PG TRB
2020-2021

UNIT-1

Chemistry

SYLLABUS: CHEMISTRY

UNIT- I

PERIODIC PROPERTIES – ATOMIC RADIUS – IONIC RADIUS, IONIZATION POTENTIAL, ELECTRON AFFINITY AND ELECTRONEGATIVITY – THEIR SIGNIFICANCE IN CHEMICAL BONDING.

VB THEORY, MO THEORY – APPLICATIONS – COMPARISION OF VB AND MO THEORIES – VSEPR THEORY – BOND ORDER – BOND ENERGY – BOND LENGTH BOND POLARITY – PARTIAL IONIC CHARACTER OF BONDS – THE CONCEPT OF MULTI-CENTRE BOND – ELECTRON DEFICIENT COMPOUNDS – HYDROGEN BOND – ITS INFLUENCES.

NON AQUEOUS SOLVENTS – A GENERAL STUDY OF TYPICAL REACTIONS IN NON AQUIEOUS MEDIA – COMPARISON WITH REACTIONS IN AQUEOUS MEDIA.

SOLID STATE CHEMISTRY – IONIC BONDING – LATTICE ENERGY – BORN EQUATION – BORN HABER CYCLE – RADIUS RATIO RULE – BORN MEYER EQUATION – KAPUSTINSKI'S MODIFICATION – ENERGETICS OF THE DISSOLUTION OF IONIC COMPOUNDS IN POLAR SOLVENTS – DIFFERENT TYPES OF ELECTOSTATIC INTERACTIONS.

STRUCTURAL ASPECTS OF SOLIDS – FOURIER SYNTHESIS AND ANALYSIS STRUCTURE FACTORS – SCATTERING FACTORS – SPINELS AND INVERSE SPINELS – DEFECTS IN STOINCHIOMETRIC AND NON STOICHIOMETRIC CRYSTALS.

ELECTRICAL PROPERTIES OF SOLIDS – BAND THEORY SEMI CONDUCTORS – JUNCTION DEVICES – SUPER CONDUCTIVITY – IONIC CONDUCTIVITY – OPTICAL PROPERTIES OF SOLIDS – LASERS AND PHOSPHORS – PHOTOVOLTAIC EFFECT – SOLAR ENERGY.

MAGNETIC PROPERTIES OF SOLIDS – DIFFERENT TYPES – DIA, PARA, FERRO, ANTIFERRO AND FERRI MAGNETISM – MAGNETIC HYSTERESIS.

Periodic Properties:

* Periodic Properties also called Atomic Properties.
* They are
  (i) Atomic radii / Atomic radius
  (ii) Ionic radii / Ionic radius
  (iii) Ionisation energy
  (iv) Electron affinity
  (v) Electron negativity.

(I) ## Atomic radius:

*Def: "Distance between the nucleus and the outer most shell of electrons of the atomic particles".

* These distance are called Internuclear distance (or) bond length (or) bond distances (or) Inter^{ionic}nuclear distances.

Classification of atomic radius:
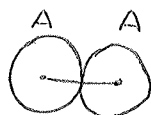
* Atomic radius are subdivided into three types.
  (i) covalent radii / radius
  (ii) Metallic radii / radius.
  (iii) vander waals radii / radius.

† (i) covalent radii / radius:-

Def: It is defined as half of the distance between the nuclei of two like atoms bonded together by a single covalent bond.

* <u>eg:</u> Homodinuclear diatomic molecule, A_2.

$*$ Distance between the nuclei of these two atoms (d_{A-A}) is equal to the sum of the single bond covalent radius of the both the atom.

$$d_{A-A} = r_A + r_A$$

$$2r_A = d_{A-A}$$

$$\boxed{r_A = \frac{d_{A-A}}{2}}$$

$\quad\quad\quad\quad\quad\quad\quad\quad$ (r_A = covalent radius of atom A).

$*$ If in a hetero-nuclear diatomic molecule, AB.

$\Rightarrow$ The atoms A and B are bonded together by purely covalent bond, then the internuclear distance d_{A-B} is equal to the sum of r_A and r_B.

$$\boxed{d_{A-B} = r_A + r_B}; \text{ when } x_A = x_B$$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ [Electronegativity of atom $A = x_A$]

$\Rightarrow$ If x_A is not equal to x_B

$$\boxed{d_{A-B} < r_A + r_B}$$

eg:
$$d_{(C-I)exp} = 2.14 A°$$

$$d_{(C-I)cal} = r_C + r_I = 0.77 + 1.33 = 2.10 A°$$

The deviation is due to a number of factors.

(i) Electronegativity difference between the atom A and B

(ii) Multiplicity of the bond between A and B

$\Rightarrow$ Stevenson suggested the equation to calculate d_{A-B}

$$\boxed{d_{A-B} = r_A + r_B - 0.09(x_A - x_B)}$$

$\Rightarrow$ Pauling given the equation.

$$d_{A-B} = r_A + r_B - C(X_A - X_B)$$

$C = $ Stevenson coefficient.

Types of covalent radius :-

* covalent radius may be single bond, double bond and triple bond covalent radii

* Double bond and triple bond covalent radii are called multiple covalent radius.

eg: $B \Rightarrow 0.76, 0.68$; $C \Rightarrow 0.67, 0.60$

(ii) (ii) Metallic radius :

* Def: one half of the distance between the nuclei of two adjacent metal atoms in the metallic to close packed crystal lattice in which metal exhibit a coordination number of 12.

eg: Na metal $\Rightarrow 3.80 A°$ Na Na

* Metallic radius are about 10 to 15% higher than the single bond covalent radius.

* Metallic radius are smaller than the vander waals radius.

* The bonding forces in the metallic crystal lattice are much stronger than the vander waals forces.

eg: The distance between the two adjacent potassium atom in solid potassium is $4.62 A°$. Therefore, the metallic radius of potassium is

$$\frac{4.62}{2} = 2.31 A°$$

MCQ:

1. The size of the ion change in the order —
   (a) $Na^+ > Mg^{2+} > Si^{4+} > Cl^{7+}$
   (b) $Cl^{7+} > Si^{4+} > Mg^{2+} > Na^+$
   (c) $Cl^{7+} > Na^+ > Mg^{2+} > Si^{4+}$
   (d) $Na^+ > Mg^{2+} > Cl^{7+} > Si^{4+}$.

2. Al^{3+} has a lower ionic radius than Mg^{2+} ion because —
   (a) Mg atom has less number of neutrons than Al
   (b) Al^{3+} has a higher nuclear charge than Mg^{2+}.
   (c) Their electronegativities are different
   (d) Al has a lower ionisation potential than Mg atom.

3. which indicates the correct variation in electro-negativities?
   (a) $F > N < O > C$ (b) $F > N > O > C$
   (c) $F < N < O < C$ (d) $F > N > O < C$.

4. The decreasing order of second ionization potential of K, Ca and Ba is —
   (a) $K > Ca > Ba$ (b) $Ca > Ba > K$
   (c) $Ba > K > Ca$ (d) $K > Ba > Ca$.

5. The screening effect of inner electrons of the nucleus causes.

(a) Decreases in the ionisation energy

(b) Increases in the ionisation energy

(c) No effect on the ionisation energy

(d) Increases in the attraction of the nucleus to the electrons.

6. Which among the following factor is most important in making fluorine the strongest oxidising halogen?

(a) Bond dissociation energy.

(b) Ionisation enthalpy

(c) Hydration enthalpy

(d) Electron affinity.

7. Greater the value of electron affinity of an element, greater is its —

(a) coordination character   (b) Electropositive character

(c) Electronegative character   (d) None of the above.

8. Calculate the electronegativity values of fluorine and chlorine on Mulliken scale, given that $(IP)_F = 1.74$ ev/atom, $(EA)_F = 3.62$ ev/atom, $(IP)_{Cl} = 13.0$ ev/atom, $(EA)_{Cl} = 4.0$ ev/atom

(a) 2.75, 3.03   (b) 3.75, 3.03

(c) 3.03, 2.75   (d) 3.85, 3.00

9. Electronegativity of beryllium and ___ are the same.
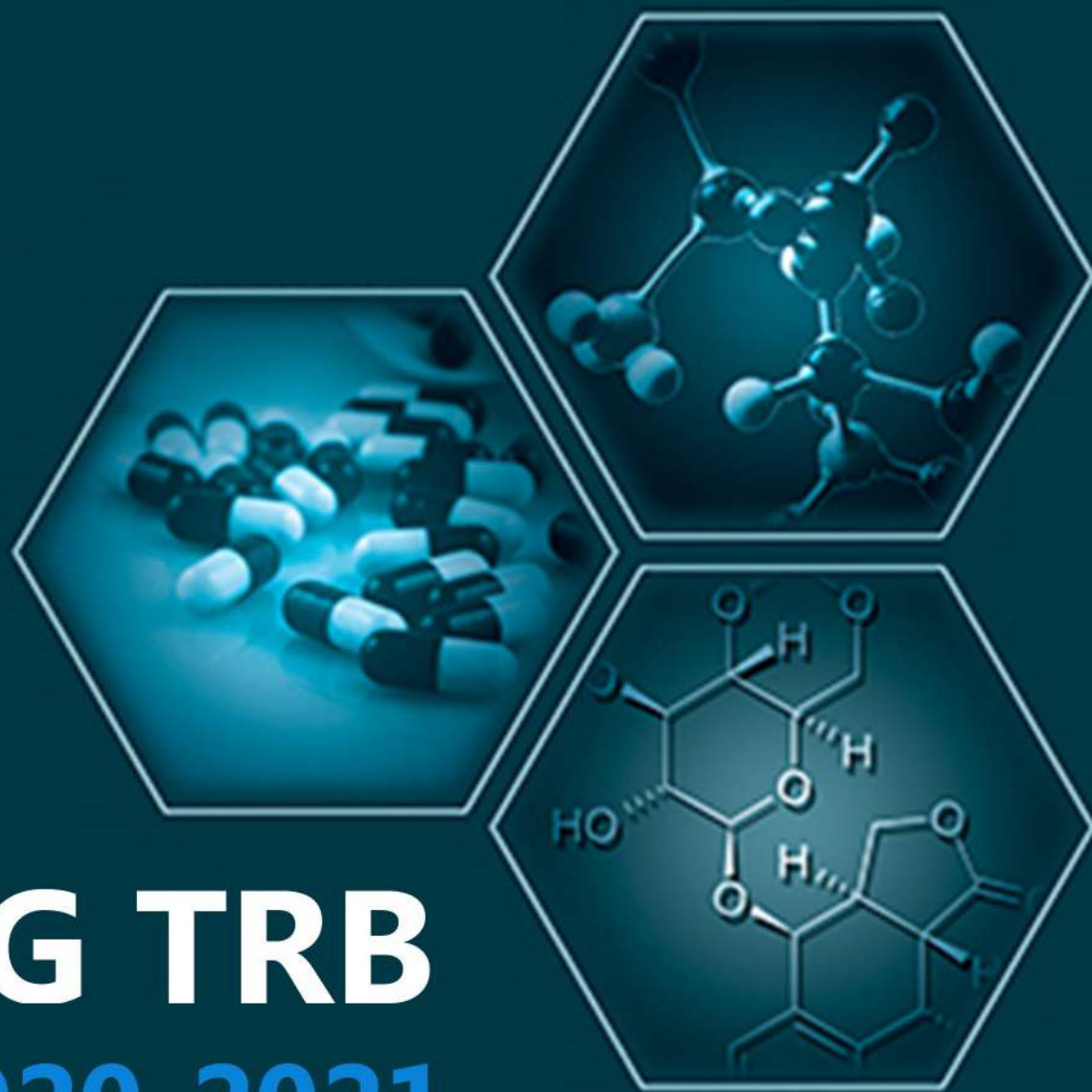
(a) Aluminium   (b) Carbon

(c) Gallium   (d) Silicon

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UNIT-2

SYLLABUS: CHEMISTRY

UNIT- II

CO-ORDINATION CHEMISTRY – METHODS OF PREPARATION OF COMPLEXES – ISOMERISM IN COMPLEXES – APPLICATIONS OF COMPLEX FORMATION IN ANALYTICAL CHEMISTRY – COMPLEXES AND THEIR STABILITY CHELATE EFFECT STABILITY CONSTANTS – THEIR DETERMINATION – COMPLEXES OF METALS IN DIFFERENT OXIDATION STATES AND THEIR STABILITY.

OPTICAL ACTIVITY AND CONCEPT OF CHIRALITY – DIFFERENT KINDS OF OPTICALLOY ACTIVE COMPOUNDS – CONFIGURATION – FOSCHER, SAWHORSE AND NEWMAN PROJECTIONS – ABSOLUTE CONFIGURATION R AND S NOTATIONS – METHODS WITH MORE THAN ONE CHIRAL CENTER – ASYMMETRIC SYNTHESIS – OPTICAL PURITY.

GEOMETRICAL ISOMERISM RESULTING FROM DOUBLE BONDS – THE E.Z.SYSTEM OF NEMENCLATURE – GEOMETRICAL ISOMERISM OF MONOCYCLIC COMPOUNDS AND FUSED RING SYSTEMS – STEROSPECIFIC AND STEREO SELECTIVE REACTIONS WITH EXAMPLES.

CONFERMATIONAL ANALYSIS – CONFORMATION AND REACTIVITY IN ACYLIC AND CYCLO – HEXANE SYSTEMS – CONFORMATION OF DECALINS, CYCLOHEXANE AND CYCLOHEXANONE.

UNIT-II

Coordination Chemistry

* Coordination chemistry is the study of a class of compounds formed by metals.

* Eg: When an excess of aqueous potassium cyanide is added to aqueous ferrous sulphate, a yellow solution is formed.

$$Fe^{2+} + 6CN^- \longrightarrow [Fe(CN)_6]^{4-}$$
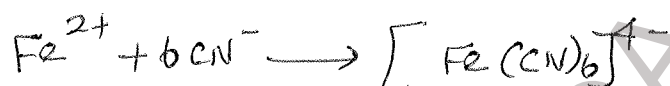
⇒ The product $K_4[Fe(CN)_6]^{4-}$ is called a metal complex ion; it can be isolated as its potassium salt $K_4[Fe(CN)_6]$. This product is called a coordination compound.

⇒ The formation of coordination compound from a metal is called complexation.

Coordination number:

* The total number of monodentate ligand attached to the central metal in a complex is called the coordination number.

eg: $[Cu(NH_3)_4]^{2+}$

⇒ four monodentate ligands are attached to the central metal, the coordination number is four.

⇒ coordination number from two to nine are known in complexes.

⇒ 4 and 6 are the common coordination numbers. The coordination number 3 is rare.

* Coordination sphere:-

⇒ The central metal ion and the ligands that are directly attached to it are enclosed in a square bracket which werner has called coordination sphere.

$$\left[\begin{array}{c} NH_3 \quad\quad NH_3 \\ Cu \\ NH_3 \quad\quad NH_3 \end{array} \right]^{2+}$$
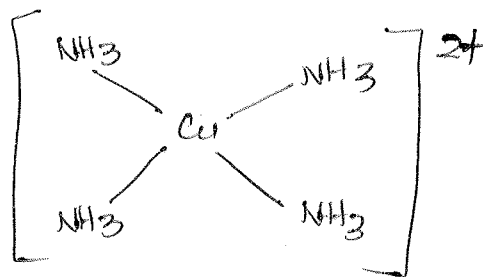
* Ligands:-

⇒ The neutral molecules or ions which are attached with the central metal ion are called ligands.

eg: NO^+, CN^-, Cl^-, Br^-, NH_3, H_2O, etc.

Methods of preparation of complexes:-

Metal complexes are prepared commonly by the following methods.
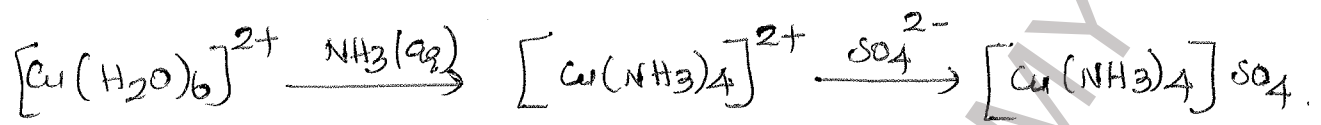
1. Direct reaction between the metal salt and the ligands:-

- The reaction between $ZnSO_4(s)$ and $NH_3(l)$ directly produces the complexes $[Zn(NH_3)_4]SO_4$.

$$ZnSO_4{}_{(s)} + 4NH_3{}_{(l)} \longrightarrow [Zn(NH_3)_4]SO_4.$$

2. <u>Substitution reaction in aqueous medium:-</u>

This is a convenient way of preparing a complex; in this reaction, the water ligands are replaced by other ligands.

$$[Cu(H_2O)_6]^{2+} \xrightarrow{NH_3(aq)} [Cu(NH_3)_4]^{2+} \cdot \xrightarrow{SO_4^{2-}} [Cu(NH_3)_4]SO_4$$

3. <u>Substitution reaction in non-aqueous solvent:-</u>

* A non-aqueous solvent is used if the reactant aqua complex is too stable to undergo substitution.

eg: $[Cr(H_2O)_6]^{3+}$ is very stable; therefore, when attempts are made to convert it to its ethylenediamine complex, only the following reaction occurs:

$$[Cr(H_2O)_6]^{3+} + 3en \xrightarrow{H_2O} [Cr(H_2O)_3(OH)_3] \downarrow + 3enH^+$$
Violet   Green
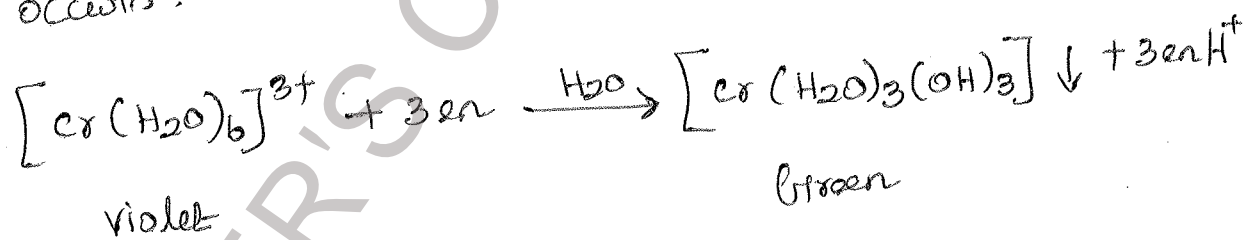
* However, when the same reaction is repeated in ether, the ethylenediamine complex is obtained;

$$CrCl_3 + 3en \xrightarrow{Ether} [Cr(en)_3]Cl_3$$
Purple   Yellow

* If the reactant ligand is insoluble in water, then also a non-aqueous solvent is employed for the preparation of the complex. For eg:

MLQ:

1. Stabilisation of highest oxidation states of transition metals by strong electronegative ligands is due to

(a) $d_\pi(M) \rightarrow d_\pi(L)$ bonding

(b) $d_\pi(M) \rightarrow P_\pi(L)$ bonding

(c) $P_\pi(L) \rightarrow d_\pi(M)$ bonding

(d) $d_\pi(M) \rightarrow d_\pi(M)$ bonding.

Answer : (c)

2. Which of the following sequence follows the Irwing-william order?

(a) $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}$

(b) $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$

(c) $Mn^{2+} < Fe^{2+} > Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$

(d) $Mn^{2+} > Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}$

Answer : ( )

3. An example of a hexadentate ligand is ____

(a) 2,2'- bipyridyl

(b) Ethylene diamine tetraacetate ion

(c) Dimethyl glyoxime

(d) Iminodiacetate ion.

Answer : ( )

4. Haemoglobin, a complex containing iron is a constituent of blood. The oxidation state of iron in the complex is____

(a) zero   (b) +1   (c) +2   (d) +3

Answer : ( )

5. $[Co(NH_3)_5 Br] SO_4$ and $[Co(NH_3)_5 SO_4] Br$ are examples of which type of isomerism?

(a) Linkage   (b) Geometrical

(c) Ionisation   (d) optical.

Answer : ( )

6. The Coordination number of a central metal atom in a complex is determined by ___

(a) The number of only anionic ligands bonded to the metal ion.

(b) The number of ligands around a metal ion bonded by Pi bond

(c) The number of ligands around a metal ion bonded by sigma and Pi bond

(d) The number of ligands around a metal ion bonded by sigma bond.

Answer : ( )

7. which one of the following complexes is an outer orbital complex?

(a) $[Ni(NH_3)_6]^{2+}$ (b) $[Mn(CN)_6]^{4+}$

(c) $[Co(NH_3)_6]^{3+}$ (d) $[Fe(CN)_6]^{4-}$

Answer : ( )

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UNIT-3

SYLLABUS: CHEMISTRY

UNIT- III

ORGANIC REACTION MECHANISMS – GENERAL METHODS OF INVESTIGATING REACTION MECHANISMS – KINETIC AND NON-KINETIC METHODS – DIFFERENT TYPES OF REACTION INTERMEDIATES.

ALIPHATIC NUCLEOPHILIC SUBSTITUION SN1, SN2 AND SNI REACTIONS – SUBSTITUTION AT VINYLIC AND BENZYLIC CARBON – STEREO CHEMISTRY OF NUCLEOPHILIC REACTION – SOLVENTS AND SUBSTITUENT EFFECTS – NUCLEOPHILICITY NEIGHBORING GROUP PARTICIPATION.

ADDITION TO DOUBLE AND TRIPLE BONDS – MECHANISM HYDRATION – HYDROBORATION – HYDROXIYLATION – EPOXIDATION.

ELIMINATION REACTIONS E1, E2, E1CB MECHANISM – ORIENTATION EFFECTS IN ELIMINATION REACTIONS – STEREO CHEMISTRY OF ELIMINATION REACTORS - DEHYDRATION OF ALCOHOLS – DEHYDRO HALOGENATION – COPE ELEMINATION.

HETEROCYCLICS – SYNTHESIS AND REACTIVITY OF FURAN, THIOPHENE, PYRROLE PYRIDINE, QUINOLINE, ISOQUINOLINE, INDOLE, FLAVENES, AND ANTHOCYANINS – SKRAUP SYNTHESIS – FISCHER INDOLE SYNTHESIS.

THE CHEMISTRY OF NATURAL PRODUCTS STRUCTURE ELUCIDATIONS AND BIOGENESIS OF THE FOLLOWING:

    ALKALOIDS   : RETICULENE, RESERPINE, MORPHINE

    TERPENOIDS   : ZINGIBERENE, SQUALENE, LANOSTEROAL

    STEROIDS   : CHOLESTEROL, OESTRONE, PROGRESTERONE

    CARBOHYDRATES: MALTOSE, STARCH, CELLULOSE (BIOGENIS NOT EXPECTED)

STRUCTURE AND FUNCTIONS OF BIOPOLYMER SUCH AS PROTEINS AND NUCLEIC ACIDS – PRIMARY, SECONDARY AND TERTIARY STRUCTURES OF PROTEINS – MECHANISM OF ENZYME ACTION – DNA AND RNA.

Organic reaction mechanisms

*Def: A detailed study of the sequence of steps which are involved in the conversion of reactants into products is known reaction mechanism.

* Reaction mechanism are of two types.

(a) concerted mechanism

(b) Non-concerted mechanism.

(a) concerted mechanism :-

* The mechanism which involves the breaking and making of bond that takes place simultaneously on approach of reacting molecules without the formation of any intermediate is called 'concerted mechanism'.

* The activation energy diagram for a concerted mechanism is given below
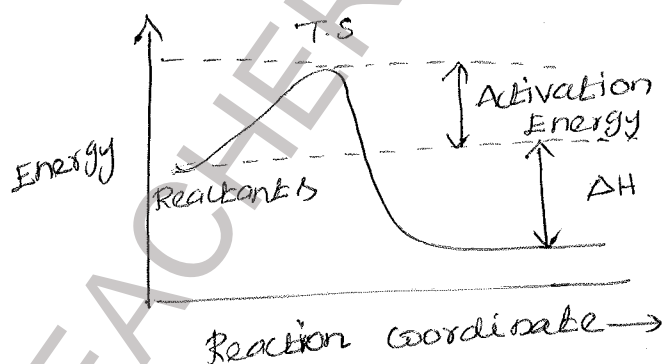
(b) Non-concerted mechanism :-

* The mechanism of those reactions which proceeds through the formation of intermediate species before the product species are finally formed are called 'non-concerted mechanism'.

Reaction coordinate →
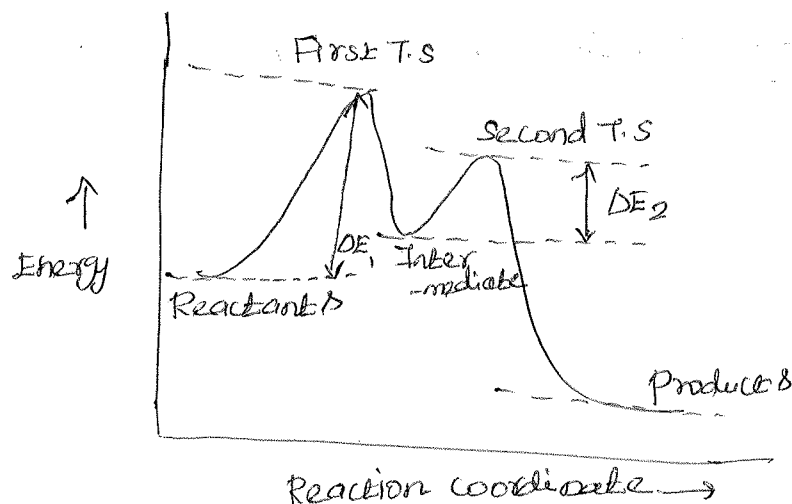
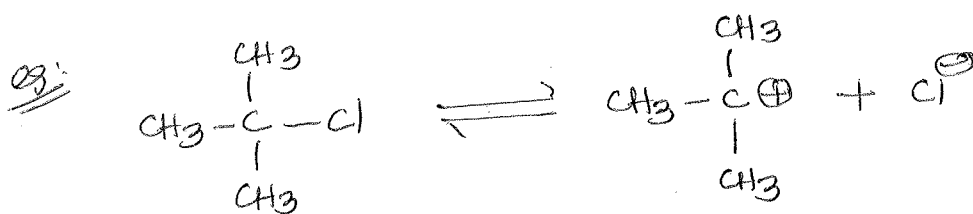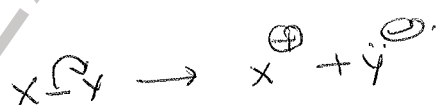* The above reaction mechanism occur through one or more of the following steps.

Bond Fission :-

* In a molecule, xy there are two ways by which the covalent bond between x and y may be broken, viz.

(a) Heterolytic and

(b) Homolytic.

(a) Heterolytic Fission :-

* The covalent bond is broken in the shared electron pair remains attached with only one of the two originally bonded atoms.

* Heterolytic bond fission results in ions

$$X \overset{\curvearrowleft}{-} Y \longrightarrow \overset{\ominus}{\underset{\cdot\cdot}{X}} + \overset{\oplus}{Y}$$

Ions'

$$X \overset{\curvearrowright}{-} Y \longrightarrow X^{\oplus} + \overset{\ominus}{Y}$$

eg:

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - Cl \rightleftharpoons CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}^{\oplus} + Cl^{\ominus}$$
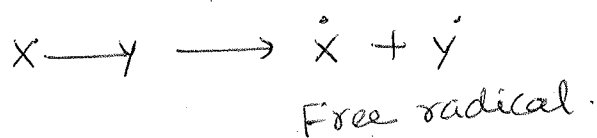
t - Butyl chloride

* A full arrowhead denotes the shift of an electron pair.

(b) Homolytic bond fission:-

* The covalent bond is broken symmetrically so that one electron of the bonding pair remains with each of the originally bonded atoms.

$$X \longrightarrow y \longrightarrow \dot{x} + \dot{y}$$

Free radical.

eg:

$$Br \frown Br \longrightarrow \dot{Br} + \dot{Br}$$

* The shift of a single electron is represented by a fish hook arrow.

General methods of investigating reaction mechanism:-

* The following techniques are useful in the detection of the intermediates.

(i) Isolation of the intermediate

(ii) kinetic studies

(iii) Isotopic tracers

(iv) Direct observation of the intermediate by spectral means

(v) Trapping of intermediates

(vi) Determination of the stereochemistry of the reaction.

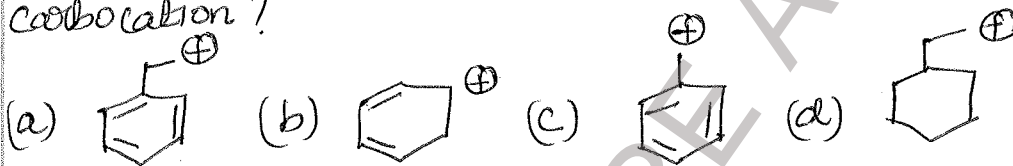* There are two major methods of determination of reaction mechanisms. They are kinetic and non-kinetic methods.

MCQ

1. The right order of stability of free radicals is

(a) $\overset{\bullet}{C}H_3 > (CH_3)_2 \overset{\bullet}{C}H > (CH_3)_3 \overset{\bullet}{C}$

(b) $(CH_3)_3 \overset{\bullet}{C} > (CH_3)_2 \overset{\bullet}{C}H > \overset{\bullet}{C}H_3$

(c) $\overset{\bullet}{C}H_3 > (CH_3)_3 C > (CH_3)_2 \overset{\bullet}{C}H$

(d) $(CH_3)_3 \overset{\bullet}{C} > \overset{\bullet}{C}H_3 > (CH_3)_2 \overset{\bullet}{C}H$

Answer :( )

2. Which of the following is an example of non classical carbocation ?

(a) (b) (c) (d)

Answer:( )

3. One of the modern methods of studying free radicals is
(a) IR Spectra (b) UV Spectra (c) CIDNP (d) Microwave spectra.
Answer:( )

4. In an SN² reaction there is.

4. For a reaction between an alkyl halide and $OH^\ominus$ increase in solvent polarity generally —

(a) Increases the rate of SN^1 reaction

(b) Decreases the rate of SN^1 reaction

(c) Increases the rate of SN^2 reaction

(d) Does not alter the rate of SN^1 and SN_2 reactions.

Answer.( )

5. The reaction

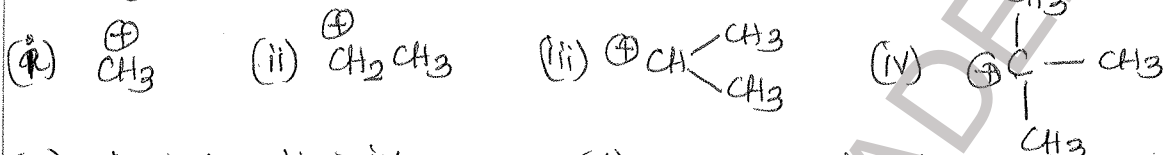$$CH_3CH_2Br + OH^{\ominus} \longrightarrow CH_3CH_2OH + Br^{\ominus}$$ is an example of

(a) Nucleophilic substitution   (b) Electrophilic substitution

(c) Nucleophilic addition   (d) Electrophilic addition.

Answer : (c)

6. The order of the stability of the following Carbocation is

(i) $\overset{\oplus}{C}H_3$ (ii) $\overset{\oplus}{C}H_2CH_3$ (iii) $\overset{\oplus}{C}H{<}^{CH_3}_{CH_3}$ (iv) $\overset{CH_3}{\underset{CH_3}{\overset{\oplus}{C}-CH_3}}$

(a) i > ii > iii > iv   (b) iv > iii > ii > i

(c) ii > iii > iv > i   (d) ii > iii > i > iv

Answer : ( )

7. The hybridisation of the carbon atom of carbocation is of the type

(a) sp   (b) sp^2 (c) sp^3 (d) dsp^2

Answer : ( )

8. The most stable carbanion among the following is

(a) $\overset{\ominus}{C} = CCH_3$ (b) $\overset{\ominus}{C}H = C(CH_3)_2$ (c) $\overset{\ominus}{C}H_2 - C(CH_3)_2$ (d) $Ph^{\ominus}$

Answer : ( )

9. The number of unshared electrons present on the Carbon atom of carbene is

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

Answer : ( )

10. Benzyne is represented as

(a)   (b)   (c)   (d)

Answer : ( )

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UNIT-4

SYLLABUS: CHEMISTRY

UNIT- IV

THE OLD QUANTUM THEORY – INADEQUACY OF CLASSICAL MECHANICS – FAILURE OF CLASSICAL MECHANICS – SUCCESS OF QUANTUM HYPOTHESIS EXPLAINING BLACK BODY RADIATION – PHOTO ELECTRIC EFFECT – THE HYDROGEN SPECTRUM – BOHR'S EXPLANATION OF HYDROGEN SPECTRUM – FAILURE OF BOHR'S MODEL.

DE BROGLIE'S POSTULATES OF MATTER WAVES – EXPERIMENTAL OBSERVATION OF MATTER WAVES – HEISENBERG'S UNCERTAINLY PRINCIPLE – WAVE PARTICLE DUALISM – DAVISSON, GARMER EXPERIMENTS – POSTULATES OF QUANTUM MECHANICS – TIME DEPENDENT SCHRODINGER EQUATION – NEEDS OF AN ACCEPTABLE WAVE FUNCTION – PHYSICAL SIGNIFICANCE OF PSI FUNCTION.

OPERATORS IN QUANTUM MECHANICS. OPERATOR ALGEBRA – LINEAR AND HERMITIAN OPERATORS –M EIGEN FUNCTIONS AND EIGEN VALUES – HAMILTONIAN OPERATORS – ANGULAR MOMENTUM.

APPLICATION OF SCHRODINGER EQUATION – PARTICLE IN ONE AND THREE DIMENSIONAL BOXES – QUANTUM MECHANICAL RESULTS FOR A SIMPLE HARMONIC OSCILLALTOR AND RIGID ROTATOR - APPROXINATION METHODS – PERTURBATION METHODS – VARIATION METHOD – VB AND MO METHODS.

SYMMETRY ELEMENTS AND SYMMETRY OPERATIONS – POINT GROUPS – REPRESENTATION OF GROUPS REDUCIBLE AND IRREDUCIBLE REPRESENTATIONS CHARACTERS TABLES – ORTHOGONALITY THEOREM AND ITS CONSEQUENCES.

SYMMETRY SELECTION RULE FOR IR AND RAMANSPECTRA – SYSTEMATIC PROCEDURE FOR DETERMINING SYMMETRIES OF NORMAL MODES OF VIBRATION – SYMMETRY APPLIED TO MO THEORY AND ORBITAL HYBRIDIZATION.

UNIT - IV

The old quantum theory - Inadequacy of classical mechanics - Failure of classical mechanics.

The old quantum theory is a collection of results from the year 1900 - 1925, which predate modern quantum mechanics.

The old quantum theory was instigated by the 1900 Work of Max Planck on the emission and absorption of light, and began in earnest after the work of Albert Einstein on the specific heats of solids. Einstein, followed by Debye, applied quantum principles to motion of atoms, explaining the specific heat anomaly.

In 1913, Niels Bohr identified the Correspondence Principle and used it to formulate a model of the hydrogen atom which explained the line spectrum. In the next few years Arnold Sommerfeld extended the quantum rule to arbitrary integrable systems making use of the Principle of adiabatic invariance of the quantum numbers introduced by Lorentz and Einstein.

Sommerfeld made a crucial contribution by quantizing the z-component of the angular momentum, which in the old quantum era was called space quantization (Richtungsquantelung). This allowed the orbits of the electron to be ellipses instead of circles, and introduced the concept of quantum degeneracy. The theory would have correctly explained the Zeeman effect, except for the issue of electron spin. Sommerfeld's model was much closer to the modern quantum mechanical picture than Bohr's.

Throughout the 1910s and well into the 1920s, many problems were attacked using the old quantum theory with mixed results. Molecular rotation and vibration spectra were understood and the electron's spin was discovered, leading to the confusion of half-integer quantum numbers. Max Planck introduced the zero point energy and Arnold Sommerfeld semi classically quantized the relativistic hydrogen atom. Hendrik Kramers explained the stark effect. Bose and Einstein gave the correct quantum statistics for photons.

Kramers gave a prescription for calculating transition probabilities between quantum states in terms of Fourier components of the motion, ideas which were extended in collaboration with Werner Heisenberg to a semiclassical matrix-like description of atomic transition probabilities. Heisenberg went on to reformulate all of quantum theory in terms of a version of these transition matrices, creating matrix mechanics.

In 1924, Louis de Broglie introduced the wave theory of matter, which was extended to a semiclassical equation for matter waves by Albert Einstein a short time later. In 1926 Erwin Schrödinger found a completely quantum mechanical wave equation, which reproduced all the successes of the old quantum theory without ambiguities and inconsistencies. Schrödinger's wave mechanics developed separately from matrix mechanics until Schrödinger and others proved that the two methods predicted the same experimental consequences. Paul Dirac later proved in 1926 that both methods can be obtained from a

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_h	3	0	1	3	0	1

Find that

$$\Gamma_h = A_1' + E$$

The three hybrids gets formed by the combination of a A_1' type orbital and two degenerate orbitals of E symmetry. A_1' is the totally symmetric irreducible representation and s-orbital which is invariant with respect to any symmetry operation belongs to A_1' (x,y) or (xy, x^2-y^2), transform like E'. Hence the following combinations can be suggested. (S, P_x, P_y) (ie) sp^2 or $(S, d_{xy}, d_{x^2-y^2})$ or sd^2; on energy considerations only sp^2 is allowed for Boron. sd^2 hybridization is discounted due to the prohibitively high promotion for $2s \rightarrow 3d$.

————————— x —————————

Objective questions

1. The _____ elements of the body, generating symmetry operations are called symmetry elements.
   (a) position   (b) axis   (c) geometry   (d) angle

② The symmetry _____ do not alter the energy of the molecule.

(a) centre (b) point (c) operations (d) direction

③ The description of the symmetry of an isolated molecule is called ____ symmetry.

(a) Point (b) axis (c) plane (d) angle

④ The highest-fold rotation axis in a molecule is known as the _____ axis.

(a) principal (b) angle (c) orientation (d) reversed

⑤ The ____ plane contains the highest order rotation axis.

(a) σ_h (b) C_2 (c) i (d) σ_v

⑥ The Point group of HCl molecule is _____.

(a) D_{2h} (b) T_d (c) C_2 (d) $C_{\alpha v}$

⑦ D_{6h} Point group belongs to ____ molecule.

(a) CH_4 (b) SF_6 (c) C_6H_6 (d) BCl_3

⑧ C_2 Point group belong to the _____ molecule.

(a) H_2O (b) NH_3 (c) BCl_3 (d) H_2O_2

⑨ Representation can be classified into ____.

(a) one (b) three (c) two (d) zero

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Chemistry

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UNIT-5

SYLLABUS: CHEMISTRY

UNIT- V

THERMODYNAMIC EQUATIONS OF STATE – CLOSED AND OPEN SYSTEMS – PARTIAL MOLAL QUANTITIES – CHEMICAL POTENTIAL WITH TEMPERATURE AND PRESSURE – THIRD LAW OF THERMODYNAMICS.

FUGACITY – METHODS OF DETERMINATION – ACTIVITY AND ACTIVITY CO-EFFICIENT – STANDARD STATES FOR GASES,

LIQUIDS – SOLIDS AND SOLUTIONS – MEAN ACTIVITY CO-EFFICIENTS OF ELECTROLYTES.

MAXWELL'S DISTRIBUTION OF MOLECULAR VELOCITIES – DERIVATION OF EXPRESSION FOR AVERAGE, MOST PROBABLE AND RCOT MEAN SQUARE VELOCITIES – MICROSTATES MACROSTATES – PARTIAL FUNCTIONS – SACKUR TETRODE EQUATION – STATISTICAL APPROACH TO THE THIRD LAW OF THERMODYNAMICS – MAXWELL BOLTZMANN – BOSE EINSTEIN AND FERMI DIRACE STATISTICS – HEAT CAPACITIES OF SOLIDS – EINSTEIN AND DEBYE MODELS LOW TEMPERATURE – NEGATIVE ABSOLUTE TEMPERATURE.

CHEMICAL EQUILIBRIUM – THERMODYNAMIC DERIVATION OF EQUILIBRIUM CONSTANT – STANDARD FREE ENERGY – CALCULATIONS.

PHASE EQUILIBRIUM – THERMODYNAMIC DERIVATION OF PHASE RULE APPLICATION OF PHASE RULE – THREE COMPONENT SYSTEMS.

CHROMOTOGRAPHY – COLUMN, PAPER, THINLAYER, GAS-LIQUID, HIGH PRESSURE LIQUID CHROMATOGRAPHY **HPLC** PRINCIPLE AND APPLICATIONS.

THERMAL ANALYSIS – DIFFERENT THERMAL ANALYSIS **(DTA)** – PRINCIPLE AND APPLICATIONS – THERMOGRAVIMETRIC ANALYSIS **(TGA)** PRINCIPLE AND APPLICATION.

CHEMICAL CRYSTALLOGRAPHY – DIFFRACTION METHODS – X RAY NEUTRON, ELECTRON DIFFRACTION METHODS. PRINCIPLE AND APPLICATIONS.

POLARIMETRY – CIRCULAR ICHROISM – OPTICAL ROTATORY DISPERSION (ORD) PRINCIPLE AND APPLICATIONS.

UNIT - V

Thermodynamic Equation of state

closed and open systems

closed system

A system which can exchange but not matter with its surroundings is called a closed system.

open system

A system which can exchange matter as well as energy with its surroundings is said to be an open system.

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 derivation of the various thermodynamic equations described, the change of state was considered to be due to change in temperature and pressure only. A tacit assumption was made that the system under consideration was a closed system (ie) 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 moles 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 $n_1, n_2, n_3, \ldots n_j$ be the respective numbers of moles of the constituents, $1, 2, 3, \ldots j$. The property X must be function of temperature, pressure and the number of moles of the various constituents, ie.,

$$X = f(T, P, n_1, n_2, n_3, \ldots n_j) \quad —①$$

Where $n_1 + n_2 + n_3 + \cdots + n_j$ = 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

$$dx = \left(\frac{\partial x}{\partial T}\right)_{P, N} dT + \left(\frac{\partial x}{\partial P}\right)_{T, N} dP + \left(\frac{\partial x}{\partial n_1}\right)_{T, P, n_2, \ldots n_j} dn_1 +$$

$$\left(\frac{\partial x}{\partial n_2}\right)_{T, P, n_1, n_3, \ldots n_j} dn_2 + \cdots + \left(\frac{\partial x}{\partial n_j}\right)_{T, P, n_1, n_2, \ldots} dn_j$$

$$—②$$

The quantity $\left(\dfrac{\partial x}{\partial n_i}\right)_{T,P,n_1,n_2,\ldots n_i} dn_i$

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 $\Big\}= \left(\dfrac{\partial U}{\partial n_i}\right)_{T,P,n_1,n_2\ldots} = \overline{U_i}$

Partial molar enthalpy $= \left(\dfrac{\partial H}{\partial n_i}\right)_{T,P,n_1,n_2,n_3\ldots} = \overline{H_i}$

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

Partial molar Volume $= \left(\dfrac{\partial V}{\partial n_i}\right)_{T,P,n_1,n_2,\ldots} = \overline{V_i}$

— x —

Partial molar Free Energy : <u>Concept of chemical Potential</u>

The Partial molar free energy designated as chemical potential and is represented as

$$\left(\dfrac{\partial G}{\partial n_i}\right)_{T,P,n_1,\ldots n_i} = \overline{G_i} = \mu_i \qquad — ③$$

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

Objectives

1) Cotton effect is known as _____ curves.
(a) anomalous (b) effective (c) original
(d) none of these

2) The assignment of absolute configurations can be done by ___.
(a) CD (b) ORD (c) positive (d) negative

3) ORD and CD are known as _____ properties.
(a) optical (b) electrical (c) chiroptical (d) All the above

4) There are ___ different types of ORD curves.
(a) two (b) one (c) three (d) four

5) Cotton curves exhibit two _____ known as maxima and minima.
(a) origin (b) extrema (c) breadth (d) amplitude

6) _____ are measurements are taken in a spectrophotometer.
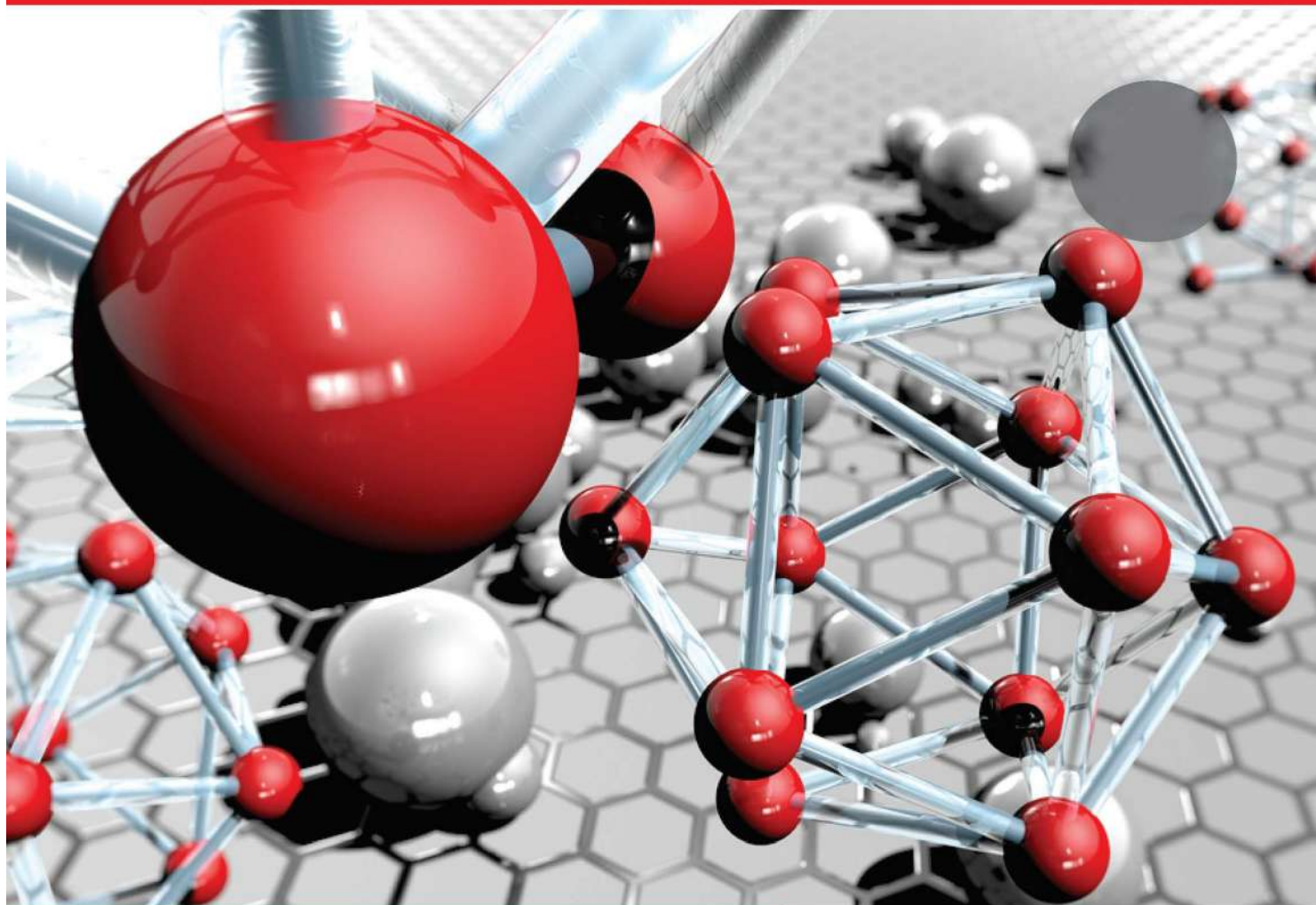(a) ORD (b) CD (c) polarimetry (d) None of these

— x —

Chemistry
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UNIT-6

SYLLABUS: CHEMISTRY

UNIT- VI

NUCLEAR – CHEMISTRY – NUCLEAR NADII SPIN AND MOMENTS – NUCLEAR STRUCTURE – NUCLEAR FORCES – NUCLEAR STABILITY – NUCLEAR MODES – MODES OF RADIOACTIVITY DECAY. NUCLEAR ISOMERISATION NUCLEAR REACTION ENERGY – COULOMB BARRIER CROSS SECTION – EXCITATION FUNCTION – RADIACTIVE EQUILIBERIA – TYPES OF NECLEAR REACTIONS – NUCLEAR FISION NUCLEAR REACTORS – ATOMIC POWER PROJECT IN INDIA – RADIATION HAZARDS – RADIATION DESIMETRY – NUCLEAR FUSION – STELLAR ENERGY.

APPLICATION OF RADIOACTIVITY – TRACER TECHNIQUES – NEUTRON - ACTIVATION ANALYSIS – ISOTOPE DILUTION ANALYSIS – INTERACTION OF RADIATION WITH MATTER – RANGE OF ALPHA AND BETA PARTICLES – ABSORPTION CO-EFFICIENT.

ORGNOMETALLIC COMPOUNDS – METALLECENCES – ARENE COMPLEXES – NONAROMATIE OLEFINS AND ACETYLENES COMPLEXES – CATALYSIS BY ORGANOMETALLIC COMPOUNDS WILKINSON'S CATALYST – OXOPROCESS – WECKER PROCESS – ZIEGLER – NATTA CATALYSIS.

INORGANIC PHOTO CHEMISTRY – PHOTOCHEMICAL REACTIONS OF COORDINATION AND ORGAN METALLIC COMPOUNDS – PROPERTIES OF EXCITED STATES – CHARGE TRANSFER PHOTO OXIDATION, PHOTO REDUCTION, PHOTO SUBSTITUTION, PHOTO ISOMERISATION - PHOTO CHEMICAL CONVERSION – SOLAR ENERGY.

Nuclear chemistry:-

* Nuclear chemistry deals with the study of nuclear particles, nuclear forces and nuclear reactions.

Nuclear radii:-

* The nuclear radius, R, can be defined as the distance from the centre to the point where the density has decreased to half of its original value.

* These radii can be obtained experimentally by deflection experiments using fast neutrons.

* The nuclear radius is proportional to $A^{1/3}$ where A is the mass number.

$$\boxed{R = r_0 A^{1/3}.}$$

where

R = Radius of the nucleus.

A = mass number

r_0 = constant , 1.3×10^{-15} m.

Nuclear spin and moment:-

* Nucleus having nuclear spin quantum number, I, there are $(2I+1)$ spin states.

* There are three broad principles for the nuclear spin.

(i) If the sum of the protons and neutrons is even, I is zero (or) integers (0, 1, 2, 3 ....).

If the spins of all the particles are paired, there will be no net spin and I will be zero.

eg: ^{12}C, ^{16}O, ^{18}O, ^{32}S.

(ii) If the sum of the protons and neutrons is odd, I is the half integral ($1/2$, $3/2$, $5/2$ etc).

eg: ^{1}H, ^{19}F, ^{13}C and ^{31}P. $\rightarrow$ $I = 1/2$

^{11}B, ^{35}Cl, ^{79}Br, ^{81}Br $\rightarrow$ $I = 3/2$.

(iii) If both protons and neutrons are even numbered. I is zero.

eg: ^{12}C and ^{16}O.

No. of Protons	No. of Neutrons	Spin quantum number, I	Examples.
Even	Even	0	^{12}C, ^{16}O, ^{32}S
Odd	Even	$1/2$, $3/2$	H^1, F^{19}, P^{31}, B^{11}, Br^{79}
Even	Odd	$1/2$, $3/2$	C^{13}, I^{127}
Odd	Odd	1	H^2, N^{14}

Nuclear structures:-

* The nuclear structure made progress only after the discovery of neutrons by James Chadwick in 1932.

* Two models have been suggested regarding the nuclear structure. They are.

   (i) The Nuclear shell model :

   (ii) The liquid drop model.

(i) <u>The Nuclear shell model</u> :-

* If the <u>nucleons</u> also exist in certain energy shells like the <u>electrons</u>.

* The electronic shell rule $2, 8, 18, 18, 32$ is applicable for the closing of nuclear shells as well.

* The nuclei containing certain specific number of protons or neutrons are particularly stable in comparison to their immediate neighbours.

* Some of the evidence is given below.

(i) Helium with mass number 4 ($z = 2$, $N = 2$; where 'z' stands for the no. of protons and 'N' for the no. of neutrons) and oxygen with mass number 16 ($z = 8$, $N = 8$) are highly stable. "The numbers 2 and 8 of neutrons and protons <u>indicate</u> high <u>nuclear stability</u>".

(ii) There is a group of <u>isotones</u> (i.e. elements having the same no. of neutrons) with $\underline{N = 82}$ (i.e. Ce^{140}_{58} and Ba^{138}_{56}) which are <u>highly stable</u>

MCQ:

1. ^{23}Na is the more stable isotope of Na. Find out the Process by which $^{23}_{12}Mg$ can undergo radioactive decay—

(a) β-emission
(b) α-emission
(c) β^+-emission
(d) k-electron capture.

Answer: ( )

2. The half-life period of $^{232}_{90}Th$ is 1.3×10^{10} years. 1.0×10^{-3} kg of this will be reduced to 5.0×10^{-4} kg in

(a) 1.3×10^{10} years
(b) 0.65×10^{10} years
(c) 2.6×10^{10} years
(d) 0.65×10^5 years.

Answer: ( )

3. In neutron activation analysis, the atom is identified by —

(a) Decay characteristic of the daughter element
(b) The velocity of the neutron
(c) Nuclear recoil
(d) Threshold energy of the reaction.

Answer: ( )

4. The plot of mean binding energy per nucleon versus atom number Z —

(a) Increases as Z increases
(b) Decreases as Z decreases
(c) Increases, reaches a max and decreases
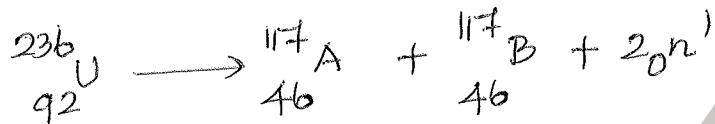(d) Reaches a limiting value as Z increases.

Answer: ( )

5. The particle having a major role in binding the nucleus is ___

(a) Neutron   (b) Electron

(c) Meson   (d) Proton

Answer: (c)

6. What is the energy released in the nuclear reaction?

$$^{236}_{92}U \longrightarrow \; ^{117}_{46}A + \; ^{117}_{46}B + 2\,_0n^1$$

(Binding energy per nucleon A and B = 8.5 MeV; Binding energy of ^{236}U = 7.6 MeV)

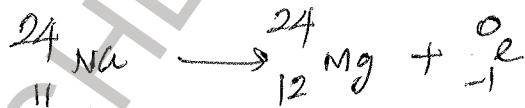(a) 20 MeV   (b) 180 MeV   (c) 200 MeV   (d) 300 MeV

Answer: ( )

7. The energy released by fission of a single uranium atom is 200 MeV. What is the number of fission per sec required to obtain 3.2 W of power?

(a) 10^9 (b) 10^{10} (c) 10^{11} (d) 10^{12}

Answer: ( )

8. During the disintegration of sodium as

$$^{24}_{11}Na \longrightarrow \; ^{24}_{12}Mg + \; ^{0}_{-1}e$$

The ratio of no. of neutron / no. of proton —

(a) Increases   (b) Decreases

(c) Remains constant   (d) Increases and decreases both

Answer: ( )

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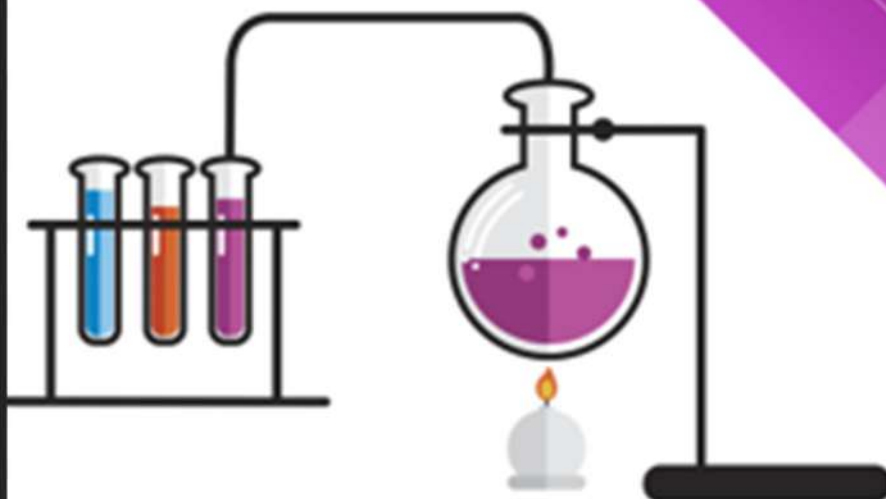38/23, Vaigundaperumal Koil Street, Kanchipuram-1
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CHEMISTRY

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UNIT-7

SYLLABUS: CHEMISTRY

UNIT- VII

TERM SYMBOLS AND TERM STATES – DN - IONS ENERGY LEVELS – DIAGRAMS WEAKFIELD AND STRONG FIELD AND STRONG FIELD CONCEPTS – SPIN ORBIT COUPLING – THE NEPHELANXETIC EFFECT CHARGE TRANSFER SPECTRA – APPLICATIONS OF UV, IR, NMR, BSR AND MOSSBAVER SPECTROSCOPY TECHNIQUES IN THE STUDY OF CO-ORDINATION CHEMISTRY.

MAGNETIC INTERACTIONS – MAGNETIC SUSCEPTIBILITIES DETERMINATION – APPLICATION IN CO-ORDINATION CHEMISTRY. APPLICATION OF VB, MO, CF AND LF THEORIES IN CO-ORDINATION CHEMISTRY – GROUP THEORETICAL APPROACH – SPLITTING OF D-ORBITALS – SPECTRO-CHEMICAL SERIES – CONCEPT OF WEAK AND STRONG FIELDS – THERMODYNAMIC AND CHEMICAL EFFECT OF D-ORBITALS SPLITTING – JAHN TELLER DISTORTION.

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY – THEORY – STUDY OF PMR – CHEMICAL SHIFT – TYPE OF SHIELDING – SPIN-SPIN COUPLING SPIN DECOUPLING – SPPLICATIONS TO SIMPLE NATURAL PRODUCTS.

ELECTRON SPIN RESONANCE SPECTRO SCOPY – PARAMAGNETISM – NUCLEAR HYPERFINE STRUCTURE – HYPERFINE COUPLING.

UNIT - VII

Term symbols and term states

An electronic configuration is the assignment of a given number of electrons to a certain set of orbitals without caring about the electrostatic and other interactions between the electrons.

For example, d^2 configuration tells us that there are two electrons in a set of five degenerate d orbitals. It does not tell us as to which d orbital is occupied and which is not.

It is important to note that for the same configuration, the placement of electrons even in degenerate orbitals may lead to electronic arrangements which may be of different energies. Consider the example of a metal ion with d^2 configuration. Let us say that we have a situation (a) in which the metal ion has one electron in dx^2-y^2 orbital and one electron in dxy orbital. Let us have another situation (b) in which the metal ion has one in dx^2-y^2 orbital and one

electron in d_{z^2} orbital. Now an electron in $d_{x^2-y^2}$ orbital has its regions of maximum electron-charge density along the x and y directions whereas an electron in d_{xy} orbital has the regions of maximum electron charge density in between the x and y directions and an electron in d_{z^2} orbital has regions of maximum electron charge density mainly in the z-direction. Therefore, the two electrons in $d_{x^2-y^2}$ and d_{xy} orbitals, both of which have their electronic charge spread in the xy plane (situation a) will repel each other to a greater extent compared to the extent with which they will repel each other when present in $d_{x^2-y^2}$ and d_{z^2} orbitals (situation b). Both situations (a) and (b) correspond to the same configuration but are associated with different energies. We can write many more arrangements for the d^2 configuration some g which will have different energies (non-degenerate arrangements due to different electrostatic repulsions between electrons) and some others will have the same energy (degenerate arrangements due to the same electrostatic repulsion between the electrons.

non-polar hydrocarbon chains of a membrane.

The hyperfine structure of an ESR spectrum is a kind of fingerprint that helps to identify the free radicals present in the sample. Again, since the magnitude of the splitting depends on the distribution of the unpaired electron near the magnetic nuclei present, the ESR spectrum can be used to map the molecular orbital occupied by the unpaired electron. This mapping is aided by the McConnell Equation,

$$a = Q P, \text{ where } Q = 2.25 \, mT$$

Here P is the unpaired electron spin density on a C atom and a is the hyperfine splitting constant observed for the H-atom to which it is attached.

— x —

Objectives

52. The proton and the neutron each has spin ____.

    (a) 1   (b) ½   (c) 3/2   (A) 0

53. The angular momentum is associated with a ____ spin is given by $[I(I+1)]^{1/2}(h/2\pi)$

    (a) nuclear   (b) proton   (c) neutron   (d) electron

54. The ____ momentum I can be parallel or antiparallel vectors.

(a) spin (b) nuclear (c) angular (d) None of these

55. The value of the electron ____ factor has been very accurately calculated to be equal to 2.0023.

(a) g (b) f (c) h (d) d

56. A ____ nucleus is an ideality.

(a) full (b) bare (c) forbidden (d) allowed

57. M_N is the ____ magneton.

(a) nuclear (b) spin (c) nucleon (d) electron

58. Each nucleus can be thought of being equivalent to a minute ____ having a magnetic moment.

(a) spin (b) magnet (c) vector (d) scalar

59. $^{12}_{6}C$ and $^{16}_{8}O$ are ____.

(a) paramagnetic (b) diamagnetic (c) ferro-magnetic

(d) non-magnetic

60. $^{11}_{5}B$, the nuclear spin I is ____.

(a) 1 (b) ½ (c) 3/2 (d) 0

CHEMISTRY

UNIT
8

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SYLLABUS: CHEMISTRY

UNIT- VIII

HUCKEL'S RULE AND CONCEPT OF AROMATICITY – AROMATICITY OF BENZENOID – NONBENZENOID AROMATICS. THE ANNULENES - AROMATICITY IN CHARGED RINGS AND FUSED RING SYSTEMS. AROMATIC ELECTROPHILIC SUBSTITUTION – MECHANISM AND REACTIVITY, TYPICAL REACTIONS TO INCLUDE DIAZONIUM COUPLING – HALOGNATION, SULPHONATION. FRIEDAL CRAFT ALKYLATION AND ACYLATION. AROMATIC NUCLEOPHILIC SUBSTITUTION – BENZYNE MECHANISM – EXAMPLES. OXIDATION – REDUCTION REACTIONS – MECHANISMS – SELECTIVITY IN OXIDATIONS AND REDUCTIONS.

MOLECULAR REARRANGEMENTS – REARRANGEMENTS WITH CARBON TO NITROGEN, CARTON TO OXYGEN AND CARBON MIGRATIONS. CURTIVS, LOSSEN, SCHMITTS BAEYER – VILLIGER, PINACOL – PINACOLENE, BENZOIL – BENZILICACID, BENZIDINE, FAVORSKI AND FRIES REARRANGEMENTS – SIGMATROPIC REARRAGEMENTS – CLAISEN AND COPE. PERICYCLIC REACTIONS, SELECTION RULES – ORBITAL SYMMETRY – LECTROCYCLIC REACTIONS – CYCLE ADDITIONS SIGMATROPIC REACTIONS.

MODERN SYNTHETIC REACTIONS – DIELS ALDER REACTION WITTING REACTIONS – STORK ENAMINE REACTIONS – MANNICH REACTIONS, BIRCH REDUCTIONS.

Concept of aromaticity:

* The aromatic compounds contain alternate double bond and single bond in a cyclic structure, and resembles benzene in chemical behaviour. They undergo substitution rather than addition reactions. This characteristic behaviour is called Aromatic character (or) Aromaticity.

*Def: Aromaticity is infact a property of the sp^2 hybridised planar rings in which the P-orbital allow cyclic delocalisation of π-electrons.

* If a cyclic conjugated system has significant increase in the stability due to delocalisation compared to acyclic structural analogues, then it is said to possess aromatic character.

Criteria for Aromaticity:

On the basis of the above considerations, can be laid down criteria or rules which help us in knowing whether a particular compound is aromatic or a non-aromatic.

(i) The π system must be conjugated (one P orbital from each atom in the cyclic system is necessary and hence each atom of the ring must be either sp^2 or sp hybridised).

(ii) The π system must be cyclic. (Linear systems can never be aromatic)

(iii) The π system must be planar. (This is necessary for a good overlap between the p-orbitals).

(iv) If the above three conditions are met, then according to the huckle's rule, the π system with $(4n+2)$ π electrons are aromatic.

Huckle's rule / $(4n+2)$ rule:

Planar, mon cyclic, fully conjugated molecules or ions that contain $(4n+2)$ electrons (where, $n=0,1,2,\ldots$) will display aromatic character.

eg: 1

 Benzene.

*It is a cyclic and planar compound.

* It has a P orbital on each carbon of the ring involved in a double bond. It has three double bond and six π-electrons, which is in accordance with Huckle rule.

$$\therefore \ 4n+2 = 6 \quad (or) \quad 4n = 6-2$$
$$4n = 4 \quad and \quad n = 1$$

eg: 2

 Toluene

It is a cyclic, planar, conjugated, follows $(4n+2)$ huckle rule. So it is aromatic.

Craig's rule of aromaticity:-

* To apply this rule, the molecule is labelled with equal number of spin symbols, α and β, giving different symbols to the end of all the double bonds in one resonance structure.

* A C_2 symmetry operation which converts one resonance structure into itself or into another of the same canonical set is characterised by two numbers P and q.

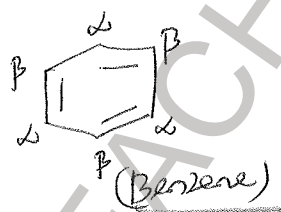* The number 'p' refers to the number of interchanges of π-electrons centres effected by the symmetry operation, or

* 'q' represents the number of interchanges of spin symbols needed to bring back the original labeling from the changed one.

* According to V.B theory, the character of the transformation of the ground state of the molecule is given by

$$x = (-1)^{P+q}$$

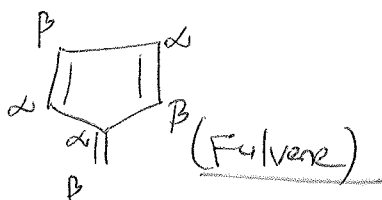* If the sum of p and q is even number, then the molecule is aromatic and if it is odd number, it is not aromatic.

(Benzene)
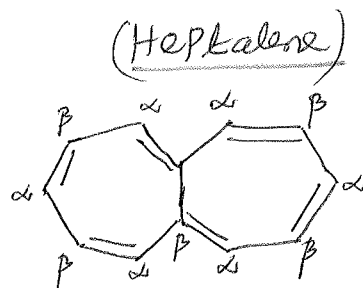
P=2
q=0
$x = (-1)^{2+0}$
$x = +1$
Symmetric & aromatic.

(Fulvene)

P=2
q=2
$x = (-1)^{2+2}$
$x = +1$
Symmetric aromatic.

(Heptalene)
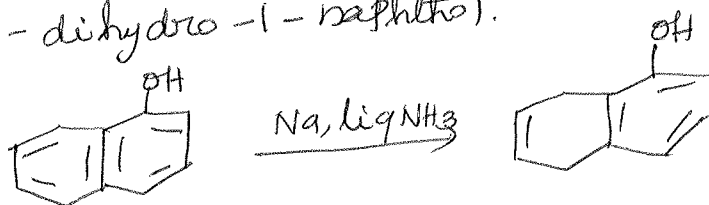
P=5
q=0
$x = (-1)^{5+0}$
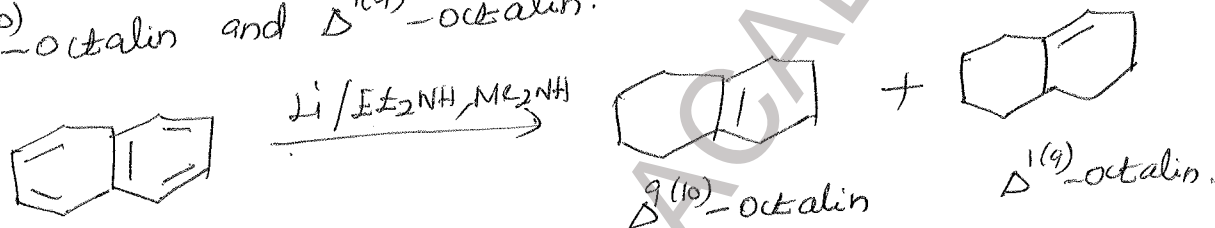$x = -1$
antisymmetric
Not aromatic

Applications:

* 1- Napthol on reduction with Na/liq. ammonia gives

5,8 - dihydro -1 - naphthol.

Na, LiqNH₃

* Similarly, naphthalene on reduction with Li and diethylamine and dimethylamine gives a mixture of $\Delta^{9(10)}$-octalin and $\Delta^{1(9)}$-octalin.

Li / Et₂NH, Me₂NH

$\Delta^{9(10)}$-octalin $\Delta^{1(9)}$-octalin.

MCQ:

1. Diels - Alder reaction is

(a) [2+2] cycloaddition   (b) [4+2] cycloaddition

(c) [1+2] cycloaddition   (d) [2+6] cycloaddition

Answer:

2. In Diels - Alder reaction, the dienes and dienophiles to form an

(a) an intermediate   (b) Transition state

(c) carbocation   (d) Adduct

Answer:

3. _____ conformation of dienes, the Diels - Alder reaction does not takes place.

(a) cisoid   (b) Transoid   (c) Exo   (d) Endo

Answer: (b)

(4) Diels-Alder reaction is

(a) Irreversible (b) Reversible (c) quasireversible (d) None of these

Answer :( )

(5) Wittig rearrangement is related to

(a) Favorskii rearrangement (b) Beckmann rearrangement
(c) Stevens rearrangement (d) Neber rearrangement

Answer :( )

(6) The intermediate for the acylation or alkylation of aldehydes or ketone is

(a) carbocation   (b) carboanion

(c) Enamine   (d) free radical
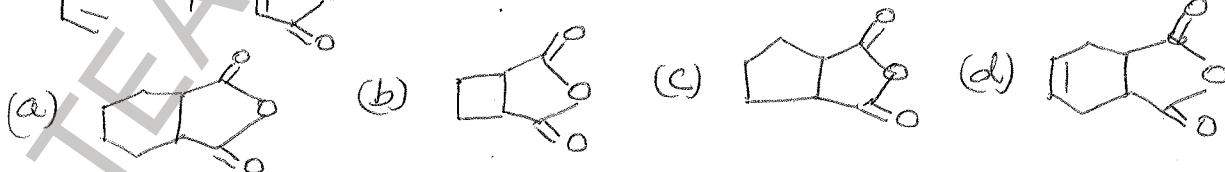
Answer :( )

(7) The mannich reaction gives

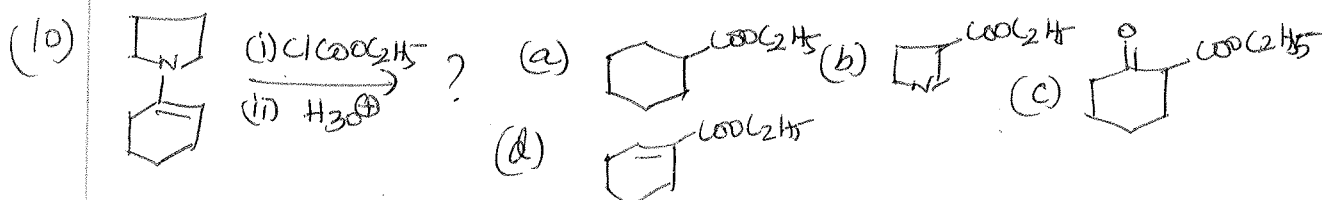(a) Mannich base (b) Intermediate (c) Transition state

(d) free radical

Answer :( )

(8) In birch reduction alkyne gives

(a) cis-alkene (b) Trans-alkene

(c) Meso alkene (d) Erythro-alkene

Answer :( )

(9) → ?
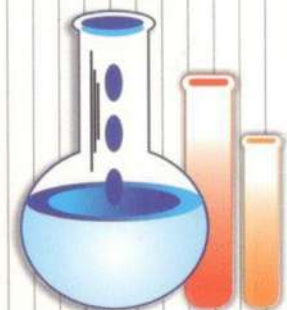
(a)   (b)   (c)   (d)

Answer :( )

(10) $\frac{(i) ClCOOC_2H_5}{(ii) H_3O^{\oplus}}$? (a) $COOC_2H_5$ (b) $COOC_2H_5$ (c) $COOC_2H_5$

(d) $COOC_2H_5$

CHEMISTRY

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UNIT-9

SYLLABUS: CHEMISTRY

UNIT- IX

THEORIES OF REACTION RATES – SIMPLE COLLISION THEORY – ABSOLUTE REACTION RATE THEORY (ARRT) – REACTION CO-ORDINATE – POTENTIAL ENERGY SURFACES. HAMMETT – TAFT EQUATION – HAMMETT ACIDITY FUNCTION – ACID BASE CATALYSIS BRONSTED RELATION ENZYME CATALYSIS – MICHAELIS MENTON LAW – INFLUENCE OF PH AND TEMPERATURE. SURFACE PHENOMENON – HETEROGENEOUS CATALYSIS – ABSORPTION ISOTHERMS. ELECTROLYTIC CONDUCTANCE – APPLICATIONS – SOLUBILITY PRODUCT – INTERIONIC ATTRACTION THEORY – DEBYE – HUCKEL – ONSAGER EQUATION – EQUIVALENT CONDUCTIVITY OF ELECTRO LYTES.

ELECTRO POTENTIALS – ELECTROCHEMICAL CELLS – ELECTRODE – ELECTROLYTE INTERFACE – ELECTRICAL DOUBLE LAYER ELECTRO CAPILLARY PHENOMENA – ELECTRO KINETIC PHENOMENA – MEMBRANE POTENTIAL – POLARISATION – OVER POTENTIAL – POLAROGRAPHY – CONCENTRATION POLARIZATION – ELECTRO CHEMICAL POLARIZATION – SUTLER – VOLMER EQUATION.

UNIT- $\overline{IX}$

Theories of Reaction Rate

There are two important theories of reaction rates. These are the collision theory developed by Arrhenius and Van't Haff and the modern transition theory, also called the activated complex theory.

The simple collision theory (or)
The collision theory of Bimolecular Gaseous reactions

This is the earliest theory of reaction rates. Since reaction between two species takes place only when they are in contact, it is reasonable to suppose that the reactant species must collide before they react. Since our knowledge of molecular collisions is more complete for the gaseous phase than for the liquid phase, we will restrict our discussion to bimolecular reactions in the gaseous phase.

From the kinetic theory of gases, the number of bimolecular collisions per second per cm^{-1}

among molecules of one species is given by

$$Z = 2\pi^2\sigma^2 \left(8\pi kT/\mu\right)^{1/2} \quad —①$$

For a reaction involving two different gases A and B, the rate of bimolecular collisions between unlike molecules is given by

$$Z_{AB} = n_A n_B \left(\sigma_{av}\right)^2 \left(8\pi kT/\mu\right)^{1/2} \quad —②$$

Where n_A and n_B are numbers of A and B molecules respectively; σ_{av} is the average collision diameter defined as $\left(\sigma_A + \sigma_B\right)^{1/2}$ and μ is the reduced mass, defined as $\mu = \left(m_A m_B\right)/\left(m_A + m_B\right)$. The collision number Z_{AB} is given, in terms of molar masses m_A and m_B of the two gases, by the expression

$$Z_{AB} = n_A n_B \left(\sigma_{av}\right)^2 \left[\frac{\left(M_A + M_B\right) 8\pi RT}{M_A M_B}\right]^{1/2} \quad —③$$

In a special case, when the reducing species A and B are the same $\sigma_{av} = \sigma$ and $n_A = n_B$ and if we also take account of the indistinguishability of the colliding molecules by dividing by 2 then equation ② reduces to equation ①.

Let us calculate Z_{AB} for the reaction between H_2 and I_2 at 700 K and 1 atm pressure, the

Here, putting the de-electronation current densities $\overleftrightarrow{i}$, first is meant to imply that when the magnitude of $\overleftrightarrow{i}$ is greater than the magnitude of $\overrightarrow{i}$, the net current i is taken as positive. Hence, there is net flow of electrons from solution to metal, the net current is taken as positive.

Where $\Delta\phi$ is the non-equilibrium potential difference across the interface $(\Delta\phi \neq \Delta\phi_e)$ corresponding to the current density i. One can split this non-equilibrium $\Delta\phi$ into the equilibrium potential difference $\Delta\phi_e$ and another portion, namely, the extra part η by which the potential of the electrode departs from that at equilibrium, (ie) $(\Delta\phi - \Delta\phi_e) = \eta$ and write it as

$$\Delta\phi = \Delta\phi_e + (\Delta\phi - \Delta\phi_e) = \Delta\phi_e + \eta \quad —⑤$$

One can write a net current density

$$i = \overleftarrow{i} - \overrightarrow{i} = \left\{ F\overrightarrow{k_c}\, C_D\, e^{(1-\beta)F\Delta\phi_e/RT} \right\} e^{(1-\beta)F\eta/RT}$$

$$- \left\{ F\overrightarrow{k_c}\, C_{A^+}\, e^{-\beta F\Delta\phi_e/RT} \right\} e^{-\beta F\eta/RT}$$

$$—⑥$$

The two terms inside the brackets are simply

the expressions for the equilibrium exchange current density (io).

Hence a convenient way of writing is

$$i = i_o \left[e^{(1-\beta)F\eta/RT} - e^{\beta F\eta/RT} \right] \quad -①$$

This is rather fundamental equation in electrodes. It may be termed as Butler–Volmer equation. It shows how the current density across a metal solution interface depends on the difference η between the actual non-equilibrium and equilibrium potential differences small changes in η produce large changes in i.

———— x ————

Objectives

1. ———— are the phenomena related to changes in the surface energy of the dropping mercury electrode.
   (a) electro capillary phenomena (b) electro kinetic phenomena (c) electrode interface (d) All the above.

2. ———— phenomena are a family of several different effect that occur in heterogeneous

fluids, or in porous bodies filled with fluid, or in a fast flow over a flat surface.

(a) Electro capillary (b) electrokinetic

(c) Electrolytic (d) None of these

③ Influence of an external force on the diffuse layer generates ———— motion of a fluid with respect to an adjacent charged surface.

(a) circular (b) linear (c) tangential (d) relative

④ $S_t = \dfrac{h \cdot r \cdot g \cdot d}{2}$ is the equation of ——

tension.

(a) Surface (b) interfacial (c) water (d)
electrolyte

⑤ ———— potential is the difference in electric potential between the interior and the exterior of a biological cell.

(a) membrane (b) polarized (c) gradient (d) All the above

⑥ A double layer is also called as ————.

(a) EL (b) EC (c) EDL (d) EF

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UNIT-10

CHEMISTRY

SYLLABUS: CHEMISTRY

UNIT- X

THEORY AND APPLICATIONS OF THE FOLLOWING SPECTROSCOPIC METHODS; ELECTONICS SPECTRA-UV-VISIBLE SPECTRA – IR SPECTRA – RAMAN SPECTRA – LASER – RAMAN SPECTRA – NMR – WCR- ESR SPECTRA – MOSSBAVER SPECTRO SCOPY – PHOTOELECTRON SPECTRO SCOPY – POLY MERISATION REACTIONS – MECHANISM – STEROCHEMICAL ASPECTS. TYPES OF POLYMERS – ORGANIC AND INORGANIC POLYMERS – PREPARATION – PROPERTIES – STRUCTURE – POLYSTYRENE – POLYVINYLCHLORIDE – POLYESTERS – NYLON – PHENOL RESIN – AMINO RESINS – EPOXY RESINS. PHOSPHONITRILIC COMPOUNDS – SILICONS – BORAZINES APPLICATIONS OF POLYMERS.

UNIT–X

Theory and applications of the UV-Visible Spectroscopy

The absorption of radiation in the ultra-violet and visible regions of the spectrum results in the transition of an electron from the
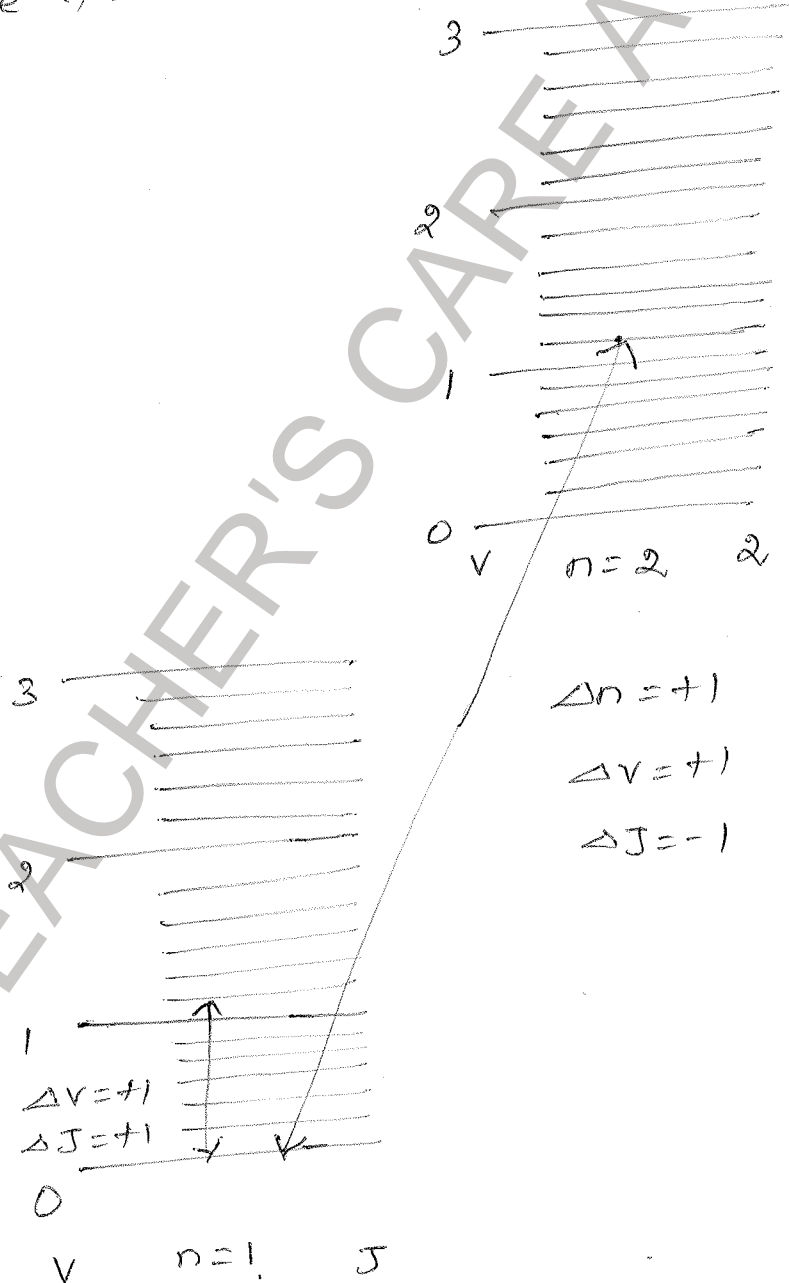

$\Delta n = +1$

$\Delta V = +1$

$\Delta J = -1$

$\Delta V = +1$
$\Delta J = +1$

Fig.1 Energy level diagram indicating the Rotational, Vibrational and Electronic Transition

ground state to an excited state (electronic excitation). For simplicity, the ultraviolet region is divided into the far ultraviolet (upto 200 nm) and the near ultraviolet (200 to 375 nm) regions. The far ultraviolet region is also known as the vacuum ultraviolet region. For measurement in this region, oxygen is excluded by evacuation since oxygen itself absorbs below 200 nm.

The total energy of a molecule is made up of translational, rotational, vibrational and electronic energies. The change in energy ΔE in the energy of a molecule, when exposed to radiation is given by

$$\Delta E = \Delta E_{trans} + \Delta E_{rot} + \Delta E_{vib} + \Delta E_{Elec}$$

ΔE_{trans} is the change in energy of the molecule due to its movement through space in all directions but usually this term is neglected. ΔE_{elec} is the energy difference between two allowed energy levels. ΔE_{vib} is the difference in energy between two allowed vibrational levels within the same electronic level and ΔE_{rot} is the spacing between two allowed rotational levels within a vibrational level.

2. Toys, pipes, radio and TV cabinets

3. Milk crates, plastic buckets, moulded articles, etc

4. Adhesive, lacquer bases, industrial fibres, etc

5. Rubber articles resistant to ozone.

6. Resins for advanced reinforced composits, can be used as elevated temperature.

7. Hosiery, yarn fibre, carpets, ropes, nets, belts and tyre cord.

8. Electrical goods, buttons, laminates, glues, and paint bases.

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objectives

1. ~~condensation~~ polymerization is generally accompanied by the elimination of a small molecule such as ____

   (a) Cl_2 (b) Br_2 (c) I_2 (d) H_2O

2. The mechanism of ____ polymerization involves the production of a growth centre.

   (a) step-wise   (b) addition   (c) condensation

   (d) chain

3. ___ and polyesters are the products of condensation polymerization.

(a) radical (b) carbanion (c) Nylon (d) All the above

4. The most common variety of polyester, the so-called ___ .

(a) PVC (b) polyethylene (c) glycol (d) PET

5. ___ Weight of a polymer is defined as the sum of the atomic weight of each of the atoms in the molecules, which is present in the polymer.

(a) atomic (b) molecule (c) normal (d) average

6. The ___ average molecular weight is the total weight of the polymer molecules divided by the total number of polymer molecules

(a) size (b) ratio (c) number (d) fraction

7. Glass transition temperature is always lower than the ___ temperature, of the crystalline state of the material.

(a) melting (b) boiling (c) existing (d) flowing

8. ___ of a material characterizes the range of temperatures over which this glass

transition occurs.

(a) glass-transition (b) transition (c) boiling
(d) melting.

9. An amorphous solid that exhibits a glass transition is called a ___.

(a) rubber (b) glass (c) liquid (d) plastics

10. The ___ transition, achieved by super cooling a viscous liquid into the glass state, is called Vitrification.

(a) irreverse (b) normal (c) reverse (d) none of these

11. In the ___ state, they are soft and flexible.

(a) rubbery (b) glass (c) plastic (d) All the above

12. Rubber elastomers like polyisoprene and polyisobutylic are used ___ their Tg.

(a) below (b) above (c) in between (d) none of these

13. Hard plastics like polystyrene are used we ___ their Tg. [1]

(a) below (b) above (c) not used (d) All the above

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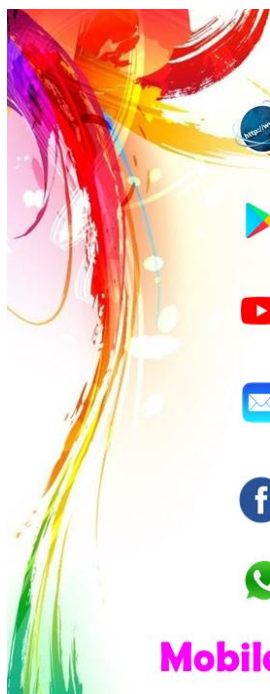### (Classes : Saturday, Sunday & Govt. Holidays)

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