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**Graduate Aptitude Test In Engineering**

**GATE**

**CHEMISTRY**

**UP TO DATE**

**Solved Papers**

**2007- Till Date**

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# GATE CY Chemistry Syllabus

## Section 1: Physical Chemistry

**Structure:** Postulates of quantum mechanics. Operators. Time dependent and time independent Schrödinger equations. Born interpretation. Dirac bra-ket notation. Particle in a box: infinite and finite square wells; concept of tunnelling; particle in 1D, 2D and 3D-box; applications. Harmonic oscillator: harmonic and anharmonic potentials; hermite polynomials. Rotational motion: Angular momentum operators, Rigid rotor. Hydrogen and hydrogen-like atoms : atomic orbitals; radial distribution function. Multi-electron atoms: orbital approximation; electron spin; Pauli exclusion principle; Slater determinants. Approximation Methods: Variation method and secular determinants; first order perturbation techniques. Atomic units. Molecular structure and Chemical bonding: BornOppenheimer approximation; Valence bond theory and linear combination of atomic orbitals – molecular orbital (LCAO-MO) theory. Hybrid orbitals. Applications of LCAO-MO theory to  $H_2^+$ ,  $H_2$ ; orbital theory (MOT) of homo- and heteronuclear diatomic molecules. Hückel approximation and its application to annular  $\pi$  – electron systems.

**Group theory:** Symmetry elements and operations; Point groups and character tables; Internal coordinates and vibrational modes; symmetry adapted linear combination of atomic orbitals (LCAOMO); construction of hybrid orbitals using symmetry aspects.

**Spectroscopy:** Atomic spectroscopy; Russell-Saunders coupling; Term symbols and spectral details; origin of selection rules. Rotational, vibrational, electronic and Raman spectroscopy of diatomic and polyatomic molecules. Line broadening. Einstein's coefficients. Relationship of transition moment integral with molar extinction coefficient and oscillator strength. Basic principles of nuclear magnetic resonance: gyromagnetic ratio; chemical shift, nuclear coupling.

**Equilibrium:** Laws of thermodynamics. Standard states. Thermochemistry. Thermodynamic functions and their relationships: Gibbs-Helmholtz and Maxwell relations, Gibbs-Duhem equation, van't Hoff equation. Criteria of spontaneity and equilibrium. Absolute entropy. Partial molar quantities. Thermodynamics of mixing. Chemical potential. Fugacity, activity and activity coefficients. Ideal and Non-ideal solutions, Raoult's Law and Henry's Law, Chemical equilibria. Dependence of equilibrium constant on temperature and pressure. Ionic mobility and conductivity. Debye-Hückel limiting law. Debye-Hückel-Onsager equation. Standard electrode potentials and electrochemical cells. Nernst Equation and its application, relationship between Electrode potential and thermodynamic quantities, Potentiometric and conductometric titrations. Phase rule. Clausius-Clapeyron equation. Phase diagram of one component systems:  $CO_2$ ,  $H_2O$ , S; two component systems: liquid- vapour, liquid-liquid and solid-liquid systems. Fractional distillation. Azeotropes and eutectics. Statistical thermodynamics: microcanonical, canonical and grand canonical ensembles, Boltzmann distribution, partition functions and thermodynamic properties.

**Kinetics (Topic have been rearranged):** Elementary, parallel, opposing and consecutive reactions. Steady state approximation. Mechanisms of complex reactions. Unimolecular reactions. Potential energy surfaces and classical trajectories, Concept of Saddle points, Transition state theory: Eyring equation, thermodynamic aspects. Kinetics of polymerization. Catalysis concepts and enzyme catalysis. Kinetic isotope effects. Fast reaction kinetics: relaxation and flow methods. Diffusion controlled reactions. Kinetics of photochemical and photophysical processes.

**Surfaces and Interfaces:** Physisorption and chemisorption. Langmuir, Freundlich and Brunauer– Emmett–Teller (BET) isotherms. Surface catalysis: Langmuir-Hinshelwood mechanism. Surface tension, viscosity. Self-assembly. Physical chemistry of colloids, micelles and macromolecules.

## Section 2: Inorganic Chemistry

**Main Group Elements:** Hydrides, halides, oxides, oxoacids, nitrides, sulfides – shapes and reactivity. Structure and bonding of boranes, carboranes, silicones, silicates, boron nitride, borazines and phosphazenes. Allotropes of carbon, phosphorus and sulphur. Industrial synthesis of compounds of main group elements. Chemistry of noble gases, pseudohalogens, and interhalogen compounds. Acid-base concepts and principles (Lewis, Brønsted, HSAB and acid-base catalysis).

**Transition Elements:** Coordination chemistry – structure and isomerism, theories of bonding (VBT, CFT, and MOT). Energy level diagrams in various crystal fields, CFSE, applications of CFT, Jahn-Teller distortion. Electronic spectra of transition metal complexes: spectroscopic term symbols, selection rules, Orgel and Tanabe-Sugano diagrams, nephelauxetic effect and Racah parameter, charge-transfer spectra. Magnetic properties of transition metal complexes. Ray-Dutt and Bailar twists, Reaction mechanisms: kinetic and thermodynamic stability, substitution and redox reactions. Metal-metal multiple bond.

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**Lanthanides and Actinides:** Recovery. Periodic properties, spectra and magnetic properties.

**Organometallics:** 18-Electron rule; metal-alkyl, metal-carbonyl, metal-olefin and metal-carbene complexes and metallocenes. Fluxionality in organometallic complexes. Types of organometallic reactions. Homogeneous catalysis - Hydrogenation, hydroformylation, acetic acid synthesis, metathesis and olefin oxidation. Heterogeneous catalysis - Fischer-Tropsch reaction, Ziegler-Natta polymerization.

**Radioactivity:** Detection of radioactivity, Decay processes, half-life of radioactive elements, fission and fusion processes.

**Bioinorganic Chemistry:** Ion ( $\text{Na}^+$  and  $\text{K}^+$ ) transport, oxygen binding, transport and utilization, electron transfer reactions, nitrogen fixation, metalloenzymes containing magnesium, molybdenum, iron, cobalt, copper and zinc.

**Solids:** Crystal systems and lattices, Miller planes, crystal packing, crystal defects, Bragg's law, ionic crystals, structures of AX, AX<sub>2</sub>, ABX<sub>3</sub> type compounds, spinels, band theory, metals and semiconductors.

**Instrumental Methods of Analysis:** UV-visible, fluorescence and FTIR spectrophotometry, NMR and ESR spectroscopy, mass spectrometry, atomic absorption spectroscopy, Mössbauer spectroscopy (Fe and Sn) and X-ray crystallography. Chromatography including GC and HPLC. Electroanalytical methods- polarography, cyclic voltammetry, ion-selective electrodes. Thermoanalytical methods.

### Section 3: Organic Chemistry

**Stereochemistry:** Chirality and symmetry of organic molecules with or without chiral centres and determination of their absolute configurations. Relative stereochemistry in compounds having more than one stereogenic centre. Homotopic, enantiotopic and diastereotopic atoms, groups and faces. Stereoselective and stereospecific synthesis. Conformational analysis of acyclic and cyclic compounds. Geometrical isomerism and optical isomerism. Configurational and conformational effects, atropisomerism, and neighbouring group participation on reactivity and selectivity/specificity.

**Reaction Mechanisms:** Basic mechanistic concepts – kinetic versus thermodynamic control, Hammond's postulate and Curtin-Hammett principle. Methods of determining reaction mechanisms through kinetics, identification of products, intermediates and isotopic labelling. Linear free-energy relationship – Hammett and Taft equations. Nucleophilic and electrophilic substitution reactions (both aromatic and aliphatic). Addition reactions to carbon-carbon and carbon-heteroatom (N and O) multiple bonds. Elimination reactions. Reactive intermediates – carbocations, carbanions, carbenes, nitrenes, arynes and free radicals. Molecular rearrangements.

**Organic Synthesis:** Synthesis, reactions, mechanisms and selectivity involving the following classes of compounds – alkenes, alkynes, arenes, alcohols, phenols, aldehydes, ketones, carboxylic acids, esters, nitriles, halides, nitro compounds, amines and amides. Uses of Mg, Li, Cu, B, Zn, P, S, Sn and Si based reagents in organic synthesis. Carbon-carbon bond formation through coupling reactions - Heck, Suzuki, Stille, Sonogoshira, Negishi, Kumada, Hiyama, Tsuji-Trost, olefin metathesis and McMurry. Concepts of multistep synthesis - retrosynthetic analysis, strategic disconnections, synthons and synthetic equivalents. Atom economy and Green Chemistry, Umpolung reactivity – formyl and acyl anion equivalents. Selectivity in organic synthesis – chemo-, regio- and stereoselectivity. Protection and deprotection of functional groups. Concepts of asymmetric synthesis – resolution (including enzymatic), desymmetrization and use of chiral auxiliaries, organocatalysis. Carbon-carbon and carbon-heteroatom bond forming reactions through enolates (including boron enolates), enamines and silyl enol ethers. Stereoselective addition to C=O groups (Cram, Prelog and Felkin-Anh models).

**Pericyclic Reactions and Photochemistry:** Electrocyclic, cycloaddition and sigmatropic reactions. Orbital correlations - FMO and PMO treatments, Woodward-Hoffmann rule. Photochemistry of alkenes, arenes and carbonyl compounds. Photooxidation and photoreduction. Di- $\pi$ -methane rearrangement, Barton-McCombie reaction, Norrish type-I and II cleavage reaction.

**Heterocyclic Compounds:** Structure, preparation, properties and reactions of furan, pyrrole, thiophene, pyridine, indole, quinoline and isoquinoline.

**Biomolecules:** Structure, properties and reactions of mono- and di-saccharides, physicochemical properties of amino acids, chemical synthesis of peptides, chemical structure determination of peptides and proteins, structural features of proteins, nucleic acids, lipids, steroids, terpenoids, carotenoids, and alkaloids.

**Experimental techniques in organic chemistry:** Optical rotation (polarimetry). Applications of various chromatographic techniques such as thin-layer, column, HPLC and GC. Applications of UV-visible, IR, NMR and Mass spectrometry in the structural determination of organic molecules.

# Graduate Aptitude Test In Engineering (GATE)

## Chemistry - 2007

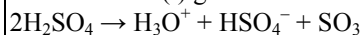
### Solved Paper

1. The rate of sulphonation of benzene can be significantly enhanced by the use of
- a mixture of  $\text{HNO}_2$  and  $\text{H}_2\text{SO}_4$
  - conc.  $\text{H}_2\text{SO}_4$
  - a solution of  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$
  - $\text{SO}_3$

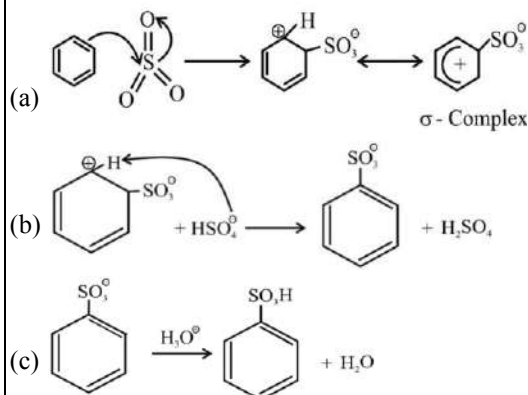
**Ans. (c) :** The rate of sulphonation of benzene can be significantly enhanced by the use of a solution of  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$ .

Sulphonation of benzene is technique in which benzene is heated with the presence of fuming sulphonic acid or  $\text{SO}_3$ , it give benzene sulphonic acid.

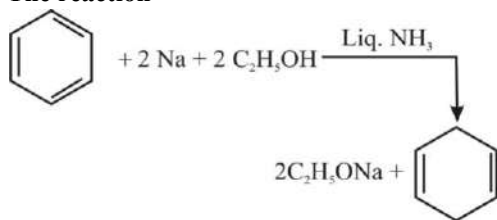
**Mechanism-** (i) generation of electrophile.



(ii) Attack of electrophile on benzene ring – Benzene reacts with  $\text{SO}_3$  as a result sigma complex is formed and finally benzene sulphonic acid is formed as a final product.



2. The reaction



in an example of

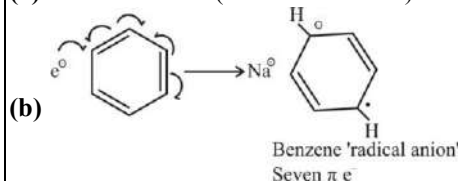
- Birch reduction
- Clemmenson reduction
- Wolff-Kishner reduction
- hydride reduction

**Ans. (a) : Birch Reduction-** When benzene is treated with metallic sodium/lithium in liquid  $\text{NH}_3$  as a solvent, in the presence of a proton source (eg. ethanol, methanol, or butanol) the net result is the net reduction of one of the double bonds of the benzene ring to give 1,4-cyclohexadiene.

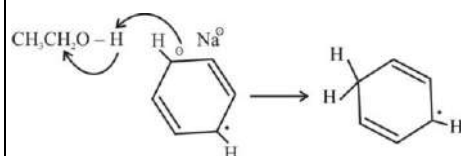
**Mechanism-**

(i) Reduction of benzene to the benzene radical anion-

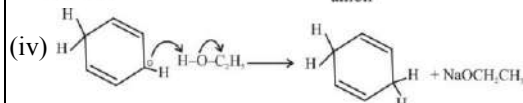
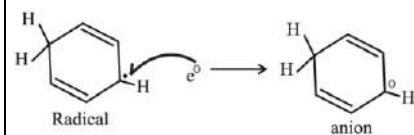
(a)  $\text{Na} \rightarrow \text{Na}^+ + e^-$  (solvated electron)



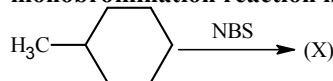
(ii) Protonation of the benzene 'radical anion'



(iii) Reduction of the radical to an anion by the electron

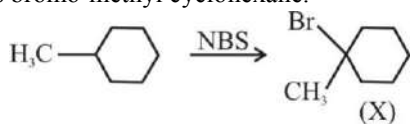


3. The major product (X) of the monobromination reaction is



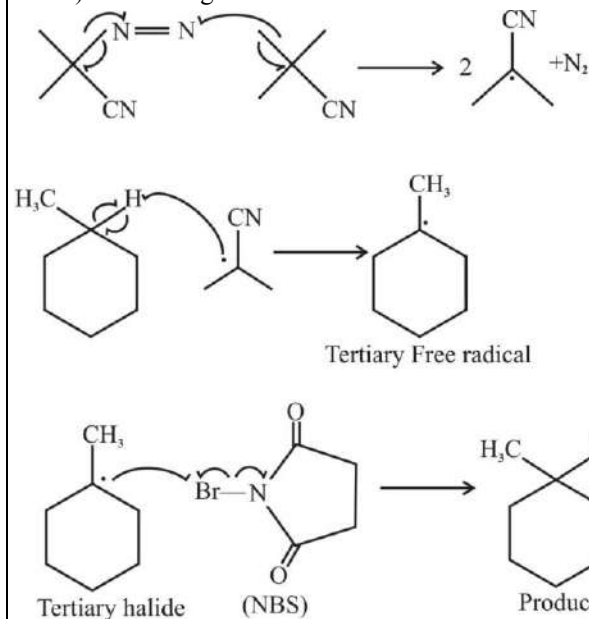
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**Ans. (d) :** NBS, N-bromo succinamide gives Br free radical, which attacks on tertiary free radical Carbon produces bromo-methyl cyclohexane.



**Mechanism-**

NBS in the presence of radical (AIBN-Azo isobutyl nitrile) initiate or gives radical substitution reaction.



4. Benzene can not be iodinated with  $\text{I}_2$  directly. However in presence of oxidants such as  $\text{HNO}_3$ , iodination is possible. The electrophile formed in this case is

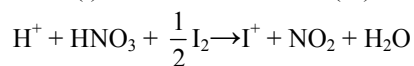
- (a)  $[\text{I}^+]$       (b)  $[\text{I}^-]$   
 (c)  $[\text{I}^{\delta+} \dots \text{OH}_2^{\delta+}]^+$       (d)  $[\text{I}^{\delta+} \dots \text{OH}_2^{\delta-}]^+$

**Ans. (a) : Iodination of Benzene-** Under conventional reaction conditions  $\text{I}_2$  adds to the benzene reversibly generating HI, it is a strong reducing agent and it regenerates  $\text{I}_2$  on reaction with the aryl iodide giving the starting material benzene.

**Oxidising agents oxidise  $\text{I}_2$  to iodonium ion  $\text{I}^\oplus$ .**

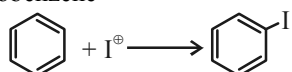
It is produced in the presence of  $\text{HNO}_3/\text{H}_2\text{SO}_4$  (in atmosphere of acetic acid). The cation ( $\text{I}^\oplus$ ) then reacts with benzene to give Iodobenzene,  $\text{NO}_2$  and  $\text{H}_2\text{O}$ .

**Mechanism-** (i) Generation of cation ( $\text{I}^\oplus$ )



Iodonium ion

(ii) Electrophilic attack of ion on benzene ring producing iodobenzene-



5. Classify the following species as electrophiles (E) and nucleophiles (N) in routine organic synthesis

- $\text{SO}_3$   $\text{Cl}^+$   $\text{CH}_3\text{NH}_2$   $\text{H}_3\text{O}^+$   $\text{BH}_3$   $\text{CN}^-$
- (a) E =  $\text{SO}_3$ ,  $\text{Cl}^+$ ,  $\text{BH}_3$  ; N =  $\text{CH}_3\text{NH}_2$ ,  $\text{H}_3\text{O}^+$ ,  $\text{CN}^-$   
 (b) E =  $\text{Cl}^+$ ,  $\text{H}_3\text{O}^+$  ; N =  $\text{SO}_3$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{BH}_3$ ,  $\text{CN}^-$   
 (c) E =  $\text{Cl}^+$ ,  $\text{H}_3\text{O}^+$ ,  $\text{BH}_3$  ; N =  $\text{SO}_3$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{H}_3\text{O}^+$ ,  $\text{CN}^-$   
 (d) E =  $\text{SO}_3$ ,  $\text{Cl}^+$ ,  $\text{H}_3\text{O}^+$ ,  $\text{BH}_3$  ; N =  $\text{CH}_3\text{NH}_2$ ,  $\text{CN}^-$

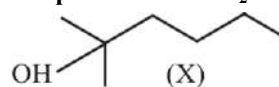
**Ans. (d) : Nucleophile-** A nucleophile is a reactant with either lone pair (neutral) or having negative charge over it (negative). Generally nucleophiles are shown by  $\text{Nu}^\ominus$ .

Example- E= $\text{SO}_3$ ,  $\text{Cl}^+$ ,  $\text{H}_3\text{O}^+$ ,  $\text{BH}_3$

**Electrophiles-** An electrophile is the species either having positive charge or electron deficient in nature. Generally electrophiles are shown by symbol  $\text{E}^\oplus$ .

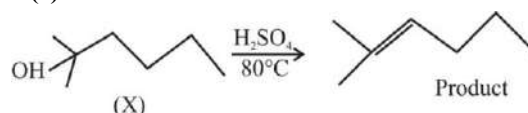
Example- N= $\text{CH}_3$ ,  $\ddot{\text{N}}\text{H}_2$ ,  $\text{CN}^-$

6. The major product obtained upon treatment of compound X with  $\text{H}_2\text{SO}_4$  at  $80^\circ\text{C}$  is

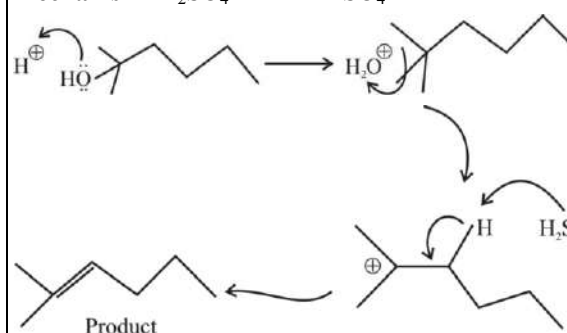


- (a)      (b)
- (c)      (d)

**Ans. (c) :**



**Mechanism-**  $\text{H}_2\text{SO}_4 \rightarrow \text{H}^\oplus + \text{HSO}_4^\ominus$

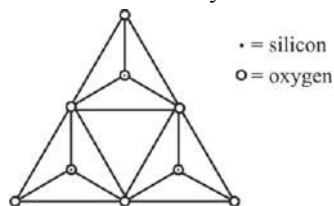


7.  $\text{BaTi}[\text{Si}_3\text{O}_9]$  is a class of

- (a) ortho silicate      (b) cyclic silicate  
 (c) chain silicate      (d) sheet silicate

**Ans. (b) :** The primary unit of BaTi ( $\text{Si}_3\text{O}_9$ ) or ( $\text{Si}_3\text{O}_9^{6-}$ ) is ( $\text{SiO}_3$ ) $^{2n-}$ ,  $n = 3$ .

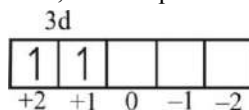
Thus it is formed by sharing of two oxygen per Si atoms and results in the formation of cyclic silicate.



8. The ground state term of  $\text{V}^{3+}$  ion is  
 (a)  ${}^3\text{F}$  (b)  ${}^2\text{F}$   
 (c)  ${}^3\text{P}$  (d)  ${}^2\text{D}$

**Ans. (a) :**  $\text{V}(23) = [\text{Ar}] 3d^3, 4s^2$   
 $\text{V}^{3+} = [\text{Ar}] 3d^2, 4s^0$

In 3d orbitals, no of unpaired electrons are two



$$S = \frac{1}{2} + \frac{1}{2} = 1$$

$$(2S + 1) = (2 \times 1 + 1) = 3$$

$$L = +2 + 1 = 3$$

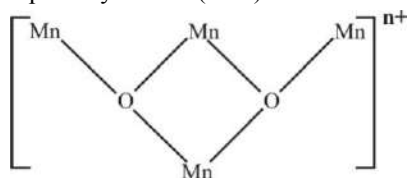
For  $L = 3$ , Term = F

Hence, ground state term of ion  $\text{V}^{3+} = (2S + 1)L = {}^3\text{F}$

9. In photosynthesis the predominant metal present in the reaction centre of photosystem II is

- (a) Zn (b) Cu  
 (c) Mn (d) Fe

**Ans. (c) :** Metals exert important functions in the Chloroplast of plants, where they act as co.factors and catalysts in the photosynthetic electron transport chain. In particular manganese (Mn) has a key function because of its indispensable role in the water-splitting reaction of photosystem-II (PSII).



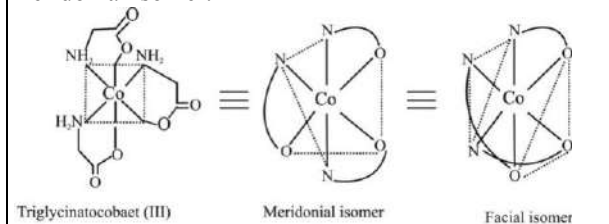
Mn (ii) and Mn (III) are present in above structure.

Oxidised Mn (III) catalyses the oxidation of  $\text{H}_2\text{O}$  to  $\text{O}_2$ .

10. The octahedral complex/complex ion which shows both facial and meridional isomers is

- (a) Triglycinatocobalt (III)  
 (b) Tris (ethylenediamine) cobalt (III)  
 (c) Dichlorodiglycinatocobalt (III)  
 (d) Trioxalatocobaltate (III)

**Ans. (a) :** Triglycinatocobalt (III) shows both face and meridional isomer.

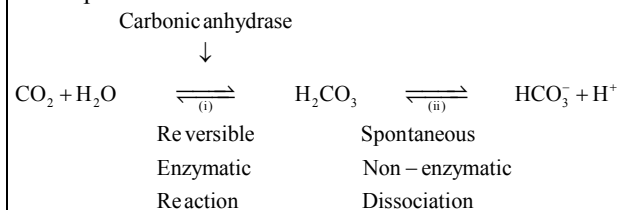


11. Zn in carbonic anhydrase is coordinated by three histidine and one water molecule. The reaction of  $\text{CO}_2$  with this enzyme is an example of

- (a) electrophilic addition  
 (b) electron transfer  
 (c) nucleophilic addition  
 (d) electrophilic substitution

**Ans. (a) :** Carbonic anhydrases catalyze a reaction, the bi-directional conversion of carbon dioxide ( $\text{CO}_2$ ) and water ( $\text{H}_2\text{O}$ ) into bicarbonates ( $\text{HCO}_3^-$ ) and protons ( $\text{H}^+$ ).

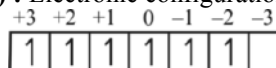
In this reaction  $\text{CO}_2$  acts as an electrophile and  $\text{H}_2\text{O}$  as a nucleophile which attacks  $\text{CO}_2$ . Hence it's an electrophilic addition reaction.



12. The difference in the measured and calculated magnetic moment (based on spin-orbit coupling) is observed for

- (a)  $\text{Pm}^{3+}$  (b)  $\text{Eu}^{3+}$   
 (c)  $\text{Dy}^{3+}$  (d)  $\text{Lu}^{3+}$

**Ans. (b) :** Electronic configuration of  $\text{Eu}^{3+} = [\text{Xe}] 4f^6$



Total spin quantum Number,  $S = 3$

Total angular momentum,  $L = 3$

For less than half filled-

$$J = L - S = 3 - 3 = 0$$

hence  $\mu_J = 0$

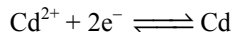
The calculated value of magnetic moment for  $\text{Eu}^{3+} = 0$  while experimental value for magnetic moment of  $\text{Eu}^{3+}$  is 3.4 BM.

This difference in magnetic moment is due to the fact that the spin orbital coupling constant ( $\lambda$ ) is about  $1000 \text{ cm}^{-1}$  for all lanthanides except  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$ .

13. For a redox reaction  $\text{Cd}^{2+} + 2e^- \rightleftharpoons \text{Cd}$ , the  $(E_p)_{\text{anodic}}$  observed in cyclic voltametry at hanging mercury drop electrode is  $-650 \text{ mV}$  vs. SCE. The expected value for  $(E_p)_{\text{cathodic}}$  is

- (a)  $-780 \text{ mV}$  (b)  $-679 \text{ mV}$   
 (c)  $-650 \text{ mV}$  (d)  $-621 \text{ mV}$

**Ans. (d) :** For reversible redox reaction–



$$\Delta E_p = \frac{0.0565}{n}$$

$(E_p \text{ anodic} - E_p \text{ cathodic}) = \Delta E_p$

$$= \frac{-0.0565}{2} \times 1000 \text{ mV}$$

$$E_p \text{ Cathode} = -(E_p \text{ anodic} - \Delta E_p) \\ = -650 \text{ mV} + 28.25 \text{ mV} \\ = -621.75 \text{ mV} \approx -621 \text{ mV}$$

**14. The dimension of Planck's constant is (M, L and T denote mass, length and time respectively)**

- (a)  $\text{ML}^3\text{T}^{-2}$  (b)  $\text{ML}^2\text{T}^{-1}$   
(c)  $\text{M}^2\text{L}^{-1}\text{T}^{-1}$  (d)  $\text{M}^{-1}\text{L}^2\text{T}^{-2}$

**Ans. (b) :** Form formula,  $E = h\nu$

where  $E = \text{energy (Force} \times \text{displacement)}$

$$= \text{M}^1\text{L}^2\text{T}^{-2} \times \text{L} \\ = \text{M}^1\text{L}^3\text{T}^{-2} \quad \dots\dots\dots \text{(I)}$$

$$\nu = \text{frequency (inverse of time)} \\ = \text{T}^{-1} \quad \dots\dots\dots \text{(II)}$$

$$\therefore h = \frac{E}{\nu}$$

$\therefore$  from eq (i) and (ii).

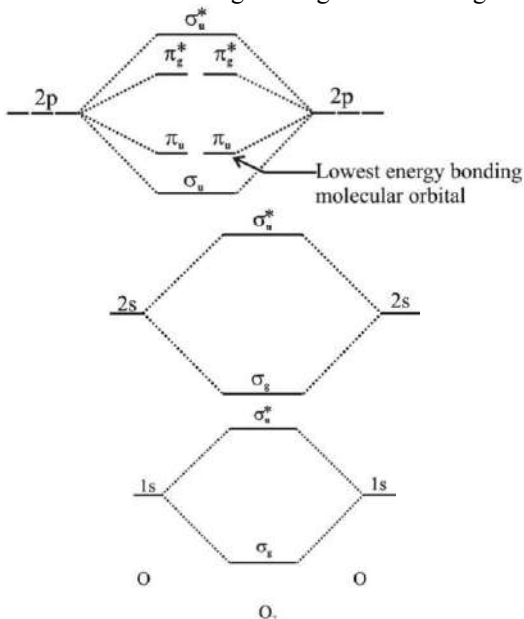
$$\text{Dimension of } h = \frac{\text{Dimension of Energy}}{\text{Dimension of frequency}}$$

$$= \frac{\text{M}^1\text{L}^3\text{T}^{-2}}{\text{T}^{-1}} = [\text{M}^1\text{L}^3\text{T}^{-1}]$$

**15. For a homonuclear diatomic molecule, the bonding molecular orbital is**

- (a)  $\sigma_u$  of lowest energy  
(b)  $\sigma_u$  of second lowest energy  
(c)  $\pi_g$  of lowest energy  
(d)  $\pi_u$  of lowest energy

**Ans. (d) :** For a homonuclear diatomic molecule, like 'O<sub>2</sub>' Molecular orbital diagram is given following.



**16. The selection rules for the appearance of P branch in the rotational-vibrational absorption spectra of a diatomic molecule within rigid rotor-harmonic oscillator model are**

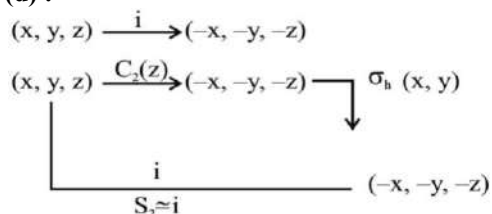
- (a)  $\Delta v = \pm 1$  and  $\Delta J = \pm 1$   
(b)  $\Delta v = +1$  and  $\Delta J = +1$   
(c)  $\Delta v = +1$  and  $\Delta J = -1$   
(d)  $\Delta v = -1$  and  $\Delta J = -1$

**Ans. (c) :** The transition  $\Delta J = 0$ , but where  $V_0 = 0$  and  $\Delta v = +1$ , is forbidden and the pure vibrational transition is not observed in most cases. The rotational selection rule gives rise to an 'R' branch for  $\Delta J = +1$  and 'P' branch for  $\Delta J = -1$ .

**17. The S<sub>2</sub> operation on a molecule with the axis of rotation as the z axis, moves a nucleus at (x, y, z) to**

- (a)  $(-x, -y, z)$  (b)  $(x, -y, -z)$   
(c)  $(-x, y, -z)$  (d)  $(-x, -y, -z)$

**Ans. (d) :**



**18. The expression which represents the chemical potential of the i<sup>th</sup> species ( $\mu_i$ ) in a mixture ( $i \neq j$ ) is**

- (a)  $(\partial E / \partial n_i)_{s, v, n_j}$  (b)  $(\partial H / \partial n_i)_{s, v, n_j}$   
(c)  $(\partial A / \partial n_i)_{s, v, n_j}$  (d)  $(\partial G / \partial n_i)_{s, v, n_j}$

**Ans. (a) :** Consider a thermodynamic system containing n constituent species with no of particle  $n_1, n_2, \dots, n_j$  for each species U, S, and V.

$$U = U(S, V, n_1, \dots, n_n)$$

where U = Internal energy (E)

S = Entropy

V = Volume

The chemical potential of the i<sup>th</sup> species,  $\mu_i$  is defined as partial derivative

$$\mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{S, V, n_j}$$

where the subscripts simply emphasize that the entropy, Volume and the other particle numbers are to be kept constant.

**19. Which of the following statements is NOT correct for a catalyst?**

- (a) It increases the rate of a reaction  
(b) It is not consumed in the course of a reaction  
(c) It provides an alternate pathway for the reaction  
(d) It increase the activation energy of the reaction

**Ans. (d) :** A catalyst is a substance that can be added to a reaction to enhance the reaction rate without getting consumed in the process. Catalysts typically speed up a reaction by lowering the activation energy or changing



the reaction mechanism. Catalyst does not take part in balancing the chemical reaction hence catalysts are not required in stoichiometric amounts.

Most common catalysts are Aluminosilicates, Iron Vanadium, Nickel, Platinum etc.

20. The value of the rate constant for the gas phase reaction  $2\text{NO}_2 + \text{F}_2 \rightarrow 2\text{NO}_2\text{F}$  is  $38 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 300K. The order of the reaction is

- (a) 0 (b) 1  
(c) 2 (d) 3

Ans. (c) : Reaction,



Temperature = 300K

unit of rate constant  $k = \text{L}^{n-1} \text{ mol}^{1-n} \text{ T}^{-1}$

Comparing the given unit of 'k' with the above equation is  $\text{mol}^{1-n} = \text{mol}^{-1}$

comparing both side power in above equation

$$1 - n = -1$$

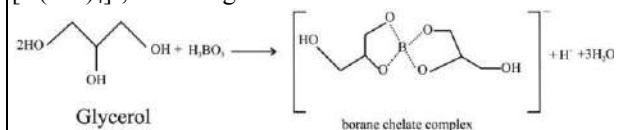
$$n = 2$$

21. Boric acid in aqueous solution in presence of glycerol behaves as a strong acid due to the formation of

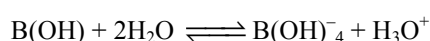
- (a) an anionic metal-chelate  
(b) borate anion  
(c) glycerate ion  
(d) a charge transfer complex

Ans. (a) : When certain organic polyhydroxy compounds like glycerol, mannitol, catechol or sugars are added to Boric acid  $[\text{B}(\text{OH})_3]$  behaves a strong monobasic acid.

Glycerol forms very stable chelate complex with  $[\text{B}(\text{OH})_4]^-$ , removing it from the solution.



Thus removal of one of the product shifts the equilibrium in the forward direction and pH is increased.



22. Match the compounds in List-I with the corresponding structure/property given in List-II

List-I

- A.  $(\text{Ph}_3\text{P})_3\text{RhCl}$   
B.  $\text{LiC}_6$   
C.  $\text{PtF}_6$   
D.  $\text{Ni}_3\text{S}_4$

List-II

- (i) Spinel  
(ii) Intercalation  
(iii) Oxidising agent  
(iv) Catalyst for alkene hydrogenation

- | A         | B     | C     | D    |
|-----------|-------|-------|------|
| (a) (iii) | (i)   | (ii)  | (iv) |
| (b) (iv)  | (ii)  | (iii) | (i)  |
| (c) (iii) | (ii)  | (i)   | (iv) |
| (d) (iv)  | (iii) | (ii)  | (i)  |

Ans. (b)

(A)  $(\text{Ph}_3\text{P})_3\text{RhCl}$  is also called as Wilkinson's catalyst and it is used for hydrogenation of alkanes

(B)  $\text{LiC}_6$  - Li is intercalated between these layers to form  $\text{Li-C}_6\text{-Li-C}_6$  - strings parallel to the C-axis and cause 10% increase of the inter larger spacing in the final stage.

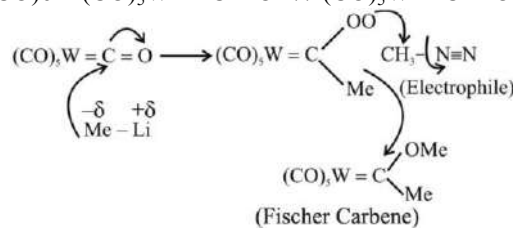
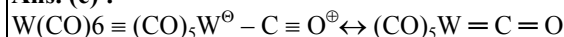
(C)  $\text{PtF}_6$  - It is a strong oxidising agent. Capable of oxidising xenon and  $\text{O}_2$ .

(D)  $\text{Ni}_3\text{S}_4$  is found in nature to be mineral polydymite and has a cubic spinel structure.

23.  $\text{W}(\text{CO})_6$  reacts with  $\text{MeLi}$  to give an intermediate which upon treatment with  $\text{CH}_2\text{N}_3$  gives a compound X. X is represented as

- (a)  $\text{WMe}_6$   
(b)  $(\text{CO})_5\text{W} - \text{Me}$   
(c)  $(\text{CO})_5\text{W} = \text{C}(\text{Me})\text{OMe}$   
(d)  $(\text{CO})_5\text{W} = \text{CMe}$

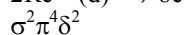
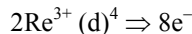
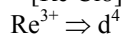
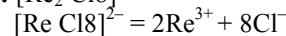
Ans. (c) :



24. Considering the quadrupolar nature of M-M bond in  $[\text{Re}_2\text{Cl}_8]^{2-}$ , the M-M bond order in  $[\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4]^+$  and  $[\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4]$  respectively are

- (a) 3.0 and 3.0 (b) 3.0 and 3.5  
(c) 3.5 and 3.5 (d) 3.5 and 3.0

Ans. (d) :  $[\text{Re}_2\text{Cl}_8]^{2-}$



bond order = 4 (quadruple bond)

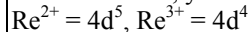
•  $[\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4]^+$

Assuming the oxidation states of two Re atoms are 'x' and 'y'

$$x + y - 4 = +1$$

$$x + y = +5$$

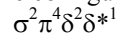
$$x = +2, y = +3$$



Therefore total no of electrons comprising both  $\text{Re}^{2+}$  and  $\text{Re}^{3+}$  ions = 5 + 4

$$= 9$$

Electronic configuration in this complex ion



$$\text{Bond order} = \frac{1}{2} (8 - 1)$$

$$= 3.5$$

•  $[\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4]$

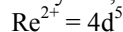
Assuming oxidation states of two Re atoms are x and y

$$x + y - 4 = 0$$

$$x + y = +4$$

$$x = 2$$

$$y = 2,$$



Total number of electrons = 5 + 5  
 = 10  
 Electronic configuration in this cluster ion  
 =  $\sigma^2 \pi^4 \delta^2 \delta^* 2$   
 Bond order =  $\frac{1}{2} \times (8 - 2)$   
 = 3

25. A student recorded a polarogram of 2.0 mM  $\text{Cd}^{2+}$  solution and forgot to add KCl solution. What type of error do you expect in his results?
- Only migration current will be observed
  - Only diffusion current will be observed
  - Both migration current as well as diffusion current will be observed
  - Both catalytic current as well as diffusion current will be observed

**Ans. (c) :** When a different electrolyte is added in very large amount carrying essentially all current the migration current can be removed. So, when a student forgot to add KCl salt both diffusion and migration current are observed.

26. The separation of trivalent lanthanide ions,  $\text{Lu}^{3+}$ ,  $\text{Yb}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Eu}^{3+}$  can be effectively done by a cation exchange resin using ammonium o-hydroxy isobutyrate as the eluent. The order in which the ions will be separated is
- $\text{Lu}^{3+}$ ,  $\text{Yb}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Eu}^{3+}$
  - $\text{Eu}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Yb}^{3+}$ ,  $\text{Lu}^{3+}$
  - $\text{Dy}^{3+}$ ,  $\text{Yb}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Lu}^{3+}$
  - $\text{Yb}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Lu}^{3+}$ ,  $\text{Eu}^{3+}$

**Ans. (a) :** The trivalent lanthanide ions are separated on the basis of the difference in their ionic radii and hydration energies. The cation exchange resin has fixed negative charges, which attract the positively charged trivalent lanthanide ions.

According to question the eluent used in the separation process is ammonium o-hydroxy isobutyrate, which is a weak organic acid. The eluent competes with the lanthanide ions for negative charge on the resin, causing the lanthanide ions to be poured into the solution.

The stronger the complex formed, the greater energy is required to remove the ion from the resin. Smaller is required to remove the ion from the resin.

Smaller ionic radius and greater hydration energy makes the complexes more stable.

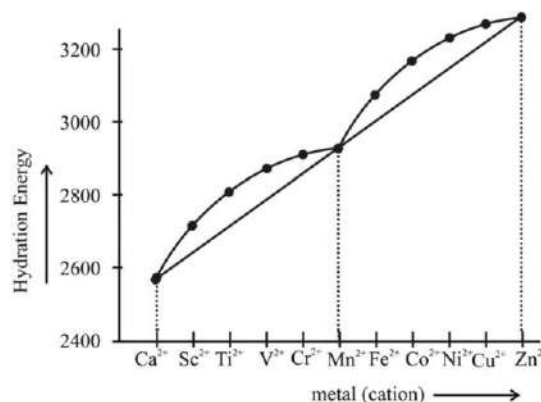
So the order of separation of ions-  
 $\text{Lu}^{3+} > \text{Yb}^{3+} > \text{Dy}^{3+} > \text{Eu}^{3+}$

27. Arrange the following metal complexes in order of their increasing hydration energy
- |  |  |
|--|--|
| $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ | $[\text{V}(\text{H}_2\text{O})_6]^{2+}$  |
| P  | Q  |
| $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ | $[\text{Ti}(\text{H}_2\text{O})_6]^{2+}$ |
| R  | S  |
- $P < S < Q < R$
  - $P < Q < R < S$
  - $Q < P < R < S$
  - $S < R < Q < P$

**Ans. (\*) :** When the gaseous metal cation gets hydrated, energy is released, called hydration energy. It depends upon the following factors—  
 (i) Effective nuclear charge—

Hydration energy  $\propto$  Effective nuclear charge  
 (ii) sized central atom (cation)—  
 Hydration energy  $\propto \frac{1}{\text{size of cation}}$

- For transition metal (cations)—



• Hydration energy = Theoretical Value + CFSE

So, order of hydration energy—

$\text{Ca}^{2+} < \text{Sc}^{2+} < \text{Ti}^{2+} < \text{V}^{2+} > \text{Cr}^{2+} > \text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$

• So,  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} > [\text{V}(\text{H}_2\text{O})_6]^{2+} > [\text{Mn}(\text{H}_2\text{O})_6]^{2+} > [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$   
 (R) (Q) (P) (S)

28. In the complex,  $[\text{Ni}_2(\eta^5\text{-Cp})_2(\text{CO})_2]$ , the IR stretching frequency appears at  $1857 \text{ cm}^{-1}$  (strong) and  $1897 \text{ cm}^{-1}$  (weak). The valence electron count and the nature of the M–CO bond respectively are

- $16e^-$ , bridging
- $17e^-$ , bridging
- $18e^-$ , terminal
- $18e^-$ , bridging

**Ans. (d) :**  $[\text{Ni}_2(\eta^5\text{-Cp})_2(\text{CO})_2]$



• Total Valence electron (TVE) in each Ni central metal ion

= valence electron of Ni + electron donated by  $\eta^5\text{Cp}$  + electron donated by CO ligand + M–M bond.  
 =  $10 + 5 + (2 \times 1) + 1$   
 = 18 electron

• TVE = 18, and the nature of M–CO bond is bridging.

29. The correct classification of  $[\text{B}_5\text{H}_5]^{2-}$ ,  $\text{B}_5\text{H}_9$  and  $\text{B}_5\text{H}_{11}$  respectively is

- closo, arachno, nido
- arachno, closo, nido
- closo, nido, arachno
- nido, arachno, closo

**Ans. (c) :**  $[\text{B}_5\text{H}_5]^{2-}$

Total number of valence electron

=  $(5 \times 3) + (5 \times 1) + 2$   
 = 22

Number of electrons for each BH unit =  $(5 \times 2) = 10$

No of skeletal electron =  $(22 - 10) = 12$

No of skeletal electron pair =  $\frac{12}{2} = 6$

$n + 1 = 6$

$n = 5$ , 'closo structure'

$[B_5H_{11}]$

Number of skeletal electron = 16

Number of skeletal electron pair

$$= \frac{16}{2} = 8$$

$n + 1 = 8$

So,  $n = 8 - 1$

$= 7$

This is an 'arachno' compound

$[B_5H_9]$

Total number of skeletal electron = 14

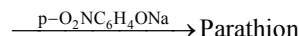
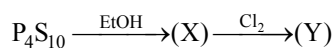
Number of skeletal electron pair =  $\frac{14}{2} = 7$

$n + 1 = 7$

$n = 6$

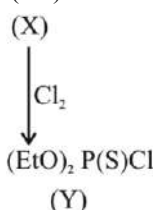
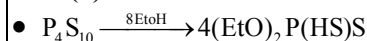
This is a 'nido' structure'

30. The compounds X and Y in the following reaction are

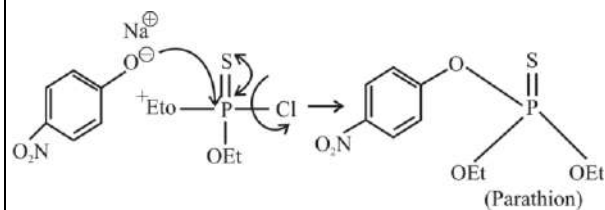


- (a)  $X = (Et)_2P(S)SH$  ;  $Y = (Et)_2P(S)Cl$   
 (b)  $X = (EtO)_2P(S)SH$  ;  $Y = (EtO)_2P(S)Cl$   
 (c)  $X = (EtO)_2PSH$  ;  $Y = (EtO)_2PCl$   
 (d)  $X = (Et)_3PO$  ;  $Y = (Et)_3PCl$

Ans. (b) :



• The complex 'y' further reacts with.  $p-NO_2$ .  $Et_3ONa$



31. Consider the reactions

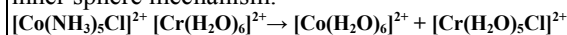
- $[Cr(H_2O)_6]^{2+} + [CoCl(NH_3)_5]^{2+} \rightarrow [Co(NH_3)_5(H_2O)]^{2+} + [CrCl(H_2O)_5]^{2+}$
- $[Fe(CN)_6]^{4-} + [Mo(CN)_8]^{3-} \rightarrow [Fe(CN)_6]^{3-} + [Mo(CN)_8]^{4-}$

Which one of the following is the correct statement?

- (i) Both involve an inner sphere mechanism

- (ii) Both involve an outer sphere mechanism  
 (iii) Reaction 1 follows inner sphere and reaction 2 follows outer sphere mechanism  
 (iv) Reaction 1 follows outer sphere and reaction 2 follows inner sphere mechanism  
 (a) i (b) ii  
 (c) iv (d) iii

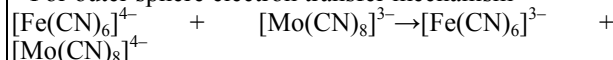
Ans. (d) : The reaction proceeding electron transfer by inner sphere mechanism.



Low spin High spin High spin  
 Inert labile labile inert

• In above reaction electron transfer happens from eg ( $\sigma$ ) of the complex  $[Cr(H_2O)_6]^{2+}$  to eg ( $\sigma$ ) of the complex  $[Co(NH_3)_5Cl]^{2+}$  and the electron transfer takes place by inner sphere mechanism.

• For outer sphere electron transfer mechanism



The above reaction is outer sphere mechanism. as illustrated by Marcus equation.

32. The pair of compounds having the same hybridization for the central atom is

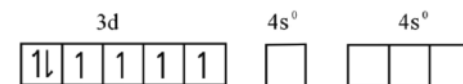
- (a)  $XeF_4$  and  $[SiF_6]^{2-}$   
 (b)  $[NiCl_4]^{2-}$  and  $[PtCl_4]^{2-}$   
 (c)  $Ni(CO)_4$  and  $XeO_2F_2$   
 (d)  $[Co(NH_3)_6]^{3+}$  and  $[Co(H_2O)_6]^{3+}$

Ans. (d) : Atomic No. of cobalt is 27  $Co^{3+}(24e^-) \Rightarrow [Ar] 3d^6 4s^0 4p^0$

In case of  $Co^{3+}$  both  $\ddot{N}H_3$  and  $H_2\ddot{O}$

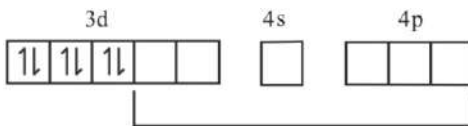
act as strong field ligand. Hence both  $[Co(NH_3)_6]^{3+}$  and  $[Co(H_2O)_6]^{3+}$  are inner orbital complex.

$Co^{3+} -$

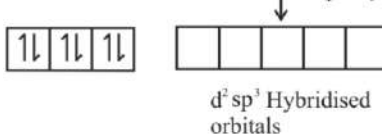


After approaching ligands ( $NH_3$  or  $H_2O$ ), pairing of inner d-orbital electrons :-

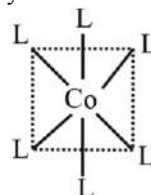
$Co^{3+} -$



$\downarrow d^2sp^3$  Hybridisation



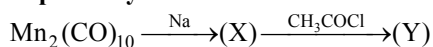
Electron pairs donated by ligands come to the  $d^2sp^3$  hybridised orbitals.



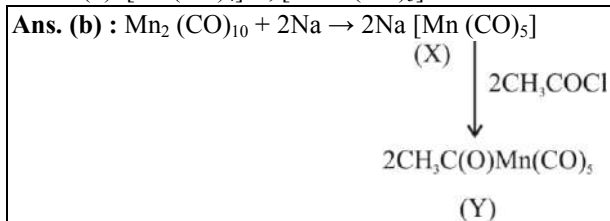
• Geometry and shape- Octahedral

• Hybridisation-  $d^2sp^3$

33. In the reaction shown below, X and Y respectively are

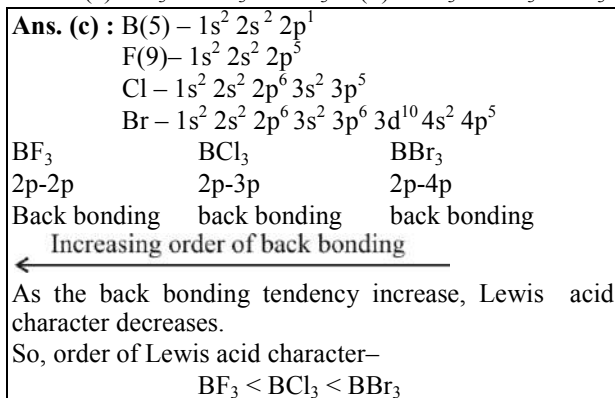


- (a)  $[\text{Mn}(\text{CO})_4]^{2-}$ ,  $[\text{CH}_3\text{C}(\text{O})\text{Mn}(\text{CO})_5]^-$   
 (b)  $[\text{Mn}(\text{CO})_5]^{2-}$ ,  $\text{CH}_3\text{C}(\text{O})\text{Mn}(\text{CO})_5$   
 (c)  $[\text{Mn}(\text{CO})_5]^-$ ,  $\text{ClMn}(\text{CO})_5$   
 (d)  $[\text{Mn}(\text{CO})_4]^{2-}$ ,  $[\text{ClMn}(\text{CO})_5]^-$



34. The Lewis acid character of  $\text{BF}_3$ ,  $\text{BCl}_3$  and  $\text{BBr}_3$  follows the order

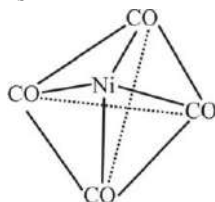
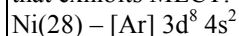
- (a)  $\text{BF}_3 < \text{BBr}_3 < \text{BCl}_3$  (b)  $\text{BCl}_3 < \text{BBr}_3 < \text{BF}_3$   
 (c)  $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$  (d)  $\text{BBr}_3 < \text{BCl}_3 < \text{BF}_3$



35. The compound which shows L←M charge transfer is

- (a)  $\text{Ni}(\text{CO})_4$  (b)  $\text{K}_2\text{Cr}_2\text{O}_7$   
 (c)  $\text{HgO}$  (d)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$

**Ans. (a) :**  $\text{Ni}(\text{CO})_4$  is a classic example of a compound that exhibits MLCT.



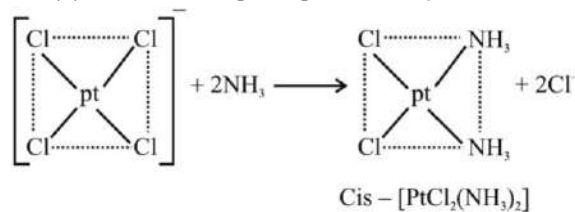
Shape— Tetrahedral, Hybridization—  $sp^3$

MLCT in  $\text{Ni}(\text{CO})_4$  occurs when one of these. (d electrons) is excited from a d-orbital to a high energy level, which could be a vacant anti bonding orbital of the CO ligand. This results in the formation of a Ni-CO bond with a weakened Co bond which makes  $\text{Ni}(\text{CO})_4$  a useful metal carbonyl compound for various applications in organic synthesis, catalysis and material science.

36. The reaction of  $[\text{PtCl}_4]^{2-}$  with  $\text{NH}_3$  gives rise to

- (a)  $[\text{PtCl}_4(\text{NH}_3)_2]^{2+}$  (b)  $\text{trans}-[\text{PtCl}_2(\text{NH}_3)_3]$   
 (c)  $[\text{PtCl}_2(\text{NH}_3)_4]$  (d)  $\text{cis}-[\text{PtCl}_2(\text{NH}_3)_2]$

- Ans. (d) :** Reaction of  $[\text{PtCl}_4]^{2-}$  with  $\text{NH}_3$ —



37. Zeise's salt is represented as

- (a)  $\text{H}_3\text{PtCl}_6$  (b)  $[\text{PtCl}_4]^{2-}$   
 (c)  $[\text{ZnCl}_4]^{2-}$  (d)  $[\text{PtCl}_3(\eta^2-\text{C}_2\text{H}_4)]^-$

**Ans. (d) :** Zeise's salt is potassium trichloro (ethylene) platinate (II)hydrate,  $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$ . The anion of this yellow co-ordination complex contains an  $\eta^2$ -ethylene ligand.



Zeise's Salt

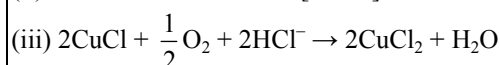
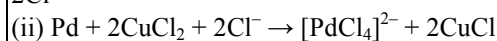
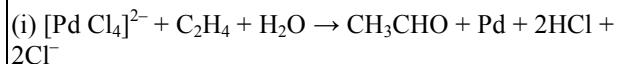
38. The catalyst used in the conversion of ethylene to acetaldehyde using Wacker process is

- (a)  $\text{HCo}(\text{CO})_4$   
 (b)  $[\text{PdCl}_4]^{2-}$   
 (c)  $\text{V}_2\text{O}_5$   
 (d)  $\text{TiCl}_4$  in the presence of  $\text{Al}(\text{C}_2\text{H}_5)_3$

**Ans. (d) :** The conversion of ethylene to acetaldehyde using 'Wacker Process'—

The Wacker process is the oxidation of olefins using using Pd (II) catalysis to produce acetaldehyde from ethylene and water.

Reaction Mechanism :—



All catalysts are regenerated and only the alkene and oxygen are consumed. Without copper (II) Chloride and HCl as oxidising agents, the palladium would precipitate out and the reaction would come to the halt. Air, pure oxygen, or a number of other oxidisers can then oxidise the resultant  $\text{CuCl}$  back to  $\text{CuCl}_2$  allowing the cycle to repeat.

39. The temperature of 54 g of water is raised from  $15^\circ\text{C}$  to  $75^\circ\text{C}$  at constant pressure. The change in the enthalpy of the system (given that  $C_{p,m}$  of water  $-75 \text{ JK}^{-1} \text{ mol}^{-1}$ ) is

- (a) 4.5 kJ (b) 13.5 kJ  
 (c) 9.0 kJ (d) 18.0 kJ

**Ans. (b) :** Given

Mass of water = 54 gram

$$\text{no of moles of water} = \frac{54}{18} = 3$$

$$T_1 = 15^\circ\text{C}, T_2 = 75^\circ\text{C}$$

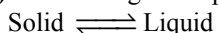
$$C_p = -75 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned}
 \text{Enthalpy change} &= \Delta H \\
 &= nC_p\Delta T \\
 &= 3 \times (-75) \times (75 - 15) \\
 &= -3 \times 75 \times 60 \\
 &= -180 \times 75 \\
 &= -13500 \text{ Joule} \\
 &= 13.500 \times 10^3 \text{ joule} \\
 &= -13.5 \text{ KJ}
 \end{aligned}$$

40. The specific volume of liquid water is  $1.0001 \text{ mL g}^{-1}$  and that of ice is  $1.0907 \text{ mL g}^{-1}$  at  $0^\circ\text{C}$ . If the heat of fusion of ice at this temperature is  $333.88 \text{ J g}^{-1}$ , the rate of change of melting point of ice with pressure in  $\text{deg atm}^{-1}$  will be

- (a)  $-0.0075$  (b)  $0.0075$   
 (c)  $0.075$  (d)  $-0.075$

Ans. (a) : According to Clapeyron- Clausius equation.



(ice) (water)

$$\frac{dp}{dT} = \frac{\Delta H_f}{T_f(V_i - V_s)}$$

$$\frac{dP}{dT} = \frac{T_f(V_i - V_s)}{\Delta H_f}$$

given heat of fusion of ice =  $333.88 \text{ Jg}^{-1}$

$V_i$  = volume of the liquid =  $1.001 \text{ cm}^3$

$V_s$  = volume of the solid =  $1.0907 \text{ cm}^3$

$(V_i - V_s) = (1.0001 - 1.0907) \text{ cm}^3$

$$= -0.0906 \text{ cm}^3$$

$T_f = 0^\circ\text{C} = 273 \text{ K}$

Putting above values in the formula.

$$\begin{aligned}
 \frac{dP}{dT} &= \frac{333.88 \text{ Jg}^{-1}}{273(0.0906) \text{ cm}^3 \text{ g}^{-1} \text{ K}} \\
 &= -13.4989 \text{ J cm}^{-3} \text{ K}^{-1} \\
 &= 13.4989 \times (0.0098 \text{ Latm}) \text{ cm}^{-3} \text{ K}^{-1} \\
 &= 0.1333 \text{ Latm} \times (10^{-3} \text{ Lk})^{-1}
 \end{aligned}$$

or 
$$\frac{dP}{dT} = -\frac{1}{133.30} \text{ katm}^{-1} = -0.0075 \text{ k atm}^{-1}$$

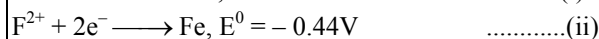
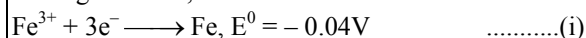
41. Given that  $E_{0(\text{Fe}^{3+}, \text{Fe})} = -0.04 \text{ V}$  and  $E_{0(\text{Fe}^{2+}, \text{Fe})} = -0.44 \text{ V}$ , the value of  $E_{0(\text{Fe}^{3+}, \text{Fe}^{2+})}$  is

- (a)  $0.76 \text{ V}$  (b)  $-0.40 \text{ V}$   
 (c)  $-0.76 \text{ V}$  (d)  $0.40 \text{ V}$

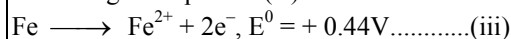
Ans. (d) : Given

$E_{0(\text{Fe}^{3+}, \text{Fe})} = -0.04 \text{ V}$  and  $E_{0(\text{Fe}^{2+}, \text{Fe})} = -0.44 \text{ V}$

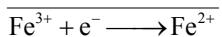
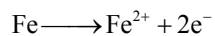
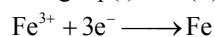
From given data,



Reversing the equation (II)



adding eq (i) and (ii)



$$E_{0(\text{Fe}^{3+}, \text{Fe}^{2+})} = +0.40 \text{ V}$$

42. For the reaction  $\text{P} + \text{Q} + \text{R} \rightarrow \text{S}$ , experimental data for the measured initial rates is given below

Expt.	Initial conc. P (M)	Initial conc. Q (M)	Initial conc. R (M)	Initial rate ( $\text{M s}^{-1}$ )
1	0.2	0.5	0.4	$8.0 \times 10^{-5}$
2	0.4	0.5	0.4	$3.2 \times 10^{-4}$
3	0.4	2.0	0.4	$1.28 \times 10^{-3}$
4	0.1	0.25	1.6	$4.0 \times 10^{-5}$

The order of the reaction with respect to P, Q and R respectively is

- (a) 2, 2, 1 (b) 2, 1, 2  
 (c) 2, 1, 1 (d) 1, 1, 2

Ans. (c) : By rate law,

$$r = k[\text{P}]^x[\text{Q}]^y[\text{R}]^z$$

taking order w.r.t. P = x

order w.r.t. Q = y

order w.r.t. R = z

From the given data,

For experiment (1)

$$8.0 \times 10^{-5} = k(0.2)^x(0.5)^y(0.4)^z$$

For experiment (2)

$$3.2 \times 10^{-4} = k(0.4)^x(0.5)^y(0.4)^z$$

For experiment (3)

$$1.28 \times 10^{-3} = k(0.4)^x(2.0)^y(0.4)^z$$

For experiment (4)

$$4.0 \times 10^{-5} = k(0.1)^x(0.25)^y(0.6)^z$$

From exp. (1) and (2)

$$\frac{3.2 \times 10^{-4}}{8.0 \times 10^{-5}} = (2)^x$$

$$4 = (2)^x$$

$$x = 2$$

From exp. (1) and (3).

$$\frac{1.28 \times 10^{-3}}{3.2 \times 10^{-4}} = (4)^y$$

$$4 = (4)^y$$

$$y = 1$$

From exp. (1) and (4)

$$\frac{8 \times 10^{-5}}{4 \times 10^{-5}} = (2)^x(2)^y\left(\frac{1}{4}\right)^z = (4)(2)\left(\frac{1}{4}\right)^z$$

$$z = 1$$

Hence,

order w.r.t. P = 2

order w.r.t. Q = 1

order w.r.t. R = 1

43. Sucrose is converted to a mixture of glucose and fructose in a pseudo first order process under alkaline conditions. The reaction has a half life of 28.4 min. The time required for the reduction of a 8.0 mM sample of sucrose to 1.0 mM is

- (a) 56.8 min. (b) 170.4 min.  
 (c) 85.2 min. (d) 227.2 min

**Ans. (c) :** Given–

$$t_{1/2} = 28.4 \text{ min}$$

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = 0.0244 \text{ min}^{-1}$$

Equation for first order kinetics

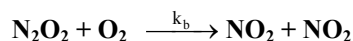
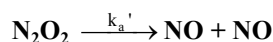
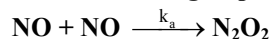
$$t = \frac{2.303}{k} \log \frac{[A_0]}{[A]}$$

$[A_0]$  = Initial amount,  $[A]$  = amount at time 't'

$$t = \frac{2.303}{0.0244} \log \frac{8}{1}$$

$$\begin{aligned} t &= 94.38 \times \log (2)^3 \\ &= 94.38 \times 3 \times \log (2) \\ &= 94.38 \times 3 \times 0.3010 \\ &= 85.2 \text{ min} \end{aligned}$$

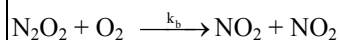
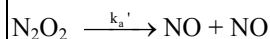
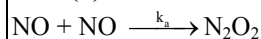
**44. The reaction  $2\text{NO}(\text{g}) + \text{O}_2 \rightarrow 2\text{NO}_2(\text{g})$  process via the following steps**



**The rate of this reaction is equal to**

- (a)  $2k_b[\text{NO}][\text{O}_2]$   
 (b)  $(2k_a k_b [\text{NO}]^2 [\text{O}_2]) / (k_a + k_b [\text{O}_2])$   
 (c)  $2k_b [\text{NO}]^2 [\text{O}_2]$   
 (d)  $k_a [\text{NO}]^2 [\text{O}_2]$

**Ans. (b) :** The Given reaction–



using steady state approximate (s.s.a), w.r.t  $[A]$

$$k_a [\text{NO}]^2 - k_a' [\text{N}_2\text{O}_2] - k_b [\text{N}_2\text{O}_2] [\text{O}_2] = 0$$

$$k_a [\text{NO}]^2 = [\text{N}_2\text{O}_2] \{k_a' + k_b [\text{O}_2]\}$$

$$[\text{N}_2\text{O}_2] = \frac{k_a [\text{NO}]^2}{k_a' + k_b [\text{O}_2]} \dots\dots\dots(i)$$

The rate of reaction–

$$r = \frac{-d[\text{NO}]}{2dt} = + \frac{d[\text{N}_2\text{O}_2]}{2dt} = -k_b [\text{N}_2\text{O}_2][\text{O}_2]$$

$$\text{or } r = \frac{-d[\text{NO}]}{dt} = -2k_b [\text{N}_2\text{O}_2][\text{O}_2] \dots\dots\dots(ii)$$

putting value of  $[\text{N}_2\text{O}_2]$  from equation (i)

$$r = -2k_b [\text{N}_2\text{O}_2][\text{O}_2] = \frac{-2k_b \cdot k_a [\text{NO}]^2 [\text{O}_2]}{k_a' + k_b [\text{O}_2]}$$

**45. 40 millimoles of NaOH are added to 100 mL of a 1.2 M HA and Y M NaA buffer resulting in a solution of pH 5.30. Assuming that the volume of the buffer remains unchanged, the pH of the buffer ( $K_{\text{HA}} = 1.00 \times 10^{-5}$ ) is**

- (a) 5.30 (b) 5.00  
 (c) 0.30 (d) 10.30

**Ans. (a) :** Given, pH = 5.30

$$K_{\text{HA}} = 1.0 \times 10^{-5}$$

$$\begin{aligned} \text{So, pKa} &= -\log k_a \\ &= -\log (1.0 \times 10^{-5}) \\ &= 5 \end{aligned}$$

$$\begin{aligned} [\text{OH}] &= 40 \text{ m mol} \\ &= 40 \times 10^{-3} \text{ mol} \\ &= 0.04 \text{ mol} \end{aligned}$$

$$[\text{AH}] = 1.2 \text{ M}$$

$$[\text{NaA}] = Y \text{ M}$$

After addition of 0.04 mole NaOH, concentration of acid decrease by 0.04 mol and concentration of salt increases by 0.04 mol.

using Hendersen-Hasselbalch equation

$$\text{pH} = \text{pka} + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{pH} = \text{pKa} + \log \frac{[\text{A}^\ominus]}{[\text{HA}]}$$

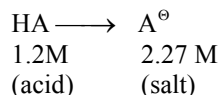
$$\therefore 5.3 = 5.0 + \log_{10} \frac{[y+0.04]}{[1.16]}$$

$$5.3 - 5.0 = \log_{10} \frac{y+0.04}{1.16}$$

$$(10)^{0.30} = \frac{y+0.04}{1.16}$$

$$\begin{aligned} y &= (1.9952 \times 1.16) - 0.04 \\ &= 2.314 - 0.04 \\ &= 2.274 \end{aligned}$$

Hence,



$$\begin{aligned} \text{pH} &= 5 + \log_{10} \frac{2.27}{1.2} \\ &= 5 + 0.2768 \\ &= 5.2768 \\ &\approx 5.30 \end{aligned}$$

**46. The entropy of mixing of 10 moles of helium and 10 moles of oxygen at constant temperature and pressure, assuming both to be ideal gases, is**

- (a)  $115.3 \text{ JK}^{-1}$  (b)  $5.8 \text{ JK}^{-1}$   
 (c)  $382.9 \text{ JK}^{-1}$  (d)  $230.6 \text{ JK}^{-1}$

**Ans. (a) :** Given,

no of moles of Helium, He = 10 moles

no of moles of oxygej,  $\text{O}_2$  = 10 moles

The entropy of mixing.

$$S = -R[n_A \ln X_A + n_B \ln X_B]$$

where

R = Gas constants,  $8.314 \text{ Jmol}^{-1}\text{K}^{-1}$

$n_A$  = no of moles of species 'A'

$X_A$  = mole fraction of species 'A'

$n_B$  = no of moles of species 'B'

$X_B$  = mole of species 'B'

$$\begin{aligned} X_{\text{He}} &= \frac{10}{10+10} \\ &= 0.5 \end{aligned}$$

putting the values of  $n_{\text{He}}$ ,  $n_{\text{O}_2}$ ,  $X_{\text{He}}$  and  $X_{\text{O}_2}$  in equation—

$$\begin{aligned} S &= -8.314 [10 \ln 0.5 + 10 \ln 0.5] \\ S &= -8.314 [10 \times (-0.69) + 10 \times (-0.69)] \\ &= -8.314 [-6.9 + (6.9)] \\ &= -8.314 \times (-13.8) \\ &= 114.7332 \text{ JK}^{-1} \\ &\cong 115.3 \text{ JK}^{-1} \end{aligned}$$

47. The ionisation potential of hydrogen atom is 13.6 eV. The first ionization potential of a sodium atom, assuming that the energy of its outer electron can be represented by a H-atom like model with an effective nuclear charge of 1.84, is

- (a) 46.0 eV                      (b) 11.5 eV  
(c) 5.1 eV                        (d) 2.9 eV

**Ans. (c) :** Given

$I_E$  of hydrogen atom is 13.6 eV  
Effective nuclear charge = 1.84 for H-like atom

$$\begin{aligned} \text{Ionisation energy} &= \frac{13.6z^2}{n^2} & [z = 1.84] \\ &= \frac{13.6 \times (1.84)^2}{3^2} \\ &= \frac{13.6 \times 1.04 \times 1.84}{9} \\ &= 5.1 \text{ eV} \end{aligned}$$

48. The quantum state of a particle moving in a circular path in a plane is given by  $\psi_m(\phi) = (1/\sqrt{2\pi})e^{im\phi}$ ,  $m = 0, \pm 1, \pm 2$

When a perturbation  $H_1 P = \cos\phi$  is applied ( $P$  is constant), what will be the first order correction to the energy of the  $m^{\text{th}}$  state

- (a) 0                                      (b)  $P/(2\pi)$   
(c)  $P/(4\pi)$                               (d)  $Pm^2/(4\pi^2)$

**Ans. (a) :** Given,

Quantum state of a particle moving in a circular path in a plane is given by

$$\psi_{m(\phi)} = (1/\sqrt{2\pi})e^{im\phi}, \quad M = 0, \pm 1, \pm 2, \dots$$

Perturbation,  $H_1 P = \cos\phi$

$$\begin{aligned} &\int_0^{2\pi} \frac{1}{2\pi} \cdot e^{im\phi} \cdot P \cos\phi \cdot \frac{1}{2\pi} \cdot e^{-im\phi} d\phi \\ &= \frac{1}{2\pi} \int_0^{2\pi} P \cos\phi \cdot d\phi \\ &= \frac{P}{2\pi} (\sin 2\pi - \sin 0) \\ &= 0 \end{aligned}$$

49. The correct statement(s) among the following is/are

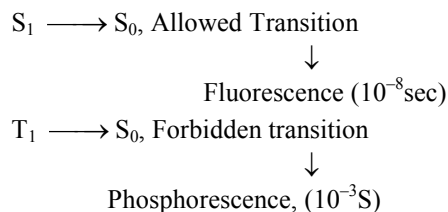
- (i) The vibrational energy levels of a real diatomic molecule are equally spaced.  
(ii) At 500K, then reaction  $A \rightarrow B$  is spontaneous when  $\Delta H = 18.83 \text{ kJ mol}^{-1}$  and  $\Delta S = 41.84 \text{ J K}^{-1} \text{ mol}^{-1}$ .

(iii) The process of fluorescence involves transition from a singlet electronic state to another singlet electronic state by absorption of light.

(iv) When a constant  $P$  is added to each of the possible energies of a system, its entropy remains unchanged.

- (a) only i                              (b) only ii  
(c) both i and iii                      (d) both ii and iv

**Ans. (b) :** Those transitions which involve the return of the activated molecule from the singlet excited state  $S_L$  and triplet excited state  $T_1$  to the ground state  $S_0$ , called radiative transitions. Their emission of radiation takes place.



• According to the thermodynamics,

$\Delta G = -ve$ , for an spontaneous reaction or process

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = 18830 - (500) \times (41.84)$$

$$\Delta G = -2090 \text{ J/mole}$$

Hence, Reaction  $A \rightarrow B$  is spontaneous.

• In an anharmonic oscillator vibrational levels are not more equally spaced but become closer to each other with increasing value of  $V$  unlike a harmonic oscillator.

50. Assuming  $H_2$  and  $HD$  molecules having equal bond lengths, the ratio of the rotational partition functions of these molecules, at temperatures above 100 K is

- (a) 3/8                                      (b) 3/4  
(c) 1/2                                      (d) 2/3

**Ans. (a) :** Rotational Partition function

$$q_r = \frac{T}{\sigma \theta_r}, \quad (\theta_r = \text{characteristic rotational temperature} \dots (i))$$

$$q_{H_2} = \frac{T}{2(\theta_r)_{H_2}}, \quad q_{HD} = \frac{T}{(\theta_r)_{HD}}$$

$$\frac{\theta_{H_2}}{\theta_{HD}} = \frac{I_{HD}}{I_{H_2}} \quad \left( \theta_r = \frac{h^2}{8\pi^2 KI} \right)$$

$$\left( \theta_r \propto \frac{1}{I} \right)$$

$$I_{H_2} = \frac{1 \times 1}{1 + 1} = \frac{1}{2} \quad I_{HD} = \frac{1 \times 2}{1 + 2} = \frac{2}{3}$$

$$\text{So, } \frac{\theta_{H_2}}{\theta_{HD}} = \frac{4}{3}$$

From eq. (i)

$$\frac{q_{H_2}}{q_{HD}} = \frac{\theta_{HD}}{\theta_{H_2}} = \frac{3}{(4) \times 2} = \frac{3}{8}$$

51. N non interacting molecules are distributed among three non degenerate energy levels  $\epsilon_0 = \epsilon_1 = 1.38 \times 10^{-21}$  J and  $\epsilon_2 = 2.76 \times 10^{-21}$  J at 100 K. If the average total energy of the system at this temperature is  $1.38 \times 10^{-18}$  J, the number of molecules in the system is

- (a) 1000 (b) 1503  
(c) 2354 (d) 2987

**Ans. (a) :** Given Total energy of the system,  $U = 1.38 \times 10^{-18}$  J

$$U = \sum niE_i$$

( $E_i$  = number of particles in  $i$ th energy level with  $E_i$  energy value)

$$n_i = \frac{N}{q} g_i e^{-(B E_i)} \text{ (Boltzmann expression)}$$

$$U = \frac{N}{q} e^{-(B E_0)} \cdot E_0 + \frac{N}{q} \cdot e^{-(B E_1)} \cdot E_1 + \frac{N}{q} e^{-(B E_2)} \cdot E_2$$

$$U = \frac{N}{q} e^{-(B E_0)} \times 0 + \frac{N}{q} \cdot e^{-(B E_1)} \cdot E_1 + \frac{N}{q} \cdot e^{[B(2E_1)]} \cdot (2E_1)$$

$$U = \frac{N}{q} E_1 (e^{-B E_1} + 2e^{-2B E_1})$$

$$U = \frac{N}{q} \cdot E_1 \times q \quad \left( q = \sum g_i e^{-B E_i} \right)$$

$$U = N E_1$$

$$N = \frac{U}{E_1}$$

$$= \frac{1.38 \times 10^{-18}}{1.38 \times 10^{-21}} = 10^3 = 1000$$

52. The  $J = 0 \rightarrow 1$  rotational transition for  $^1\text{H}, ^{79}\text{Br}$  occurs at 500.72 GHz. Assuming the molecule to be a rigid rotor, the  $J = 3 \rightarrow 4$  transition occurs at

- (a) 50.1  $\text{cm}^{-1}$  (b) 66.8  $\text{cm}^{-1}$   
(c) 16.7  $\text{cm}^{-1}$  (d) 83.5  $\text{cm}^{-1}$

**Ans. (b) :** Energy required for transition.

$$J \longrightarrow J + 1 \quad \text{(rotational energy level)}$$

$$\Delta E = 2B(J + 1)$$

$$\Delta E_{0 \rightarrow 1} = 2B(J + 1) = 2B$$

$$2B = \frac{500.72 \times 10^9 \text{ s}^{-1}}{C}$$

$$= \frac{500.72 \times 10^9 \text{ s}^{-1}}{3 \times 10^{10}} = 16.69 \text{ cm}^{-1}$$

$$\text{or } B = \frac{16.69}{2} \text{ cm}^{-1} = 8.345 \text{ cm}^{-1}$$

$$\Delta E_{3 \rightarrow 4} = 2B(3 + 1) = 8B = 8 \times 8.345 = 66.76 \text{ cm}^{-1}$$

53. The rate constants of two reactions at temperature T are  $k_1(T)$  and  $k_2(T)$  and the corresponding activation energies are  $E_1$  and  $E_2$  with  $E_2 > E_1$ . When temperature is raised from  $T_1$  to  $T_2$ , which one of the following relations is correct?

- (a)  $\frac{k_1(T_2)}{k_1(T_1)} = \frac{k_2(T_2)}{k_2(T_1)}$  (b)  $\frac{k_1(T_2)}{k_1(T_1)} > \frac{k_2(T_2)}{k_2(T_1)}$   
(c)  $\frac{k_1(T_2)}{k_1(T_1)} \geq \frac{k_2(T_2)}{k_2(T_1)}$  (d)  $\frac{k_1(T_2)}{k_1(T_1)} < \frac{k_2(T_2)}{k_2(T_1)}$

**Ans. (d) :** Arrhenius equation-  $K = A e^{(-E_a/RT)}$

Ignoring the pre exponential factor 'A' to make simple calculation,

• Activation energy  $E_1$ , rate constant  $K_1$  at  $T_1$  and  $T_2$  respectively,

$$K_1(T_1) = e^{\left(\frac{E_{a1}}{RT_1}\right)} \quad \dots\dots\dots (i)$$

$$K_1(T_2) = e^{\frac{-E_{a1}}{RT_2}} \quad \dots\dots\dots (ii)$$

• Activation energy  $E_2$ , rate constant  $K_2$  at  $T_1$  and  $T_2$  respectively,

$$K_2(T_1) = e^{\left(\frac{-E_{a2}}{RT_1}\right)} \quad \dots\dots\dots (iii)$$

$$K_2(T_2) = e^{\left(\frac{-E_{a2}}{RT_2}\right)} \quad \dots\dots\dots (iv)$$

• According to problem given that,  $E_2 > E_1$  and  $T_2 > T_1$   
Taking ratio of (i) and (ii)

$$\frac{K_1(T_1)}{K_2(T_2)} = \frac{e^{\left(\frac{-E_{a1}}{RT_1}\right)}}{e^{\left(\frac{-E_{a2}}{RT_2}\right)}} = e^{\left(\frac{E_{a1}}{RT_1} - \frac{-E_{a2}}{RT_2}\right)} = e^{\frac{1}{RT_1}(E_{a2} - E_{a1})} \quad \dots\dots\dots (v)$$

Taking ratio of (ii) and (iv)

$$\frac{K_1(T_2)}{K_2(T_2)} = \frac{e^{\frac{-E_{a1}}{RT_2}}}{e^{\frac{-E_{a2}}{RT_2}}} = e^{\frac{-E_{a2} + E_{a1}}{RT_2}} = e^{\frac{1}{RT_2}(E_2 - E_1)} \quad \dots\dots\dots (vi)$$

Given that  $T_2 > T_1$ , hence,  $\frac{1}{RT_1} > \frac{1}{RT_2}$  and  $(E_2 - E_1)$  is same for both.

$$e^{\frac{1}{RT_1}(E_2 - E_1)} > e^{\frac{1}{RT_2}(E_2 - E_1)} \quad \dots\dots\dots (vii)$$

$$\text{or } \frac{K_1(T_1)}{K_2(T_1)} > \frac{K_1(T_2)}{K_2(T_1)}, \text{ or } \frac{K_2(T_2)}{K_2(T_1)} > \frac{K_1(T_2)}{K_1(T_1)}$$

54. The number of degrees of freedom for a system consisting of  $\text{NaCl}(s)$ ,  $\text{Na}^+(\text{aq})$  and  $\text{Cl}^-(\text{aq})$  at equilibrium is

- (a) 2 (b) 3  
(c) 4 (d) 5



**Ans. (c) :** According to Gibbs phase rule  
 $F = C - P + 2$   
 where, F = degree of freedom  
 C = no of components  
 P = Phase  
 So, no of degree of freedom for NaCl(S), Na<sup>+</sup>(aq) and Cl<sup>-</sup>(aq) in equilibrium—  
 $F = 3 - 1 + 2$   
 $F = 4$

55. 'Match the structures in List-I with their correct names given in List-II

List-I		List-II	
(P)		(i)	3-methyl furan
(Q)		(ii)	Imidazole
(R)		(iii)	5-hydroxy benzothiazole
(S)		(iv)	2-amino piperidine
(T)		(v)	3-amino morpholine

**Choose the correct option**

- (a) P-i, Q-ii, R-v, S-iii, T-iv  
 (b) P-ii, Q-iii, R-iv, S-v, T-i  
 (c) P-iii, Q-iv, R-v, S-i, T-ii  
 (d) P-iv, Q-v, R-i, S-ii, T-iii

**Ans. (a) :**

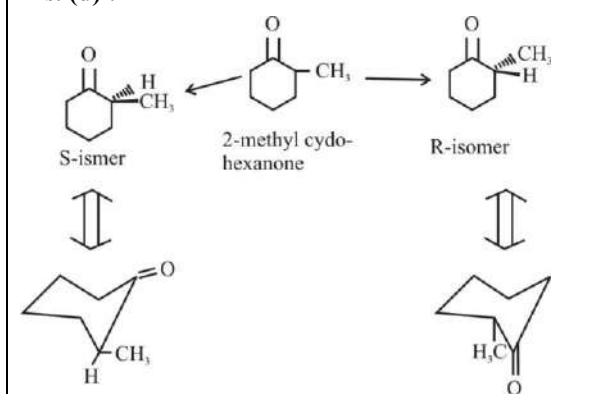
List-I		List-II	
(P)		(i)	3-methyl furan
(Q)		(ii)	Imidazole
(R)		(v)	3-amino morpholine

(S)		(iii)	5-hydroxy benzothiazole
(T)		(iv)	2-amino piperidine

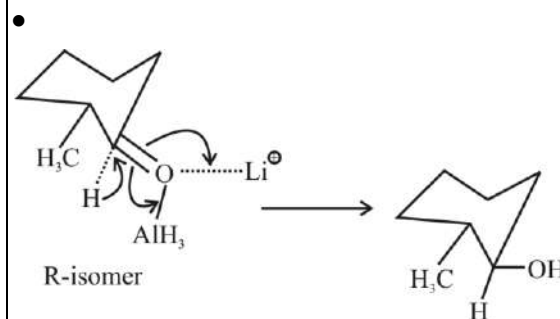
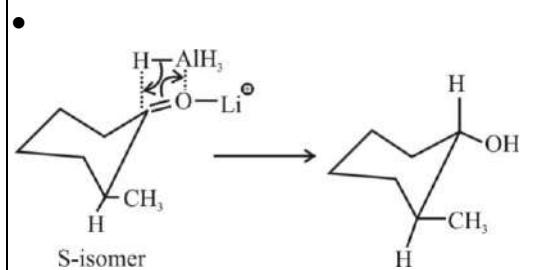
56. The result of the reduction of either (R) or (S) 2-methylcyclohexanone, in separate reactions, using LiAlH<sub>4</sub> is that the reduction of

- (a) the R enantiomer is stereoselective  
 (b) the R enantiomer is stereospecific  
 (c) the S enantiomer is stereospecific  
 (d) both the R and S enantiomers is stereoselective

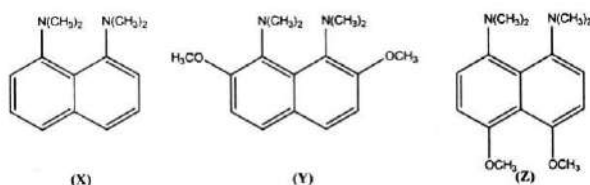
**Ans. (d) :**



- There is stereoselectivity is seen during reduction of cyclohexanone (different isomer) by either LiAlH<sub>4</sub> or NaBH<sub>4</sub> predominantly more stable among two isomer is obtained.

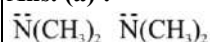


57. The increasing order of basicity among the following is



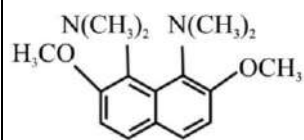
- (a)  $Y < X < Z$                       (b)  $Y < Z < X$   
 (c)  $X < Z < Y$                       (d)  $X < Y < Z$

Ans. (a) :



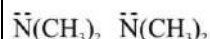
(X)

No electron donating or withdrawing group so act as base as usual, due to presence of  $\text{-N(CH}_3)_2$  on both benzene rings.



(Y)

Electron donating group  $\text{-OCH}_3$  present at ortho position, hence disruptures the planarity and do not donate electron pairs to the ring.

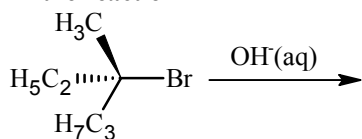


(Z)

Electron donating group  $\text{-OCH}_3$  present at para position, donates electron pair to the ring, hence enhances basicity.

So correct order  $\text{-Y < X < Z}$

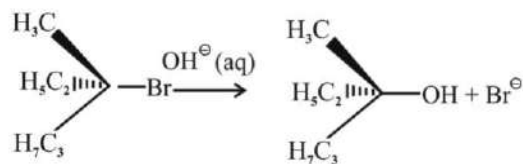
58. In the reaction



if the concentration of both the reactants is doubled, then the rate of the reaction will

- (a) remain unchanged                      (b) quadruple  
 (c) reduce to one fourth                      (d) double

Ans. (d) :



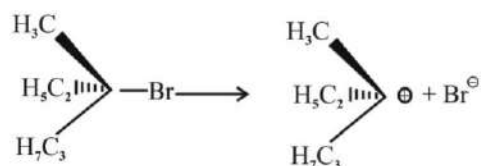
Above reaction occurs through the  $\text{S}_{\text{N}}1$  mechanism, because reagent is a tertiary halide.

$$\text{rate} = K [\text{3}^\circ\text{carbocation}]$$

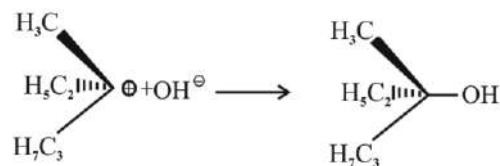
So if amount of reactant i.e. alkyl bromide is doubled, then rate of reaction is also doubled.

Mechanism-

(i) Rate determining step i.e. carbocation formation



(ii) Attack of nucleophile i.e.  $\text{OH}^\ominus$  at carbocation



59. Match the structure in List-I with the coupling constant [ $^1\text{H J}(\text{Hz})$ ] given in List-II

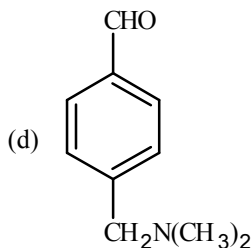
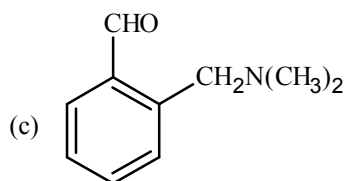
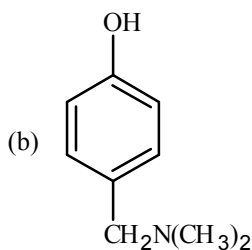
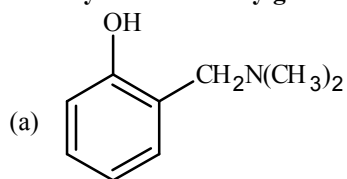
List-I	List-II
A.	(i) $\sim 1\text{Hz}$
B.	(ii) $\sim 10\text{Hz}$
C.	(iii) $\sim 15\text{Hz}$

A	B	C
(a) i	ii	iii
(b) ii	iii	i
(c) iii	ii	i
(d) iii	i	ii

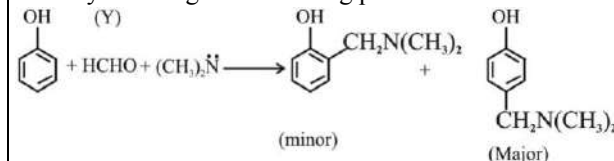
Ans. (b) : The molecules and their respective J values are given following

Molecules	J-value Range
	$^2J = 1 - 3 \text{ Hz}$
	$^3J = 9 - 12 \text{ Hz}$
	$^3J = 15 - 18 \text{ Hz}$

60. Phenol on reaction with formaldehyde and dimethyl amine mainly gives

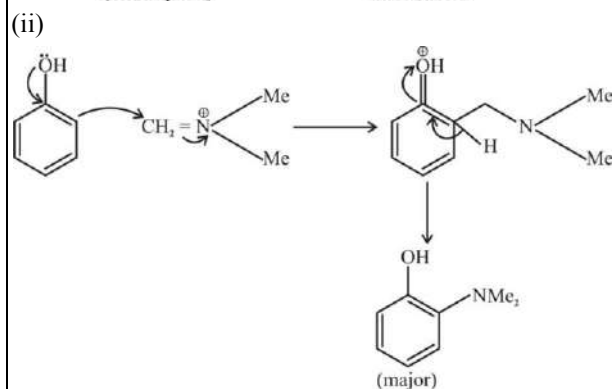
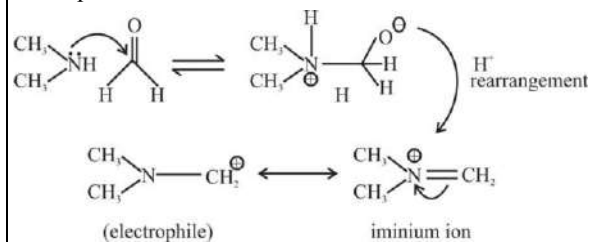


**Ans. (a) :** Phenol on reaction with formaldehyde and dimethyl amine gives following products



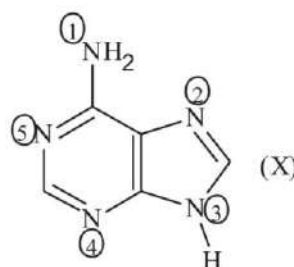
• The above reaction is Mannich reaction. The para product is major product due to smaller steric hindrance than ortho product.

**Mechanism– (i)** Initially an iminium ion is formed due to nucleophilic addition of amine to formaldehyde and subsequent loss of water molecule.



**Note :** There is much electron density at ortho-position than para-position, so ortho product is major product. Hydrogen bonding is also present in ortho product.

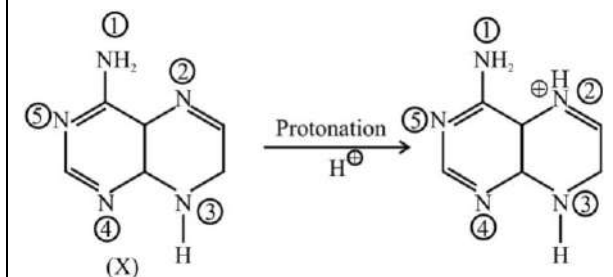
61. The mono protonation of adenine (X) in acidic solution



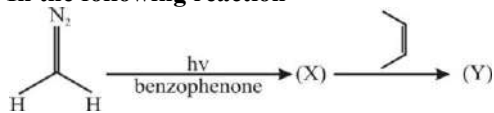
mainly occurs at

- (a) position 1                      (b) position 2  
(c) position 3                      (d) either position 4 or 5

**Ans. (b) :** Adenine is monoprotonated on N (2) under acidic conditions.



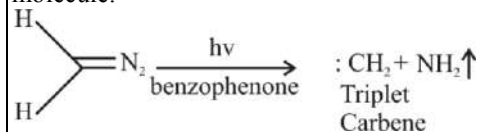
62. In the following reaction



(X) and (Y) respectively are

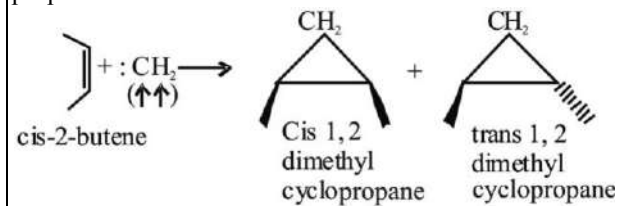
- (a)  $^1\text{CH}_2$  and cis 1, 2 dimethylcyclopropane  
 (b)  $^3\text{CH}_2$  and cis 1, 2 dimethylcyclopropane  
 (c)  $^1\text{CH}_2$  and a mixture of cis/trans 1, 2 dimethylcyclopropane  
 (d)  $^3\text{CH}_2$  and a mixture of cis/trans 1, 2 dimethylcyclopropane

**Ans. (d) :** Diazomethane can be exposed to light/heat to facilitate the loss of  $\text{N}_2$  gas and formation of the simplest Carbon methylene. The process is driven by the formation of the nitrogen gas which is a very stable molecule.

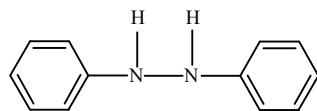


• Due to presence of benzophenone triplet ( $\uparrow\uparrow$ ) carbene is formed.

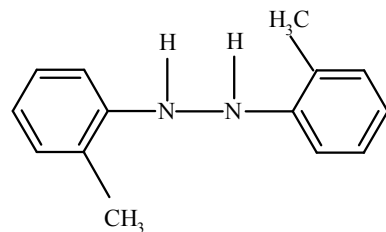
Now  $\text{:CH}_2$  formed reacts with cis-2 butene gives cis 1, 2 dimethyl cyclopropane and trans 1, 2 dimethyl cyclopropane.



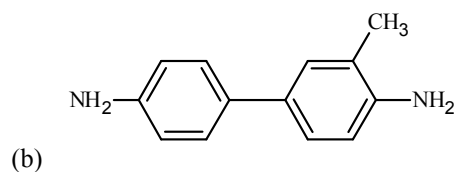
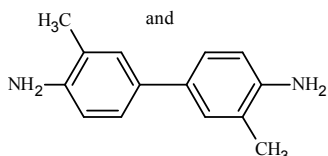
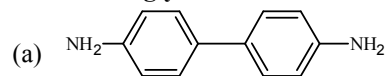
63. The major products obtained upon treating a mixture of



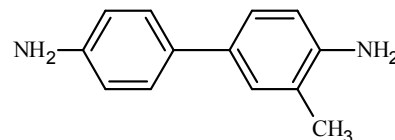
and



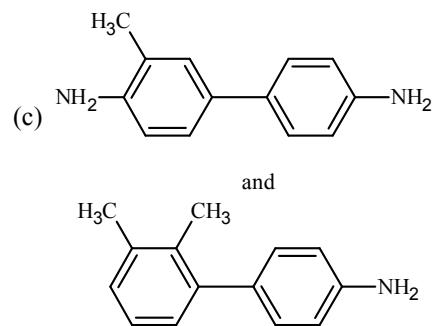
with a strongly acidic solution of  $\text{H}_2\text{SO}_4$  is



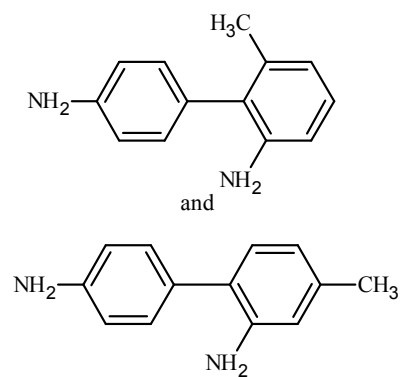
and



and

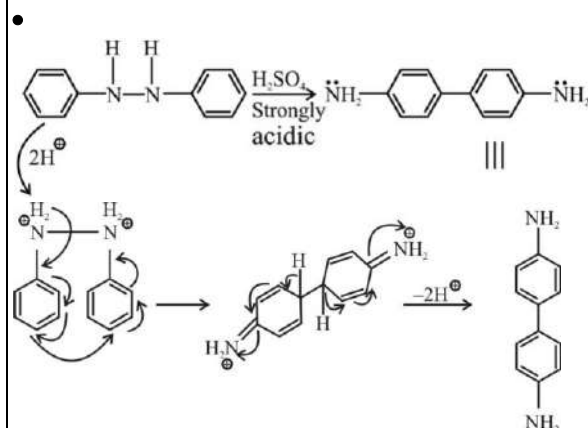


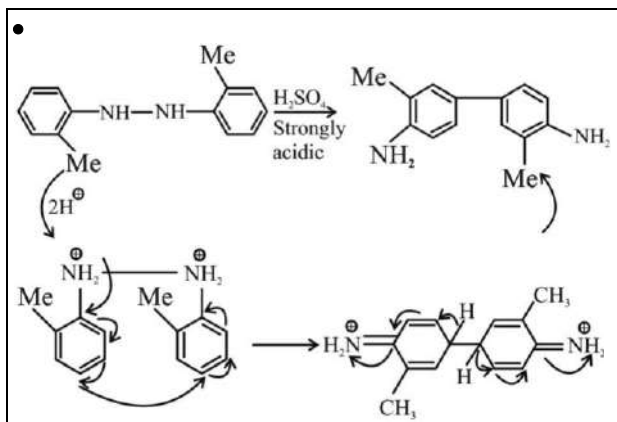
(d)



**Ans. (a) :** The given reactant undergo benzidine reaction. In this reaction/rearrangement hydroazobenzene is converted to benzidine under acidic environment.

**Reactions :-**





64. Match the observed principal absorptions in the visible spectrum shown in List-I with the bond that shows this absorption in List-II

List-I		List-II	
(A) $\sigma \rightarrow \sigma^*$		(i) C - C	
(B) $n \rightarrow \sigma^*$		(ii) C - O	
(C) $n, \pi^*$		(iii) C = O	
(D) $\pi, \pi^*$		(iv) C = C	
A	B	C	D
(a) i	ii	iii	iv
(b) i	iii	ii	iv
(c) ii	i	iv	iii
(d) iv	ii	iii	i

**Ans. (a) :  $\sigma \rightarrow \sigma^*$  Transition**— This transition is high energy transition and found in alkanes. In this case promotion of an electron takes from a bonding sigma orbital to the associated anti bonding  $\sigma^*$  orbital.

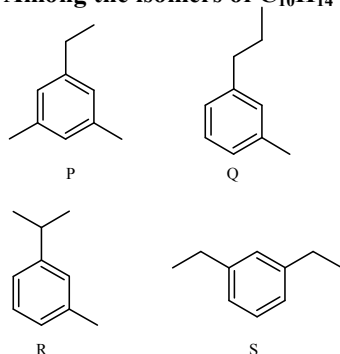
$\sigma \rightarrow \sigma^* \Rightarrow$  alkanes  
(C - C)

**$n \rightarrow \sigma^*$  Transition**→ This type of transition occurs if an electron from a non-bonding orbital to an anti bonding  $\sigma^*$ -orbital. Usually compounds having non-bonding electrons on hetero atom show this kind of transition. This is lower energy transition than  $\sigma \rightarrow \sigma^*$  transitions. Ex. alcohols, ethers etc.

**$n \rightarrow \pi^*$  Transitions**→ The promotion of a non-bonding electron to a  $\pi$ -bonding orbital, It's a low energy transition. This type of transition is shown by saturated aldehydes and ketones.

**$\pi \rightarrow \pi^*$  Transition**→ usually this kind of transition is shown in compounds containing one or more covalently unsaturated groups like C=C, C=O, NO<sub>2</sub> etc.

65. Among the isomers of C<sub>10</sub>H<sub>14</sub> shown,

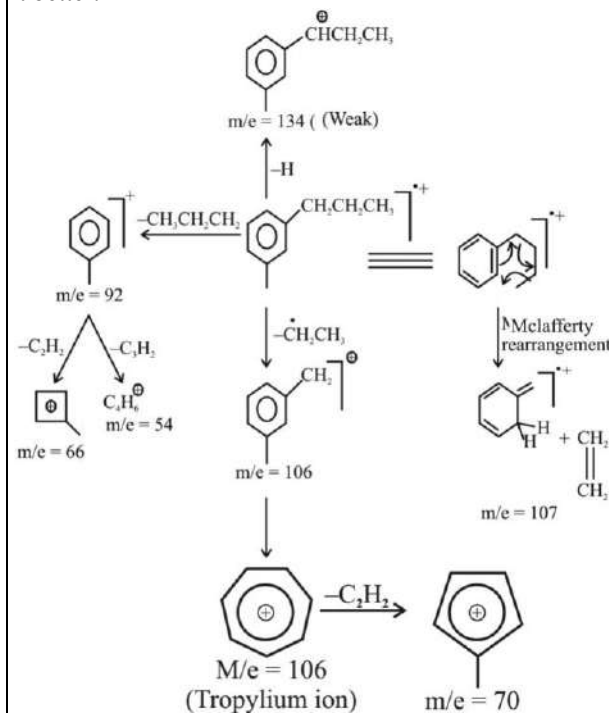


the isomer that can be identified uniquely by mass spectrometry alone is

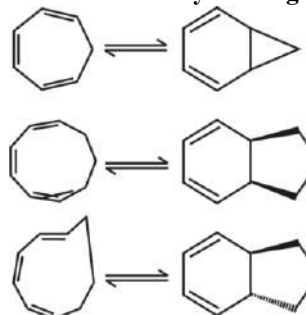
- (a) P (b) Q  
(c) R (d) S

**Ans. (b) :** Mass spectroscopy→ It is an analytical method useful for calculating the mass to charge ratio (m/z) of one or more molecules in the sample.

The most stable cation is required to show uniquely spectrometry. From the given options, option (Q) shows it better.



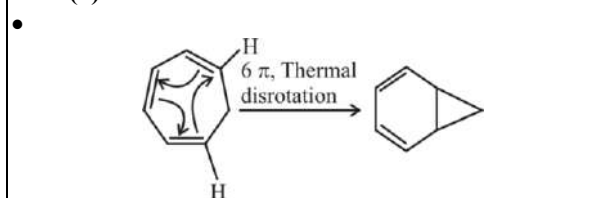
66. The direction of rotation of the following thermal electrocyclic ring closures

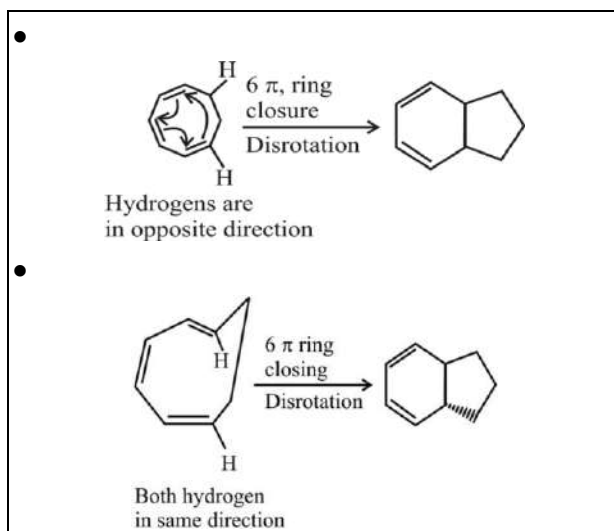


respectively is :

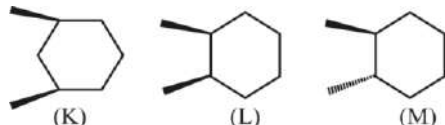
- (a) disrotatory, disrotatory, disrotatory  
(b) conrotatory, conrotatory, conrotatory  
(c) disrotatory, disrotatory, conrotatory  
(d) disrotatory, conrotatory, disrotatory

**Ans. (a) :**





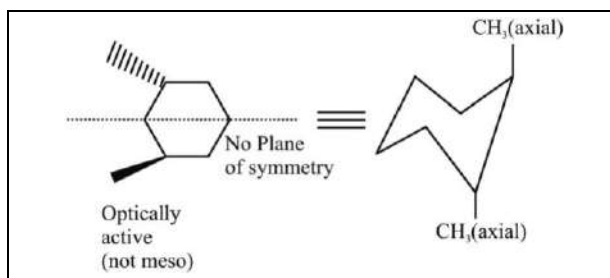
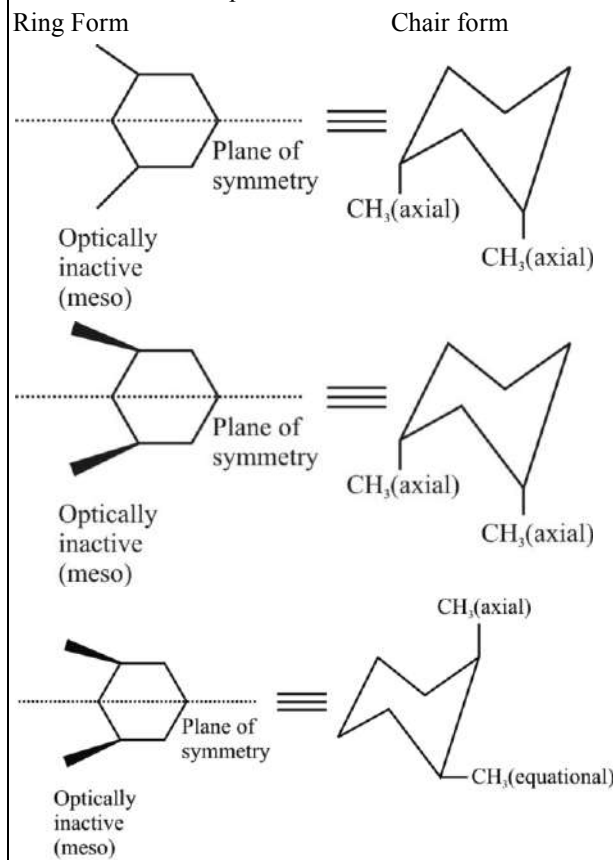
67. The molecule(s) that exist as meso structure(s)



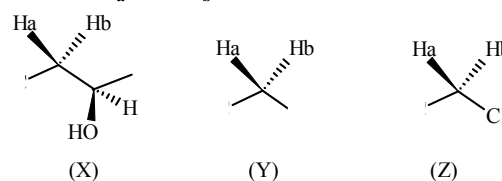
is/are

- (a) only M (b) both K and L  
 (c) only L (d) only K

**Ans. (b) :** Both 'K' and 'L' are optically inactive due to presence of plane of symmetry, hence optically inactive, hence are meso compounds.



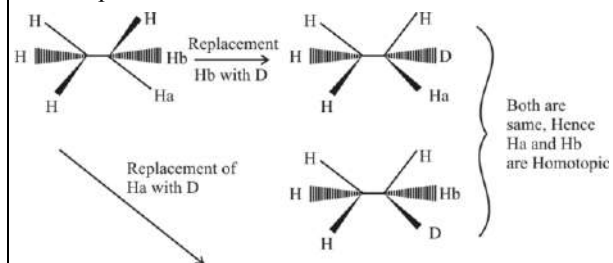
68. The stereochemical descriptors for the atoms labeled H<sub>a</sub> and H<sub>b</sub> in the structures



respectively are

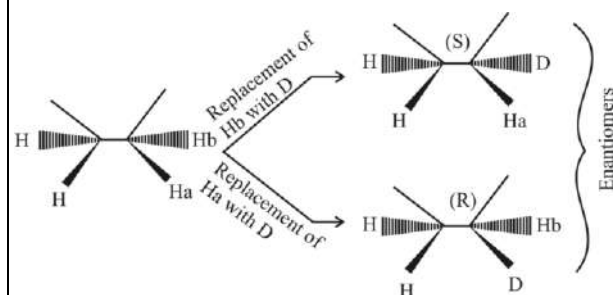
- (a) X-homotopic, Y-enantiotopic and Z-diastereotopic  
 (b) X-enantiotopic, Y-homotopic and Z-diastereotopic  
 (c) X-diastereotopic, Y-homotopic and Z-enantiotopic  
 (d) X-homotopic, Y-diastereotopic and Z-enantiotopic

**Ans. (c) :** When replacement of each H with D results in the same product, these hydrogen are called 'homotopic'.



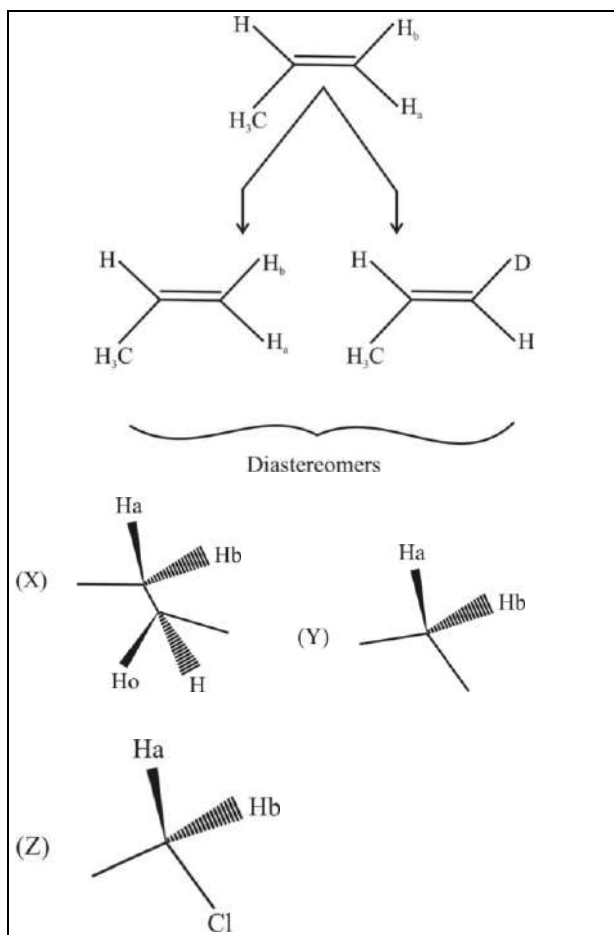
When replacement of each H with D results in enantiomers, these hydrogen are called 'enantiotopic'.

Ex.



When replacement of each 'H' with D result in diastereomers, these hydrogens are called diastereotopic.

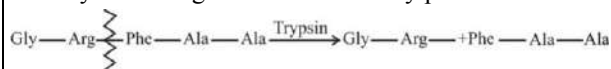
Example :-



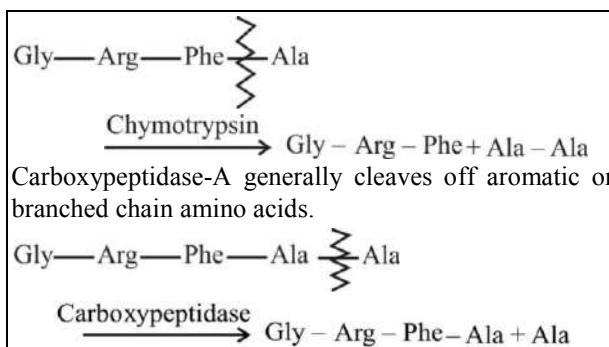
69. Treatment of the pentapeptide Gly-Arg-Phe-Ala-Ala, in separate experiments, with the enzymes Trypsin, Chymotrypsin and Carboxypeptidase A respectively, gives

- Gly-Arg+Phe-Ala-Ala ; Gly-Arg -Phe+Ala-Ala ; Gly-Arg-Phe-Ala+Ala
- Gly-Arg-Phe+Ala-Ala ; Gly-Arg -Phe+Ala-Ala ; Gly-Arg-Phe-Ala+Ala
- Gly-Arg+Phe-Ala-Ala ; Gly-Arg -Phe+Ala-Ala ; Gly-Arg-Phe+Ala-Ala
- Gly-Arg+Phe-Ala-Ala ; Gly-Arg -Phe+Ala-Ala ; Gly+Arg-Phe-Ala+Ala

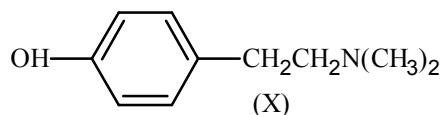
**Ans. (a) :** The highly specific protease trypsin is used to hydrolyse a protein completely. Proteolysis is carried out with high level of trypsin to ensure total proteolysis. It cleaves the peptide bond between -COOH group of Arginine or carboxylic group of lysine and the amino group of adjacent amino acid. Cleavage does not occur when lysine or arginine is followed by proline.



Chymotrypsin is an enzyme of family called serine protease. It cleaves on the C-terminal phenyl alanine, tryptophan and tyrosine on peptide chain. It shows specificity towards aromatic amino acids because of its hydrophobic pocket.



70. Hordenine (X), an alkaloid, undergoes Hoffman degradation to give compound (Y).



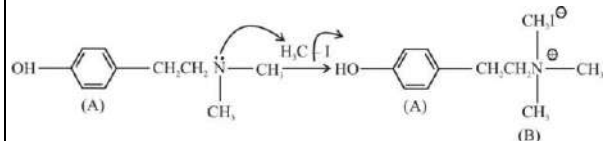
(Y) on treatment with alkaline permanganate gives (Z). Y and Z respectively are

- 
- 
- 
- 

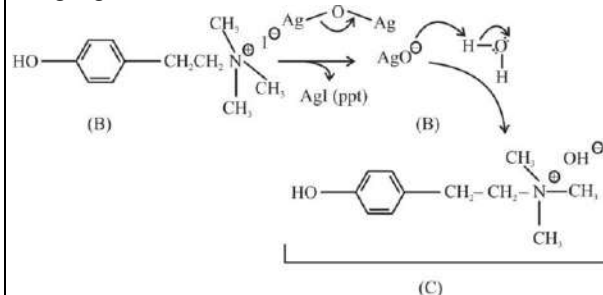
**Ans. (a) :** Hofmann's elimination is the process of creating tertiary ammonium and alkenes from the treatment of quaternary ammonium with excess methyl iodide and treatment of the resulting compound with silver oxide, water and heat. The product formed from the treatment of quaternary ammonium iodide salt. The replacement of the iodine by a hydroxyl anion is replacement of the

iodine by a hydroxyl anion is followed by an elimination reaction to form the alkene as well.

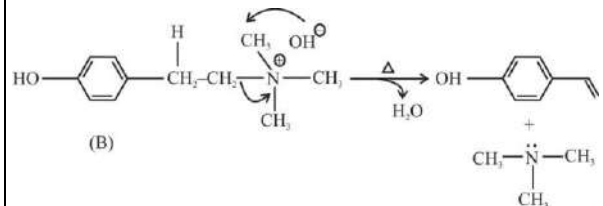
**Mechanism-** (i) Formation of quaternary ammonium iodide salt.



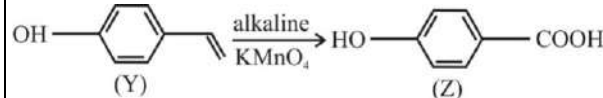
(ii) Substitution of the iodide ion with the  $\text{OH}^\ominus$  ion using  $\text{Ag}_2\text{O}$ .



(iii) compound (c) is heated to facilitate elimination reaction.



• (Y) On treatment with alkaline  $\text{KMnO}_4$  gives following compound (z).



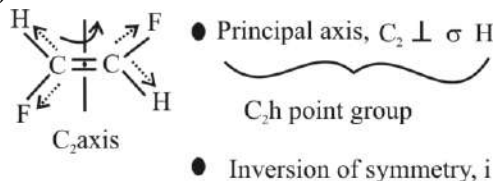
**Common Data for Questions 71, 72, 73 :**

**Trans 1, 2 difluoroethylene molecule has a 2-fold rotational axis, a symmetry plane perpendicular to the rotational axis and an inversion centre.**

71. The number of distinct symmetry operations that can be performed on the molecule is

- (a) 2 (b) 4  
(c) 6 (d) 8

**Ans. (b) :**



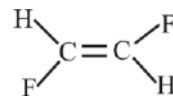
• There are total 4 symmetry operations.

- E (identity operation)  
 $C_2$   
 $\sigma_h$   
 $i$

72. The number of irreducible representations of the point group of the molecule is

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

**Ans. (d) :**



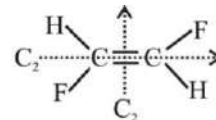
• Since having 4 symmetry operations, number of irreducible representation are also four. i.e.  $A_g, B_g, A_u, B_u$ .

$C_{2h}$	E	$C_2$	i	$\sigma_h$		
$A_g$	1	1	1	1	$R_z$	$x^2, y^2, z^2, xy$
$B_g$	1	-1	1	-1	$R_x, R_y$	$zx, yz$
$A_u$	1	1	-1	-1	$z$	
$B_u$	1	-1	-1	1	$x, y$	

73. When two H atoms of the above molecule are also replaced by F atoms, the point group of the resultant molecule will be

- (a)  $C_1$  (b)  $C_{2h}$   
(c)  $C_{2v}$  (d)  $D_{2h}$

**Ans. (d) :** Resultant molecule after replacing two hydrogen with Fluorine atoms.

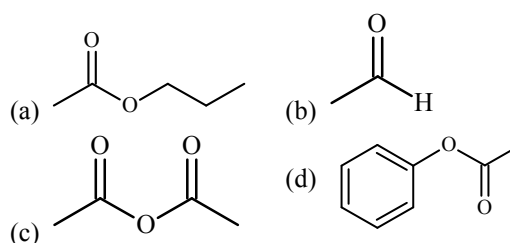


- $2C_2$  axis  $\perp$  molecular plane,  $\sigma_h$
- Two  $\sigma_h$  planes perpendicular to each other.
- It has eight irreducible representations as  $A_g, B_{1g}, B_{2g}, B_{3g}, A_u, B_{1u}, B_{2u}, B_{3u}$ .

**Common Data for Questions 74, 75 :**

**Reactivity of aryl amines towards electrophilic aromatic substitution is much higher than that of aliphatic amines. Hence differential reactivity of the amino group is desirable in many reactions.**

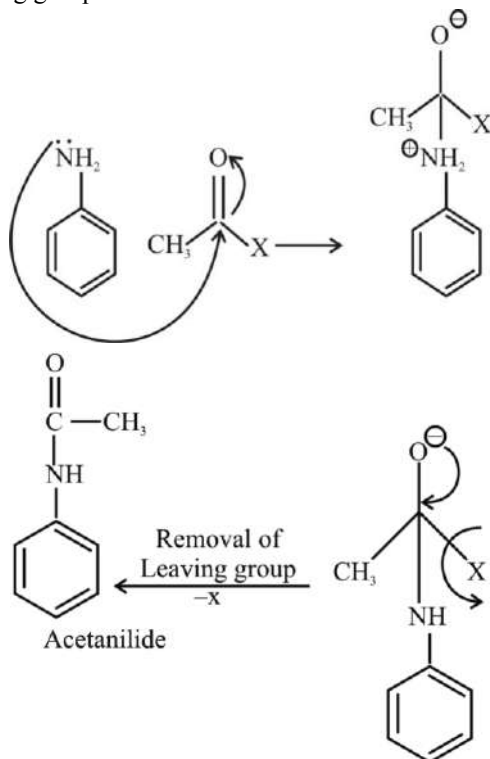
74. The compound which on reacting with aniline will NOT form an acetanilide is





**Ans. (b) :** The  $\overset{\ominus}{\text{O}}\text{C}-\text{X}$  species, where x is a leaving group (ex. -OR,  $\text{O}-\text{C}-\text{R}$ , halogen, - OAr etc) reacts with aniline gives acetanilide.

In formation of acetanilide lone pair present on Nitrogen in aniline attacks on electrophile carbonyl carbon and C - N bond is formed after removal of leaving group.

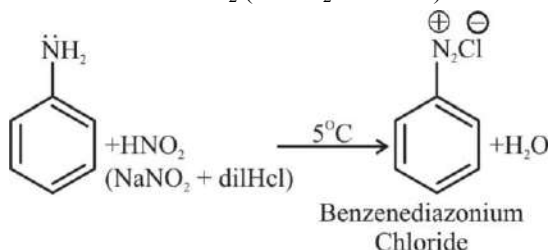


•  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$  has no leaving group, hence it will not form acetanilide.

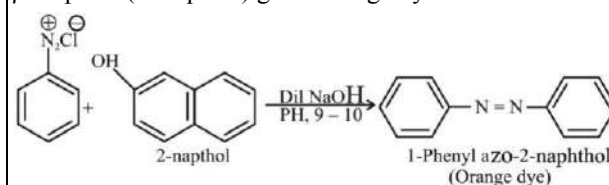
**75. Aniline can be distinguished from methylamine by its reaction with**

- (a) p-toluene sulphonyl chloride/KOH  
 (b) (i)  $\text{NaNO}_2/\text{HCl}$ ,  $0-5^\circ\text{C}$  (ii) alkaline  $\beta$  naphthol  
 (c)  $\text{Sn}/\text{HCl}$  (d) acetyl chloride

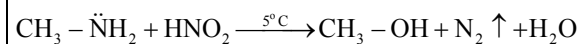
**Ans. (b) :** Aniline can be distinguished from methylamine by azodye test. 'A' dye is obtained when aromatic amines react with  $\text{HNO}_2$  ( $\text{NaNO}_2 + \text{dil HCl}$ ) at  $0^\circ\text{C}$ .



Benzenediazonium chloride on reaction with alkaline  $\beta$ -naphthol (2-naphthol) gives orange dye.

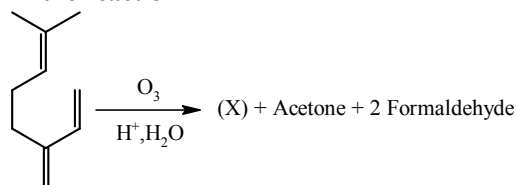


Aliphatic amines on treatment with  $\text{HNO}_2$ ,  $5^\circ\text{C}$  give a brisk effervescence due to evolution of  $\text{N}_2$  gas.

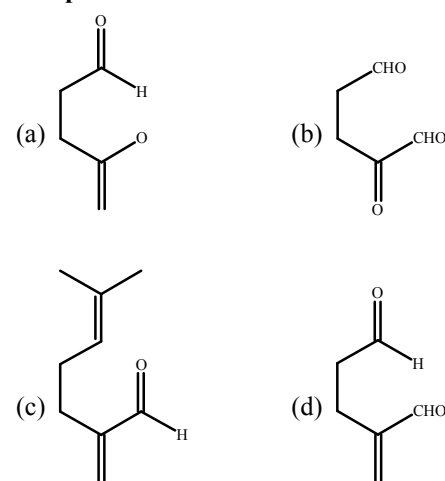


**Linked Answer Questions 76 & 77 :**

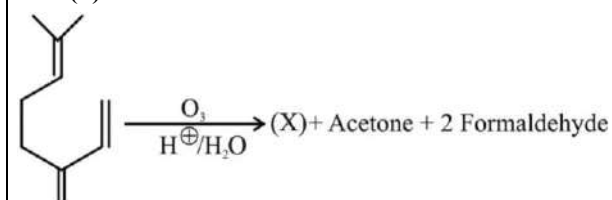
**76. In the reaction**



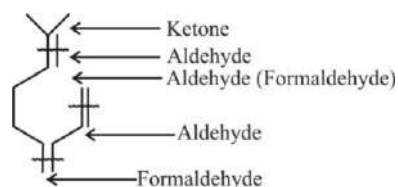
**Compound X is**



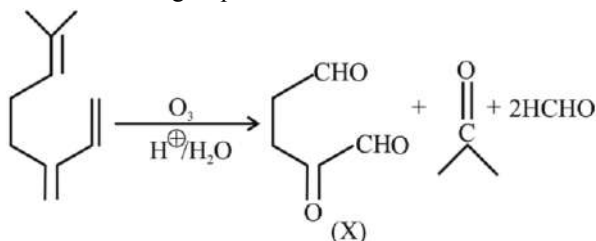
**Ans. (b) :**



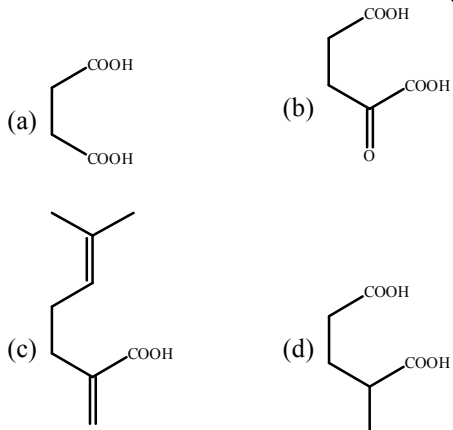
The above reaction is an example of ozonolysis reaction in which double bonded carbon having either single or double hydrogen forms aldehyde and double bonded carbon having no hydrogen or two alkyl groups form ketones.



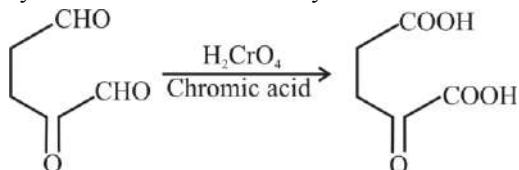
Hence there will be formation of 2 formaldehydes one acetone and a compound having two aldehydic group and an acetonic group.



77. Oxidation of X with chromic acid chiefly gives

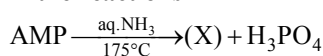


**Ans. (b) :** Chromic acid does not oxidise ketones but aldehydes are oxidised to carboxylic acid.



**Linked Answer Questions 78 & 79 :**

78. In the reactions

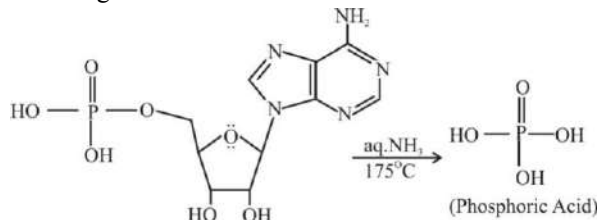


**Compound X is**

- (a) Adenine (b) Xanthine  
(c) 2, 6-diaminopurine (d) Adenosine

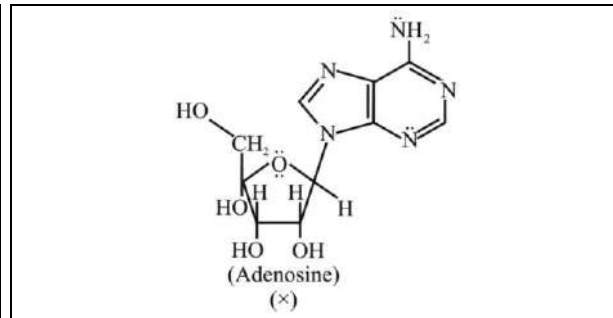
**Ans. (d) :** On treating with aqueous  $\text{NH}_3$  at  $175^\circ\text{C}$ , adenosine mono phosphate (AMP) gives adenosine and phosphoric acid.

The compound [X] is nucleoside adenosine, containing ribose sugar and adenine base.



Adenosine Monophosphate (AMP)

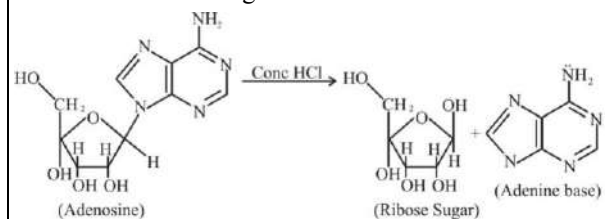
5' - adenylic acid



79. Compound X on treatment with conc. HCl gives

- (a) Uric acid (b) Adenine  
(c) Hypoxanthine (d) Guanine

**Ans. (b) :** Adenosine on treating with conc HCl gives adenine and ribose sugar.

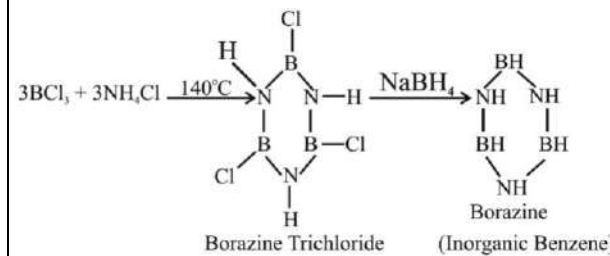


**Linked Answer Questions 80 & 81 :**

80. The reaction of ammonium chloride with  $\text{BCl}_3$  at  $140^\circ\text{C}$  followed by treatment with  $\text{NaBH}_4$  gives the product X. The formula of X is

- (a)  $\text{B}_3\text{N}_3\text{H}_3$  (b)  $\text{B}_3\text{N}_3\text{H}_6$   
(c)  $\text{B}_3\text{N}_3\text{H}_{12}$  (d)  $[\text{BH}-\text{NH}]_n$

**Ans. (b) :** When boron trichloride ( $\text{BCl}_3$ ) is treated with ammonium chloride ( $\text{NH}_4\text{Cl}$ ) at  $140^\circ\text{C}$  borazine trichloride is formed which on further treatment with  $\text{NaBH}_4$  gives borazine ( $\text{B}_3\text{N}_3\text{H}_6$ ).

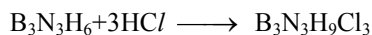


81. Which of the following statement(s) is/are true for X?

- (i) X is not isoelectronic with benzene.  
(ii) X undergoes addition reaction with HCl  
(iii) Electrophilic substitution reaction on X is much faster than that of benzene.  
(iv) X undergoes polymerization at  $90^\circ\text{C}$
- (a) i and ii (b) only ii  
(c) ii and iii (d) i and iv

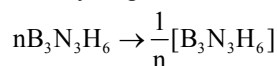
**Ans. (c) :** (i) Benzene is isoelectronic with benzene hence statement is incorrect.

(ii) One molecule of borazine adds 3 molecules of HCl or HBr in the cold without a catalyst. These molecules gets attached with all the three B atoms of borazine, since B atom is more electronegative than N is B - N or B = N bond.



(iii) Borazine is more reactive than benzene towards electrophilic aromatic substitution reactions because in borazine molecule nitrogen is more electronegative than boron. Nitrogen acquires partial negative charge and boron acquires partial positive charge and boron bonding takes place between boron and nitrogen, and it is more as compared with benzene because borazine is less soluble and more reactive towards electrophilic aromatic substitution reaction.

(iv) Borazine is polymerised into polyborazylene by heating it at 70°C. The polymer is formed when borazine loses some hydrogen atoms from its sides.



**Linked Answer Questions 82 & 83 :**

**82. Consider a particle of mass of moving in a one-dimensional box under the potential  $V = 0$  for  $0 \leq x \leq a$  and  $V = \infty$  outside the box. When the particle is in its lowest energy state the average momentum ( $\langle P_x \rangle$ ) of the particle is**

- (a)  $\langle p_x \rangle = 0$                       (b)  $\langle p_x \rangle = \frac{h}{a}$   
 (c)  $\langle p_x \rangle = \frac{h}{2a}$                       (d)  $\langle p_x \rangle = \frac{h}{2\pi a}$

**Ans. (a) :** Either inside a box, hydrogen like atom or for S.H.O. average value of momentum is always zero. Hence,

$$\langle P_x \rangle = 0$$

A particle in one dimensional box in ground state,  $n = 1$

$$\text{From, } \Psi_1 = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$$

For a normalized wave function

$$\begin{aligned} \langle p \rangle &= \int_0^a \Psi_1 \left| \frac{h}{2\pi i} \cdot f \frac{d}{dx} \right| \Psi_x \\ &= \frac{h}{2\pi i} \int_0^a \left(\frac{2}{a}\right) \sin\left(\frac{\pi x}{a}\right) \left| \frac{a}{ax} \right| \sin\left(\frac{\pi x}{a}\right) dx \\ &= \frac{h}{2\pi i} \left(\frac{\pi}{a}\right) \int_0^a \left(\frac{2}{a}\right) \sin\left(\frac{\pi x}{a}\right) \cos\left(\frac{\pi x}{a}\right) dx \\ &= 0 \end{aligned}$$

**83. The uncertainty in the momentum ( $\Delta p_x$ ) of the particle in its lowest energy state is**

- (a)  $\Delta p_x = 0$                       (b)  $\Delta p_x = \frac{h}{a}$   
 (c)  $\Delta p_x = \frac{h}{2a}$                       (d)  $\Delta p_x = \frac{h}{2\pi a}$

**Ans. (c) :** We know that either inside a box, hydrogen like atom or for S.H.O, the average value of momentum,

$$\begin{aligned} \langle p_x \rangle &= 0 \\ \langle p_x^2 \rangle &= \frac{n^2 h^2}{4a^2} \end{aligned}$$

The uncertainty in the momentum of the particle,

$$\begin{aligned} \Delta p_x &= \sqrt{\langle p_x^2 \rangle - \langle p_x \rangle^2} \\ &= \sqrt{\frac{n^2 h^2}{4a^2}} = \frac{nh}{2a} \end{aligned}$$

**Linked Answer Questions 84 & 85 :**

**84. In the mixture obtained by mixing 25.0 mL  $1.2 \times 10^{-3}$  M  $\text{MnCl}_2$  and 35.0 mL of  $6.0 \times 10^{-4}$  M KCl solution the concentrations (M) of  $\text{Mn}^{2+}$ ,  $\text{K}^+$  and  $\text{Cl}^-$  ions respectively are**

- (a)  $6.0 \times 10^{-4}$ ,  $3.0 \times 10^{-4}$ ,  $1.5 \times 10^{-3}$   
 (b)  $6.0 \times 10^{-4}$ ,  $3.0 \times 10^{-4}$ ,  $9.0 \times 10^{-4}$   
 (c)  $5.0 \times 10^{-4}$ ,  $3.5 \times 10^{-4}$ ,  $1.35 \times 10^{-3}$   
 (d)  $5.0 \times 10^{-4}$ ,  $3.5 \times 10^{-4}$ ,  $8.5 \times 10^{-4}$

**Ans. (c) :** Given,

$$\begin{aligned} &25 \text{ mL of } 1.2 \times 10^{-3} \text{ M } \text{MnCl}_2 \\ &35 \text{ mL } 6.0 \times 10^{-4} \text{ M, KCl} \\ &\equiv 0.6 \times 10^{-3} \text{ M KCl} \end{aligned}$$

After mixing-

$$\begin{aligned} \text{Total Volume} &= 25 \text{ ml} + 35 \text{ ml} \\ &= 60 \text{ ml} \end{aligned}$$

$$\begin{aligned} \text{Now concentration of } \text{Mn}^{2+} &= \frac{1.2 \times 10^{-3} \times 25}{60} \\ &= 5.0 \times 10^{-4} \text{ M} \end{aligned}$$

In case of KCl Solution,

$$\begin{aligned} \text{Concentration of } \text{K}^+ &= \frac{6 \times 10^{-4} \times 35}{60} \\ &= 3.5 \times 10^{-4} \text{ M} \end{aligned}$$

$\text{MnCl}_2$  on ionization will give  $2\text{Cl}^-$  ions and KCl will give one  $\text{Cl}^-$  ion per molecule, so the counteraction to  $\text{Cl}^-$  ions =  $(2 \times 5 \times 10^{-4} + 3.5 \times 10^{-4})$   
 $= 1.35 \times 10^{-3} \text{ M}$

**85. The activity (M) of  $\text{Mn}^{2+}$  ions in the above solution is**

- (a)  $1.0 \times 10^{-4}$   
 (b)  $2.0 \times 10^{-4}$   
 (c)  $3.0 \times 10^{-4}$   
 (d)  $4.0 \times 10^{-4}$

**Ans. (d) :** For a dilute solution activity of an ion =  $\gamma m$   
 $\gamma$  = activity coefficient (For dilute solution,  $\gamma = 1$ )  
 activity = Molality  $\approx$  Molarity  
 $= 5 \times 10^{-4}$  (closer value)

# Graduate Aptitude Test In Engineering (GATE)

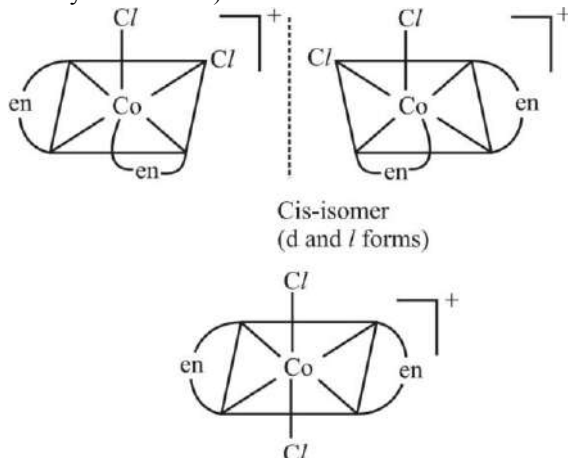
## Chemistry - 2008

### Solved Paper

1. The total number of isomers of  $\text{Co(en)}_2\text{Cl}_2$  (en- ethylenediamine) is

- (a) 4 (b) 3  
(c) 6 (d) 5

Ans. (b) : The total number of isomers of  $\text{Co(en)}_2\text{Cl}_2$  (en- ethylenediamine) is 3.



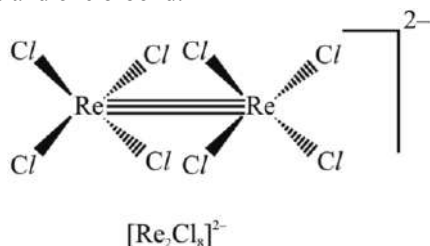
2. Metal-metal quadruple bonds are well-known for the metal

- (a) Ni (b) Co  
(c) Fe (d) Re

Ans. (d) : A quadruple bond is a type of chemical bond between two atoms involving 8 electrons. This bond is an extension of the more familiar types double bonds and triple bonds. Quadruple bonds are most common among the middle members of transition metal elements such as Rhenium, (Re), Tungsten (W), Molybdenum (Mo) and Chromium (Cr). Typically the ligands that support quadruple bonds are  $\pi$ -donors, not  $\pi$ -acceptors.

The quadruple bond was first characterized in Potassium octachlorodirhenate(III) or  $\text{K}_2[\text{Re}_2\text{Cl}_8] \cdot 2\text{H}_2\text{O}$  by F.A. Cotton in 1964.

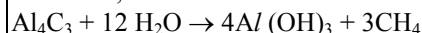
Rhenium metal complex dimers contain quadruple bonds. An example of this is in  $[\text{Re}_2\text{Cl}_8]^{2-}$  shown below. The quadruple Re-Re- bond is made of one  $\sigma$ -bond, two  $\pi$ -bonds and one  $\delta$ -bond.



3. The reaction of  $\text{Al}_4\text{C}_3$  with water leads to the formation of

- (a) methane (b) propyne  
(c) propene (d) propane

Ans. (a) : Aluminium carbide ( $\text{Al}_4\text{C}_3$ ) reacts with water to form methane ( $\text{CH}_4$ ). The chemical reaction can be written as;



4. The correct statement about  $\text{C}_{60}$  is

- (a)  $\text{C}_{60}$  is soluble in benzene  
(b)  $\text{C}_{60}$  does not react with tert-butyllithium  
(c)  $\text{C}_{60}$  is made up of 10 five-membered and 15 six-membered rings  
(d) Two adjacent five-membered rings share a common edge

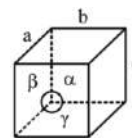
Ans. (a) :  $\text{C}_{60}$  molecules are held together by weak Vander Waals' force. They are insoluble in ionic solvents like water, ammonia and HCl, as it is non-ionic. As it is an organic molecule it is soluble in Benzene.

- \*  $\text{C}_{60}$  react with tert-butyl lithium.
- \*  $\text{C}_{60}$  contains 20 hexagons and 12 pentagons.
- \* Six membered rings are fused with both six membered as well as five membered rings while five membered rings are attached only with six membered rings.

5. The lattice parameters for a monoclinic crystal are

- (a)  $a \neq b \neq c; \alpha = \gamma = 90^\circ$   
(b)  $a = b \neq c; \alpha \neq \beta \neq \gamma$   
(c)  $a \neq b \neq c; \alpha \neq \beta \neq \gamma$   
(d)  $a = b = c; \alpha = \gamma = 90^\circ$

Ans. (a) : The monoclinic lattice has no sides of equal length, but two of the angles are equal at  $90^\circ$ , with the other angle (usually defined as  $\beta$ ) being something other than  $90^\circ$ . It is a tilted parallelogram prism with rectangular bases. This system also includes base centered monoclinic.



monoclinic

$$a \neq b \neq c$$

$$\alpha = \gamma = 90^\circ \neq \beta$$

6. The magnetic moment of  $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$  corresponds to the presence of

- (a) four unpaired electrons  
(b) three unpaired electrons  
(c) two unpaired electrons  
(d) zero unpaired electrons

Ans. (d) : Magnetic Moment of  $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$   
The magnetic moment of this complex ion can be calculated using the formula -

$$\mu = \sqrt{n(n+2)} \text{ BM}$$

where,

$\mu$  = magnetic moment

$n$  = no. of unpaired electrons

BM = Bohr magneton ( $9.27 \times 10^{-24}$  J/T)

Electronic configuration of Ruthenium ion  $[\text{Ru}]^{2+} = [\text{Kr}]4d^6$ .

According to Hund's rule, the seven electrons in the d-subshell will occupy separate orbitals with parallel spins before pairing up. Therefore, the Ruthenium ion has five unpaired electrons.

Using the formula we get,

$$\mu = \sqrt{4(4+2)} \text{ BM}$$

$$\mu = \sqrt{24} \text{ BM}$$

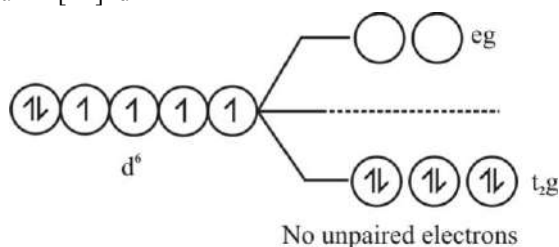
$$\mu = 4.90 \text{ BM}$$

But  $\mu_{\text{OBS}} = 0$

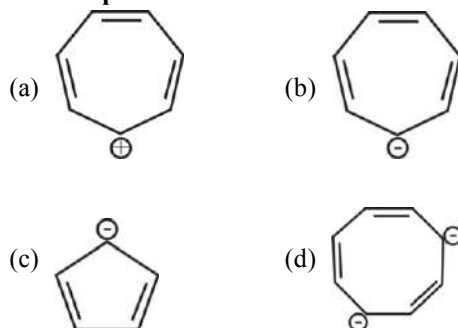
This means that all the electrons in the Ruthenium ion are paired up.

In  $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$  all d-electrons are paired up and goes to  $t_{2g}$  orbitals.

$\text{Ru}^{2+} - [\text{Kr}]4d^6$



7. The compound that is NOT aromatic is

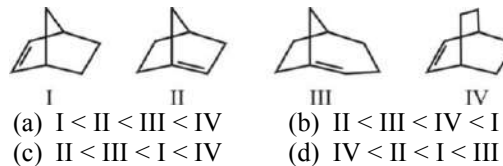


**Ans. (b) :** A conjugated cyclic planar compound having  $(4n+2)\pi$  electrons is aromatic. If the number of  $\pi$ -electrons in the compound is not equal to  $(4n+2)$  then the compound is non-aromatic.

In the option (b) cycloheptatrienyl anion has 8  $\pi$ -electrons. Thus the number of  $\pi$ -electrons in cycloheptatrienyl anion is not equal to 2, 6, 10, 14 ..... Hence, cycloheptatrienyl anion is not an aromatic compound.

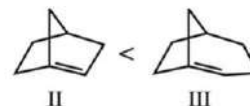


8. The order of stability for the following cyclic olefins is

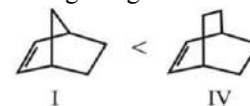


**Ans. (c) :** In small bridged cyclic compounds (olefins) the double bond at bridged carbon makes unstable the alkenes – Bredt's rule.

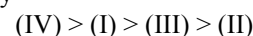
So structures (II) and (III) both are unstable but (III) is comparatively more stable, so these structures do not exist.



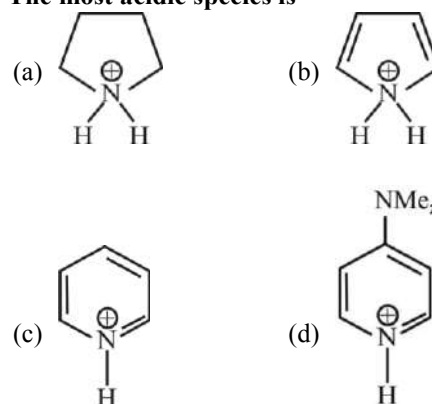
• In case of structures (I) and (IV), the structure (IV)<sup>th</sup> is more stable due to large ring size.



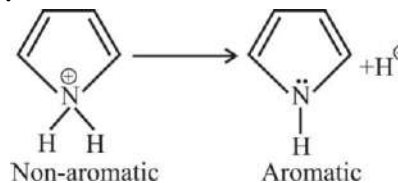
Order of stability –



9. The most acidic species is

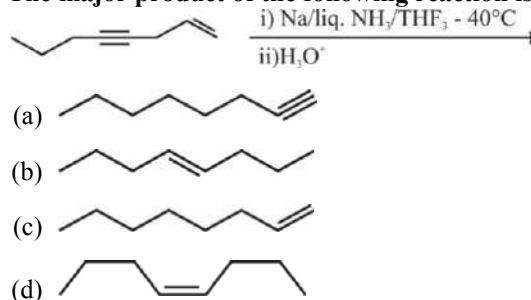


**Ans. (b) :**



The given compound is most acidic species because it is non-aromatic, after de-protonation it will aromatic.

10. The major product of the following reaction is



Ans. (c) :

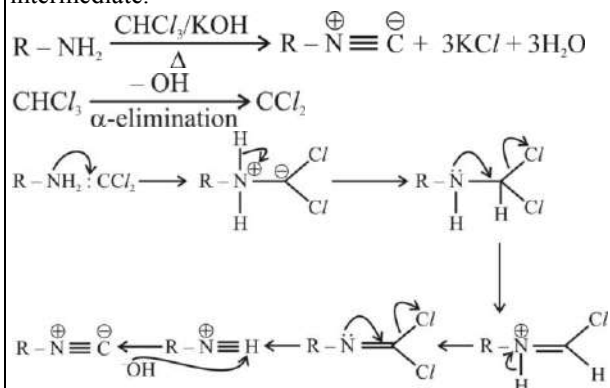


Reduction (Birch Reduction) of alkynes give trans - alkenes or E- alkenes.

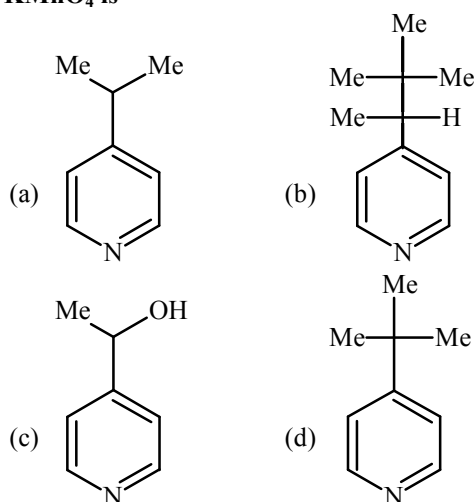
11. In the carbylamine reaction, R - X is converted to R - Y via the intermediate Z. R - X, R - Y and Z, respectively, are

- R - NH<sub>2</sub>, R - NC, carbene
- R - NH<sub>2</sub>, R - NC, nitrene
- R - NC, R - NH<sub>2</sub>, carbene
- R - OH, R - NC, nitrene

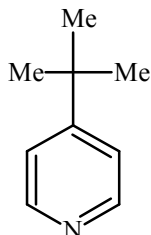
Ans. (a) : Carbylamine reaction involves the reaction between primary amine and chloroform in basic medium. In carbylamine reaction, -NH<sub>2</sub> group is converted into -NC group via reaction with carbene intermediate.



12. The compound that is NOT oxidized by KMnO<sub>4</sub> is



Ans. (d) :



The given compound does not oxidized by KMnO<sub>4</sub> because if head carbon does not have any hydrogen then KMnO<sub>4</sub> does not oxidise this. So, the correct option is d.

13. Cyanogen bromide (CNBr) specifically hydrolyses the peptide bond formed by the C-side of

- methionine
- glycine
- proline
- serine

Ans. (a) : Chemical reagents, such as cyanogen bromide (CNBr), which cleaves peptide bonds on the C-terminal side of a methionine residue can also be used to cut larger proteins into smaller peptides. Common proteins performing this activity are found in the digestive system.

14. The Hammett reaction constant ρ is based on

- the rates of alkaline hydrolysis of substituted ethyl benzoates
- the dissociation constants of substituted acetic acids
- the dissociation constants of substituted benzoic acids
- the dissociation constants of substituted phenols

Ans. (c) : The Hammett equation describes a linear free energy relationship that relates the reaction rates and equilibrium constants for many reactions involving benzoic acid derivatives with meta and para - substituent to each other with just two parameters - a substituent constant and a reaction constant.

$$\log \frac{k}{k_0} = \sigma \rho$$

where, k = equilibrium constant  
k<sub>0</sub> = Reference constant  
σ = Substituent constant  
ρ = Reaction constant.

The reaction constant ρ (sensitivity constant), describes the susceptibility of the reaction to substituents, compared to the ionization of benzoic acid. It is equivalent to the slope of the Hammett plot.

15. The lifetime of a molecule in an excited electronic state is 10<sup>-10</sup>s. The uncertainty in the energy (eV) approximately is

- 2 × 10<sup>-3</sup>
- 3 × 10<sup>-6</sup>
- 0
- 10<sup>-14</sup>

Ans. (b) : According to the formula,

$$\Delta E = \frac{h}{4\pi\Delta t}$$

As given Δt = 10<sup>-10</sup> s

h = Planck's constant

$$\Delta E = \frac{6.6 \times 10^{-34} \text{ J.S}}{4\pi(10^{-10} \text{ S})}$$