No charge
Proton	$^{1}_{1}H$	+ Ve
Neutrino	$^{0}_{0}n$	No charge

Points to be remembered

- German physicist, E.Goldstein performed positive rays experiment.
- Positive rays are also called canal rays or anode rays.
- Rutherford suggested a name proton for positive rays particle.
- Chadwick discovered neutron in 1932.
- [Fast neutron] Travel with an energy 1.2Mev
- [Slow neutron] Travel with energy below 1ev

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PROPERTIES OF POSITIVE RAYS

Positive Rays
Production They are produced when electric current is passed through gas at low pressure
Charge Have +ve charge as deflected towards -ve pole of electric field.
Move in straight line.
e/m ratio ▪ Smaller than electron ▪ Depends upon the gas filled in tube. ▪ Highest value was obtained when H_2 gas was filled.
▪ Penetration power is very low. ▪ They can ionize gases.
▪ They produce shadow of an opaque object. ▪ They were named canal rays because they travel through perforated cathode electrodes

PROPERTIES OF NEUTRONS

Neutrons
Production They are produced when stream of α-particles are directed at beryllium ($^{9}_{4}Be$).
Charge They are passed undeflected through electric field and magnetic field.
Move in straight line.
▪ Penetration power is very high. ▪ They cannot ionize gases.

MEASUREMENT OF e/m VALUE OF ELECTRON

- Joseph John Thomson calculated the e/m value of electron in 1897.
- Cathode rays are allowed to pass
  - (i) When both fields (electric and magnetic fields) are off.
  - (ii) When only magnetic field is applied.
  - (iii) When only electric field is applied.
  - (iv) When both fields are applied simultaneously so that canceling the effect of each other and electrons are passed undeflected.
  - (v) Strengths of the two fields are compared.
- The e/m value of electron is -1.7588×10^{11} C/kg.
- One Kg of electrons have 1.7588×10^{11} Coulombs of charge.

m/e value of electron is 5.686×10^{-12} kg/C

MILLIKAN'S OIL DROP METHOD

An American physicist Robert Millikan determined the charge on an electron.

Mass of Electron	
Method I	Method II
$e/m = 1.7588\times10^{11}$ C/kg	$m/e = 5.686\times10^{-12}$ kg/C
Mass of electron $= \frac{1.6022\times10^{-19}C}{1.7588\times10^{11}C/kg}$	Mass of e $= 5.686\times10^{-12}$ kg/C x 1.6022×10^{-19}C
Mass of electron $= 9.1095\times10^{-31}$ kg	Mass of electron $= 9.1095\times10^{-31}$ kg

RUTHERFORD'S ATOMIC MODEL

- Rutherford discovered nucleus in 1911.

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Experiment

- Bombardment of alpha particles on 0.00004 cm thick gold foil.

Observations

- Rutherford observed the various angle of deflections of alpha particles.
  - ➢ Most of the alpha particles were passed un-deflected.
  - ➢ Some alpha particles were deflected at various angles

Conclusion

- Most of the part of atom is empty.
- Central part is tiny and positively charged. It is called nucleus.
- Almost the whole mass of an atom is concentrated in the nucleus (i.e. atom has non-uniform density).

Objections

If electron is revolving continuously then it will radiate energy continuously then

- Atomic assembly must collapse that doesn't happen.
- Atomic spectrum must be continuous rather than the line spectrum.

AMAZING

If we were to use a golf ball to represent the nucleus, the atom would be about three miles in diameter.

PLANCK'S QUANTUM THEORY

In 1900 Plank put forward his theory to explain the emission and absorption of radiations. This theory gives the relationship of energy, frequency, wavelength and wave number of photon of light.

- Energy is emitted or absorbed only in terms of wave packets in a discontinuous manner. These wave packets are called quanta or photon.
- Energy of photon or quanta $E \propto \nu$.
- $E = h\nu = hc/\lambda = hc\bar{\nu}$

Where, h = planks constant = 6.625×10^{-34} Js.
ν = frequency
c = velocity of light = 3×10^8 m/s
λ = wavelength in $\mathring{A}$, nm, pm
$\bar{\nu}$ = wave number

Important Terminologies

- **Frequency:(ν)**
  Number of waves passing through a point in one second.
- **Wavelength:(λ)**
  The distance between two adjacent crests or troughs.
- **Wave number:($\bar{\nu}$)**
  The number of waves per unit length

BOHR'S ATOMIC MODEL

Postulates

(i) Electron revolves in one of the circular orbits outside the nucleus.

(ii) Electron can revolve only in those orbits in which its angular momentum is integral multiple of unit $h/2\pi$.

$mvr = nh/2\pi$

Such orbits are called allowed orbits or stationary state or Bohr's orbits.

(iii) As long as an electron remains revolving in its allowed orbit, the energy of electron remains constant.

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(iv) When an electron jumps from higher to lower orbit, it radiates energy in the form of photon of energy as given below.

$$\Delta E = E_2 - E_1 = h\nu$$

Objections

Bohr's Atomic model cannot explain

- The spectrum of poly electron system.
- The fine lines in the atomic spectrum.
- The three-dimensional movement of electrons.
- Zeeman Effect and Stark Effect.

SOMMERFELD'S MODIFICATION OF BOHR'S ATOMIC MODEL

In 1915, Sommerfeld suggested the moving electrons might describe in addition to the circular orbits elliptic orbits as well wherein the nucleus lies at one of the focii of the ellipse.

DERIVATION OF RADIUS OF n^{th} ORBIT

(i) The electrostatic force of attraction between the electron and nucleus is

$$\frac{Ze^2}{4\pi\varepsilon_o r^2}$$

(ii) Centrifugal force balance coulomb's force.

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\varepsilon_o r^2}$$

$$r = \frac{Ze^2}{4\pi\varepsilon_o mv^2}$$

on further proceeding, we get;

$$r = \frac{\varepsilon_o n^2 h^2}{\pi me^2}$$

$$r = a_0\, n^2 (constant)$$

$$a_0 = \frac{\varepsilon_o h^2}{\pi me^2} = 0.529 A^o$$

By putting the value of n as 1,2,3,4....., we get

$n_1 = 1$	$r_1 = 0.529\ \text{Å}$	$n_4 = 4$	$r_4 = 8.4\ \text{Å}$
$n_2 = 2$	$r_2 = 2.11\ \text{Å}$	$n_5 = 5$	$r_5 = 13.22\ \text{Å}$
$n_3 = 3$	$r_3 = 4.75\ \text{Å}$		

Conclusion

(i) The orbits are not equally spaced

$r_2 - r_1 < r_3 - r_2 < r_4 - r_3 < \ldots\ldots\ldots\ldots$

(ii) The second orbit is four times away from the nucleus than first orbit, third orbit is nine times away and similarly fourth orbit is sixteen times away.

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ENERGY OF REVOLVING ELECTRON

$E = E_{kinetic} + E_{potential}$

$$E = \frac{Ze^2}{8\pi\varepsilon_0 r} - \frac{Ze^2}{4\pi\varepsilon_0 r}, \quad KE = \frac{1}{2}mv^2 = \frac{Ze^2}{8\pi\varepsilon_0 r}$$

Energy of nth orbit

$$E_n = -\frac{me^4}{8\varepsilon_0^2 h^2}\left[\frac{1}{n^2}\right]$$

$$E_n = -2.178\times10^{-18}\left[\frac{1}{n^2}\right] J \text{ per electron}$$

$$E_n = -\frac{1313.315}{n^2} \text{ kJmol}^{-1}$$

$E_1 = -1313.315 \text{kJmol}^{-1}$

$E_2 = -328.32 \text{kJmol}^{-1}$

$E_3 = -145.92 \text{kJmol}^{-1}$

$E_4 = -82.08 \text{kJmol}^{-1}$

$E_\infty = 0 \text{ kJmol}^{-1}$

Conclusion

The difference in the values of energy go on decreasing from lower to higher orbits.

$E_2-E_1 > E_3-E_2 > E_4-E_3 > \ldots\ldots\ldots\ldots$

SPECTRUM

A visual display or dispersion of the components of white light, when it is passed through a prism is called a spectrum.

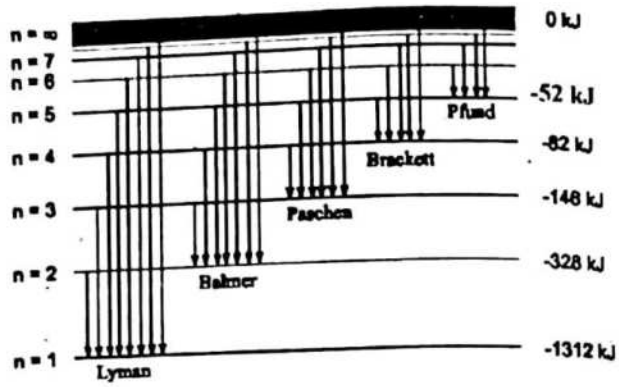
Difference between continuous spectrum and line spectrum

Continuous spectrum	Line spectrum
In this spectrum line or waves are diffused into one another.	In this spectrum lines are separated from each other by some dark spaces.
There is no sharp boundary between the colours.	There is gap between the lines.
It can be formed by dispersing some typical lights like sun light incandescent bulbs light etc.	It is produced by heating the element or its compound on flame or some other source of heat.
It is an effect of polychromatic light	It is an effect of monochromatic light.
Examples: rainbow, sunlight, electric bulb light.	Heating of sodium or potassium or their salts on flame.
Atomic Emission spectra	**Atomic Absorption spectra.**
It is formed when the substance is in excited state.	It is formed when the substance is in its ground state.
It is produced when the substance reaches the gaseous or vapour state after absorbing energy	It is produced by gases and transparent liquids and solids.
It consists of bright lines present in a dark background.	It consists of black lines present in a bright background.
Emission spectrum of sodium gives two yellow lines of 589.0nm 589.6nm.	Absorption spectrum of sodium gives two dark lines at 589.0nm and 589.6nm.
Origin: When an excited electron jumps from higher to a lower energy level, it emits energy that form colored lines in emission spectra.	Origin: when an electron absorbs energy and moves to higher energy level, dark lines in absorption spectrum indicate the absorbed radiations.

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EMISSION SPECTRUM OF HYDROGEN

$n_1=1$;
$n_2=2,3,4,$.....(Lyman series)(U.V region)
$n_1=2$;
$n_2=3,4,5,$.....(Balmer series)(Visible region)
$n_1=3$;
$n_2=4,5,6,$.....(Paschen series)(I.R region)
$n_1=4$;
$n_2=5,6,7,$.....(Brackett series)(I.R region)
$n_1=5$;
$n_2=6,7,$.....(Pfund series)(I.R region)

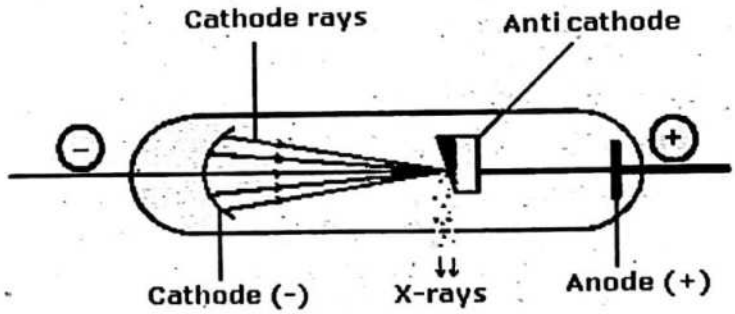


$$\Delta E = 2.18\times10^{-18}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right] J \quad , \quad \bar{v} = 1.0967\times10^{7}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right] m^{-1}.$$

X-RAYS AND ATOMIC NUMBER

Definition

The rays which are produced when rapidly moving electrons collide with heavy metal anode in the discharge tube is called x-rays.



- Wavelength of X-rays depends upon nature of metal.
- Mosley's research work covers the range of wavelength 0.04-8A°.
- Spectral line of shorter wavelength is K-series and of longer wavelength is called L-series.
- X-rays become very short wavelength in case of heavy metals.

Mosley's equation

$$\sqrt{v} = a\,(z-b).$$

DUAL NATURE OF MATTER

According to de-Broglie "All matter particles (electrons, protons, neutrons, atoms and molecules) possess the characteristics of both the material particle and a wave".

de-BROGLIE'S RELATIONSHIP

$$\lambda = \frac{h}{mv}$$

HEISENBERG'S UNCERTAINTY PRINCIPLE

"It is impossible to determine simultaneously both the position and momentum of an electron with accuracy"

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MATHEMATICALLY

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

REASON

- The wavelength of visible light is million times larger as compared to diameter of electron. So the position becomes uncertain.
- The x-rays of short wavelength have high energy. So the collision of X-rays with electron will bring about the great uncertainty in momentum.

QUANTUM NUMBERS

The sets of numerical values, which give the acceptable solution to Schrodinger wave equation, are called quantum numbers.

The quantum numbers are;

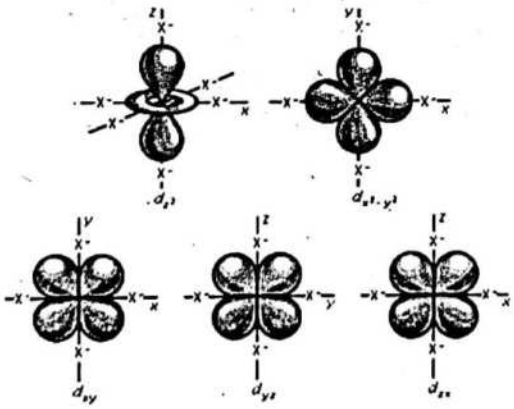
1- Principal quantum number (n)
2- Azimuthal quantum number (ℓ)
3- Magnetic quantum number (m)
4- Spin quantum number (s)

Schrodinger wave equation brings revolution by giving quantum numbers

ORBITAL

The area around the nucleus, where the probability of finding an electron is maximum is called an orbital.

Sub shell	Orbitals	shape
s	1 s-atomic orbital	spherical
p	3 p-atomic orbitals p_x, p_y, p_z	dumb-bell
d	5 d-atomic orbitals d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$, d_{z^2}	sausage
f	7 f-atomic orbitals	complex



Arrangement of sub-shells

The sub-shells are arranged in the increasing order of $(n+l)$ value and if any two sub-shells have same $(n+l)$ value, then that sub-shell is placed first whose n value is smaller.

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Principal Quantum Number		Azimuthal Quantum Number		Magnetic Quantum Number	Spin Quantum Number	Number of Electrons in Shell	
1	K	0	s	0	+1/2, -1/2	2	
2	L	0	s	0	+1/2, -1/2	2	8
		1	p	+1, 0, -1	+1/2, -1/2	6	
3	M	0	s	0	+1/2, -1/2	2	18
		1	p	+1, 0, -1	+1/2, -1/2	6	
		2	d	+2, +1, 0, -1, -2	+1/2, -1/2	10	
4	N	0	s	0	+1/2, -1/2	2	32
		1	p	+1, 0, -1	+1/2, -1/2	6	
		2	d	+2, +1, 0, -1, -2	+1/2, -1/2	10	
		3	f	+3, +2, +1, 0, -1, -2, -3	+1/2, -1/2	14	

Electronic Distribution

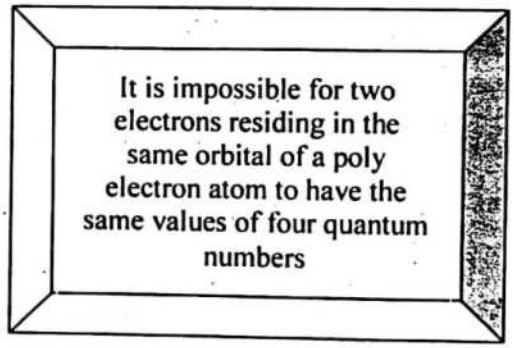
The following rules are adopted in order to distribute the electrons in the orbitals of sub-shells of shells in an atom.

Auf-Bau principle

The electrons should be filled in energy sub shells in order of increasing energy values. The electrons are first placed in 1s, 2s, 2p and so on.

Pauli's exclusion principle

Two electrons in the same orbital must have opposite spins.



Hund's rule

If degenerate orbitals are available and more than one electrons are to be placed in them, they should be placed in separate orbitals with the same spin rather than putting them in the same orbital with opposite spins.

Note

Half filled and completely filled sub-shells, are more stable e.g. Cr and Cu.

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s and so on.

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PRACTICE EXERCISE

35 mins Time Yourself

1. **All of the following were theorized by Bohr in his description of the atom except**
   (a) Angular momentum of electrons in multiples of $h/2\pi$
   (b) Electrons revolve in discrete circular orbits.
   (c) Energy of each electron is directly proportional to n^2.
   (d) Electrons radiate energy continuously in a given orbit.
2. **The letters s,p,d and f are used to represent which quantum numbers.**
   (a) Principal (b) Azimuthal
   (c) Magnetic (d) Spin
3. **The magnetic quantum number (QN) has its values determined directly by the value of**
   (a) Principal (QN) (b) Azimuthal (QN)
   (c) Spin (QN) (d) Both a and b
4. **The atomic number of an element having maximum number of unpaired electrons in p-subshell, is**
   (a) 7 (b) 10
   (c) 12 (d) 16
5. **The maximum number of electron in a sub shell with $\ell = 3$ is**
   (a) 6 (b) 10
   (c) 14 (d) 18
6. **Radius of the third shell of H-atom is**
   (a) 5.761 A° (b) 4.761 A°
   (c) 6.671 A° (d) 3.716 A°
7. **When an atom absorbs energy the lines in the spectrum will appear which are**
   (a) Brighter (b) Darker
   (c) Colourless (d) Hard to locate
8. **Colour of fluorescence produced by cathode rays depends upon**
   (a) Temperature (b) Pressure
   (c) Volume (d) Composition of glass
9. **Which one is not true about cathode rays?**
   (a) 9.11×10^{-31} Kg (b) Cast shadow
   (c) Heat up the platinum foil (d) Cannot ionize
10. **Positive rays are produced**
    (a) By burning of gas
    (b) By cooling of the gas
    (c) By the bombardment of cathode rays on gas molecules
    (d) From anode like cathode rays, produced from cathode
11. **A fast moving neutron can eject from nitrogen**
    (a) γ-rays (b) α-rays
    (c) β-rays (d) electrons
12. **Rutherford's planet like structure was defective and unsatisfactory because**
    (a) Moving e⁻ accelerate towards the nucleus
    (b) Continuous spectrum
    (c) Behavior of electron remain unexplained
    (d) All

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13. **The relationship between energy of a photon of light and its frequency is given by**
(a) de-Broglic dual nature of matter (b) Bohr's model
(c) Planck's Quantum theory (d) Rutherford's atomic model

14. **Splitting of spectral lines when atom is subjected to magnetic field is called**
(a) Zeeman's effect (b) Stark's effect
(c) Photo electric effect (d) Compton effect

15. **The velocity of the photon**
(a) Is independent of wavelength (b) Depends upon source
(c) Depends upon its frequency (d) Equals to the square of amplitude

16. **Which one of the following explain the shape of orbitals?**
(a) Principal of quantum number (b) Azimuthal quantum number
(c) Magnetic quantum number (d) Spin quantum number

17. **Atom cannot be divided into simple units, theorized by**
(a) Rutherford (b) Dalton
(c) Bohr (d) Schrodinger

18. **Pressure in gas discharge tube was kept**
(a) 10 torr (b) 1 torr
(c) 0.1 torr (d) 0.01 torr

19. **The number of fundamental particles in an atom of the lightest isotope of carbon are**
(a) 6 (b) 12
(c) 18 (d) 20

20. **Angle of deflection was studied by**
(a) Hittorf (b) Stoney
(c) William Crookes (d) J.Perrin

21. **Increase in atomic number is observed during**
(a) Alpha emission (b) Beta emission
(c) Both a and b (d) Radioactivity

22. **Positive rays give flash on**
(a) $AgNO_3$ plate (b) AgCl plate
(c) ZnO (d) ZnS

23. **Free neutron changes into proton with the emission of**
(a) Neutrino (b) Electron
(c) Both a and b (d) Meson

24. **The value of e/m ratio of electron is**
(a) 6.02×10^{23} C/kg (b) 1.7588×10^{20} C/kg
(c) 9.1095×10^{-31} C/kg (d) 1.7588×10^{11} C/kg

25. **Charge of electron was measured by**
(a) J.J Thomson (b) Millikan
(c) Rutherford (d) Perrin

26. **Rutherford bombarded _____ particles in discovery of nucleus.**
(a) Gamma-rays (b) Alpha rays
(c) Beta-rays (d) X-rays

27. **Plank's theory says energy is emitted**
(a) In continuous manner (b) Discontinuous manner
(c) Simultaneously (d) In the form of heat

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28. Angular momentum of an electron

(a) $n^2h/2\pi$ (b) $nh^2/2\pi$
(c) $nh/4\pi$ (d) $nh/2\pi$

29. 2nd orbit is _____away from nucleus of H-atom as compared to 1st orbit is

(a) 2-times (b) 3-times
(c) 4-times (d) 6-times

30. The maximum number of orbitals present in a sub-shell that is represented by Azimuthal quantum number = 3, will be

(a) 1 (b) 3
(c) 5 (d) 7

31. The correct electronic configuration of Cu is

(a) $[Ar]4s^1$ (b) $[Ar]4s^2$
(c) $[Ar]3d^{10}4s^1$ (d) $[Ar]3d^94s^2$

32. Pfund series are produced in the spectrum of hydrogen atom

(a) When electrons jump down to 2nd-orbit
(b) When electrons jump down to 3rd-orbit
(c) When electrons jump down to 4th-orbit
(d) When electrons jump down to 5th-orbit

33. Atomic orbitals having same energy are called

(a) Degenerate orbitals (b) Bonding molecular orbitals
(c) Anti bonding molecular orbitals (d) Half filled orbitals

34. Sommerfeld's modification in Bohr's model is

(a) Orbit is cylindrical (b) Orbit is elliptical
(c) Orbit is longitudinal (d) Orbit is asymmetrical

35. When electrons collide with heavy metals, then _____ are produced.

(a) Beta-rays (b) Alpha-rays
(c) X-rays (d) Gamma-rays

36. Planck's equation is

(a) $E = mc^2$ (b) $mvr = nh/2\pi$
(c) $E = h\upsilon$ (d) $\lambda = h/mv$

37. Atom with higher atomic number produces X-rays of

(a) Shorter wavelength (b) Larger wavelength
(c) X-ray not produced (d) All are possible

38. Wavelength of electron was verified by

(a) Moseley (b) Davisson and Germer
(c) Einstein (d) Roentgen

39. Space around nucleus where finding probability of electrons is maximum is called

(a) Orbital (b) Orbit
(c) subshell (d) Electron cloud

40. Quantum number which tells the energy of electron, is;

(a) n (b) l
(c) m (d) s

41. Electronic configuration of K is

(a) $[Ar]4s^2$ (b) $[Ar]4s^1$
(c) $[Kr]5s^1$ (d) $[He]2s^1$

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42. **_____ can expel protons from paraffins.**
(a) Electron (b) Positron
(c) Neutron (d) None of above

43. **Millikan used _____ in his atomizer.**
(a) Milk (b) Honey
(c) Oil (d) Water

44. **Centrifugal forces are balanced in atom by**
(a) Attractive forces (b) Repulsive force
(c) Electrons (d) Neutrons

45. **Spectrum is produced due to**
(a) Different wavelength (b) Different colours
(c) Different intensities (d) all have little contribution

46. **When 6d orbital is complete, the entering electron goes into**
(a) 7f (b) 7s
(c) 7p (d) 7d

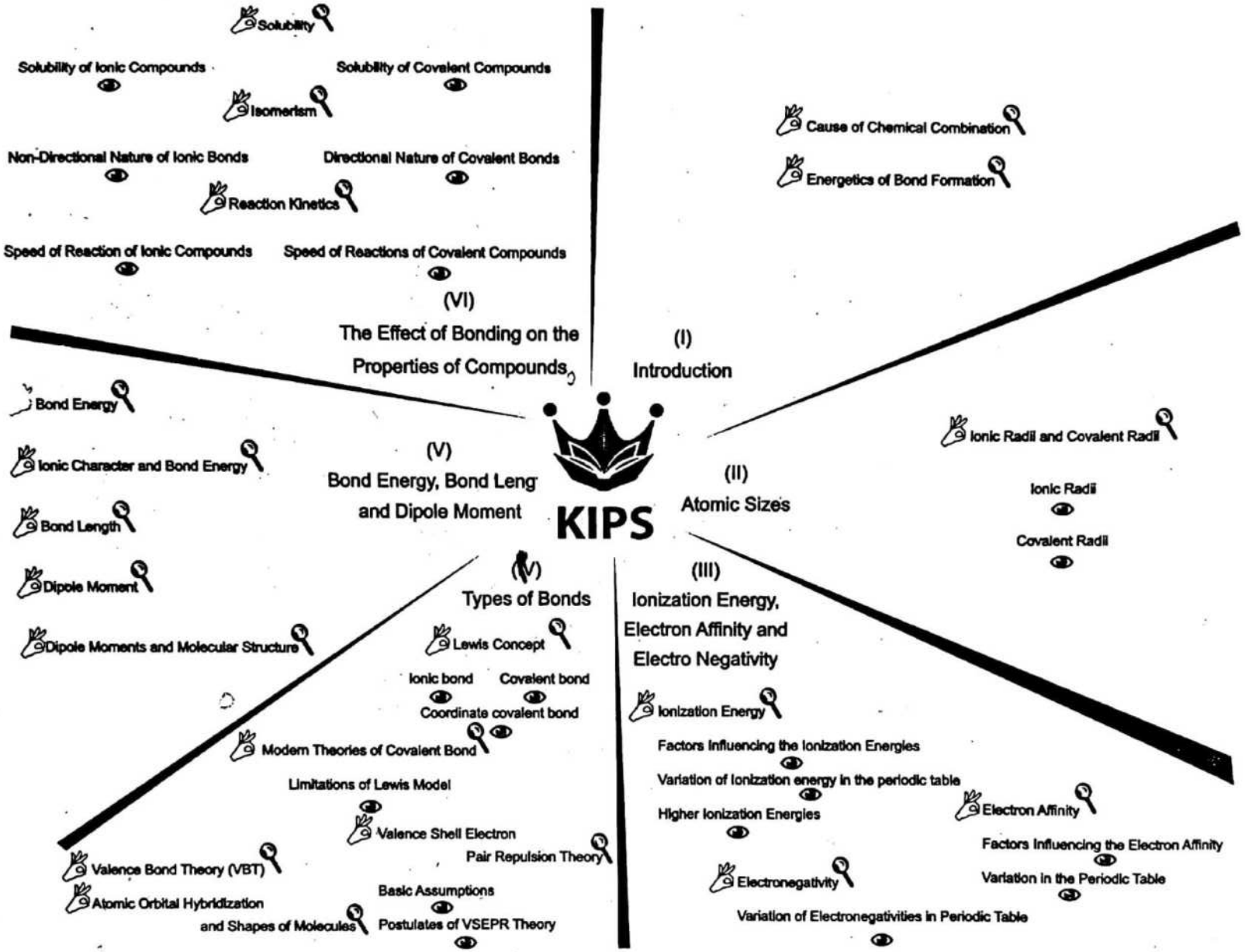
47. **When electron jump into orbit 1, then series obtained is**
(a) Lyman (b) Paschen
(c) Pfund (d) Brackett

48. **Neutrons moving with an energy of 1.2 MeV, are called**
(a) Fast neutrons (b) Slow neutrons
(c) Moderate neutrons (d) All are possible

49. **Splitting of spectral lines when atoms are subjected to strong electric field is called**
(a) Zeeman effect (b) Stark effect
(c) Photoelectric effect (d) Compton effect

50. **Three quantum number have been derived from equation of**
(a) de-Broglie (b) Planck's
(c) Schrodinger (d) Heisenberg

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CHEMICAL BOND

The force which holds two or more atoms or ions to form a large variety of compounds is called chemical bond.

CAUSES OF CHEMICAL COMBINATION

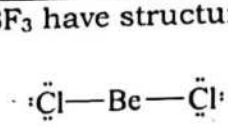
Atoms of elements combine with each other to stabilize themselves. Two factors are necessary for their satisfaction;

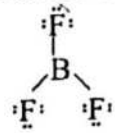
(a) Every atom tries to attain electronic configuration near to a noble gas. (wants to follow octet rule). The tendency of atoms to attain a maximum of eight electrons in the valence shell is called octet rule.

(b) Each atom tries to attain lowest energy state because it is a stable state.

MOLECULES WITH INCOMPLETE OCTETS

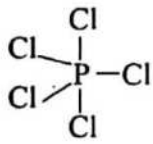
$BeCl_2$ and BF_3 have structure with less than an octet of electrons.





CENTRAL ATOM WITH MORE THAN AN OCTET (extended octet rule)

In the case of PCl_5, the phosphorous has 10 electrons surrounding it while in SF_6, 12 electrons surround the sulphur atom. The elements having d-sub-shell will follow this rule.



Atomic radius is measured by;
- X-ray diffraction
- Spectroscopy

ATOMIC, IONIC and COVALENT RADII

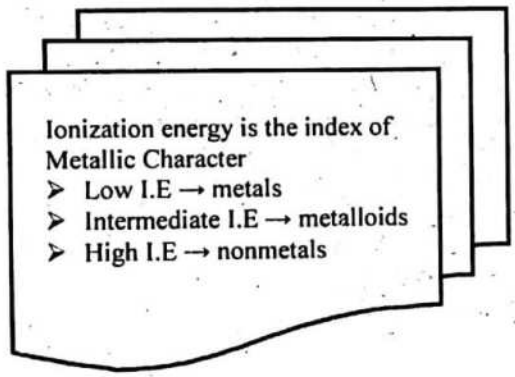
Particulars	Atomic radii	Ionic radii	Covalent radii
Definition	It is the average distance between the nuclei of an atom and its outermost electronic shell	It is the average distance between the nuclei of an ion and its outermost electronic shell	It is the half of the single bond length between two similar atoms covalently bonded in a molecule
Trend along the period	From left to right, it decreases	From left to right, it decreases	From left to right, it decreases
Trend down the group	Increases from top to bottom	Increases from top to bottom	Increases from top to bottom
Effect of the shielding effect	Greater shielding effect results in larger radii	Greater shielding effect results in larger radii	Greater shielding effect results in larger radii

Note: Cationic radius is smaller than parent atom while the anionic radius is larger than the parent atom.

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IONIZATION POTENTIAL, ELECTRON AFFINITY and ELECTRONEGATIVITY

Particular	I.P/I.E	E.A	E.N
Definition	Energy required to remove an electron from the outer most shell of gaseous atom	Energy released when an electron is added to the outer most shell of gaseous atom	Tendency of an atom to attract a shared pair of electron
First, second and third energies	1st I.P is lesser, 2nd is higher and 3rd is much higher	1st E.A is high, 2nd is higher, 3rd is much higher	Not applicable
Trend down the group	Top to bottom decreases	Top to bottom decreases; sometimes energy is absorbed	Top to bottom decreases
Trend along the period	Left to right increases	Left to right increases	Left to right increases
Effect of atomic size	I.P decreases as atomic size decreases	E.A decreases as atomic size increases	E.N decreases as atomic size increases
Effect of nuclear charge	High nuclear charge, high value of I.P	High nuclear charge, high value of E.A	High nuclear charge, high value of E.N
Effect of the shielding effect	Greater shielding effect results in lesser I.P value	Greater shielding effect results in lesser E.A value	Greater shielding effect results in lesser E.N value



Exceptional Cases of Ionization energy:

- Among Li, Be, B, Be has maximum I.E
- Among N, O, F, Ne, Ne has maximum I.E because Ne has stable electronic configuration
- Among B,C,N,O, N has maximum I.E because N has half filled p-sub-shell
- Among Ga, In, Tl, Tl has highest I.E because of poor shielding effect
- Among Ca, Sr, Ba, Sr has maximum I.E because of poor shielding effect
- Among F, Cl, Cl has more electron affinity
- The element of group IIA, VA, and VIII shows abnormal trend. This can be understood from the distribution of the electrons.

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IONIC BOND, COVALENT BOND and CO-ORDINATE COVALENT BOND

Particulars	Ionic bond	Covalent bond	Co-ordinate Covalent bond
Definition	By complete transfer of electrons	By mutual sharing of electrons	By donation of electron pair by one of the bonded atoms
Special	-	▪ Single bond when one electron is shared by each atom ▪ Double bond when 2-electrons are shared by each atom ▪ Triple bond when 3-electrons are shared by each atom	▪ The atom that donates an electron pair is called donor ▪ The atom that accepts an electron pair is called acceptor
Types of atoms involved	More electropositive and more electronegative atoms	Usually the atoms of non-metals.	One group, electron deficient; other group electron rich or have lone pair of electrons
E.N difference	Difference more than 1.7	Difference less than 1.7	-
Ionic nature	Completely ionic	Atoms having more E.N will attain δ^- charge, while other will get δ^+ charge	Donor will bear δ^{+ve} charge while accepter will have δ^{-ve} charge
Alignment	It is non-directional.	It is directional.	It is directional.
Representation	It is represented as positive and negative charge e.g. (Na^+Cl^-)	$-$, $=$, $\equiv$ **Examples** $H_3C\text{-}CH_3$, $H_2C{=}CH_2$ $HC{\equiv}CH$	$\longrightarrow$ **Example** $H_3N: \rightarrow BF_3$

Properties Of ionic Compounds and Covalent Compounds

No.	Properties	Ionic Compounds	Covalent Compounds
1	Conductivity	Conduction of electricity ➢ Non-conductor in solid state. ➢ Conductor in fused or aqueous state.	Non conductor but electrolytic solutions are conductor
2	Thermodynamic properties	High melting point	Low melting point and boiling point
3	Alignment	The bond is non-directional and non-rigid.	The bond is directional and rigid
4	Crystalline properties	Show polymorphism and isomorphism.	Show isomerism
5	Reaction rate	Rate of reaction is very high	Rate of reaction is low
6	Solubility	Soluble in polar solvents.	Like dissolve like

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TYPES OF COVALENT BONDS

Non Polar Bond	Polar Bond.
A covalent bond between two similar atoms or those having negligible electronegativity difference.	A covalent bond between two dissimilar atoms having appreciable electronegativity difference but less than 1.7.
The shared pair of electrons is equally attracted by the two bonded nuclei	The shared pair of electron is un- equally attracted by the two bonded nuclei.
Electron cloud is symmetrical around the two nuclei.	Electron cloud is unsymmetrical around the two nuclei.
No partial charges appear on the molecule because of symmetrical electrons cloud.	Partial positive and partial negative charges appear because of unsymmetrical electrons cloud.
No polarity is developed on the molecule.	There is polarity in the molecule.
Compounds having non-polar bonds have weak intermolecular attraction.	Compounds having polar bonds have strong intermolecular attraction usually
Compounds having non-polar bond have low boiling point and melting point with less solubility in water.	Compounds having polar bonds have high melting point and boiling point with high solubility in water.
It is a weak bond	It is a strong bond.
Example: H — H	Example: $H^{\delta+}$ — $Cl^{\delta-}$

VALENCE SHELL ELECTRON PAIR REPULSION THEORY (VSEPR THEORY)

"The valence electron pairs (lone pairs and the bond pairs) are arranged around the central atom to remain at a maximum distance apart to keep repulsion at a minimum."

NOTE
Lone Pair is not involved in determining the shape of the molecules.

The acronym "VSEPR" is pronounced "vesper"

Introduction

- Sidgwick and Powell
- Nylholm and Gillespie

Postulates

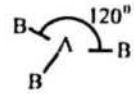
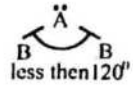
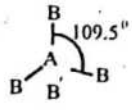
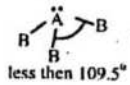
- Both lone pair and bond pair determine the geometry of the molecules
- Lone pair occupies more space than a bond pair
- The magnitude of repulsion (van der Waal's repulsion) is in the following order
  Lone pair – Lone pair > Lone pair – Bond pair > Bond pair – Bond pair
- Double bond and triple bond behaves like a single bond in determining the geometry of the molecule.

Limitations

- VSEPR Theory predicts and explains the shapes of molecules but does not give reasons for the formation of bonds.
- It is not applicable for single bond pair system means di-atomic molecules.
- Complexes do not follow this theory.

✓ CFT and LFT are applied to describe the geometry of complexes

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Type	Electron Pairs			Arrangement of pairs	Molecular geometry	Shape	Examples
	Total	Bonding	Lone				
AB_2	2	2	0	Linear	Linear	B–A–B	$BeCl_2$ $HgCl_2$
AB_3	3	3	0	Trigonal planar	Trigonal planar		BH_3, BF_3 $AlCl_3$
		2	1		Bent (or angular		$SnCl_2, SO_2$
AB_4	4	4	0	Tetrahedral	Tetrahedral		$CH_4, SiCl_4$ CCl_4, BF_4^- NH_4^+, SO_4^{2-}
		3	1		Trigonal pyramidal		NH_3, NF_3 PH_3
		2	2		Bent (or angular)		H_2O, H_2S

VALANCE BOND THEORY (VBT)

It is an approximate theory to explain the bond pair or covalent bond formation by quantum mechanics.

Basic Theory

According to VBT, a bond between two atoms is formed only when;

1. The two partially filled atomic orbitals should overlap each other.
2. Electrons with opposite spin pair up to stabilize themselves during bond formation (overlaping).

Strength

The strength of bond depends on the extent of overlapping. Greater overlapping results in stronger bond.

COMPARISON BETWEEN SIGMA BOND AND PI BOND

Sigma bond	Pi bond
A bond formed by linear overlapping of two half filled atomic orbitals of adjacent atoms is called a sigma bond.	A bond formed by the sidewise overlapping of two half filled parallel atomic orbitals of adjacent atoms is called a pi bond.
Electron density is concentrated around the bond axis.	Electron density lies above and below the bond axis.
It has only one lobe of electron density between the nuclei.	It has two lobes of electron density on opposite sides of bond axis.
Only one sigma bond can exist between two atoms.	One or more pi bonds can exist between two atoms.
It offers free rotation about the bond axis	It offers no free rotation about the bond axis.
It has no nodal plane.	It has a nodal plane along the bond axis.
The sigma bonds present in the molecule determine its shape.	Pi bond has no effect on the shape of the molecule.

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FORMATION OF SOME IMPORTANT COMPOUNDS

Particulars	H_2 molecule	H_2O molecule	NH_3 molecule
Atomic orbital participating	1s will take part	1s of H and $2p_y$, $2p_z$ of O will take part	$2p_x$, $2p_y$, $2p_z$ of N, and 1s of H will take part
Nature of bond	Sigma bond	Sigma bond	Sigma bond
Angle of bond	No	104.5°	107.5°
Number of lone pair of electrons	No	Two lone pairs at O atom	One lone pair at nitrogen atom

HYBRIDIZATION

A process in which atomic orbitals of different energies and shapes are mixed together to form a new set of equivalent orbitals of the same energy and same shape is called hybridization

- Hybridization is a process of mixing of orbitals in a single atom (or ion).
- Only orbitals of comparable (relatively close) energies can be mixed to form hybrid orbitals.
- The number of hybrid orbitals is always equal to the number of orbitals which are mixed.
- Once an orbital has been used to form hybrid orbitals, it is no longer available for the electrons.

Hybrid atomic orbitals

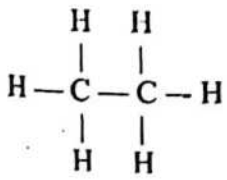
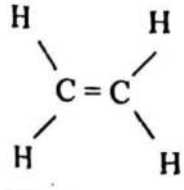
The atomic orbitals of same energy, which have been formed due to mixing of different orbitals of different energies, are called the hybrid atomic orbitals.

Types Of Hybridization

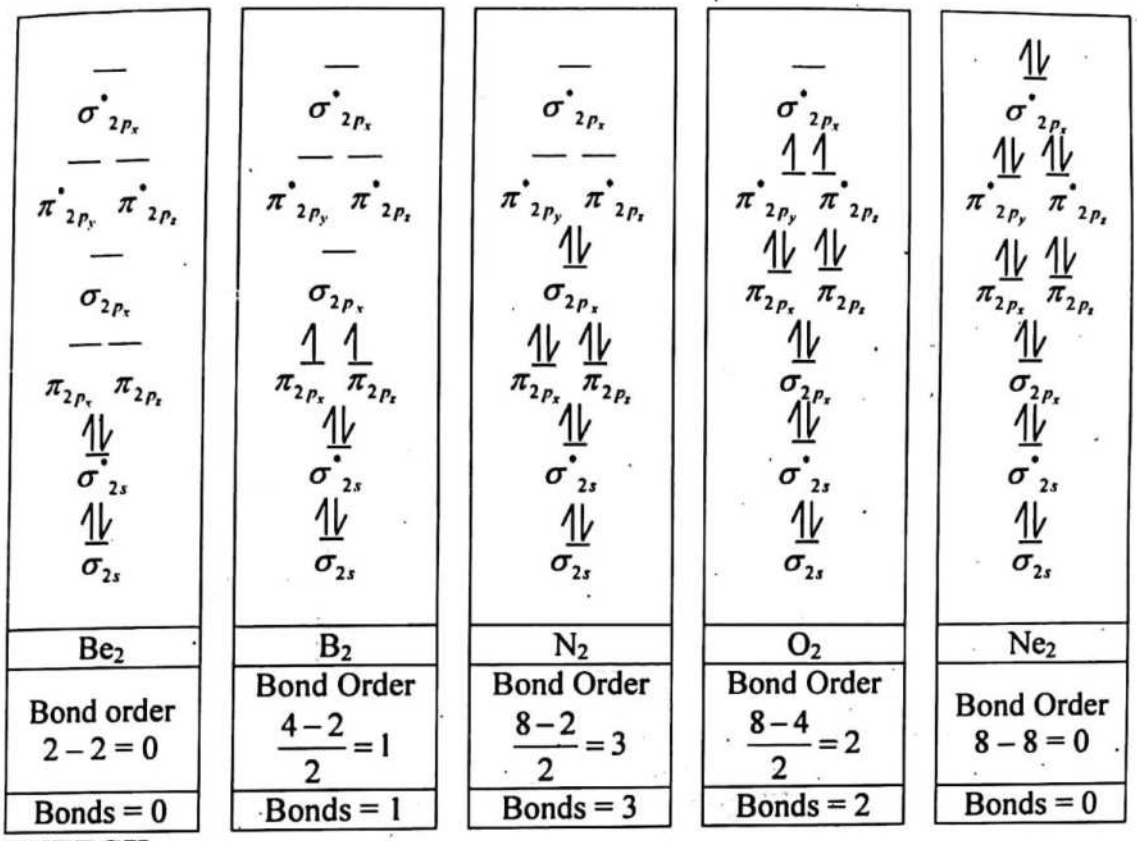
In Hydrocarbons

Particular	sp^3	sp^2	sp
Definition	Mixing of one-s and three p-atomic orbitals	Mixing of one-s and two p-atomic orbitals	Mixing of one-s and one p-atomic orbitals
Geometry	Tetrahedral	Trigonal planar	Linear
Nature of bonds	4 σ-bonds	3 σ-bonds, 1π-bond	2 σ-bonds and 2 π-bonds

STRUCTURE OF HYDROCARBONS ON BASIS OF HYBRIDIZATION

Structure	Number of bonds	Hybridization	Bond angle	Sigma bonds	Pi bonds
	7	sp^3	109.5°	7	0
	6	sp^2	120°	5	1
H – C ≡ C – H	5	sp	180°	3	2

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Be_2	B_2	N_2	O_2	Ne_2
Bond order $2-2=0$	Bond Order $\frac{4-2}{2}=1$	Bond Order $\frac{8-2}{2}=3$	Bond Order $\frac{8-4}{2}=2$	Bond Order $8-8=0$
Bonds = 0	Bonds = 1	Bonds = 3	Bonds = 2	Bonds = 0

BOND ENERGY

The average amount of energy required to break all bonds of a particular type in one mole of the substance is called bond energy.

- Unit of bond energy is kJ/mole.

Factors Effecting Bond Energy

The bond energy is the measure of the strength of bond. The strength of a bond depends upon the following factors.

1- Electronegativity difference of bonded atoms
2- Sizes of the atoms
3- Bond length

BOND LENGTH

The distance between the nuclei of two atoms forming a covalent bond is called bond length.

- Techniques used to determine bond length are electron diffraction, X-ray diffraction or spectral studies.
- Greater the E.N difference between bonded atoms, shorter will be bond length.
- Ionic character shortens bond length.
- Greater the atomic radii of the bonded atoms larger will be the bond length.
- Involvement of π-bond reduces bond length.
- Greater s-character in the hybrid orbital results in shorting of bond length.
- Along the period, bond length decreases.
- Down the group, bond length increases.

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Compound	Bond	Bond length (pm)
BF_3 (sp^2 hybridized)	B–F	130
BCl_3 (sp^2 hybridized)	B–Cl	175
SiH_4 (sp^3 hybridized)	Si–H	148
SiF_4 (sp^3 hybridized)	Si–F	155
C_2H_6 (sp^3 hybridized)	C–C	154
C_2H_4 (sp^2 hybridized)	C=C	133
C_2H_2 (sp hybridized)	C ≡ C	120
$(CH_3)_2C=O$ (sp^2 hybridized)	C=O	122

Applications of bond energy

- Relative strength of bonds
- % of ionic character in bond
- Estimation of ΔH

DIPOLE MOMENT

The product of the electric charge and the distance between the positive and negative centers is called dipole moment. Dipole moment is a vector quantity. Mathematically, it can be written as;

$$\mu = q \times r$$

Units

(i) Coulomb metre (Cm)

(ii) Debye (D)

$$1D = 3.336 \times 10^{-30} Cm$$

Applications

- % of ionic character
- Geometry of molecules

RELATION BETWEEN MOLECULAR GEOMETRY AND DIPOLE MOMENT

Formula	Molecular Geometry	Dipole Moment
AX	Linear	Can be non zero
AX_2	Linear	Zero
	Bent	Can be non zero
AX_3	Trigonal planar	Zero
	Trigonal pyramidal	Can be non zero
	T-shaped	Can be non zero
AX_4	Tetrahedral	Zero
	Square planar	Zero
	Seesaw	Can be non zero
AX_5	Trigonal bipyramidal	Zero
	Square pyramidal	Can be non zero
AX_6	Octahedral	Zero

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1. **The relative attraction of the nucleus for the electrons in a chemical bond is called**
   (a) Ionization energy (b) Electron affinity
   (c) Electro negativity (d) None of the above
2. **The ionization energy**
   (a) Generally increases from left to right in a period
   (b) Does not change in a period
   (c) Increase from top to bottom in a group
   (d) Does not change in a group
3. **Which of the following will have highest value of electron affinity**
   (a) F (b) Cl
   (c) Br (d) I
4. **Which type of bond is formed by overlap of p orbitals**
   (a) Pi(π) (b) Sigma(σ)
   (c) Both (d) Neither
5. **The octet rule does not always hold for which of the following elements?**
   (a) C (b) O
   (c) F (d) P
6. **Which of the solid does not contain covalent bond**
   (a) Copper (b) Ice
   (c) Diamond (d) Graphite
7. **Which of the following is the best explanation that CO_2 is non polar molecule**
   (a) Linear geometry (b) Dipole moment is zero
   (c) sp hybridization (d) None of these
8. **Shielding effect across the period**
   (a) Increases (b) Decreases
   (c) Constant (d) 1st Increase and then decreases
9. **Which one is not the absolute term of the element?**
   (a) Ionization energy (b) Electron affinity
   (c) Electro negativity (d) Atomic size
10. **Which one has maximum number of unpaired electrons?**
    (a) $_6X$ (b) $_7Y$
    (c) $_9Z$ (d) $_{13}W$
11. **The molecule having π-bond**
    (a) H_2O (b) C_2H_6
    (c) O_2 (d) NH_3
12. **When 2 lone pair and 2 bond pair are around the central atom, reduction in the bond angle is up to.**
    (a) 109.5° (b) 104.5°
    (c) 107.5° (d) 102°

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13. **In O_2, each oxygen atom is hybridized**
(a) sp^3 (b) sp^2
(c) sp (d) All

14. **Molecular orbitals are filled according to**
(a) Auf bau principle (b) Hund's rule
(c) Pauli's Exclusion principle (d) All these

15. **Measurement of the degree of polarity is**
(a) Electron affinity (b) Ionic character
(c) Ionization energy (d) Dipole moment

16. **Which one shows high %age of the ionic character?**
(a) H_2O (b) HF
(c) HCl (d) HBr

17. **Which of the following has largest ionic size?**
(a) F^- (b) Na^+
(c) Mg^{+2} (d) Al^{+3}

18. **Which of the following have their outer most shell complete in atomic form?**
(a) Noble gases (b) Alkali metals
(c) Coinage metals (d) Gun metals

19. **Force responsible to hold atoms together in a compound is called**
(a) Bond (b) Attractive force
(c) Interaction (d) All of above represent same entity

20. **Energy of atom in compound is**
(a) Higher than individual (b) Lesser than individual
(c) No change (d) Impossible to predict

21. **In a period, the atomic radii**
(a) Increases (b) Decreases
(c) Remain same (d) First decreases, then increases

22. **An atom loses or gains electrons, to**
(a) Gain stability (b) Form a bond
(c) Complete its outermost shell (d) All are accurate justifications

23. **In a group, ionic radii**
(a) Increases (b) Decreases
(c) No change (d) Variable trend

24. **Energy required to remove electron from an atom**
(a) Ionization potential (b) Electronegativity
(c) Electron affinity (d) Activation energy

25. **Factor which is not responsible for variation in I.E down the groups**
(a) Shielding effect (b) Atomic size
(c) Nature of orbital (d) Nuclear attraction

26. **Greater shielding effect corresponds to ionization energy value**
(a) Greater (b) Lesser
(c) Remain same (d) No effect

27. **Elements having high I.P values are**
(a) Metals (b) Non metals
(c) Liquids (d) Solids

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28. **Energy released or absorbed when electrons are added in atom is**
(a) Ionization potential (b) Electronegativity
(c) Electron affinity (d) Activation energy

29. **In a period, electronegativity from left to right**
(a) Increases (b) Decreases
(c) Remain constant (d) Variable trend

30. **Ionic bond is produced after complete transfer of**
(a) Nucleus (b) Neutrons
(c) Electrons (d) Protons

31. **Elements of group IA, IIA are**
(a) Electronegative
(b) Electropositive
(c) IIA is electropositive, while IA is electronegative
(d) IA is electropositive, while IIA is electronegative

32. **Bond will be ionic, when E.N difference of bonded atom is**
(a) Equal to 1.7 (b) Greater than 1.7
(c) Less than 1.7 (d) No specificity exists

33. **Mostly ionic compound are produced in between elements of**
(a) IA and VIA (b) IA, IIA and VIIA
(c) IB and VIIB (d) IA and IB

34. **Which one of the following has polar covalent bond?**
(a) HF (b) CH_4
(c) H_2 (d) N_2

35. **The Lewis acids are**
(a) Electron deficient (b) Electron rich
(c) Octet is complete (d) No such acids exist

36. **Sharing of 1 electron pair by one specie forms**
(a) Single covalent bond (b) Hydrogen bond
(c) Double covalent bond (d) Coordinate covalent bond

37. **Bond angle in water molecule is**
(a) 104.9° (b) 104.5°
(c) 109.5° (d) 107°

38. **The geometry of ammonia is**
(a) Tetrahedral (b) Square planner
(c) Trigonal bipyramidal (d) Trigonal Pyramidal

39. **Orbitals of same energy produced after mixing of orbitals of different energy are called**
(a) Degenerate orbitals (b) Molecular orbitals
(c) Hybrid orbitals (d) All of these

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40. By combining "n" atomic orbitals, number of hybrid orbitals will be
(a) 2n (b) n
(c) 3n (d) Impossible to predict

41. In sp^3 hybridization
(a) All p-orbitals are involved (b) One s and 3 p-orbitals are involved
(c) One p-orbital is involved (d) Four p-orbitals are involved

42. Geometry of simple molecule having sp^3 hybrid orbital is
(a) Triangular (b) Tetrahedral
(c) Square planner (d) Linear

43. Geometry of molecule will be pyramidal, if the outer most shell of the central atom has
(a) 3 bond pair, one lone pair (b) 2 bond pair, 2 lone pair
(c) 1 bond pair, 3 lone pair (d) 3 lone pair, 1 bond pair

44. Pi bonds are produced by overlapping of
(a) Un-hybrid orbitals (b) Hybrid orbitals
(c) Hybrid and un-hybrid orbitals (d) Atomic orbital and hybrid orbital

45. According to VSEPR Model, the geometry of molecule having 5 bond pair in outer most shell will be
(a) Triangular (b) Square planner
(c) Trigonal bipyramidal (d) Octahedral

46. Molecular orbital, which have higher energy than atomic orbitals is called
(a) Bonding molecular orbital (b) Antibonding molecular orbital
(c) Hybrid orbital (d) Degenerate atomic orbital

47. Unpaired electron in a molecule gives _____character
(a) Ferromagnetic (b) Paramagnetic
(c) Diamagnetic (d) Both a and b

48. Bond order for N_2 molecule is
(a) 2 (b) 1
(c) 3 (d) 4

49. Product of charge and distance is called
(a) Pressure (b) Bond length
(c) Work (d) Dipole moment

50. Unit of dipole moment is
(a) Debye (b) Poise
(c) Pascal (d) Newton

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Chapter 7

THERMOCHEMISTRY

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THERMOCHEMISTRY

The study of heat changes during a chemical reaction is called thermochemistry.

ENERGY

"Ability of a body to do work is called energy."

TYPES OF ENERGIES

(i) Kinetic energy (K.E)→Energy due to motion
(ii) Potential energy (P.E)→Energy due to position, shape and orientation
(iii) Sound energy
(iv) Heat energy
(v) Magnetic energy
(vi) Mechanical energy
(vii) Solar energy

UNITS OF ENERGY

Units	Relation
Joule (SI Unit)	$J=kgm^2s^{-2}$
British thermal unit	$1B.T.U=1.055x10^3J$
Kilo watt hour	$1Kwh = 3.6x10^6J$
Calorie	$1\ Cal = 4.184J$
erg	$1J=10^7ergs$

SYSTEM

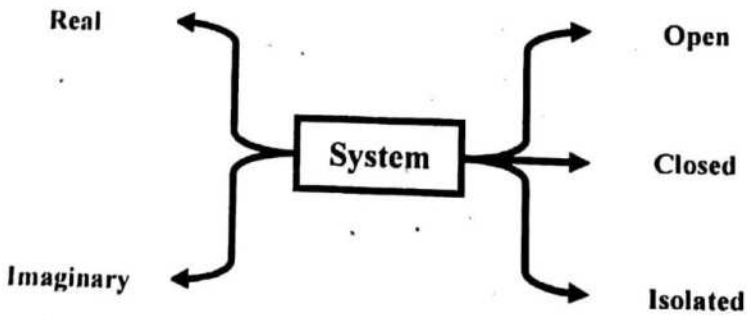
"The portion of universe which is set aside for consideration, observation, discussion, argumentation or experimentation is called system"

OR

"The substance under consideration is called chemical system"

Examples

(i) $Pb(NO_3)_2$ under consideration is a system.
(ii) The liquid whose boiling point is to be measured is a system.



Isolated System

If a system is isolated, then nothing can enter or leave. Its energy and matter remain the same. Any changes go on inside the system, and since it is isolated, we cannot know anything about an isolated system from the outside.

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Open System

When both matter and energy can be exchanged, the system is called open. Clearly when you do a titration matter is added. In this case the system is the beaker.

Closed System

When only energy can be exchanged but matter can not exchanged between system and surrounding, the system is called closed. A bomb calorimeter only allows heat to be exchanged. Such a system is called closed.

SURROUNDING

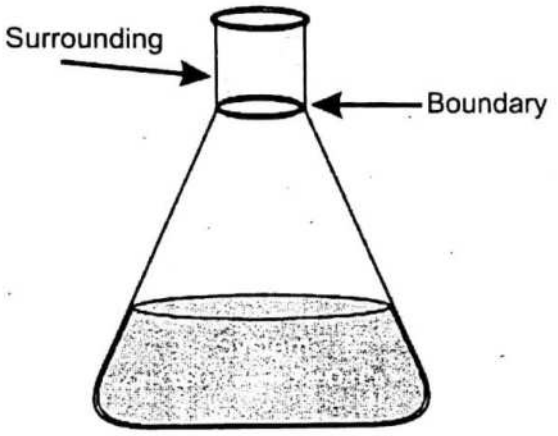
The portion of universe except system is called surrounding.

Example

A chemical reaction happening in a test tube is a system, while the walls of the test tube and the atmosphere are its surrounding.

BOUNDARY

The real or imaginary surface, separating the system from surrounding is called boundary of a system.



FLASK

STATE

The condition of a system is called state of the system.

EXAMPLES

Volume, Temperature, Pressure, Energy etc

	State	Examples
1	Conditions describing the system before it undergoes a change are called initial states of system.	V_1, T_1, P_1, E_1
2	Conditions describing the system after it undergoes a change are called final states of system.	V_2, T_2, P_2, E_2

CHANGE IN THE STATE OF SYSTEM

$\Delta V = V_2 - V_1$ (Change in volume)

$\Delta P = P_2 - P_1$ (Change in pressure)

$\Delta G = G_2 - G_1$ (Change in free energy)

$\Delta H = H_2 - H_1$ (Change in enthalpy)

$\Delta T = T_2 - T_1$ (Change in temperature)

$\Delta E = E_2 - E_1$ (Change in internal energy)

$\Delta S = S_2 - S_1$ (Change in entropy)

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STATE FUNCTION

A macroscopic property of a system which has some definite values for initial and final states, and which is independent of the path adopted to bring about a change.

Examples

Pressure (P), Temperature (T), Volume (V), Internal energy (E) and enthalpy (H) are all state functions.

- Capital symbols are used for state function.
- Heat and work are not state functions.
- Internal energy E is a state function.

INTERNAL ENERGY

"The sum of potential energy and kinetic energy of a substance is called its internal energy."

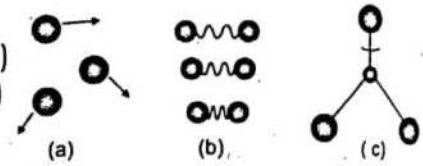
OR

"The sum of all the possible kinds of energies of a system is called its internal energy (E)."

$$E_T = K.E + P.E + \ldots\ldots$$

Internal energy

- **Kinetic energy**
  - Translational kinetic energy (a) (mono-atomic)
  - Rotational kinetic energy (b) (tetra-atomic)
  - Vibrational kinetic energy (c) (di-atomic)



- **Potential energy**
  - Intra-molecular forces
  - Inter-molecular forces
- **Effect of increase in Internal Energy:**
  - i) The temperature of the system may increase
  - ii) A phase change may occur.
  - iii) A chemical reaction may take place.

FIRST LAW OF THERMODYNAMICS (LAW OF CONSERVATION OF ENERGY)

"Energy can neither be created nor be destroyed, but can be changed from one form to another."

$$\Delta E = q + P\Delta V$$

$$\Delta E = q_v$$

ENTHALPY

The total heat content of a system is called enthalpy of a system.

- It is a state function.
- In a given state, enthalpy cannot be calculated.
- Change in enthalpy is equal to heat of reaction at constant pressure

  $\Delta H = q_p$
- Enthalpy change ΔH of a reaction is the change that occurs when certain number of moles of reactants converts into products under standard conditions i.e. 25°C and 1 atm.
- Change in enthalpy, which occurs when one mole of a compound is produced from reactants, is called molar enthalpy of formation (ΔH_f).

  e.g. ΔH°_f for CO_2=-393.7 kJmole^{-1}

  ΔH°_f for MgO =-692 kJmole^{-1}
- Standard enthalpy of a substance is chosen 'zero'.
- $q_p > q_v$ or $\Delta H > \Delta E$

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Enthalpy	Definition	Symbol
Enthalpy of reaction	The enthalpy change which occurs when the certain number of moles of reactants as indicated by the balanced chemical equation, react together completely to give the products under standard condition. $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$ $\Delta H^\circ = -285.8 kJmol^{-1}$	ΔH°_r
Enthalpy of formation	The change of enthalpy when one mole of the compound is formed from atoms of its elements. $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H^\circ_f = -393.7 kJmol^{-1}$	ΔH°_f
Enthalpy of atomization	The enthalpy change when one mole of gaseous atoms are formed from a molecule or an element under standard conditions. $1/2H_{2(g)} \rightarrow H_{(g)}$ $\Delta H^\circ_{at} = +218 kJmol^{-1}$	ΔH°_{at}
Enthalpy of neutralization	The amount of heat evolved when one mole of hydrogen ions H^+ from an acid, react with one mole of hydroxide ions (OH^-) from a base to form one mole of water. Example:- The enthalpy of neutralization of sodium hydroxide by hydrochloric acid is $-57.4 kJmol^{-1}$. $NaOH + HCl \rightarrow NaCl + H_2O$ $\Delta H_n = -57.4 kjmol^{-1}$	ΔH°_n
Enthalpy of combustion	The enthalpy change when one mole of a substance is completely burnt in excess of oxygen under standard conditions. $C_2H_5OH_{(l)} + 3O_2 \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ $\Delta H^\circ_c = -1368 kJmol^{-1}$	ΔH°_c
Enthalpy of solution	The amount of heat absorbed or evolved when one mole of a substance is dissolved in so much solvent that further dilution results in no detectable heat change. $NH_4Cl_{(s)} + (aq) \rightleftharpoons NH_4Cl_{(aq)}$ $\Delta H^0_{(sol)} = +16.2 kJmol^{-1}$	ΔH°_{sol}

Enthalpy (energy) changes
Δ (delta means difference)
H (means enthalpy)
$\Delta H = E_{IN} - E_{OUT}$ (joules)

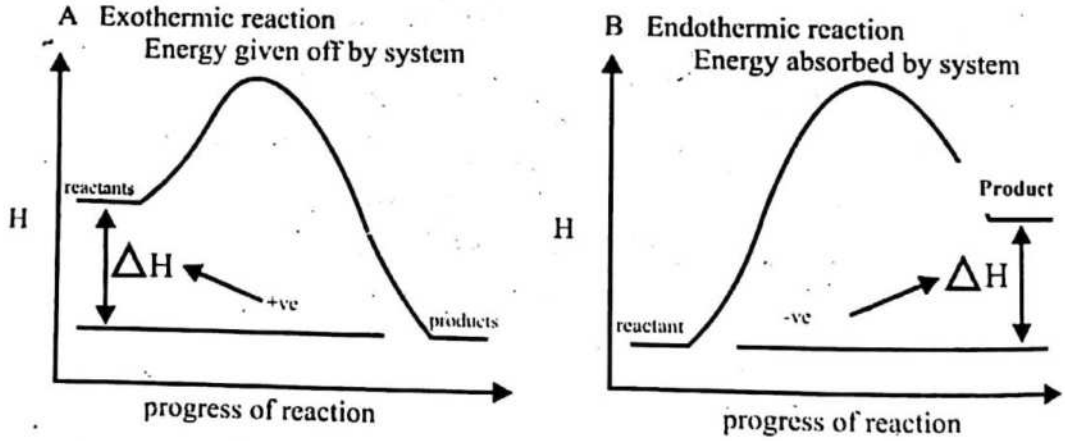
Examples of reactions when ΔH° = +ive :	Examples of reactions when ΔH° = - ive :	Examples of reactions when ΔH° = + ive or - ive :
i) Enthalpy of atomization (ΔH°_{at})	i) Enthalpy of Neutralization (ΔH°_n)	i) Enthalpy of Formation (ΔH°_f)
ii) Enthalpy of ionization (ΔH°_i)	ii) Enthalpy of Combustion (ΔH°_c)	ii) Enthalpy of Solution (ΔH°_{sol})

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Comparison of Exothermic and Endothermic Reactions

Sr.	Properties	Exothermic	Endothermic
1	Flow of heat energy	System to surrounding	Surrounding to system
2	Temperature of surrounding	Increases	Decreases
3	Temperature of the system	Decreases	Increases
4	Energy of products	Low	High
5	Energy of reactants	High	Low
6	Strength of bonds in products	Strong	Weak
7	Strength of bonds in reactants	Weak	Strong
8	Enthalpy change (ΔH)	Negative	Positive
9	Examples	$C + O_2 \rightarrow CO_2$ $\Delta H = -393.7 kj/mol$ **Respiration** $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ **Neutralization** $NaOH + HCl \rightarrow NaCl + H_2O$	$N_2 + O_2 \rightarrow 2NO$ $\Delta H = +180.51 kj/mol$ **Thermal decomposition** $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$ **Dissolving** $NH_4NO_{3(s)} \rightarrow NH_4NO_{3(aq)}$

Graphical Representation of Exothermic and Endothermic Reactions



DIFFERENCE BETWEEN INTERNAL ENERGY AND ENTHALPY

Internal energy	Enthalpy
• It is defined as the total energy of the system. • It is denoted by 'E' • It is the sum of kinetic and potential energies. • It is calculated by the formula. $E = \frac{1}{2}mv^2 + P.E$ • It is expressed in Joules or calories.	• It is defined as the sum of internal energy and product of pressure and volume of the system. • It is denoted by 'H'. • It is calculated by the formula. $H = E + PV$ • It is expressed in kcal mol^{-1} or $kJmol^{-1}$.

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DIFFERENCE BETWEEN SPONTANEOUS AND NON-SPONTANEOUS REACTIONS

Spontaneous reaction	Non-Spontaneous reaction
• A process which takes place on its own without any outside assistance is called spontaneous reaction. • It moves from a non equilibrium state towards an equilibrium state. • It is usually exothermic in nature. • It is unidirectional irreversible and a real process. **Examples** i. Water flows from higher level to the lower level. ii. Neutralization of a strong acid with a strong base is a spontaneous acid base reaction.	• A process which needs external assistance to start is called non-spontaneous reactions. • It is the reverse of spontaneous process. • It is usually endothermic in nature. • It is multidirectional, reversible and an imaginary process. **Examples** i. Pumping of water uphill. ii. Transfer of heat from cold interior part of the refrigerator to the hot surroundings

ΔG = +ve → non-spontaneous reaction
ΔG = -ve → spontaneous reaction

Do Not Mix

- It is expected that all exothermic reactions are spontaneous. But it is not always true. Some endothermic reactions are also spontaneous in nature.
- The spontaneity of a reaction can be measured by study of the free energy of the system.

$\Delta G = \Delta H - \Delta TS$

MEASUREMENT OF ENTHALPY OF A REACTION

There are two basic methods to measure the enthalpy of reactions

- Experimental methods
  - Glass Calorimeter
  - Bomb Calorimeter

Heat of reaction of those reactions can be measured by calorimeter, which are in single step.

- Theoretical methods
  - Hess's Law for constant heat summation
  - Born Haber's cycle

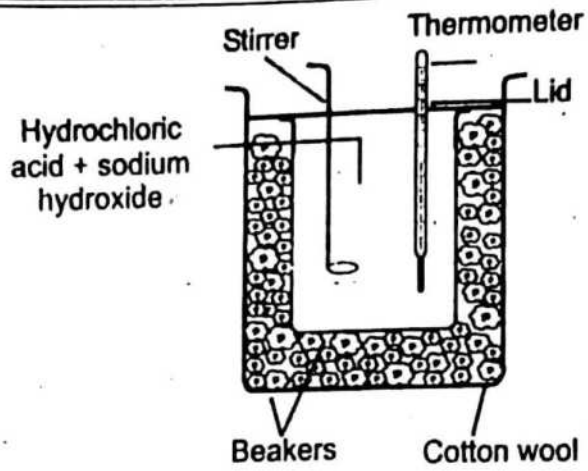
BY GLASS CALORIMETER

- Glass calorimeter is used to measure the enthalpy of reaction.
- By using following relationship, heat of reaction is calculated.

$$q = m \times s \times \Delta T$$

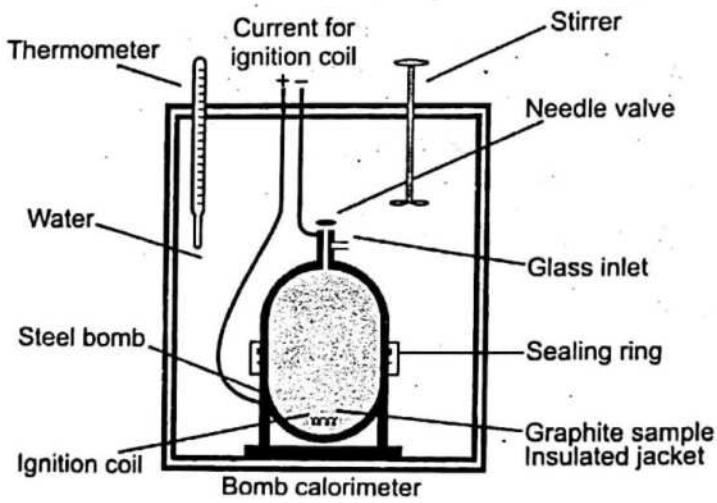
where
m = mass of reactant, Units = 'g' or 'Kg'
s = specific heat of reacting mixture, Units = $JK^{-1}g^{-1}$
ΔT = change in temperature, Units = K

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BY BOMB CALORIMETER

- It gives more accurate enthalpy of combustion for food, fuel etc.
- It contains steel vessel lined with enamel to prevent corrosion.
- Platinum crucible is used inside bomb calorimeter.
- Pressure of O_2 is maintained at 20 atm.
- When mass of reactants is in grams, then specific heat unit will be kJ/g.



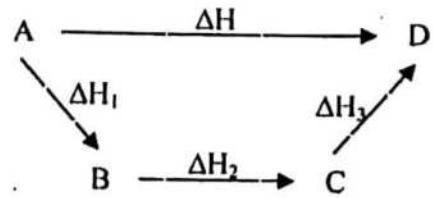
$$q = C \times \Delta T$$

where

C	=	Heat capacity,	Units	= kJK^{-1}
ΔT	=	change in temperature,	Units	= K

HESS'S LAW OF CONSTANT HEAT SUMMATION

Energy contents of a reaction remain constant either that reaction completes in single step or different steps.



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

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Example

⇒ **Single step process**

$2NaOH+CO_2 \rightarrow Na_2CO_3+H_2O$ $\quad \Delta H_1 = -89.08$ kJ

⇒ **Two step process**

$NaOH+CO_2 \rightarrow NaHCO_3$ $\quad \Delta H_2 = -48.06$ kJ

$NaHCO_3+NaOH \rightarrow Na_2CO_3+H_2O$ $\quad \Delta H_3 = -41.02$ kJ

According to Hess's law

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

$-89.08 = -48.06 - 41.02$

$-89.08 = -89.08$

BORN-HYBER CYCLE

Energy change in cyclic process is always zero. It enables us to calculate the lattice energy of binary compounds (ionic); this is called Born-Hyber cycle.

$$\sum(\Delta H)\text{cycle}=0$$

LATTICE ENERGY

- Lattice energy of an ionic crystal is the enthalpy of formation of one mole of the ionic compound from gaseous ions under STP.
- Lattice energy cannot be determined directly.
- Lattice energy can be obtained by means of Born-Haber cycle.
- Lattice energy is helpful in discussing structure, bonding and properties of ionic compounds.

Applications

It is applied to determine

- Structure of ionic compounds
- Bonding in ionic compounds
- Properties of ionic compounds

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PRACTICE EXERCISE

20 min Time Yourself

1. **Which one is not a state function**
   (a) Internal energy (b) Enthalpy
   (c) Gibbs free energy (d) Work
2. **If ΔH value is less than zero then reaction will be**
   (a) Exothermic
   (b) Endothermic
   (c) May or may not be Exothormic or Endothermic
   (d) None of these
3. **If internal energy of the system is increased.**
   (a) Change in state of the system may occur
   (b) Temperature of the system may rise
   (c) Chemical reaction may take place
   (d) All
4. **Which is true for a spontaneous endothermic process?**
   (a) $\Delta H<0$ (b) $\Delta G< 0$
   (b) $\Delta S<0$ (d) $\Delta G>0$
5. **Plants and animals are example of**
   (a) Isolated System (b) Closed System
   (c) Adiabatic System (d) Open system
6. **_____ is study about energy of a chemical system**
   (a) thermochemistry (b) thermodynamics
   (c) chemical kinetics (d) stoichiometry
7. **The environment in which a system is studied is**
   (a) state function (b) phase
   (c) surrounding (d) state
8. **Unit of heat in SI system is**
   (a) J (b) kCal
   (c) Cal (d) GJ
9. **Anything which depends upon initial and final state of a system is**
   (a) environment (b) surrounding
   (c) state function (d) enthalpy
10. **Total energy of a system is**
    (a) P.E +K.E (b) P.E+heat energy
    (c) K.E+heat energy (d) P.E +mechanical energy
11. **Mathematical form of first law of thermodynamics is**
    (a) $\Delta H=q_p$ (b) $\Delta E=q + w$
    (c) $\Delta E=q \times v$ (d) All of the above
12. **Reaction in which heat evolves is called**
    (a) endothermic (b) spontaneous
    (c) non-spontaneous (d) exothermic
13. **$CuSO_4+Zn \rightarrow ZnSO_4+Cu$ is**
    (a) Spontaneous reaction (b) Non-spontaneous reaction
    (c) Endothermic (d) Exothermic
14. **Pumping of water uphill is**
    (a) spontaneous process (b) non-spontaneous process
    (c) irreversible process (d) reversible process

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15. **State function, the macroscopic property of system, depends upon**
(a) path of reaction (b) initial state
(c) final state (d) initial and final state

16. **Which one of the following is a state function?**
(a) pressure (b) temperature
(c) enthalpy (d) all of the above

17. **When enthalpy of reactants is higher than product, then reaction will be**
(a) endothermic (b) spontaneous
(c) non-spontaneous (d) exothermic

18. **Enthalpy of a reaction can be measured by**
(a) glass calorimeter (b) manometer
(c) Barometer (d) thermometer

19. **Enthalpy of combustion for food, fuel and other compounds can be measured** accurately by
(a) glass calorimeter (b) bomb calorimeter
(c) thermometer (d) manometer

20. **The lattice energy of NaCl is**
(a) -787kJ/mole (b) 787J/mole
(c) 780kJ/mole (d) 790kJ/mole

21. **Most of thermodynamic parameters are**
(a) system (b) surrounding
(c) phase (d) state functions

22. **ΔH of a system can be calculated by which of following relationship**
(a) $q=m \times s \times \Delta T$ (b) $q=\Delta E$
(c) $q=m \times v \times \Delta T$ (d) $q=pv$

23. **Change in enthalpy(H) of a system can be calculated by following relationship.**
(a) $\Delta H=\Delta E+P\Delta V$ (b) $\Delta H=\Delta E-PV$
(c) $\Delta H=\Delta E-q$ (d) $\Delta H=\Delta E+q$

24. **Which of the following is correct**
(a) $q_p>q_v$ (b) $\Delta E<\Delta H$
(c) $\Delta E>\Delta H$ (d) Both a and b

25. **Two fundamental ways to transfer energy are**
(a) pressure and temperature (b) pressure and volume
(c) heat and work (d) heat and volume

26. **which of the following processes has always ΔH = -ve**
(a) formation of compound (b) combustion
(c) dissolution of ionic compound (d) dilution of a solution

27. **Enthalpy change can be**
(a) calculated by Hess's law (b) can be measured by calorimeter
(c) both a and b (d) none

28. **If there is interconversion of solid and liquid states then**
(a) $\Delta V = 0$ (b) $\Delta H \approx \Delta E$
(c) $\Delta H > \Delta E$ (d) both a and b

29. **In order to determine ΔH_{latt} of ionic compound which is correct relationship**
(a) $\Delta H_{latt} = \Delta H_f - \Delta H_x$ (b) $\Delta H_{latt} = \Delta H_f + \Delta H_x$
(c) $\Delta H_{latt} = \Delta H_a + \Delta H_v$ (d) $\Delta H_{latt} = \Delta H_f - \Delta H_{sol}$

30. **Hess's law can be applied to determine**
(a) ΔH_f (b) ΔH_{latt}
(c) ΔH_{comb} (d) All of the above

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Chapter 8

CHEMICAL EQUILIBRIUM

KIPS

(I) Reversible and Irreversible Reactions
- State of Chemical Equilibrium
- Law of Mass Action
- Equilibrium Constant Expressions or Some Important Reactions
- Relationship Between Equilibrium Constants
- Applications of Equilibrium Constants
- The Le-Chatelier's Principle

(II) Applications of Chemical Equilibrium in Industry
- Synthesis of Ammonia by Haber's Process
- Preparation of Sulphur Trioxide

(III) Ionic Product of Water

(IV) Ionization Constants of Acids (K_a)

(V) Ionization Constant of Bases (K_b)

(VI) Lowry Bronsted acid and BaseConcept
- Examples of Common Ion Effect

(VII) Common Ion effect
- Effect of Common Ion on Solubility
- Determination of Solubility from K_{sp}
- Determination of K_{sp} from solubility
- Applications of solubility product

(VIII) Buffer Solutions
- Buffer Capacity

(IX) Equilibria of Slightly Soluble Ionic Compounds

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RATE OF CHEMICAL REACTION

The change in the molar concentration of the reactants or products per unit time is called rate of chemical reaction.

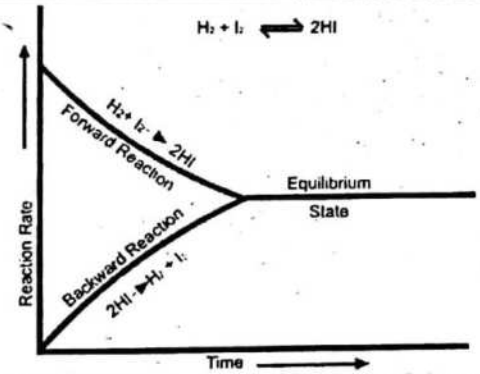
Its units are $mol.dm^{-3}s^{-1}$.

CHEMICAL EQUILIBRIUM

An apparent state of rest in a reversible chemical reaction where the rate of forward chemical reaction becomes equal to the rate of reverse reaction is called chemical equilibrium.

- **Characteristics of Chemical Equilibrium:**
  - It is established only in close system
  - It can be established from either side
  - It is a microscopic property
  - When chemical equilibrium is established even then minute changes continuously take place. These changes are called microscopic properties.
  - It is a dynamic state.
- **Types of Equilibria**

Homogeneous Equilibrium	Heterogeneous equilibrium
A chemical equilibrium in which the reaction mixture and catalyst are in the same phase is called a homogeneous equilibrium e.g.	A chemical equilibrium in which the reaction mixture and catalyst are present in different phases is called a heterogeneous equilibrium e.g.
$2SO_{2(g)} + O_{2(g)} \underset{}{\overset{NO_{(g)}}{\rightleftharpoons}} 2SO_{3(g)}$	$2SO_{2(g)} + O_{2(g)} \underset{}{\overset{V_2O_{5(s)}}{\rightleftharpoons}} 2SO_{3(g)}$



Difference between reversible and irreversible reaction

Reversible Reactions	Irreversible Reactions
Proceed in both directions i.e. forward and reverse	Proceed in one direction i.e. forward.
Reaction does not go to completion.	Reaction goes to completion usually.
Represented by $\left(\rightleftharpoons\right)$	Represented by $(\rightarrow)$
Dynamic equilibrium state is present	Dynamic equilibrium state is absent.
Examples $N_2 + 3H_2 \underset{}{\overset{Fe/450^{\circ}C}{\rightleftharpoons}} 2NH_3$ $PCl_5 \underset{}{\overset{High\ Pressure}{\rightleftharpoons}} PCl_3 + Cl_2$	**Examples** $2Na + 2H_2O \rightarrow 2NaOH + H_2$ $2H_2 + O_2 \rightarrow 2H_2O$

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LAW OF MASS ACTION

C.M Guldberg and P.Waage introduced this law in 1864.

Statement:

It states that the rate at which the reaction proceeds is directly proportional to the product of the active masses of the reactants or their molar concentration.

Explanation:

Consider a general reaction in which A and B are the reactants and C and D are the products.

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C + D$$

$R_f \propto [A][B]$

$R_f = k_f [A][B]$

$R_r \propto [C][D]$

$R_r = k_r [C][D]$

$R_f = R_r$

$k_f[A][B] = k_r [C][D]$

On rearranging, we get

$$\frac{k_f}{k_r} = \frac{[C][D]}{[A][B]}$$

$$\frac{k_f}{k_r} = K_c$$

$$K_c = \frac{[C][D]}{[A][B]}$$

Active mass means the concentration in mole dm^{-3} of the reactants which alter as a result of chemical reaction

The constant K_c is called the equilibrium constant of the reaction.

For a more general reaction

$$aA + bB \underset{k_r}{\overset{k_f}{\rightleftharpoons}} cC + dD$$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

WHAT IS K_c

The ratio of the products of the concentrations of the products to the product of the concentrations of the reactants is called equilibrium constant (K_c)

CHARACTERISTICS OF K_c

Factors	Expression
Depends upon	Greater the temperature, greater will be the K_c value for endothermic reactions and vice versa
Independent of	• Initial concentration of reactants • Direction of reaction • Catalyst
Units	• When Number of moles of reactants = number of moles of products Then Kc has no units • When Number of moles of reactants ≠ number of moles of products Then K_c has some units either conc. or $(conc)^{-1}$

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EQUILIBRIUM CONSTANT EXPRESSIONS OF DIFFERENT REACTIONS

Particular	Ester formation	Dissociation of PCl_5	Decomposition of N_2O_4	Synthesis of NH_3
Reaction	$RCOOH+ROH \rightarrow RCOOR+H_2O$	$PCl_5 \rightarrow PCl_3+Cl_2$	$N_2O_4 \rightarrow 2NO_2$	$N_2+3H_2 \rightarrow 2NH_3$
Initial conc. of reactants	(a) = [RCOOH] (b) = [ROH]	(a) = $[PCl_5]$	(a) = $[N_2O_4]$	(a) = $[N_2]$ (b) = $[H_2]$
Final conc. of reactants	(a-x) = [RCOOH] (b-x) = [ROH]	(a-x) = $[PCl_5]$	(a-x) = $[N_2O_4]$	(a-x) = $[N_2]$ (b-3x) = $[H_2]$
Rate expression	$K_c = \frac{[RCOOR][H_2O]}{[RCOOH][ROH]}$	$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$	$K_c = \frac{[NO_2]^2}{[N_2O_5]}$	$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$
	$K_c = \frac{x^2}{(a-x)(b-x)}$	$K_c = \frac{x^2}{V(a-x)}$	$K_c = \frac{4x^2}{V(a-x)}$	$K_c = \frac{4x^2V^2}{(a-x)(b-3x)^3}$

RELATION BETWEEN DIFFERENT EQUILIBRIUM CONSTANTS

When concentrations are expressed in mole dm^{-3}, then

$$aA + bB \rightleftharpoons cC + dD$$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$K_c = \frac{C_C^c C_D^d}{C_A^a C_B^b}$$

In case of gases, we use partial pressure and K_c changes to K_p.

$$K_c = \frac{p_C^c p_D^d}{p_A^a p_B^b}$$

$K_p = K_c (RT)^{\Delta n} = K_x (P)^{\Delta n} = K_n (P/N)^{\Delta n}$

Δn = number of moles of products – number of moles of reactants
R = General gas constant
T = Absolute temperature
When $\Delta n = 0$ then
$K_p = K_c = K_x = K_n$

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Applications of K_c:

Direction of Reaction	Extent of reaction
• When $K_c<1$, then backward reaction will be dominant before the equilibrium is reached • When $K_c>1$, then forward reaction will dominant before the equilibrium is reached • When $K_c = 1$, then reaction is at equilibrium	• Larger value of K_c shows forward reaction. $2O_3 \rightleftharpoons 3O_2$ ($K_c=10^{55}$ at 25°C) • Smaller value of K_c shows backward reaction $2HF \rightleftharpoons H_2 + F_2$ ($K_c = 10^{-13}$ at 2000°C) • Neither very small nor very large value of K_c shows equilibrium. $N_2 + 3H_2 \rightleftharpoons 2NH_3$ ($K_c= 0.1$ at 25°C)

Characteristics of K_c:

- K_c is independent of the initial concentrations
- K_c changes with change in temperature
- K_c may or may not have units
  a) K_c has no unit when $\Delta n = 0$
  b) K_c has certain unit when $\Delta n \neq 0$
  (Δn = no of moles of products – no of mole of reactants)

Note

If K_c is very small then products will be very much unstable.
If K_c is very large then the products will be very much stable.

THE LE-CHATELIER'S PRINCIPLE

Statement

This principle states that if a stress is applied to a system at equilibrium, the system acts in such a way so as to nullify, as far as possible, the effect of that stress.

Applications of Le-Chatelier's principle

There are four aspects
(i) Effect of change of concentration.
(ii) Effect of change of pressure.
(iii) Effect of change of temperature.
(iv) Effect of catalyst on equilibrium.

Effect of change of concentration

- The addition of substance among the reactants, or the removal of a substance among the products at equilibrium stage disturbs the equilibrium position and reaction is shifted to forward direction.
- The addition of a substance among the products or the removal of a substance among the reactants will drive the equilibrium towards the backward direction.

Effect of change in pressure or volume

- The change in pressure or volume is important only for the reversible gaseous reactions where the number of moles of reactants and products are not equal.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

$$K_c = \frac{4x^2V}{(a-2x)^2(b-x)}$$

Conclusion

In the above example by increasing pressure, the position of equilibrium will shift towards the forward direction to attain equilibrium and vice versa.

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Effect of change in Temperature

i) On Endothermic reactions.

- By increasing the temperature, reaction is favored in forward direction.
- By decreasing the temperature, reaction is favored in backward direction.

$$H_2 + I_2 \rightleftharpoons 2HI \qquad \Delta H = +ve$$

ii) On Exothermic reactions.

- By decreasing the temperature, reaction is favored in forward direction.
- By increasing the temperature, reaction is favored in backward direction.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \Delta H = -ve$$

Effect of catalyst on Equilibrium Constant

A catalyst does not affect the equilibrium position and equilibrium constant of the reaction. It increases the rates of both forward and backward reactions, as it reduces the time to attain the equilibrium.

APPLICATIONS OF CHEMICAL EQUILIBRIUM IN INDUSTRY

Particulars	Synthesis of NH_3	Synthesis of SO_3
Introduction	F. Haber prepared in 1933.	In contact process H_2SO_4 is prepared.
Reaction	$N_2+3H_2 \rightleftharpoons 2NH_3$ $\Delta H = -92.46kJ$	$2SO_2 + O_2 \rightleftharpoons 2SO_3$ $\Delta H = -194$ kJ
Conditions for maximum production	▪ Removal of ammonia after regular intervals. ▪ Increase in pressure. ▪ Decrease in temperature.	▪ Continuous supply of O_2. ▪ Increase in pressure. ▪ Decrease in temperature.
Catalyst	Pieces of iron crystals are embedded in fused mixture of MgO, Al_2O_3 and SiO_2.	V_2O_5, NO or Pt are used as catalyst.
Favorable conditions	P= 200-300atm T= 673K(400°C)	P= 1atm T= 400-500°C / 650°C.
Others	▪ Equilibrium mixture contain 35% NH_3 by volume. ▪ Ammonia is separated by refrigeration. ▪ 110 million tons ammonia is produced per anum. ▪ 80% is used in fertilizer. ▪ 13% Nitrogen fixation is done by Haber's process.	

IONIC PRODUCT OF WATER

Water undergoes self-ionization as follows and the reaction is reversible.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \qquad H_2O \rightleftharpoons H^+ + OH^-$$

$$K_c[H_2O] = [H^+][OH^-]$$

$$K_w = [H^+][OH^-] = 10^{-14} \text{ at } 25°C$$

K_w is called ionic product of water or dissociation constant of water.

K_w VARIES WITH TEMPERATURE

Temperature (°C)	K_w
0	0.11×10^{-14}
10	0.30×10^{-14}
25	1.0×10^{-14}
40	3.00×10^{-14}
100	7.5×10^{-14}

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pH

The negative log of hydrogen ion concentration $[H^+]$ is called pH

$$pH = -\log[H^+]$$

- The idea of pH and pOH was introduced by a Danish biochemist, **Sorenson**, in 1909.
  - pH means potential of hydrogen ion concentration
  - pOH means potential of hydroxyl ion concentration

pOH

The negative log of hydroxyl ion concentration $[OH^-]$ is called pOH.

$$pOH = -\log[OH^-]$$

Conclusion:
For neutral water

$$pH = -\log 10^{-7} = 7$$
$$pOH = -\log 10^{-7} = 7$$

pH = 7, → solution is neutral
pH < 7, → solution is acidic
pH > 7, → solution is basic

pK_w

The negative log of K_w is called pK_w

$$pK_w = -\log K_w$$

APPROXIMATE pH OF SOME COMMON MATERIALS AT 25°C

Material	pH	Material	pH
1.0MHCl	0.1	Bread	5.5
0.1M HCl	1.1	Potatoes	5.8
0.1M CH_3COOH	2.9	Rainwater	6.2
Gastric juice	2.0	Milk	6.5
Lemons	2.3	Saliva	6.5-6.9
Vinegar	2.8	Pure water	7.0
0.1M $NaHCO_3$	8.4	Eggs	7.8
Soft drinks	3.0	Apples	3.1
Cherries	3.6	Seawater	8.5
Tomatoes	4.2	Milk of magnesia	10.5
Bananas	4.6	0.1M NH_3	11.1
Grapefruit	3.1	0.05M Na_2CO_3	11.6
Oranges	3.5	0.1M NaOH	13.0

IONIZATION CONSTANT OF ACIDS (K_a)

The dissociation constant of an acid is the ratio of the product of molar concentration of the ionized species to the molar concentration of unionized species.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

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- Dissociation constant of an acid shows the strength of an acid.
- When $K_a < 10^{-3}$, acid is weak.
- When $K_a = 1$ to 10^{-3}, acid is moderately strong.
- When $K_a > 1$, acid is strong.

$$\text{Percentage of ionization} = \frac{\text{Amount of an acid ionized}}{\text{Acid initially available}} \times 100$$

DISSOCIATION CONSTANTS OF SOME ACIDS AT 25°C

Acid	K_a	Relative strength
HCl	Very large	Very strong
HNO_3	Very large	Very strong
H_2SO_4	Large	Very strong
HSO_4^-	1.3×10^{-4}	Strong
HF	6.7×10^{-5}	Weak
CH_3COOH	1.85×10^{-5}	Weak
$H_2CO_3(H_2O+CO_2)$	4.4×10^{-7}	Weak
H_2S	1.0×10^{-7}	Weak
NH_4^+	5.7×10^{-10}	Weak
HCO_3^-	4.7×10^{-11}	Weak
H_2O	1.8×10^{-16}	Very weak

IONIZATION CONSTANT OF BASES (K_b)

The dissociation constant of a base is the ratio of the product of molar concentration of the ionized species to the molar concentration of unionized species.

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

- Strength of base is expressed by K_b.
- Any substance that accepts H^+ or generates OH^- is a base.

DISSOCIATION CONSTANTS OF SOME BASES AT 25°C

Base	K_b	Relative strength
NaOH	Very high	Very strong
KOH	Very high	Very strong
$Ca(OH)_2$	High	Strong
NH_4OH	1.81×10^{-5}	Weak
CH_3NH_2(Methylamine)	4.38×10^{-4}	Weak
$C_6H_5NH_2$ (Aniline)	4.7×10^{-10}	Very weak

pK_a and pK_b

The value of pK_a and pK_b can be defined and related as follow:

$$pK_a = -\log K_a$$
$$pk_b = -\log K_b$$

Conclusion

- Larger the pK_a weaker is the acid and vice versa.
- Larger the pK_b weaker is the base and vice versa.
- If the difference of pK_a value of the two acids is one, then acid with smaller pK_a is ten times stronger than the other.

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LOWRY BRONSTED ACID AND BASE CONCEPT

Acid Those species which donate the proton or have a tendency to donate protons are called acids.	**Points to be Remembered:** ➢ Smaller is pKa value stronger is the acid. ➢ Smaller the pK_b value stronger is the base. ➢ Conjugate base of a very weak acid is relatively very strong base. ➢ Conjugate acid of a very strong base is relatively very weak acid.
Base Those species which accept the proton or have tendency to accept the proton are called bases.	

Example

$$\underset{\text{(Acid)}}{HA} + \underset{\text{(Base)}}{H_2O} \rightleftharpoons \underset{\text{Conjugate Acid}}{H_3O^+} + \underset{\text{Conjugate Base}}{A^-}$$

$$K_a \times K_b = [H^+][OH^-]$$

$$K_a \times K_b = K_w = 10^{-14} \text{ at } 25^\circ C$$

$$K_a \propto \frac{1}{K_b}$$

$$pK_a + pK_b = pK_w \ (pK_w = 14, \text{ at } 25^\circ C)$$

$$pK_a + pK_b = 14 \text{ at } 25^\circ C$$

COMMON ION EFFECT

The addition of a common ion to the solution of a less soluble electrolyte suppresses its ionization and the concentration of unionized species increases, which may come out as a precipitates.

Examples

1- The solubility of a less soluble salt $KClO_3$ in water is suppressed by the addition of a more soluble salt KCl by common ion effect.

$$KClO_{3(S)} \rightleftharpoons K^+_{(aq)} + ClO_3^-{}_{(aq)}$$

$$KCl_{(S)} \rightleftharpoons K^+_{(aq)} + Cl^-_{(aq)}$$

2- An addition of NH_4Cl in NH_4OH solution suppresses the concentration of $OH^-_{(aq)}$ due to the presence of a large excess of NH_4^+ from NH_4Cl.

$$NH_4Cl_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + Cl^-_{(aq)}$$

$$NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

BUFFER SOLUTIONS

The solutions, which resist the change in their pH when a small amount of an acid or a base is added to them, are called buffer solutions.

BUFFER CAPACITY

The buffer capacity of a solution is the capability of a buffer to resist the change of pH in a particular ange of pH.

Buffer capacity is developed by varying the molarities of its components.

Best Buffer	Ideal Buffer
$pH = pK_a$ $pOH = pK_b$	$pH = 7$ $pOH = 7$

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Henderson's Equation for Acidic Buffer

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

Henderson's Equation for Basic Buffer

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

Points to be Remembered

If [salt] = [acid] then pH = pKa
If [salt] > [acid] then pH > pKa
If [salt] < [acid] then pH < pKa

- **Characteristics of Buffer Solutions**
  i) It has definite pH
  ii) Its pH does not alter either on keeping for a long time or on dilution.
  iii) Its pH is very slightly altered by the addition of strong acid or by strong base.
- **Applications**
  The applications of buffer solutions are found in the study of
  - Clinical analysis
  - Chemical reactions
  - Nutrition
  - Soil sciences
  - Biochemistry
  - Molecular biology
  - Cell biology

SOLUBILITY PRODUCT (Equilibria of Slightly Soluble ionic compounds)

The product of the concentration of ions raised to an exponent equal to the co-efficient of the balanced equation.

General Expression

$$A_xB_y \rightleftharpoons xA^{+y} + yB^{-x}$$

$$K_{sp} = [A^{+y}]^x [B^{-x}]^y$$

Examples

$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$ $K_{sp} = 1.6 \times 10^{-5}$
$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$ $K_{sp} = 1.8 \times 10^{-10}$

Applications

- Determination of K_{sp} from solubility of salts
- Determination of solubility from K_{sp}
- Prediction of precipitation
- Effect of common ion effect on solubility

Applicable for sparingly soluble substances $PbCl_2$, AgCl, $Ca(OH)_2$, $PbCrO_4$.

It is only applicable for those substances whose molar concentrations are less than 0.01.

- **If ionic product = K_{sp}** solution is saturated,
- **If ionic product < K_{sp}** solution is unsaturated,
- **If ionic product > K_{sp}** solution is supersaturated

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PRACTICE EXERCISE

30 min Time Yourself

1. **The pH of 10^{-3} mol dm^{-3} of an aqueous solution of H_2SO_4 is**
   (a) 3.0 (b) 2.7
   (c) 2.0 (d) 1.5
2. **Kc value has**
   (a) No units (b) Units
   (c) Both a and b (d) None
3. **If a buffer solution of higher pH than seven is to be made we use**
   (a) Strong acid and strong base
   (b) Weak acid and strong base
   (c) Weak acid and its salt with strong base
   (d) Weak base and its salt with strong acid
4. **Sodium benzoate and benzoic acid are mixed in equimolar ratio to form buffer if pKa is 2 what will be the pH?**
   (a) 0 (b) 1
   (c) 2 (d) any one
5. **AgCl dissolved with conc (2×10^{-2}) K_{sp} will be**
   (a) 3.6×10^{-6} (b) 3.6×10^{-5}
   (c) 7.2×10^{-6} (d) 4×10^{-4}
6. **In which of the following equilibria will K_c and K_p have the same value?**
   (a) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ (b) $N_2 + 3H_2 \rightleftharpoons 2NH_3$
   (c) $2CO + O_2 \rightleftharpoons CO_2$ (d) $N_2 + O_2 \rightleftharpoons 2NO$
7. **Which of the following will not change the concentration of ammonia at the equilibrium?**
   (a) Increase of pressure (b) Increase of volume
   (c) Addition of catalyst (d) Decrease of temperature
8. **pH of an aqueous solution is 5.0. The hydroxyl ion conc. in the solution would be**
   (a) 1×10^{-7}
   (c) 1×10^{-9} (b) 1×10^{-5}
   (d) 1×10^{-8}
9. **For a reaction involving only gases at 25°C, the equilibrium constant can be expressed in terms of molarity, K_c, or partial pressure, K_p. Which is true about the numerical value of K_p?**
   (a) K_c is generally greater than K_p
   (b) K_c is generally less than K_p
   (c) K_c is generally equal to K_p
   (d) K_c is equal to K_p if the total moles of reactants and products are equal
10. **Which of following is not a base**
    (a) KOH (b) NH_3
    (c) PH_3 (d) BF_3
11. **The unit of K_c for the reaction. $N_2 + O_2 \rightleftharpoons 2NO$ will be**
    (a) mole dm^{-3} (b) mol dm^{-3}
    (c) mol^{-2} dm^{+6} (d) No unit
12. **Which one of the following aqueous solutions will be basic?**
    (a) NaCl (b) Na_2SO_4
    (c) Na_2CO_3 (d) $FeCl_3$
13. **The value of K_w in an acidic aqueous solution at 298 K is**
    (a) $>10^{-14}$ (b) $<10^{-14}$
    (c) 10^{14} (d) 10^{-14}

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14. **Reaction which proceeds in both directions is called**
(a) reversible (b) irreversible
(c) spontaneous (d) non-spontaneous

15. **Chemical equilibrium state is**
(a) dynamic state (b) static state
(c) free state (d) unidirectional state

16. **Conversion of reactant into product in unit time is called**
(a) rate of forward reaction (b) rate of backward reaction
(c) rate constant (d) rate co-efficient

17. **At start of reaction, the concentration of reactants is**
(a) high (b) low
(c) according to K_c (d) constant

18. $\frac{[\text{products}]}{[\text{reactant}]} > K_c$ **favors**
(a) Law of mass action (b) Rate expression
(c) Forward reaction (d) Backward reaction

19. **Unit of K_c is**
(a) $\text{moles}^2\text{dm}^{+6}$ (b) $\text{moles}^{-2}\text{dm}^{+6}$
(c) $\text{moles}^{+2}\text{dm}^{-6}$ (d) K_c may or may not have units

20. **In case of gases, K_c is replaced by**
(a) K_a (b) K_b
(c) K_p (d) K

21. **Rate expression for ammonia synthesis is**
(a) $K_c=x^2/(a-x)(b-x)$ (b) $K_c=x^2/v(a-x)$
(c) $K_c=4x^2/(a-2x)^2(b-x)$ (d) $K_c=4x^2v^2/(a-x)(b-3x)^3$

22. $X_A=\frac{n_A}{n_t}$ **is**
(a) Mole fraction (b) Partial pressure
(c) Partial temperature (d) Molality

23. $\frac{[\text{Product}]}{[\text{Reactant}]} < K_c$
(a) Forward reaction (b) Backward reaction
(c) Equilibrium stage (d) Reaction completed.

24. **When the value of K_c is very small, then**
(a) Reaction is at start (b) Product conc. is maximum
(c) Reactant conc. is minimum (d) Reaction is completed

25. **Catalyst used to speed up the reaction of ammonia synthesis is**
(a) V_2O_5
(b) V_2O_5 and Pt
(c) Fe
(d) Pieces of Fe crystals are embedded in fused mixture of MgO, Al_2O_3 and SiO_2

26. **Temperature for preparation of SO_3 is**
(a) 400-500°C (b) 400°C
(c) 600°C (d) 200°C

27. **By the addition of base in water, pH will be**
(a) More than 7 (b) Less than 7
(c) Equal to 7 (d) No effect

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28. **Idea of pH and pOH was put forward by**
(a) Gibbs (b) Einstein
(c) Sorenson (d) Chadwick

29. **Negative log of molar concentration of H^+ ions is called**
(a) pH (b) pOH
(c) pKa (d) pKw

30. **Ka<10^{-3} means**
(a) Very strong base (b) Very weak acid
(c) Very strong acid (d) Very strong salt

31. **Any substance which accepts H^+ is base, favors the concept**
(a) Lowry's (b) Lewis
(c) Arrhenius (d) None of these

32. **Conjugated base of a weak acid is**
(a) weak (b) strong
(c) moderately weak (d) unstable

33. **When sparingly soluble salt is in equilibrium with molar concentration of its oppositely charged ion then the product is called**
(a) common ion effect (b) solubility product
(c) dissociation constant (d) dissociation constant for an acid

34. **Solution having the property of a very little change in pH on adding a small amount of strong acid or base is called**
(a) buffer solution (b) normal solution
(c) standard solution (d) neutral solution

35. **Addition of CH_3COOH and CH_3COONa gives in water**
(a) Standard solution (b) buffer solution
(c) acidic buffer solution (d) both b and c

36. **Which one of the following is a buffer solution?**
(a) brine (b) blood
(c) glue (d) solution of $CuSO_4$

37. **Solubility of any salt can be determined from**
(a) K_a (b) K_b
(c) K_c (d) K_{sp}

38. **The pH of human blood is**
(a) 7.00 (b) 7.35
(c) 7.50 (d) 7.80

39. **By decreasing the pressure, the reaction will go to that direction where**
(a) volume is decreased (b) volume increased
(c) heat absorbed (d) no. of moles of specie decreased

40. **Equilibrium state is achieved quickly by the addition of.**
(a) reactants (b) acid
(c) base (d) catalyst

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Chapter 9

SOLUTIONS

KIPS

(I) Concentration Units of Solutions
- Percentage Composition
- Molarity (symbol, M)
- Molality (symbol, m)
- Mole Fraction (symbol, x)
- Parts per Million (symbol, ppm)
- Interconversion of Various Concentration Units of Solutions

(II) Types of Solutions
- Solutions of Solids in Liquids
- Solutions of Liquids in Liquids
  - Completely Miscible Liquids
  - Partially Miscible Liquids
  - Practically Immiscible Liquids

(III) Ideal and Non-Ideal Solutions
- Raoult's Law

(IV) Vapour Pressures of Liquid-Liquid Solutions
- Ideal Solutions
  - Fractional Distillation of Ideal Mixture of two Liquids
- Non-Ideal Solutions (azeotropic mixtures)
  - Positive Deviations
  - Negative Deviations

(V) Solubility and Solubility Curves
- Solubility Curves
  - Continuous Solubility Curves
  - Discontinuous Solubility Curves
  - Fractional Crystallisation

(VI) Colligative Properties of Solutions
- Why some of the Properties are called colligative
- Lowering of Vapour Pressure
- Elevation of Boiling point
- Measurement of Boiling Point Elevation
- Depression of the Freezing Point of a Solvent by a Solute
- Measurement of Freezing point Depression
  - Beckmann's Freezing point Apparatus
- Application of Boiling Point Elevation and Freezing Point Depression Phenomena

(VII) Hydration and Hydrolysis
- Hydration
- Hydrates
- Hydrolysis

(VIII) Energetics of Solution
- Hydration Energy of Ions

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PHASE

Every sample of matter with uniform properties and a fixed composition is called a phase.

SOLUTION

A homogeneous mixture of two or more kinds of different molecular or ionic substances is called solution.

COMPONENTS OF A SOLUTION

Solute

(i) In the case of a solution of a gas or solid dissolved in a liquid, the gas or solid is the solute.

(ii) Generally, the component of a solution, which is in smaller amount, is called solute.

Solvent

(i) In the case of a solution of a gas or solid in a liquid, the liquid is the solvent.

(ii) Generally, the component of a solution, which is in larger amount, is called solvent.

Example

When sodium chloride is dissolved in water, sodium chloride is the solute and water is the solvent.

CONCENTRATION UNITS OF SOLUTIONS

Particular	Percentage composition
Definition	Solute in percent of solvent. Four ways of expression of percentage composition 1- $\frac{w}{w}$% it is a weight of solute dissolved per 100g of solution 2- $\frac{v}{w}$% it is volume of solute (cm^3) dissolved per 100g of solution. 3- $\frac{w}{v}$% it is a weight of solute (g) dissolved per 100cm^3 of solution 4- $\frac{v}{v}$% it is volume of solute (cm^3) dissolved per 100 cm^3 of solution
Expression	Expressed by percentage (%).
Units	In volumetric analysis

MOLARITY

The number of moles of a solute dissolved per dm^3 of a solution.

Molar Solution
A solution whose molarity is one e.g. 1M NaOH solution.
(40g/1dm^3 of soln)

Symbol

It is denoted by 'M'.

Examples

0.1M NaOH solution and 0.02M $KMnO_4$ solution

Formulae

1- $$\text{Molarity(M)} = \frac{\text{Moles of solute}}{\text{Volume of solution in dm}^3}$$

2- $$\text{Molarity(M)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Volume of Solution in dm}^3}$$

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MOLALITY

Definition

The number of moles of a solute dissolved per kg of a solvent.

Molal Solution
A solution whose molality is one e.g. 1m NaOH solution. (40g/1kg of water)

Symbol

It is denoted by 'm'.

Example

0.1m NaOH solution, 0.01m HCl etc.

Formulae

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

2- $$\text{Molality (m)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Mass of solvent in kg}}$$

MOLE FRACTION

Definition

The ratio of the number of moles of a component to the total number of moles of all the components of solution.

Symbol

It is denoted by 'X'.

Explanation

Let us have components A,B and C making a solution and their number of moles are n_A, n_B and n_C respectively. X_A, X_B and X_C are their mole fractions and are given below:-

$$X_A = \frac{n_A}{n_A + n_B + n_C}$$

$$X_B = \frac{n_B}{n_A + n_B + n_C}$$

$$X_C = \frac{n_C}{n_A + n_B + n_C}$$

Normality (N)
The number of gram equivalent of the solute dissolved per dm^3 of a solution.
0.1N NaOH 0.02N $KMnO_4$

- The sum of the mole fractions of all the components of solution must be unity (one).
- To get mole percent mole fractions is multiplied by 100.
- There are no formal units of mole fraction.

PARTS PER MILLION

Definition

The number of parts (by weight or volume) of a solute per million parts (by weight or volume) of the solution.

$$\text{ppm} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

Symbol

It is denoted by 'ppm'.

Formula

Mass Percent	Symbol	Formula
Parts per million	ppm	$\text{ppm} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$
Parts per billion	ppb	$\text{ppb} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^8$
Parts per trillion	ppt	$\text{ppt} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^{11}$

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A COMPARISON OF VARIOUS CONCENTRATION UNITS

Name	Symbol	Units	Advantages	Disadvantages
Molarity	M	moles dm^{-3}	Useful in stoichiometry, measure by volume.	Temperature dependent, must know density to find solvent mass.
Molality	m	moles kg^{-1}	Temperature independent, useful in special applications	Measure by mass, must know density to convert to molarity.
Mole Fraction	X	None	Temperature independent, useful in all kinds of solutions.	Measure by mass, must know density to convert to molarity.
Parts Per million	ppm	ppm	Temperature independent, useful for small amount.	Measure by mass, must know density to convert to molarity.

TYPES OF SOLUTION

State of Solute	State of Solvent	Examples
Solid	Liquid	Sugar in water, jellies.
Solid	Gas	Dust particles in smoke
Solid	Solid	Metal alloys pearls, opals
Liquid	Gas	Mist, fog, clouds
Liquid	Liquid	Alcohol in water, milk
Liquid	Solid	Mercury in silver, butter
Gas	Gas	Air
Gas	Liquid	O_2 in water, CO_2 in water
Gas	Solid	H_2 adsorbed by palladium

Types of solutions on the basis of number of substances

Binary Solution	Ternary Solution	Quaternary Solution
A homogenous mixture of two substances is called binary solution	A homogenous mixture of three substances is called ternary solution	A homogenous mixture of four substances is called quaternary solution
water + sugar	salt + sugar + water	salt + sugar + water + lemon

Types on the basis of saturation

Unsaturated Solution	Saturated Solution	Super Saturated Solution
An unsaturated solution is a solution, which contains less amount of solute than is required to saturate it at that temperature.	A solution that can hold no more of the solute at a particular temperature is said to be a saturated solution at that temperature.	Solution that is more concentrated than a saturated solution is known as super saturated solution. If a crystal of solute is added to this solution, the excess of solute crystallizes.

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Types on the basis of miscibility

Solution of completely miscible liquids	Solution of partially miscible liquids	Solution of immiscible liquids
Alcohol and Water Alcohol and Ether	Phenol and Water Triethylamine and Water Nicotine and Water	Benzene and Water Carbon disulphide and Water

Upper Consulate Temperature

Water - Aniline system = 167°C
15% water solution.
Methanol – Cyclohexane = 49.1°C
29% methanol solution.

Dilute Solution
A solution, which contains relatively lower concentration of solute.

Concentrated Solution
A solution, which contains relatively higher concentration of solute.

PHENOL WATER SYSTEM

- At 25°C, Solution of phenol and water contains two layers.
  - Upper layer is saturated phenol with water.
    - 5% solution of phenol in water.
      Phenol is solute while water acts as a solvent
  - Lower layer is saturated water with phenol.
    - 30% solution of water in phenol
      Water is solute while phenol acts as a solvent
- At 65.9°C, the both layers merge in each other to form a homogenous mixture containing 34% phenol and 66% water.
- The temperature at which two conjugated mixtures merge in one another called critical solution temperature or upper consulate temperature.

IDEAL AND NON-IDEAL SOLUTION

Ideal solution	Non-ideal solution
A – B attractive forces are equal in strength with A – A and B – B attractive forces	A – B attractive forces are not equal in strength with A – A and B – B attractive forces
Volume of solution is equivalent to sum of volumes of all components i.e. $\Delta V = 0$.	Volume of solution is not equal to sum of volumes of all components i.e. $\Delta V \neq 0$
Enthalpy change is zero i.e. $\Delta H = 0$	Enthalpy change is not zero i.e. $\Delta H \neq 0$.
Obeys Raoult's law	Shows deviations from Raoult's law

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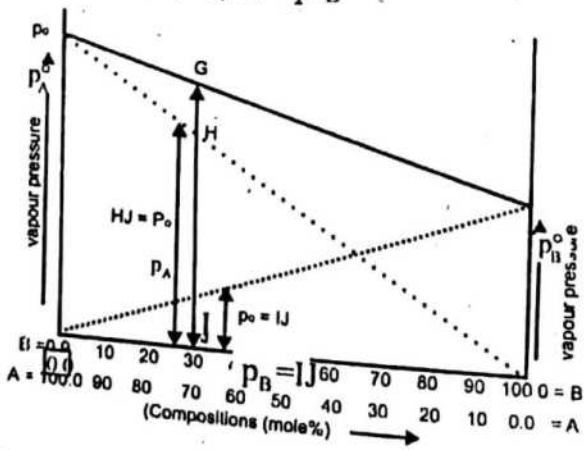
RAOULT'S LAW

Statements	Mathematical Representation	Symbols	Conclusions
The vapour pressure of a solvent above a solution is equal to the product of the vapour pressure of pure solvent and the mole fraction of solvent in solution.	$p = p^\circ x_1$	**p** - vapour pressure of solvent in solution. **p°** - vapour pressure of pure solvent. x_1 - mole fraction of solvent. x_2 - mole fraction of solute. **Δp** = lowering of vapour pressure. **Δp / p°** = relative lowering of vapour pressure	The relative lowering of vapour pressure is:- ➢ Independent of temperature ➢ Dependent on conc. of solute. ➢ constant when equi-molar proportions of different solutes are dissolved in the same mass of same solvent.
The lowering of vapour pressure is directly proportional to the mole fraction of solute.	$\Delta p = p^\circ x_2$		
The relative lowering of vapour pressure is equal to the mole fraction of solute.	$\frac{\Delta p}{p^\circ} = x_2$		

Raoult's Law (when both components are volatile)

- Graph is plotted between compositions on x-axis and vapour pressure on y-axis
- If composition of solution is;
  - Component A is 70% (highly volatile thus low boiling)
  - Component B is 30% (less volatile thus high boiling)
- p^0_A and p^0_B are partial pressures of pure components.
- If the solution is ideal then straight line will produce in graph.
- At point G P_t of solution will be sum of partial pressures of components i.e.

$$P_t = p_A + p_B$$
$$P_t = (p^0_A - p^0_B)x_A + p^0_B$$



Vapour Pressures of Liquid-Liquid Solutions

Binary mixtures of miscible liquids may be classified as

(i) Ideal solutions
(ii) Non-ideal or real solutions

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(i) Ideal Solutions

A solution which obeys Raoult's law is called ideal solution.

Examples

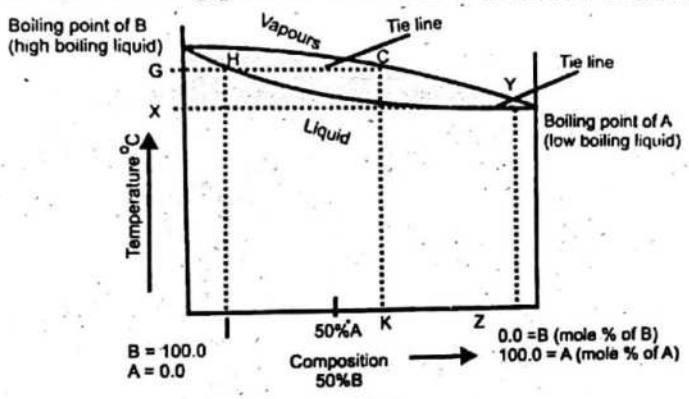
(i) benzene-toluene solution
(ii) benzene ether solution
(iii) chlorobenzene-bromobenzene solution
(iv) ethyl iodide-ethylbromide solution

Zeotropic Mixture

A mixture or solution which distills over with the change in composition is called zeotropic mixture.

Fractional Distillation of Ideal Mixture of two liquids

A technique by which different liquids are separated from each other on the basis of their different boiling points is called fractional distillation.



Non-Ideal Solutions

A solution or mixture which does not obey Raoult's law is called non-ideal solution.

- They show deviations from Raoult's law due to difference in their molecular structures i.e. size, shape and intermolecular forces.
- Formation of such solution is accompanied by changes in volume and enthalpy.

Azeotropic Mixtures

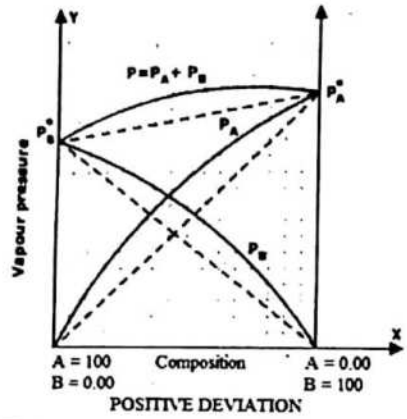
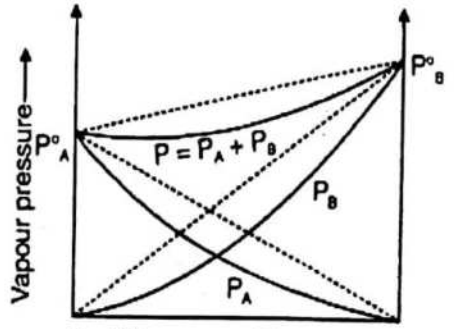
Those mixtures which boil at constant temperature and distills over without change in composition at any temperature like a pure chemical compound are called azeotropic mixtures.

Types of Deviation

The deviation of non-ideal solutions are of two types:-

- Positive deviations
- Negative deviations

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	Positive Deviations	Negative Deviations
Definition	When the vapour pressure is greater than that predicted by Raoult's Law	When the vapour pressure is lesser than that predicted by Raoult's Law
Reason	Solute – solvent interaction is weaker than solute – solute or solvent – solvent interaction.	Solute – solvent interaction is stronger than solute – solute or solvent – solvent interaction.
Graphical Representation	 POSITIVE DEVIATION	 NEGATIVE DEVIATION
Examples	Ethanol-water mixture boils at 78.1°C with 4.5% water and 95.5% alcohol. 78.1°C is lower than the boiling point of ethanol (78.5°C) and water (100°C).	Hydrochloric acid solution in water is an example of negative deviation. HCl forms an azeotropic mixture with water, boiling at 110°C and containing 20.24% of the acid.

SOLUBILITY

The concentration of the solute in the solution when it is in equilibrium with the solid substance at a particular temperature is called solubility

OR

Number of grams of solute dissolved in 100g of solvent at a particular temperature is called solubility.

Examples

(i) Saturated solution of NaCl in water at 0°C contains 37.5g of NaCl in 100g of water.

(ii) The solubility of $CuSO_4$ in water at 0°C is 14.3g/100g while at 100°C it is 75.4g/100g.

Factors Affecting Solubility

- Nature of solute
- Nature of solvent
- Pressure (in case of gas)
- Temperature

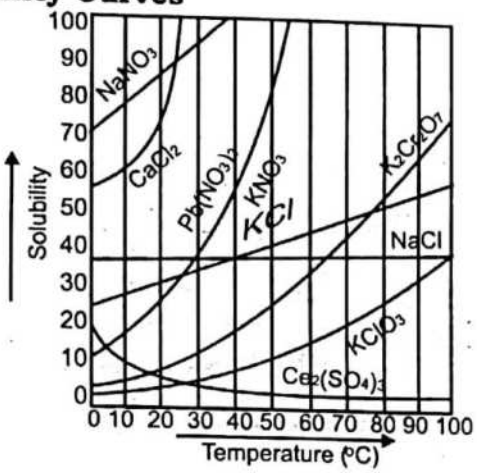
Solubility Curves

A graphical representation between temperature and solubility of its solution is called solubility curves.

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Types of Solubility Curves

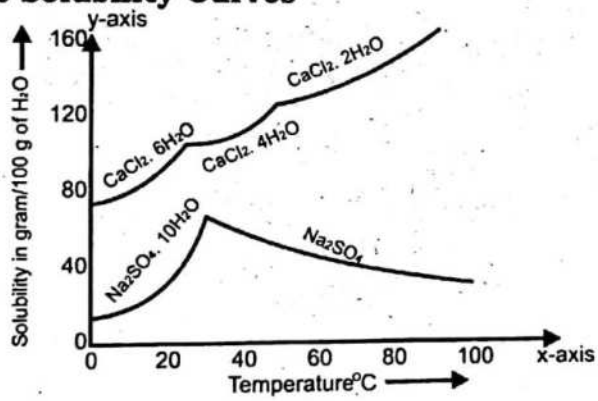
(a) Continuous Solubility Curves



Continuous curved lines are analyzed as

- Lines
  - Straight — $NaNO_3$, KCl, NaCl
  - Abrupt — $CaCl_2$, KNO_3
  - Decline — $Ce_2(SO_4)_3$

(b) Discontinuous Solubility Curves



COLLIGATIVE PROPERTIES OF SOLUTIONS

Liquid Properties

Colligative Property
The property which depends upon the number of particles of solute and solvent but independent of the nature of the solute.

Constitutive Property
The property which depends upon the arrangements of atoms in a molecule.

Additive Property
Those properties which are sum of individual component of a substance e.g. molar mass of H_2SO_4

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Examples of Colligative Properties

(i) Lowering of vapour pressure
(ii) Elevation of boiling point
(iii) Depression of freezing point
(iv) Osmotic pressure

The word colligative means "bound together in a collection" and is used because a collection of solute particles is responsible for the observed effects.

Conditions for study of colligative properties

(i) Solution should be dilute.
(ii) Solute should be non-volatile.
(iii) Solute should be non-electrolyte.

Lowering of Vapour Pressure

- Addition of solute in solvent decreases the vapour pressure of solvent.
- Lowering of vapour pressure depends upon no. of molecules of solute and mass of solute.

$$\frac{\Delta p}{p^\circ} = x_2$$

$$\frac{\Delta p}{p^\circ} = \frac{n_2}{n_1+n_2} \quad \text{(1 for solvent and 2 for solute)}$$

$$\frac{\Delta p}{p^\circ} = \frac{n_2}{n_1} \quad (n_2 = 0)$$

$$\frac{\Delta p}{p^\circ} = \frac{n_2}{n_1} = \frac{\dfrac{\text{mass in g of solute}\,(W_2)}{\text{Molar mass}\,(M_2)}}{\dfrac{\text{mass in g of solvent}\,(W_1)}{\text{Molar mass}\,(M_1)}}$$

$$\frac{\Delta p}{p^\circ} = \frac{W_2 M_1}{M_2 W_1}$$

$$M_2 = \frac{p^\circ}{\Delta p} \cdot \frac{W_2 M_1}{W_1}$$

Elevation of Boiling point

- Addition of solute in solvent increases the boiling point of solvent.
- Boiling point of H_2O in 0.1 molal solution of urea and glucose will rise by 0.052°C i.e 100.052°C.
- Boiling point elevation value is called molal boiling point constant or ebullioscopic constant denoted by K_b.
- Higher the concentration of solute, greater will be boiling point elevation.

$\Delta T_b = T_2 - T_1$
ΔT_b (Elevation in boiling point)
$\Delta T_b \alpha$ molality
$\Delta T_b \alpha\ m$
$\Delta T_b = K_b m$

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$$\Delta T_b = K_b \cdot \frac{W_2}{M_2} \cdot \frac{1000}{W_1}$$

$$M_2 = \frac{K_b}{\Delta T_b} \times \frac{W_2}{W_1} \times 1000$$

Measurement of Boiling point elevation

The boiling point elevation can be measured by Landsberger's method. The apparatus consists of four major parts.

(i) An inner tube
(ii) A boiling flask
(iii) An outer tube
(iv) A thermometer (Beckmann's thermometer)

Depression of Freezing point

- Addition of solute in solvent will decrease the freezing point of solvent.
- Freezing point of H_2O will decrease by 1.86°C in solution of urea and glucose i.e -1.86°C.
- Decrease in freezing point is called molal freezing point constant or cryoscopic constant denoted by K_f.

$\Delta T_f = T_1 - T_2$

$\Delta T_f \propto$ molality

$\Delta T_f = K_f m$

ΔT_f is called depression in freezing point

$$\Delta T_f = K_f \frac{1000\, W_2}{M_2 \times W_1}$$

$$\text{Molar mass of solute } (M_2) = \frac{K_f}{\Delta T_f} \frac{1000\, W_2}{W_1}$$

Measurement of Freezing Point Depression

There are two important methods for the measurement of depression of freezing point.

1. Beckmann's method.
2. Rast's camphor method.

Beckmann's method.

The apparatus consists of three major parts.

a. A freezing tube.
b. An outer larger tube.
c. A large jar containing a freezing mixture.

No.	Solvent	B.P. (°C)	K_b (°C/m)	F.P. (°C)	K_f (°C/m)
1	Acetic acid	118	3.07	17	3.90
2	Water	100	0.52	0.00	1.86
3	Benzene	80	2.70	5.5	5.10
4	Ethanol	79	1.75	-114.5	1.99
5	Ether	34.4	2.16	-116.3	1.79

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ENERGETICS OF SOLUTIONS

The quantity of heat energy, that is absorbed or released when a substance forms solution, is termed as heat of solution.

Enthalpy of Solution

The enthalpy or heat of solution of a substance is defined as the heat change when one mole of the substance is dissolved in a specified number of moles of solvent at a given temperature

HYDRATION

The phenomenon in which water molecules surround and interact with solute ions or molecules is called hydration.

- The number of water molecules surrounding an ion depends upon the charge density of the ion
- Charge density = charge/size, higher the charge density greater will be the number of molecule surrounding it.
  - Positive ion will be surrounded by greater number of water molecules as compare to –ve ion because of its high charge density due to its smaller size.
  - Negative ion will be surrounded by less number of water molecules as compare to +ve ion because it has less charge density due to its larger size.
- The ion which is surrounded by water molecule is called hydrated ion.
- The number of water molecules which surround an ion are called water molecules of hydration.
- The number of water molecules which are part of the crystals are called water of crystallization
- The compounds that have specific number of water molecules are called hydrates.
- Water of crystallization can be removed by heating of substance.

Hydration Energy of Ions

The hydration energy is the amount of heat evolved when one mole a gaseous ions are dissolved in water to give infinitely dilute solution.

$$H^+_{(g)} + H_2O_{(l)} \rightarrow H^+_{(aq)} \quad \Delta H_h = -1075 \text{ kJ/mol}$$

HYDROLYSIS

The interactions between salts and water to produce acidic or basic solutions are called hydrolytic reactions and this phenomenon is known as hydrolysis.

The Result of Salt Hydrolysis

No.	Salt made from	Example	Nature of solution
1	Strong acid with high pK_a + Strong base with high pK_b	NaCl, KNO_3, Na_2SO_4	Neutral
2	Strong acid with high pK_a + Weak base with low pK_b	NH_4Cl, $AlCl_3$, $CuSO_4$	Acidic
3	Weak acid with low pK_a + Strong base with high pK_b	Na_2CO_3, $NaHCO_3$, CH_3COONa	Alkaline
4	Weak acid with low pK_a + Weak base with low pK_b	CH_3COONH_4	Almost neutral

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PRACTICE EXERCISE

25 mins Time Yourself

1. **Which of the following solutions of H_2SO_4 is more concentrated?**
(a) 1 molar solution (b) 1 molal solution
(c) 1 normal solution (d) All have same concentration

2. **Which of the following unit of concentration is dependent on temperature?**
(a) Molarity (b) Molality
(c) Mole fraction (d) All

3. **Which of the following is an example of liquid in gas solution**
(a) Opals (b) Dust particles in smoke
(c) Paints (d) Fog

4. **The molal boiling point constant is the ratio of the elevation of boiling point to**
(a) Molarity (b) Molality
(c) Mole fraction of solvent (d) Mole fraction of solute

5. **Which of the following are the conditions of colligative properties**
(a) Non-electrolyte solute (b) Non-volatile solute
(c) Dilute solution (d) All of the above

6. **Which has the minimum freezing point?**
(a) One molal NaCl (b) One molal KCl solution
(c) One molal $CaCl_2$ (d) One molal urea solution

7. **Which of the following is not a colligative property?**
(a) Lowering of vapour pressure (b) Freezing point
(c) Osmotic pressure (d) Elevation of boiling point

8. **Which of the following substance do not show continuous solubility curve?**
(a) $KClO_4$ (b) $Na_2SO_4.10H_2O$
(c) $K_2Cr_2O_7$ (d) $PbCl_2$

9. **When common salt is dissolved in water?**
(a) Boiling point of water decrease (b) Boiling point of water increase
(c) Boiling point of water remains same (d) None of the above

10. **Every sample of matter with uniform properties and fixed composition is called**
(a) Solute (b) Solvent
(c) Solution (d) Phase

11. **Homogeneous mixture of two or more than two compounds is called**
(a) Solution (b) Compound
(c) Radical (d) Ion

12. **The component of solution which is in smaller amount is called**
(a) Solvent (b) Solute
(c) Phase (d) Ion

13. **Solution with maximum concentration of solute at given temperature is called**
(a) Super saturated solution (b) Unsaturated solution
(c) Saturated solution (d) Dilute solution

14. **10ml of alcohol dissolve in 90ml of water, unit of concentration used is**
(a) % w/w (b) % w/v
(c) % v/v (d) % v/w

15. **Number of moles in 1kg of solvent is called**
(a) Normality (b) Molarity
(c) Molality (d) Mole fraction

16. **58.5g of NaCl per $1dm^3$ of solution of NaCl in water, the concentration of** solution will be
(a) 0.1M (b) 1m
(c) 1M (d) 0.1N

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17. **In partially miscible liquids, the two layers are**
(a) Saturated solutions of each liquid (b) Unsaturated solutions of each liquid
(c) Normal solution of each liquid (d) No layer formation takes place

18. **If the volume of solution is equal to sum of volumes of its all components then** the solution
(a) Will be an ideal solution
(b) Will be non-ideal solution (c) Will show deviations from Raoult's law
(d) Both b and c

19. **The relative lowering of vapour pressure is**
(a) Equal to the mole fraction of solvent
(b) Equal to the mole fraction of solute
(c) Directly proportional to the mole fraction of solute
(d) Both b and c

20. **The solution which distils over with change in composition.**
(a) Ideal solution (b) Aeotropic solution
(c) Azeotropic solution (d) Non-ideal solution

21. **Mixtures which distill over without change in composition called**
(a) Zeotropic mixture (b) Azeotropic mixture
(c) Amphoteric mixture (d) Ideal solution

22. **Concentration of solute molecule when they are in equilibrium with solid substance at particular temperature is called**
(a) Saturated solution (b) Solubility
(c) Unsaturated solution (d) Super saturated solution

23. **Solubility of $KClO_3$ gives**
(a) Continuous and falling solubility curve
(b) Discontinuous and falling solubility curve
(c) Continuous and rising solubility curve
(d) Discontinuous and rising solubility curve

24. **The determination of correct molecular weight from Raoult's law is applicable to**
(a) A volatile solute in dilute solution
(b) A non-electrolyte and non volatile solute in concentrated solution
(c) A non-electrolyte and non volatile solute in concentrated solute
(d) non volatile solute in a dilute solution

25. **Boiling point elevations can be measured by**
(a) Beckmann's method (b) Landsberger's method
(c) Lind's method (d) None of the above

26. **Beckmann's apparatus is used to measure**
(a) Boiling point elevation (b) Depression in freezing point
(c) Lowering of vapour pressure (d) Lowering of osmotic pressure

27. **Water molecules surrounds more around**
(a) +ve ion (b) complex ion
(c) –ve ion (d) neutral atom

28. **The compounds in which water molecules are added are called**
(a) Hydrated ions (b) Double salts
(c) Hydrates (d) Complexes

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29. Hydration is a process in which

(a) Molecules are surrounded by solvent molecules
(b) Ions are surrounded by solvent molecules
(c) Both ions and molecules are surrounded by solvent molecules
(d) Both ions and molecules are surrounded by water molecules

30. Solution of Na_2SO_4 will be

(a) Basic
(b) Acidic
(c) Neutral
(d) Cannot be predicted without data

31. ppm means

(a) Parts of solute in 1000 parts of solvent
(b) Parts of solvent in 1000 parts of solute
(c) Parts of solute in one million parts of solution
(d) Parts of solvent in one million parts of solute

32. 1 molar solution of glucose in water contains weight of glucose

(a) $180g/dm^3$
(b) $170g/\ dm^3$
(c) $190g/\ dm^3$
(d) $195g/\ dm^3$

33. Water of crystallization can be removed by

(a) Drying
(b) Heating
(c) Evaporation
(d) All of the above

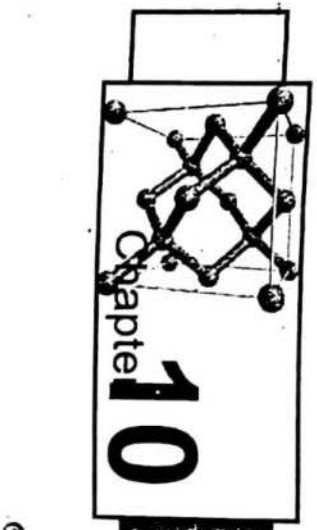
34. The relative lowering of vapour pressure is directly proportional to molality if the solution is

(a) Concentrated
(b) Dilute
(c) Saturated
(d) All of the above

35. Which one of the following salt does not hydrolyzed

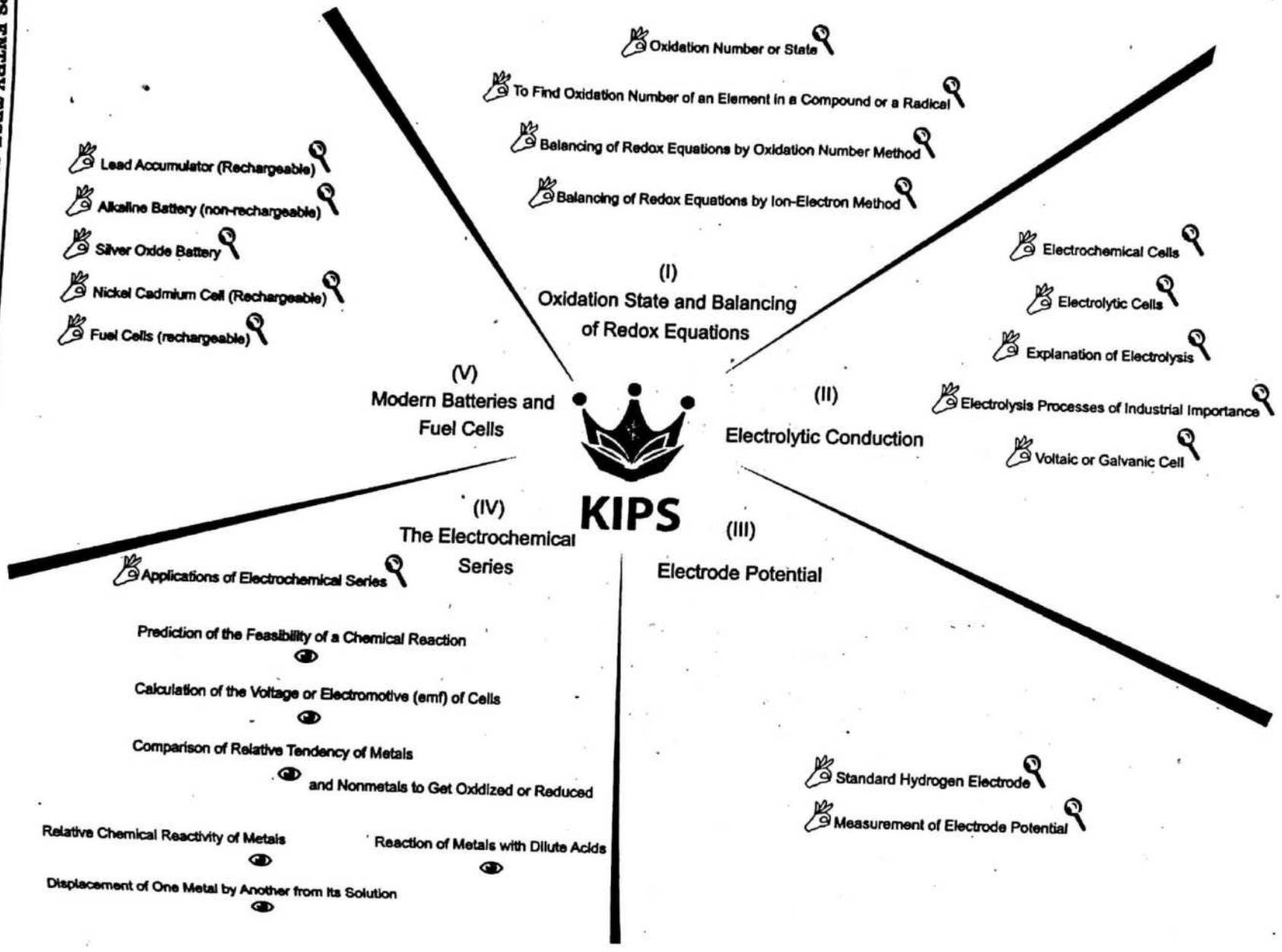
(a) Na_2SO_4
(b) $AlCl_3$
(c) $CuSO_4$
(d) NH_4Cl

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Chapter 10

ELECTROCHEMISTRY



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ELECTROCHEMISTRY

It is the branch of chemistry which is concerned with the inter-conversion of chemical energy and electrical energy.

- Electrical energy is converted into chemical energy through electrolytic cells.
- Chemical energy is converted into electrical energy through galvanic or voltaic cells.

OXIDATION STATE OR NUMBER

It is the apparent charge on an atom of an element in a molecule or an ion. It may be positive or negative or zero.

Rules for assigning oxidation number

Element	• Molecular form • Bulk / chunk	H_2, S_8 0 Diamond (C) 0
Compound	• Covalent compound ➢ Molecular / Bulk / chunk *Non-Metal – Non-Metal* • Less electronegative non-metal = +ve • More electronegative non-metal = -ve • Algebraic sum of oxidation numbers = 0 • Ionic compound ➢ *Metal – Non-Metal* Metal = +ve Non-metal = –ve Algebraic sum of oxidation numbers = 0	Molecular HCl ; (+1)+ (-1) = 0 Bulk / chunk SiO_2 ; [+4+2(-2)] = 0 Ionic compound NaCl (+1)+ (-1) = 0
Ion	• Mono-atomic ion ➢ Oxidation number will be equal to the charge on the ion. • Poly-atomic ion ➢ The algebraic sum of oxidation number is equal to charge on that ion.	Mono-atomic ion Cl^{-1} -1 Poly-atomic ion SO_4^{-2} +6+[–2(4)] = -2
Hydrogen	• Ionic compound ➢ Always –ve oxidation number • Covalent compound ➢ Always +ve oxidation number	Ionic compound NaH (+1)+(–1) = 0 Covalent compound H_2O [+1(2)]+(–2) = 0
Oxygen	• With all elements. ➢ –2 oxidation number(normal oxides) ➢ –1 oxidation number(per oxides) ➢ –1/2 oxidation state (super oxides) • With Fluorine ➢ + 2 oxidation state	H_2O; -1(2) –2 = 0 H_2O_2; +1 – 1 = 0 KO_2; [+1+2(–1/2)] = 0 OF_2; [+2+2(–1)] = 0

Oxidation	Reduction
➢ Gain in oxygen	➢ Loss in oxygen
➢ Loss of hydrogen	➢ Gain of hydrogen
➢ Loss of electrons including anode reactions	➢ Gain of electrons including cathode reactions
➢ Increase in oxidation state	➢ Decrease in oxidation state

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	Oxidation number of IA group (+1) Oxidation number of II-A group (+2) Oxidation number of III-A group (+3)

Examples

$K_2Cr_2O_7$

$(+1)2+2Cr-2(7) = 0$
$+2+2Cr-14 = 0$
$2Cr = +14-2 = +12$
$Cr = +6$

$NaBrO_3$

$1+Br+(-2)(3) = 0$
$1+Br-6 = 0$
$Br - 5 = 0$
$Br = +5$

ELECTROLYTIC CONDUCTION

Electrolytic Conduction	Electronic Conduction
• Conduction through fused or aqueous electrolyte	• Conduction through solid metal
• It is due to mobile ions	• Due to free electrons
• Conduction increases with increase in temperature due to increase in ionization	• Conduction decreases with temperature due to increase in oscillations of cations

Products of electrolysis
(when electrodes take part in the reaction)

Electrolyte	Copper cathode	Copper anode
$CuSO_{4(aq)}$	Cu deposits	$Cu_{(s)}$ dissolves to form Cu^{2+} ions
Electrolyte	Silver cathode	Silver anode
$AgNO_{3(aq)}$ and $HNO_{3\ (aq)}$	Ag deposits	$Ag_{(s)}$ dissolves to form Ag^{+} ions

Products of electrolysis
(using inert electrodes of platinum or graphite)

Electrolyte	Cathode	Anode
$PbBr_2$(molten)	$Pb_{(s)}$	$Br_{2(g)}$
NaCl (molten)	$Na_{(s)}$	$Cl_{2(g)}$
$NaCl_{(aq)}$	$H_{2\ (g)}$	$Cl_{2(g)}$
$CuCl_{2\ (aq)}$	$Cu_{(s)}$	$Cl_{2(g)}$
$CuSO_{4(aq)}$	$Cu_{(s)}$	$O_{2(g)}$
$KNO_{3(aq)}$	$H_{2(g)}$	$O_{2(g)}$
$NaOH_{(aq)}$	$H_{2(g)}$	$O_{2(g)}$
$H_2SO_{4(aq)}$	$H_{2(g)}$	$O_{2(g)}$

USES OF ELECTROLYSIS

Particular	Description
Extraction of Na metal	Fused NaCl is used Down's cell is an example
Caustic soda from brine	Nelson cell (aqueous NaCl is used)
Mg and Ca extraction	Extraction occurs from their fused chlorides
Extraction of Al	Electrolysis of fused bauxite is conducted
Anodized Al	Prepared by making anode of Al
Purification of Cu	Anode is made up of impure copper
Electroplating	Copper, silver, nickel or chromium plating is done in electrolytic cell

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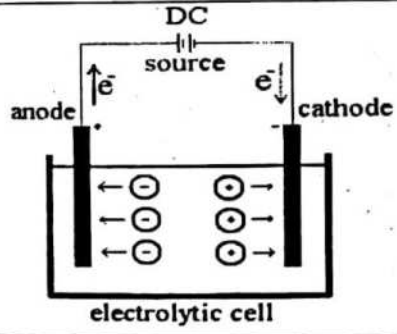
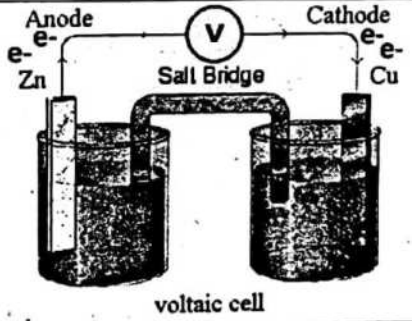
ELECTROCHEMICAL CELLS

The cells consisting of electrodes dipped into an electrolyte which make the inter-conversion of electrical energy and chemical energy possible, are called electrochemical cells.

Types of electrochemical cells:

(i) Electrolytic cell:

(ii) Voltaic or galvanic cell:

Electrolytic Cell	Voltaic/Galvanic Cell
A cell in which a redox reaction occurs at the expense of electrical energy is called electrolytic cell.	A cell in which redox reaction generates electric current through chemical reaction is called voltaic or galvanic cell.
Anode is +vely charged	Anode is –vely charged.
Cathode is –vely charged.	Cathode is +vely charged.
Electrical energy → chemical energy	Chemical energy → electrical energy
Both reduction reaction and oxidation reaction occur in the same compartment.	Reduction reaction and oxidation reaction occur in the separate compartment.
Non-spontaneous redox reaction occurs.	Spontaneous redox reaction occurs.
Salt bridge is not used.	Salt bridge is used.
Used for the extraction of metals, purification, electroplating and anodizing.	Used for the measurement of electrode potential.
It consumes heat (endothermic)	It generates heat (exothermic)
 electrolytic cell	 voltaic cell
Nelson's Cell and Down's Cell	Daniel's cell, Ni-Cd cell, fuel cell

VOLTAIC OR GALVANIC CELL

Two half cells are present in voltaic cell

- **Left Half Cell (Oxidation Half Cell)**
  Zn – electrode is dipped in 1M solution of $ZnSO_4$
- **Right Half Cell (Reduction Half Cell)**
  Cu – electrode is dipped in 1M solution of $CuSO_4$.
- **Salt Bridge**
  It is aqueous solution of KCl in a gel.
- **Working**
  - Connect both the half cells electrolytically through the salt bridge
  - Close the external circuit by connecting the Zn and Cu electrodes.
  - The electrons will flow from Zn to Cu through external circuit. The following reactions will occur at respective electrodes.
    - At anode
      $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$ oxidation
    - At cathode
      $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ reduction
    - The voltaic cell reaction is represented by

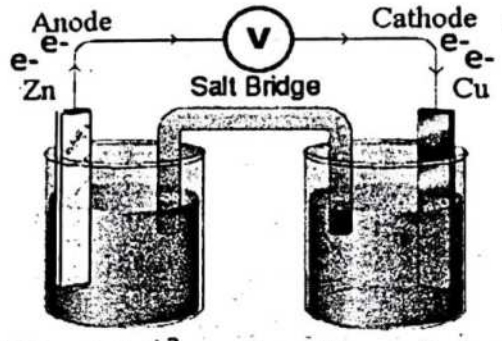
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$Zn_{(s)} / Zn^{2+}_{(aq)}$ 1M || $Cu^{2+}_{(aq)}$ 1M / $Cu_{(s)}$

- emf of the cell

  $E° = 1.10$ V

- **Function of salt bridge**
  - Salt bridge acts as a passage for the transfer of negative ions (SO_4^{2-}) from right half-cell to left half-cell.
  - If the exchange of SO_4^{2-} ions is stopped, then the oxidation-reduction reaction will stop due to charge accumulation in both half cells



$Zn \longrightarrow Zn^{+2} + 2e^- \| Cu^{+2} + 2e^- \rightarrow Cu$

Replacing the external circuit by a source of high voltage can reverse the voltaic cell reactions. Such cell is called reversible cell.

ELECTRODE POTENTIAL

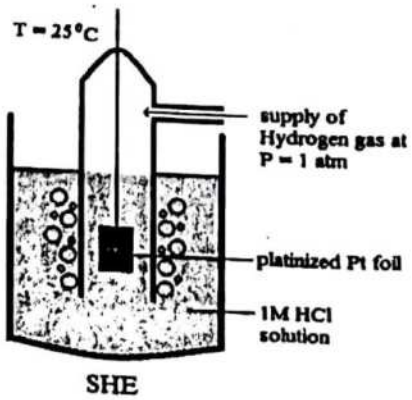
The potential set up when an electrode is dipped in one molar solution of its own ions at 298K called standard electrode potential or standard reduction potential, denoted by E°.

- Electrode potential, of any element, can be calculated by comparing it with standard hydrogen electrode (SHE).

STANDARD HYDROGEN ELECTRODE (SHE)

SHE consists of

- Glass Tube filled with H_2 gas at 1 atm. Pt–foil, coated with finally divided platinum black is suspended in it.
- The whole system mentioned above is dipped in 1M solution of HCl
- Electrode Potential of SHE is arbitrarily considered as zero



SHE

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MEASUREMENT OF ELECTRODE POTENTIAL

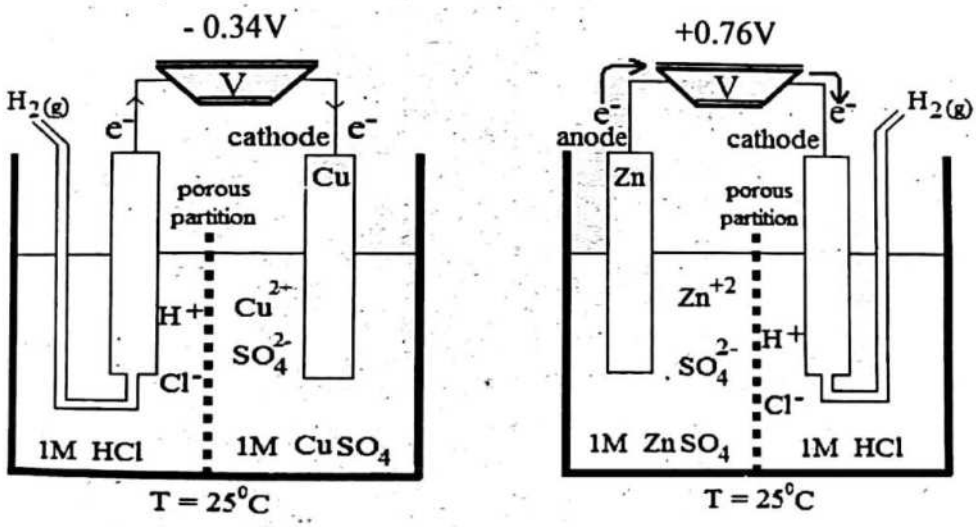
- Concerned electrode is joined with SHE and form a voltaic cell
- Salt bridge is used to connect both cells, filled with solution of KCl
- Voltmeter is attached to measure electrode potential
- Oxidation or Reduction occurs at SHE depending on the nature of the concerned electrode.
- When reduction occurs on SHE then volt meter reading will be +ve.

$$2H^{+}_{(aq)} + 2e^{-} \longrightarrow H_{2(gas)}$$

- When oxidation occurs on SHE then voltmeter reading will be in –ve

$$H_{2(gas)} \longrightarrow 2H^{+}_{(aq)} + 2e^{-}$$

- Potential of Zn is called oxidation potential
- Potential of Cu is called reduction potential



Electrode	Plate which carries electricity into the liquid
Anode	plate at which oxidation occurs
Cathode	plate at which reduction occurs
Conductor	A substance which conducts electricity but is not chemically changed
Insulator	A solid non-conductor
Strong electrolyte	A liquid which is fully ionized
Weak electrolyte	A liquid which is not fully ionized
Non-electrolyte	A liquid which does not undergo ionization.
Electrolysis	Decomposition of an electrolyte by passage of electricity
Anion	Negatively charged ion that travels to the anode during electrolysis
Cation	Positively charged ion that travels to the cathode during electrolysis

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THE ELECTROCHEMICAL SERIES

When elements are arranged in the order of their increasing standard electrode potentials on the hydrogen scale, the resulting list is known as electrochemical series.

Electrochemical series

Element	Electrode	Standard Reduction Potential (E°)
Li	$Li^+ + e^- \rightarrow Li$	-3.045
K	$K^+ + e^- \rightarrow K$	-2.925
Ca	$Ca^{2+} + 2e^- \rightarrow Ca$	-2.87
Na	$Na^+ + e^- \rightarrow Na$	-2.714
Mg	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37
Al	$Al^{3+} + 3e^- \rightarrow Al$	-1.66
Zn	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
Cr	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.74
Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
Cd	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.403
Ni	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.25
Sn	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14
Pb	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.126
H_2	$2H^+ + 2e^- \rightarrow H_2$	0.000
Cu	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
Cu	$Cu^+ + e^- \rightarrow Cu$	+0.521
I_2	$I_2 + 2e^- \rightarrow 2I$	+0.535
Fe	$Fe^{3+} + 3e^- \rightarrow Fe$	+0.771
Ag	$Ag^+ + e^- \rightarrow Ag$	+0.794
Hg	$Hg^{2+} + 2e^- \rightarrow Hg$	0.885
Br_2	$Br_2 + 2e^- \rightarrow 2Br^-$	+1.08
Cl_2	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.360
Au	$Au^{3+} + 3e^- \rightarrow Au$	+1.50
F_2	$F_2 + 2e^- \rightarrow 2F^-$	+2.87

Increasing strength as an oxidizing agent
Increasing reduction potentials

Increasing strength as a reducing agent
decreasing reduction potentials

APPLICATIONS OF ELECTROCHEMICAL SERIES

Applications

(i) Prediction of the feasibility of a chemical reaction

The Electrochemical series tells us that whether a reaction is feasible or not. If the sum of E° values of the two half cell reaction is positive, the reaction is feasible and if it is negative then the reaction will not be feasible.

(ii) Calculation of the voltage or emf of the cell

- Electrode having higher position in series will act as an anode, oxidation will take place on it
- Electrode having lower position in series, will act as cathode, reduction will take place on it

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(iii) **Comparison of relative tendency of metals and non metals to get oxidized or reduced**

- Value of the electrode potential shows, either the metal or non metal is oxidized or reduced

Greater value of standard reduction electrode potential greater will be the tendency to accept electron and undergo reduction and vice versa

(iv) **Relative chemical reactivity of metals**

Greater value of the standard reduction potential of a specie lesser will be its tendency to lose electron to form +ve ion hence lesser will be its reactivity.

(v) **Reaction of metals with dilute acids**

Greater the value of standard reduction potential of a metal, lesser its tendency to lose electrons to form metal ions and so weaker its tendency to displace H_2 from acids. For example Au, Pt, Ag and Cu do not liberate hydrogen from acids.

(vi) **Displacement of one metal by another from its solution**

Metal will displace another metal from the aqueous solution of its salt if it lies above the electrochemical series. For example Fe can displace Cu from $CuSO_4$, Zn does not displace Mg from solution of $MgSO_4$.

MODERN BATTERIES AND FUEL CELLS

Primary cells	Secondary cells:
Those cells which cannot be recharged are called primary cells.	Those cells, which can be recharged, are called secondary cells.
Dry cell, alkaline battery, mercury and silver oxide battery.	Ni-Cd battery and fuel cells.

LEAD STORAGE BATTERY OR LEAD ACCUMULATOR

Introduction:

- It is a secondary cell.

Anode:

- Metallic Lead (Pb)

Cathode:

- PbO_2

Electrolyte:

- 30% H_2SO_4 having density 1.25g/dm^3

Discharging:

- $Pb + PbO_2 + 4H^+ + 2SO_4^{-2} \longrightarrow 2PbSO_4 + 2H_2O$

Recharging:

- Anode and Cathode of the battery is connected to the anode and cathode of a source of high voltage.

$$2PbSO_4 + 2H_2O \longrightarrow Pb + PbO_2 + 4H^+ + 2SO_4^{-2}$$

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Note:

- Concentration of H_2SO_4 decreases during discharging and it is restored on recharging.
- Density of H_2SO_4 decreases from $1.25g/dm^3$ to $1.15g/dm^3$ during discharging and is restored on recharging.
- Lead Storage Battery consists of 6–cells and each cell produces energy of 2 volts.

Uses:

- It is used in car batteries

DIFFERENT BATTERIES

Particulars	Alkaline battery	AgO battery	Ni-Cd cell	Fuel cell
Type of cell	Primary	Primary	Secondary	Secondary
Anode	Zn rod	Zn metal	Cadmium	Porous carbon impregnated with Pt
Cathode	MnO_2	Ag_2O mixed with NaOH	NiO_2	Porous carbon impregnated with Pt
Nature of Electrolyte	Electrolyte is basic	Electrolyte is basic	Electrolyte is basic	KOH is electrolyte. It operates at high temperature.
Voltage	1.5V	1.5V	1.4V	75% bond energy into electricity
Uses	Toys, watches, tape recorder etc.	Battery, electronic watches, auto exposure camera	Mobile phones	Used in rocket as a fuel cell

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PRACTICE EXERCISE

30 mins Time Yourself

1. **Which of the following element act as inert electrode**
(a) Cu (b) Ag
(c) Pt (d) None

2. **If electricity is passed through $CuSO_4$ solution by using Pt electrode then which of the following possible change occurs?**
(a) H_2 is deposited at cathode (b) Colour of the solution becomes fade
(c) Cu is deposited at anode (d) All are possible

3. **Stronger the oxidizing agent, greater is the**
(a) Oxidation potential (b) Reduction potential
(c) Redox potential (d) emf of cell

4. **Which has maximum oxidation number?**
(a) N (b) Cr
(c) S (d) Mn

5. **Which of the following cell is not rechargeable?**
(a) Lead storage battery (b) Silver oxide cell
(c) Fuel cell (d) Ni-Cd cell

6. **In an electrolytic cell current flows?**
(a) From cathode to anode in outer circuit
(b) From anode to cathode outside the cell
(c) From cathode to anode inside the cell
(d) both b and c

7. **Which of the following is true in the case of Zn-Cu cell?**
(a) The flow of electrons takes place from copper to zinc
(b) E^0_{red} of copper electrode is less than that of zinc electrode
(c) Zinc acts as an anode and copper as cathode
(d) All are correct

8. **In a galvanic cell**
(a) Chemical energy is converted into electricity
(b) Chemical energy is converted into heat
(c) Electrical energy is converted into chemical energy
(d) Electrical energy is converted into heat

9. **The degree of dissociation of week electrolyte increases as**
(a) Pressure increases (b) Dilution decreases
(c) Dilution increases (d) None

10. **Molten NaCl conducts electricity due to the presence of**
(a) Free electrons (b) Free molecules
(c) Free ions (d) Atoms of Na and Cl

11. **In which of the following reactions, occur at cathode?**
(a) $Cu^{2+} + 2e^- \rightarrow Cu$ (b) $Cu + 2e^- \rightarrow Cu^{2+}$
(c) $Hg + O_2 \rightarrow HgO$ (d) $Mg + O_2 \rightarrow MgO$

12. **Electricity in voltaic cell is produced due to**
(a) neutralization (b) oxidation
(c) reduction (d) both b and c

13. **In electrolytic solution conductance of electricity is due to**
(a) free electrons (b) ions
(c) metals (d) electrodes

14. **In electrolytic cell, electricity carries**
(a) spontaneous reaction (b) non-spontaneous reaction
(c) neutralization (d) all of above

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15. **Reaction at anode is called**
(a) oxidation (b) reduction
(c) redox (d) decomposition

16. **In an electrolytic cell cathode provides electrons to**
(a) +ve ion (b) –ve ion
(c) neutral atom (d) does not provide any electron

17. **In Galvanic cell, electrons flow from anode to cathode through**
(a) external electric circuit (b) salt bridge
(c) movement of ions (d) all of the above

18. **Decrease in oxidation number is called**
(a) oxidation (b) reduction
(c) oxidation-reduction (d) all of above represent same entity

19. **For the measurement of standard electrode potential, Zn is dipped in**
(a) 1M ZnO solution (b) 1M $ZnSO_4$ solution
(c) 1.5M $ZnSO_4$ solution (d) 0.1M $ZnSO_4$ solution

20. **Right half cell contains_____ electrode**
(a) Al (b) Zn
(c) Cu (d) Fe

21. **$Zn_{(s)}/Zn^{+2}{}_{(aq)}$ 1M $||$ $Cu^{+2}{}_{(aq)}$ 1M/$Cu_{(s)}$ is representation of reaction in**
(a) Daniel cell (b) Down's cell
(c) Voltaic cell (d) Nelson's cell

22. **Salt bridge transfers**
(a) electrons (b) anion
(c) current (d) ions

23. **Voltaic cell can be recharged by**
(a) by addition of fresh solution
(b) by replacing external circuit with external source of electricity
(c) by removal of solution
(d) by heating it

24. **E°_{red} of an element can be calculated by comparing it with**
(a) New electrode of same element
(b) SHE
(c) 1M solution of ions of respective element
(d) 2M solution of HCl

25. **Temperature for the measurement of standard electrode potential is**
(a) 298K (b) 300K
(c) 30°C (d) 310K

26. **H_2 gas in SHE is filled at pressure of**
(a) 760mm of Hg (b) 750mm of Hg
(c) 780mm of Hg (d) 800mm of Hg

27. **Potential of SHE is considered as**
(a) zero (b) unity
(c) constant (d) multiple of 1

28. **Chemical used in salt bridge is**
(a) KOH (b) KCl
(c) KNO_3 (d) KBr

29. **Electrode potential of Zn is**
(a) oxidation
(b) reduction
(c) oxidation-reduction
(d) depends on the nature of the coupled electrode

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30. **List of elements based on hydrogen scale is called**
(a) periodic table (b) groups
(c) periods (d) electrochemical series

31. **The element that act as anode always have_____ position in electrochemical cell**
(a) higher (b) lower
(c) in middle (d) no effect of position

32. **In galvanic cell Zn acts as an anode so its value of standard reduction potential in comparison to coupled electrode would be**
(a) greater (b) lesser
(c) (reduction + oxidation potentials) (d) none

33. **Greater value of standard reduction potential greater will be tendency**
(a) to get oxidized (b) To get reduced
(c) to accept electrons (d) both b and c

34. **Greater value of standard reduction potential, smaller will be tendency**
(a) to form positive ions (b) to form negative ions
(c) gain electrons (d) all are possible

35. **Secondary cell is**
(a) rechargeable (b) non rechargeable
(c) electrolytic cell (d) Daniel cell

36. **Lead accumulators are**
(a) secondary cell (b) primary cell
(c) voltaic cell (d) both a and c

37. **Density of H_2SO_4 in lead accumulator is**
(a) 1.25g/cm^3 (b) 1.3g/cm^3
(c) 1.20g/cm^3 (d) 1.15g/cm^3

38. **Capacity of one lead accumulator cell is**
(a) 1.5volts (b) 2 volts
(c) 3 volts (d) 1 volts

39. **In alkaline battery, the anode is made up of**
(a) MnO_2 (b) Zn
(c) AgO_2 (d) cadmium

40. **The strength of solution of an element whose electrode potential is to be measured is**
(a) 2M (b) 1N
(c) 1m (d) 1M

41. **Apparent charge on atom in molecule is**
(a) valency (b) coordination number
(c) oxidation number (d) charge number

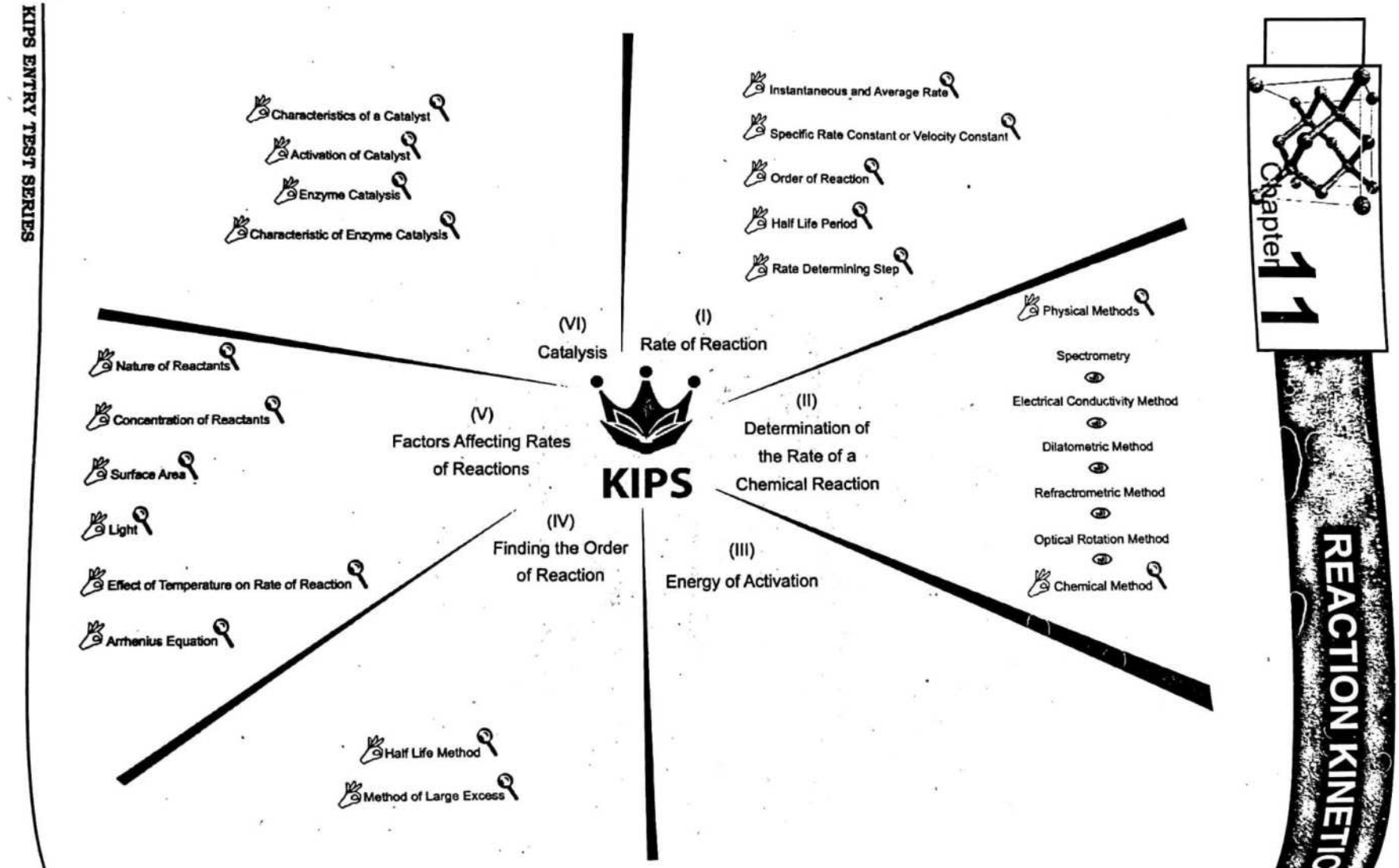
42. **Voltaic cell is a**
(a) irreversible cell (b) reversible cell
(c) alkaline cell (d) all of the above

43. **In $K_2Cr_2O_7$, the oxidation number of chromium is**
(a) +7 (b) +6
(c) -7 (d) -6

44. **Percentage of sulphuric acid in lead accumulator is**
(a) 40% (b) 25%
(c) 30% (d) 50%

45. **The reduction potential of Zn is**
(a) 0.76 (b) –0.76
(c) –0.55 (d) 0.55

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REACTION KINETICS

The studies concerned with rates of chemical reactions and factors that affect the rates of chemical reactions and the mechanism of reactions constitute the subject matter of reaction kinetics

CHEMICAL REACTIONS

The breaking of pre-existing bonds and the formation of new bond is called chemical change or chemical reaction.

On the basis of rate of reaction, chemical reactions can be broadly classified into three types;

(1) Very fast reaction $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$

(2) Very slow reaction $2Fe + 3H_2O + O_2 \rightarrow Fe_2O_3.3H_2O$

(3) Moderately slow reactions $C_2H_5OH + CH_3COOH \rightarrow CH_3COOC_2H_5 + H_2O$

RATE OF REACTION

The change in concentration of a reactant or a product divided by the time taken for the change is called rate of reaction.

$$\text{Rate of reaction} = \frac{\text{Change in concentration of the substance}}{\text{Time taken for the change}}$$

Units of rate of reaction:

The units for rate of reaction are moles $dm^{-3}s^{-1}$

Types of reaction rate:

Average rate

The rate of reaction between two specific time intervals is called average rate.

Rate of reaction = dx/dt

> **NOTE**
>
> For a gas phase reaction, units of pressure are used in place of molar concentration.

Instantaneous rate

The rate at any one instant during a specific interval of time is called instantaneous rate.

Comparison of instantaneous and average rate:

- The average rate and instantaneous rate are equal for only one instant in any time interval.
- At the beginning of reaction, the instantaneous rate is higher than the average rate.
- At the end of reaction, the instantaneous rate is less than the average rate
- The average rate will be equal to instantaneous rate, when the time interval approaches zero.

The rate of a general reaction.

$A \rightarrow B$ can be expressed as

$$\text{Rate of reaction} = \frac{-d[A]}{dt} = \frac{+d[B]}{dt}$$

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RATE LAWS FOR ELEMENTARY REACTIONS

Elementary Reaction	Molecularity	Rate Law
A→ Products	Unimolecular	Rate = k [A]
A+A→ Products	Bimolecular	Rate = k[A]^2
A+B→ Products	Bimolecular	Rate = k [A][B]
A+A+B→ Products	Termolecular	Rate = k [A]^2[B]
A+B+C→ Products	Termolecular	Rate = k[A][B][C]

SPECIFIC RATE CONSTANT OR VELOCITY CONSTANT

Definition:

The rate of reaction when the concentrations of the reactants are unity is called specific rate constant of a chemical reaction.

Explanation

According to law of mass action for a general chemical reaction.

$$aA + bB \rightarrow cC + dD$$

$$\text{Rate of reaction} = k[A]^a[B]^b$$

Here 'k' is called specific rate constant or velocity constant for the reaction.

- Let [A]=1mol dm^{-3} and [B] = 1 mol dm^{-3}

$$\text{Rate of reaction} = k \times 1^a \times 1^b = k$$

- Under the given conditions, k remains constant, but it changes with temperature.

> **NOTE:**
> There is only one factor i.e. temperature which affects the specific rate constant

Difference Between Rate of Reaction and Rate Constant of Reaction

Rate of reaction	Rate constant of reaction
• The change in concentration of a reactant or a product divided by the time taken for the change is called rate of reaction. • Its unit is mol dm^{-3}s^{-1}. • It depends upon concentrations of reactants. • It varies with the passage of time under given conditions. • Example: $aA + bB \rightarrow cC + dD$ Rate of reaction = k[A]^a[B]^b	• It is the proportionality constant, which is represented by k, in rate equation. • Its units depend on the order of reaction. • It is independent of the concentration of reactant or products. • It always remains constant under the given conditions. • Example: aA+bB→ Product $k = \frac{\text{Rate}}{[A]^a[B]^b}$

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RATE DETERMINING STEP

When the reaction completes in more than one step, then the slowest step will give the overall rate of reaction, thus slowest step of such a reaction is called rate determining step.

DETERMINATION OF RATE OF REACTION

- Determination of rate of reaction involves the measurement of concentration of reactants.
- Graph is plotted between concentration of reactant and time & we get a curve.
- Select any two points in a curve.
- Make a right angle triangle of these points.
- Getting the tanθ of right angle triangle, we shall get

$$\text{Rate of reaction} = \frac{\text{Change in concentration of reactant}}{\text{Change in time}}$$

METHODS FOR THE DETERMINATION OF RATE OF A CHEMICAL REACTION

Physical Methods

Techniques	Details
Spectrometry	▪ Spectrophotometer is used. ▪ Reactants and products absorbs U.V, I.R radiations ▪ Amount of radiation absorbed give rate of reaction
Electrical conductivity method	▪ Conductometer is used ▪ Conductivity depends on the concentration of ions in the solution. ▪ Conductivity of ions of reactants give rate of reaction
Dilatometric method	▪ It is applied to the reaction in which volume of solution is changed. ▪ Volume change of a reaction is proportional to extent of reaction.
Optical rotation method	▪ Polarimeter is used ▪ Reacting molecules rotates angle of rotation of plane polarized light ▪ Value of angle of rotation gives information about rate of reaction
Refractometric method	▪ Refractometer is used ▪ It is applied to the reaction in which change in refractive indices occurs. ▪ Transformation of glucose into alcohol can be analyzed regarding rate of reaction through this method

Chemical Method

- Titration

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FACTORS AFFECTING THE RATE OF REACTION

Name	Details
Nature of reactant	▪ More active reactants give fast rate of reaction ▪ No. of electrons present in innermost shell affects the reactivity of reactant ▪ Elements of IA are more reactive than IIA. ▪ Neutralization reactions and decomposition reactions are very fast. ▪ Oxidation reduction reactions are slower ▪ Ionic reactions are very fast
Concentration of reactant	▪ Reaction is due to effective collision of reactant molecules. ▪ Greater concentration of reactants, more effective collisions, thus rate of reaction will be high ▪ In case of reactants in gases, their concentration is increased by increasing their partial pressures ▪ Rate of reaction is directly proportional to concentration of reactants ▪ Sometime concentration of reactant become double and rate of reaction increases four times
Surface area	▪ Greater the surface area, greater will be chance of contact of molecules ▪ Greater surface area of molecules, greater will be rate of reaction.
Light	▪ Light travel in the form of photons. ▪ Photons have energy depending on frequency of light. ▪ Light gives the energy to reactants to form activated complex in minimum time. ▪ Light increases the rate of reaction.
Temperature	▪ By increasing temperature, the number of collisions of molecule increases ▪ Rate of reaction increases by increase in temperature of reaction ▪ On increasing temperature by 10K, the rate of reaction becomes doubled. ▪ Arrhenius equation: $K = Ae^{-Ea/RT}$ (it gives us the quantitative effect of temperature on rate of reaction.

ORDER OF REACTION

The sum of all the exponents to which the concentrations in the rate equation are raised is called order of reaction.

OR

The number of reacting molecules, whose concentration alter as a result of the chemical change, is called order of reaction.

$$aA + bB \longrightarrow P$$

$$\frac{dx}{dt} = k[A]^a[B]^b$$

Order of reaction = a+b

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IMPORTANT POINTS

- The order of a reaction is an experimentally determined quantity and cannot be inferred simply by looking at the reaction equation.
- The sum of the exponents in the rate equation may or may not be the same as in a balanced chemical equation.
- The order of reaction provides valuable information about the mechanism of a reaction.
- Maximum order of reaction is three
- Order of reaction can be zero or can be in fraction
- Order of reaction is related with rate equation and is controlled by rate law.
- Order of reaction help us to determine mechanism of reaction
- If the molecularity and order of reaction is same then it is said to be a simple reaction. Otherwise it is complex reaction.

The chemical reactions are classified as;

- Zero order reaction
- First order reaction
- Second order reaction
- Third order reaction
- Pseudo first order reaction
- Fractional order reaction

EXAMPLES OF ORDER OF REACTIONS

Zero order reactions

Photochemical reactions are usually zero order.

First order reaction

$N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$

Second order reactions

(i) $2CH_3CHO \rightarrow 2CH_4 + 2CO$

(ii) $NO + O_3 \rightarrow NO_2 + O_2$

Third order reactions

(i) $SnCl_2 + 2FeCl_3 \rightarrow SnCl_4 + 2FeCl_2$

(ii) $2NO + Cl_2 \rightarrow 2NOCl$

HALF LIFE PERIOD

The time required to convert 50% of the reactants into products is called half-life period.

Example

(i) Half-life period of N_2O_4 at 45°C is 24 minutes.

(ii) Half-life period of $^{235}_{92}U$ is 7.1×10^8 or 710 million years.

IMPORTANT POINTS

- Half-life period of second order reaction is inversely proportional to the initial concentration of the reactants.
- Half-life period of third order reaction is inversely proportional to the square of initial concentration of reactants.

In general for the reaction of nth order:

$$\left[t_{1/2}\right]_n \propto \frac{1}{a^{n-1}}$$

METHODS TO DETERMINE THE ORDER OF REACTION

Five methods are available.

(i) Method of hit and trial

(ii) Graphical method

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(iii) Differential method
(iv) Half life method
(v) Method of large excess

ENERGY OF ACTIVATION

The minimum amount of energy, in addition to the average kinetic energy, which the particles must have for effective collisions, is called activation energy.

IMPORTANT POINTS

- Reactants go into transition state before going into product called activated complex.
- Energy of activated complex is higher than reactants and products.
- Amount of energy to form transition state is called energy of activation.
- Effective collision produces products.
- In effective collision, molecules have certain amount of energy and collide in certain orientation.
- When the energy of products is lesser than reactants, the reaction is exothermic.
- When the energy of products is higher than reactants, the reaction is endothermic.
- Energy of activation of forward reaction is less than backward reaction for an exothermic reaction.
- Energy of activation for backward reaction is less than forward reaction for an endothermic reaction.

ARRHENIUS EQUATION

According to Arrhenius

$K = Ae^{-E_a/RT}$

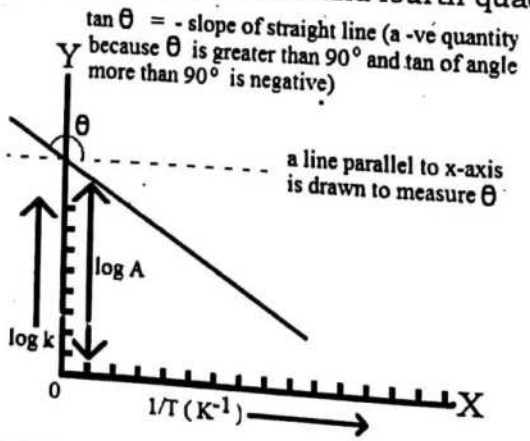
In this equation

K = specific rate constant
A = Arrhenius constant.

It tells us about collision frequency.

Points to be remembered:

- This equation explains the effect of temperature on the rate constant of reaction.
- k is exponentially related to activation energy and temperature.
- When a graph is plotted between $\frac{1}{T}$ on x-axis and log k at y-axis, a straight line is obtained with a negative slope. Actually, $\frac{E_a}{RT}$ has negative sign so the straight line has two ends in second and fourth quadrants.



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- $Slope = \frac{-E_a}{2.303R}$ Unit of slope is Kelvin
- This equation helps us to determine activation energy of the reaction.
- E_a = -Slope x 2.303R
- Unit of activation energy is Joule mole^{-1}, greater is value of activation energy smaller is k value hence smaller will be the rate

CATALYST

A substance, which alters the rate of a chemical reaction, but remains chemically unchanged at the end of the reaction, is called catalyst.

CATALYSIS

The process, which takes place in the presence of a catalyst, is called catalysis.

Types of Catalysis

1- **Homogeneous catalysis**

In this type of catalysis, the catalyst and the reactants are in the same phase and the reacting system is homogenous throughout.

Examples

$$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{NO(g)} 2SO_{3(g)}$$

$$CH_3COOH_{(aq)} + C_2H_5OH_{(aq)} \xrightleftharpoons{H+} CH_3COOC_2H_{5(aq)} + H_2O_{(\ell)}$$

2- **Heterogeneous catalysis**

When the phase of catalyst differ from phase of reactant, catalysis is called heterogeneous catalysis.

Example

$$4NH_{3(g)} + 5O_{2(g)} \xrightleftharpoons{Pt(s)} 4NO_{(g)} + 6H_2O_{(g)}$$

CHARACTERISTICS OF A CATALYST

- Catalyst remains chemically unchanged.
- Catalyst is more effective when it is in finely divided powder form.
- Catalyst should not affect chemical equilibrium state of reaction.
- Catalyst cannot start a reaction; it only lowers the energy of activation.
- Catalysts are specific in their nature.
- Catalytic poisoning occurs when any foreign particle affect the activity of catalyst.
- Addition of impurity in catalyst is called poisoning of catalyst.

  It may be
  - Permanent poisoning
  - Temporary poisoning

Examples

- HCl can poison Pt in decomposition of H_2O_2.
- CO in Haber's Process can poison V_2O_5/Pt.

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ACTIVATION OF CATALYST

Promoter

Substance that increases the activity of catalyst is called promoter or activators or catalyst.

Example

Cu promotes activity of Ni in hydrogenation of oil.

Inhibitor

When a substance reduces the rate of reaction then it is called inhibitor or negative catalyst.

Example

Tetraethyl lead is added to petrol which acts as inhibitor or negative catalyst.

Autocatalyst

In some reactions, products formed act as catalyst called autocatalysis.

Examples

- Hydrolysis of ester gives acetic acid which act as catalyst.
- The reaction of oxalic acid with acidified $KMnO_4$, $MnSO_4$ is produced Mn^{+2} ions act as auto catalyst.

ENZYME CATALYSIS

Enzymes are biocatalytical proteins, which increase the rate of biochemical reactions.

- The substance on which an enzyme can attack is called substrate.
- The point through which an enzyme attacks on substrate called active site.
- Each enzyme has its own active site.
- Enzymes are highly specific for substrate.
- Enzyme and substrate forms enzyme-substrate complex, which then breaks into product and enzyme.
- The name of enzyme usually ends on "ase".

Examples

- Urease, Zymase, Dehydrogenase, Hydrolase, Maltase

CHARACTERISTICS OF ENZYME CATALYSIS

- The catalytic activity of enzymes is greatly enhanced by the presence of a co- enzyme or activator
- Enzyme catalysis is highly specific e.g. urease catalyses the hydrolysis of urea only and it cannot hydrolyse any other amide even methyl urea.
- Enzyme catalytic reactions have the maximum rates at an optimum temperature.
- The pH of the system also controls the rates of the enzyme catalysed reaction
- and the rate passes through a maximum at a particular pH, known as an optimum pH. The activity of enzyme catalyst is inhibited by a poison.

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PRACTICE EXERCISE

30 mins Time Yourself

1. **The rate of reaction**
   (a) Increases as the reaction proceeds.
   (b) Decreases as the reaction proceeds.
   (c) Remains the same as the reaction proceeds.
   (d) May decrease or increase as the reaction proceeds.
2. **The addition of a catalyst to the reaction system.**
   (a) Increases the rate of forward reaction only.
   (b) Increases the rate of reverse reaction.
   (c) Increases the rate of forward but decreases the rate of backward reaction.
   (d) Increases the rate of forward as well as backward reaction equally.
3. **The specific rate constant of a first order reaction depends on the**
   (a) Time
   (b) Concentration of the reactant
   (c) Temperature
   (d) Concentration of the product.
4. **On increasing the temperature, the rate of reaction increases mainly because**
   (a) The activation energy of the reaction increases
   (b) Concentration of the reacting molecules increases
   (c) Collision frequency increases
   (d) None of these
5. **$-d[N_2O_5]/dt$ represents**
   (a) Rate of formation of N_2O_5
   (b) Rate of decomposition of N_2O_5
   (c) Order of the reaction
   (d) None.
6. **The value of activation energy is primarily determined by**
   (a) Temperature
   (b) Effective collision
   (c) Concentration of reactants
   (d) Chemical nature of reactants and products
7. **Sum of exponents of molar concentration is called**
   (a) Order of reaction
   (b) Molecularity
   (c) Rate of reaction
   (d) Average of reaction
8. **Spontaneous reactions are**
   (a) Moderate
   (b) Slow
   (c) Fast
   (d) not natural
9. **In rate expression, the concentration of reactants is negative. It shows**
   (a) Concentration of reactant does not change
   (b) Concentration of product increases
   (c) Concentration of reactant decreases
   (d) Concentration of reactant increases
10. **Unit of rate of reaction is**
    (a) Moles dm^{-3} sec^{-1}
    (b) Moles dm^{-3}
    (c) Moles sec^{-1}
    (d) Mol^{-1} dm^3 sec^{-1}
11. **When a graph is plotted between $\frac{1}{T}$ on x-axis and log k on y-axis a straight line is obtained with a negative slope which has two end in**
    (a) I and II quadrant
    (b) II and III quadrant
    (c) III and IV quadrant
    (d) II and IV quadrant
12. **Rate of disappearance of reactant is equal to**
    (a) Rate of reaction
    (b) Rate of formation of product
    (c) Energy released during reaction
    (d) a and b

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13. **Rate of reaction, when concentration of reactants are taken as unity is called**
(a) Arrhenius constant (b) Molecularity
(c) Specific rate constant (d) Ideal rate constant

14. **Order of reaction of $2N_2O_5 \rightarrow 2N_2O_4 + O_2$ is**
(a) First order (b) Second order
(c) Third order (d) Zero order

15. **For 3rd order reaction, the half life is inversely proportional to initial concentration of reactants**
(a) Single (b) Square
(c) Cube (d) Raise to power four

16. **Which order of reaction obeys the relation $t_{1/2} = 1/k_a$**
(a) First order (b) Second order
(c) Third order (d) Zero order

17. **Radiations are absorbed in**
(a) Spectrophotometer method (b) Dilatometric method
(c) Optical relation method (d) Refractometric method

18. **Activated complex is formed due to**
(a) Pressure (b) Effective collisions
(c) Ineffective collisions (d) Temperature

19. **Energy of reactant higher than energy of product favours**
(a) Endothermic (b) Exothermic
(c) Moderate reaction (d) No reaction

20. **Energy required to form transition complex state is called**
(a) Ea (b) P.E
(c) V (d) K.E

21. **Which of the following will have very high rate of reaction?**
(a) Double decomposition reaction (b) Neutralization reaction
(c) Ionic reactions (d) all of above

22. **Greater the conc. of reactant**
(a) Greater will be dx/dt (b) Lesser will be dx/dt
(c) dx/dt will be moderate (d) any of above

23. **Anything which increases rate of reaction without being involved in the reaction.**
(a) Promoter (b) Catalyst
(c) Inhibitor (d) All of the above

24. **The substances that reduces the effectiveness of a catalyst are called**
(a) Promoters (b) Poisoning catalysts
(c) Inhibitors (d) pro-catalysts

25. **When catalysts and reactants are in more than one phase, it is**
(a) Homogeneous catalysis (b) Heterogeneous catalysis
(c) Catalysis (d) Ea

26. **Each catalyst has**
(a) Specificity (b) Special structure
(c) Its own Ea (d) All of above

27. **Biocatalytical proteins are**
(a) Enzymes (b) Substrate
(c) Lipids (d) Any of above

28. **A catalyst can not effect**
(a) Products (b) Chemical equilibrium
(c) Reactants (d) both a & b

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29. **An enzyme has its specificity due to**
(a) Substrate (b) Structure
(c) Temperature (d) Pressure

30. **Co-enzymes are**
(a) Non proteineous (b) Proteineous
(c) sugars (d) lipids

31. **A substance which increases the reactivity of enzyme is called**
(a) Promoters (b) Inhibitors
(c) Stimulators (d) Non-activators

32. **Addition of tetraethyl lead in petrol is example of**
(a) +ve catalysis (b) –ve catalysis
(c) auto catalysis (d) anti catalysis

33. **When a product acts as catalyst then it is called**
(a) Autocatalysis (b) –ve catalysis
(c) +ve catalysis (d) self catalysis

34. **End name of enzyme is**
(a) yl (b) ase
(c) one (d) al

35. **When the reaction completes in more than one steps, rate of reaction will be determined by**
(a) Fast step (b) Slowest step
(c) All steps (d) Molecularity of the reaction

36. **For determining the order of reaction, we use**
(a) Refractometric method (b) Dilatometric method
(c) Optical activity method (d) Half life method

37. **Energy of activation for backward reaction is less than forward reaction for_____ reaction**
(a) Endothermic (b) Exothermic
(c) Moderate (d) Fast

38. **The unit of slope in Arrhenius plot to calculate the energy of activation is**
(a) K^{-1} (b) ^0F
(c) K (d) ^0C

39. **Which statement is incorrect about catalyst**
(a) it is used in smaller amount (b) decrease activation energy
(c) specific in action (d) it affects specific rate constant

40. **Which of the following type of reaction is 3rd order reaction**
(a) $2N_2O_5 \rightleftharpoons 2N_2O_4 + O_3$ (b) $NO + O_3 \longrightarrow NO_2 + O_2$
(c) $2FeCl_3 + 6KI \longrightarrow 2FeI_2 + 6KCl + I_2$ (d) None of these

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KIPS DIAGNOSTIC TEST

1	C	11	C	21	B	31	B	41	C	51	C
2	B	12	B	22	A	32	C	42	D	52	D
3	C	13	C	23	C	33	C	43	C	53	C
4	D	14	D	24	C	34	B	44	B	54	C
5	C	15	C	25	B	35	B	45	D	55	B
6	B	16	C	26	D	36	D	46	C	56	C
7	D	17	D	27	A	37	A	47	B	57	C
8	D	18	C	28	B	38	B	48	A	58	B
9	D	19	C	29	C	39	B	49	B	59	C
10	D	20	A	30	D	40	C	50	C	60	A

CHAPTER-1

1	C	11	A	21	A	31	D
2	D	12	D	22	C	32	A
3	B	13	D	23	B	33	C
4	D	14	C	24	D	34	C
5	C	15	C	25	C	35	A
6	D	16	C	26	A	36	D
7	D	17	A	27	C	37	D
8	D	18	A	28	A	38	A
9	A	19	C	29	C	39	C
10	C	20	B	30	A	40	A

CHAPTER-2

1	A	11	A	21	D	31	B
2	D	12	C	22	A	32	B
3	C	13	B	23	C	33	C
4	B	14	B	24	C	34	B
5	B	15	C	25	B	35	D
6	C	16	B	26	B	36	C
7	B	17	B	27	A	37	A
8	C	18	B	28	B	38	A
9	C	19	D	29	B	39	B
10	B	20	B	30	B	40	C

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CHAPTER-3

1	A	11	D	21	B	31	D
2	B	12	B	22	B	32	B
3	A	13	D	23	C	33	A
4	B	14	A	24	C	34	B
5	C	15	D	25	A	35	A
6	D	16	B	26	C	36	C
7	D	17	A	27	B	37	D
8	D	18	C	28	D	38	C
9	C	19	A	29	A	39	D
10	B	20	C	30	A	40	D

CHAPTER-4

1	C	11	D	21	A	31	B	41	B
2	D	12	C	22	B	32	B	42	B
3	B	13	C	23	A	33	D	43	C
4	A	14	B	24	C	34	B	44	B
5	A	15	A	25	A	35	C	45	D
6	C	16	B	26	B	36	A	46	D
7	B	17	C	27	B	37	B	47	C
8	D	18	D	28	D	38	B	48	B
9	B	19	B	29	A	39	B	49	C
10	B	20	C	30	A	40	A	50	C

CHAPTER-5

1	D	11	B	21	B	31	C	41	B
2	B	12	D	22	D	32	D	42	C
3	B	13	C	23	C	33	A	43	C
4	A	14	A	24	D	34	B	44	A
5	C	15	A	25	B	35	C	45	A
6	B	16	B	26	B	36	C	46	C
7	B	17	B	27	B	37	A	47	A
8	D	18	D	28	D	38	B	48	A
9	D	19	C	29	C	39	A	49	B
10	C	20	D	30	D	40	A	50	C

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CHAPTER-6

1	C	11	C	21	B	31	B	41	B
2	A	12	B	22	D	32	B	42	B
3	B	13	B	23	A	33	B	43	A
4	C	14	D	24	A	34	A	44	A
5	D	15	D	25	C	35	A	45	C
6	A	16	B	26	B	36	D	46	B
7	B	17	A	27	B	37	B	47	B
8	C	18	A	28	C	38	D	48	C
9	C	19	A	29	A	39	C	49	D
10	B	20	B	30	C	40	B	50	A

CHAPTER-7

1	D	11	B	21	D
2	A	12	D	22	A
3	D	13	A	23	A
4	B	14	B	24	A
5	D	15	D	25	C
6	A	16	D	26	B
7	C	17	D	27	C
8	A	18	A	28	B
9	C	19	B	29	A
10	A	20	A	30	D

CHAPTER-8

1	B	11	D	21	D	31	A
2	C	12	C	22	A	32	B
3	D	13	D	23	A	33	B
4	C	14	A	24	A	34	A
5	D	15	A	25	D	35	D
6	D	16	A	26	A	36	B
7	C	17	A	27	A	37	D
8	C	18	D	28	C	38	B
9	D	19	D	29	A	39	B
10	D	20	C	30	B	40	D

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CHAPTER-9

1	A	11	A	21	B	31	C
2	A	12	B	22	B	32	A
3	D	13	C	23	C	33	B
4	B	14	C	24	D	34	B
5	D	15	C	25	B	35	A
6	C	16	C	26	B		
7	B	17	A	27	A		
8	B	18	A	28	C		
9	B	19	B	29	D		
10	D	20	B	30	C		

CHAPTER-10

1	C	11	A	21	C	31	A	41	C
2	B	12	D	22	D	32	A	42	D
3	B	13	B	23	B	33	D	43	B
4	D	14	B	24	B	34	A	44	C
5	B	15	A	25	A	35	A	45	B
6	B	16	A	26	A	36	D		
7	C	17	A	27	A	37	A		
8	A	18	B	28	B	38	B		
9	C	19	B	29	D	39	B		
10	C	20	C	30	D	40	D		

CHAPTER-11

1	B	11	D	21	D	31	A
2	D	12	A	22	A	32	B
3	C	13	C	23	B	33	A
4	C	14	A	24	B	34	B
5	B	15	B	25	B	35	B
6	B	16	B	26	D	36	D
7	A	17	A	27	A	37	A
8	C	18	B	28	D	38	C
9	C	19	B	29	B	39	D
10	A	20	A	30	A	40	C

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Part - II

KIPS PUBLICATION

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Chapter 1

PERIODIC CLASSIFICATION OF ELEMENTS AND PERIODICITY

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PURPOSE OF PERIODIC TABLE

The periodic table provides a basic framework to study the periodic behaviour of physical and chemical properties of elements as well as their compounds.

HISTORICAL BACKGROUND

Name of Scientist	Country	Contributions	Basis of Classification
Al-Razi	Arab	First ever classification	Physical and chemical properties of substances
Dobereiner	German	Law of triads	Elements can be classified in triads where the atomic weight of middle element of each triad is almost equal to the arithmetic mean of atomic weights of the other two elements.
Newland	English	Law of octaves	If elements are arranged in increasing order of their atomic weights, every 8th element starting from a given one has similar properties as that of first one. It includes 62 elements.
Mendeleev	Russian	Periodic law	The physical and chemical properties of elements are periodic functions of their atomic weights. His periodic table contains 12 periods and 8 groups.
Moseley	English	Modern periodic law	The physical and chemical properties of elements are periodic functions of their atomic numbers. It contains seven periods and eight groups.

Advantages of Mendeleev's Periodic Table

- Mendeleev left many vacant spaces in his periodic table for unknown elements and predicted their properties e.g. germanium.
- Mendeleev's Periodic Table helped to correct the doubtful atomic weights of elements e.g. beryllium.

Improvements in Mendeleev's Periodic Table

- Arrangement of elements in ascending order of atomic numbers to rectify four misfit pairs of elements in the Mendeleev's Periodic Table i.e. Ar and K, Co and Ni, Te and I and Th and Pa.
- Addition of group VIII to place the newly discovered noble gases properly.
- Introduction of two types of vertical groups A and B to eradicate the misplacement of Zn, Cd, Hg and Be, Mg, Ca, Sr, Ba in same vertical group and so many others in same manner.

MODERN PERIODIC TABLE

Modern periodic law (Moseley)

The physical and chemical properties of elements are the periodic function of their atomic numbers.

Fact File of Modern Periodic Table

Periodic Table	Elements arranged in order of increasing proton number
Group Number	Number of electrons in outermost shell (valence electrons)
Period Number	Number of shells of atom
Valence Electron	Electron in outermost shell
Metals	Elements with 1-3 valence electrons except boron
Non-metals	Elements with 4-7 valence electrons
Inert gases	Elements with completely filled outermost-shell

Essential Features

Following are the essential features of the modern periodic table:-

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Groups

- The vertical columns of elements in the periodic table are called groups. Each group represents number of valence electrons.
- All the elements in a group have similar properties and similar electronic configuration of valence shell.
- There are eight groups that are shown by Roman numerals I to VIII.
- Each group has two sub-groups A and B.

'A' contains normal or typical elements while 'B' contains transition elements.

Periods

- The horizontal rows of elements in the periodic table are called periods.
- All elements in a period have same number of shells according to the period number.
- There are seven periods in the periodic table that are known by Arab numerals 1 to 7.

Sr#.	Peculiarity	Sub-groups present	No. of elements	s-block elements	p-block elements	d-block elements	f-block elements
1	Shortest	A	2	2	0	0	0
2	Short	A	8	2	6	0	0
3	Short	A	8	2	6	0	0
4	Long	A and B	18	2	6	10	0
5	Long	A and B	18	2	6	10	0
6	Longest	A and B	32	2	6	10	14
7	Incomplete	A and B	26	2	-	10	14

Families

Name	Contents
Alkali metals	Group-I A
Alkaline earth metals	Group II A
Chalcogens	Group-VI A
Halogens	Group VII A
Noble gases/Inert gases	Group VIII A
Coinage metals	Group I B
Rare earth elements / Inner transition metals	f-block elements
Actinides	fourteen elements that follow Actinium ($_{89}$Ac)
Lanthanides	fourteen elements that follow lanthanum ($_{57}$La)
Outer transition metals	d-block elements

Blocks

There are four blocks on basis of the valance sub-shell (s and p block) and involvement of orbitals in valancy (d and f block)

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Block	Contents
s	IA, IIA and He
p	IIIA to VIIIA except He
d	Transition elements (outer) 3d-series, 4d-series and 5d-series
f	Actinides and Lanthanides 4f-series and 5f-series

Fact File

Lanthanide Contraction

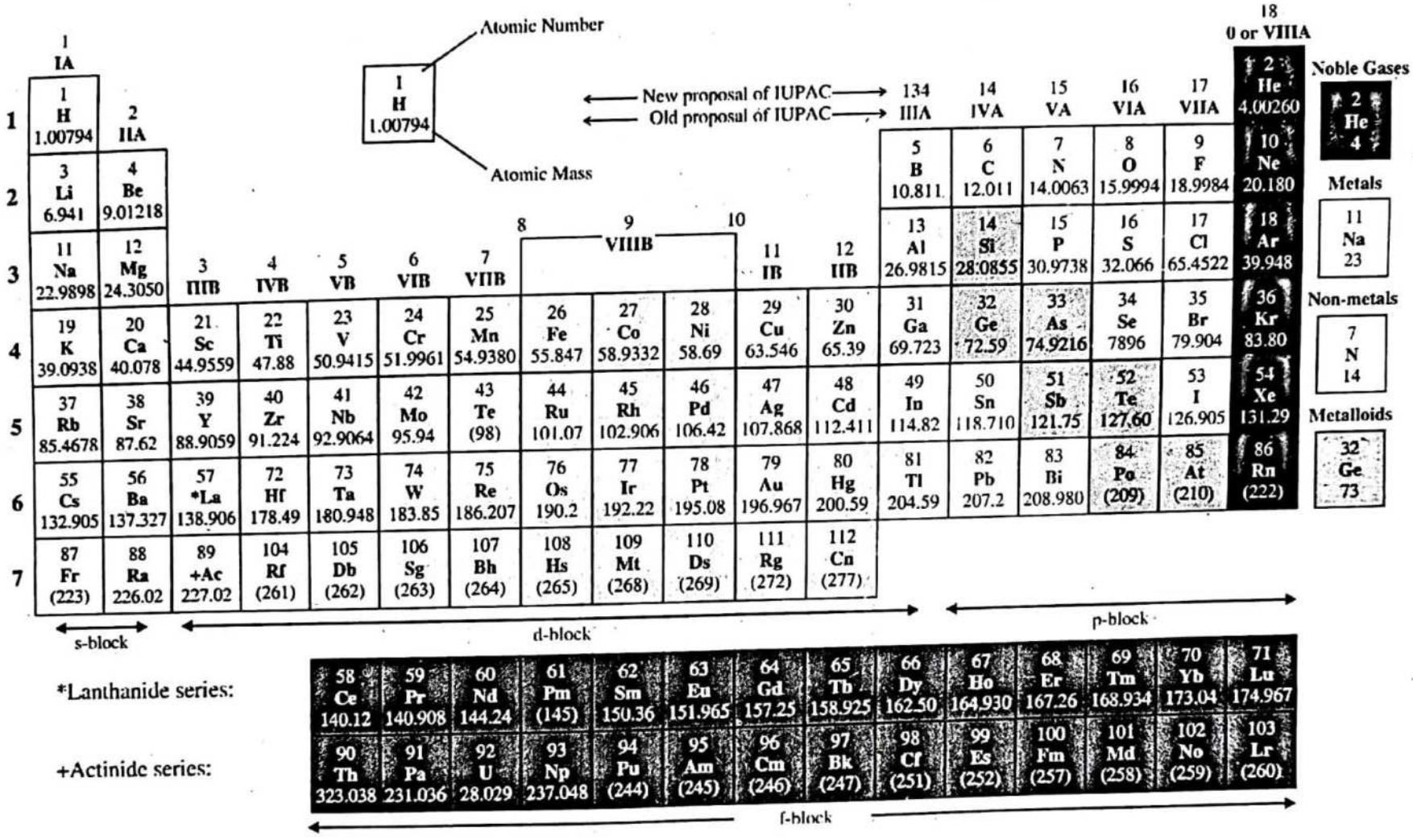
Increase in nuclear charge along a period reduces atomic size due to greater attractive forces; the effect is remarkable in longer periods therefore gradual reduction in the size of lanthanides is significant and known as lanthanide contraction.

Positive ion is always smaller than the neutral atom, whereas negative ion is always larger than the neutral atom.

$$M^+ < M$$
$$X^- > X$$

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MODERN PERIODIC TABLE OF THE ELEMENTS



	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 0 or VIIIA
1	1 H 1.00794																	2 He 4.00260
2	3 Li 6.941	4 Be 9.01218											5 B 10.811	6 C 12.011	7 N 14.0063	8 O 15.9994	9 F 18.9984	10 Ne 20.180
3	11 Na 22.9898	12 Mg 24.3050											13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 65.4522	18 Ar 39.948
4	19 K 39.0938	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.59	33 As 74.9216	34 Se 7896	35 Br 79.904	36 Kr 83.80
5	37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Te (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.82	50 Sn 118.710	51 Sb 121.75	52 Te 127.60	53 I 126.905	54 Xe 131.29
6	55 Cs 132.905	56 Ba 137.327	57 *La 138.906	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.59	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra 226.02	89 +Ac 227.02	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (264)	108 Hs (265)	109 Mt (268)	110 Ds (269)	111 Rg (272)	112 Cn (277)						

*Lanthanide series:	58 Ce 140.12	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
+Actinide series:	90 Th 323.038	91 Pa 231.036	92 U 28.029	93 Np 237.048	94 Pu (244)	95 Am (245)	96 Cm (246)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Noble Gases: 2 He 4

Metals: 11 Na 23

Non-metals: 7 N 14

Metalloids: 32 Ge 73

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METALS, NON-METALS AND METALLOIDS

Metals	Non-metals	Metalloids
• Usually solids at room temperature (except Hg) • High melting and boiling points (except Group I) • Good conductors of heat and electricity • Often shiny, ductile, malleable and possess great tensile strength • Mostlly form ionic compound • Oxides are usually basic or amphoteric • Often form hydrogen gas with dilute acids • Always form positive ions (cations)	• Often gases (except $Br_{(l)}$, $S_{(s)}$, P(s), I(s), C(s), B(s) and Si(s) • Low melting and boiling points (except B, C and Si) • Poor conductor of heat and electricity (except Graphite) • Normally dull, soft and can not be drawn out into wires or made into flat sheets. • Most compounds are covalent in nature • Oxides are usually neutral or acidic • Always form negative ions (anions)	• Their electron losing and gaining capabilities are intermediate between metals and non metals. • Their electrical and thermal conductivities are intermediate between metals and non metals. • Their oxides are amphoteric, which means that they can act as acidic as well as basic oxides.

POSITION OF HYDROGEN IN PERIODIC TABLE

Hydrogen resembles with elements of groups IA, IVA and VIIA. Its actual position is still confusing because of its behaviour.

Position over Alkali Metals (I-A)

Similarities	Differences
• One electron in outermost shell • Ability to lose electron and form positive ions • Strong tendency to combine with electronegative elements like halogens. • Formation of H^+ on ionization of its ionic compounds • Collection at cathode during electrolysis	• It is a gas where as I-A elements are solid metals. • It needs only one electron to complete its outer most shell others need seven. • It prefers to form covalent compounds. • It exists in diatomic state. • It can form H^- ion. • Its oxide is neutral e.g. H_2O.

Position over Halogens (Group-VII-A)

Similarities	Differences
• Gaseous state • Stable diatomic molecules Requirement of only one electron to complete their valence shell • Formation of hydrides similar to alkali metal halides Formation of hydride ion H^- like F^-, Cl^-, I^- etc.	• It has only one valence electron while halogens have seven. • H^- ion is unstable in aqueous solution but halide are stable. • It can form H^+ ion. • It is liberated at cathode during electrolysis but halides at anode. • Its oxide is neutral but the oxides of halogens are acidic.

Position over Carbon-Silicon Family (Group-IVA)

Similarities	Differences
• Half-filled valence shell • Mutual sharing of electrons during chemical interactions • Remarkable reducing property	• It is a gas. • It needs only one electron to complete its valence shell. • It exists as diatomic molecules.

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PERIODIC TRENDS IN PHYSICAL PROPERTEIS

Property	Definition	Trend in a group (down the group)	Responsible Factors.	Trend along a period (from left to right)
Atomic radius	Half of the distance between the centers of two adjacent atoms of any element.	Increases	Nuclear charge and number of shells	Decreases
Ionic radius	Distance between the center of an ion and the outer boundary of its electron cloud.	(for similar charged ions)increases	Nuclear charge and number of shells.	Decreases for iso-electronic +ve and –ve ions.
Ionization energy	Minimum quantity of energy, which is required to remove an electron from the outer most shell of its isolated, gaseous atom in its ground state.	Decreases	Nuclear charge, atomic size and shielding effect.	Increases
Electron affinity	Energy released or absorbed, when an electron is added to a gaseous atom to form a negative ion.	Decreases	Size of atom, nuclear charge and vacancies in valence shell.	Increases
Metallic character	Tendency to lose electron and form cations and basic oxides.	Increases	Atomic size and nuclear charge.	Decreases
Melting and boiling points	Specific temperature at which an element changes to liquid or gaseous state.	In case of IA and IIA decreases and for VIIA increases	Number of valence electrons.	I-A to IV-A increases V to VIII decreases
Oxidation state	Apparent charge, which an element could carry in a compound.	Usually same	Electrons lost or gained	I to IV same as group number V,VI,VII is equal to vacancy or group number
Electrical conductance	Ability to conduct electricity.	(increases for IA and IIA) no regular trend for transition metals	Lose electrons in outer shell	Decreases
Hydration energy	Heat absorbed or evolved, when one mole of gaseous ion dissolves in water to give an infinitely dilute solution.	Decreases	Charge to size ratio	Increases

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PERIODIC RELATIONSHIP IN COMPOUNDS

Halides

- The binary compounds of halogens with other elements are called halides.
- There are three classes of halides: ionic, covalent and polymeric.

Characteristics	Ionic	Covalent	Polymeric
Intramolecular forces	Purely ionic	Covalent	Partly ionic
Elements (Other than halogen) involved	Strongly electropositive	Less electropositive	Less electropositive
Lattice structure	Crystalline solid	Gases or liquids	Layer or chain form
Basic unit	Discrete ions	Discrete molecules	Discrete molecules
Melting and boiling point	High	Low	Moderate
Examples	NaCl, $CaCl_2$	CCl_4	$AlCl_3$, $BeCl_2$ and $SiCl_4$

- If an element forms more than one halides, the halide in its lower oxidation state tends to be ionic e.g. $PbCl_2$ is mainly ionic and $PbCl_4$ is fairly covalent due to high polarizing power.
- Order of decreasing ionic character of halides:

  fluoride > chloride > bromide > iodide
- Bonding Character of Chlorides of Third Period

Groups	I A	II A	III A	IV A	V A	VI A
Chlorides	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	S_2Cl_2
Character	Ionic	Partly ionic	Partly ionic	Polar covalent	Polar covalent	Polar covalent

Hydrides

- The binary compounds of hydrogen with other elements are called hydrides.
- There are three classes of hydrides: ionic, covalent and intermediate.

Characteristics	Ionic	Covalent	Intermediate
Intramolecular forces	Purely ionic	Covalent	Partly ionic
Elements (other than hydrogen) involved	Strongly electropositive	Less electropositive	Less electropositive
Structure	Crystalline solid	Gases or volatile liquids	Polymeric (layer or chain form)
Basic unit	Discrete ions	Discrete molecules	Discrete molecules
Melting point and Boiling point	High	Low	-
Electrical conductance	Conductors in molten state	Non-conductors	-
Examples	NaH, CaH_2	H_2O, H_2S and PH_3	BeH_2 and MgH_2

- Boiling point of water is greater than HF although it is less polar

Oxides

The binary compounds of oxygen are called oxides

Classification of Oxides

Oxides can be classified on the basis of

(i) Nature of chemical bonding

(ii) Acidic, basic or neutral

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Classification on the basis of Acidic properties

(i) Basic oxides (Na_2O, K_2O, MgO, CaO etc)
(ii) Acidic oxides (CO_2, SO_3, SiO_2, NO_2 etc)
(iii) Amphoteric oxides (ZnO, Al_2O_3, BeO, Ga_2O_3, In_2O_3, GeO_2, SnO_2, PbO, As_2O_3, Sb_2O_3, Bi_2O_3,

MAXIMAS AND MINIMAS OF PERIODIC TABLE

Characteristics	Element (s) / Group
Largest block of periodic table	d-block (40 elements)
Longest period of periodic table	6th period (32 elements)
Largest group of periodic table	VIII-B (12 elements)
Most metallic element	Cesium
Most powerful reducing agent	Cesium
Most reactive metal	Cesium
Most powerful oxidizing agent	Fluorine
Least metallic element	Fluorine
Most reactive non-metal	Fluorine
Element having highest ionization energy	Helium
Element having highest electron affinity value	Chlorine
Lowest value of oxidation state	0 for an element in free state
Metal with highest value of oxidation state	Os^{+8}
Elements with no vacancy in valence shell	Noble gases (0-group)
Elements with highest electrical conductance values	I-B (coinage metals)
Halides having highest lattice energies	Fluorides
Halides with strongest Vander Waals forces	Iodides
Element forming most stable hydrides	Fluorine
Elements forming least stable hydrides	Thallium, Lead, Bismuth
Non-metal with highest value of oxidation state	Xe^{+8}

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PRACTICE EXERCISE

35 mins Time Yourself

1. **Elements in the same vertical group of the periodic table have same.**
   (a) Number of valence electrons (b) Atomic number
   (c) Atomic mass (d) Atomic volume
2. **An element having low value of ionization energy and low value of electron** affinity is likely to belong to
   (a) Group IA (b) Group IB
   (c) Group VIIA (d) Group VIII
3. **Which set of elements is listed in order of increasing ionization energy?**
   (a) Sb<As<S<P<Cl (b) Cl<Sb<P<As<S
   (c) As<Cl<P<S<Sb (d) Sb<As<Cl<S<P
4. **Which of the following always increases on going from top to bottom in a group?**
   (a) Metallic character (b) Electronegativity
   (c) Oxidizing power (d) Tendency to get reduced
5. **Which of the p-block elements are not representative elements?**
   (a) Alkali metals (I-A) (b) Group-14 elements (IV-A)
   (c) Group-18 elements (VIII-A) (d) Halogens (VII-A)
6. **Among halogens, the highest boiling point is of**
   (a) Fluorine (b) Chlorine
   (c) Bromine (d) Iodine
7. **Which of the following will not form crystalline structure with oppositely charged ions**
   (a) H^+ (b) H^-
   (c) Mg^{2+} (d) Ca^{2+}
8. **Which statement is incorrect?**
   (a) All the metals are conductor of electricity.
   (b) All the metals are conductor of heat.
   (c) All the metals form positive ions.
   (d) All the metals form acidic oxides.
9. **Periodic table provides a basic framework to study elements with respect to their**
   (a) Physical properties (b) Chemical properties
   (c) Properties of their compounds (d) All
10. **The scientist who did not contribute in the construction of periodic table?**
    (a) Al-Razi (b) Moseley
    (c) Dobereiner (d) Democritus
11. **Concept of Triads was introduced by**
    (a) Dobereiner (b) Newland
    (c) Mendeleev (d) Al-Razi
12. **Which element was not known when Mendeleev proposed his classification?**
    (a) Hydrogen (b) Sodium
    (c) Copper (d) Germanium

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13. **Elements with similar chemical properties appear in the**
(a) Same family (b) Same period
(c) p-block elements (d) Right upper corner

14. **Noble gases are named so because they are**
(a) Least reactive (b) Zero group elements
(c) Having completely filled valence shell (d) All.

15. **In modern periodic table, all the elements are arranged in ascending order of**
(a) Valency (b) Atomic mass
(c) Atomic number (d) Valence electrons

16. **The longest period in the modern periodic table is**
(a) 6th (b) 7th
(c) 2nd and 3rd both (d) 5th

17. **Inner transition elements are called**
(a) Lanthanides (b) Actinides
(c) Rare earth metals (d) All

18. **Seventh period contains _____normal elements.**
(a) 2 (b) 4
(c) 6 (d) 8

19. **Modern periodic table has been divided in _____blocks.**
(a) 2 (b) 4
(c) 8 (d) 7

20. **Non-metals usually form _____ oxides.**
(a) Acidic (b) Amphoteric
(c) Neutral (d) All of the above

21. **Amphoteric oxides are those, which possess _____ properties.**
(a) Acidic (b) Basic
(c) Acidic and basic (d) Neutral and acidic

22. **Best position of hydrogen in the periodic table is above I.A Group which is mainly due to**
(a) Both are electropositive
(b) Similar outer most shell electronic configuration
(c) Both form ionic compounds
(d) All

23. **Hydrogen resembles with carbon because of having**
(a) Same number of electrons in the valence shell
(b) Similar physical state
(c) Remarkable reducing properties
(d) Homovalent (show same valency)

24. **Which one of the following sets consists of all coinage metals?**
(a) Cu, Hg, Au (b) Cu, Ag, Au
(c) Ag, Au, Hg (d) Cu, Fe, Au

25. **In which of the following pairs are elements belonging to the same group?**
(a) Boron and Beryllium (b) Nitrogen and Phosphorous
(c) Magnesium and Aluminium (d) Gallium and Helium

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26. Many properties of an element and its compounds can be predicted from the position of the element in the periodic table. What property could not be predicted in this way?
(a) The nature of its oxides
(b) The charge on its ions
(c) The formula of its oxide
(d) Its number of isotopes

27. Which one of the following is not a periodic property?
(a) Melting point of elements
(b) Boiling point of elements
(c) Ionization energy of elements
(d) Coordination number of ions

28. The atomic radii decreases by increasing atomic number in
(a) Alkali metal
(b) Alkaline earth metal
(c) Elements from Li to Ne
(d) Halogens

29. Which discovery caused a revision in the periodic law as stated by Mendeleev?
(a) Location of nucleus by Rutherford
(b) Atomic number by Moseley
(c) X-rays by Roentgen
(d) Natural radioactivity by Henry Bacquerel

30. An element has electronic configuration $1s^2$, $2s^2$, $2p^2$. It belongs to
(a) Group II-A
(b) Group IV-A
(c) Group VII-A
(d) Group VI-A

31. The property which increases upto group IV-A then decreases onwards
(a) Ionization energy
(b) Atomic radii
(c) Melting and boiling points
(d) Atomic volume

32. Which of the following ion is stable in aqueous solution?
(a) H^+
(b) H^-
(c) Cl^-
(d) All are stable

33. The atoms of same element having same atomic number but different mass number are called
(a) Isobars
(b) Isomers
(c) Isotopes
(d) Isotropes

34. Deuterium reacts with oxygen to form
(a) Hard water
(b) Heavy water
(c) Soft water
(d) Water gas

35. Which order of ionization energy is correct.
(a) Mg < Al
(b) Si > P
(c) Mg > Al
(d) both b and c

36. Ionization energy depends upon
(a) Nuclear charge
(b) Atomic size
(c) Shielding effect
(d) I.E depends upon all of the above and nature of orbital

37. Shielding effect across the period
(a) Increases
(b) Decreases
(c) Can not be predicted
(d) Remains constant

38. Addition of 2^{nd} electron to a uninegative ion is always
(a) Exothermic
(b) Endothermic
(c) Data is insufficient
(d) Unpredictable

39. Higher value of electron affinity means
(a) Atom will lose electron easily
(b) Atom will gain electron easily
(c) Atom may form di-positive ion
(d) The reason is unknown

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40. **Metallic characters of alkali metals**
(a) Increase down the group (b) Decrease down the group
(c) No regular trend (d) Remain same.

41. **Melting points of VII-A group elements down the group**
(a) Increasc (b) Decrease
(c) Remain constant (d) No regular trend

42. **Oxidation state of an atom represents**
(a) Number of electrons gained (b) Number of electrons lost
(c) Apparent charge in compound. (d) Its vacancies

43. **Which of the following possesses maximum hydration energy?**
(a) Na^{+} (b) K^{+}
(c) Mg^{+2} (d) Ca^{+2}

44. **Halides in which halogen atoms act as a bridge between two atoms of the other element are called**
(a) Covalent halides (b) Electronegative halides
(c) Polymeric halides (d) Polymeric hydrides

45. **Less electronegative elements such as Be, Ga, Al etc form**
(a) Polymeric halide (b) Covalent halide
(c) Ionic halide (d) All

46. **Iodine is solid due to**
(a) Strong covalent bond (b) Large value of dipole moment
(c) High polarizability (d) Strong hydrogen bonding

47. **True increasing order of acidity of the oxides of Mn is**
(a) $MnO < MnO_2 < Mn_2O_7$ (b) $Mn_2O_7 > MnO_2 > MnO$
(c) $MnO_2 > MnO > Mn_2O_7$ (d) $MnO_2 > Mn_2O_7 > MnO$

48. **Keeping in view the size of atom which order is correct one?**
(a) Mg > Sr (b) Ba > Mg
(c) Lu > Ce (d) Cl > I

49. **Which one of the following element has highest oxidation state in its compounds?**
(a) Cr (b) Mn
(c) Sn (d) O

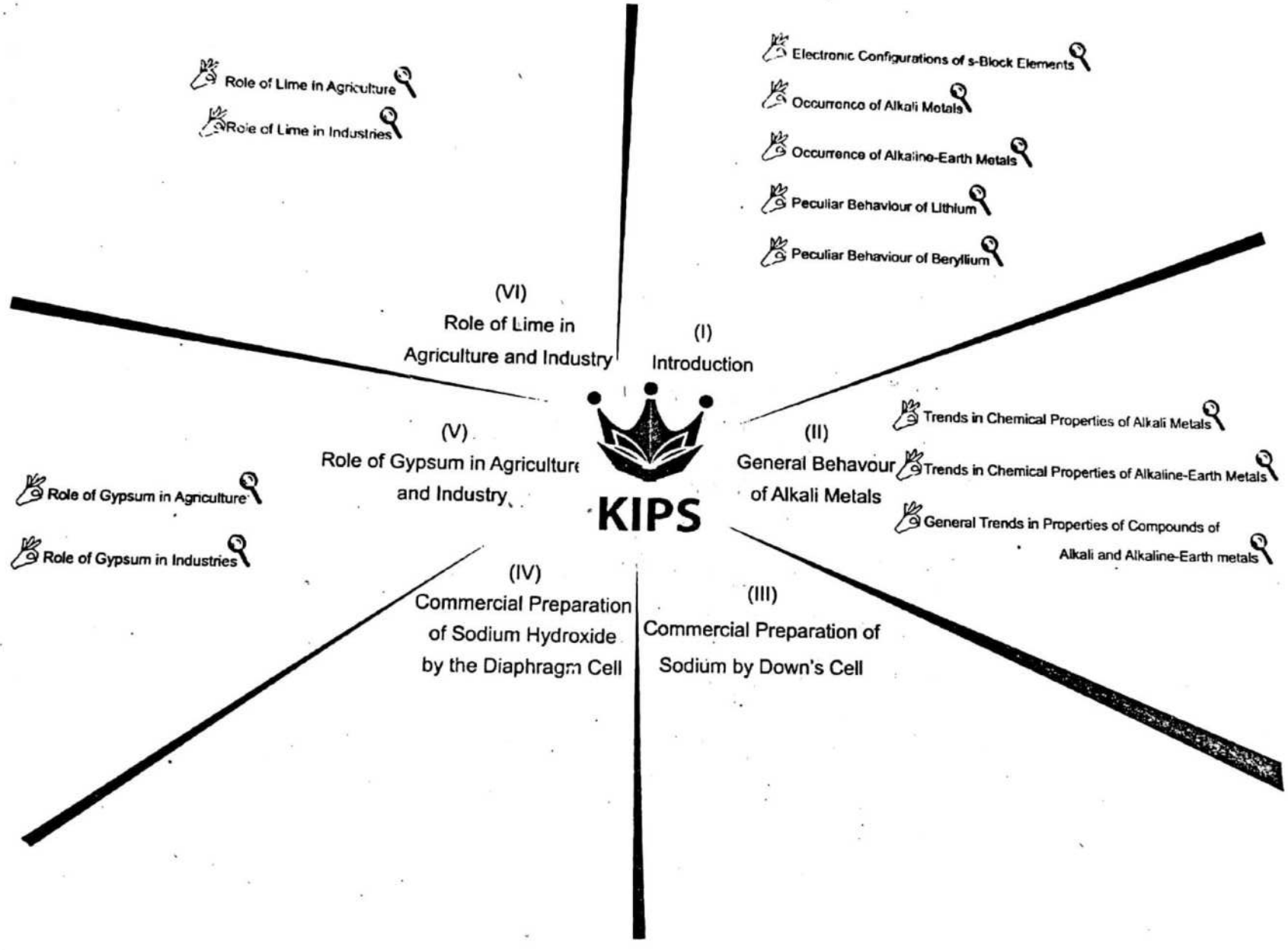
50. **Which of the following can not exist in solution**
(a) O^{-2} (b) H^{+}
(c) Cl^{-} (d) Na^{+}

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Chapter 2

S-BLOCK ELEMENTS



ALKALI METALS

The elements of group IA except hydrogen, which have only one electron in s-orbital of their valence shell, are called alkali metals.

Electronic Configurations and physical constants of Alkali Metals

Properties	Li	Na	K	Rb	Cs
Atomic number	3	11	19	37	55
Electronic configuration	$1s^2 2s^1$	[Ne] $3s^1$	[Ar] $4s^1$	[Kr] $5s^1$	[Xe]6s
Ionization energy (kJ/mol)	520	496	419	403	376
Electron affinity (kJ/mol)	-60	-53	-48	-47	-46
Electronegativity	1.0	0.9	0.8	0.8	0.7
Atomic radius	123	158	203	216	235
Ionic radius of 1+ ion (pm)	60	95	133	148	169
Melting points (^{0}C)	187	97.5	63.6	39.0	28.5
Boiling points (^{0}C)	1325	889	774	688	690
Density gm/cm^3(20^{0}C)	0.53	0.97	0.86	1.53	1.9
Heat of hydration (kJ/mol)	505	475	384	345	310

ALKALINE-EARTH METALS

The elements of group IIA, which have two electrons in s-orbital of their valence shell, are called alkaline earth metals.

Electronic configurations and physical constants of alkaline Earth Metals

Properties	Be	Mg	Ca	Sr	Ba
Atomic number	4	12	20	38	56
Electronegativity	$1s^2 2s^2$	[Ne] $3s^2$	[Ar] $4s^2$	[Kr] $5s^2$	[Xe]$6s^2$
Ionization energy (kJ/mol)	899	738	590	549	503
Electron affinity (kJ/mol)	240	230	156	168	52
Electronegativity	1.5	1.2	1.0	1.0	0.9
Atomic radius	89	136	174	191	198
Ionic radius of 2+ ion (pm)	31	65	99	113	135
Melting points (^{0}C)	1289	649	839	769	725
Boiling points (^{0}C)	2970	1107	1484	1384	1640
Density gm/cm^3(20^{0}C)	1.85	1.74	1.55	2.6	3.5
Heat of hydration (kJ/mol)	2337	1897	1619	1455	1250

HISTORY

- The name 'alkali' came from Arabic, which means " The Ashes".
- The name alkaline earth metal came from the fact that they produce alkalies in water and they are widely distributed in earth's crust.

OCCURRENCE OF ALKALI METAL

Element	Name of Mineral	Chemical Formula
Lithium	Spodumene	$LiAl(SiO_3)_2$
Sodium	Rock salt (Halite)	NaCl
	Chile saltpetre	$NaNO_3$
	Natron	$Na_2CO_3.H_2O$
	Trona	$Na_2CO_3.2NaHCO_3.2H_2O$
	Borax	$Na_2B_4O_7.10H_2O$
Potassium	Carnallite	$KCl.MgCl_2.6H_2O$
	Sylvite	KCl
	Alunite (Alum stone)	$K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$

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OCCURRENCE OF ALKALINE EARTH METALS

Element	Name of Mineral	Chemical Formula
Beryllium	Beryl	$Be_3Al_2(SiO_3)_6$
	Chrysoberyl	Al_2BeO_4
Magnesium	Magnesite	$MgCO_3$
	Dolomite	$MgCO_3.CaCO_3$
	Carnallite	$KCl.MgCl_2.6H_2O$
	Epsom salt	$MgSO_4.7H_2O$
	Soap stone(talc)	$H_2Mg_3.(SiO_3)_4$
	Asbestos	$CaMg_3(SiO_3)_4$
Calcium	Calcite (Lime stone)	$CaCO_3$
	Gypsum	$CaSO_4.2H_2O$
	Plaster of Paris	$CaSO_4.1/2H_2O$
	Fluorite	CaF_2
	Phosphorite	$Ca_3(PO_4)_2$
Strontium	Strontionite	$SrCO_3$
Barium	Barite (Heavy Spar)	$BaSO_4$

PECULIAR BEHAVIOUR OF LITHIUM AND BERYLLIUM

Li (1st Alkali Metal)	Other Alkali Metals
Li is much harder and lighter than other I-A group elements.	Other elements are soft
Li salts are insoluble in water	Salts of other elements are soluble
Forms stable complex compounds	Do not form complex compounds
Reacts slowly with water	React very fast with water
Does not form bi-carbonate, tri-iodide or hydrogen sulphide due to high polarizing power	Forms bi-carbonates, tri-iodide and hydrogen sulphide
Gives normal oxides on burning	Give peroxide and superoxide
Hydrides are very stable	Hydrides are less stable
Compounds are more covalent and soluble in organic solvent	Compounds are ionic and insoluble in organic solvent
Least reactive among IA group	Very reactive
Li does not react with acetylene	React with acetylene
Less electropositive	More electropositive
Carbonates and nitrates are unstable	Carbonates and nitrates are stable
LiOH on heating gives Li_2O	Hydroxide are stable
Gives nitride on reaction with N_2	No reaction with nitrogen
Gives carbide directly	No reaction with carbon directly

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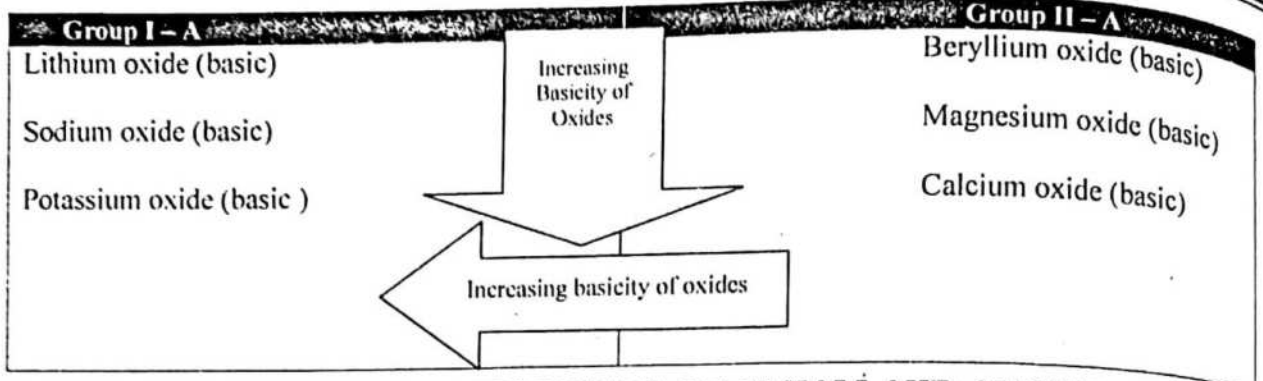
Be (1st Member of II-A)	Other members of II-A
Harder as Fe	Softr but harder than I-A group
M.P and B.P are higher	Less M.P and B.P than Be
Forms insoluble BeO with water	Form soluble oxide with water
Have resistance for complete oxidation	Oxidized completely
Liberates H_2 on reaction with alkalies	No reaction with alkalies

TREND IN CHEMICAL PROPERTIES OF ALKALI & ALKALINE METALS

	Alkali Metals	Alkaline Metals
Valency	Low I.P and forms +1	Low I.P and form +2 ion
2nd I.P.	2nd I.P is very high	2nd I.P is comparatively low
Oxides	Normal, superoxide and peroxides are formed e.g. $Li + O_2 \rightarrow Li_2O$ (Normal Oxide) $Na + O_2 \rightarrow Na_2O_2$(Peroxide) $K + O_2 \rightarrow KO_2$ (Super oxide)	Normal and peroxides are produced e.g. $2Be + O_2 \rightarrow 2BeO$(Normal Oxide) $2Mg + O_2 \rightarrow 2MgO$(Normal Oxide) $2Ba + O_2 \rightarrow BaO_2$(Per oxide)
Hydrides	Ionic hydride formation $2M + H_2 \rightarrow 2MH$	Ionic Hydride formation in presence of high pressure and catalyst(MgI_2) $Mg + H_2 \rightarrow MgH_2$
Nitrides	Only Li give nitride directly	All elements give nitride directly
Sulphides	Form sulphides with S (M_2S)	Forms sulphides with S (MS)
Reaction with water	React with water and give MOH	React with water and give $M(OH)_2$ except Be
Reaction with halogen	React with halogen to give MX	React with halogen to give MX_2

- Reaction of alkali metal oxide with water is acid-base and not oxidation-reduction reaction. $O^{-2} + H_2O \rightarrow 2OH^-$

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TREND IN PROPERTIES OF COMPOUNDS OF ALKALI AND ALKALINE EARTH METALS

Alkali Metal	Alkaline Metals
OXIDES:	
Li - forms normal oxide, Na – forms per oxide, other form super oxides.	BeO is amphoteric others are basic in nature
All oxides are soluble and forms OH^- in water	Be and Mg do not react with water while other oxides soluble in water and form OH^-
Solubility increases down the group	Solubility increases down the group
Aqueous solution is highly alkaline	Aqueous solution is less alkaline
HYDROXIDE:	
These are hygroscopic, very soluble in water except LiOH	$Be(OH)_2$ is insoluble, $Mg(OH)_2$ is sparingly soluble and $Ba(OH)_2$ is more soluble
Difficult to decompose	Decomposes on heating
CARBONATES:	
Carbonates are very soluble in water except $LiCO_3$	Carbonates are insoluble in water
Thermally stable except Lithium	Thermally less stable
Decomposition on heating decreases down the group	Decomposition on heating decreases down the group
NITRATES:	
Nitrates are soluble in water	Nitrates are soluble in water
Nitrates of Li gives Li_2O, O_2 and NO_2 on heating other form nitrite and oxygen $NaNO_3 \rightarrow NaNO_2+O_2$	Nitrates of Mg, Ca, Ba give NO_2, O_2 and metallic oxide
SULPHATES:	
Sulphates are soluble in water except Lithium	Solubility decreases down the group

Fact File

- KO_2 absorbs CO_2 and liberate O_2 used in breathing equipments.
- Milk of lime is used in test of CO_2
- Milk of Magnesia is used against acidity of stomach

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COMMERCIAL PREPARATION OF SODIUM

Melting point of NaCl is 801°C. It is reduced to 600°C by addition of $CaCl_2$ (flux).

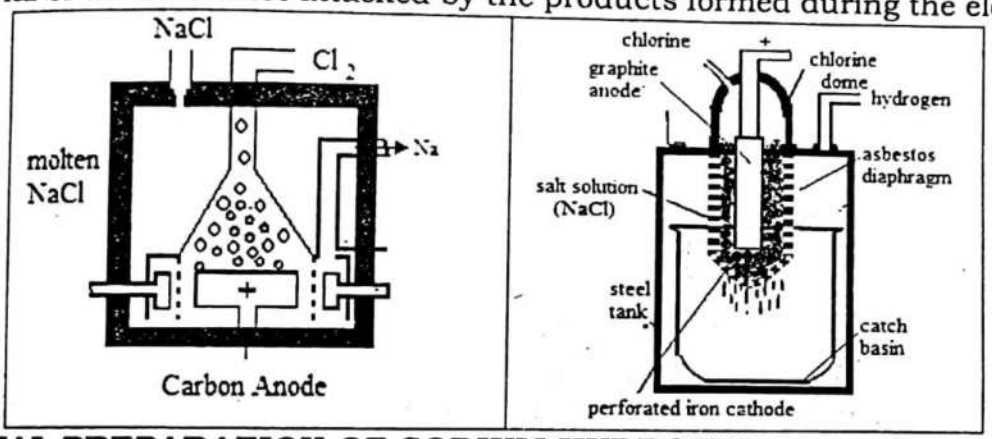
$$NaCl_{(fused)} \rightarrow Na_{(99.9\% \text{ pure})} + \tfrac{1}{2} Cl_2$$

Down's cell

- Anode is made up of graphite. (Cl_2 is collected)
- Cathode is of iron. (Na is collected)

Advantages of Down's cell

- The metallic fog is not produced
- Liquid sodium can easily be collected at 600°C
- Material of the cell is not attacked by the products formed during the electrolysis.



COMMERCIAL PREPARATION OF SODIUM HYDROXIDE

Sodium hydroxide (caustic soda) is manufactured on a large scale by the electrolysis of aqueous solution of common salt (Brine) in a diaphragm cell.

PREPARATION OF NaOH

- NaOH is prepared from brine.
- Cathode is made up of steel lined with asbestos..
- Anode is made up of graphite.
- Steam helps to keep perforation of cathode clear.
- H_2 is produced at cathode.
- Reaction between Cl_2 and OH^- is stopped by using asbestos diaphragm.
- OH^- may not contaminate Cl_2 on oxidation at anode for which anode level is slightly higher to keep liquid to flow towards cathode.
- Solution of NaOH obtained contains 11% NaOH and 16% NaCl.
- After evaporation, NaOH crystallizes and contains 50% NaOH and 1% NaCl as impurity.

Brine

- 30% aqueous solution of NaCl is called Brine.

ROLE OF GYPSUM IN AGRICULTURE

- $CaSO_4.2H_2O$ is gypsum.
- Applied to soil to provide Ca and S.
- Leached soils are supplied by gypsum.
- Sulphur develops protein and chlorophyll in plants.
- Due to deficiency of S, plants become pale green coloured.
- Root system of plants is enlarged by sulphur.

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ROLE OF GYPSUM IN INDUSTRIES

- $CaSO_4.1/2H_2O$ is plaster of Paris.
- Plaster of Paris is used in making plaster walls, casts of statuary and coins in holding of fractured bones.
- In cement, plaster is added to prolong the time of setting.
- Hard finish plasters are achieved by the calcinations of anhydrous sulphates with alum or borax.
- Hard finish plasters are used in construction of buildings as wall boards and partitions.
- Gypsum is used in paper industry as filler.

ROLE OF LIME IN AGRICULTURE

- Lime neutralizes the acidic salts.
- Lime-sulphur spray is prepared from lime and has strong fungicidal affect.
- Slaking of lime is exothermic reaction and $Ca(OH)_2$ is formed.
- It increases the solubility of phosphorous in acidic soils.
- Calcium increases the size of root hair and root system.
- Calcium is essential for normal growth of leaf.
- Calcium is important for microorganism, which produces nitrate.
- Deficiency of calcium stimulates the accumulation of Al and Mn which is harmful for plants

ROLE OF LIME IN INDUSTRY

Lime is used in:

- Extraction and refining of metal.
- Paper industry.
- Glass and ceramic industry.
- Preparation of mortar
- Mortar (contains slaked lime (one volume), sand (3 or 4 volume) and water.
- Refining of raw sugar.
- Leather industry
- Preparation of CaC_2
- As dehydrating agent in combination with NaOH forms soda lime.
- Milk of lime is used as a white-wash.

GARDEN OF EQUATIONS

Reactions of Metals with Water

$$2Li + 2H_2O \longrightarrow 2LiOH + H_2$$
$$2K + 2H_2O \longrightarrow 2KOH + H_2$$

Reactions of Metallic Oxides with Water

$$Na_2O + H_2O \longrightarrow 2NaOH$$
$$CaO + H_2O \longrightarrow Ca(OH)_2$$
$$Li_2O + H_2O \longrightarrow 2LiOH$$
$$2Na_2O_2 + 2H_2O \longrightarrow 4NaOH + O_2$$

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Effect of Heat on Hydroxides

$$Ca(OH)_2 \xrightarrow{\Delta} CaO + H_2O$$
$$2LiOH \xrightarrow{\Delta} Li_2O + H_2O$$

Reactions of Metals with Oxygen

$$4Li + O_2 \longrightarrow 2Li_2O$$ Lithium oxide
$$2Na + O_2 \xrightarrow{\Delta} Na_2O_2$$ Sodium peroxide

Effect of Heat on Carbonates

$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$
$$CaCO_3 \longrightarrow CaO + CO_2$$

Formation of Bicarbonates from Carbonates

$$Na_2CO_3 + H_2O + CO_2 \xrightarrow{\Delta} 2NaHCO_3$$
$$CaCO_3 + H_2O + CO_2 \xrightarrow{\Delta} Ca(HCO_3)_2$$

Effect of Heat on Bicarbonates

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$$
$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 + H_2O + CO_2$$

Effect of Heat on Nitrates

$$2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$$
$$4Li\,NO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$$
$$2Ca(NO_3)_2 \xrightarrow{\Delta} 2CaO + O_2 + 4NO_2$$

Role of Lime in Industries

$$CaO + H_2O \longrightarrow Ca(OH)_2$$
$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$
$$Ca(OH)_2 + SiO_2 \longrightarrow CaSiO_3 + H_2O$$
$$CaO + 3C \xrightarrow{2000^\circ C} CaC_2 + CO$$
$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

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PRACTICE EXERCISE

30 Minutes Time Yourself

1. **I – A elements are named as alkali metals because**
   (a) Their oxides are basic
   (b) Their oxide and hydroxides are water soluble
   (c) Both 'a' and 'b'
   (d) They are found in earth
2. **The word Alkali means**
   (a) Base (b) Basic salt
   (c) Ashes (d) Spirit
3. **Formula of Chile saltpetre is**
   (a) $NaNO_3$ (b) $CaCO_3$
   (c) $Ba(NO_3)_2$ (d) NH_4Cl
4. **The elements which are very abundant in earth crust are**
   (a) Si and Aℓ (b) Ca and Mg
   (c) B and Aℓ (d) All of these
5. **The oxides of beryllium BeO is**
   (a) Acidic (b) Basic
   (c) Amphoteric (d) Neutral
6. **Which element is necessary for normal leaf development?**
   (a) Si (b) Ba
   (c) Mg (d) Ca
7. **Li is different from its family members due to**
   (a) Small size (b) High charge density
   (c) Less electropositivity (d) All of these
8. **Carbonates of lithium are not stable like that of sodium due to**
   (a) Low electronegativity (b) Low electropositivity
   (c) Low charge density (d) Not known yet
9. **Nitrates of which pair of elements give different products on thermal decomposition?**
   (a) Na, K (b) Mg, Ca
   (c) Li, Na (d) Li, Ca
10. **Which one of the following is not an alkali metal?**
    (a) Francium (b) Caesium
    (c) Rubidium (d) Radium
11. **Which of the following sulphates is not soluble in water?**
    (a) Sodium sulphate (b) Potassium sulphate
    (c) Zinc sulphate (d) Barium sulphate
12. **The element cesium bears resemblance with**
    (a) Ca (b) Cr
    (c) Both Ca and Cr (d) None of these
13. **The general name of $CaSO_4 . 2H_2O$ is**
    (a) Gypsum (b) Dolomite
    (c) Calcite (d) Plaster of Paris
14. **Down's cell is used to prepare**
    (a) Sodium carbonate (b) Sodium bicarbonate
    (c) Sodium metal (d) Sodium hydroxide
15. **Which element is produced at the cathode during the electrolysis of brine in Nelson's cell?**
    (a) H_2 (b) Na
    (c) $Cℓ_2$ (d) O_2

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6. **Ammonia may be prepared by heating ammonium chloride with**
(a) Water (b) NaCl
(c) Aqueous sodium hydroxide (d) H_2SO_4

7. **Calcium carbide is prepared by heating lime with coke at**
(a) 2500°C (b) 2600°C
(c) 2700°C (d) 2800°C

8. **Crystals of Na_2CO_3. $10H_2O$ when exposed to air**
(a) Lose water and remain solid (b) Gain water and remain solid
(c) Gain water and become liquid (d) Remains unchanged.

9. **Which one of the following substances conducts electricity by the movement of ions?**
(a) Graphite (b) Copper
(c) Molten sodium chloride (d) Mercury

10. **Which one of the following gives white precipitate with aqueous solution of $BaCl_2$?**
(a) $NaHCO_3$ (b) $NaNO_3$
(c) Na_2CO_3 (d) Na_2CrO_4

11. **Which one of the following carbonate is water insoluble?**
(a) Na_2CO_3 (b) K_2CO_3
(c) $(NH_4)_2CO_3$ (d) $CaCO_3$

12. **The deliquescence is a property in which a solid**
(a) Absorbs moisture and remains solid
(b) Absorbs moisture and turns to liquid form
(c) Loses water of crystallization
(d) Increases the number of water of crystallization.

13. **In diaphragm cell, hydrogen is discharged by the reduction of**
(a) Water (b) HCl
(c) Na^+ (d) NaCl

14. **In diaphragm cell, level of brine in anode compartment is kept slightly higher which prevents**
(a) Hydroxide ions to reach anode (b) Chlorine gas to mix
(c) Cathode to decay (d) All of these

15. **Gypsum is applied to the soil as a source of**
(a) Ca and P (b) S and P
(c) Ca and S (d) we could not apply

16. **Alkali and alkaline earth metals impart colours when heated over burner. It is due to**
(a) Smaller electronegativity of alkali metals
(b) Smaller ionic radius of these metals
(c) De-excitation of electrons from higher energy levels to low energy level
(d) Excitation of electrons from low energy levels to higher energy levels.

17. **Which one of the following alkali metals forms only normal oxide when it reacts with O_2?**
(a) Lithium (b) Sodium
(c) Potassium (d) Rubidium

18. **First ionization potential of alkaline earth metal is greater than alkali metals because**
(a) They are more reactive (b) They have greater atomic radii
(c) They have smaller atomic sizes (d) They have greater shielding effect

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29. **Which one of the following pairs shows diagonal relationship in the periodic table?**
(a) Sodium and Lithium
(b) Lithium and magnesium
(c) Lithium and beryllium
(d) Boron and Beryllium

30. **NaOH is named as caustic soda because**
(a) It corrodes the organic tissues
(b) It is used in soda water
(c) It reacts with chlorine gas
(d) It reacts with fats to form soap

31. **Sodium is not observed in +2 oxidation state because of its**
(a) high first ionization potential
(b) Very high second ionization potential
(c) high ionic radius
(d) high electronegativity

32. **Carnalite has chemical formula**
(a) KCl
(b) $KCl.MgCl_2.6H_2O$
(c) $Na_2B_4O_7.10H_2O$
(d) $CaCO_3.MgCO_3$

33. **Magnesium metal does not burn in the vessel containing**
(a) N_2
(b) O_2
(c) N_2 and O_2
(d) Ne

34. **Electrolysis of dilute solution of NaCl produces at the anode**
(a) sodium
(b) hydrogen
(c) chlorine
(d) oxygen

35. **Second ionization potential of alkali metals are very high due to**
(a) being s-block elements
(b) inert gas configurations
(c) ns^1 electronic configuration
(d) being metals

36. **Which ion will have maximum value of heat of hydration?**
(a) Al^{+3}
(b) Cs^+
(c) Ba^+
(d) Mg^{+2}

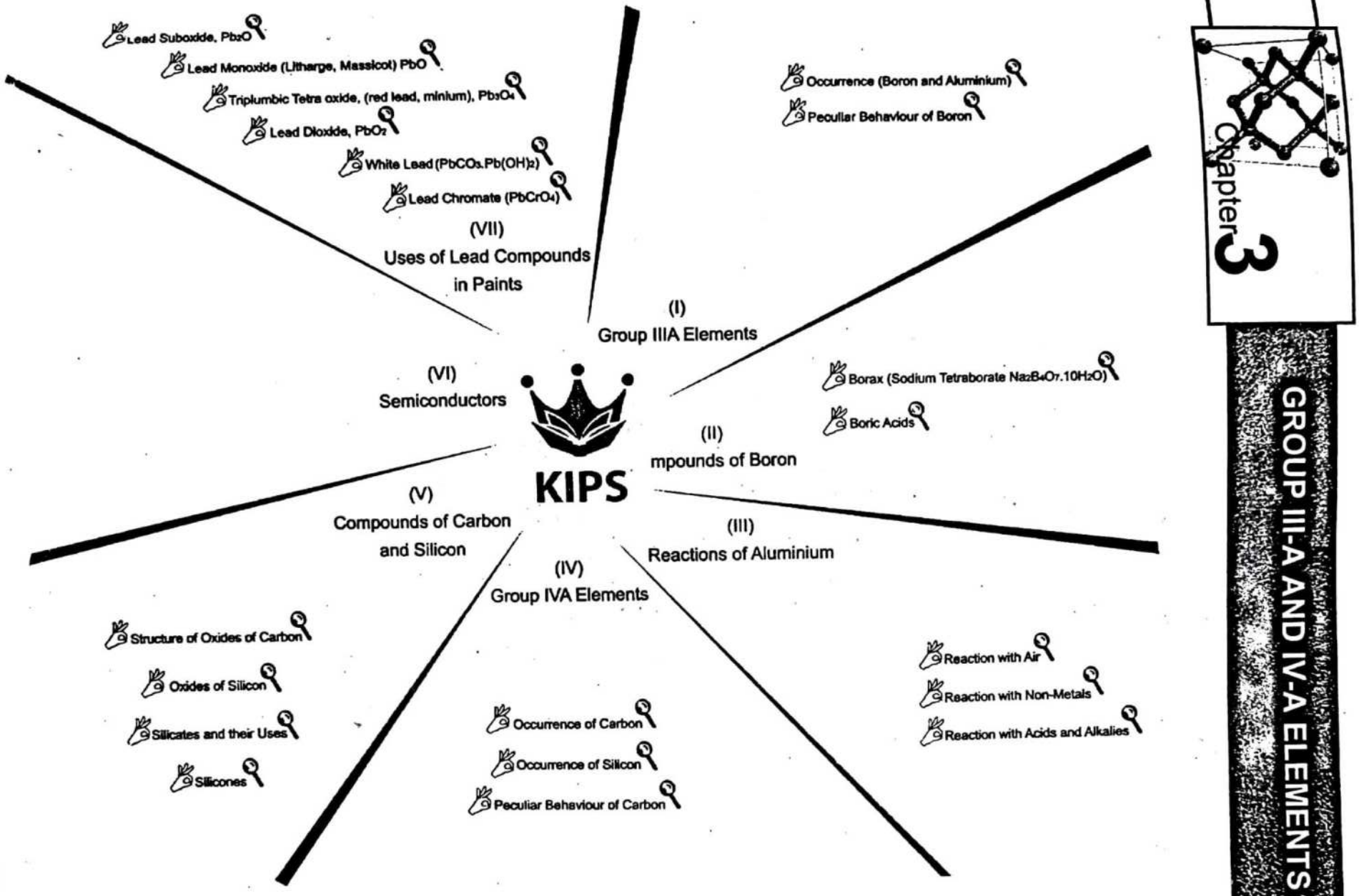
37. **Which one can form complex?**
(a) Na
(b) Cs
(c) Li
(d) K

38. **Which one is natron?**
(a) Na_2CO_3
(b) $Na_2CO_3.10H_2O$
(c) $Na_2CO_3.H_2O$
(d) $NaHCO_3$

39. **Addition of 2% gypsum in cement**
(a) Triggers hydration
(b) Triggers hydrolysis
(c) Prevents rapid hardening
(d) All of these

40. **Which one is least ionic in nature and decompose on heating.**
(a) LiOH
(b) NaOH
(c) KOH
(d) CsOH

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GROUP IIIA ELEMENTS

Group IIIA of the periodic table consists of five elements as boron (B), aluminium (Al), gallium (Ga), indium (In) and thallium (Tl).

GENERAL TREND OF IIIA GROUP

Elements of III-A
• Metallic character increases down the group
• B is non–metal others are metals.
• p-atomic orbital is in the process of completion
• Lesser shielding effect
• Elements show +3 oxidation state.
• Elements give normal oxides
• Gives halides MX_3
• Al is present as Aluminosilicates
• Gallium, Indium and Thallium are rare elements

OCCURRENCE OF BORON

Boron is always found in nature combined with oxygen usually as oxyborate ions and salts of various polyboric acids.

Element	Name of mineral	Chemical formula
Boron	Borax or tincal	$Na_2B_4O_7.10H_2O$
	Colemanite	$Ca_2B_6O_{11}.5H_2O$
	Orthoboric acid	H_3BO_3

PECULIAR BEHAVIOUR OF BORON

Boron	Other elements of III-A
Only non metal with less than four valence electrons.	Metallic
Boron has oxidation state +3,-3	Other elements has +3
Molecular addition compounds are formed	No reaction
Does not form ionic compound	Formation of ionic compound
It forms acidic oxides,	Amphoteric oxides except Tl
It can form acids like HBO_2, H_3BO_3 etc.	Do not form.

COMPOUNDS OF BORON

BORAX($Na_2B_4O_7.10H_2O$)

- Present as natural deposit called **tincal** after drying of lake.
- Lakes are present in Tibet and California.

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PREPARATION OF BORAX

Detail of reaction	Chemical formula	Remarks
From boric acid and soda ash	▪ $4H_3BO_3+Na_2CO_3 \rightarrow Na_2B_4O_7+6H_2O+CO_2$	▪ It is an old method ▪ Hot solution of boric acid is used
From calcium borate	▪ $Ca_2B_6O_{11}+2Na_2CO_3 \rightarrow 2CaCO_3+Na_2B_4O_7+2NaBO_2$ ▪ $NaBO_2+CO_2 \rightarrow Na_2CO_3+Na_2B_4O_7$	▪ It is a modern method ▪ Solution of borax and sodium metaborate leave to crystallize borax ▪ To get more borax, add CO_2 gas
From tincal	–	▪ Tincal is dissolved in water ▪ Evaporation is carried out ▪ Crystal of borax will separate out.

PROPERTIES OF BORAX

- Solubility is 3g/100g water at 10°C
- Solubility is 99.3g/100g water at 100°C
- Above 62°C, pentahydrated octahedral crystals exist
- Below 62°C, decahydrated monoclinic crystals exist
- Borax Bead Test is conducted through heating of borax
- Reaction with acids like HCl and H_2SO_4 gives boric acid
- Reaction with NH_4Cl gives boron nitride
- Solution of borax is alkaline in nature

USES OF BORAX

- Preparation of borate glass (heat resistant).
- Water softening agent.
- Detection of coloured metallic cations (Borax Bead Test).
- Metallurgy
- Welding flux
- Leather industry for tanning & dying.
- Cosmetic, soap, textiles, paints, medicines, match industry and as preservative of food.

BORIC ACIDS

Formulas of four boric acids are as follows:

a) Orthoboric acid, H_3BO_3 or $B_2O_3.3H_2O$
b) Meta boric acid, HBO_2 or $B_2O_3.H_2O$
c) Tetra boric acid, $H_2B_4O_7$ or $2B_2O_3.H_2O$
d) Pyroboric acid, $H_6B_4O_9$ or $2B_2O_3.3H_2O$

ORTHOBORIC ACID

- Orthoboric acid is stable, while others are stable only in solid form.
- Others change into ortho form in aqueous solution.
- Crystal of orthoboric acid is triclinic.
- It is sparingly soluble in cold water (2.6% at 40°C) but more soluble in warm water (37% at 107°C).

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PROPERTIES OF BORIC ACID (H_3BO_3)

Particulars	Reaction Involved	Remarks
Physical appearance	-	Crystalline solid, soft, soapy touch.
Solubility	-	Fairly soluble in water (cold)
Effect of steam	-	Become volatile
Reaction with C_2H_5OH	$H_3BO_3+C_2H_5OH \rightarrow (C_2H_5)_3BO_3+H_2O$	-
Effect of heat	$H_3BO_3 \rightarrow HBO_2$ (metaboric acid) $HBO_2 \rightarrow H_2B_4O_7$ (tetraboric acid) $H_2B_4O_7 \rightarrow B_2O_3$(Boric anhydride)	Loss of water
Acidic behaviour	$H_3BO_3 + H_2O \longrightarrow [B(OH)_4]^- + H^+$	Monobasic Lewis acid
Effect on litmus paper		▪ No effect on methyl orange ▪ Turns blue litmus to red.
Effect of NaOH	$H_3BO_3+NaOH \rightarrow Na_2B_4O_7+H_2O$	▪ Partially neutralized ▪ Borax is produced
Titration with alkali		▪ No titration in normal condition ▪ Titrated in presence of glycerol ▪ Phenolphthalein is an indicator

ALUMINIUM

Occurrence

Element	Name of mineral	Chemical formula
Aluminium	Feldspar	$KAlSi_3O_8$
	Mica (Muscovite)	$KH_2Al_3(SiO_4)_3$
	Kaolin	$Al_2O_3.2SiO_2.2H_2O$
	Corundum	Al_2O_3
	Emerald	$Al_2F_2SiO_4$
	Gibbsite	$Al_2O_3.3H_2O$
	Bauxite	$Al_2O_3.2H_2O$
	Cryolite	Na_3AlF_6
	Diaspore	$Al_2O_3.H_2O$

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REACTION OF ALUMINIUM

Particulars	Chemical reaction	Remarks
Reaction with H_2	$2Al + 3H_2 \rightarrow 2AlH_3$	
Reaction with O_2	$4Al + 3O_2 \rightarrow 2Al_2O_3$	▪ Intense light is produced ▪ Used in flash light photography ▪ When burnt in air, AlN is produced.
Reaction with N_2	$2Al + N_2 \rightarrow 2AlN$	This reaction is used in removing of air bubbles in molten metals ▪ Salt solution corrode aluminium and aluminium alloys badly, so are not suitable for marine use.
Reaction with X_2	$2Al + 3X_2 \rightarrow 2AlX_3$	Exothermic
Action of acids	▪ $2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$ ▪ $2Al + 6H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3SO_2 + 6H_2O$ ▪ $Al + HNO_3 \rightarrow$ No reaction	▪ H_2 is evolved with reaction of dil. acid ▪ On reaction with conc. H_2SO_4, SO_2 is evolved
Action of alkali	▪ $2Al + 2NaOH + 6H_2O \rightarrow 2NaAl(OH)_4 + 3H_2$	Al is dissolved in alkali forms soluble sodium aluminate and liberates H_2

USES

1- Aluminium is very light and is used in the construction of air craft's, ships and cars.
2- Due to its conductivity, it is used in a manufacture of heavy duty electrical cables.
3- Due to its reflection power it is commonly used to insulate buildings.
4- It is non magnetic and is thus used in navigational equipment.
5- It is non-toxic and can be used for making food and brewing equipments and in packaging.
6- Aluminium readily forms alloys with other metals like copper, magnesium, nickel and zinc.
7- At homes, aluminium is found in the form of cooking utensils, window frames and kitchen foil.
8- Aluminium is used for making petrol and milk storage tanks because it reflects heat and prevents them of being over heated in the sun.
9- Aluminium is excellent reflector of radiation and energy.
10- It is good reducing agent.

VA GROUP

Group IVA of the periodic table consist of five elements including carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb).

ommon Properties of Group IVA Elements

1- All the elements of this group show a valency of four except tin and lead which either show four or two valency. Two due to inert pair effect.
2- All of them form hydrides, MH_4.
3- They form tetrachlorides, MCl_4.
4- They also form the dioxides, MO_2.

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CARBON

Occurrence of Carbon

Carbon can be found in free and combined state.

Element	Name of Ore	Chemical formula
Carbon	Limestone	$CaCO_3$
	Dolomite	$MgCO_3.CaCO_3$
	Magnesite	$MgCO_3$

Uniqueness Of Carbon

1- Carbon and silicon are non-metals while the other members of the family are metalloids (Ge,Sn) or metals (Pb).
2- Carbon shows the property of catenation or self linkage markedly.
3- Tetravalent, can combine with four same or different elements.
4- Can form multiple bonds.
5- Carbon also forms homocyclic and heterocyclic compounds.

Oxides of Carbon

There are three oxides of carbon

a. CO
b. CO_2
c. C_3O_2 (carbon suboxide)

STRUCTURE OF CO AND CO_2

CO_2	CO
Molecule is linear	Molecule is almost linear
Dipole moment is zero	Dipole moment is 0.112D.
All electrons of C-atom take part in bond formation	Two valence electrons are inert in C and two form covalent bonds.
σ and π bonds are present	σ and π bonds are present
Co-ordinate covalent bond is absent	Co-ordinate covalent bond is present
Used in soft drinks and fire extinguishers.	Toxic and form carboxy haemoglobin complex in blood.

SILICON

It occurs only in combined state.

Element	Name of material	Chemical formula
Silicon	Analcite (a zeolite)	$NaAl(SiO_3)_2.H_2O$
	Asbestos	$CaMg_3(SiO_3)_4$
	Kaolin (pottery clay)	$H_2Al_2(SiO_4)_2.H_2O$
	Zircon	$ZrSiO_4$
	Talc (soap stone)	$H_2Mg_3(SiO_3)_4$

COMPOUNDS OF SILICON

- Silica
- Silicates
- Silicones

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SILICON DIOXIDE (SiO_2)

- Every Si atom is tetrahedrally attached with four O atoms.
- Each oxygen atom is attached to two silicones.
- Ratio of atoms Si and O is 1:2

QUARTZ

- Quartz, the common crystalline form of silicon oxide, is a hard, brittle, refractor, colourless solid which differs very markedly from carbon dioxide.
- Quartz is found in the following forms: Rock crystal, amethyst quartz, smoky quartz, rose quartz, milky quartz. Opal is hydrated variety of quartz. Sand is largely silicon dioxide (silica).

VITREOUS SILICA/ SILICA GLASS (Incorrectly called fused quartz)

- On heating at high temperature, it gives viscous liquid
- On cooling, it becomes rigid without going into a regular crystal pattern.

INTERESTING AND USEFUL PROPERTIES OF VITREOUS SILICA

- High transparency to light
- Can withstand very high temperature i.e. 1500°C-1600°C
- Very low thermal expansion
- Excellent insulator
- Hard brittle and elastic
- Insoluble in water and inert with other reagents
- Inert towards acids except HF.

COMPARISON OF CO_2 AND SiO_2

CO_2	SiO_2
Double covalent bonds are present	Single covalent bonds are present
C atom is smaller	Si atom is larger
Molecule is linear	Tetrahedral geometry is present
Structure is one dimensional	Structure is three dimensional

SILICATES

The compounds derived from silicic acid are termed as silicates.

SODIUM SILICATE (Na_2SiO_3)

- It is a sodium salt of metasilicic acid (H_2SiO_3)
- It is also called water glass or soluble glass
- Prepared by Na_2CO_3 and pure sand.
- Soluble in water and its solution is alkaline
- When soluble colored salts like $NiCl_2$, $FeSO_4$ and $CuSO_4$ are dissolved in solution of water glass, they give beautiful growth called chemical garden.

ALUMINIUM SILICATES or CLAY

- Aluminium is present in important silicate rocks
- Weathering effect, effect of CO_2 and effect of H_2O (freezing and melting) disintegrate the silicate rocks into clay.
- Pure clay "$Al_2O_3.(SiO_2)_2\ 2H_2O$" also called kaolin used in preparation of porcelains and china wares.
- Ordinary clay contains Fe and it is of yellow or reddish yellow.
- Ordinary clay is used to prepare bricks, tiles and stone wares.

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S.No	Name and Formula of Silicates	Preparation	Properties	Uses
1	Sodium Silicate Na_2SiO_3	$Na_2CO_3+SiO_2 \rightarrow Na_2SiO_3+CO_2$ $2NaOH+H_2SiO_3 \rightarrow Na_2SiO_3+2H_2O$	Aqueous Solution is strongly alkaline Soluble in water	Soap – Filler Textile – Fireproof Furniture – Polish Calico – Printing Chemical Garden
2	Aluminum Silicate $Al_2O_3(SiO_2)_2.2H_2O$	$K_2O.Al_2O_3.6SiO_2+H_2CO_3+H_2O \rightarrow K_2CO_3+4SiO_2+Al_2O_3(SiO_2)_2.2H_2O$ Kaolin	Clay: Impure (Fe_2O_3,CaO, MgO) → Tiles, Bricks, Stone ware, Pottery → $NaAlO_2$, Na-Al-Silicate Pure → Porcelain Chinaware → Kaolin, Bone ash, Feldspar	
3	Talc/Soap Stone $H_2Mg_3(SiO_3)_4$		Greasy Touch	Cosmetics House hold Articles
4	Asbestos $CaMg_3(SiO_3)_4$		Hydrated Mg Silicate	Incombustible Fabrics Hard Board

SILICONES:

The compound in which Si is surrounded by two O atoms and two alkyl groups is called silicone

- Chemistry of silicon is similar to carbon
- Forms SiO_2, $SiCl_4$ and Silane (SiH_4) like C form CO_2, CCl_4 and methane CH_4.
- Silicones are very inert to oxygen at high temperature.
- Its viscosity is not affected by the change in temperature.
- Silicones are used:
  - In preparation of lubricants
  - In hydraulic brakes or hydraulic system
  - Methyl silicones of high molecular mass resemble rubber and are used in making rubber like tubing and sheets.
  - Cross linked silicones can be made
  - These have resinous properties so used in electrical insulation.
  - Silicone films can prevent water leakage and act as water repellent like a grease film.

SEMICONDUCTORS

A substance whose resistance to electric current is different under different condition is called semiconductor

- Compounds/elements acts as semiconductor are Germanium, Selenium, Silicones, Lead sulphide, Silicon carbide, Calcium sulphide, Lead telluride, Gallium arsenide, Indium antimonide.
- Electrical conductance depends upon temperature of semiconductor.
- On heating resistance of semiconductor decrease while that of metal increases.
- In light conductance of semi conductor increases
- Semi conductors are used in transistors, photoelectric cell and solar batteries.
- The junction between the different materials forms a boundary. It allows electricity to pass more properly and is used in transistors.

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USE OF LEAD COMPOUNDS

Lead Compound	Remarks	Uses
Lead suboxide (Pb_2O)	▪ It is a black powder	▪ as pigment ▪ in lead storage batteries as filler
Lead monoxide (PbO)	▪ Two crystalline forms are available: **1.** rhombic(yellow in colour) **2.** tetragonal(red in colour) ▪ it is slightly soluble in water	▪ in preparing flint glass and paints
Triplumbic tetra-oxide (Pb_3O_4)	▪ It is produced after the action of O_2 and Pb	▪ in preparation of storage batteries ▪ in anticorrosion paint.
Lead oxide (PbO_2)	▪ It is produced after the reaction of HNO_3 and red lead ▪ It is reddish brown powder ▪ It is soluble in alkaline water ▪ Unaffected by dilute acids.	▪ forms plumbates
White lead $2PbCO_3.Pb(OH)_2$	▪ It is amorphous white pigment. ▪ Prepared by Dutch process.	▪ has good covering power when mixed with linseed oil ▪ toxic and tarnished to grey by environment.

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PRACTICE EXERCISE

20 mins Time Yourself

1. **Boron is non-metal whereas Al is metal, it is due to**
   (a) Small size
   (b) High nuclear charge
   (c) Both a and b
   (d) No authorized justification yet
2. **Boron in soil has been considered micronutrient for**
   (a) Soil porocity
   (b) Proper growth of plants
   (c) Alkalinity of soil
   (d) All
3. **One of the outstanding feature of boron is its ability to form**
   (a) Molecular addition compounds
   (b) Molecular crystals
   (c) Semiconductors
   (d) Ionic compounds
4. **Substance which is found in dried up lakes of Tibet and California is**
   (a) Tincal
   (b) Boric acid
   (c) Calcium carbonate
   (d) Colemanite
5. **Borax is a white crystalline solid and it is**
   (a) More soluble in cold water
   (b) More soluble in hot water
   (c) Insoluble in water
   (d) Soluble only in organic solvents
6. **Which of the following does not give Borax bead test?**
   (a) Cu
   (b) Cr
   (c) Ni
   (d) Al
7. **Special features of borate glass is that it is**
   (a) Heat resistant
   (b) Low melting
   (c) Used to prepare chemical garden
   (d) Green in colour
8. **The metal which is used in thermite process because of its activity, is**
   (a) Iron
   (b) Copper
   (c) Aluminium
   (d) Zinc
9. **Aluminium oxide is**
   (a) Acidic oxide
   (b) Basic oxide
   (c) Amphoteric oxide
   (d) It does not exists
10. **Which of the following shows inert pair effect?**
    (a) Boron
    (b) Carbon
    (c) Silicon
    (d) Tin
11. **Which electronic configuration corresponds to an element of group IIIA?**
    (a) $1s^2, 2s^2, 2p^3$
    (b) $1s^2, 2s^2, 2p^6, 3s^2, 3p^1$
    (c) $1s^2, 2s^2, 2p^4$
    (d) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^1$
12. **Tincal is a mineral of**
    (a) Al
    (b) Si
    (c) B
    (d) C
13. **In network of silica (SiO_2), each silicon atom is surrounded by _____ atoms of oxygen**
    (a) 4
    (b) 2
    (c) 1
    (d) 6

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14. **Which one of the following is not a semiconductor?**
(a) Si (b) Ge
(c) Se (d) Sn

15. **Orthoboric acid is 2.6% soluble in water at 40°C and _____ at 107°C.**
(a) 26% (b) 27%
(c) 37% (d) < 2.6%

16. **The process of aluminium extraction is called**
(a) Hall process (b) Thermite process
(c) Haber process (d) Contact process

17. **Because of its ability to combine with both oxygen and nitrogen, aluminium metal is used**
(a) As nitrometer
(b) To remove air bubbles from molten metal
(c) To produce alloy
(d) As insulator

18. **Aqueous solution of borax above 62°C gives crystals of**
(a) $Na_2B_4O_7.4H_2O$ (b) $Na_2B_4O_7.5H_2O$
(c) $Na_2B_4O_7.2H_2O$ (d) $Na_2B_4O_7.10H_2O$

19. **Silicones differ from silica by a group of**
(a) CH_3- (b) -OH
(c) H_3CO- (d) O_2

20. **Which of the following is not a use of silicones?**
(a) Lubricants (b) Hydraulic brakes
(c) Antifreeze (d) Water repellent

21. **Boron is non metal while other elements of IIIA group are metals. This is because**
(a) It has small size
(b) It has high nuclear charge
(c) It forms molecular addition compounds
(d) All of the above

22. **CO_2 is gas while SiO_2 is solid at room temperature.**
(a) Carbon is non-metal while silicon is semi-metal
(b) CO_2 is an independent molecule while SiO_2 has network covalent structure
(c) Carbon forms multiple bond while silicon does not form multiple bonds
(d) Silicon has all sigma bonds.

23. **The coloured glassy mass in borax bead test is due to the formation of**
(a) Metal borate (b) Metal meta borate
(c) Metal boride (d) Metal silicate

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24. Identify the correct statement regarding CO

(a) It combines with H_2O to form carbonic acid

(b) It reacts with red blood cells of haemoglobin

(c) It is powerful oxidizing agent

(d) It is used to prepare aerated drinks.

25. The chief ore of Aℓ is:

(a) Na_3AlF_6 (b) $Al_2O_3 \cdot 2H_2O$

(c) $Al_2O_3 \cdot H_2O$ (d) $Al_2O_3 \cdot 3H_2O$

26. If temperature of gallium arsenide is increased then its conductivity will

(a) Decrease (b) Increase

(c) Remains constant (d) First decreases then increases

27. Boric acid cannot be used

(a) As antiseptic in medicine (b) For washing eyes

(c) In soda bottles (d) For senamel and glazes.

28. Which of the following will decompose to produce litharge

(a) $PbCrO_4$ (b) Pb_2O

(c) PbO_2 (d) All of the above

29. Which element can form tripositive ion?

(a) Beryllium (b) Carbon

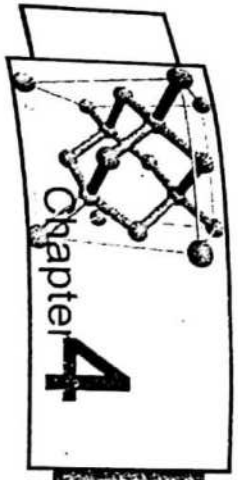
(c) Silicon (d) Aluminium

30. Which of the following is metasilicic acid?

(a) H_2SnO_3 (b) H_2SiO_3

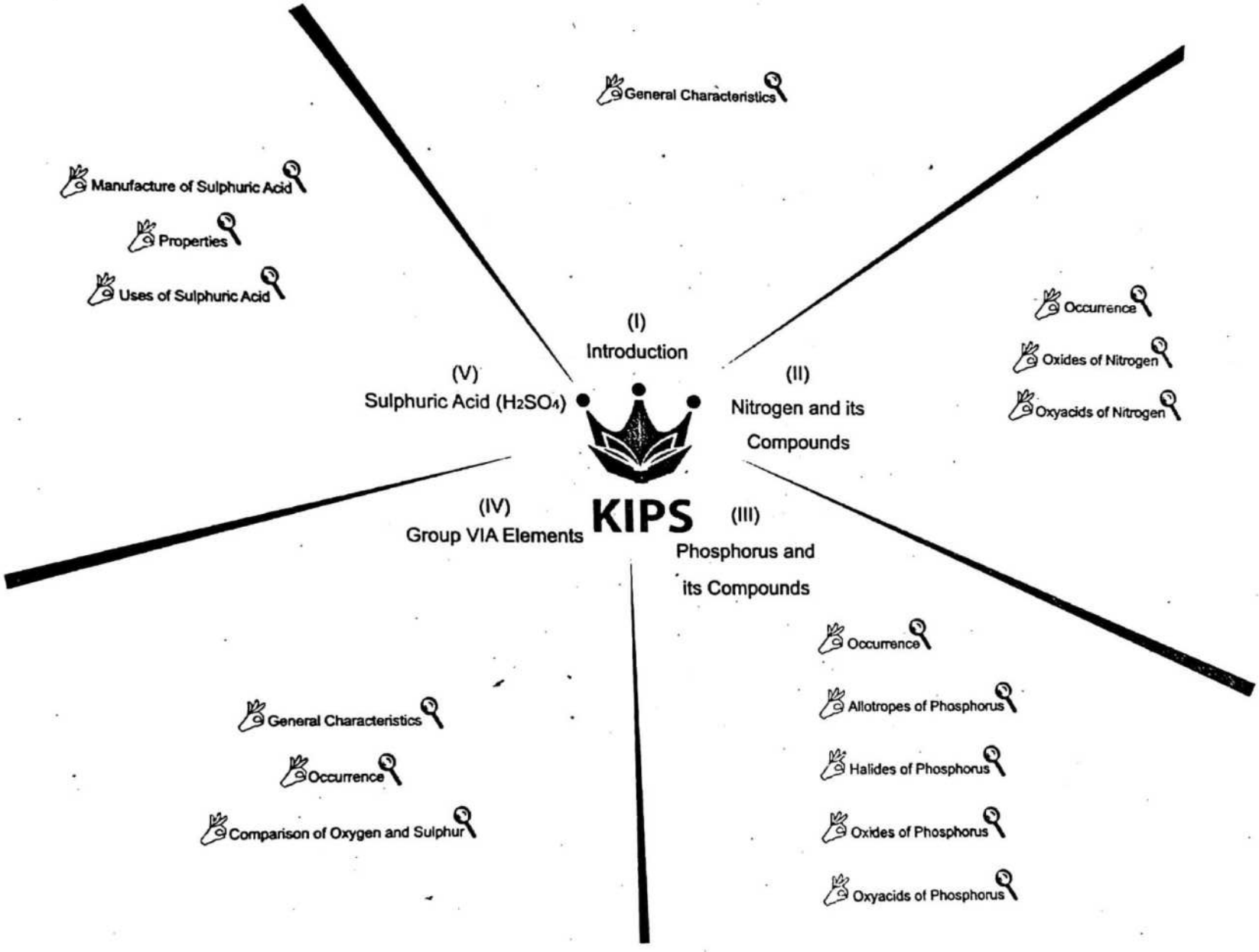
(c) H_3AsO_4 (d) H_3SbO_4

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Chapter 4

GROUP V-A AND VI-A ELEMENTS



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INTRODUCTION

Elements of VA	Elements of VIA
N and P are non-metals, As and Sb are metalloids while Bi is metal.	All elements are non-metals except Po.
Some elements show allotropy.	All elements show allotropy.
Catenation is absent.	Catenation is present.
Metallic character increases down the group.	Non-metallic character is pronounced
d–orbital is involved in bond formation except in nitrogen	d-orbital is involved in bond formation except in oxygen
Usually show +3 and +5 oxidation states.	Usually show –2, +2, +4, +6 oxidation states except oxygen.

NITROGEN AND ITS COMPOUNDS

- It is present in free state in air, 78% by volume.
- Inorganic compounds of nitrogen are not commonly found as minerals.
- In combined state, it is present in the form of proteins, urea and amino acids.

OXIDES OF NITROGEN

Particular	Nitrous Oxide (N_2O)	Nitric Oxide (NO)	Nitrogen Oxide (NO_2)
Preparation	$Zn+HNO_3 \rightarrow Zn(NO_3)_2+N_2O+H_2O$ $NH_4NO_2 \rightarrow N_2O+H_2O$	$Cu+dilHNO_3 \rightarrow Cu(NO_3)_2+NO+H_2O$ $N_2+O_2 \rightarrow 2NO$	$Pb(NO_3)_2 \rightarrow PbO+NO_2+O_2$ $Cu+HNO_3 \rightarrow Cu(NO_3)_2+NO_2+H_2O$
Colour	Colourless gas.	Colourless gas.	Reddish brown gas.
Smell and Taste	Pleasant smell and taste.	-----	Pungent smell.
Solubility	Fairly soluble in water.	Sparingly soluble.	Soluble and formed blue colour acidic solution.
Action of O_2	-----	Form reddish brown NO_2	------
Combustion	Supports combustion	Supports combustion	Supports combustion
As Reducing Agent	It converts into NO	With oxidizing agents like $KMnO_4$, HNO_3 gives HNO_3 and NO_2 respectively.	--------
As Oxidizing Agent	On reaction with red-hot Cu, it gives N_2.	With reducing agents like H_2S, H_2SO_4 etc, it gives N_2O.	As strong oxidizing agent, it oxidizes H_2S to sulphur, $FeSO_4$ to $Fe_2(SO_4)_3$ and KI to I_2.
Reaction With Water	No reaction	No reaction	In absence of air, it forms HNO_3 and HNO_2 with water.
Reaction With Alkali	No reaction	No reaction	On reaction with alkalies, it gives nitrates and nitrites

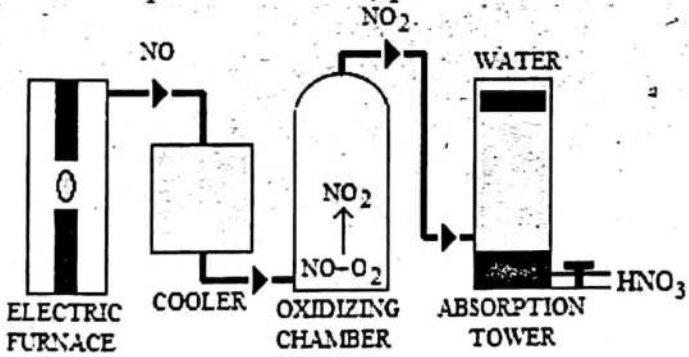
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ACIDS OF NITROGEN

Particulars	Nitrous acid (HNO_2)	Nitric acid(HNO_3)
Preparation	$N_2O_3+H_2O \rightarrow HNO_2$ $Ba(NO_2)_2+H_2SO_4 \rightarrow BaSO_4+HNO_2$	$KNO_3+H_2SO_4 \rightarrow KHSO_4+HNO_3$
Effect of heat	Decompose into HNO_3, NO and H_2O	Decompose into NO_2, O_2 and H_2O
As an oxidizing agent	Oxidizes HI to I_2, SO_2 to H_2SO_4 and $SnCl_2$ to $SnCl_4$	Oxidizes non-metals to their oxides and metalloids to corresponding acids. Oxidizes $FeSO_4$ to $Fe_2(SO_4)_3$, H_2S to S, HI to I_2
As reducing agent	Decolourizes $KMnO_4$ and changes into HNO_3	--------
Reaction with alkali	Gives salt and water	Gives salt and water
Action on organic compounds	Produces N_2 with urea or aniline.	H-atoms in hydrocarbon are replaced by $-NO_2$ group
Aqua Regia		One volume of Conc. HNO_3 and 3 volume of Conc. HCl give Aqua Regia that can dissolve noble metals

Brikland and Eyde's procedure

- Another method for preparation of nitric acid is Birkland and Eyde's process.
- Oxidation of N_2 with atmospheric O_2 gives NO which on oxidation forms NO_2 and this reacts with water in the presence of air, produces nitric acid.



Reactivity of Nitric Acid With Metals

- Au, Pt and Ti do not react.
- Fe, Co, Ni, Cr and Al are rendered passive by acid due to their oxide coating.
- W and U are changed into their oxides.
- Mg, Ca and Mn gives H_2.
- Ag, Cu and Pb give NO and NO_2 with dilute and conc. acid.
- Hg give $Hg_2(NO_3)_2$ and $Hg(NO_3)_2$ with dilute and conc. acid.
- Zn gives products depending upon HNO_3 concentration and temperature.
  - Very dilute HNO_3 gives NH_4NO_3.
  - Moderate dilute HNO_3 gives N_2O.
  - Concentrated HNO_3 gives NO_2.

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PHOSPHORUS AND ITS COMPOUNDS

OCCURRENCE OF PHOSPHORUS

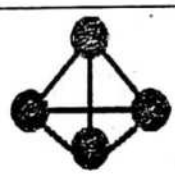
- Phosphorus is found in combined state in the form of minerals.
- It is present in seed, yolk of eggs, nerves, brain and bone marrows.
- Bone ash [80% $Ca_3(PO_4)_2$] is source of P.

ALLOTROPES OF PHOSPHORUS

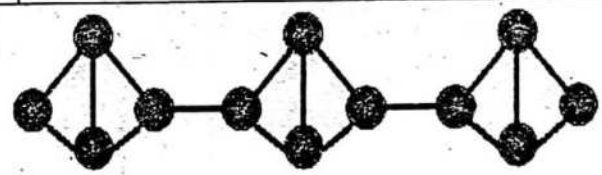
Different crystalline forms of any substance are said to be allotropes. There are six allotropes of phosphorous;

1. Yellow/ White Phosphorous
2. Red Phosphorous
3. Scarlet Phosphorous
4. α-Black Phosphorous
5. β-Black Phosphorous
6. Violet Phosphorous

White Phosphorus	Red Phosphorus	Black Phosphorus
Very reactive, poisonous, volatile, waxy and yellowish.	Less reactive and poisonous.	-
Soluble in C_6H_6 and CS_2	-	-
Exist in tetra atomic form	Tetra atomic form	-
Change into P_2 at 700°C	-	-
-	Prepared by heating white phosphorous in presence of S and I_2 at 250°C	Prepared by heating red phosphate at high temperature and pressure
Tetrahedral in shape	Tetra-atomic macromolecule	Hexagonal



WHITE PHOSPHOROUS



RED PHOSPHOROUS

HALIDES OF PHOSPHORUS

Particulars	PCl_3	PCl_5
Colour	Colourless liquid	Yellowish crystal
Boiling point	76°C	Sublims at 100°C
Freezing point	-112°C	-
Effect of heat	-	Changes into Cl_2 and PCl_3
Action of O_2	Phosphorus oxychloride is produced	-
Action of water	Forms phosphorous acid	Forms orthophosphoric acid
Action of alcohol	Forms alkyl chloride and phosphorous acid	Forms alkyl chloride and phosphorus oxychlorides

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OXIDES OF PHOSPHOROUS

Particulars	Phosphorous trioxide	Phosphorus pentaoxide
Smell and state	White waxy solid and garlic smell	White powder and garlic like smell
Melting point	22.8°C	Sublimes at 360°C
Boiling point	173°C	-
Action of Oxygen	Changes into P_2O_5	-
Action of water	• With cold water, gives phosphorus acid • With hot water, gives phosphoric acid and phosphene gas	Forms meta phosphoric acid

ACIDS OF PHOSPHORUS

Particulars	Phosphorus acid(H_3PO_3)	Phosphoric acid (H_3PO_4)
Colour and state	White crystalline solid	Colourless deliquescent crystalline solid
Melting point	73.6 °C	41°C
Effect of heat	Changes into phosphine and phosphoric acid	Changes into pyro and metaphosphoric acid $2H_3PO_4 \rightarrow H_4P_2O_7 \rightarrow 2HPO_3$
Action with O_2	Gives phosphoric acid	-
Action with alkali	Forms salts	Forms salts
As reducing agent	Reduces $CuSO_4$ to Cu and $AgNO_3$ to Ag	-

OCCURRENCE OF GROUP VI-A ELEMENT

- O_2 comprises 50% of earth crust.
- Oxygen is found in air in free state
- Water contains 89% oxygen.
- $CaCO_3$ contains 48% oxygen.
- Silica contains 53% oxygen.
- Sulphur is present in metallic ores.
- Sulphur is also present in onions, garlic, mustard, hair, oil, egg & proteins.

MINERALS OF GROUP VIA ELEMENTS

Name	Formula
Galena	PbS
Zinc blend	ZnS
Cinnabar	HgS
Stibnite	Sb_2S_3
Copper pyrite	Cu_2S
Iron pyrite, (Fool's Gold)	FeS_2
Gypsum	$CaSO_4.2H_2O$
Heavy spar	$BaSO_4$

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COMPARISON OF OXYGEN AND SULPHUR

SIMILARITIES BETWEEN OXYGEN AND SULPHUR
➢ Both have same Outer shell Electronic configuration i.e. ns^2np^4
➢ Both are usually divalent
➢ Both show allotropy
➢ Both have polyatomic molecules.
➢ Both combine with metals with oxidation state -2.
➢ Both combine with non-metals and form covalent compounds.
➢ Both are found in both free and combined states.
➢ Both are typical non-metals.

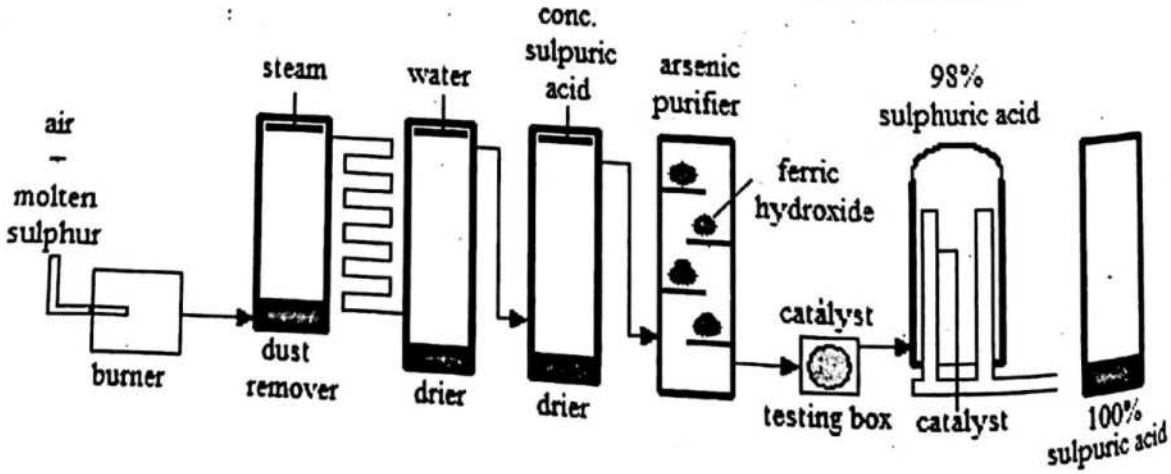
DIFFERENCES	
Oxygen	**Sulphur**
Two allotropic forms O_2 and O_3	Three allotropic forms rhombic, monoclinic and plastic.
Gas at ordinary temperature.	Solid at ordinary temperature.
Sparingly soluble in water	Insoluble in water
Helps in combustion.	It is itself combustible.
Does not react with water.	Boiling sulphur reacts with steam producing a little hydrogen sulphide and sulphur dioxide.
Does not react with acids.	Readily oxidized by conc. Sulphuric acid & nitric acid.
Does not react with alkalies.	Reacts with alkali solution & forms sulphides and thiosulphate.
It shows -2,-1,-1/2,+2oxidation states.	It shows -2, +2, +4 and +6 oxidation states
It is paramagnetic.	It is diamagnetic.

SULPHURIC ACID (H_2SO_4)

- Discovered by **Jabar-Ibn-Hayan**
- It was called **oil of vitriol.**

Contact Process

- SO_2 is produced by burning of S or FeS_2 and again oxidized to SO_3 in the presence of air and V_2O_5 at 400-500°C in contact chamber.
- SO_3 absorbed by H_2SO_4 and converts into Oleum $H_2S_2O_7$.
- Water is added to $H_2S_2O_7$ and forms H_2SO_4 of desired concentration.



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Properties of H_2SO_4

- Colourless oil liquid
- Specific gravity is 1.834 at 18°C
- Freezing point 10.5°C
- Boiling point 338°C
- Soluble in water, exothermic reaction
- Pure is non-conductor, but addition of a little water makes it good conductor.
- Corrosive to skin and causes very serious burn to all tissues.

Chemical Properties

- On heating changes into SO_3 and H_2O
- Strong acid so completely ionizes in water
- Reacts with alkali to give salt and water
- Reacts with carbonates and bicarbonates to give salt
- Reacts with NH_3 to give ammonium sulphate
- Reacts with benzene to give benzene sulphonic acid
- Reacts with metal in following manner:
  a. cold and dilute acid give salt and H_2
  b. cold and concentrated acid do not react with Cu, Ag, Au, Hg, Pt.
  c. hot and concentrated acid liberate SO_2 and metallic sulphate
- Good dehydrating agent, removes water from organic compounds and liberate CO, CO_2, and black C.
- As an oxidizing agent oxidizes C and S to their oxides, H_2S to S, HBr, HI to Br_2 and I_2 respectively.
- Reacts with $BaCl_2$ and $Pb(NO_3)_2$ to give precipitation of $BaSO_4$ and $PbSO_4$
- Reacts with $KMnO_4$ and $K_2Cr_2O_7$ and liberate O_2

GARDEN OF EQUATIONS

NITROUS OXIDE

Preparation

$$4Zn + 10HNO_3 \xrightarrow[\text{dilute}]{} 4Zn(NO_3)_2 + N_2O + 5H_2O$$

$$NH_4NO_3 \xrightarrow{200°C} N_2O + 2H_2O$$

Chemical Reactions of Nitrous Oxide

$$2N_2O + S \longrightarrow SO_2 + 2N_2$$

$$10N_2O + P_4 \longrightarrow P_4O_{10} + 10N_2$$

$$N_2O + Cu \longrightarrow CuO + N_2$$

NITRIC OXIDE

Preparation

$$3Cu + 8HNO_3 \xrightarrow[\text{dilute}]{} 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$N_2 + O_2 \rightleftharpoons 2NO$$

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Chemical Reactions of Nitric Oxide

$$NO + O_2 \longrightarrow 2NO_2$$
$$2NO \longrightarrow N_2 + O_2$$
$$2NO + Cl_2 \longrightarrow 2NOCl$$
$$FeSO_4 + NO \longrightarrow FeSO_4 . NO \text{ (Black ring of nitrosyl ferrous sulphate)}$$
$$H_2S + 2NO \longrightarrow H_2O + N_2O + S$$
$$H_2SO_3 + 2NO \longrightarrow H_2SO_4 + N_2O$$
$$2HNO_3 + NO \longrightarrow H_2O + 3NO_2$$
$$4H_2O + NO + 3I_2 \longrightarrow 6HI + 2HNO_3$$
$$6KMnO_4 + 12H_2SO_4 + 10NO \longrightarrow 6KHSO_4 + 4H_2O + 10HNO_3 + 6MnSO_4$$

NITROGEN DIOXIDE

Preparation

$$Cu + 4HNO_3 \text{ (conc.)} \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$
$$2Pb(NO_3)_2 \longrightarrow 2PbO + 2NO_2 + O_2$$

EFFECT OF HEAT

$$N_2O_4 \underset{}{\overset{140°C}{\rightleftharpoons}} 2NO_2 \overset{620°C}{\rightleftharpoons} NO + O_2$$
$$2NO_2 \longrightarrow 2NO + O_2$$

CHEMICAL REACTION S OF NITROGEN DIOXIDE

$$5NO_2 + 2P \longrightarrow P_2O_5 + 5NO$$
$$H_2O + 2NO_2 \longrightarrow HNO_3 + HNO_2$$
$$H_2S + NO_2 \longrightarrow H_2O + NO + S$$
$$2KOH + 2NO_2 \longrightarrow H_2O + KNO_2 + KNO_3$$
$$2NO_2 + 2KI \longrightarrow I_2 + 2KNO_2$$
$$2FeSO_4 + H_2SO_4 + NO_2 \longrightarrow Fe_2(SO_4)_3 + H_2O + NO$$
$$2NaOH + 2NO_2 \longrightarrow H_2O + NaNO_2 + NaNO_3$$

NITRIC ACID

Preparation

Birkland and Eyde's process

$$N_2 + O_2 \xrightarrow{3000°C} 2NO$$
$$2NO + O_2 \xrightarrow{600\text{-}1000C} 2NO_2$$
$$H_2O + 2NO_2 \longrightarrow HNO_3 + HNO_2$$
$$3HNO_2 \longrightarrow H_2O + NO + HNO_3$$

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Chemical Reactions Of Nitric Acid

REACTION WITH BASE

$$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$$

REACTIONS WITH SALTS

$$Na_2CO_3 + 2HNO_3 \longrightarrow 2NaNO_3 + H_2O + CO_2\uparrow$$

$$NaHCO_3 + HNO_3 \longrightarrow NaNO_3 + H_2O + CO_2\uparrow$$

REACTIONS WITH METALS

$$3Cu + \underset{\text{dilute}}{8HNO_3} \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$Cu + \underset{\text{conc}}{4HNO_3} \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

$$4Zn + \underset{\text{Very dilute}}{10\ HNO_3} \longrightarrow 4Zn\ (NO_3)_2 + NH_4NO_3 + 3H_2O$$

$$4Zn + \underset{\text{dilute}}{10HNO_3} \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

$$Zn + \underset{\text{conc}}{4HNO_3} \longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$$

$$3Pb + \underset{\text{dilute}}{8HNO_3} \longrightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$$

$$Pb + \underset{\text{conc}}{4HNO_3} \longrightarrow Pb(NO_3)_2 + 2NO_2 + 2H_2O$$

$$Mg + 2HNO_3 \xrightarrow{\text{dilute}} Mg(NO_3)_2 + H_2$$

$$Mn + 4HNO_3 \xrightarrow{\text{dilute}} Mn(NO_3)_2 + H_2$$

$$Hg + \underset{\text{(excess)}}{4HNO_3} \longrightarrow Hg(NO_3)_2 + 2NO_2 + 2H_2O$$

$$6Hg + \underset{\text{(excess)}}{8HNO_3} \xrightarrow{\text{dilute}} 3Hg_2(NO_3)_2 + 2NO + 4H_2O$$

$$4Sn + 10HNO_3 \xrightarrow{\text{dilute}} 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

$$Sn + 4HNO_3 \longrightarrow \underset{\text{Meta stannic acid}}{H_2SnO_3} + 4NO_2 + H_2O$$

$$Sb + 5HNO_3 \longrightarrow H_3SbO_4 + 5NO_2 + H_2O$$

REACTIONS WITH NON-METALS

$$S + 6HNO_3 \xrightarrow{\text{dilute}} H_2SO_4 + 6NO_2 + 2H_2O$$

$$As + 5HNO_3 \xrightarrow{\text{conc}} H_3AsO_4 + 5NO_2 + H_2O$$

$$As + 3HNO_3 \xrightarrow{\text{dilute}} H_3AsO_3 + 3NO_2$$

$$P + 5HNO_3 \xrightarrow{\text{Hot / conc}} H_3PO_4 + H_2O + 5NO_2$$

$$I_2 + 10HNO_3 \xrightarrow{\text{Hot / conc.}} 2HIO_3 + 10NO_2 + 4H_2O$$

$$C + 4HNO_3 \xrightarrow[\text{hot}]{\text{Conc.}} CO_2 + 4NO_2 + 2H_2O$$

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REACTIONS AS AN OXIDIZING AGENT

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

$$3H_2S + 2\underset{\text{Conc.}}{HNO_3} \longrightarrow 3S + 2NO + 4H_2O$$

$$6HI + 2HNO_3 \longrightarrow 4H_2O + 2NO + 3I_2$$

$$SnCl_2 + 2HCl + 2HNO_3 \longrightarrow SnCl_4 + 2NO_2 + 2H_2O$$

AQUA REGIA

$$HNO_3 + 3HCl \longrightarrow NOCl + Cl_2 + 2H_2O$$

$$2NOCl \longrightarrow 2NO + Cl_2$$

PHOSPHORUS TRICHLORIDE

Preparation

$$3P + 3Cl_2 \longrightarrow 2PCl_3$$

$$2P + 4SOCl_2 \longrightarrow 2PCl_3 + 2SO_2 + S_2Cl_2$$

Chemical Reactions of Phosphorus Trichloride

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

$$2PCl_3 + O_2 \longrightarrow 2POCl_3$$

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

PHOSPHORUS PENTACHLORIDE

Preparation

$$2P + 5Cl_2 \longrightarrow 2PCl_5$$

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

Chemical Reactions of Phosphorus Pentachloride

$$PCl_5 \longrightarrow PCl_3 + Cl_2$$

$$PCl_5 + Zn \longrightarrow ZnCl_2 + PCl_3$$

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$

PHOSPHORUS TRIOXIDE

Preparation

$$P_4 + 3O_2 \longrightarrow 2P_2O_3$$

Chemical Reactions of Phosphorus Trioxide

$$P_2O_3 + O_2 \longrightarrow P_2O_5$$

$$P_2O_3 + 3H_2O \xrightarrow{\text{cold}} 2H_3PO_3$$

$$P_2O_3 + 6H_2O \xrightarrow{\text{hot}} 2H_3PO_4 + PH_3$$

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PHOSPHORUS PENTOXIDE

Preparation

$$P_4 + 5O_2 \longrightarrow 2P_2O_5$$

Chemical Reactions of Phosphorus Pentaoxide

$$P_2O_5 + H_2O \xrightarrow{\text{cold}} 2HPO_3$$

$$P_2O_5 + 3H_2O \xrightarrow{\text{hot}} 2H_3PO_4$$

$$P_2O_5 + 2HNO_3 \xrightarrow{\text{hot}} N_2O_5 + 2HPO_3$$

$$P_2O_5 + C_2H_5OH \longrightarrow C_2H_4 + 2HPO_3$$

$$P_2O_5 + 2CH_3COOH \longrightarrow 2HPO_3 + (CH_3CO)_2O$$

Acetic anhydride

PHOSPHORUS ACID

Preparation

$$P_2O_3 + 3H_2O \xrightarrow{\text{cold}} 2H_3PO_3$$

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

Chemical Reactions of Phosphorus Acid

$$4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$$

$$H_3PO_3 + CuSO_4 + H_2O \longrightarrow H_3PO_4 + H_2SO_4 + Cu$$

$$H_3PO_3 + 2AgNO_3 + 2NH_4OH \longrightarrow H_3PO_4 + H_2O + 2Ag + 2NH_4NO_3$$

$$H_3PO_3 + O_2 \longrightarrow 2H_3PO_4$$

$$H_3PO_3 + 6[H] \xrightarrow{Zn/HCl} PH_3 + 3H_2O$$

ORRTHOPHOSPHORIC ACID

Preparation

$$P_2O_5 + 3H_2O \xrightarrow{\text{hot}} 2H_3PO_4$$

$$P + 5HNO_3 \xrightarrow{\text{Conc.}} H_3PO_4 + 5NO_2 + H_2O$$

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$

$$Ca_3(PO_4)_2 + 3SiO_2 \longrightarrow 3CaSiO_3 + P_2O_5$$

Chemical Reactions of Orthophosphoric Acid

DEHYDRATION

$$2H_3PO_4 \xrightarrow[-H_2O]{240^\circ C} H_4P_2O_7 \xrightarrow[-H_2O]{316^\circ C} 2HPO_3$$

Orthophosphoric aicd — Pyro-phosphoric acid — Meta phosphoric acid

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REACTION WITH BASE

$H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$

$H_3PO_4 + 2NaOH \longrightarrow Na_2HPO_4 + H_2O$

$H_3PO_4 + 3NaOH \longrightarrow Na_3PO_4 + H_2O$

SULPHURIC ACID

Preparation

Contact Process

$S + O_2 \longrightarrow SO_2$

$2SO_2 + O_2 \xrightarrow[V_2O_5.]{400\text{-}500^\circ C} 2SO_3$

$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$

$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$

Chemical Reactions of Sulphuric Acid

IONIZATION

$H_2SO_4 + H_2O \longrightarrow H_3O^+ + HSO_4^-$

$HSO_4^- + 2H_2O \longrightarrow 2H_3O^+ + SO_4^{-2}$

REACTIONS WITH BASE

(A) Arrhenius Base

$H_2SO_4 + NaOH \longrightarrow NaHSO_4 + H_2O$

Sodium bisulphate (acidic salt)

$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$

Sodium sulphate (normal salt)

(B) Lewis Base

$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$

REACTIONS WITH METALS

(A) Cold and dilute sulphuric acid

$Mg + H_2SO_4 \longrightarrow MgSO_4 + H_2$

$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$

$Sn + H_2SO_4 \longrightarrow SnSO_4 + H_2$

(B) Hot and concentrated sulphuric acid

$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

$2Ag + 2H_2SO_4 \longrightarrow Ag_2SO_4 + SO_2 + 2H_2O$

$Hg + 2H_2SO_4 \longrightarrow HgSO_4 + SO_2 + 2H_2O$

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REACTIONS WITH SALTS

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + CO_2 + H_2O$$

$$CuCO_3 + H_2SO_4 \longrightarrow CuSO_4 + CO_2 + H_2O$$

$$2NaHCO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2CO_2 + 2H_2O$$

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

REACTIONS AS AN OXIDIZING AGENTS

$$H_2S + H_2SO_4 \longrightarrow S + SO_2 + 2H_2O$$

$$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$$

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

$$2P + 4H_2SO_4 \longrightarrow H_3PO_3 + H_3PO_4 + 4SO_2 + H_2O$$

$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$

REACTIONS AS A DEHYDRATING AGENT

Concentrated sulphuric acid

$C_6H_{12}O_6 \longrightarrow 6C + 6H_2O$
(glucose)

$C_{12}H_{22}O_{11} \longrightarrow 12C + 11H_2O$
(Sucrose)

$HCOOH \longrightarrow CO + H_2O$
(Formic acid)

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \longrightarrow CO + CO_2 + H_2O$$
(oxalic acid)

$$\begin{matrix} CH_3 \\ | \\ CH_2-OH \end{matrix} \longrightarrow \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + H_2O$$
Ethyl alcohol → Ethylene

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PRACTICE EXERCISE

20 mins Time Yourself

1. **Which of the following is different with respect to physical appearance?**
   (a) Arsenic (b) Phosphorus
   (c) Antimony (d) Bismuth
2. **Which one of the followings possesses melting point below 0°C?**
   (a) Nitrogen (b) Phosphorus
   (c) Carbon (d) Bismuth
3. **Compounds of nitrogen and phosphorus are mostly**
   (a) Ionic (b) Covalent
   (c) Polar (d) All varieties are possible
4. **The most electronegative element among the following is**
   (a) Sb (b) N
   (c) As (d) P
5. **SO_3 is not absorbed in water directly because**
   (a) Reaction is exothermic (b) It is insoluble in water
   (c) Dilute acid is produced (d) All of above
6. **Phosphene gas will be produced if phosphorous acid is subjected to**
   (a) Oxidation (b) Reduction
   (c) Decomposition (d) Both b & c
7. **Which of the following will give phosphoric acid on reaction with water**
   (a) PCl_5 (b) P_2O_3
   (c) P_2O_5 (d) All of the above
8. **Which one of following is not a property of pure quartz?**
   (a) Coloured solid (b) Brittle
   (c) Hard (d) All of above
9. **Phosphorus is a Greek word and it means**
   (a) Light bearing (b) Fire
   (c) Impure (d) Tetrahedral
10. **Which of the following does not contain phosphorus?**
    (a) Yolk of egg (b) Bone
    (c) Nerves (d) Steel
11. **Allotropic form of phosphorus that is poisonous is**
    (a) White (b) Red
    (c) Black (d) Violet
12. **Which one of the following is not the use of graphite?**
    (a) Lead pencils (b) Abrasive
    (c) Lubricant (d) Electrode of electrolytic cell
13. **Acetic anhydride can be obtained by treating ethyl alcohol with**
    (a) P_2O_5 (b) H_2SO_4
    (c) Both a & b (d) PCl_5
14. **The composition of brown ring in nitrate test is**
    (a) $FeSO_4.NO$ (b) $FeSO_4.NO_2$
    (c) $FeSO_4.NO_3$ (d) $FeSO_4.N_2O$
15. **Phosphorous acid upon thermal decomposition yields phosphoric acid and**
    (a) Phosphine (b) Phosphorus
    (c) Water (d) Phosphorus pentoxide
16. **Which one of the following compounds usually smells like garlic?**
    (a) P_2O_3 (b) P_2O_5
    (c) H_3PO_3 (d) All have same smell

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17. **P_2O_5 is a hygroscopic powder which sublimes at**
(a) 260°C (b) 360°C
(c) 630°C (d) 620°C

18. **The element of group VIA, which is a non-metal is**
(a) S (b) Se
(c) Te (d) Po

19. **Phosphoric acid is a weak acid and its basicity is**
(a) 1 (b) 3
(c) Zero (d) 2

20. **All the elements in group VIA are _____ in nature.**
(a) Hygroscopic (b) Metals
(c) Polymeric (d) All of above

21. **Which of the elements show passivity when treated with conc. HNO_3.**
(a) Fe (b) Al
(c) Cr (d) All of the above

22. **Which allotropic form of phosphorous is the most stable?**
(a) White (b) Black
(c) Red (d) Violet

23. **The gas which cannot be dried by conc. H_2SO_4**
(a) SO_2 (b) H_2S
(c) CO_2 (d) C_2H_4

24. **The chemical composition of cinnabar is**
(a) ZnS (b) PbS
(c) HgS (d) FeS

25. **$FeSO_4$ forms brown ring with**
(a) N_2O_3 (b) NO_2
(c) NO (d) N_2O

26. **Oxygen and sulphur resemble in all except**
(a) Electronic configuration of valence shell electrons.
(b) Show allotropy
(c) Polymeric
(d) Show same oxidation state

27. **Oxygen does not react with all except**
(a) Alkali (b) Acid
(c) Water (d) Metals

28. **Arsenic oxides are removed by passing through**
(a) Ferric hydroxide (b) Sodium hydroxide
(c) Calcium hydroxide (d) Aluminium hydroxide

29. **In which compound nitrogen has maximum oxidation state**
(a) N_2O (b) NO_2
(c) HNO_2 (d) HNO_3

30. **When sulphuric acid is treated with ethanol, sulphuric acid behaves like**
(a) An acid (b) A dehydrating agent
(c) An oxidizing agent (d) As sulphonating agent

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Chapter 5

THE HALOGENS AND THE NOBLE GASES

KIPS

(I) Introduction

(II) Occurrence

(III) Peculiar Behaviour of Fluorine

(IV) Oxidizing Properties

(V) Compounds of Halogens
- Hydrides (hydrogen halides, HX)
- Oxides of Halogens
- Reactions of Chlorine with Cold and Hot NaOH
- Oxyacids
- Bleaching Powder

(VI) Commercial uses of Halogens and their Compounds

(VII) Noble Gases
- Introduction
- Compounds of Xenon
- Fluorides of Xenon
- Xenon Oxyfluorides
- Oxides of Xenon
- Applications of the Noble Gases

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INTRODUCTION (HALOGENS)

- VII-A group is called halogen group.
- Very reactive with non-metals.
- Exist in three states of matter with diatomic molecule.
- Halogen forms –ve ion by getting one electron (X^-).
- Have highest E.N. value among the elements of their period.

Astatine is rare element. It is a radioactive and its most stable isotope has half-life of 8.30 hrs.

	FLUORINE	CHLORINE	BROMINE	IODINE
Colour	Pale yellow	Greenish yellow	Reddish brown	metallic shiny Greyish black
Physical state	Gas	Gas	Liquid	Solid

OCCURRENCE OF HALOGENS

- Halogens are very reactive, so they are not found in free state.
- Halogens are found in the form of soluble halides.

FLUORINE	CHLORINE	BROMINE	IODINE
Fluorospar CaF_2 Cryolite Na_3AlF_6 Apatite $[CaF_3.3Ca_3(PO_4)_2]$	Halite NaCl (Salt beds, brine wells, sea water) Carnalite $KCl.MgCl_2.6H_2O$	Brine wells, Sea water NaBr, KBr, $MgBr_2$	$NaIO_3$, $NaIO_4$ deposits in Chile brine wells.

PECULIAR BEHAVIOUR OF FLUORINE

Fluorine	Other Halogen
High first I.P and E.N	Low first I.P and E.N
Low dissociation energy	High dissociation energy except I_2
Fluorides have high lattice energy .	Lattice energy of other halides is smaller than other fluorides
Most reactive	Less reactive
F reacts directly with noble gases	No other halogen reacts with the noble gases
Shows only -1 oxidation state	Others show -1,+1,+3,+5,+7 oxidation states
Does not form oxy acids.	Form oxyacids.
Has maximum reduction potential.	Others have lower reduction potential.

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OXIDIZING PROPERTIES OF HALOGENS

- The oxidizing power of halogens decreases with increase in atomic number. $F_2 > Cl_2 > Br_2 > I_2$
- The oxidizing power of halogens depend upon the following factors:
  - Energy of dissociation.
  - Electron affinity of atoms
  - Hydration energies of ions.
  - Heats of vaporization (for Br_2 and I_2)
- Fluorine and chlorine can oxidize various coloured dyes to colourless substances e.g. litmus and universal indicator can be decolourized when exposed to fluorine or chlorine.

COMPOUNDS OF HALOGEN

HYDRIDES

The binary compounds of X and H are hydrides.

- Reactivity of X_2 with H_2 is F > Cl > Br > I.
- Reaction with I_2 is reversible and very slow.
- F and Cl give their halides with conc. H_2SO_4 while Br and I do not.

Properties Of Hydrides

Properties of HF

- Zig-Zag pattern of hydrogen bonding is present in HF.
- HF is liquid while HCl, HBr and HI are gases at room temperature.
- HF attacks glass while others do not.
- Viscosity of HF is lesser than water.
- Vapour phase of HF is equilibrium mixture of monomers and cyclic hexamers.

Properties Of other Hydrogen Halide

Increasing Trends

- Intermolecular attraction, M.P, B.P, heat of fusion, heat of vaporization, bond length, reducing strength and acidic strength is in the order as

$$HCl < HBr < HI$$

Decreasing Trends

- Bond energy, Dipole moment, Strength of bond have trends as HCl > HBr > HI

OXIDES OF HALOGENS

- No reaction with Oxygen under normal conditions except fluorine.

Fluorine		Chlorine		Bromine		Iodine	
Oxide	Formula	Oxide	Formula	Oxide	Formula	Oxide	Formula
Oxygen difluoride	OF_2	Dichlorine monoxide	Cl_2O	Bromine monoxide	Br_2O	Iodine tetraoxide	I_2O_4
Dioxygen difluoride	O_2F_2	Chlorinedioxide	ClO_2	Bromine dioxide	BrO_2	Iodine iodate	I_4O_9
Trioxygen difluoride	O_3F_2	Chlorine hexaoxide	Cl_2O_6	Bromine trioxide	BrO_3 (Br_3O_8)	Iodine pentaoxide	I_2O_5
		Chlorine heptaoxide	Cl_2O_7				

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	Preparation	Colour and state	Effect of heat	Uses and other properties
O_3F_2	From mixture of F_2 and O_2 subjected to electric discharge	▪ Dark red liquid at 363°C ▪ Reddish brown solid at 350°C	Gives oxygen and oxides of flourine	On reaction with F_2, it gives O_2F_2
ClO_2	▪ By reducing $NaClO_3$ with NaCl or SO_2 or CH_3OH in acidic media ▪ By reacting H_2SO_4 and $KClO_3$ in the presence of oxalic acid	Pale yellow gas	Forms O_2 and Cl_2 on warming	▪ Paramagnetic substance ▪ Used as antiseptic for purification of water and bleach of cellulose material ▪ Decomposes in H_2O to HCl and $HClO_3$
Cl_2O_7	By dehydration of perchloric acid ($HClO_4$) with P_2O_5 at -10°C	Colourless viscous liquid	Stable at room temperature	When goes in water produces $HClO_4$.
Br_2O	By reacting bromine vapours and mercuric oxide By suspension of mercuric oxide in CCl_4 and Br_2	Dark Volatile liquid	Only stable at -20°C	It has oxidizing properties
I_2O_5	Heating iodic acid at 240°C	White crystalline solid	Stable up to 300°C	▪ Has polymeric structure ▪ Insoluble in organic solvent ▪ Acts as oxidizing agent ▪ Used in quantitative analysis of CO

DISPROPORTIONATION REACTION

A reaction in which a specie is simultaneously oxidized and reduced is called disproportionation reaction. e.g. reaction of Cl_2 with NaOH gives sodium hypochlorite and sodium chloride.

In this reaction, oxidation number of chlorine converts to (-1) in chloride and (+1) in hypochlorite in cold state. At 70°C the oxidation state changes from -1 to +5.

OXYACIDS

- *In oxyacids, X is the central atom to which one or more oxygen atoms are covalently bonded.*
- Greater number of O atom in oxyacids, more will be thermal stability.
- Acidic strength increases with increase in oxygen atom
- Strength of oxyacids is $HXO_4 > HXO_3 > HXO_2 > HXO$.
- Chloric acid is stronger than bromic acid. It is due to decrease in electronegativity and increase in the size of bromine.

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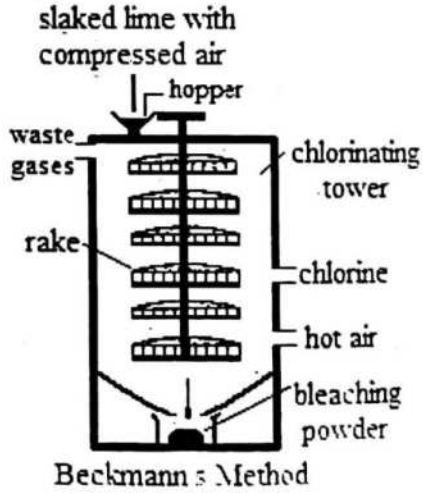
Oxidation state of halogen	Formula of oxy acids of halogens			General names of	
	Chlorine	Bromine	Iodine	Oxyacids	Salts of oxyacids
+1	HClO	HBrO	HIO	Hypohalous acid	Hypo------ite
+3	$HClO_2$	----------	----------	Halous acid	----------ite
+5	$HClO_3$	$HBrO_3$	HIO_3	Halic acid	----------ate
+7	$HClO_4$		HIO_4, H_5IO_6	Perhalic acid	Per--------ate

PERCHLORIC ACID

- It is prepared by distilling a mixture of potassium perchlorate and conc. H_2SO_4 under reduced pressure.
- Perchloric acid is a hygroscopic liquid.
- Freezes at -112°C, decomposes at 90°C
- It works as oxidizing agent.
- It is stored in 67% solution in water as decomposes explosively when heated
- Due to its oxidizing property, it is very important analytical reagent.

BLEACHING POWDER

- It is prepared by reaction of slaked lime and chlorine
- Two methods are available
  - Hasenclever method (old)
  - Beckman method (new)
- It is good oxidizing agent due to generation of hypochorite ion.
- Cl_2 liberated on reaction with excess acid is called "available chlorine" (35-40%).



Beckmann's Method

- **Uses**
  - Preparation of chloroform
  - Sterilization of water
  - Preparation of un-shrinkable wool
  - As bleaching agent in textile

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COMMERCIAL USES OF HALOGENS AND THEIR COMPOUNDS

Field of usage	Fluorine	Chlorine	Bromine	Iodine
Chemical	▪ Freon gas CCl_2F_2, $CClF_3$, CF_4 ▪ Teflon (valuable plastic) $(- CF_2 - CF_2 -)$	▪ Bleaching powder ▪ PVC ▪ CCl_4 ▪ $CHCl_3$ ▪ HCl	▪ Ethylene bromide $C_2H_4Br_2$ used in gasoline to save engine from PbO and $PbSO_4$ deposits	▪ KI, NaI are added to common salt which is known as iodized salt.
Industry	▪ Corrosion proof parts of machinery from Teflon ▪ Electric wires are coated with Teflon	▪ Bleaching powder is used in textile and paper industry.	▪ AgBr is used in photography.	▪ Pharmaceutical industry as disinfectant and germicide.
Medical /agriculture	▪ Halothane is used as anesthetic	▪ Antiseptic, insecticide weed killer, herbicide	▪ Used as fungicide	▪ To fulfill deficiency of I_2 in our diet to avoid the risk of goiter

INTRODUCTION (NOBLE / RARE GASES)

- Noble gases are placed in zero group or VIII-A group
- All elements are non-metallic, odourless and colourless gases.
- There are eight electrons in outermost shell of each element except He.
- Noble gases are isolated from air by fractional distillation.
- He is present on earth as radioactive decay, the 2nd most abundant element in the universe.
- Neon is 1/65000th part of air.
- Neon gives reddish glow in gas discharge tube.
- Neon has 40 times more refrigeration capacity than He.
- Xe is present in air as 0.08 ppm.
- Radon is product as α-decay of radium.
- Boiling point increases down the group due to increase in London forces.

COMPOUNDS OF Xe

Oxidation state of Xe	Compound	Physical state
+2	XeF_2	Colourless crystal
+4	XeF_4, $XeOF_2$	Colourless crystal
+6	XeF_6	Colourless crystal
	$XeOF_4$	Colourless liquid
	XeO_3	Colourless crystal
+8	XeO_4	Colourless gas

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FLUORIDES

Particulars	XeF_2	XeF_4	XeF_6
Preparation	Direct interaction of Xe and F_2 for 8 hours	Interaction of Xe and F_2 in 1:5 ratio in Nickel container at 6 atm for few hours	Interaction of Xe and F_2 in 3:20 ratio in stainless steel vessel at 50 atm and 300°C
State	Crystalline solid	Crystalline solid	Crystalline solid
Others	• Stored in Ni vessel • Mild fluorinating agent	• Stored in Ni vessel • Strong fluorinating agent	Yellow in colour when liquid or gas
Action of H_2	Forms Xe and HF	Forms Xe and HF	Forms Xe and HF
Hydrolysis	-	-	Forms HF and $XeOF_4$
Action of NH_3	-	Forms N_2, HF and Xe	-
Action of Hg	-	Forms Xe and HgF_2	-

XENON OXYTETRAFLUORIDE ($XeOF_4$)

- Prepared by XeF_6 and quartz (silica).
- Colourless volatile liquid
- Stored in Ni vessel
- Gives XeO_3 after reaction with water

XENON OXIDES

Particulars	XeO_3	XeO_4
Preparation	Interaction of XeF_6 and H_2O	Interaction of Ba_2XeO_6 or Na_4XeO_6 with H_2SO_4
State and other	• Crystalline solid • Explodes at very low temp. • Weak acid	Colourless crystalline solid below -35.9°C

USES OF NOBLE GASES

- He ⇒ weathering balloons, traffic signal lights and welding
- 80 % helium + 20 % oxygen ⇒ breathing cylinder
- He ⇒ cooling in nuclear reactor
- Ne ⇒ neon advertising signs, TV tubes, high voltage indicators
- Ne+He ⇒ making glass lasers
- Ar ⇒ bulbs, fluorescent tubes, radio tubes
- Ar ⇒ arc welding
- Kr ⇒ filled in fluorescent tube, flash lamps
- Xe ⇒ bactericidal lamps
- Ra ⇒ radiotherapy of cancer, earthquake prediction

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GARDEN OF EQUATIONS

OXIDES OF HALOGENS

$$2O_3F_2 \xrightarrow{\Delta} 2O_2F_2 + O_2$$

$$2O_3F_2 + F_2 \longrightarrow 3O_2F_2$$

$$5CO + I_2O_5 \longrightarrow I_2 + 5CO_2$$

OXYACIDS OF HALOGENS

$$2HClO_4 + P_2O_5 \xrightarrow{-10°C} Cl_2O_7 + 2HPO_3$$

$$HgO + 2Br_2 \xrightarrow{50°C} HgBr_2 + Br_2O$$

$$2HIO_3 \xrightarrow{240°C} I_2O_5 + H_2O$$

DISPROPORTIONATION REACTIONS

$$[Cl_2 + 2NaOH \xrightarrow{15°C} NaCl + NaClO + H_2O] \times 3$$

$$3NaClO \longrightarrow 2NaCl + NaClO_3$$

$$3Cl_2 + 6NaOH \xrightarrow{70°C} NaClO_3 + 5NaCl + 3H_2O$$

BLEACHING POWDER

IONIZATION

$$Ca(OCl)Cl \xrightleftharpoons{H_2O} Ca^{2+} + Cl^- + ClO^-$$

REACTION WITH LEWIS BASE

$$3Ca(OCl)Cl + 2NH_3 \longrightarrow 3CaCl_2 + N_2 + 3H_2O$$

REACTION WITH ARRHENIUS ACID

$$Ca(OCl)Cl + 2HCl \longrightarrow CaCl_2 + Cl_2 + H_2O$$

$$2Ca(OCl)Cl + \text{dil.}H_2SO_4 \longrightarrow CaSO_4 + CaCl_2 + 2HClO$$

$$Ca(OCl)Cl + \underset{\text{(Excess)}}{H_2SO_4} \longrightarrow CaSO_4 + H_2O + Cl_2$$

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FLUORIDES OF XENON

Preparation

$$Xe + F_2 \longrightarrow XeF_2$$
$$XeF_2 + F_2 \longrightarrow XeF_4$$
$$XeF_4 + F_2 \longrightarrow XeF_6$$

Chemical Reactions of Xenon Fluorides

AS FLUORINATING AGENTS

$$XeF_2 + H_2 \longrightarrow Xe + 2HF$$
$$XeF_4 + 2H_2 \longrightarrow Xe + 4HF$$
$$XeF_6 + 3H_2 \longrightarrow Xe + 6HF$$
$$XeF_4 + 2Hg \longrightarrow Xe + 2HgF_2$$
$$3XeF_4 + 4NH_3 \longrightarrow 3Xe + 12HF + 2N_2$$
$$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$$
$$XeF_6 + H_2O_{(less)} \longrightarrow XeOF_4 + 2HF$$

PREPARATION OF XENON OXIDE

$$Ba_2XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2BaSO_4 + 2H_2O$$
$$Na_4XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2Na_2SO_4 + 2H_2O$$

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PRACTICE EXERCISE

20 mins Time Yourself

1. **Among the halogens, the rare element is**
   (a) Fluorine (b) Chlorine
   (c) Astatine (d) Iodine
2. **The colour of chlorine gas is**
   (a) Pale yellow (b) Greenish yellow
   (c) Reddish brown (d) Greyish black
3. **Van der Waal's forces are stronger in**
   (a) F_2 (b) Cl_2
   (c) Br_2 (d) I_2
4. **The most powerful oxidizing agent among the halogens is**
   (a) F_2 (b) Cl_2
   (c) Br_2 (d) I_2
5. **Which of the following statements is incorrect about fluorine**
   (a) Fluorine is restricted to -1 oxidation state
   (b) Fluorine follows octet rule and as well as extended octet rule
   (c) Fluorine has lowest dissociation energy among the halogens
   (d) Both b and c
6. **The halogen which reacts spontaneously with gold(Au) to form Au^{+3} is**
   (a) F_2 (b) Cl_2
   (c) Br_2 (d) I_2
7. **Which one of the following is the weakest acid in water**
   (a) HF (b) HCl
   (c) HBr (d) HI
8. **The halogen, which reacts very slowly with other halogen salt**
   (a) Fluorine (b) Chlorine
   (c) Bromine (d) Iodine
9. **Which of the following represents the correct electronic configuration of VII A group elements in the ground state?**
   (a) ns^2p^2 (b) ns^2p^4
   (c) ns^2p^5 (d) ns^2p^6
10. **The halogen having highest electron affinity is**
    (a) Fluorine (b) Chlorine
    (c) Bromine (d) Iodine
11. **Which is the strongest acid?**
    (a) HClO (b) $HClO_2$
    (c) $HClO_3$ (d) $HClO_4$
12. **Bromine can be liberated from KBr solution by the action of**
    (a) Iodine solution (b) Chlorine
    (c) NaCl (d) KI

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13. **Bleaching powder is an example of**
(a) Normal salt (b) Double salt
(c) Mixed salt (d) Complex

14. **Consider the following reaction-**
$2KClO_3 + H_2C_2O_4 + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O + 2CO_2 +$ Oxide
Which oxide of chlorine is produced in the above reaction?
(a) Cl_2O (b) ClO_2
(c) Cl_2O_6 (d) Cl_2O_7

15. **Which of the following oxides of iodine is used for quantitative analysis of CO?**
(a) I_2O_4 (b) I_4O_9
(c) I_2O_5 (d) I_2O_4

16. **Consider the following reaction-**
$3Cl_2 + 6NaOH \longrightarrow NaClO_3 + 5NaCl + 3H_2O$
This reaction is
(a) Displacement reaction
(b) Double displacement reaction
(c) Disproportionation reaction
(d) Reduction reaction

17. **Which of the halogen has highest electronegativity?**
(a) Fluorine (b) Chlorine
(c) Bromine (d) Iodine

18. **Which of the halogen can displace other three elements?**
(a) Fluorine (b) Chlorine
(c) Iodine (d) Bromine

19. **Which of the following statements is incorrect about halogens?**
(a) All are non-metals
(b) All the halogens have electronic configuration ns^2p^5
(c) They have high electron affinity and ionization energy
(d) All the halogens react with noble gases to form their halides

20. **The chemical formula of sodium hypochlorite is**
(a) NaClO (b) $NaClO_2$
(c) $NaClO_3$ (d) $NaClO_4$

21. **Fluorine can react with**
(a) Xe (b) Kr
(c) Rn (d) All of these

22. **Bleaching powder is not used for bleaching**
(a) Cotton (b) Costly fabrics
(c) Linen (d) Paper pulp

23. **Which of the following is the weakest reducing agent:**
(a) HF (b) HBr
(c) HCℓ (d) HI

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24. Which statement is incorrect about bleaching powder

(a) It acts as an oxidizing agent

(b) It contains 35 – 40 % available chlorine

(c) It used in laboratory preparation of oxygen and chlorine

(d) It is partially soluble in water

25. In which compound of Xenon, the oxidation state of Xenon is + 6.

(a) XeF_4 (b) $XeOF_4$

(c) $XeOF_2$ (d) Na_4XeO_6

26. Photographic plates are coated with a thin film of:

(a) $AgNO_3$ (b) AgI

(c) AgCl (d) AgBr

27. The anhydride of $HClO_4$ is:

(a) Cl_2O (b) Cl_2O_6

(c) ClO_2 (d) Cl_2O_7

28. Indicate the correct statement about halogen:

(a) Cl_2 is the strongest oxidizing agent (b) I_2 is a volatile solid

(c) Br_2 is more reactive than Cl_2 (d) Cl_2 is insoluble in water

29. Which one of the following halogens is present in Teflon:

(a) I_2 (b) Br_2

(c) Cl_2 (d) F_2

30. Which is the paramagnetic oxide of chlorine:

(a) Cl_2O_7 (b) Cl_2O_6

(c) ClO_2 (d) Cl_2O

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Chapter 6 TRANSITION ELEMENTS

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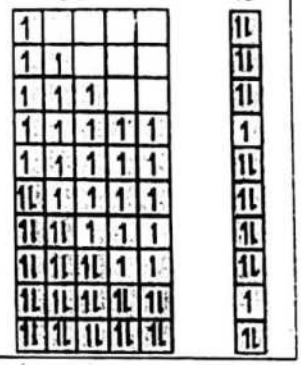
INTRODUCTION

Transition elements may be defined as those elements which have partially filled 'd' or 'f'-sub shells in atomic state or in any of their commonly occurring oxidation states.

Properties

Transition elements usually show variable oxidation states, coloured compounds and form complex compounds

3d – series elements	
Elements	Electronic Configuration
Sc (21)	$[Ar]\ 3d^1 4s^2$
Ti (22)	$[Ar]\ 3d^2 4s^2$
V (23)	$[Ar]\ 3d^3 4s^2$
Cr (24)	$[Ar]\ 3d^5 4s^1$
Mn (25)	$[Ar]\ 3d^5 4s^2$
Fe (26)	$[Ar]\ 3d^6 4s^2$
Co (27)	$[Ar]\ 3d^7 4s^2$
Ni (28)	$[Ar]\ 3d^8 4s^2$
Cu (29)	$[Ar]\ 3d^{10} 4s^1$
Zn (30)	$[Ar]\ 3d^{10} 4s^2$



Typical and Non-Typical Transition Elements

- Elements of group II-B(Zn, Cd and Hg), III-B(Sc,Y, La) are non-typical transition elements.
- Coinage metals (Cu, Ag and Au) are considered as transition elements as their d-orbitals are in process of completion in their ionic states.
-
  - Cu^{+2} ----------$3d^9$
  - Ag^{+2} ---------- $4d^9$
  - Au^{+3}---------- $5d^8$
- d-block elements are called outer transition elements while f-block elements are called inner transition elements.

GENERAL CHARACTERISTICS OF TRANSITION ELEMENTS

Characteristic	Description
Binding energies	• Metals are hard having high value of binding energy due to the involvement of electrons of d-atomic orbitals along with s-atomic orbitals • From Left to Right in a period, the number of unpaired electrons increases up to VI-B and then there is a decrease up to the end of the period. • Binding energy increases up to VI-B and then weakened up to II-B
Melting point and Boiling point	• High M.P and B.P due to high binding energy up to 'Vanadium' • And then decreases upto end of series
Covalent and ionic radii	• Covalent radii decreases rapidly in the start (Sc to V) then become constant in middle (V to Co) and then begin to increase at the end of

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	series (Ni to Zn) • Ionic radii remain irregular throughout series
Para magnetism	• Weakly attracted by strong magnetic field hence are paramagnetic • Unpaired electron favours paramagnetism.
Oxidation state	• Elements shows variable oxidation state +2,+3.....+7 • It is due to the involvement of unpaired d-electrons in bonding in addition to outer s electrons. • Sc upto Mn oxidation states increases and after that it decreases
Colour	• When d-orbitals are involved in the bonding they split up into two energy levels. One set has a higher energy than the other. • d-d transition occur when light energy is absorbed by electrons of lower atomic orbital. • Each ions absorb a particular set of wavelength and transmits the remaining set of wavelength giving colour • Energy difference between two sets of d-orbitals varies from ion to ion
Interstitial compounds	• The interatomic spaces among metal atoms is called interstices • C,B,N,H can enters into these interstices and form interstitial compounds. • They are non-stoichiometric compounds
Alloy formation	• Owing to the similarity in their sizes, some transition elements replace each other in crystal lattice to form substitutional alloys • In alloy steel, Fe is replaced by Cr, Mn, Ni • Examples include brass, bronze etc.

COMPLEX COMPOUNDS

The compounds containing the complex molecules or complex ions and capable of independent existence are called coordination compounds complexes.

A complex compound may contain

(i) A simple cation and a complex anion

(ii) A complex cation and a simple anion

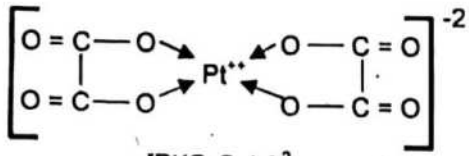
COMPONENT OF COMPLEX COMPOUND

Component	Description
Central metal atom or ion	• Metal atom or metal ion surrounded by number of ligands in the complex compound
Ligand	• Ion, atom or neutral molecule that donates electron pairs to central metal atom/ion. • Ligand with two donor atoms is called bidentate
Co-ordination Number.	• The number of lone pair of electrons provided by ligands to central atom or ion.
Co-ordination sphere	• The central metal atom or ion along with ligands is called co-ordination sphere. It is usually placed in square brackets.
Charge on co-ordination sphere	• Algebraic sum of charges present on central metal ion and the total charge on the ligands

Chelates:

A complex compound, in which one or more than one ring is formed due to donation of electrons by poly dentate ligand. e.g. $[Pt(C_2O_4)_2]^{2-}$

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$[Pt(C_2O_4)_2]^{-2}$

Dioxalato-platinate (II) ion

Nomenclature

The IUPAC rules for naming the complex compounds are as follows.

(1) Cations are named before anions.

(2) In naming the coordination sphere, ligands are named in alphabetical order regardless of the nature and number of each followed by the name of central metal ion.

(3) The prefixes di, tri, tetra, penta, hexa, etc, are used to specify the number of coordinated same ligand.

(4) The names of anionic ligands end in suffix "O" e.g. hydroxo, OH- carbonato CO_3^{-2}

(5) The names of neutral ligands are usually unchanged, e.g. for NH_3 ammine and for H_2O, aqua.....etc.

(6) The suffix 'ate' comes at the end of the name of metal if the co-ordination sphere is negative otherwise it remains unchanged.

(7) The oxidation number of the metal ion is represented by a Roman numeral in parenthesis following the name of the metal.

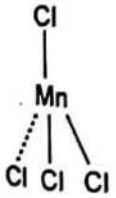
Examples:

$K_4[Fe(CN)_6]$ Potassium hexacayno ferrate(II)

$[PtCl(NO_2)(NH_3)_4]SO_4$ Tetraammine chloronitro-platinum (IV) sulphate.

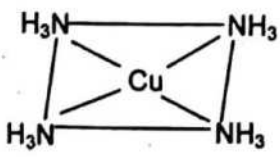
Geometry Of Complex Compound

$[Mn Cl_4]^{-2}$



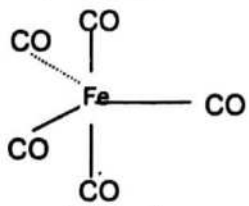
tetrahedral (sp^3)

$[Cu(NH_3)_4]^{+2}$



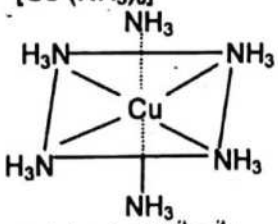
square planar (dsp^2)

$[Fe(CO)_5]$



trigonal bipyramidal (dsp^3)

$[Co(NH_3)_6]^{+3}$



octahedral (d^2sp^3)

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IRON

Ores of iron

Name	Formula
Haematite	Fe_2O_3
Magnatite	Fe_3O_4
Limonite	$Fe_2O_3.3H_2O$

COMMERCIAL FORMS OF IRON

Name	% of carbon
Pig iron or cast iron	2.5 to 4.5%
Wrought iron	0.12 to 0.25%
Steel	0.25 to 2.5%

WROUGHT IRON

Composition

Element	%
S	0.2 to 0.15%
Mn	0.25%
P	0.04 to 0.2%
Fe	Rest

Manufacturing

- Prepared from cast iron in puddling furnace.
- Haemetite ore is used
- Haemetite lining gives oxygen for the oxidation of C, S, Si, Mn and P present in cast iron.
- Oxides of Mn, P, Si and S forms slags($MnSiO_3$),($FePO_4$)
- Hammering is done on balls or blooms to remove slag

STEEL

- Steel is an alloy of Iron containing 0.25 to 2.5% carbon and traces of S,P,Si.

Types of steel

Mild steel	Medium carbon steel	High carbon steel
C=0.1to 0.2%	C=0.2 to 0.7%	C=0.7 to 1.5%
Fairly soft	Harder than mild	More Hard
Malleable and ductile	Malleable and ductile	Can be forged when the percentage of carbon is less than 1%
Nuts, bolts, bars and boiler plates are prepared	Making rails, axles, casting are prepared	A hammer, taps, dies, cutting tools, machine tools, hard steel parts of machinery are prepared.

- Steel can be prepared:
  - By removing C, S, P and Si from cast iron
  - Adding Ferromanganese to wrought iron according to the type of steel.

Manufacturing

Two methods are common

1. Open hearth process.
2. Bessemer's process.

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Open Hearth Process

- It is a modern method, carried out in open-hearth furnace.
- Open-hearth process is of two types.
  - Furnace with acidic lining e.g .SiO_2, when impurities are Mn, Si
  - . Furnace with basic lining e.g. CaO, MgO, when impurities are S and P
- Mixture of cast iron, scrap steel, quick lime heated at 1600°C in furnace
- C is removed in the form of CO
- SiO_2 combines with CaO, MgO and FeO to form slag.
- P and S reacts with Fe_2O_3 and CaO to form slag
- Slag contains $Ca_3(PO_4)_2$ sold as fertilizer.

Bessemer's Process

- Oxides of C, Si and Mn form slag($MnSiO_3$).
- CO burns at mouth of furnace with blue flame.
- Ferromanganese is added to correct the proportion of C when CO flame dies.
- Mn imparts hardness and tensile strength.
- To remove bubbles of O_2, N_2 and CO_2, Al or ferrosilicon is added.

CORROSION

- Chemical decay of metal due to action of surrounding medium is called corrosion.
- Water is main source of corrosion.
- Impurities in metal promote corrosion.
- When metal (Al) comes in contact with less active metal (Cu), a galvanic cell is produced.
- Active metals are corroded rapidly due to oxidation than less active metal.

PREVENTION OF CORROSION

- ¼th of iron's total production is damaged due to corrosion.
- We can prevent it by:
  - Coating of oil, paint varnish or enamel
  - Coating of metal with thin layer of another metal (electroplating)
  - Alloy formation.

Tin plating (cathode coating)	Zinc coating (anode coating)
Iron sheet is dipped in molten tin and then passed through hot pairs of roller	Iron sheet is dipped in $ZnCl_2$ and rolled in Zn bath and air-cooled.
Galvanic cell is formed when tin (Sn) layer is damaged	Galvanic cell is formed when Zn is damaged
Tin (Sn) acts as cathode	Fe acts as cathode
Fe acts as anode	Zn acts as anode
Electrons flow from Fe to tin (Sn)	Electron flow from Zn to Fe
Fe decays	Zn decays
	Its corrosion is called sacrificial corrosion as zinc sacrifice.

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