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2025-2026

PG TRB

G.O No. 219 New Syllabus

CHEMISTRY

UNIT-I
INORGANIC CHEMISTRY-1

Your Success is Our Goal...

CHEMISTRY

INORGANIC CHEMISTRY

PG TRB (2025-2026)

UNIT - 1

FIRST EDITION

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PG TRB CHEMISTRY

UNIT 1 - INORGANIC CHEMISTRY

SYLLABUS

Chemical Periodicity: Modern periodic law – Periodicity in properties, the trend in the atomic and ionic radii, ionization potential and electron affinity along the period. Effective nuclear charge – Slater rules and its uses.

Structure and bonding in homo – and hetero-nuclear molecules, including shapes of molecules. (VSEPR Theory): Linear combination of AOs in hybridization, Stereochemistry of the hybrid orbitals, Calculation of s & p characters of equivalence and non-equivalence of hybrid orbitals.

MO theory: MO diagram for the homo-nuclear diatomic molecules, heteronuclear diatomic molecules and triatomic molecules.

Concepts of acids and bases: HSAB concept – theory, classification, characteristics of hard and soft species – symbiosis. Bronsted-Lowry concept – conjugate acid-base theory – relative strength of acids and bases, applications. Lewis concept-characteristic features of the Lewis theory.

Non-Aqueous Solvents: Classification of solvents –characteristics of a solvent/ ionizing solvent. Advantages and disadvantages of the following non-aqueous solvents: NH_3, HF, HCN, acetic acid, H_2SO_4. Molten salts as solvents and ionic liquids, supercritical fluids in inorganic chemistry.

Nature of bonding of Main group elements: Alkali and alkaline earth metal complexes: ligands – alkyl amines, alkoxides, b-diketone and crown ethers. Electron rich and electron deficient compound of main group elements. Allotropes of carbon.

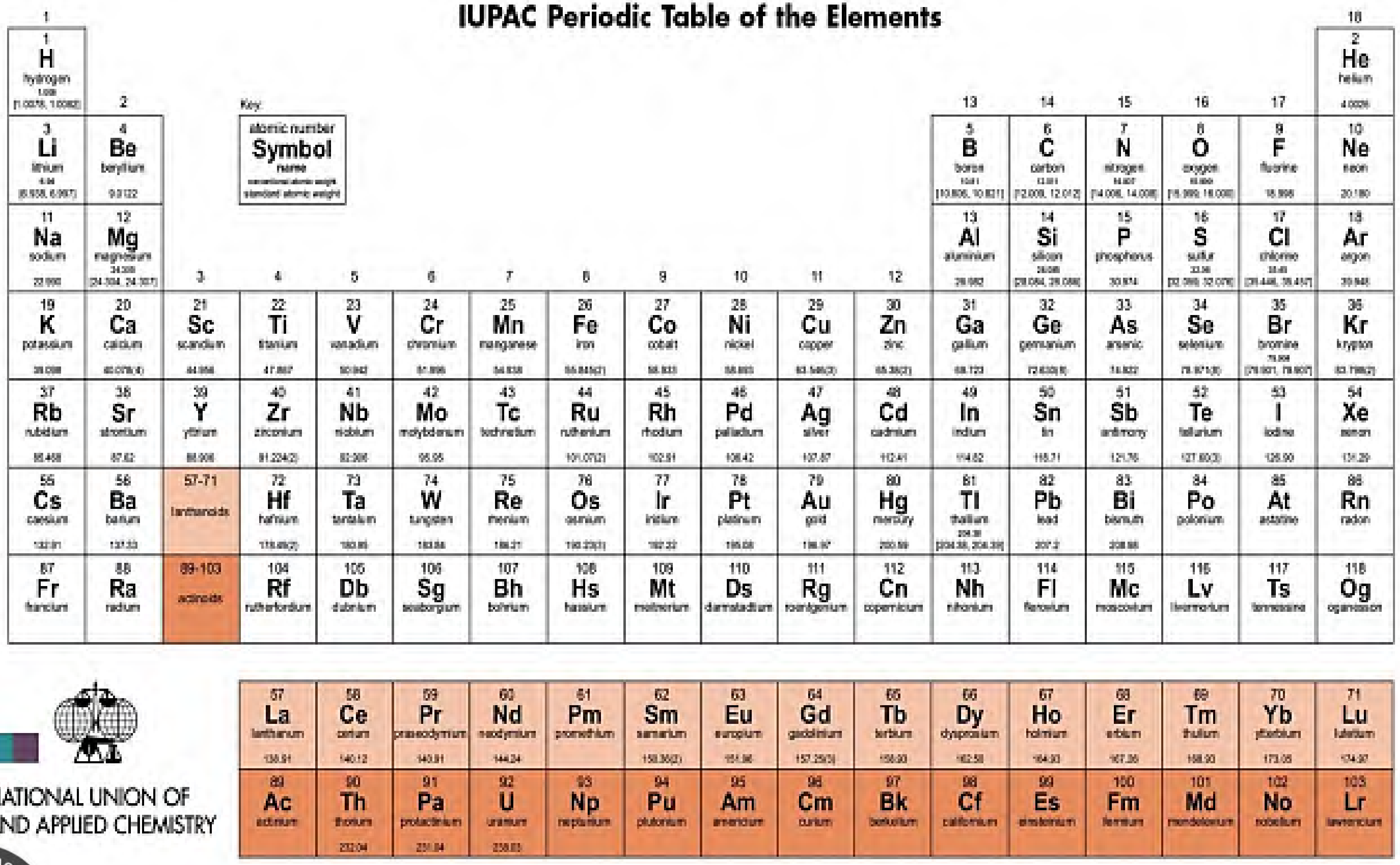
Transition elements and coordination compounds: Structure, bonding theories, spectral and magnetic properties, reaction mechanisms. Transition Elements – General group trends, Stability of various oxidation states. Difference between the first, second and third transition series. Types of transitions, selection rules for electronic transitions, ground states, correlation diagrams, Orgel and Tanabe Sugano diagrams.

Coordination compounds: Crystal field theory – splitting of d orbitals under different geometries – CFSE – Spectrochemical series – Jahn Teller distortion – Limitations of CFT – **MO theory** – sigma and pi-bonding in complexes.

Inner transition elements: Spectral, magnetic, redox properties and Its applications

1.1. CHEMICAL PERIODICITY

IUPAC Periodic Table of the Elements



Key:
atomic number
Symbol
name
conventional atomic weight
standard atomic weight

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H hydrogen 1.008 [1.0078, 1.0082]																	2 He helium 4.0026
3 Li lithium 6.94 [6.938, 6.997]	4 Be beryllium 9.0122											5 B boron 10.81 [10.806, 10.821]	6 C carbon 12.011 [12.009, 12.012]	7 N nitrogen 14.007 [14.006, 14.008]	8 O oxygen 15.999 [15.999, 16.000]	9 F fluorine 18.998	10 Ne neon 20.180
11 Na sodium 22.990	12 Mg magnesium 24.305 [24.304, 24.307]											13 Al aluminium 26.982	14 Si silicon 28.085 [28.084, 28.086]	15 P phosphorus 30.974	16 S sulfur 32.06 [32.059, 32.076]	17 Cl chlorine 35.45 [35.446, 35.457]	18 Ar argon 39.948
19 K potassium 39.098	20 Ca calcium 40.078(4)	21 Sc scandium 44.956	22 Ti titanium 47.867	23 V vanadium 50.942	24 Cr chromium 51.996	25 Mn manganese 54.938	26 Fe iron 55.845(2)	27 Co cobalt 58.933	28 Ni nickel 58.693	29 Cu copper 63.546(3)	30 Zn zinc 65.38(2)	31 Ga gallium 69.723	32 Ge germanium 72.630(8)	33 As arsenic 74.922	34 Se selenium 78.971(8)	35 Br bromine 79.904 [79.901, 79.907]	36 Kr krypton 83.798(2)
37 Rb rubidium 85.468	38 Sr strontium 87.62	39 Y yttrium 88.906	40 Zr zirconium 91.224(2)	41 Nb niobium 92.906	42 Mo molybdenum 95.95	43 Tc technetium	44 Ru ruthenium 101.07(2)	45 Rh rhodium 102.91	46 Pd palladium 106.42	47 Ag silver 107.87	48 Cd cadmium 112.41	49 In indium 114.82	50 Sn tin 118.71	51 Sb antimony 121.76	52 Te tellurium 127.60(3)	53 I iodine 126.90	54 Xe xenon 131.29
55 Cs caesium 132.91	56 Ba barium 137.33	57-71 lanthanoids	72 Hf hafnium 178.49(2)	73 Ta tantalum 180.95	74 W tungsten 183.84	75 Re rhenium 186.21	76 Os osmium 190.23(3)	77 Ir iridium 192.22	78 Pt platinum 195.08	79 Au gold 196.97	80 Hg mercury 200.59	81 Tl thallium 204.38 [204.38, 204.39]	82 Pb lead 207.2	83 Bi bismuth 208.98	84 Po polonium	85 At astatine	86 Rn radon
87 Fr francium	88 Ra radium	89-103 actinoids	104 Rf rutherfordium	105 Db dubnium	106 Sg seaborgium	107 Bh bohrium	108 Hs hassium	109 Mt meitnerium	110 Ds darmstadtium	111 Rg roentgenium	112 Cn copernicium	113 Nh nihonium	114 Fl flerovium	115 Mc moscovium	116 Lv livermorium	117 Ts tennessine	118 Og oganesson
			57 La lanthanum 138.91	58 Ce cerium 140.12	59 Pr praseodymium 140.91	60 Nd neodymium 144.24	61 Pm promethium	62 Sm samarium 150.36(2)	63 Eu europium 151.96	64 Gd gadolinium 157.25(3)	65 Tb terbium 158.93	66 Dy dysprosium 162.50	67 Ho holmium 164.93	68 Er erbium 167.26	69 Tm thulium 168.93	70 Yb ytterbium 173.05	71 Lu lutetium 174.97
			89 Ac actinium	90 Th thorium 232.04	91 Pa protactinium 231.04	92 U uranium 238.03	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fermium	101 Md mendelevium	102 No nobelium	103 Lr lawrencium

INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY

For notes and updates to this table, see www.iupac.org. This version is dated 28 November 2016.

- Dmitri Ivanovich Mendeleev (1834 – 1907), Russian chemist is introduced the periodic properties.
- Mendeleev’s name has been immortalized by naming the element with atomic number 101, as Mendelevium. This name was proposed by American scientist Glenn T. Seaborg, t.
- Mendeleev’s Periodic Law was, therefore, accordingly modified. This is known as the Modern Periodic Law and can be stated as: The physical and chemical properties of the elements are periodic functions of their atomic numbers.

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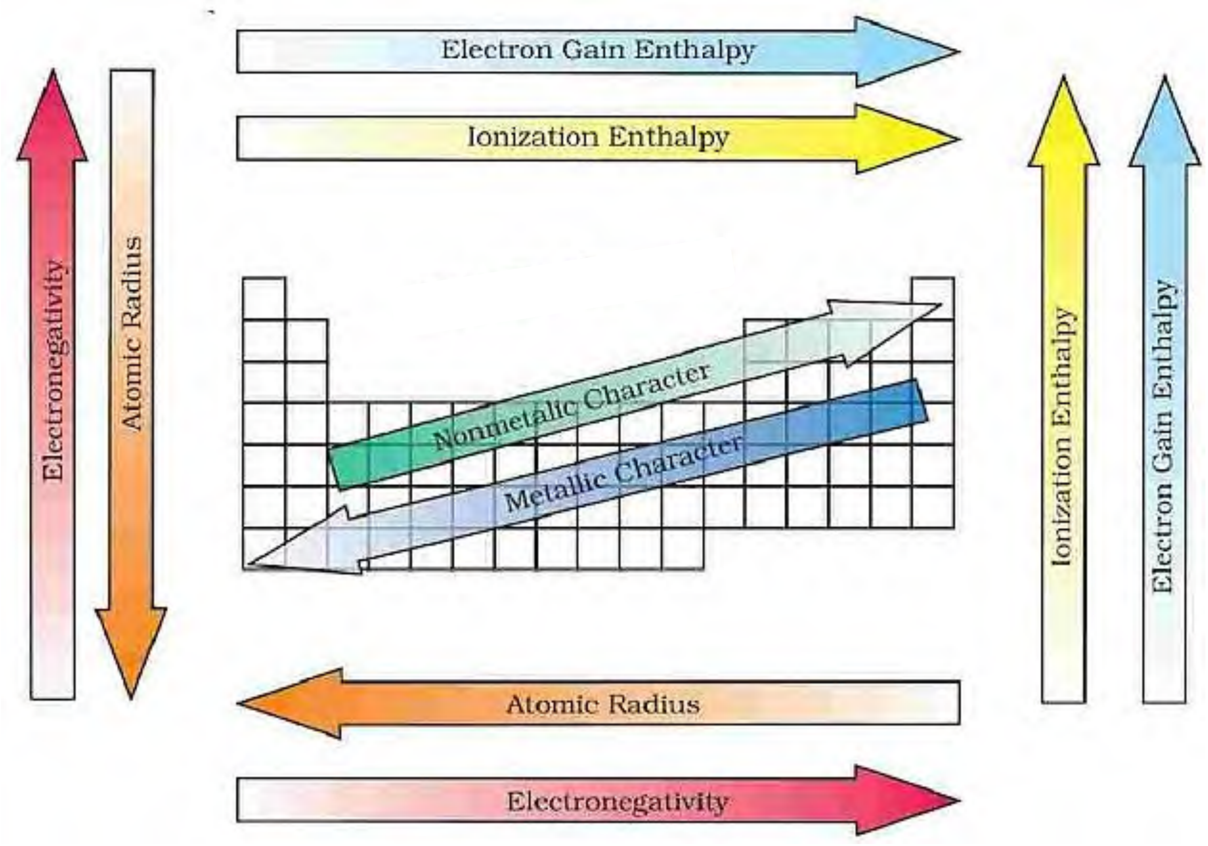
Representative elements | d-Transition elements | Representative elements | Noble gases

PERIOD NUMBER	1 IA	2 IIA	3 IIIA	4 IVA	5 VA	6 VIA	7 VIIA	8 ← VIII	9 VIII	10 VIII →	11 IB	12 IIB	13 IIIB	14 IVB	15 VB	16 VIB	17 VIIB	18 0
1	1 H $1s^1$																	2 He $1s^2$
2	3 Li $2s^1$	4 Be $2s^2$											5 B $2s^2 2p^1$	6 C $2s^2 2p^2$	7 N $2s^2 2p^3$	8 O $2s^2 2p^4$	9 F $2s^2 2p^5$	10 Ne $2s^2 2p^6$
3	11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^2 3p^1$	14 Si $3s^2 3p^2$	15 P $3s^2 3p^3$	16 S $3s^2 3p^4$	17 Cl $3s^2 3p^5$	18 Ar $3s^2 3p^6$
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^1 4s^2$	22 Ti $3d^2 4s^2$	23 V $3d^3 4s^2$	24 Cr $3d^5 4s^1$	25 Mn $3d^5 4s^2$	26 Fe $3d^6 4s^2$	27 Co $3d^7 4s^2$	28 Ni $3d^8 4s^2$	29 Cu $3d^{10} 4s^1$	30 Zn $3d^{10} 4s^2$	31 Ga $4s^2 4p^1$	32 Ge $4s^2 4p^2$	33 As $4s^2 4p^3$	34 Se $4s^2 4p^4$	35 Br $4s^2 4p^5$	36 Kr $4s^2 4p^6$
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^1 5s^2$	40 Zr $4d^2 5s^2$	41 Nb $4d^4 5s^1$	42 Mo $4d^5 5s^1$	43 Tc $4d^5 5s^2$	44 Ru $4d^7 5s^1$	45 Rh $4d^8 5s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10} 5s^1$	48 Cd $4d^{10} 5s^2$	49 In $5s^2 5p^1$	50 Sn $5s^2 5p^2$	51 Sb $5s^2 5p^3$	52 Te $5s^2 5p^4$	53 I $5s^2 5p^5$	54 Xe $5s^2 5p^6$
6	55 Cs $6s^1$	56 Ba $6s^2$	57 La* $5d^1 6s^2$	72 Hf $4f^{14} 5d^2 6s^2$	73 Ta $5d^3 6s^2$	74 W $5d^4 6s^2$	75 Re $5d^5 6s^2$	76 Os $5d^6 6s^2$	77 Ir $5d^7 6s^2$	78 Pt $5d^9 6s^1$	79 Au $5d^{10} 6s^1$	80 Hg $5d^{10} 6s^2$	81 Tl $6s^2 6p^1$	82 Pb $6s^2 6p^2$	83 Bi $6s^2 6p^3$	84 Po $6s^2 6p^4$	85 At $6s^2 6p^5$	86 Rn $6s^2 6p^6$
7	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac** $6d^1 7s^2$	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

f - Inner transition elements

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

- Long form of the periodic Table of the Elements with their atomic numbers and ground state outer electronic configurations. The groups are numbered 1-18 in accordance with the 1984 IUPAC recommendations. This notation replaces the old numbering scheme of IA-VIIA, VIII, IB-VIIB and 0 for the elements.



Modern Periodic Law

Introduction to Atom Models

- Let us recall the history of the development of atomic models from the previous classes. We know that all things are made of matter. The basic unit that makes up all matter is atom. The word ‘atom’ has been derived from the Greek word ‘a-tomio’ meaning non-divisible. Atom was considered as non-divisible until the discovery of subatomic particles such as electron, proton and neutron. J. J. Thomson’s cathode ray experiment revealed that atoms consist of negatively charged particles called electrons. He proposed that atom is a positively charged sphere in which the electrons are embedded like the seeds in the watermelon.

a. Rutherford’s Atom model

- Later, Rutherford’s α-ray scattering experiment results proved that Thomson’s model was wrong. Rutherford bombarded a thin gold foil with a stream of fast moving α–particles. It was observed that

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(i) Most of the α–particles passed through the foil

(ii) Some of them were deflected through a small angle and

(iii) Very few α–particles were reflected back by 180° Figure.

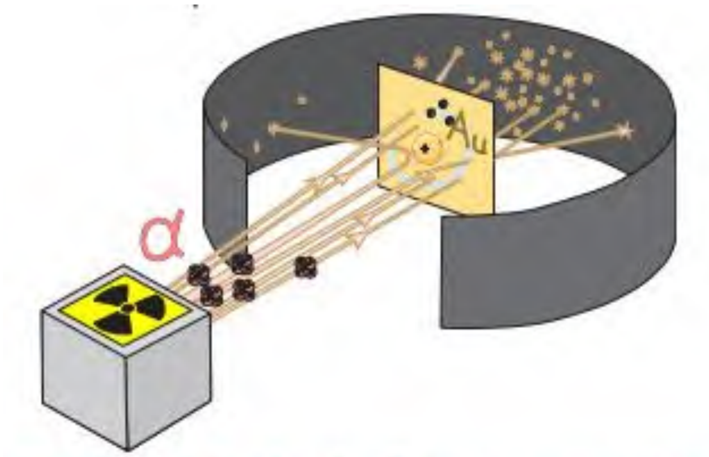

Figure. 2.1 Rutherford's α-ray scattering experiment

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

b. Bohr atom model:

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

1. The energies of electrons in an atom are quantised.
2. The electron is revolving around the nucleus in a certain circular path of fixed energy called stationary orbit.
3. Electron can revolve only in those orbits in which the angular momentum (mvr) of the electron must be equal to an integral multiple of h/2π. i.e. mvr = nh/2π -------- (2.1) where n = 1,2,3,...etc.

Periodic Law

- **"The physical and chemical properties of elements are a periodic function of their atomic masses."**
- On the basis of this law he arranged all the elements in order of increasing atomic mass and he found that **after certain regular intervals repetition in properties occur.**

A. Merits of Mendeleev's Table

(i) First systematic classification of elements by forming a table. Mendeleev's periodic table has **8 groups** and **7 periods.**

(ii) Correction of Atomic Masses of the elements was done.

(iii) He left a certain **gap** in the periodic table for **undiscovered elements** and he predicted the properties of those elements correctly. For instance, what he called **Eka-Aluminium** is now a days **Gallium** and what he called **Eka-Silicon** is now a days **Germanium**.

B. Demerits of Mendeleev's Table

(i) Anomalous position of **Hydrogen.** He failed to justify the position of Hydrogen because some properties of hydrogen were **similar to alkali metals** and some other properties were similar to **halogens**.

(ii) **Cause of periodicity**: He failed to explain **why the repetition** in properties occur after certain regular intervals.

(iii) He failed to accommodate Lanthanides & Actinides in the main body of the periodic table.

(iv) Some pairs did not obey the rule of increasing atomic masses. For instance **Tellurium with atomic number 52 had a mass of 127.60u but Iodine with atomic number 53 had a mass of 126.90** which was less than that of Tellurium.

(v) He failed to justify the **position of isotopes** in the periodic table.

Qn. No. 16, NET - 2017

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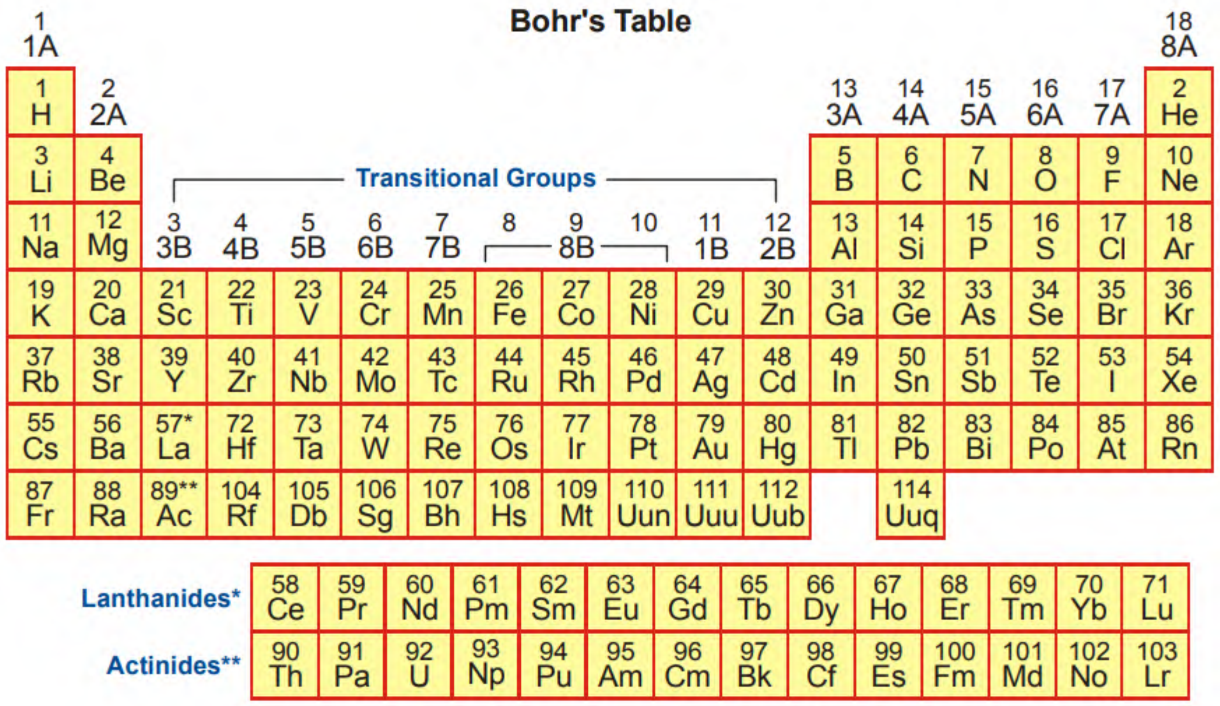
Modern Periodic Law And Modern Periodic Table

- Moseley showed that bombarding a beam of high velocity electrons on a target metal resulted in generation of X – rays. The square root of the frequency $\sqrt{\gamma}$ of these X- rays was found to be directly proportional to the atomic number (Z) of the target metal. This was be represented by the following expression.

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

- Where Z is the atomic number of the target element and (a) and (b) are Moseley's constants. The results of this experiment led to the **re-framing of the periodic law**. The modern periodic law was hence propounded as, **"The physical and chemical properties of elements are a periodic functions of their atomic numbers".**

Long Form of the Modern Periodic Table:



Bohr's Table

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
		Transitional Groups															
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57* La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89** Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub		114 Uuq				

Lanthanides*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides**	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Some Important Points about the Modern Periodic Table:

a. It consists of **eighteen groups**. Each group consists of a number of elements having the **same outer electronic configuration.**

b. The elements of **18th group** are called inert gases or noble gases.

c. The elements of groups 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 are called **transition elements.**

d. Two series each of **14 elements** are placed at the bottom of the periodic table, known as **Lanthanides and Actinides** (Inner Transition Elements)

e. There are 7 known periods (horizontal rows) in this table. Distribution of element in different periods are as below:

1st Period	2
2nd and 3rd period	8
4th and 5th period	18
6th period	32
7th period	Incomplete

Atomic Size

(i) Atomic Radius: It is the **distance from the centre of the nucleus to the outer most shell containing electron**. It is impossible to isolate the atom and determine its radius precisely because its radius on is affected by its association with its neighbourhood. On the basis of the bond formed between atoms we can estimate the radius of the atom with great precision. Some of the radii are mentioned here:

(d) Ionic Radius: The Ionic radius may be defined as the effective **distance from the centre of the nucleus of the ion upto which it exerts its influence on the electron cloud.**

Atomic radii decrease along the period in periodic table. (Qn. No: 65, PGTRB- 2001)

Ionization energy and atomic number are found in rare gases (Qn- 1,PGTRB, 2002-03)

(i) The **radius of cation is always smaller than that of its parent atom due to higher effective nuclear charge** after removal of electron.

e.g., $\underset{1s^2 2s^2 2p^6 3s^1}{Na} \rightarrow \underset{1s^2 2s^2 2p^6}{Na^+} + e^-$

Due to removal of a valence electron, the number of electrons decrease. Each electron now experiences greater nuclear pull. As a result, the size of cation is smaller than that of the parent atom.

The smallest ionic radius of potassium is 1.34Å (Qn-57, TRB-2005-06)

(i) The **radius of anion is always larger than that of its parent atom**.

$\underset{1s^2 2s^2 2p^6 3s^2 3p^5}{Cl} + e^- \rightarrow \underset{1s^2 2s^2 2p^6 3s^2 3p^6}{Cl^?}$

(ii) An anion is formed by **gain of electron**, which increases the number of electrons in the same shell. The **effective nuclear charge now decreases** and each electron **experiences reduced nuclear pull.** Repulsions between valence electrons now cause the cloud to expand making the anion larger in size than the neutral atom.

- **Iso-electronic ions**: Ions of different elements which have the same number of electrons but different magnitude of nuclear charge are called isoelectronic ions.
- **Variation of size:** The **ionic radius of iso-electronic ions decreases with the increase in the magnitude of nuclear charge.** e.g., among isoelectronic ions of the second period the order of radius should be $C_4 > N^{3-} > O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}$ and among those of the third period: $Si_4^- > P_3^- > S_2^- > Cl > K^+ > Ca^{2+}$
    - **Qn. No. 16, June, NET – 2016**

- **The Correct Order Of Decreasing Ionic Radius For The Isoelectronic Species (Qn. 2, Trb – 2002- 03)**
  - **The smallest ionic radius is (Qn.57, TRB – 2005-06), (Qn.5, TRB – 2002)**
  - **The nuclear charge increases, the ionic radius decreases.**

(iii) Factors affecting the Atomic Radii:

a. **Number of Shell:** More the **number of the shells** filled with electrons, **larger will be size.**

b. **Nuclear Charge:** Nuclear charge attracts the electrons toward itself and attempts to decrease the size. This is **nuclear charge effect.** Generally, **across the period size decreases** because **with increase in atomic number effective nuclear charge increases**. As electrons are filled in the same shell they contract towards the nucleus causing size to decrease. **Down the group size generally increases, addition of an extra shell causes effective nuclear charge to decrease on the valence electron.**

c. The atomic radii of N, O and C are 70, 74 and 77 pm respectively while electronegativities are 3.0, 3.5 and 2.5 respectively. The N-O and C-O bond lengths are respectively : 139.5 pm, 142 pm. **[PGTRB, Qn.No.6, 2019]**

d. **Screening Effect or Shielding Effect**: The inner layer of the electron act as shield between nucleus and valence electron. This is known as shielding effect or screening effect as discussed earlier. Effective screening therefore attempts to increase the size and ineffective screening causes a decrease in atomic radius.

(iv) Periodicity in Atomic Radius

a. **In a Period:** The number of orbit remains same on going from left to right in a period while effective nuclear charge increases. So, **atomic radius decreases across the period**.

b. **In a Group:** The **atomic radius increases on going down a group** due to addition of an extra shell.

Ionization Energy (Enthalpy)

- It is the amount of energy required to **remove the outer most electron** from an **isolated atom in gaseous state.**

$$M(s)\xrightarrow{\Delta H_{\text{sublimation}}}M(g)$$

$$M(g)\xrightarrow{\Delta H_{ionization}}M^{+}(g)+e^{-}$$

- Neutral isolated gaseous atom is produced by firstly subliming the metal atom from its solid state. Further on, the energy needed to **knock off the first outermost electron** is called the **first ionization enthalpy**. As this is the energy required, so **value of ionization enthalpy is always positive.**
- **The first ionization potential of calcium is greater than of potassium because**

(Qn- 2, TRB-2003-04)

- Unit wise, ionization enthalpy is expressed in kJ/mole or kCal/mol, however for an atom if the energy unit is in terms of eV then ionization enthalpy can also be referred to as **ionisation potential.**

NET – 2015

June, NET – 2014 Part – B

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- **The element with first ionization potential is (qn-56, TRB-2014-15)**
- **Ionization potential of hydrogen is 13.6v (Qn-52, TRB-2004-05)**
- **The molecules having lowest ionization potential is (Qn- 137, TRB-2012-13)**

Successive Ionisation Energy

a. **Ionisation Energy (First):** It is the amount of energy required to remove the outer most e from an atom in gaseous state.

b. **Ionisation Energy (Second):** It is the amount of energy required to remove the 2nd e- from same atom in gaseous state.

Important Fact: $I.E_2 > I.E_1$

- Because 2nd electron has to be removed from a cation which has **high effective nuclear charge** and **smaller size** than the neutral atom.
- Ionisation energy generally **increases across a period** and **decreases down the group. Successive ionization energies are always larger. There is no exception to this rule.**

Electron Gain Enthalpy

- It is the **enthalpy change** when an **electron is added to the gaseous neutral atom.**
- Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion.

$$X(g) + e^- \rightarrow X^-(g);\ \Delta H = A_{eg}H \quad ..(i)$$

- **The negative of the enthalpy change for the process shown in equation is defined as electron affinity of the atom undergoing the change for formation of anion.**

- Depending on the element, enthalpy change in process may be **endothermic** or **exothermic.** When electron is added to gaseous neutral atom that has a **natural tendency to accept an electron then energy is released, electron gain enthalpy is negative and electron affinity is positive.**
- When an electron is added to an element that **does not have a natural tendency to accept an electron then energy will be absorbed electron gain enthalpy will be positive and electron affinity will be negative.**

Electronegativity

- Electronegativity is a **measure of the tendency of an element to attract bonded electron pair** towards (itself) in a covalent bonded molecule.

(i) Factors on which electronegativity depend:

a. **Atomic Size**: **Electronegativity is inversely proportional to the size.** Small sized elements generally have higher electronegativity.

b. **Effective Nuclear Charge:** Electronegativity is **directly proportional** to the effective nuclear charge. Elements such as fluorine have highest effective nuclear charge in the second period and hence have the highest electronegativity.

c. **Hybridization:** More is the s-character in hybridization, higher will be electronegativity. The order of electronegativity among different hybridizations is: **sp hybrid carbon >sp^2 hybrid carbon > sp^3 hybrid carbon**

(ii) Electronegativity Scales:

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

a. **Mulliken Scale:** According to Mulliken, Both ionization energy and electron affinity are taken in eV/atom.

b. **Pauling Scale**: Linus Pauling developed a method for the calculation of relative electronegativity of element.

c. Pauling's Formula: $\boxed{|\chi_A - \chi_B| = 0.208\sqrt{\Delta E}}$

Where, $\Delta E =$ Bond energy of $(A-B) - \sqrt{B.E.\ of\ A-A \times B.E. of\ B-B}$

[Bond enthalpy is taken in kcal/mole]

d. **Relation between Mulliken and Pauling Scale**: The value of electronegativity for an element in **Mulliken scale is 2.8 times higher than Pauling's value.**

e. **Allred Rochow's Electronegativity**: Allred and Rochow defined electronegativity as the force exerted by the nucleus of an atom on its valence electrons:

$$\boxed{\text{Electronegativity} = 0.744 + \frac{0.359\,Z_{eff}}{r^2}}$$

- Here, Z_{eff} is effective nuclear charge and r is the radius of the atom.
- On the Pauling Scale: **Fluorine is most electronegative element** with an electronegativity value of **4.0** followed by **oxygen with a value of 3.5.**

1. **According to modern periodic law**, the properties of elements are the periodic functions of their atomic numbers. In modern periodic table, the horizontal lines are periods and the vertical lines are groups.

   The periodic table has total 7 periods and 18 groups. If elements are arranged in increasing order of their atomic numbers, there is repetition of properties after 2, 8, 18, and 32 elements. There are two elements in the first period, eight elements in each of the second and third periods, eighteen elements in each of fourth and fifth period, thirty two elements in the sixth period and only nineteen elements till now in the seventh period.

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Periodic classification of elements:

(i) s-block Elements:

- The elements of the periodic table in which the last electron enters in s-subshell, are called s-block elements. It contains elements of group s_1 and s_2 and their general configuration is ns^{1-2}, where n represents the outermost shell. The total number of s-block elements are 14. IA group elements are known as alkali metals whereas the elements of II A group are known Chemical periodicity as alkaline earth metals. Fr87 and Ra88 are radioactive elements, H and He are gaseous elements and Cs and Fr are liquid elements among the s-block elements.

(ii) p-block Elements:

- The elements of the periodic table in which the last electron enters in p-subshell are called p-block elements. p-block contains elements groups 13, 14, 15, 16, 17 and 18 of the periodic table. The general configuration of p-block elements are ns2np1-6 (where n = 2 to 6). The total number of p-block elements in the periodic table is 30 (excluding He). Most of these elements are non-metals, some are metalloids and few others are heavy elements which exhibit metallic character.

(iii) d-block Elements:

- ➢ The elements of the periodic table in which the last electron gets filled up the d-orbital called d-block elements. The general electronic configuration is $(n-1)d_{1-10}$, ns_{1-2}. The dblock contains elements of group 3 to 12 of the periodic table. In d-block elements, the electron get filled up in the d-orbital of penultimate shell, that is why, these elements are known as Transition elements. The total d-block elements in periodic table are 33. Out of all the d-block elements mercury is the only liquid elements.

(iv) f-block Elements:

- ➢ The elements of the periodic table in which the last electron gets filled up in the f orbital are called f-block elements. There is 28 f-block elements in the periodic table. The elements from atomic number 58 to 71 are called lanthanides because they come after lanthanum (57). The elements from atomic number from 90 to 103 are called Actinides because they come after actinium (39). All the actinium elements are radioactive. The general electronic configuration of these elements is $(n-2)f_{1-14}(n-1)\ d_{0-1}$, ns_2. All the elements after atomic number 92 (i.e., U_{92}) are transuranic elements.

The Types of Elements:

(i) **Inert gases:** The general electronic configuration of these elements is $ns_2\ np_6$. These have filled s and p orbitals of the outermost shell. So, these elements are stable and rarely take part in a reaction. Helium is also inert gas but its electronic configuration is 1s2.

(ii) **Representative elements:** s and p-block elements except inert gases are called representative elements. Outermost shell of these elements is incomplete.

(iii) **Transition elements:** These elements have partially d-orbitals in neutral state or in any stable oxidation state. The outermost electronic configuration is similar to d-block elements, i.e., $(n-1)d_{1-10}ns_{1-2}$. Chemical periodicity

(iv) **Inner transition element:** In these elements last three shells i.e, last, penultimate and prepenultimate shells are incomplete. These are related to III B i.e., group -3. Their outermost electronic configuration is similar to f-block elements i.e., $(n-2)f\ _{1-14}$, $(n-1)s_2$,$(n-1)p_6$, $(n-1)d_{0-1}ns_2$.

MULTIPLE CHOICE QUESTIONS - 1

1. The atom having the valence-shell configuration $4s^2\ 4p^5$ would be in:

A) Group VIA and Period 5 B) Group IVB and Period 4

C) Group VIB and Period 7 D) Group VIIA and Period 4

E) Group VIIB and Period 4

2. Select the term best describing the series of elements: Mn, Fe, Co, Ni, Cu.

A) d-transition metals B) representative elements

C) metalloids D) alkaline earth metals

E) halogens

3. Which element has the **largest** atomic radius?

A) Li B) Na C) Rb D) F E) I

4. Which of the following terms accurately describes the energy associated with the process?

$$Li(g) \rightarrow Li^{+}(g) + e^{-}$$

A) electron affinity B) binding energy

C) ionization energy D) electronegativity

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E) none of these

5. The species that contains 24 protons, 26 neutrons and 22 electrons would be represented by the symbol:

A) $^{50}V^{3+}$ B) $^{26}Cr^{2+}$ C) $^{50}Cr^{2+}$ D) $^{50}Mn^{2+}$

E) none of these

6. Which element has the **lowest** first ionization energy?

A) He B) Ne C) Ar D) Kr E) Xe

7. Which element has the **highest** first ionization energy? (Note: this is an exception to the general trend - see notes- you may be responsible for this.)

A) Be B) B C) C D) N E) O

8. Which of these isoelectronic species has the **smallest** radius?

A) Br^{-} B) Sr^{2+} C) Rb^{+} D) Se^{2-}

E) They are all the same size because they have the same number of electrons.

9. Which of the following elements has the greatest attraction for electrons in a covalent bond?

A) Ge B) As C) Se D) Br E) Bi

10. Which statement is **wrong**?

A) The atomic weight of carbon is about 12.

B) The most stable ion of lithium is Li^{+}.

C) A phosphorus atom is larger than an antimony atom.

D) The radius of a sodium atom is larger than that of a sodium cation.

E) Oxygen has a less negative electron affinity than fluorine.

11. All of the following properties of the alkaline earth metals increase going down the group **except**

A) atomic radius
B) first ionization energy
C) ionic radius
D) atomic mass
E) atomic volume

12. Which of the following is an ionic hydride?

A) PH_3
B) H_2S
C) HI
D) KH
E) CH_4

13. Which of the following is the most basic oxide?

A) N_2O_3
B) N_2O_5
C) P_4O_6
D) P_4O_{10}
E) Bi_2O_5

1.2. PERIODICITY IN PROPERTIES

- Periodicity refers to trends or recurring variations in element properties with increasing atomic number. The properties of elements are periodic functions of their atomic numbers. If elements are arranged in increasing order of their atomic number, there is repetition of properties of elements with similar properties after certain regular intervals is known as periodicity. The periodic repetition of properties is due to the recurrence of similar valence shell configurations after regular intervals.

Example of some periodic properties of atoms:

(i) melting and boiling point
(ii) density
(iii) atomic radii and ionic radii
(iv) ionization potential
(v) electron affinity
(vi) electronegativity etc.

Aperiodicity: Not periodic; not occurring at regular intervals.

MULTIPLE CHOICE QUESTIONS - 2

1. Which statement is **false**? A sigma molecular orbital

A) may result from overlap of p atomic orbitals perpendicular to the molecular axis (side-on).

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G.O No. 219 New Syllabus

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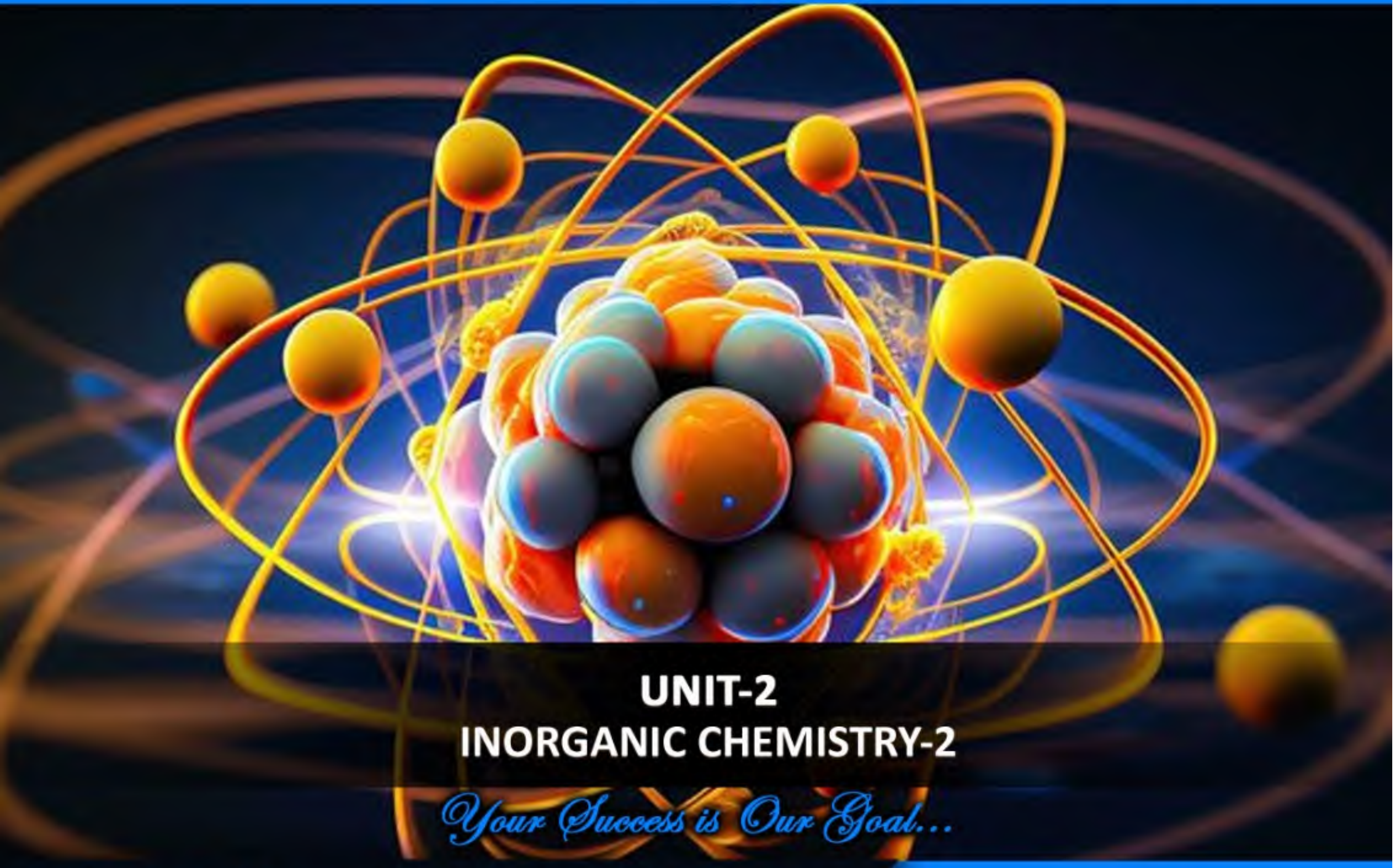

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UNIT 2 - INORGANIC CHEMISTRY

SYLLABUS

ORGANOMETALLIC COMPOUNDS:

Synthesis, Structure of Bonding and Important Types of Reactions of Organometallic Compounds – Oxidative Addition, Reductive Elimination. Catalysis – Hydrogenation, Hydroformylation, Monsanto and Wacker Processes, Alkene Polymerization.

CAGES AND CLUSTERS:

Chemistry and Molecularity of Metal Clusters such as Binuclear and Trinuclear Metal Clusters, Metal Carbonyl, Halide Type Clusters, Borazines and Phosphazenes.

BIOINORGANIC CHEMISTRY:

Structures and Biological Importance of Porphyrin Ring System, Metalloporphyrin, Haemoglobin, Myoglobin and CHLOROPHYLL. IRON-SULPHUR Proteins, Metalloenzymes, Photosynthesis – Photosystem-I and Photosystem-II. Metal Storage and Transport – Fe, Cu and Zn Storage and Transport.

NUCLEAR CHEMISTRY:

Nuclear Fission and Fusion Reactions, Radio-Analytical Techniques and Activation Analysis. Decay Modes, Types of Nuclear Reaction – Threshold Energy, Energy Barrier, Q-Value, Nuclear Cross Section, Photonuclear Reaction, Nuclear Fission, Spallation, Fragmentation and Fusion. Fission as a Chain Reaction – Nuclear Fuels: Fertile and Fissile Isotopes, Radiation Hazards – Nuclear Reactors in India.

2.1. ORGANOMETALLIC COMPOUNDS

- All transition elements exhibit a characteristic property of complex ion formation. The compounds containing complex ions are called coordination compounds. The branch of chemistry in which coordination compounds are studied that is called coordination chemistry.

(1) Double Salts and Co-Ordination Compounds:

- When solutions of two or more stable compounds are mixed in stoichiometric (simple molecular) proportions new crystalline compounds called molecular or addition compounds are formed. These are of two types, (1) Double salts, (2) Co-ordination or Complex compounds (1) Double salts : Addition compounds, stable in solid state. Dissociate into ions in aqueous solution as such give test for each constituent ion.

Examples:

Double Salt	Responds test for the ions
Carnalite: $KCl \cdot MgCl_2 \cdot 6H_2O$	K^+, Mg^{2+}, Cl^-
Potash alum: $K_2SO_4 \cdot Al_2(SO_4)_3 24H_2O$	K^+, Al^{3+}, SO_4^{2-}

(2) Co-ordination or Complex compounds:

- Addition compound, stable in solid state. Retain their identity even in solution. Central metal ion form dative or coordinate bond with the species surrounding it (ligands).

Examples:

Complex compound	Cation	Anion
$\left[Cu(NH_3)_4\right]SO_4$	$\left[Cu(NH_3)_4\right]^{+2}$	SO_4^{2-}
$K_2\left[PtF_6\right]$	$2K^+$	$\left[PtF_6\right]^{2-}$
$\left[Co(NH_3)_6\right]\left[Cr(CN_3)_6\right]$	$\left[Co(CN_3)_6\right]^{2+}$	$\left[Cr(CN)_6\right]^{3-}$

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(3) Terminology of co-ordination compounds

(1) Central metal atom or ion: A complex ion contains a metal atom or ion known as the central metal atom or ion. It is sometimes also called a nuclear atom.

(2) Complex ion: It is an electrically charged radical which is formed by the combination of a simple cation with one or more neutral molecules or simple anions or in some cases positive groups also.

(3) Ligands: Neutral molecules or ions that attach to central metal ion are called ligands. The donor atom associated with the ligands supplies lone pair of electrons to the central metal atom (forming dative bond) may be one or two more. Monodentate (one donor atom), bidentate (two donor atom), tridentate (three donor atom) etc.

Monodentate Ligands (with one donor site)

Formula	**Name**	**Formula**	**Name**
X^-	Halo	O_2^{2-}	Peroxo
$:OH^-$	Hydroxo	CH_3COO^-	Acetato
CN^-	Cyano	NO_3^-	Nitrato
O^{2-}	Oxo	$S_2O_3^{2-}$	Thiosulphato
NH_2^-	Amido	NO_2^-	Nitrito
S^{2-}	Sulphido	CO_3^{2-}	Carbonato
CNS^-	Thiocyanato	SO_4^{2-}	Sulphato

Table: 20.2 Neutral Ligands

Formula	**Name**	**Formula**	**Name**
CO	Carbonyl	$:NH_3$	Amminato
PH_3	Phosphine	H_2O	Aqua
NO	Nitrosyl	$C_5H_5N:$	Pyridine (py)

Table: 20.3 Cationic Ligand (Positive)

Formula	**Name**	**Formula**	**Name**
NO_2^+	Nitronium	NO^+	Nitrosonium
$H_2NNH_3^+$	Hydrazinium		

Polydentate Ligands (with two or more donor site)

Table 20.4 Bidentate (Two donor sites)

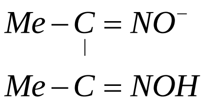
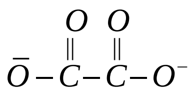
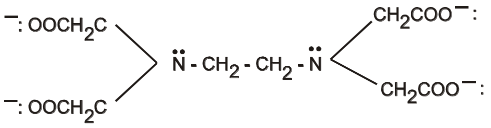
Formula	Name	Formula	Name
$H_2NCH_2CH_2NH_2$	Ethylenediamine (en)	 $\begin{array}{c} Me-C=NO^- \\ \vert \\ Me-C=NOH \end{array}$	Dimethylglyoximeto(dmg)
 $\overset{-}{O}-\overset{\overset{O}{\parallel}}{C}-\overset{\overset{O}{\parallel}}{C}-O^-$	Oxalato (ox)	$NH_2-CH_2-COO^-$	Glycinate ion (gly)

Table 20.5

	Formula	Name
Tridentate	$H_2\ddot{N}(CH_2)_2-\ddot{N}H-(CH_2)_2\ddot{N}H_2$	Diethylenetriaminediamine(dien)
Tetradebtate	$H_2\ddot{N}(CH_2)_2-\ddot{N}H-(CH_2)_2\ddot{N}H(CH_2)_2\ddot{N}H_2$	Triethylenetetra-mine (trien)
Hexadentate		Ethylenediamine tetraacetic acid (EDTA)[4]

Chelating Ligand:

- When polydentate ligands bind to the central metal ion they form a ring called chelate and the ligand is referred as chelating ligand.

Ambidentate Ligands:

- A ligand which possesses two donor atom but in forming complex it utilizes only one atom depending upon the condition and type of complex.
- NO_2 (Nitro), ONO (nitrito), CN (cyano), NC (isocyano), SCN (thiocyanide), NCS (isothiocyanide)

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π-Acid Ligand:

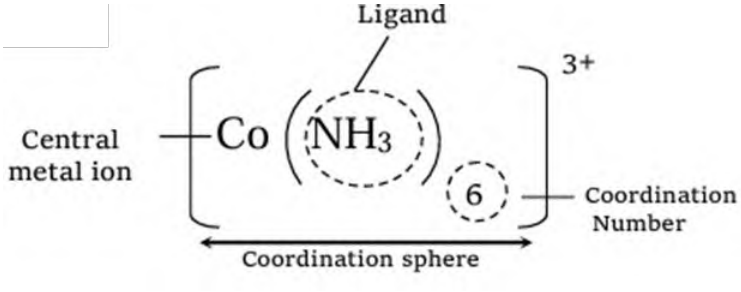
- Ligands which are capable of accepting an appreciable amount of π - e^- density from the metal atom into emptying π or $\pi*$orbital or their own called π - acceptor of π - acid ligands eg. CO.

(4) Co-Ordination Sphere:

- Ligand with central metal ion is kept in square bracket [ ] retains its identity in the same form is called co-ordination sphere (non-ionisable)

(5) Co-Ordination Number:

- Number of monodentate ligands attached to central atom/ion are called coordination number of the central metal atom/ion.



(6) Ionisation Sphere:

- The part present outside of the square bracket is called ionization sphere (ionisable).

IUPAC Nomenclature of complex compounds In order to name complex compounds certain rules have been framed by IUPAC. These are as follows

(1) The positive part of a coordination compound is named first and is followed by the name of negative part.

(2) The ligands are named first followed by the central metal. The prefixes di-, tri-, tetra-, etc., are used to indicate the number of each kind of ligand present. The prefixes bis (two ligands), tris (three ligands), etc., are used when the ligands includes a number e.g., dipyridyl, bis (ethylenediamine).

(3) In polynuclear complexes, the bridging group is indicated in the formula of the complex by separating it from the rest of the complex by hyphens. In polynuclear complexes (a complex with two or more metal atoms), bridging ligand (which links two metal atoms) is denoted by the prefix □ before its name.

(4) Naming of ligands : The different types of ligands i.e. neutral, negative or positive are named differently in a complex compound. When a complex species has negative charge, the name of the central metal ends in – ate. For some elements, the ion name is based on the Latin name of the metal (for example, argentate for silver). Some such Latin names used (with the suffix – ate) are given below.

(OR) Additional notes

Organometallic Compounds

- Organometallic compounds are those “compounds in which central metal atoms are directly bonded with the carbon atoms of the hydrocarbon radical or molecule” or An Organometallic compound is defined as one that possesses a metal-carbon bond.

- The term “Organometallic” generally denotes compound in which organic groups are directly linked to the metal through at least one carbon atom.
- The bonding is ionic or covalent or delocalised between organic groups and a metal atom. Simple organometallic compounds are one which a metal-carbon bond which is typically similar with respect to the derivative of associated constituent.

Further divided in to a) Symmetrical:

- Example: [Hg $(C_2H_5)_2$] Diethyl mercury

b) Unsymmetrical: Example: CH_3-Hg-C_2H_5 Ethyl methyl mercury A mixed organometallic compounds are those in which a metal atom bonded with more than one identity of organic or inorganic constituent. Example: C_2H_5-Mg-Br Ethyl magnesium bromide.

Classification of Organometallic Compounds:

- On this basis of nature of metal- carbon bond organometallic compounds are classified in to ″ Ionic bonded organometallic compounds: The organometallic compounds of alkali, alkaline earth metals, Lanthanides and Actinides are predominantly form ionic compounds. These are generally colourless compounds extremely reactive, non-volatile solids and insoluble in organic solvents. Examples: $Ph_3C^-Na^+$, Cp_2Ca, Cs^+Me^- , Na^+Cp^-.

[PGTRB – 2007, Qn.No. 48]

Covalent Bonded Organometallic Compounds:

1) σ- bonded organometallic compounds: These are the compounds in which carbon atom of the organic ligand is bonded to the metal by a 2 electron, 2 centered (2e-2c) covalent bond. Generally formed by most of the elements with values of electronegativity are higher than 1.

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- Examples: Ni $(CO)_4$, Fe $(CO)_5$

2) π- bonded organometallic compounds: These are alkene, alkyne or some other carbon group has a system of electron in π-orbitals overlap of these π- orbitals with vacant orbitals of the metal atom gives rise to arrangement in which the metal atom is bonded to several carbon atom instead of to one. Examples: [(η_5 -$C_5H_5)_2$Fe)], K [$PtCl_3$ (η_2 -C_2H_2)] (Zeise’s salt) ″**[PGTRB 2014-2015, Qn. No. 8]**

Multicentre Bonded Organometallic Compounds:

- The compounds in which a loosely bonded electron deficient species exist with the coordination of metal like Li, Be, Al…etc Examples: MeLi or $(CH_3)_4Li_4$, Al_2Me_6.
- Classification of ligands based on hapticity: In hapto classification organic ligands are classified according to “number of carbon atoms within a bonding distance of metal atom

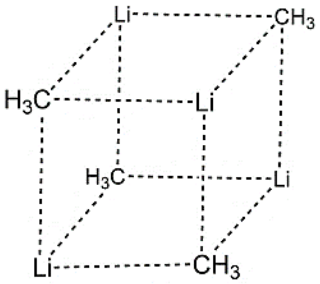
or the no. of carbon atoms through which an organic ligand is attached to central metal atom” is known as “hapticity” of the ligand. This is represented by the symbol “ ηn” appearing beforethe symbol of the ligand. Where, n- hapticity of the ligand.

Monohepto Ligands (η_1):

- Organic ligands attached to the metal through one carbon.
  - Ex: $-CH_3$, $-C_2H_5$
- Dihepto ligands (η_2): Example: $CH_2=CH_2$, $K[PtCl_3(\eta_2 -C_2H_2)]$ (Zeise’s salt)
- Trihepto ligands (η_3): Example: Allylic radical $CH_2=CH-CH_2^-$
- Tetrahepto ligands (η_4): Example: Butadiene $CH_2=CH-CH= CH_2$
- Pentahepto ligands (η_5): Example: Metallocene $M (\eta_5 -C_5H_5)_2$
- Hexahepto ligands (η_6): Example: Dibenzene ChromiumCr $(\eta_6 -C_6H_6)$

Structure of Methyl Lithium:

- CH_3Li in nonpolar solvents consists of tetrahedron of Li atoms with each face ridged by a methyl group.
- The bonding in CH_3Li consists of a set of localized molecular orbitals. The symmetric combination of three Li 2s orbitals on each face of the Li^4 tetrahedron and one sp^3 hybrid orbital from CH_3 gives an orbital that can accommodate a pair of electron to form a 4c-2e bond.
- The lower energy of the C - orbital compared with the Li orbitals indicates that the bonding pair of electrons will be associated primarily with the CH_3 group, thus supporting the carbanionic character of the molecule.
- Some analysis has indicated that about 90% ionic characters for the $Li-CH_3$ interaction.



Structure of Zeise’s salt: $K [PtCl_3 (\eta_2-CH_2=CH_2)]$:- Potassiumtrichloro (ethene) platinate (II)

1) Zeise’s salt was the first organometallic compond to be isolated in pure form (1825 by William Zeise). It is a square planar complex with 16 electrons.

Zeise's salt is represented as (a) H_3PtCl_6 (b) $[PtCl_4]^{2-}$ (c) $[ZnCl_4]^{2-}$ (d) $[PtCl_3(\eta_2 - C_2H_4)]^-$ Ans. (d) : Zeise's salt is potassium trichloro (ethylene) platinate (II)hydrate, $K[PtCl_3(C_2H_4)].H_2O$. The anion of this yellow co-ordination complex contains an η_2 – ethylene ligand. $K[PtCl_3(C_2H_4)].H_2OK \leftrightarrow K^+ + [PtCl_3(C_2H_4)]^-$ Zeise's Salt**[GATE EXAM 2007, 2012]**

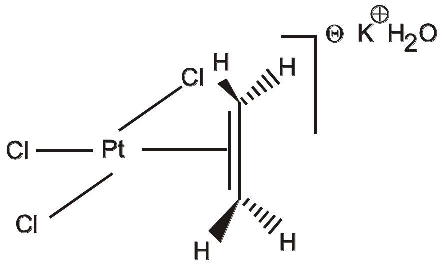
2) The π-acid ligand donates electron density into a metal d-orbital. The metal donates electrons back from a filled d-orbital into the empty π* antibonding orbital of the ligand (hence the description π-acid ligand). Both of these effects tend to reduce the C-C bond order, leading to an elongated C-C distance.

3) The interaction can cause carbon atoms to "rehybridize” from sp^2 towards sp^3 , which is indicated by the bending of the hydrogen atoms on the ethylene back away from the metal.

4) The Pt-Cl bond trans to the ethylene group is significantly longer than the cis- Pt-Cl bonds.

5) The C-C distance, 1.375 Å, is slightly longer than the value found in free ethylene (1.337 Å), indicating some dπ-pπ* back-bonding from the platinum atom to C_2H_4.

6) Back-bonding is also indicated by a bending of the four hydrogen atoms away from the Pt atom.



Zeise’s Salt - the first olefin complex

Figure 1. Zeise’s salt

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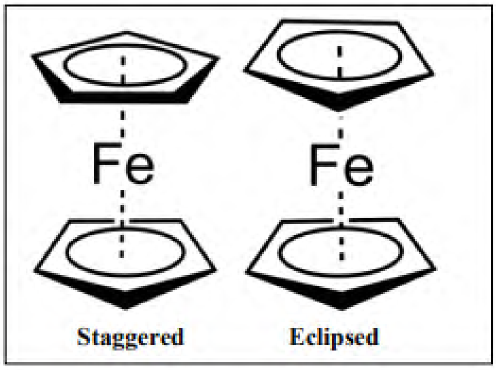
Structure of ferrocene $[Fe(\eta_5 - C_5H_5)_2]$:- bis (η_5 -cyclopentadienyl) iron (II)

1. Ferrocene is known as a “sandwich” compound.
2. It occurs as highly stable orange crystals with a melting point of 174° C.
3. In solid state at low temperature, the rings are staggered.
4. The rotational barrier is very small, with free rotation of the rings.
5. Extreamly low temperature that is Below 110 K, the Cp rings are ordered and eclipsed.
6. Terms of bonding, the iron center in ferrocene is usually assigned to the +2 oxidation state.
7. Each cyclopentadienyl (Cp) ring is then allocated a single negative charge, bringing the number of π-electrons on each ring to six, and thus making them aromatic.

8. These twelve electrons (six from each ring) are then shared with the metal via covalent bonding. When combined with the six d-electrons on Fe^{2+}, the complex attains an 18-electron configuration.



The number of metal – metal bonds in $[(C_5H_5) Fe (CO)_2]_2$ is (a) zero (b) one (c) two (d) three

Ans. (b)

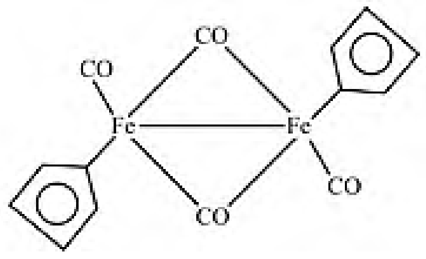
Ligands	No of e^- donated
C_5H_5	2
CO	2

So, Total valence electron in the compound

TVE = $8\times2+(5\times2)+(4\times2)$

= 16 + 10 + 8

= 34



No. of metal-metal bond = $\dfrac{(n\times18-A)}{2}$

Where n = 2

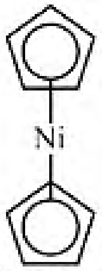
A = 34

M – M bond = $\dfrac{2\times18-34}{2}=1$

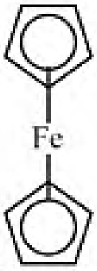
Compound

[GATE EXAM 2008]

- Structurally nickellocene is similar to ferrocene. Nickellocene attains stability due to the formation of (a) a monocation (b) a dication (c) a monoanion (d) a dianion Ans. (b) : Nickelocene is the chemical compound with the formula ( ) 5 5 5 2 Ni C H . η − Also known as bis (Cyclopentadienyl) nickel or NiCp2. Nickelocene is type of metallocene in which metal ion is sandwitched between two parallel cyclopentadienyl rings. The Ni center can be considered to have a 2+ charge and Cp rings are each considered to be cyclopentadienyl anion (Cp^-), related to cyclopentadiene by deprotonation (this structure is similar to ferrocene).



(Nickelocene)



(Ferrocene)

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- So, nickalocene attains stability due to formation of dications. According molecular orbital diagram ferrocene contains 18 valence electrons in bonding and non-bonding MOs and ABMOs are vacant because only BMOs donated by both cyclopenta dienyl ring ($6 \times 2 = 12e^-$) in BMOs 6 electrons are supplied by Fe^{2+} cation, filled in nonbonding e_2g and a1g orbitals. The a_1g is HOMO and e1g is LUMO in ferrocene.**[GATE EXAM 2010]**

[GATE EXAM 2017]

- The correct molecular representation of W(Cp)$_2$(CO)$_2$ is (Cp = cyclopentadienyl) (a) [W(η_1 – Cp) (η_3 – Cp) (CO)$_2$] (b) [W(η_1 – Cp) (η_5 – Cp) (CO)$_2$] (c) [W(η_3 – Cp) (η_5 – Cp) (CO)$_2$] (d) [W(η_5 – Cp)$_2$ (CO)$_2$]
  - Ans. (c): The complex [W(η_3 –Cp) (η_5 –Cp) (CO)$_2$] is correct representation, as it follows $18e^-$ rule. Total valence electron (TVE) = Number of electrons in valence shell of metal + Total no. of electrons donated by ligands. TVE = electron in valence shell of 'W' + electron donated by 'η^3 –Cp' + electrons donated by 'η_5 –Cp' + electrons donated by CO lingads. TVE = 6 + 3 + 5 (2×2) = 18 electron

Multiple Choice Questions - 1

1. Which of the following is considered an organometallic compound?

A) Sodium chloride
B) Ethyl magnesium bromide
C) Ammonium sulfate
D) Acetic acid

2. What is the central metal in ferrocene $\left(\mathbf{C_5H_5C_5H_5C_5H_5\,2Fe}\right)$?

A) Copper B) Iron C) Chromium D) Nickel

3. Which of the following ligands is commonly found in organometallic compounds?

A) Chloride $(Cl - Cl^{-}Cl-)$ B) Carbonyl (COCOCO)

C) Hydroxide $(OH - OH^{-}OH-)$ D) Ammonia $\left(NH_3NH_3NH_3\right)$

4. What type of bonding is observed in organometallic compounds involving carbon monoxide (CO)?

A) Ionic bonding B) Covalent bonding only

C) Coordinate and back-donation bonding D) Hydrogen bonding

5. Which of the following is an application of organometallic compounds?

A) Catalysis in polymerization reactions B) As fertilizers in agriculture

C) As antiseptics in medicine D) As oxidizing agents

6. Which of the following statements is correct about Grignard reagents (R−MgXR-MgXR−MgX)?

A) They are stable in water.

B) They are used in nucleophilic addition reactions.

C) They do not react with carbon dioxide.

D) They are not organometallic compounds.

7. Which of the following is not an organometallic compound?

A) Tetraethyl lead $\left(Pb\left(C_2H_5\right)4Pb\left(C_2H_5\right)_4 Pb\left(C_2H_5\right)_4\right)$

B) Sodium methoxide $\left(CH_3ONaCH_3ONaCH_3ONa\right)$

C) Methyl lithium $\left(CH_3LiCH_3LiCH_3Li\right)$

D) Dimethyl zinc $\left(Zn\left(CH_3\right)_2 Zn\left(CH_3\right)_2 Zn\left(CH_3\right)_2\right)$

8. The 18-electron rule in organometallic chemistry is analogous to which rule in organic chemistry?

A) Octet rule B) Hund’s rule

C) Aufbau principle D) VSEPR theory

9. Which metal is commonly used in organometallic catalysts for olefin polymerization?

A) Aluminum B) Palladium C) Titanium D) Sodium

10. In which type of reaction are organometallic compounds such as Wilkinson's catalyst commonly used?

A) Oxidation B) Reduction C) Hydrogenation D) Hydrolysis

2.1.1. Synthesis

- Simple transition metal carbonyls are made by various methods, the important ones are
  - (a) Direct reaction
  - (b) Reductive carbonylation
  - (c) Photolysis and thermolysis

TCA

(a) Direct Reaction

- First of all tetracarbonyl nickel $\left[Ni(CO)_4\right]$ and pentacarbonyl iron $\left[Fe(CO)_5\right]$ were discovered in 1888. • The synthesis of $\left[Ni(CO)_4\right]$ is inducstrially important because the reaction is reversible and this is the basis of the Mond’s process for purification of metallic nickel.

$$\underset{\text{Impure}}{Ni} + 4CO \xrightarrow[1\ atm]{25^o C} Ni(CO)_4 \xrightarrow[\Delta]{Distill} \underset{Pure}{Ni} + 4CO$$

- The simplest metal carbonyls are the neutral binary Mx (CO)y compounds, these may be mononulear (x=1) or polynuclear (x>1). The majority of metal carbonyls are ow melting point solids that can be sublimated in vacuo. A small number of the compounds are volatile liquids.
- The other mononuclear metal carbonyls are prepared by direct reaction of metal with gaseous CO at appropriate temperatures and pressures.
  - ➢ Example

$$Fe + 5Co \xrightarrow[100\ atm]{200^o C} Fe(CO)_5,\ Mo + 6CO \xrightarrow[250\ atm]{200^o C} Mo(CO)$$

(b) Reductive Carbonylation

- Mononuclear and polynuclear metal caarbonyls are synthesized by a process known as reductive carbonylation in which a transition metal in a high oxidation state is reduced to zero oxidation state in presence of CO gas.
- Often these reactions are performed at very high pressures in steel bombs

- To reduce the possibility of an accident the bombs are usually operated in explosion proof rooms, located on the top floor of a chemistry building.
- Some typical metal carbonyls synthesis employing reductive carbonylation are shown as

$$CrCl_3 + Al + 6CO \xrightarrow[C_6H_6]{AlCl_3} Cr(CO)_9 + AlCl_3$$

- When halide is not present, CO can serve as the reducing agent

$$\mathrm{Re}_2O_7 + 17CO \rightarrow \mathrm{Re}_2(CO)_{10} + 7CO_2$$

$$2CoCO_3 + 2H_2 + 8CO \xrightarrow[250\ atm]{150^{o}C} Co_2(CO)_8 + 2CO_2 + 2H_2O$$

(c) Photolysis and Thermolysis

- In addition to direct reaction and reductive carbonylation methods, carbonyl compounds can also be synthesized by a route called occurs photolysis. Photochemical bond cleavage occurs during synthesis
  - Eg. Synthesis of iron near carbonyl.

$$2Fe(CO)_5 \xrightarrow{hv} Fe_2(CO)_9 + CO$$

$$2Na\left[V(CO)_6\right] + 2HCl \xrightarrow{hv} 2V(CO)_6 + 2NaCl + H_2$$

18 Electron Rule:

- 18 electron rule of metal carbonyls
- The 18-electron rule is used primarily for predicting and rationalizing formulae for stable metal complexes, especially organometallic compounds.
- The rule is based on the fact that the valence shells of transition metals consist of nine valence orbitals (one s orbital, three p orbitals and five d orbitals), which collectively can accommodate 18 electrons as either bonding or nonbonding electron pairs.
- This means that, the combination of these nine atomic orbitals with ligand orbitals creates nine molecular orbitals that are either metalligand bonding or non-bonding.
- When a metal complex has 18 valence electrons, it has achieved the same electron configuration as the noble gas in the period.
- The rule and its exceptions are similar to the application of the octet rule to main group elements. 18 electron rule of metal carbonyls
- This rule applies primarily to organometallic compounds, and the 18 electrons come from the 9 available orbitals in d orbital elements (1 s orbital, 3 p orbitals, and 5 d orbitals).

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UNIT 4 - INORGANIC CHEMISTRY

SYLLABUS

Classical Thermodynamics

Partial Molar properties, chemical potential, Gibb's-Duhem equation. Determination of partial molar quantities, thermodynamics of real gases, fugacity-determination of fugacity by graphical and equation of states methods, dependence of temperature, pressure and composition, thermodynamics of ideal and non-ideal mixtures, Activity and acitivity coefficients.

Statistical Thermodynamics

Concepts of statistical thermodynamics, distinguishable and non-distinguishable particles, Assemblies, ensembles, canonical particles, Boltzmann distribution, Bose-Einstein, Fermi-Dirac statistics, comparison and application, kinetic theory of gases, partition function and their relation to thermodynamic quantities, calculation for model systems.

Phase Rule:

Phase, degrees of freedom, component, One component system, water system, triple point-two component systems, reduced phase rule-eutectic temperature-lead-silver system-congruent and incongruent melting point-Zn and Mg system – NaCl and water system – CST – phenol and water system. Henry's law – Raoult's law – Nernst distribution law – solvent extraction – steam distillation – fractional crystallisation – Park's process.

Colloids and Surfaces:

Stability and properties of colloids, gold number, types of adsorption, Freundlich's and Langmuir's isotherms and surface area, heterogeneous catalysis.

4.1. CLASSICAL THERMODYNAMICS

4.1.1. Partial Molal Quantities (or) Thermodynamics of Open Systems:

- The thermodynamic properties U, H, S, A and G are extensive properties because their values change with change in the mass of the system. In the derivative of the various thermodynamic equations described, the change of state was considered to be due to change in temperature and pressure only. A taint assumptions was made that the system under consideration was a closed system (i.e.,) there could be no change in the mass of the system. However, in the case of an open system containing two or more components, there can be change in the number of more of various components as well. In that case, an extensive property, say X must be a function not only of temperature and the pressure but also the number of moles of the various components present in the system.
- Let *T* and *P* be the temperature and pressure respectively, of a system. Let $n_1, n_2, n_3, ..., n$ be the respective numbers of moles of the constituents 1, 2, 3, ….,j. The property *X* must function of temperature, pressure and the number of moles of the various constituents i.e.,

$$X = f\left(T, P, n_1, n_2, n_3, ...n_j\right) \qquad \text{\_\_\_\_\_\_\_\_\_\_ (1)}$$

Where $n_1 + n_2 + n_3 + ... + n_j$ = total number of moles = N

For a small change in temperature, pressure and the number of moles of the components the change in property *dx* will be given by the expression

$$dx = \left(\frac{\partial x}{\partial T}\right)_{P_1N} dT + \left(\frac{\partial x}{\partial P}\right)_{T_1N} + \left(\frac{\partial x}{\partial n_1}\right)_{T_1P_1n_2,....,n_i} d_{n_1} +$$

$$\left(\frac{dx}{dn_2}\right)_{T_1P_1n_1n_3...n_i} dn_2 + ... + \left(\frac{\partial x}{\partial n_i}\right)_{T_1p_1n_1,n_2} dn_i ... \qquad \text{\_\_\_\_\_\_\_\_\_\_ (2)}$$

The quantity $\left(\frac{\partial x}{\partial n_i}\right)_{T_1P_1n_1n_2....n_i} dn_i$ is called the partial molar property of the concerned component. This is more often represented as $\overline{X_i}$.

Thus, for the ith component of a system

Partial molar internal energy = $\left(\frac{\partial u}{\partial n_i}\right) T_1P_1n_1, n_2, ... = \overline{U_i}$

TCA

Partial molar enthalpy = $\left(\frac{\partial H}{\partial n_i}\right)T_1P_1n_1,n_2,n_3... = \overline{H_i}$

Partial molar entropy = $\left(\frac{\partial S}{\partial n_i}\right)T,P,n_1,n_2,n_3... = \overline{S_i}$

Partial molar volume = $\left(\frac{\partial V}{\partial n_i}\right)T,P,n_1,n_2,... = \overline{V_i}$

4.1.2. Partial molar Free energy: Concept of Chemical Potential

- The partial molar free energy is designated as chemical potential and is represented as

$$\left(\frac{\partial G}{\partial n_i}\right)T,P,n_1,...n_j = \overline{G_i} = \mu_i \qquad \text{\_\_\_\_\_\_\_\_\_ (3)}$$

- The chemical potential of a given substance is, evidently the change in free energy of the system that results on the addition of one mole of that particular substance at a constant temperature and pressure, to such a large quantity of the system that there is no appreciable change in the overall composition of the system **(PGTRB 2001, 12-13; CSIR DEC-2013).**
- Chemical potential is an intensive property **(PGTRB 2002)**.
- For a small force energy change, equation (2) may be written as

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P_1N} dT + \left(\frac{\partial G}{\partial P}\right)_{T_1N} dp + \mu_1 d_{n_1} + \mu_2 dn_2 + ...+ \mu_j d_{n_j} \qquad \text{\_\_\_\_\_\_\_\_\_ (4)}$$

- Where $\mu_1, \mu_2, ...$ and μ_j are chemical properties of the components 1, 2, … and j, respectively.
- If temperature and pressure remain constant then

$$(\partial G)_{T_1P} = \mu_1 d_{n_1} + \mu_2 d_{n_2} + ...+ \mu_j d_{n_j} \qquad \text{\_\_\_\_\_\_\_\_\_ (5)}$$

- If a system has a definite composition having $n_1, n_2, ...n_j$ moles of the constituents 1, 2, …, j respectively, then on integrating equation (5) we have

$$(G)_{T_1P_1N} = n_1\mu_1 + n_2\mu_2 + ...+ n_2\mu_i \qquad \text{\_\_\_\_\_\_\_\_\_ (6)}$$

- From equation (6), chemical potential may be taken as the contribution per mole of each particular constituent of the mixture of the total free energy of the system under conditions of constant temperature and pressure.
- It readily follows that for a total of 1 mole of a pure substance $G = \mu$ (i.e.,) free energy is identical with chemical potential.

4.1.3. Gibbs – DuhemEquation

- Equation (6) shows that the free energy of a system, at constant temperature and pressure, can be expressed as a sum of $n\mu$ terms for the individual components of the system.
- From equation (6), the total differential of G is written as

TCA

$$dG = \mu_1 d_{n_1} + \mu_2 d\mu_1 + n_2 d\mu_2 ... \mu_i d_{n_j} + n_i d\mu_j$$

$$= \left(\mu_1 d_{n_1} + \mu_2 d_{n_2} + ... \mu_i dn_i\right) + \left(n_1 du_1 + n_2 du_2 + ... + n_i du_j\right) \quad \_\_\_\_\_\_\_\_\_ (7)$$

- But according to equation (5), the first term on right hand side of equation (7), is equal to dG, at constant temperature and pressure, for a system of a definite composition.

$$n_1 du_1 + n_2 du_2 + ... + n_i du_i = 0 \quad \_\_\_\_\_\_\_\_\_ (8)$$

(or)

$$\sum n_i du_i = 0 \quad \_\_\_\_\_\_\_\_\_ (9)$$

- This simple relationship is known as Gibbs-Duhem equation.**(PGTRB-2001; 2022; CSIR JUN-2015))**

4.1.4. Variation of Chemical Potential with Temperature:

- The variation of chemical potential of any constituent i of a system with temperature can be derived by differentiating equation (3), with respect to temperature and equation

$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S$ with respect to n_i. The results are:

$$\frac{\partial^2 G}{\partial n_i \partial T} = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} \quad \_\_\_\_\_\_\_\_\_ (10)$$

$$\frac{\partial^2 G}{\partial i \partial n_i} = -\left(\frac{\partial S}{\partial \mu_i}\right) T, P, n_1, ..., \overline{S_i} \quad \_\_\_\_\_\_\_\_\_ (11)$$

- Where $\overline{S_i}$ by definition, is the partial molar entropy of the component i.
- It follows from equations (10) and (11), that

$$\left(\frac{\partial \boldsymbol{\mu_i}}{\partial \boldsymbol{T}}\right)_{\boldsymbol{P,N}} = -\overline{\boldsymbol{S}}_{\boldsymbol{i}} \quad \_\_\_\_\_\_\_\_\_ (12)$$

- Equation (12) gives the variation of chemical potential (μ_i) of any constituent i of the system with temperature **(PGTRB 2015)**.

4.1.5. Variation of Chemical Potential with Pressure:

- The variation of chemical potential of any constituent i of the system with pressure may be desired by differentiating equation (3) with respect to pressure and equation

  $\left(\frac{\partial G}{\partial P}\right)_{P,N} = V$ with respect to n_i. The results are:

$$\left(\frac{\partial^2 G}{\partial P\ \partial n_i}\right) = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} \qquad \text{\_\_\_\_\_\_\_\_\_ (13)}$$

and $$\left(\frac{\partial^2 G}{\partial n_i \partial P}\right) = -\left(\frac{\partial V}{\partial n_i}\right) T, P, n_1, ...n_j = \overline{V_1} \qquad \text{\_\_\_\_\_\_\_\_\_ (14)}$$

- Where $\overline{V_i}$ by definition, is the partial molar volume of the component i.
- It follows from equations (13) and (14), we get

$$\left(\frac{\partial^2 G}{\partial n_i \partial P}\right) = -\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \overline{-V_i} \qquad \text{\_\_\_\_\_\_\_\_\_ (15)}$$

- Equation (15) gives the variation of chemical potential (μ_i) of any constituent of the system and pressure **(PGTRB 2004, 2011-12)**.

4.1.6. Determination of Partial Molar Properties:

Experimental Determination of Partial Molar Volumes

- A straight forward method for determining $V_{1,pm}$ of component 1 in a binary solution of known composition is to measure volumes of solutions obtained by adding varying amount of component 1 in a fixed amount of component 2. A graph between volume of solution and amount of component 1 is plotted. The slope of the line at the given composition of the solution gives the partial molar volume of the component 1.

Method of Intercept

- A considerably more precise method for the determination of partial molar volumes (or in general any partial molar quantity) is the *method of intercepts*. The principle underlying this method is described below.
- Let $V_{m,mix}$ be the volume of mixture containing a total of one mole of the two components, Obviously, it will be given as

$$V_{m,mix} = \frac{V}{n_1 + n_2} \qquad (1)$$

- Where V_1 is the volume of the mixture containing the amounts n_1 and n_2 of components 1 and 2, respectively. Since partial molar volume of component 1 is defined $\left(\partial V/\partial n_1\right)_{\sum,p,n_2,}$ (Written hereafter a $\left(\partial V/\partial n_1\right)_{n_2,}$ since T and p remain constant during the experiment), it follows that

$$V_{1,pm}=\left(\frac{\partial V}{\partial n_1}\right)_{n_2}=\left(\frac{\partial\left(n_1+n_2\right)V_{m,mix}}{\partial n_1}\right)_{n_2}$$

$$=V_{m,mix}+\left(n_1+n_2\right)\left(\frac{\partial V_{m,mix}}{\partial n_1}\right)_{n_2} \qquad (2)$$

- Since $x_1+x_2=1$, the total molar volume $V_{m,mix}$ at a given temperature and pressure will depend only on one of the mole fraction terms. Writing it as

$$V_{m,mix}=f\left(x_2\right) \qquad (3)$$

- We get $$dV_{m,mix}=\left(\frac{dV_{m,mix}}{dx_2}\right)dx_2 \qquad (4)$$

- Division of the above equation by dn_1, and restriction to constant n_2 gives

$$\left(\frac{\partial V_{m,mix}}{\partial n_1}\right)_{n_2}=\left(\frac{\partial V_{m,mix}}{dx_2}\right)\left(\frac{\partial x_2}{\partial n_1}\right)_{n_2} \qquad (5)$$

TCA

- Now since $$x_2=\frac{n_2}{n_1+n_2}$$

- We have $$\left(\frac{\partial x_2}{\partial n_1}\right)_{n_2}=-\frac{n_2}{\left(n_1+n_2\right)^2}=-\frac{x_2}{\left(n_1+n_2\right)} \qquad (6)$$

- Hence, Eq. (5) becomes

$$\left(\frac{\partial V_{m,mix}}{\partial n_1}\right)_{n_2}=\left(\frac{\partial V_{m,mix}}{\partial x_2}\right)\left(-\frac{x_2}{n_1+n_2}\right)$$

- Substituting the above equation in Eq. (2), we have

$$V_{1,pm}=V_{m,mix}-x_2\left(\frac{\partial V_{m,mix}}{\partial x_2}\right)\ i.e.,\ V_{m,mix}=V_{1,pm}+x_2\left(\frac{\partial V_{m,mix}}{dx_2}\right) \qquad (7)$$

- A similar treatment for $V_{2,pm}$ yields

$$V_{m,mix}=V_{2,pm}+x_1\left(\frac{\partial V_{m,mix}}{dx_1}\right) \qquad (8)$$

- Geometrical interpretation of Eq. (7) for (or 8) is straightforward. This represents the tangent line drawn to the plot of $V_{m,mix}$ versus x_2 (or $V_{m,mix}$ versus x_1) with intercept equal to $V_{1,pm}$ (or $V_{2,pm}$) and slope equal to $dV_{m,mix}/dx_1$). Both the plots of $V_{m,mix}$ versus x_2 and $V_{m,mix}$ versus x_1 represent a single plot as $x_1 + x_2$ is always equal to 1. This is illustrated in Fig 1 where the intercepts are $V_{1,pm}$ at $x_2 = 0$ (or $x_1 = 1$) and V_2 at $x_2 = 1$ (or $x_1 = 0$). In fact, Eq. (8) may be derived from figure 1. The slope of $V_{m,mix}$ versus x_2 at P is given by expression

$$\frac{dV_{m,mix}}{dx_2} = \frac{V_{2,pm} - V_{m,mix}}{1 - x_2}$$

- On rearranging this expression, we get

$$V_{m,mix} = V_{2,pm} - \left(1 - x_2\right)\frac{dV_{m,mix}}{dx_2}$$

- Since $x_1 + x_2 = 1$, it follows that $dx_1 = -dx_2$. Hence, the above expression becomes

$$V_{m,mix} = V_{2,pm} + x_2\frac{dV_{m,mix}}{dx_1}$$

- Since $x_1 + x_2 = 1$, it follows that $dx_1 = -dx_2$. Hence, the above expression becomes

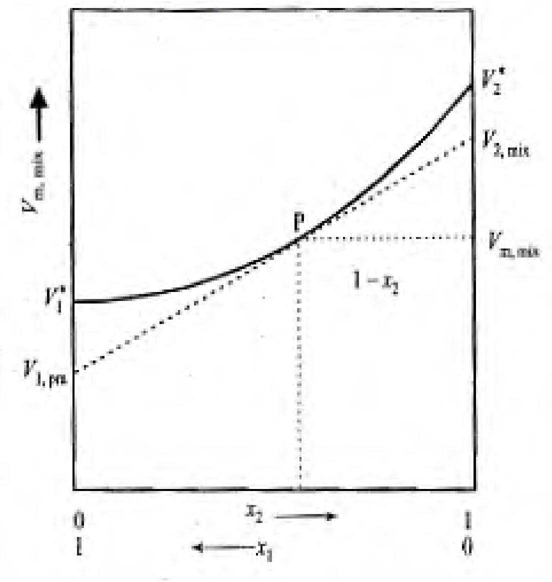
$$V_{m,mix} = V_{2,pm} + x_1\frac{dV_{m,mix}}{dx_1}$$

- Equations (7) and (8) are valid for any extensive property Y(say V, U, H.S.A and G) of the mixture. Hence, the equations may be generalized to

$$Y_{m,mix} = Y_{1,pm} + x_2\left(\frac{dV_{m,mix}}{dx_2}\right)$$

$$Y_{m,mix} = Y_{2,pm} + x_1\left(\frac{dV_{m,mix}}{dx_1}\right)$$

Figure 1: The method of intercepts to determine the partial molar volumes of components of a binary solution



Alternative Method:

- In older literatures, partial molar volumes have been determined by plotting a graph between the reciprocal of the density of the solution versus the mass per cent of component 1 (or component 2), rather than $V_{m,mix}$ versus x, equation (7) can be rewritten in terms of the reciprocal of density of the mixture $\left(1/\rho_{mix}\right)$ and mass per cent of component 2 $\left(w_2\right)$, we have

$$V_{m,mix} = \frac{x_1M_1 + x_2M_2}{\rho_{mix}} = \frac{M_1 + x_2\left(M_2 - M_1\right)}{\rho_{mix}} \tag{9}$$

- Therefore

$$\frac{dV_{m,mix}}{dx_2} = \frac{M_2 - M_1}{\rho_{mix}} + \left\{M_1 + x_2\left(M_2 - M_1\right)\right\}\left(\frac{d\left(1/\rho_{mix}\right)}{dx_2}\right) \tag{10}$$

- The dx will be related to dw as shown below.

$$w_2 = \frac{m_2}{m_1 + m_2}\times 100 = \frac{n_2M_2}{n_1M_1 + n_2M_2}\times 100 = \frac{x_2M_2}{x_1M_1 + x_2M_2}\times 100$$

or $$w_2 = \frac{x_2M_2}{M_1 + x_2\left(M_2 - M_1\right)}\times 100 \tag{11}$$

- Taking inverse of the above expression, we have

$$\frac{1}{w_2} = \frac{M_1}{x_2M_2\times 100} + \frac{M_2 - M_1}{M_2\times 100}$$

TCA

- Differentiating the above expression, we have

$$-\frac{1}{w_2^2}dw_2 = -\frac{M_1}{x_2^2 M_2 \times 100}dx_2 \text{ or } dx_2 = \frac{x_2^2 M_2 \times 100}{M_1 w_2^2}\left(dw_2\right)$$

- Substituting dx_2 from the above expression in Eq. (10), we get

$$\frac{dV_{m,mix}}{dx_2} = \frac{M_2 - M_1}{\rho_{mix}} + \left\{M_1 + x_2\left(M_2 - M_1\right)\right\}\frac{M_1 w_2^2}{x_2^2 M_2 \times 100}\frac{d\left(1/\rho_{mix}\right)}{dw_2}$$

- Making use of Eq. (11), we get

$$\frac{dV_{m,mix}}{dx_2} = \frac{M_2 - M_1}{\rho_{mix}} + \frac{x_2 M_2 \times 100}{w_2}\frac{M_1 w_2^2}{x_2^2 M_2 \times 100}\frac{d\left(1/\rho_{mix}\right)}{dw_2}$$

$$= \frac{M_2 - M_1}{\rho_{mix}} + \frac{M_1 w_2}{x_2}\frac{d\left(1/\rho_{mix}\right)}{dw_2} \qquad (12)$$

- Substituting Eqs. (12) and (9) in Eq. (7), we get

$$\frac{M_1 + x_2\left(M_2 - M_1\right)}{\rho_{mix}} = \frac{M_1}{\rho_{1,pm}} + x_2\left[\frac{M_2 - M_1}{\rho_{mix}} + \frac{M_1 w_2}{x_2}\frac{d\left(1/\rho_{mix}\right)}{dw_2}\right]$$

- On simplifying, we get

$$\frac{1}{\rho_{mix}} = \frac{1}{\rho_{1,pm}} + w_2\frac{d\left(1/\rho_{mix}\right)}{dw_2} \qquad (13)$$

- Similarly, Eq. (8) will become

$$\frac{1}{\rho_{mix}} = \frac{1}{\rho_{2,pm}} + w_1\frac{d\left(1/\rho_{mix}\right)}{dw_1} \qquad (14)$$

- Hence, a tangent to the curve $1/\rho_{mix}$ versus w_2 at any particular w_2 has an intercept on $1/\rho_{mix}$ axis of $1/\rho_{1,pm}$, whereas a tangent to the curve $1/\rho_{mix}$ versus w_2 at any particular w_1 has an intercept on $1/\rho_{mix}$ of $1/\rho_{2,pm}$, Both the curves can be represented by a single plot as $w_1 + w_2$ is always equal to 100. The partial molar volumes are obtained by multiplying the two intercepts with the respective molar masses.

Objective Questions - 1

1. The partial molar free energy is designated as _______.

(A) Gibbs Duhem equation
(B) Free – energy
(C) Chemical potential
(D)All the above

2. Which of the following is the correct expression for the partial molar Gibb's free energy (G_i) of a component *i* in a mixture?

   (A) $G_i = \frac{\partial G}{\partial n_i}$ (B) $G_i = \frac{\partial G}{\partial P}$ (C) $G_i = \frac{\partial G}{\partial T}$ (D) $G_i = \left.\frac{\partial G}{\partial n_i}\right|_{T,P}$

3. The partial molar enthalpy of a component is defined as:

   (A) The heat required to change the temperature of the mixture by one degree.

   (B) The enthalpy change of the system when an infinitesimal amount of component iii is added, keeping the temperature and pressure constant

   (C) The heat released when one mole of a component is dissolved in the solvent

   (D) The enthalpy change of the system when the pressure is changed by an infinitesimal amount

4. The Gibb's-Duhem equation is

   (A) $\sum n_i d\mu_i = 0$ (B) $\sum \mu_i dn_i = 0$ (C) $n_i d\mu_i = 0$ (D) $\sum \mu_i = 0$

5. The correct expression for variation of chemical potential with temperature is

   (A) $\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} = \bar{S}_i$ (B) $\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = -\bar{S}_i$

   (C) $\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} = -\bar{S}_i$ (D) $\left(\frac{\partial \mu_i}{\partial T}\right) = -\bar{S}_i$

6. The correct expression for variation of chemical potential with Pressure is

   (A) $\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \bar{S}_i$ (B) $\left(\frac{\partial \mu_i}{\partial P}\right) = V_i$

   (C) $\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} = -V_i$ (D) $\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = -\bar{V}_i$

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4.1.7. Fugacity

4.1.7.1. Concept of Fugacity:

- By using the free energy function, G Lewis introduced the concept of fugacity for representing the actual behaviour of real gases which is distinctly different from the behaviour of ideal gas**(PGTRB 2003)**. The unit of fugacity is same as pressure **(PGTRB 2004-05)**.
- Variation of free energy with pressure at constant temperature is given by equation

$$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad \text{\_\_\_\_\_\_\_\_ (1)}$$

- This equation is applicable to all gases whether ideal or non-ideal
- If one mole of a gas is under consideration, then V refers to molar volume. For an ideal gas the above equation may be written as,

$$(dG)_T = \frac{RTdP}{P} \qquad \text{\_\_\_\_\_\_\_\_ (2)}$$

and for n moles as, $(dG)_T = \frac{nRTdp}{p}$

$$= \frac{nRTd}{(\ln p)} \qquad \text{\_\_\_\_\_\_\_\_ (3)}$$

- Integrating of Eq. 167 yields

$$G = G_0 + nRT\ln P \qquad \text{\_\_\_\_\_\_\_\_ (4)}$$

- Where G^o, the integration constant is the free energy of n moles of the ideal gas at temperature T when the pressure P is unity
- Equation (4), gives the free energy of an ideal gas at temperature T and pressure P.
- Integration of Equation (3) between pressures P_1 and P_2, at constant temperature T, yields,

$$\Delta G = \int_{P_1}^{P_2} nRT\frac{dp}{p} - nRT\ln\frac{P_2}{P_1} \qquad \text{\_\_\_\_\_\_\_\_ (5)}$$

- The corresponding equation for 1 mole of the gas would be

$$\Delta G = Rn\ln\frac{P_2}{P_1} \qquad \text{\_\_\_\_\_\_\_\_ (6)}$$

- Equations (4) and (6) are not valid for real gases since V is not exactly equal to RT/P for real gases.
- In order to make these simple equations applicable to real gases, Lewis introduced a new function f, called fugacity function. It takes the place of P in Eq. (3) which, for real gases, may be expressed as

$$(dG)_T = nRTd(\ln f) \qquad \text{\_\_\_\_\_\_\_\_ (7)}$$

and equation (4) may be represented as

$$G = G^0 + nRT\ln f \qquad \_\_\_\_\_\_\_ \text{ (8)}$$

- Where G^0 is the free energy of n moles of a real gas when its, fugacity happens to be 1.Thus, fugacity is a sort of "factitious pressure" which is used in order to retain for real gases simple forms of equations which are applicable to ideal gases only. The escaping tendency of a substance from a given state is called fugacity **(PGTRB 2011-12; CSIR DEC-2014; JUN 2017)**.
- Equation (8), gives the free energy of a real gas at temperature T and pressure P at which the fugacity can be taken as f.
- Equation (7), on integration between fugacities f_1 and f_2 at constant temperature T, yields

$$\Delta G = nRT\ln\left(\frac{f_2}{f_1}\right) \qquad \_\_\_\_\_\_\_ \text{ (9)}$$

- The corresponding equation for 1 mole of the gas would be

$$\Delta G = RT\ln\left(\frac{f_2}{f_1}\right) \qquad \_\_\_\_\_\_\_ \text{ (10)}$$

- Equations (9) and (10) are applicable to real gases.

4.1.7.2. Fugacity at Low Pressures:

- The ratio f/p, where p is the actual pressures approaches unity when P approaches zero since in that case a real gas approximates to ideal behaviour **(PGTRB 2001)**. The fugacity function, may be defined as

$$\lim_{p \to 0} \frac{f}{p} = 1 \qquad \_\_\_\_\_\_\_ \text{ (11)}$$

- Evidently, at low pressures, fugacity is equal to pressure. The two terms differ materially only at high pressures**(PGTRB – 2015)**.

4.1.7.3. Determination of Fugacity of a Gas:

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- Equation (8), for one mole of a gas, may be put as

$$G = G^0 + RT\ln f \qquad \_\_\_\_\_\_\_ \text{ (12)}$$

- Differentiation of equation (12) with respect to pressure at constant temperature and constant number of moles of the various constituents (i.e.,) in a closed system, gives

$$\left(\frac{\partial G}{\partial P}\right)_T = RT\left(\frac{\partial(\ln f)}{\partial P}\right)$$ _______ (13)

Since $\left(\frac{\partial G}{\partial P}\right)_T = V$ _______ Equation (1)

It follows that,

$$\left(\frac{\partial(\ln f)}{\partial P}\right)_T = \frac{V}{RT}$$ _______ (14)

- Thus, at a definite temperature, equation (14) may written as

$$RTd(\ln f) = Vdp$$ _______ (15)

- Since one mole of a gas is under consideration. V is the molar volume of the gas.
- Knowing that for an ideal gas, $V = \frac{RT}{P}$, the quantity α, defined as departure from ideal behavior at a given temperature, is given by

$$\alpha = \frac{RT}{P} - V$$ _______ (16)

- Multiplying by dpthrough out, we get

$$\alpha dp = RT\left(\frac{dp}{p}\right) - Vdp$$ _______ (17)

- Combining equations (15) and (16), we have

$$RTd(\ln f) = RT\frac{dp}{p} - \alpha dp$$

(or)

$$d(\ln f) = d(\ln p) - \alpha\frac{dp}{dT}$$ _______ (18)

- Integrating equation (182) between pressures O and P_1 we have

$$\ln\frac{f}{p} = -\frac{1}{RT}\int_0^P d(dp)$$ _______ (19)

- Now, α as given by equation (16), can be determined experimentally, at different pressures

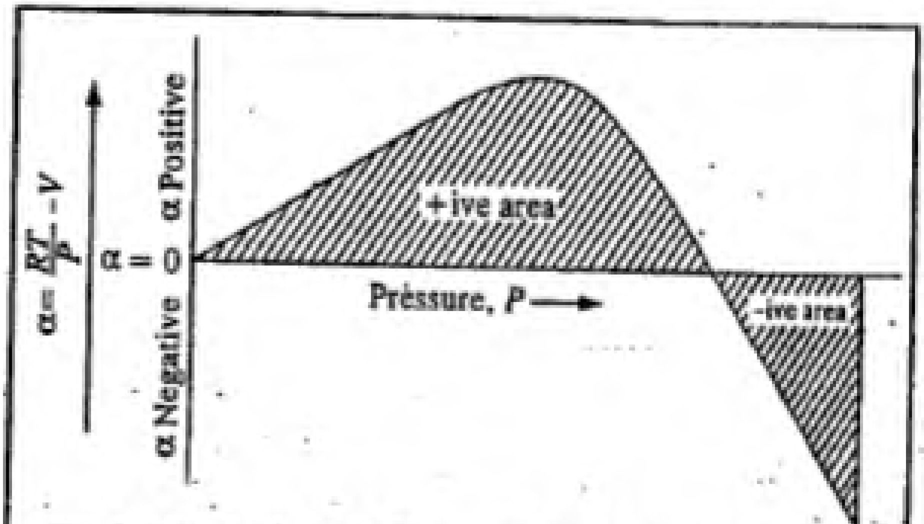

Fig. 6. Plot of α (=RT/P−V) versus P for the determination of fugacity of the gas.

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Figure: Plot of $\alpha = \left(\frac{RT}{P} - V \right)$ **versus P for the determination of fugacity of the gas**

- These values of α are then plotted against correspond pressures, as shown figure. The area under the curve between pressure P = 0 and any given pressure P, yield the value of the integral $\int_0^P \alpha(dp)$, as illustrated in shaded portion in figure. Incorporating this value in equation (19), the fugacity f can be evaluated at a given pressure P of the gas.
- Since α, the departure from ideal behaviour can be both positive as well as negative, the area under the curve can be both positive as well as negative. Thus, the fugacity of the gas can be both less than or more than the pressure P.
- As is evident from figure the area and hence the value of $\int_0^P \alpha(dp)$ is positive at low pressures and negative at very high pressures. Hence, in accordance with equation (19), fugacity *f* of the gas would be less than the pressure P at low pressures and more than the pressure P at high pressure.
- For hydrogen and Helium, PV is greater than RT for all pressures at ordinary temperatures. Hence, fugacity in those gases always remains greater than the pressure**(PGTRB 2005-06)**.

4.1.8. Thermodynamics of IDEAL and Non-Ideal Mixtures

- A **mixture** consists of two or more components that are physically combined but not chemically bonded.

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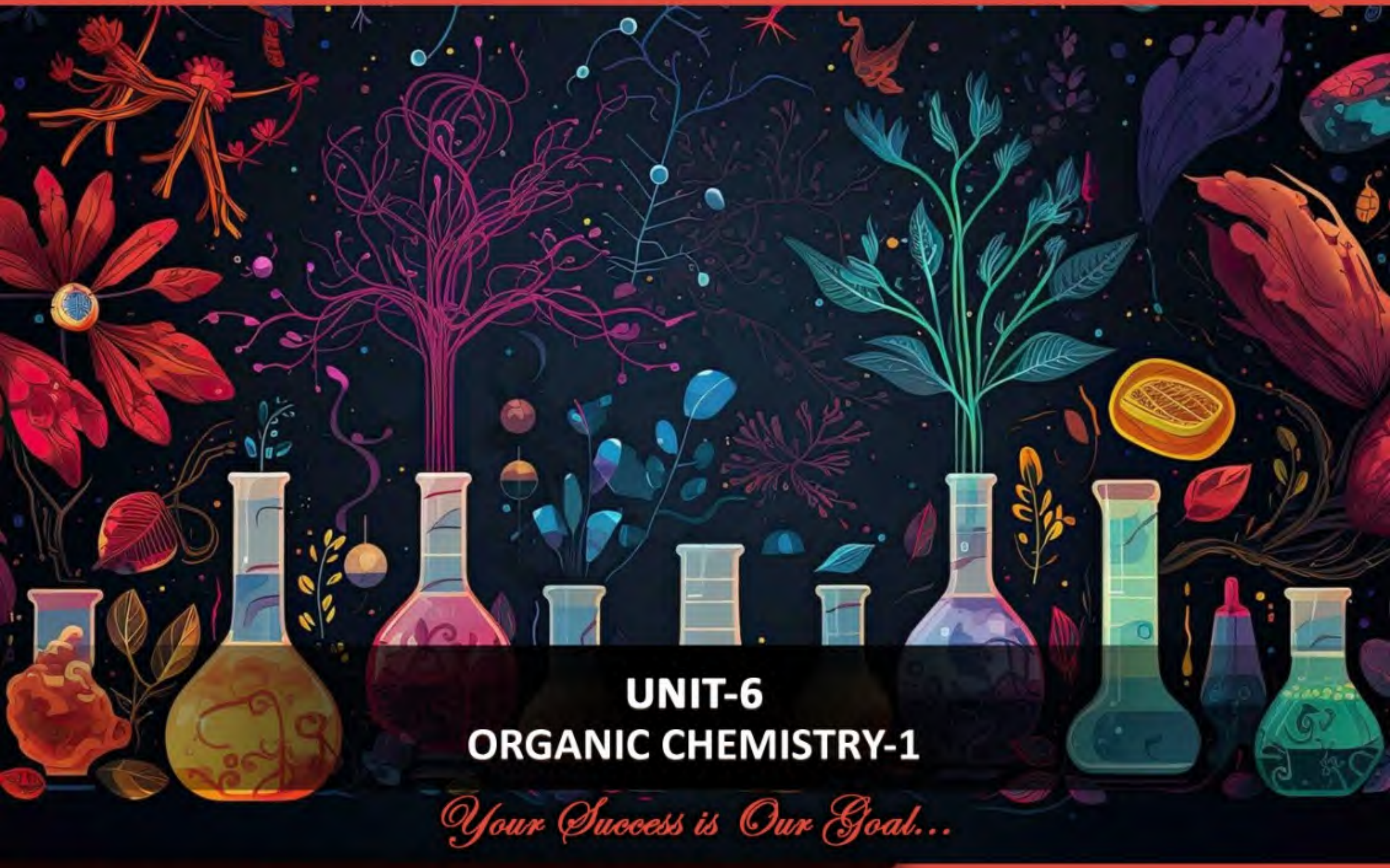

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PG TRB CHEMISTRY

UNIT 6 - ORGANIC CHEMISTRY

SYLLABUS

IUPAC Nomenclature:

Organic molecules including regio and stereoisomers.

Principles of Stereochemistry:

Configurational and conformational isomerism in acyclic and cyclic compounds, stereogenicity, stereoselectivity, enantioselectivity, diastereo selectivity and asymmetric induction. Geometrical isomerism resulting from double bonds – E, Z system of nomenclature, monocyclic compounds and fused ring systems, stereo specific and stereo selective reactions with examples.

Aromaticity:

Benzenoid and non-benzenoid compounds, generation and reactions.

Organic Reactive Intermediates:

Generation, stability and reactivity of carbocations, carbanions, free radicals, carbenes, benzynes and nitrenes. Organic reaction mechanisms involving the addition, elimination and substitution reactions with the electrophilic, nucleophilic or radical species. Reaction pathways determination.

Common Named Reactions and Rearrangements:

Still Coupling, Heck reaction, Pusond-Kahn Reaction, Suzuki Coupling, Mitsunobu reaction, Baylis-Hillman reaction, Mukiayama's reaction, Metathesis reaction. Nef reaction, Henry reaction, Ritter reaction. Pinacol-Pinacolone, Wagner-Meerwein, Demjanov, dienone-phenol, Favorskii, Baeyer-Villiger, Wolff, Wittig, Neber, Stevens, Hofmann, Lossen, Curtius, Beckmann, Benzidine and Von Richter rearrangements. Applications in organic synthesis.

Polarimetry:

Circular dichroism, Optical Rotatory Dispersion, principles and applications.

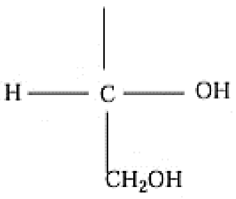
6.1. IUPAC NOMENCLATURE

6.1.1. Nomenclature of Optical Isomers

- Following three nomenclatures are used for optically active compounds:

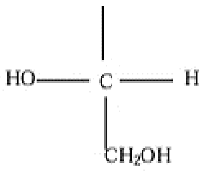
6.1.2. D.L System of Nomenclature

- This nomenclature is mainly used in sugar chemistry or optically active polyhydric carbonyl compounds. This is a relative nomenclature because all the configurations described with respect to glyceraldehydes. All sugars whose Fischer projection formula shows the OH group on the right hand side of the chiral atom belong to the D-series.



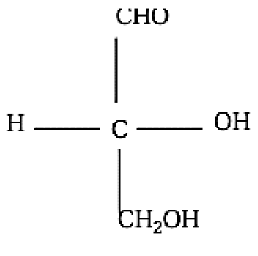
D-series.

Similarly, if OH is on the left hand side, then the sugar belongs to the L-series.

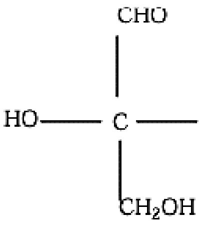


L-series

Examples:



D(+) glyceraldehyde



L(-) glyceraldehydes

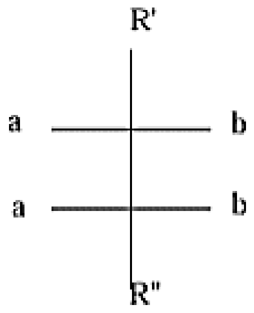
- It must be noted that there is no relation between sign of rotation and (+, - or d,l) and configuration (D and L) of enentiomer.
- Any compound that can be prepared from, or converted in to D(+) glyceraldehydes will belong to D-series and similarly any compound that can be prepared from, or converted in to L(-) glyceraldehydes will belongs to the L-series.

6.1.3. Erythro and Threo System of Nomenclature

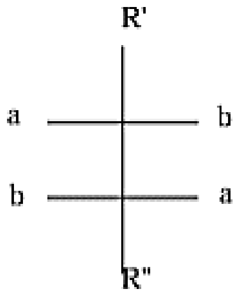
- This nomenclature is mainly used only in those compounds which have only two chiral carbons and the following structures:

$$R'-Cab-Cab-R'' \quad \text{or} \quad R'-Cab-Cbc-R''$$

- i.e. out of six substituent on two asymmetric carbons, at least one should be same in both the carbons. When two like groups in fisher projection formula are drawn on the same side of vertical line, the isomer is called erythro form; if these are placed on the opposite sides the isomer is said to be threo form. (TRB 2017)



erythro form



threo form

Following are some examples of threo and erythro form.

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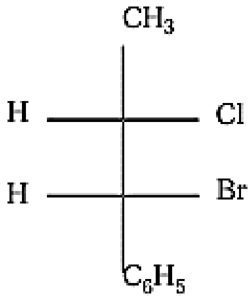
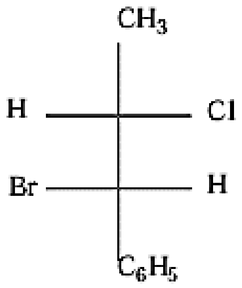
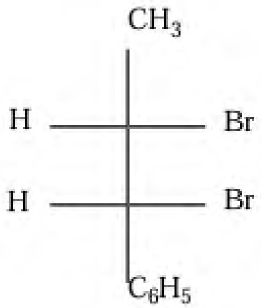


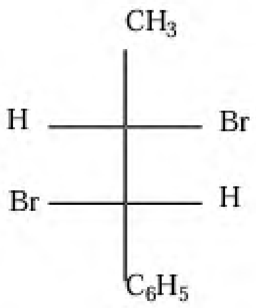
erythro form



threo form



erythro form



threo form

6.1.4. R.S. Nomenclature

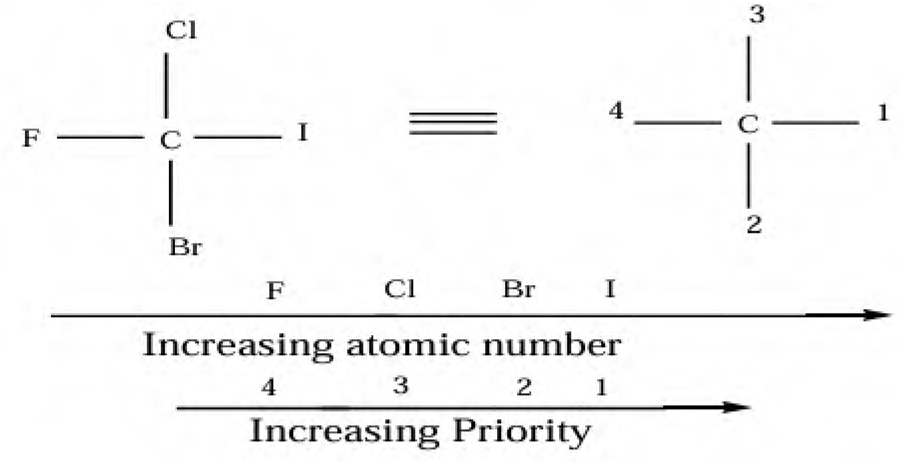
- The order of rearrangement of four groups around a chiral carbon is called the absolute configuration around that atom. System which indicates absolute configuration was given by three chemists R.S. Cahn, C.K. Ingold and V. Prelog. This system is known as (R) and (S) system or the Cahn-Ingold Prelog system. The letter (R) comes from the Latin rectus (means right) while (S) comes from the Latin sinister (means left).
- Any Chiral carbon atoms have either an (R) configuration or a (S) configuration. Therefore, one enantiomer is (R) and the other is (S). (TRB 2024)
- A recemic mixture may be designated as (RS), meaning a mixture of the two.
- The R, S nomenclature involves two steps:

Step I:

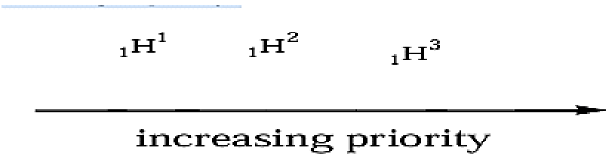
- The four ligands (atom or groups) attached to the chiral centre are assigned a sequence of priority according to sequence rules.

Rule 1: If all the four atoms directly attached to the chiral carbon are different, priority depends on their atomic number. The atom having highest atomic number gets the highest priority, i.e., (1).The atom with lowest atomic number is given lowest priority, i.e. (2), the group with next higher atomic number is given the next higher priority (3) and so on.

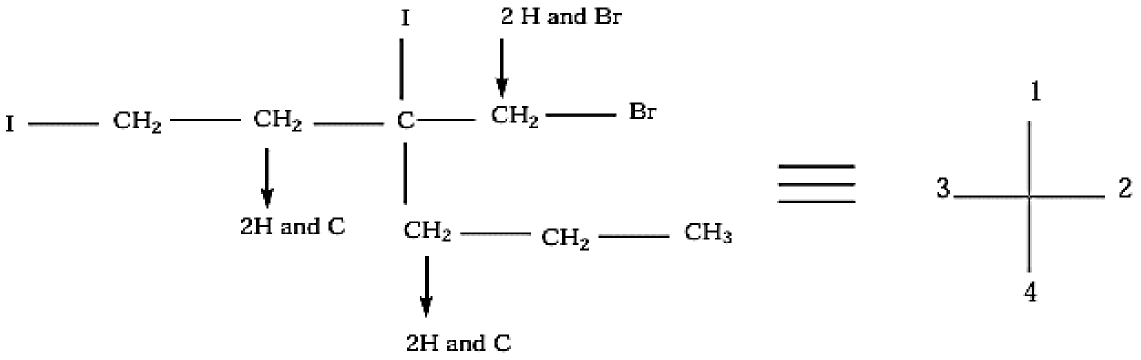
For example:



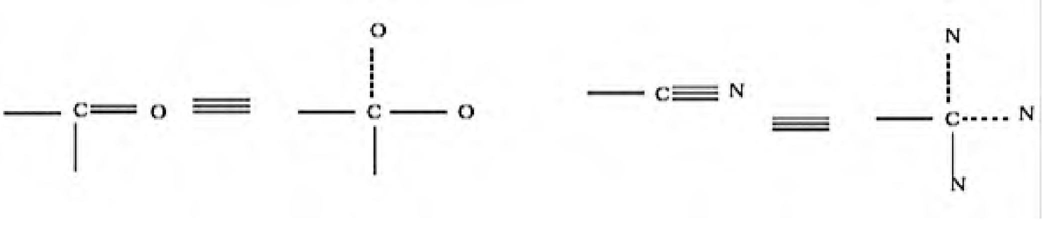
Rule 2: if two or more than two isotopes of the same element are present, the isotope of higher mass receives the higher priority.

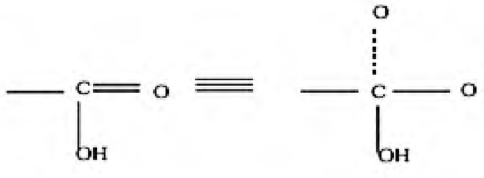


Rule 3: if two or more of the atoms directly bonded to the chiral carbon are identical, the atomic number of the next atom is used for priority assignment. If these atoms also have identical atoms attached to them, priority is determined at the first point of difference along the chain. The atom that has attached to it an atom of higher priority gets the higher priority.

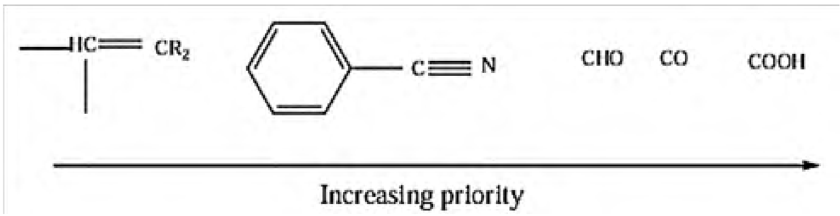


- In the above example, the atoms connected directly to the chiral carbon are iodine and three carbons. • Iodine has the highest priority. • Connectivity of other three carbons are 2H and Br, 2H and C and 2H and C. • Bromine has the highest atomic number amongst C, H, Br and thus CH_2Br has highest priority among these three groups (i.e. priority number 2). • The remaining two carbon are still identical (C and 2H) connected to the second carbon of these groups are 2H and I and 2H and C. Iodine has highest priority. • Amongst these atoms, so that-CH_2-CH_2-I is next in priority list and CH_2-CH_2-CH_3 has the last priority. Rule 4: If a double or a triple bond is linked to chiral centre, the involved electrons are duplicated or triplicated respectively.





- By this rule, we obtain the following priority sequence:

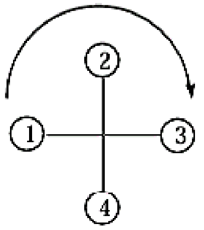


Step-II:

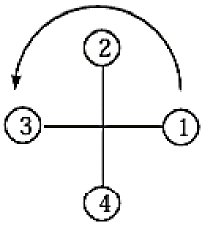
- The molecule is then visualised so that the group of lowest priority (4) is directed away from the observer (at this position the lowest priority is at the bottom of the plane). The remaining three groups are in a plane facing the observer. If the eye travels clockwise as we look from the group of highest priority to the group of second and third priority (i.e. 1 → 2 → 3 with respect to 4) the configuration is designated R. If arrangement of groups is in anticlockwise direction, the configuration is designated as S.

For example:

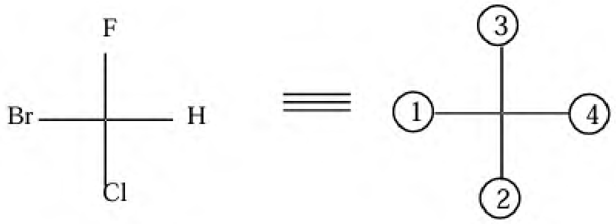
- Let us apply the whole sequence to bromochlorofluoromethane



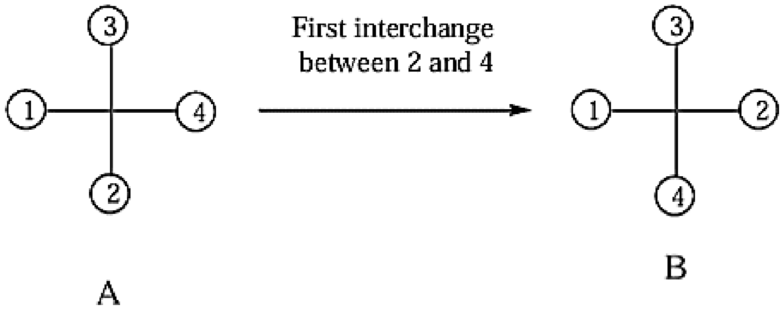
Clockwise arrangement of
① ② and ③ → R



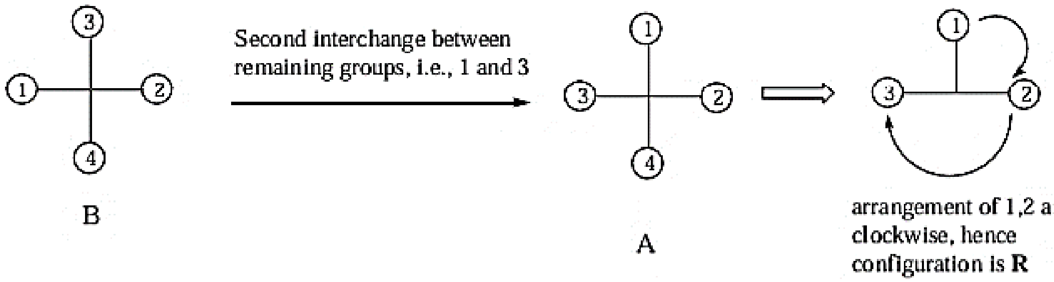
Anticlockwise arrangement of
① ② and ③ → S



- In this Fischer projection, the least priority number is not at the bottom of the plane. In such cases, the Fisher projection formula of the compound is converted in to another equivalent projection formula in such a manner that atom the lowest priority is placed vertically downward. This may be drawn by two interchanges between four priority numbers. The first interchange involves the two priority numbers, one is the least priority number and the other is the priority number which is present at the bottom of the plane. In the above case, first interchanges will takes place between 2 and 4.

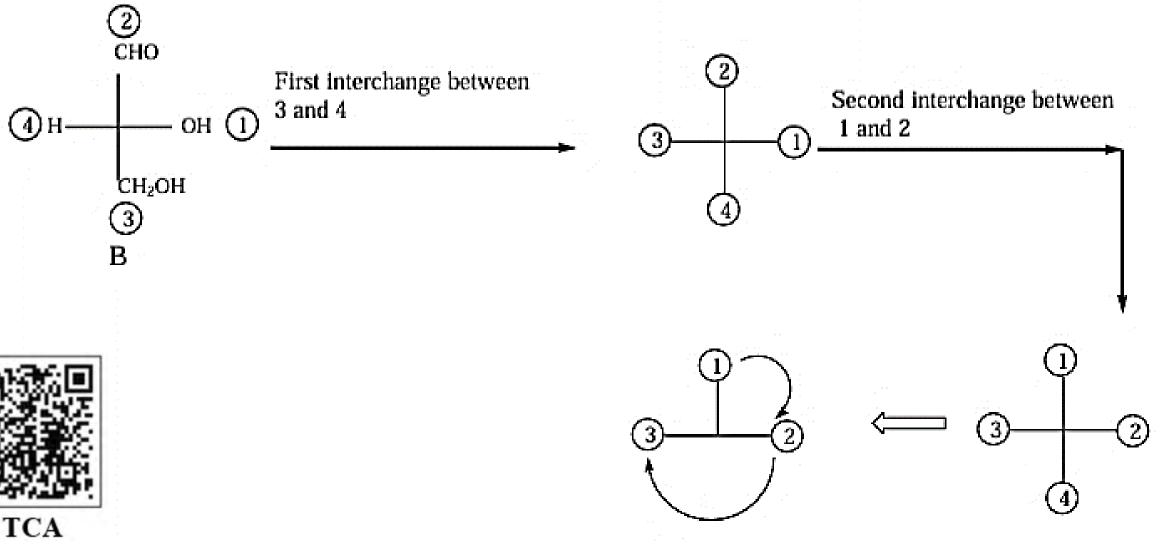


- A second inter change creates the original molecule (i.e. A).



arrangement of 1,2 and 3 are clockwise, hence configuration is **R**

Example:-

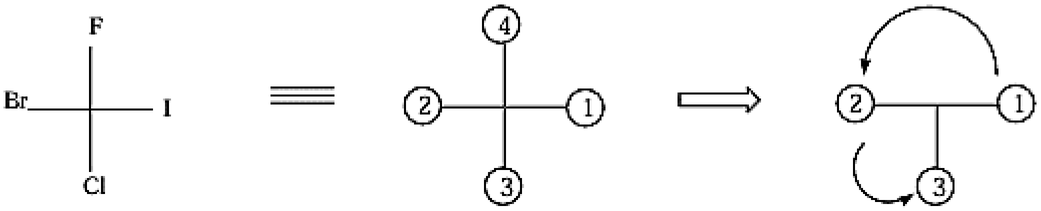


TCA

clockwise, hence configuration is **R**

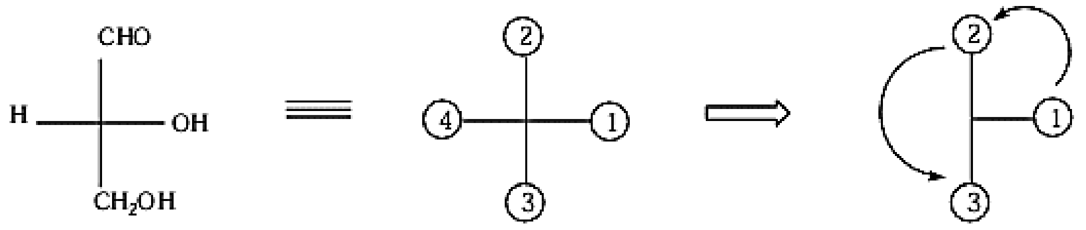
Note: • An odd number of interchange of positions of groups on chiral carbon gives different compound. • An even number of interchange of positions of groups on chiral carbon gives same compound. An alternative, simple and most widely accepted procedure used now (Epling,1982) to assign R,S configuration in the case of Fischer projections is as followes: Case-I: R and S nomenclature from Fischer projection formula (Golden rule): If in a Fischer projection, the group of lowest priority (4) is on a vertical line, then the assignment of configuration is R for a clockwise sequence of 1 to 2to 3 and S for anticlockwise sequence. (TRB 2015)

For example:



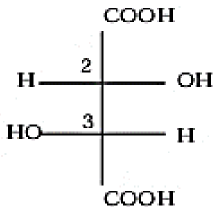
Anticlockwise arrangement hence S- configuration

- However, if the group of lowest priority is on horizontal line, then the assignment of configuration is S for a clockwise sequence of 1 to 2 to 3, and R for the anticlockwise sequence.

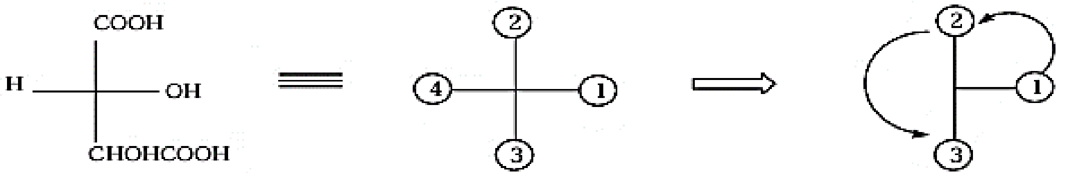


Anticlockwise arrangement
but lowest priority at horizontal
line hence R- configuration

- When molecule contain two or more chiral centres, each chiral centre is assigned an R or S configuration according to the sequence and conversion rules. Thus (+) tartaric acid is (2R, 3R) (+) tartaric acid.

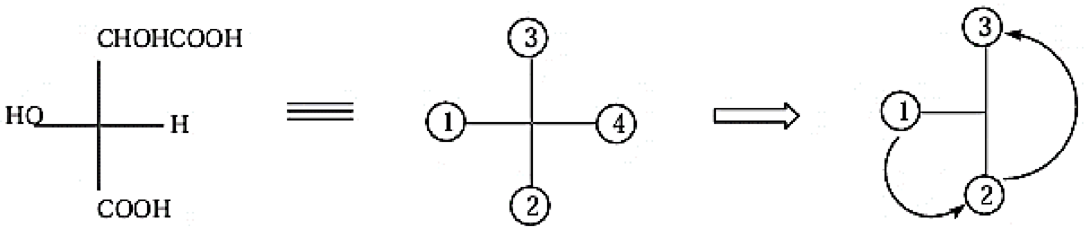


Configuration at chiral carbon - 2.



Anticlockwise arrangement
but lowest priority at horizontal
line hence R- configuration

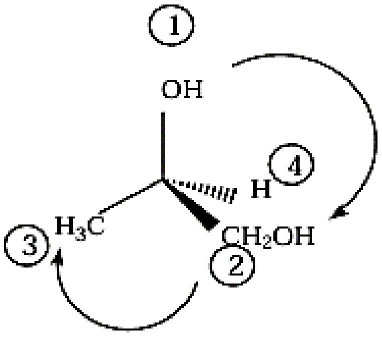
Configuration at chiral carbon - 3.



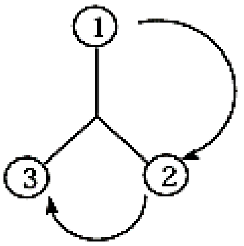
Anticlockwise arrangement
but lowest priority at horizontal
line hence R- configuration

6.1.5. R.S- Nomenclature from Flying-Wedge Formula.

- If the group of the lowest priority is away from the observer (i.e., bonded by dashed line) and the priority sequence (1 2 3) is clockwise, then the configuration is assigned as R. If the priority sequence is anticlockwise then the configuration is S.

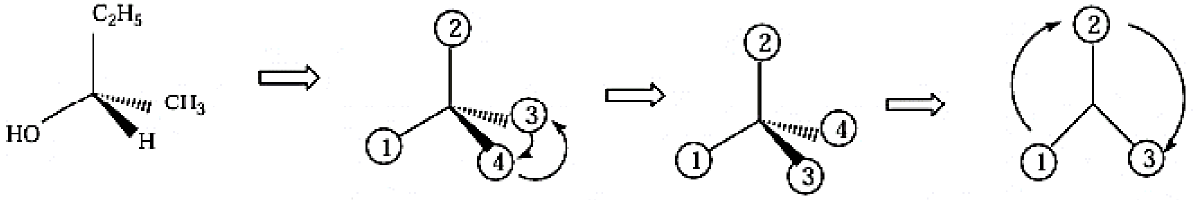


Lowest priority order is on deshed line



Clockwise arrangement thus configuration is R

- If the group of lowest priority is not bonded by dashed line then interchange a pair of groups so that the group with the lowest priority is bonded by dashed line. Now see the sequence (1 2 3), if it is clockwise then the configuration is assigned as S and if anticlockwise R. This is because you have interchanged a pair of groups and now you are determining the configuration of enantiomer of original molecule.



Least priority order is not bonded with deshed line , so interchange the group 3 and 4

This is R configuration, which means that the original compoundI has S configuration

Exercise Questions 1:

1.What is the prefix used to indicate the presence of a stereocenter in a molecule?

A) "iso-" B) "stereo-" C) "R/S-" D) "cis/trans-"

2. What is the term used to describe isomers that differ in the arrangement of atoms in space?

A) Structural isomers B) Stereoisomers

C) Conformational isomers D) Tautomers

TCA

3. What is the prefix used to indicate the presence of a geometric isomer?

A) "cis-" B) "trans-" C) "geo-" D) Both A and B

4. What is the term used to describe isomers that differ in the arrangement of atoms around a double bond?

A) Structural isomers B) Stereoisomers

C) Geometric isomers D) Conformational isomers

5. What is the term used to describe isomers that differ in the arrangement of atoms in a ring?

A) Structural isomers B) Stereoisomers

C) Geometric isomers D) Conformational isomers

6. What is the prefix used to indicate the presence of an optical isomer?

A) "d-" B) "l-" C) "R-" D) Both A and B

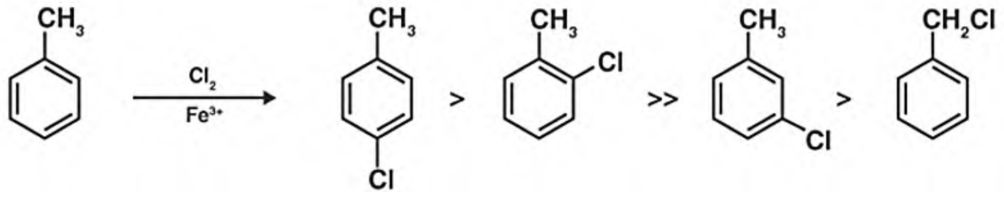
7. What is the term used to describe isomers that differ in the arrangement of atoms in a molecule, but not in the arrangement of atoms around a double bond?

A) Structural isomers B) Stereoisomers

C) Conformational isomers D) Tautomers

6.2. REGIOCHEMISTRY

Regiochemistry is the discipline of chemistry that explains chemical processes' regioselectivity. In a chemical reaction with many products, it identifies which one is the major product and which one is the minor product. This is dependent on the target molecule's probable sites to which the reagent molecules will be attached. In a substituted benzene ring, for example, the reagent molecule can attach to one of three potential places, *ortho*, *para*, or *meta*, depending on the substituent already present in the benzene ring.



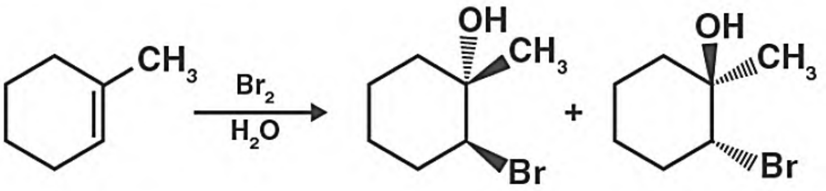
- The chlorination of toluene is seen in the above reaction. The chlorine atom can bind to the toluene molecule in a number of different places. The para replacement, on the other hand, is the most reliable. As a result, it is the main product of this reaction.

6.2.1. Regioselectivity

- The preference of chemical bonding or breaking in one direction over all other potential orientations is referred to as regioselectivity in chemistry. It can refer to any of the numerous possible positions that a reagent can affect, such as which proton a strong base will extract from an organic molecule or where an additional substituent will be applied to a substituted benzene ring.
  - In the presence of water, the synthesis of halohydrin from an alkene is regioselective.
  - This reaction follows the Markovnikov pathway and proceeds with anti stereospecificity.
  - The nucleophile is connected to the more substituted carbon and the electrophile to the less substituted carbon.

TCA

- A halohydrin production from an alkene is an example:

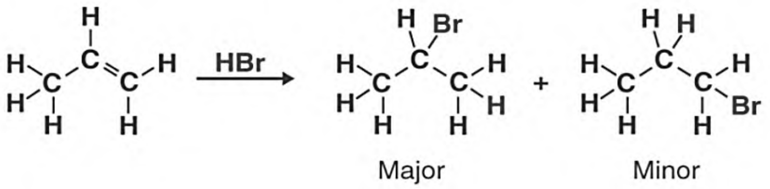


- Bromine works as an electrophile in the given case, whereas the OH group from water acts as a nucleophile.

6.2.2. Markovnikov's Rule

- The result of some chemical addition reactions can be described using Markovnikov's Rule, also known as Markownikoff's Rule. This rule was initially proposed in 1865 by Russian scientist Vladimir Vasilyevich Markovnikov. Markovnikov's rule is an empirical rule for predicting the regioselectivity of alkene and alkyne electrophilic addition processes.(TRB 2015)
- When a protic acid (HX) is introduced to an asymmetric alkene, the acidic hydrogen binds to the carbon with the most hydrogen substituents, while the halide group binds to the carbon with the most alkyl substituents.

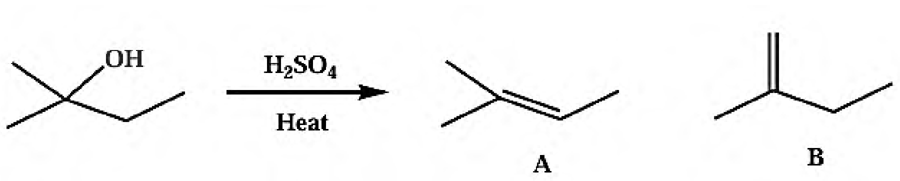
- “Hydrogen is added to the carbon with the most hydrogens, and halide is added to the carbon with the least hydrogens,” as a simplified version of the rule goes.
- The addition of hydrobromic acid (HBr) to propene, as shown below, is an example of a reaction that follows Markovnikov’s rule.



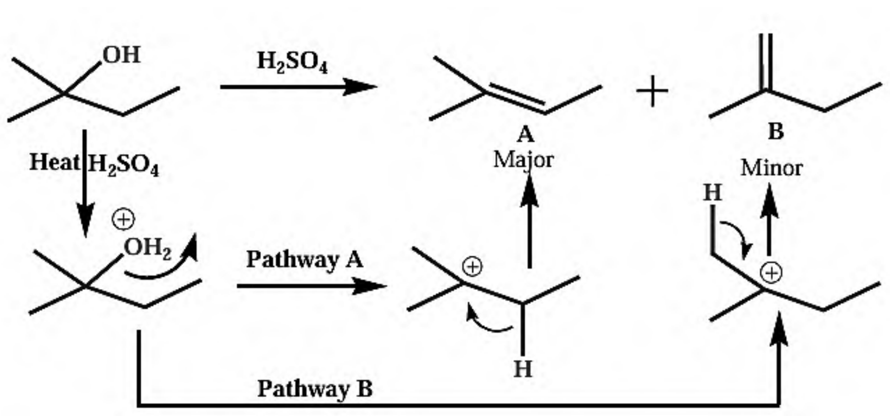
- The reaction depicted above shows that the bulk of the products generated follow Markovnikov’s rule, while the minority do not.
- It’s worth noting that Markovnikov’s rule was designed especially for use in the addition reaction of hydrogen halides to alkenes. Based on the regioselectivity of the reaction, Anti-Markovnikov addition reactions are the opposite of ‘Markovnikov’ addition reactions.

6.2.3. Regioselective and Regiospecific reactions

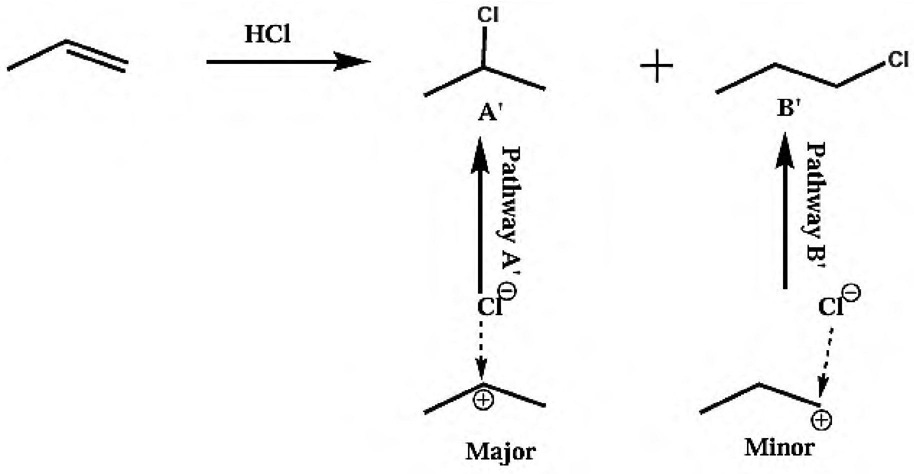
- Suppose, you are walking 100 metre distance in a straight path and you suddenly find two different routes A and B from the same starting point. After walking 100 metres on route A, you find the house of your friend A and after walking 100 metres on route B, you find the house of your friend B. If you analyze the situation, then you are providing the same physical effort and energy to walk 100 metres in two different routes, and you are getting two targets, houses of friend A and friend B. For chemical reactions, you can start with the same starting materials and reaction conditions, and the reactants can react with each other via different pathways. Each pathway will lead us to different product.
- Let us take the following example:



- In the above reaction after heating the alcohol with sulphuric acid, we get two products A and B, which have different position of double bonds. Product A, which is the tri-substituted alkene is the major product and Product B is the minor product. They differ by the position of double bond and are generated by two different pathways, Pathway A and Pathway B as shown below:



- Let us take another example as shown below:



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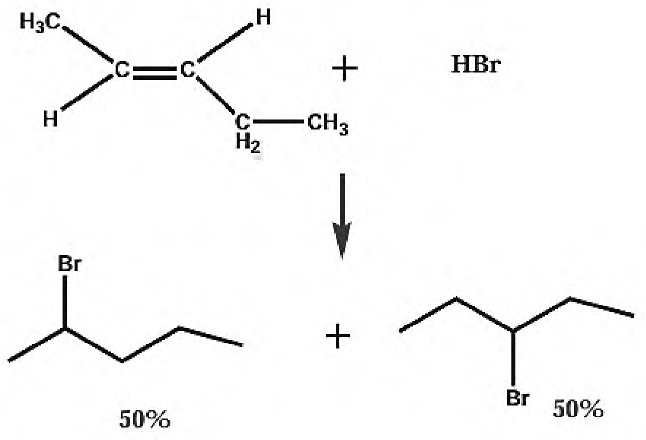
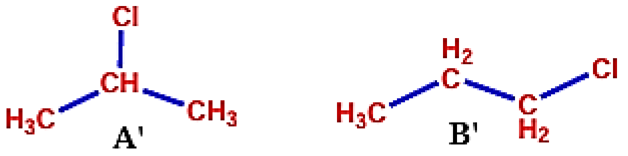
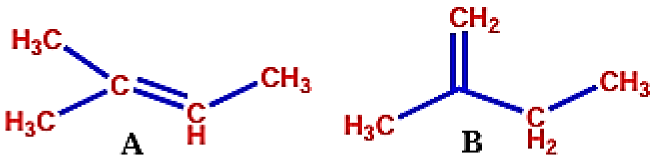
- In the second example, 2-chloropropane, A' is the major product. Here, pathway A' involves a secondary carbocation, which is more stable than the primary carbocation formed in pathway B'. So, we get two different products A' and B', by two different pathways and product A' is formed in greater proportion than product B'. If a reaction takes place on an unsymmetrical compound and more than one reacting pathways are possible due to site selectivity of one functional group in a reaction, then the reaction is called regiochemical reaction. Now, all regiochemical reactions are not regioselective. For example, consider the following reaction:



- In this case, the reaction is regiochemical as it can occur by two different pathways. But, the reaction is not regioselective as the two products are formed in equal proportions and no product is major product for this reaction. Thus, If out of the several pathways, one pathway predominates, then the reaction is called regioselective reaction. In regioselective reactions, if only one product is formed exclusively, then the reaction is called regiospecific reaction. Regiochemistry is the study of different pathways that two reactants can take during a reaction. In the first example, products A and B are called regioisomers and in the second example, products A' and B' are regioisomers of each other. Now why these are called regioisomers? It is because, they are formed by two different pathways of a regiochemical reaction. Now, let us study what is the nature of isomerism present in case of regioisomers.   Do you remember the term constitutional isomers? Constitutional isomers are compounds that have the same molecular formula and different connectivity. Regioisomers are constitutional isomers. So, regioisomers will be generated from the same chemical reaction, they will have the different bond connectivity and the same chemical formula.



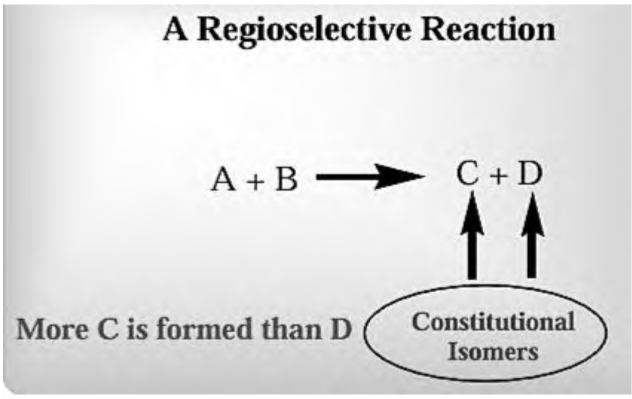
Same Molecular Formula: C_3H_7Cl



Same Molecular Formula: C_5H_{10}

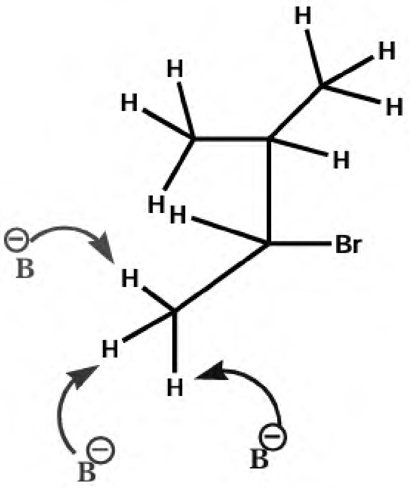
- It is clearly evident that A and B have the same molecular formula, but different bond connectivity, and they are formed by two different pathways of one chemical reaction. Hence, they are regioisomers of each other. Similarly, A' & B' are also the regioisomers.
- Regioselectivity is a type of substrate selectivity in which substrates have the capability to react at more than one centre but react at one centre at a higher rate than the other. For example, 2-methylcyclohexanone on base induced alkylation gives mostly 2,2 dimethylcyclohexanone and only small amount of 2,6-dimethylcyclohexanone.   Thus, If we add a non-symmetrical reagent (i.e. A-B where A is not equal to B) to nonsymmetrical starting materials (think an alkene, where the groups at each end of the double bond are

different), then two isomeric products that are constitutional isomers can be obtained. The reaction is regiochemical reaction. If one product predominates over the other, then it is called regioselective. According to IUPAC Gold Book, "A regioselective reaction is one in which one direction of bond making or breaking occurs preferentially over all other possible directions. Reactions are termed completely (100%) regioselective if the discrimination is complete, or partially (x%), if the product of reaction at one site predominates over the product of reaction at other sites.".



E2 reaction is regioselective in nature. Let us explain how?

- Generally, in a E2 reaction, we have a halide and a proton to be removed and form a double bond. Now, if there are option of two protons to be removed, then the two options might lead to two different products. Thus, such reactions can have different regiochemical outcomes, which means the reaction can occur at two different places of the molecule. The removal of proton in E2 generally leads to the most-substituted alkene as the major product. However, steric factor is also important for removal of proton. If the hydrogen leading to more substituted double bond is crowded and not easy to approach, then the base approaches other proton more easily which is less crowded. If the bases have a bulky structure, then in some cases, the least substituted alkene is formed as the major product.

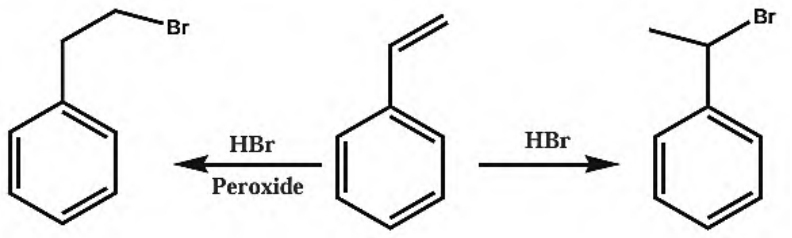


TCA

- Now, let us study regioselectivity observed in some commonly known reactions such as addition reactions, hydration, epoxidation, electrophilic substitution, Diels Alder reaction and 1, 3-Dipolar cycloaddition reactions.

6.2.4. Addition of HBr to alkenes

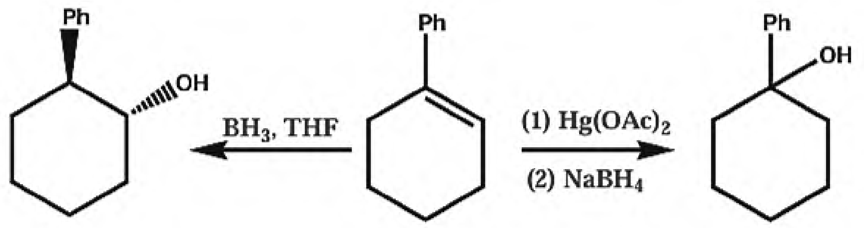
- When compound I reacts with HBr, it gives II as the major product and when compound I reacts with HBr in presence of peroxide, it gives III as the major product. Both these reactions are regioselective. In case of regioselective reactions, there is preferential reactivity of one site over the other of the same functional group, which is the olefinic double bond in this case.



III Major I II Major

(a) Hydration of Alkenes

- When compound IV reacts with $Hg(OAc)_2$ followed by $NaBH_4$, it gives V as the major product and when compound IV reacts with BH_3.THF, it gives VI as the major product. Both these reactions are regioselective. In case of regioselective reactions, there is preferential reactivity of one site over the other of the same functional group, which is the olefinic double bond in this case.



VI Major IV V Major

(b) Hydration of Alkynes

- When compound VII reacts with $HgSO_4/H_2SO_4$, it gives VIII as the major product and when compound VII reacts with BH_3.THF followed by $NaOH/H_2O_2$, it gives XI as the major product. Both these reactions are regioselective. In case of regioselective

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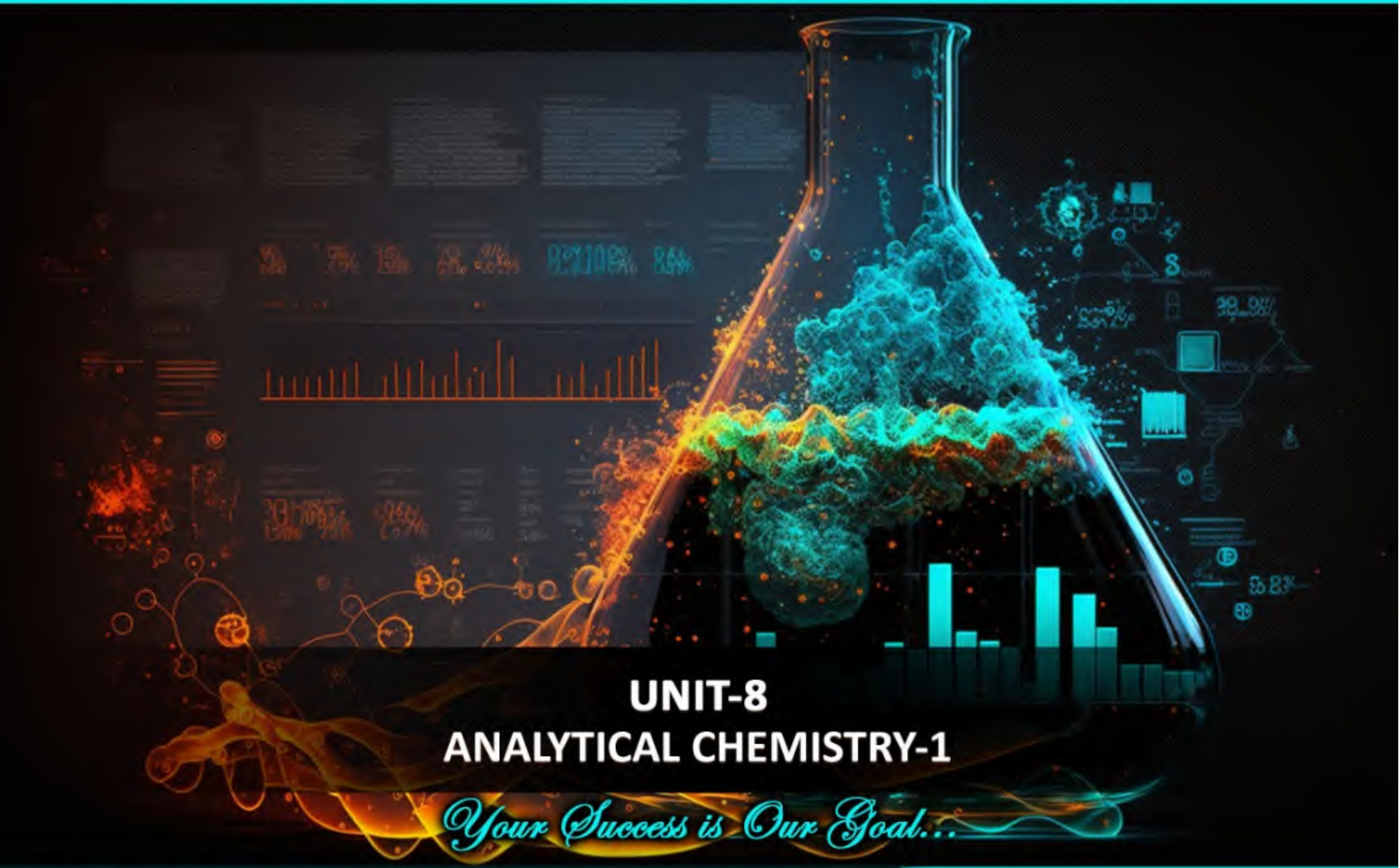

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INDEX

SYLLABUS

DATA ANALYSIS:

Nature of quantitative measurements and treatment of data. Mean, median, precision and accuracy, standard deviation, significant figures, Gaussian distribution curves, Null Hypothesis, Confidence interval of mean, Rejection of data (Q test), Student’s t, F tests. Errors – absolute and relative errors, linear regression, covariance and correlation coefficient.

SAMPLING:

Principles of sampling methods for solid, liquids and gases. Gross sampling, Sampler’s responsibility and pitfalls, hazards of sampling.

SEPARATION TECHNIQUES:

Classical forms of chromatography – Introduction, principle and applications of column, thin layer chromatography and paper chromatography, Gas and High-Performance Liquid Chromatography.

THERMO ANALYTICAL TECHNIQUES:

Principles and applications of TGA, DTA and DSC.

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7) Fundamentals of Analytical Chemistry" by Douglas A. Skoog, Donald M. West, F. James Holler, and Stanley R. Crouch
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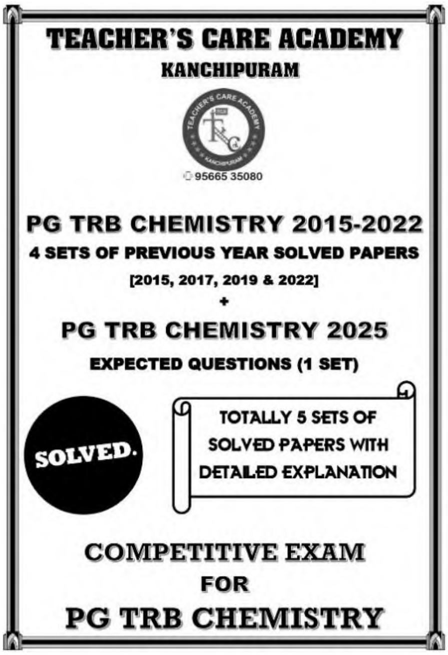

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PG TRB CHEMISTRY – UNIT 8

8. ANALYTICAL CHEMISTRY

INTRODUCTION:

Historically chemistry could be divided into five main areas. Analytical chemistry is an unique experimental science wherein there are phenomenal developments each year. This results in progress in the formulation of better methods of analysis with more selectivity as well as sensitivity. Many advances and changes in these areas were made possible by analytical results.

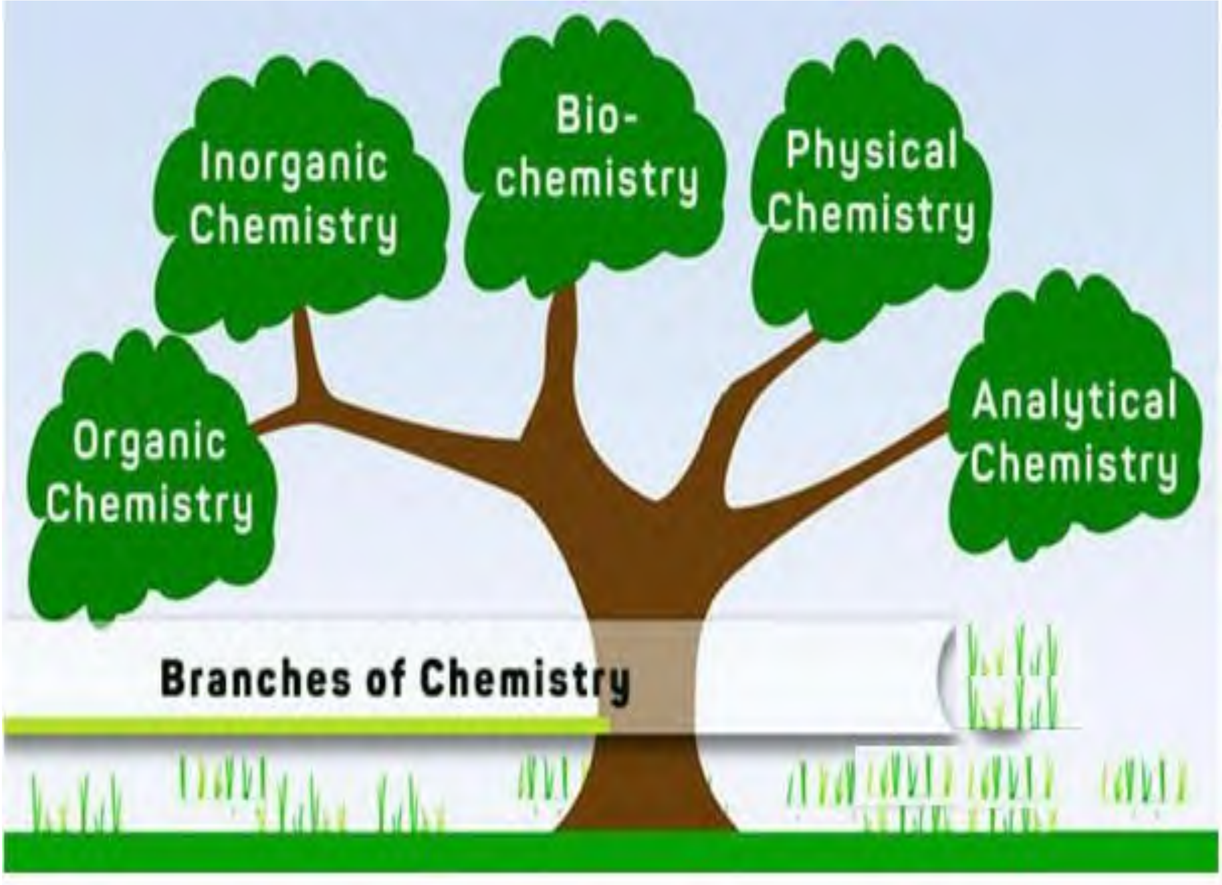

Figure 1: Branches of Chemistry

Analytical chemistry is the study of separation, identification and quantification of the chemical components of natural and artificial materials. A complete chemical analysis is essential to understand the chemistry of a substance.

This involves the quantitative and qualitative treatment of the substance under study.Infact, analytical chemistry is the science of chemical identification and determination of the composition (atomic, molecular, phase) of substances and materials and their chemical structure.

Analytical chemistry seeks ever improved means of measuring the chemical composition of natural and artificial materials. The techniques of this science are used to identify the substances which may be present in a material and to determine the exact amounts of the identified substances.

An Analytical chemist tries to serve the needs of many fields:

- In medicine, analytical chemistry is the basis of clinical laboratory tests which help physicians to diagnose diseases and chart progress in recovery.
- In industry, analytical chemistry provides the means of testing raw materials and for assuring the quality of finished product whose chemical composition is critical.
- Many house-hold products, fuels, paints, pharmaceuticals, etc. are analyzed by the procedures developed by the analytical chemists before being sold to the consumer.
- Environmental quality is often evaluated by testing for suspected contaminants using the techniques of analytical chemistry.
- The nutritional value of food is determined by chemical analysis for major components such as proteins and carbohydrates and trace components such as vitamins and minerals.
- Indeed, even the calories in food are often calculated from its chemical analysis.
- An analytical chemist also makes important contribution to fields as diverse as forensics, archaeology and space science.

Types:

Analytical chemistry consists of two types of analysis:

i) Qualitative Analysis:

It deals with the identification of elements, ions or compounds present in a sample.

ii) Quantitative Analysis:

It deals with the determination of how much of one or more constituents are present in the sample which may be solid, liquid, gas or a mixture.

DIFFERENCES:

S. No	Qualitative Analysis	Quantitative Analysis
1	It identifies the presence or absence of a particular substance in a sample.	It measures the amount or concentration of a substance in a sample.
2	It is performed using simple chemical tests that produce a visual change, such as a colour change or a precipitate formation.	It is performed using instrumental methods that produce a numerical result, such as a mass or a volume.
3	It is used to identify unknown substances or to confirm the identity of a known substance.	It is used to determine the purity or composition of a substance.
4	It is less precise and less accurate than quantitative analysis because it relies on subjective observations.	It is more precise and more accurate than qualitative analysis because it relies on objective measurements.
5	It can be performed using a small sample size.	It requires a larger sample size to obtain accurate results.

Table:1

METHODS OF ANALYSIS:

To select an appropriate method of analysis, following important factors must be taken into account:

(a) The nature of the information which is sought.

(b) The size of the sample available and the proportions of the constituents to be determined and,

(c) The purpose for which analytical data are required.

TCA

i) Classical methods

Classical methods are routine, simple methods that are used in laboratories. They are simple procedures and cost-effective. They do not need sophisticated instruments and so these methods are preferred where high accuracy is not essential. The classical methods can be subdivided into two types namely –

(a) Gravimetric analysis – This method involves the quantitative measurement of the analyte through the measurement of mass. This method involves determining the mass of the analyte or some compound chemically related to it.

(b) Volumetric analysis – This method involves titrations. The volume of a solution containing sufficient standard reagent to react completely with the analyte is measured.

Analytical methods are divided into two categories, as follows,

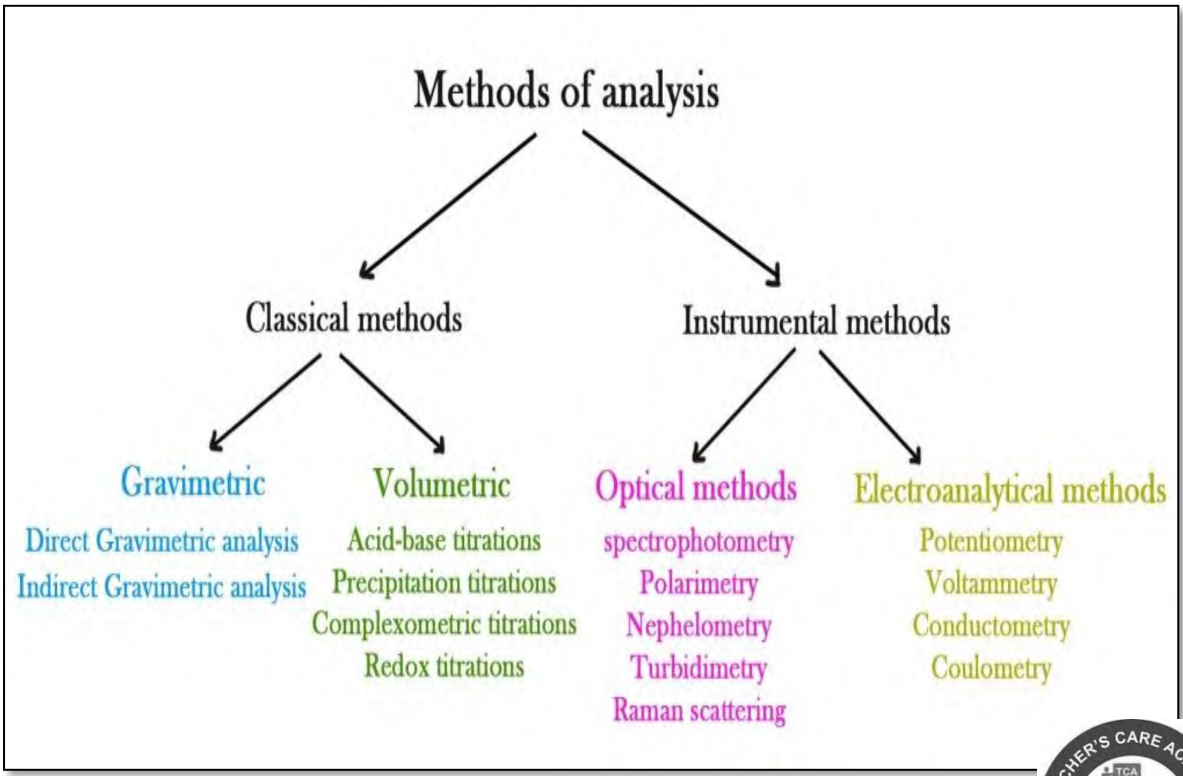

Figure 2: Method of Analysis

ii) Instrumental methods:

These methods involve use of instruments. These involve very accurate measurements.

Some physical property of the analyte is measured by an instrument, which gives us information about the analyte. Depending on the physical property under study, the instrumental methods can be broadly classified as –

(a) Optical methods – These are based on the interaction of the analyte with electromagnetic radiations (i.e light).

(b) Electroanalytical methods – These involve measuring some electric property (e.g.– conductance, electrical potential, etc.) of the analyte.

EXERCISE: 1

1. The primary purpose of analytical chemistry is -----------

A) To synthesize new compounds	B) To study the properties of matter
C) To separate and identify substances	D) To design new laboratory instruments

2. Which of the following is a common technique used in qualitative analysis?

A) Gas chromatography	B) Atomic absorption spectroscopy
C) Titration	D) X-ray diffraction

3. What does a calibration curve represent in analytical chemistry?

A) The relationship between the sample’s composition and its color

B) The relationship between sample concentration and instrument response

C) The time required for a reaction to complete

D) The accuracy of a measurement technique

4. Which of the following is an example of a destructive analytical method?

A) Spectrophotometry B) Chromatography

C) Atomic absorption spectroscopy D) Titration

5. ---------- is used to measure the concentration of an analyte in a solution?

A) Refractometer B) pH meter

C) Spectrophotometer D) Thermometer

6. Which of the following is a common sample preparation method in analytical chemistry?

A) Filtration B) Evaporation C) Drying D) All of the above

7.What is the purpose of a blank sample in analytical experiments?

A) To ensure that the sample is completely free from contaminants

B) To measure the background noise and instrument response without the analyte

C) To determine the calibration of the instrument

D) To test the final product after analysis

8.Quantification in analytical chemistry is ------------

A) Determining the molecular structure of a compound

B) Measuring the physical properties of a sample

C) Measuring the amount or concentration of an analyte in a sample

D) Identifying the components present in a sample

TCA

8.1.DATA ANALYSIS:

It is defined as researching, organizing, analyzing and changing data in order to bring out the useful information. In analytical chemistry, quantitative measurement and data treatment involves determining the amount of a substance in a sample, and using calculations to determine the concentration of that substance

8.1.1. NATURE OF QUANTITATIVE MEASUREMENTS AND TREATMENT OF DATA:

Quantitative analysis:

- A method used to determine the amount or concentration of a substance in a sample. It involves measuring the sample's physical properties, such as mass, volume, and density.

Data treatment:

- Involves using statistical methods to evaluate the precision of data sets and determine if a questionable data point should be discarded.

Analytical methods:

There are several analytical methods used in quantitative analysis, including:

- **Gravimetric analysis:** Determines the mass of an analyte or a compound related to it.
- **Volumetric analysis:** Uses the volume of a solution containing a reagent to react with the analyte.
- **Electroanalytical analysis:** Measures electrical properties of a sample to determine its composition.
- **Spectroscopic analysis:** Based on the interaction of electromagnetic radiation with the analyte's atoms and molecules.

Steps in Quantitative analysis:

The important steps involved in determination are:

i) Procurement of samples
ii) Its conversion to measurable state
iii) Measurement of desired constituent
iv) Calculation and interpretation of numerical data.

The most difficult problem is the isolation, before the measurement step. The important steps encountered are:

(a) Sampling: It should be representative of the mass of the material. This is possible provided the material is reasonably pure and is homogeneous in nature.

(b) Conversion of desired constituent to measurable form: This step involves method of separation. The selection of the separation technique for a specific situation will depend upon a number of factors. Such selection is generally decided on the basis of accuracy and the precision required.

(c) Measurement of desired constituent: Any physical or chemical property can be used as a means of qualitative identification and quantitative measurement or both. If the property is specific and selective for measurement, then separation and pretreatment of the sample can be minimized, e.g. analysis involving atomic absorption spectroscopy.

(d) Calculation and interpretation of analytical data: An analysis is not complete until the results have been expressed in such a manner that the person for whom the results are intended can understand their significance. In recent years greater attention has been paid to statistical techniques both in development and in assaying the value of the final analytical results. This has led to the establishment of a new branch of science termed as Chemometrics.

Statistical measures of Data:

In analytical chemistry, the mean and median are both statistical measures used to characterize measurements and results Statistical measures like the mean, median, and standard deviation are used to quantify errors, precision, and accuracy. In reporting results, it's important to include the standard deviation to indicate the sample variance.

8.1.2. MEAN ($\bar{x}$):

Mean or average is the quotient obtained when the sum of a set of replicate measurements by then number of individual results in the set.

$$\bar{x} = \frac{x_1 + x_2 + x_3 + \ldots\ldots + x_n}{n}$$

TCA

Example:

- Calculate the mean for the following set of values 5, 10 & 15.

  Mean = $\bar{x} = \frac{5+10+15}{3}$ = 30/3 = 10

- To calculate the mean, we add together the results for all measurements

  3.080, 3.094, 3.107, 3.056, 3.112, 3.174 &3.198

  $\bar{x}$ = 3.080+3.094+3.107+3.056+3.112 +3.174+3.198 = $\frac{21.821\text{g}}{7}$

  $\bar{x}$ = 3.117 g

8.1.3. MEDIAN (M):

The median is the average (or) middle value in a set. For an odd number of values, the middle value is the median and for even number values, the average of the middle pair gives the median.

Example:

i) For the odd values 18, 19, 20, 21 & 22.

Median (M) = 20

ii) For the even values 18, 19, 20, 21, 22 & 23

Median (M) = 20+21 / 2 = 20.5

8.1.3.1. MEAN DEVIATION ($\overline{d}$):

The mean deviation of a value in a set of values is the average of the deviations of all the individual values from their average.

$$\overline{d} = \frac{d_1 + d_2 + d_3 + \ldots\ldots + d_n}{n}$$

Example:

Calculate the mean deviation for the following set of values: 30.42, 30.32 and 30.22

Solution:

The following steps should be used for calculating mean deviation.

i) The average of the given set of values is calculated.

ii) The deviation of each value from the average is calculated.

iii) The average of all these deviation (ignoring signs) gives the average deviation.

$$\text{Average} = \frac{30.42 + 30.32 + 30.22}{3}$$

$$\overline{x} = 30.32$$

S. No	Value x_i	$\left|x_i - \overline{x}\right| = \overline{d}$
1.	30.42	30.42 – 30.32 = 0.10
2.	30.32	30.32 – 30.32 = 0
3.	30.22	30.22 – 30.32 = 0.10

Total = 0.20

$$\text{Mean deviation} = \frac{0.20}{3}$$

$$\mathbf{\overline{d} = 0.0667}$$

If the mean deviation of a set of measurements is small it means that the average of that set is nearly precise.

EXERCISE: 2

1. Mean of the data set: 3, 7, 5, 9, 2 is -----------

A) 4.5 B) 5.2 C) 5 D) 6

TCA

2. Which of the following is true about the median of a dataset?

A) The median is always equal to the mean.

B) The median is the middle value when the data is ordered.

C) The median is the sum of all values divided by the total number of values.

D) The median cannot be used with an odd number of values.

3. Calculate the median of the data set: 12, 18, 24, 30, 36, 42

A) 24 B) 30 C) 18 D) 36

4. If the data set consists of the numbers: 8, 10, 12, 14, 16, what is the mean?

A) 12 B) 13 C) 10 D) 14

5. Which of the following is true about the relationship between mean and median in a skewed distribution?

A) In a negatively skewed distribution, the mean is greater than the median.

B) In a positively skewed distribution, the mean is less than the median.

C) In a symmetrical distribution, the mean and median are equal.

D) The mean and median are never equal.

6. For the data set: 5, 7, 10, 12, 15, what is the median?

A) 12 B) 10 C) 7 D) 9

7. Calculate mean of the data set: 1, 3, 3, 6, 7

A) 4 B) 5 C) 6 D) 4.2

8. For the data set: 2, 3, 5, 7, 11, 13, what is the median?

A) 5 B) 7 C) 6 D) 8

9. If the dataset is: 3, 5, 7, 10, 12, 14, what is the median?

A) 8 B) 9 C) 7 D) 10

10. If the median of a data set is 20, what can be inferred?

A) The data set is symmetrical.

B) The sum of all values equals 20.

C) 50% of the values are less than or equal to 20.

D) The mean is always greater than 20.

8.1.4. PRECISION:

Definition:

It is the degree of agreement between two (or) more measured value of a property under identical conditions.

Explanation:

Let the weight of a silica crucible be 25.1234 g when weighed in a particular set of conditions. If the same crucible is weighed under identical conditions and if the weight got is the same, then we say that there is precision in the weighing. Thus if a value is reproducible, then it called a precise value.

Method of expressing precision:

Precision is expressed in terms of absolute method (or) relative method.

i. Absolute method:

The precision is expressed in terms of mean deviation in this method. The smaller the value of average mean deviation the greater will be the precision.

ii. Relative method:

The precision is expressed in terms of percentage deviation from the mean of a set of values.

Percentage deviation from the mean = $\frac{\bar{x} - x_i}{Mean}$ x 100

Where,

$\bar{x}$ -- Mean of a set of values

x_i -- Particular value

Terms of Precision:

There are three terms, widely used to describe the Precision of a set of replicate

i. Standard Deviation

ii. Variance

iii. Co-efficient of variation

8.1.5. STANDARD DEVIATION(σ):

Definition:

It is the square root of the quotient obtained by dividing the sum of the squares of the individual deviations from their mean by the number of measurements made.

$$\sigma = \frac{\sqrt{d_1^2 + + d_2^2 + \ldots . . + d_n^2}}{n-1}$$

Explanation:

The following steps should be used to calculate standard deviation.

i) The mean ($\bar{x}$) is calculated.

ii) The individual deviation of each measurement from the average (x_i - $\bar{x}$) is calculated.

iii) Each individual deviation is squared $(x_i - \bar{x})^2$

iv) All the individual deviation square is added $\sum (x_i - \bar{x})^2$

v) The value obtained from step (4) is divided by the number of measurements made $\sum (x_i - \bar{x})^2 \div n\text{-}1$

vi) The standard deviation σ = $\sqrt{\dfrac{\sum(x_i - \bar{x})^2}{n-1}}$

viii) For small number of measurements 'S' = $\sqrt{\dfrac{\sum(x_i - \bar{x})^2}{n-1}}$

TCA

Example:

Calculate the standard deviation for the following set of values 92.10; 92.50; 92.70; 92.80 & 92.90.

i) Mean (or) average = $\dfrac{92.10 + 92.50 + 92.70 + 92.80 + 92.90}{5}$

$\bar{x}$ = 92.60

ii) Calculation of $|x_i - \bar{x}|$ and $|x_i - \bar{x}|^2$

S. No	**Value x_i**	$\lvert x_i - \bar{x} \rvert = \bar{d}$	$\lvert x_i - \bar{x} \rvert^2 = \bar{d}^2$
1.	92.10	92.10 – 92.60 = 0.50	0.25
2.	92.50	92.50 – 92.60 = 0.10	0.01
3.	92.70	92.70 – 92.60 = 0.10	0.01
4.	92.80	92.80 – 92.60 = 0.20	0.04
5.	92.90	92.90 – 92.60 = 0.30	0.09

iii) $\sum (x_i - \bar{x})^2$ = 0.25+ 0.01 + 0.01 + 0.04+ 0.09 = 0.40

iv) $\dfrac{\sum(x_i - \bar{x})^2}{n-1} = \dfrac{0.40}{5-1}$ = 0.10

v) $$S = \sqrt{\frac{\sum(x_i - \bar{x})^2}{n-1}} = \sqrt{0.1}$$

$$S = 0.3162$$

Variance:

The Square of the standard deviation is called variance. It is denoted by S^2. It is also important in statistical calculations.

Co-efficient of Variation:

The Co-efficient of variation(C>V) is an accurate measure of the precision and is given by,

$$C.V = \frac{S \times 100\%}{X}$$

Where, S=Standard deviation, X =data asset mean value

8.1.6. ACCURACY:

Definition:

It is the degree agreement between the measured value and the true value of a property.

Explanation with example:

The accuracy of a measurement is how close a result comes to the true value. Determining the accuracy of a measurement usually requires calibration of the analytical method with a known standard.

As per analytical data available the solubility product of $CaSO_4$ is $2.4 \times 10^{-5} mol^2 dm^{-}$. If an analyst gets the same experimental (or) measured value then it is called as the accuracy of the result. If it differs, then we calculate the deviation. This deviation gives a measure of the accuracy of experiment.

Methods of expressing accuracy:

Accuracy is expressed in terms of absolute error (or) relative error. The lower these values are, the more will be the accuracy.

Absolute error (E):

It is defined as the difference between the accepted value (x_t) and the observed value (x_i).

$$E = xi - x_t$$

Relative error (RE):

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It is the error percentage of the acceptable value.

RE = $E / x_t \times 100$

RE = $x_i – x_t / x_t \times 100$

Explanation:

The dissociation constant of acetic acid at 25°C is 1.75×10^{-5}. It is the accepted value (x_t). A student determines it as 1.80×10^{-5}. It is the observed value (x_i).

Absolute error (E) = $xi – x_t$

$= 1.80 \times 10^{-5} - 1.75 \times 10^{-5}$

$E = 0.05 \times 10^{-5}$

Relative error (RE) = $xi – x_t / x_t \times 100$

$= 0.05 \times 10^{-5} / 1.75 \times 10^{-5} \times 100$

RE = 2.86 %

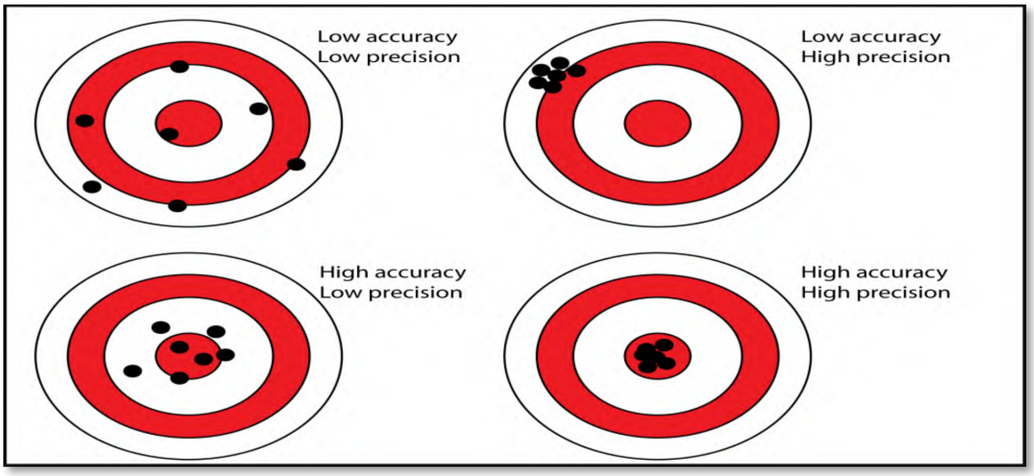

Figure 3: Representation of Precision and Accuracy

Differences:

S.no	Precision	Accuracy
1.	It is the degree of agreement between two (or) more measured value of a property under identical conditions.	It is the degree agreement between the measured value and the true value of a property.
2.	It may be achieved	It is never known
3.	Expresses the reproducibility of the results	Expresses correctness of a measurement

Table:2

EXERCISE:3

1. Accuracy means ------------

A) The degree to which repeated measurements under unchanged conditions show the same results.

B) The degree to which a measured value agrees with the true value.

C) The spread of measurements around the true value.

D) The closeness of measurements to each other.

2. Which of the following best describes precision?

A) The closeness of a measurement to the true value.

B) The closeness of multiple measurements to each other.

C) The ability to measure the true value.

D) The difference between the maximum and minimum values in a set of measurements.

3. If a set of measurements is consistently close to each other but far from the true value, they are:

A) Accurate and precise.

B) Accurate but not precise.

C) Not accurate but precise.

D) Neither accurate nor precise.

4. -----------an example of high precision but low accuracy

A) Measurements are spread out but close to the true value.

B) Measurements are clustered close to each other but far from the true value.

C) Measurements are scattered and far from the true value.

D) All measurements are identical and correct.

5. Which of the following would indicate both high accuracy and high precision?

A) Measurements are all close to each other and close to the true value.

B) Measurements are all far from each other but close to the true value.

C) Measurements are all close to each other but far from the true value.

D) Measurements are scattered far from each other and far from the true value.

6. A set of measurements has a high degree of accuracy but low precision. What does this mean?

A) The measurements are close to the true value but vary widely.

B) The measurements are far from the true value but consistent.

C) The measurements are both close to each other and the true value.

D) The measurements are neither accurate nor precise.

இன்றைய *TRB* பயிற்சியாளரே நாளைய அரசு பள்ளி ஆசிரியரே!

Teacher's Care Academy **கடந்த *14* ஆண்டுகளாக *TRB* தேர்வுகளுக்கான சிறப்பு பயிற்சியை வழங்கி வருகிறது. இதுவரை *10,000*-க்கும் மேற்பட்ட ஆசிரியர்களை அரசு வேலைகளில் வெற்றிகரமாக நியமிக்க உதவியதில் நாங்கள் பெருமிதம் கொள்கிறோம். எங்கள் நிறுவனத்தில் அனைத்து *TRB* தேர்வுகளுக்கும் விரிவான பயிற்சிகள் உள்ளன, அவை:**

- ***PGTRB***
- ***UGTRB***
- ***SGT***
- ***POLYTECHNIC TRB***
- ***BEO***
- ***TET Paper I & II***
- ***College TRB***
- ***Special Teachers***

95665 35080

கூடுதலாக, தமிழ்நாடு அரசு இப்போது அனைத்து அரசு பணிக்கான தேர்வாணையங்களுக்கு (*TRB, TNPSC, MRB, TNUSRB*) தமிழ் மொழி கட்டாய தகுதி தேர்வு (*Tamil Compulsory Exam*) முதற்கட்ட தேர்வாக அறிவித்துள்ளது இதற்காக தமிழ் மொழி கட்டாய தகுதி தேர்வு என்ற புத்தகத்தை பிரத்தியேகமாக உங்கள் *Teacher's Care Academy* வெளியிட்டுள்ளது. இந்த புத்தகம் அமேசானிலும் கிடைக்கிறது ஆனால் எங்களை நேரடியாக தொடர்பு கொண்டு வாங்கும் போது உங்களுக்கு கூடுதல் தள்ளுபடி கிடைக்கும்

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PGTRB

PGTRB தேர்விற்கு நாங்கள் அனைத்து மொழி பாடத்திற்கும் பயிற்சிகளை வழங்கி வருகிறோம் அதாவது

- *Tamil*
- *English*
- *Mathematics*
- *Physics*
- *Chemistry*
- *Botany*
- *Zoology*
- *Economics*
- *Commerce*
- *Computer Science*
- *History*

மேற்கண்ட அனைத்து படப்பிரிவுகளுக்கான *Study Material*-களுடன் *Psychology, Tamil Eligibility Book, Question Bank* மற்றும் *General Knowldge Material*-களும் வழங்கப்படும்

TET (Teachers Eligibility Test)

TET தேர்விற்கு நம் *Teachers Care Academy*-யில் *Paper I* மற்றும் *Paper II* என இரண்டு தாள்களுக்கும் பிரத்தியேகமாக பயிற்சிகளை வழங்குகிறோம்

இதற்கு தமிழ்நாடு அரசால் வழங்கப்பட்டுள்ள பள்ளி பாட புத்தகத்தில் இருந்து குறிப்புகளை எடுத்து *Study Material*-களாக வழங்குகிறோம்

மேலும் *Psychology*-க்கு *TRB*-ஆல் வழங்கப்பட்டுள்ள பாடத்திட்டத்தை பின்பற்றி பல்வேறு *Reference Book*-லிருந்து குறிப்புகளை எடுத்து *Study Material*-களாக வழங்குகிறோம்

UGTRB

TET தேர்வில் வெற்றி பெற்ற ஆசிரியர்களுக்கு நடத்தப்படும் *UGTRB* போட்டி தேர்வுக்காக_அனைத்து மொழி பாடத்திற்கும் பயிற்சிகளை வழங்கி வருகிறோம் அதாவது

- *Tamil*
- *English*
- *Mathematics*
- *Physics*
- *Chemistry*
- *Botany*
- *Zoology*
- *History*
- *Geography*

SGTRB

TET **தேர்வில் வெற்றி பெற்ற ஆசிரியர்களுக்கு நடத்தப்படும்** ***SGTRB*** **போட்டி தேர்வுக்காக தமிழ்நாடு அரசால் வழங்கப்பட்டுள்ள பள்ளி பாட புத்தகத்தில் இருந்து குறிப்புகளை எடுத்து** ***Study Material*****-களாக வழங்குகிறோம்**

BEO

BEO **தேர்வுக்காக** ***TRB*****-ஆல் பாடத்திட்டம் வெளியிடப்பட்டுள்ளது அந்த பாடத்திட்டத்தின் அடிப்படையில் அனைத்து பாடத்திற்கும் உங்கள்** ***Teachers Care Academy*** **அலகு** ***(Unit-Wise)*** **வாரியாக** ***Study Material*****-களை வழங்குகிறது.**

POLYTECHNIC TRB

Polytechnic **தேர்விற்காக உங்கள்** ***Teachers Care Academy*** **பின்வரும் மொழி பாடத்திற்கு பயிற்சிகளை வழங்கி வருகிறது. அதாவது,**

- ***Civil***
- ***EEE***
- ***ECE***
- ***CSE***
- ***Mechanical***
- ***English***
- ***Mathematics***
- ***Physics***
- ***Chemistry***

College TRB

தமிழ்நாட்டில் அரசு கல்லூரிகளில் காலியாக உள்ள உதவி பேராசிரியர் பணிக்கு ***TRB*** **வெகு விரைவில் போட்டித் தேர்வை நடத்த இருக்கிறது**

அந்த தேர்வுக்காக நம் ***Teachers Care Academy*****-யில் பின்வரும் மொழி பாடத் திட்டத்திற்கும் பயிற்சிகளை வழங்கி வருகிறது**

- ***Tamil***
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- ***Chemistry***
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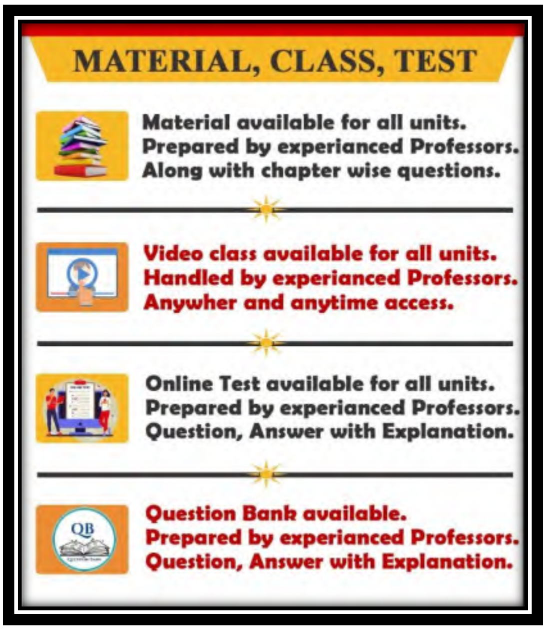

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