MAULANA ABUL KALAM AZAD UNIVERSITY OF TECHNOLOGY, WEST BENGAL

Paper Code : BS-CH-101

PUID : 01034 (To be mentioned in the main answer script)

CHEMISTRY-I

Time Allotted : 3 Hours　　　　*Full Marks* : 70

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

GROUP – A
(Multiple Choice Type Questions)

1. Choose the correct alternatives for any *ten* of the following : 10×1=10

i) Energy required to remove an electron from outermost shell of an isolated gaseous atom is called

a) potential energy　　b) kinetic energy

c) electron affinity　　d) ionization energy.

ii) At inversion temperature Joule-Thomson coefficient is

a) zero　　b) positive

c) negative　　d) none of these.

iii) If uncertainty in position and momentum are equal, the uncertainty in velocity is

a) $\sqrt{h/\pi}$ b) $\frac{1}{2m}\sqrt{h/\pi}$

c) $\sqrt{h/2\pi}$ d) none of these.

iv) For transition metal octahedral complexes, the choice between high spin and low spin electronic configurations arises only for

a) d^1 to d^3 complexes

b) d^4 to d^7 complexes

c) d^8 to d^9 complexes

d) d^1, d^2 and d^8 complexes.

v) Which one of the following correctly represents the formation of bonding molecular orbital from the atomic orbitals having wave functions ψA and ψB ?

a) $\psi A \times \psi B$ b) $\psi A / \psi B$

c) $\psi A + \psi B$ d) $\psi A - \psi B$.

vi) IR spectra detects

a) functional group

b) unsaturation

c) number of protons

d) nature of nuclei.

vii) What is the fingerprint region range in IR ?

a) 4000 – 400 cm^{-1} b) 4000 – 1600 cm^{-1}

c) 1600 – 400 cm^{-1} d) No range.

viii) During the motion, if the centre of gravity of molecule changes, the molecule possesses
a) Electronic energy b) rotational energy c) Translational energy d) Vibrational energy.

ix) The strength of van der Waals forces depends upon
- a) size of the molecule
- b) molecular structure
- c) number of electrons present in the molecule
- d) all of these.

x) In which of the following reactions is H = U ?
- a) $H_2(g) + I_2(g) \rightarrow 2HI(g)$
- b) $KI(aq) + I_2(s) \rightarrow KI_3(aq)$
- c) $6NaOH(aq) + 3Cl_2(g) \rightarrow 5NaCl(aq) + NaClO_3(aq) + 3H_2O(l)$
- d) $N_2O_4(g) \rightarrow 2NO_2(g)$.

xi) Water at 4°C, under pressure of 1 atm, $(C_p - C_v)$ is

a)	positive	b)	negative
c)	zero	d)	*R*.

xii) In which of the following processes does the entropy decrease ?
- a) The dissolving of NaCl in water
- b) The evaporation of water
- c) The conversion of $CO_2(g)$ into dry ice
- d) When one dozen marbles are taken out of a small bag and dropped on the ground.

GROUP – B

(Short Answer Type Questions)

Answer any *three* of the following. 3 × 5 = 15

2. Explain the following reactions with a suitable example :

   a) Wolff-Kishner reduction

   b) Cannizzaro reaction. 3 + 2

3. a) State the reason for the presence of only one electron in the 4*s* subshell of chromium ?

   b) Which of the following has larger size and why ?

   i) Mg^{2+} ii) N^{3-}. 2 + 3

4. a) Give molecular orbital energy level diagram of CO. Write its electronic configuration, magnetic behaviour and bond order.

   b) Discuss types and conditions for hydrogen bonding. 3 + 2

5. a) For a reaction both H and S are positive. Under what conditions will the reaction be spontaneous ?

   b) What will be the conjugate acids for the following Bronsted bases ?

   NH_3, HCO_3^-, CH_3COO^-, $H_2PO_2^-$. 1 + 4

6. Why violet coloured $[Ti(H_2O)_6]Cl_3$ becomes colourless when heated ?

GROUP – C

(Long Answer Type Questions)

Answer any *three* of the following. 3 × 15 = 45

7. a) Phenol on treatment with Br_2 in CS_2 at low temperature gives two isomeric monobromophenols *X* and *Y*. But phenol on treatment with bromine water gives a white precipitate *Z*. Identify the products *X, Y* and *Z* with chemical reactions. 6

b) What do you mea by enantiomer and diastereomer ? Differentiate them with examples. 4

c) Give one example of each of Friedel-Crafts' alkylation and acylation reaction. 2

d) Predict the major product(s) of the following reactions and explain their formation : 2

i) $H_3C{-}CH{=}CH_2 \xrightarrow[HBr]{(Ph-CO-O)_2}$

ii) $H_3C - CH = CH_2 \xrightarrow{HBr}$.

e) Write down the criteria for aromaticity. 1

8. a) Calculate the force constant for the bond in HCl from the fact that the fundamental vibration frequency is $8{\cdot}667 \times 10^{13}\ s^{-1}$.

b) Calculate the energy of one photon of light of wavelength 2450 Å. Will it be able to dissociate a bond in diatomic molecule which absorbs this photon and has a bond energy equal to 95 kcal per mole ?

c) "All adiabatic reversible expansions lead to a fall of temperature." — Comment or justify. 4 + (3 + 3) + 5

9. a) What is screening constant ? Calculate the effective nuclear charge ($Zeff$) of one 4s electron of the following :
Cu (Z = 29) and K (Z = 19).

b) Determine the bond order of each member of the following groups, and determine which member of each group is predicted by the molecular orbital model to have the strongest bond :

i) H_2, H_2^+, H_2^-

ii) O_2, O_2^{2+}, O_2^{2-} .

c) *p*-block elements form acidic, basic and amphoteric oxides. Explain each property by giving two examples and also write the reactions of these oxides with water. 5+4+6

10. a) What is the necessary and sufficient condition to exhibit optical activity ?

b) Draw all the stereo-isomers for the following :

$CH_3CH(OH)-CH(Cl)COOH$

c) Arrange the different conformations of *n*-butane in terms of their stability. 5+5+ 5

11. a) Nitration is also in absence of H_2SO_4 yet H_2SO_4 has no effect on benzene under the conditions employed. Show the mechanism of nitration of benzene.

b) What is the condition of spontaneity in terms of entropy ? The condition of spontaneity :

$$G_{x,\,y} < 0 \ ; \quad A_{p,\,r} < 0,$$

where G is the Gibbs free energy and A is the Helmholtz free energy. Identify x, y, p and r.

c) State whether the following properties are extensive or intensive properties :

Pressure, Concentration, Entropy, Viscosity, Temperature. 4+(2+4)+5

12. a) pH of a solution of a strong acid is 5. What will be the pH of the solution obtained after diluting the given solution 100 times ?

b) Write the Nernst equation for the cell reaction in the Daniel cell. How will the E_{cell} effected when the concentration of Zn^{2+} is increased ?

c) Draw and explain the energy level diagrams for conductor, semiconductor and insulator.

d) Explain enantiomers and diastereoisomers with examples.

e) Write the principle and application of NMR and MRI. 3+3+3+2+4

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CHEMISTRY-1

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Group – A

(Multiple Choice Type Questions)

1. Choose the correct alternatives for *any ten* of the following: 1×10=10

(i) Which of the following is the expression of Schrödinger wave equation?

(a) $\nabla^2\Psi + (h^2/8\Pi^2 m)(E - V)\Psi = 0$ (b) $\nabla^2\Psi + (8\Pi^2 m/h^2)(E - V)\Psi = 0$

(c) $(-\hbar^2/2m\nabla^2 + E)\Psi - V\Psi = 0$ (d) $(-2m/\hbar^2\nabla^2 + V)\Psi - E\Psi = 0$

(ii) All living body is the example of

(a) open system (b) closed system

(c) isolated system (d) exothermic system

(iii) The correct order of bond dissociation energy is

(a) $O_2 < O_2^+ < O_2^- < O_2^{2-}$ (b) $O_2^{2-} < O_2^- < O_2 < O_2^+$

(c) $O_2^{2-} < O_2 < O_2^- < O_2^+$ (d) $O_2 < O_2^{2-} < O_2^+ < O_2^-$

(iv) What is the hybridization of XeF_4?

(a) Sp^2 (b) Sp^3

(c) Sp^3d (d) Sp^3d^2

(v) (2R, 4S)–2, 4-dichloropentane and (2S, 4R) –2, 4-dichloropentane are

(a) enantiomers (b) diastereomers

(c) identical (d) constitutional isomers

(vi) In electrochemical corrosion
- (a) oxidation occurs at the anode
- (b) reduction occurs at the anode
- (c) both oxidation-reduction occurs at the anode
- (d) it is not an example of oxidation-reduction reaction

(vii) Which of these exhibit fluorescence?
- (a) NaCl
- (b) BaF_2
- (c) CaF_2
- (d) $CaCl_2$

(viii) Unit of frequency is
- (a) cm
- (b) sec
- (c) hertz
- (d) gm

(ix) Which of the following is not part of a polarimeter?
- (a) NICOL
- (b) Diffraction grading
- (c) Simple tube
- (d) Analyser

(x) The nucleus which will not show any peak in the NMR spectrum is
- (a) ^{1}H
- (b) ^{17}o
- (c) ^{16}o
- (d) ^{2}H

(xi) Which of the following is true for the Galvanic cell?
- (a) The cell potential is always negative.
- (b) The product are less stable than the reactants.
- (c) ΔG for the cell reaction is positive.
- (d) Chemical energy is converted to Electrical energy.

(xii) van der Waals type of bond is formed by
- (a) sharing of electron.
- (b) transfer of electron from one atom to other atom.
- (c) sharing of electron by one atom only.
- (d) weak electrostatic force of interaction among fluctuating dipoles.

(xiii) Silicon doped with gallium forms
- (a) *p*-type semiconductor
- (b) *n*-type semiconductor
- (c) insulator
- (d) None of these

Group – B

(Short Answer Type Questions)

Answer *any three* of the following. 5×3=15

2. (a) Explain the term chemical potential.

(b) Derive the relation of EMF of cell with ΔG and ΔH. 1+4=5

3. (a) Draw the molecular energy level diagram for O_2.

(b) Explain the paramagnetic behaviour of O_2 under the light of MO theory as an evidence of failure of VBT.

3+2=5

4. Prove that, $\left(V - \frac{h^2}{8\pi^2 m}\nabla^2\right)\Psi = E\Psi$. 5

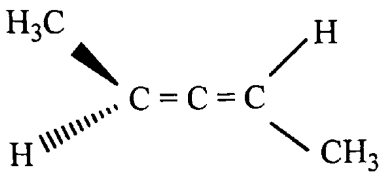
5. (a) Show that, entropy of mixing of ideal gases $\Delta S_{mix} > 0$.

(b) What is the physical significance of free energy change (ΔG)? 3+2=5

6. (a) Define specific rotation for an optically active molecule.

(b) What is the necessary and sufficient condition for a molecule to be optically active?

(c) The following compound does not have a chiral center still it shows optical activity— comment.



1+2+2=5

Group – C

(Long Answer Type Questions)

Answer *any three* of the following. 15×3=45

7. (a) State Hund's rule of spin multiplicity and Pauli Exclusion principle. Write down the electronic configuration of Fe (Z = 26).

(b) Calculate the effective nuclear charge of 4s electrons of Fe (Z = 26) with the help of Slater's rule.

(c) Define Pauling's Scale of electronegativity.

(d) Electron affinity of Cl is greater than F explain the phenomenon.

(e) Between $BeCl_2$ and $BaCl_2$ which one has more melting point and why?

(f) Show the hybridization and calculate the CFSE of $[Fe^{2+}(H_2O)_6]^{2+}$ and $[Fe^{3+}(H_2O)_6]^{3+}$ complex ions.

(1+1+1)+2+2+2+2+4=15

8. (a) Draw all possible stereoisomers for butane-2, 3-diol. Are all of them optically active? Give reason.

(b) Draw the Fischer projection formula of following stereoisomers:

(i) (2R, 3R) –2, 3-dibromobutanedioic acid

(ii) S-2-Hydroxy-2-phenylpropanoic acid

(c) How enantiomers differ from diastereomers?

(d) S_N1 mechanism proceeds through partial racemization of the product. Explain.

(e) Halogens are ortho-para orienting and deactivating. Give reason. 4+(1+1)+3+3+3=15

9. (a) Define the following elements of symmetry with a suitable example in each case:
   - (i) Rotational axis of symmetry
   - (ii) Plane of symmetry
   - (iii) Centre of symmetry
   - (iv) Alternating axis of symmetry

   (b) What is Beer-Lambert law? Show that absorption is linearly proportional to concentration of the solution.

   (c) Explain-trans-Stilbene absorbs at a longer wavelength than cis-Stilbene. (4×2)+(2+3)+2=15

10. (a) Define corrosion. What are different types of corrosion?

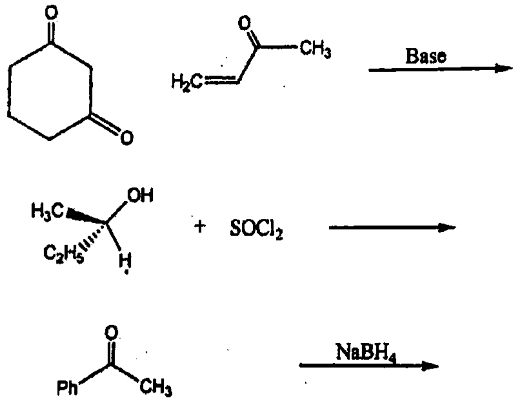
    (b) What do you mean by hardness of water? Explain how hard water fails to form lather with soap? What are different types of hardness?

    (c) Explain the potentiometric titration with suitable diagram of precipitation reactions between NaCl and $AgNO_3$. (1+4)+(1+2+2)+5=15

11. (a) State the postulates of Crystal Field Theory.

    (b) Calculate the de Broglie wavelength associated with a stone having velocity 1 m s^{-1} and mass 100g; on the other side an electron having velocity 6×10^5 m s^{-1} and mass $9{\cdot}1\times10^{-31}$ kg. Which one of these is meaningful and why?

    (c) Predict the product of the following reaction with a plausible mechanism.



    (d) How do you measure the pH of unknown solution using calomel electrode?

    (e) What type of storage cell is used in your mobile cell? 3+3+(2+2+1)+3+1=15

12. Write the short notes on *any five* of the following: 5x3=15
    - (i) Fluorescence and its application
    - (ii) Hard soft acids and bases
    - (iii) Gibbs-Helmholtz equation
    - (iv) Fajan's rule
    - (v) *n* and *p*-type semiconductor
    - (vi) Features of Ellingham diagram

CS/B.TECH/BME/ECE/EE/EEE/EIE/ICE/PWE(N)/ODD/
SEM-1/BS-CH-101/2019-20

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a) potential energy　　b) kinetic energy

c) electron affinity　　d) ionization energy.

ii) At inversion temperature Joule-Thomson coefficient is

a) zero　　b) positive

c) negative　　d) none of these.

iii) If uncertainty in position and momentum are equal, the uncertainty in velocity is

a) $\sqrt{h/\pi}$ [✓ b)] $\frac{1}{2m}\sqrt{h/\pi}$

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v) Which one of the following correctly represents the formation of bonding molecular orbital from the atomic orbitals having wave functions ψ_A and ψ_B?

a) $\psi_A \times \psi_B$ b) ψ_A / ψ_B

[✓ c)] $\psi_A + \psi_B$ d) $\psi_A - \psi_B$.

vi) IR spectra detects

a) functional group

b) unsaturation

c) number of protons

d) nature of nuclei.

vii) What is the fingerprint region range in IR ?

a) 4000 – 400 cm^{-1} b) 4000 – 1600 cm^{-1}

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viii) During the motion, if the centre of gravity of molecule changes, the molecule possesses .

a) Electronic energy b) rotational energy

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ix) The strength of van der Waals forces depends upon

a) size of the molecule

b) molecular structure

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d) all of these.

x) In which of the following reactions is $\Delta H = \Delta U$?

a) $H_2(g) + I_2(g) \rightarrow 2HI(g)$

b) $KI(aq) + I_2(s) \rightarrow KI_3(aq)$

c) $6NaOH(aq) + 3Cl_2(g) \rightarrow 5NaCl(aq) + NaClO_3(aq) + 3H_2O(l)$

d) $N_2O_4(g) \rightarrow 2NO_2(g)$.

xi) Water at 4°C, under pressure of 1 atm, ($C_p - C_v$) is

a) positive b) negative

[✓ c)] zero d) R.

xii) In which of the following processes does the entropy decrease ?

a) The dissolving of NaCl in water

b) The evaporation of water

[✓ c)] The conversion of $CO_2(g)$ into dry ice

d) When one dozen marbles are taken out of a small bag and dropped on the ground.

GROUP – B

(Short Answer Type Questions)

Answer any *three* of the following. 3 × 5 = 15

2. Explain the following reactions with a suitable example :

   a) Wolff-Kishner reduction

   b) Cannizzaro reaction. 3 + 2

3. a) State the reason for the presence of only one electron in the 4s subshell of chromium ?

   b) Which of the following has larger size and why ?

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4. a) Give molecular orbital energy level diagram of CO. Write its electronic configuration, magnetic behaviour and bond order.

   b) Discuss types and conditions for hydrogen bonding. 3 + 2

5. a) For a reaction both ΔH and ΔS are positive. Under what conditions will the reaction be spontaneous ?

   b) What will be the conjugate acids for the following Bronsted bases ?

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6. Why violet coloured [Ti (H_2O)$_6$] Cl_3 becomes colourless when heated ?

GROUP – C

(Long Answer Type Questions)

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7. a) Phenol on treatment with Br_2 in CS_2 at low temperature gives two isomeric monobromophenols *X* and *Y*. But phenol on treatment with bromine water gives a white precipitate *Z*. Identify the products *X*, *Y* and *Z* with chemical reactions. 6

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   i) $H_3C-CH=CH_2 \xrightarrow[HBr]{(Ph-CO-O)_2}$

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   Cu (Z = 29) and K (Z = 19).

   b) Determine the bond order of each member of the following groups, and determine which member of each group is predicted by the molecular orbital model to have the strongest bond :

   i) H_2, H_2^+, H_2^-

   ii) O_2, O_2^{2+}, O_2^{2-}.

   c) *p*-block elements form acidic, basic and amphoteric oxides. Explain each property by giving two examples and also write the reactions of these oxides with water. 5 + 4 + 6

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    b) Draw all the stereo-isomers for the following :

    $CH_3CH(OH)-CH(Cl)COOH$

    c) Arrange the different conformations of *n*-butane in terms of their stability. 5 + 5 + 5

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    b) What is the condition of spontaneity in terms of entropy ? The condition of spontaneity :

    $$\Delta G_{x,y} < 0 ;\ \Delta A_{p,r} < 0,$$

    where *G* is the Gibbs free energy and *A* is the Helmholtz free energy. Identify *x*, *y*, *p* and *r*.

e) State whether the following properties are extensive or intensive properties :

Pressure, Concentration, Entropy, Viscosity, Temperature. 4 + (2 + 4) + 5

12. a) pH of a solution of a strong acid is 5. What will be the pH of the solution obtained after diluting the given solution 100 times ?

b) Write the Nernst equation for the cell reaction in the Daniel cell. How will the E_{cell} effected when the concentration of Zn^{2+} is increased ?

c) Draw and explain the energy level diagrams for conductor, semiconductor and insulator.

d) Explain enantiomers and diastereoisomers with examples.

e) Write the principle and application of NMR and MRI. 3 + 3 + 3 + 2 + 4

ANSWER

Group - A

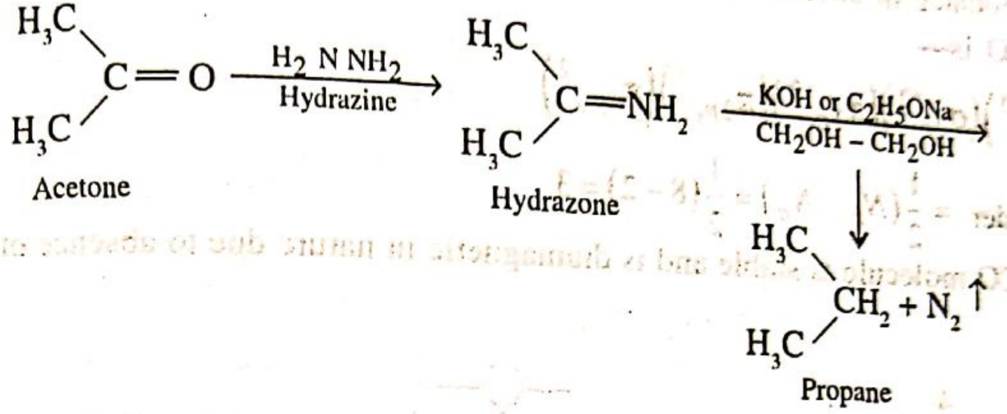
(Multiple Choice Type Questions)

1. (i) d, (ii) a, (iii) b, (iv) b, (v) c, (vi) a, (vii) c, (viii) d, (ix) d, (x) a, (xi) c, (xii) c

GROUP - B

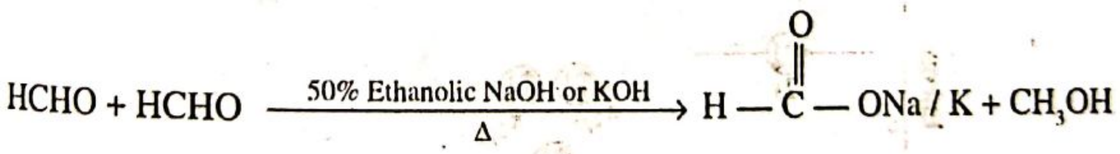
(Short Answer Type Questions)

2. (a) **Wolff - Kishner reduction :** In this reaction, acetone initially reacts with hydrazine to produce hydrazone which on heating at 180°C in presence of KOH or C_2H_5OH in ethylene glycol solvent yields propane.



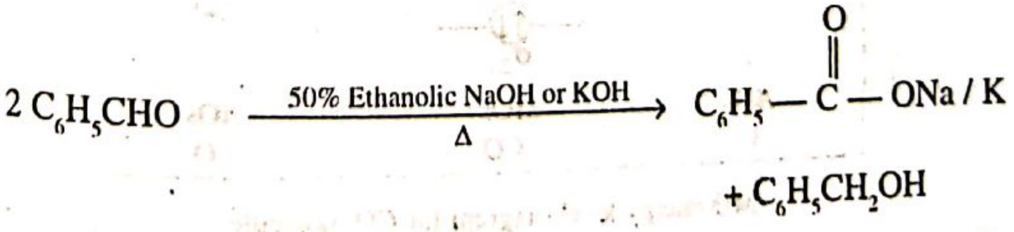
(b) **Cannizzaro's Reaction :** Aldehydes having no α-hydrogen undergo self oxidation reduction reaction in presence of strong base like ethanolic KOH to produce corresponding acid and alcohol. This is called Cannizzaro's reaction.

Example : Reaction between two formaldehyde molecules (having no α-hydrogen) produces sodium or potassium formate and methyl alcohol in presence of 50% ethanolic NaOH or KOH solution.



$$HCHO + HCHO \xrightarrow[\Delta]{50\%\ \text{Ethanolic NaOH or KOH}} H-\overset{\overset{\displaystyle O}{\|}}{C}-ONa/K + CH_3OH$$

Similarly benzaldehyde molecules may undergo similar reaction.



$$2\,C_6H_5CHO \xrightarrow[\Delta]{50\%\ \text{Ethanolic NaOH or KOH}} C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-ONa/K + C_6H_5CH_2OH$$

3. (a) The ground state electronic configuration of Chromium (24) is :- $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^1$ It has only one electron in 4s subshell as the second electron is shifted to 3d subshell to make it half filled to achieve additional stability.

(b) Mg^{2+} and N^{3-} ions have same number of valence electrons. Both are having total 10 electrons but Mg is a 3rd period element with one more orbital than N (2nd period) element. But in +2 state Mg is having only two orbitals, as N.

As, atomic number of Mg is 12 and that of N is 7, no number of proton present i is more than N and therefore exerting greater pull on outermost electrons resulting sm size.

Hence, we can conclude that N^{3-} has larger size than Mg^{2+}.

4. (a) Molecular orbital diagram of Carbon monoxide molecule (CO) : The elec configuration of C and O are —

C : $1s^2\ 2s^2\ 2p^2$

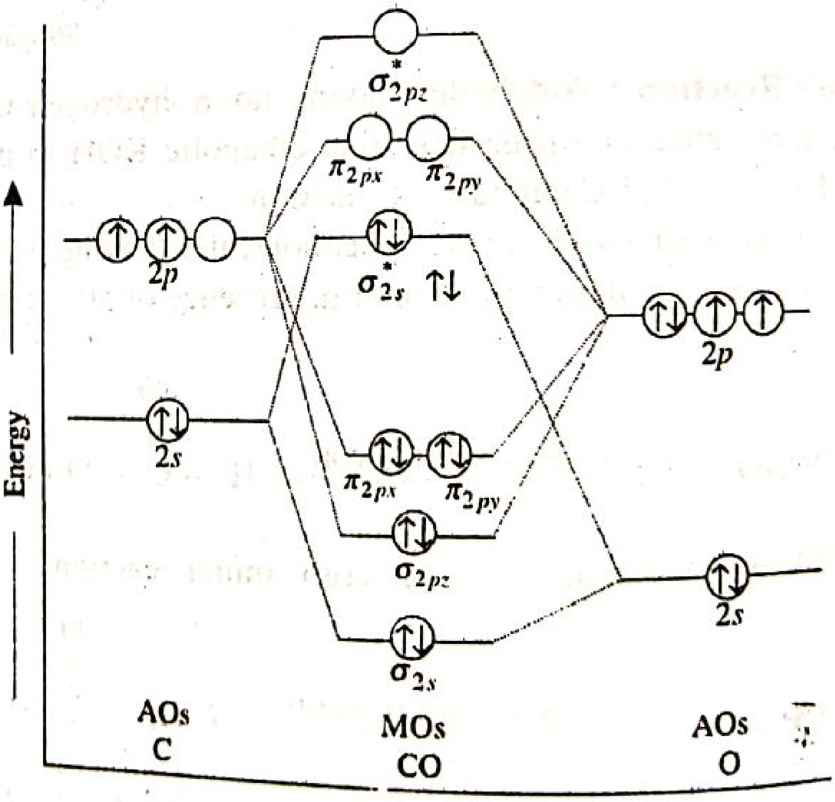
O : $1s^2\ 2s^2\ 2p^4$

Total number of electrons in CO is 6 (from C) + 8 (from O) = 14. These 14 electron to be accomodated in different molecular orbitals of CO. Thus, the molecular orbital confi ration of CO is—

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

Bond order $=\frac{1}{2}(N_b - N_a) = \frac{1}{2}(8-2) = 3$

Hence, CO molecule is stable and is diamagnetic in nature due to absence of any unp electron.



MO energy level diagram for CO molecule

CO^+ ion has one less electron in σ_{2p_z} orbital than CO molecule. The molecular or configuration is—

$$KK\left(\sigma_{2s}{}^{2}\right)\left(\sigma_{2s}{}^{*2}\right)\left(\pi_{2p_x}{}^{2}\right)\left(\pi_{2p_y}{}^{2}\right)\left(\pi_{2p_z}{}^{1}\right)$$

Bond order $=\frac{1}{2}(7-2) = 2.5$

(b) Conditions for the formation of Hydrogen-bonding

Hydrogen bond formation depends on few factors —

(i) Hydrogen bonding takes place with an atom having high electronegativity. Higher the electronegativity of the atom, stronger is the hydrogen bonding.

(ii) The atom which is involved in Hydrogen bonding should be small in size because smaller atoms can attract the electron density of the covalent bond more efficiently, thus can produce the polarity in the molecule and consequently the strength of the hydrogen bonding increases.

Types of hydrogen - bonding

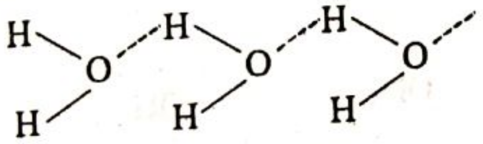
Hydrogen bonding is classified into two groups :

(i) Intermolecular hydrogen - bonding.

(ii) Intra-molecular hydrogen bonding.

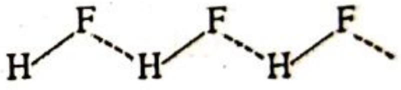
(i) **Inter-molecular Hydrogen - bonding :** If the hydrogen bonding takes place between two seperate molecules of same type or different type then that kind of hydrogen bonding is called intermolecular hydrogen bonding.

Example : H_2O, HF, ROH etc.



H_2O molecules

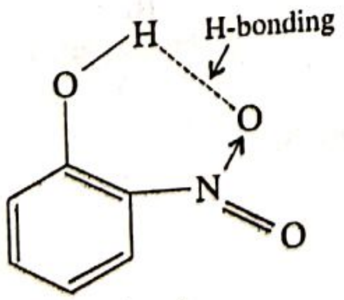
and



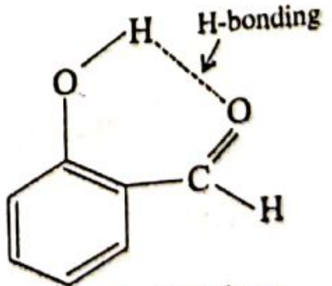
HF molecules

(ii) **Intra-molecular Hydrogen - bonding :** If the hydrogen bonding takes place within the molecule itself, then that is called intra-molecular Hydrogen bonding.

Example : Salicyldehyde, Ortho - nitro phenol etc.



O-nitro phenol



Salicyldehyde or
Ortho hydroxyl benzaldehyde

5\. (a) If $T\Delta S > \Delta H$ the reaction will be spontaneous.

(b) Bronsted base	Conjugate acid
(i) NH_3	NH_4^+
(ii) HCO_3^-	H_2CO_3
(iii) CH_3COO^-	CH_3COOH
(iv) $H_2PO_2^-$	H_3PO_2

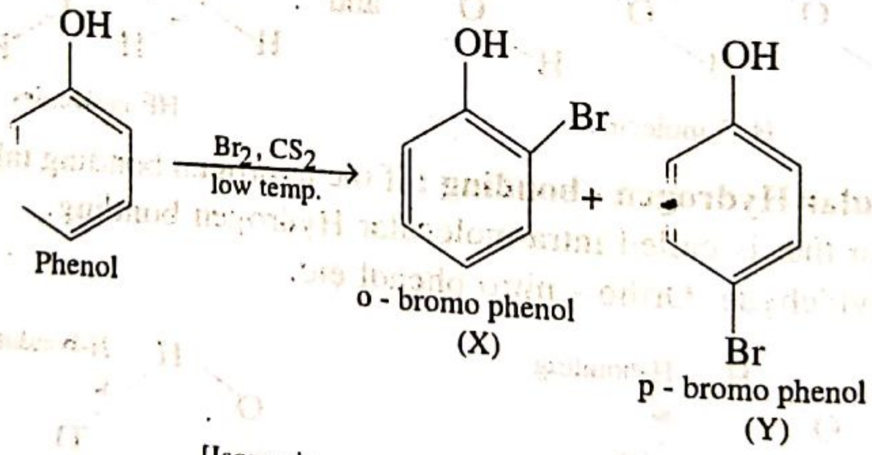
6. Co-ordination compounds exhibits colour, which is attributed to the crystal field theory, corresponding to the d - d transition of elements.

In case of $[\mathrm{Ti}(H_2O)_6]^{3+}$, excitation of an electron from the empty state will absorb light and will get excited from t_{2g} to e_g.

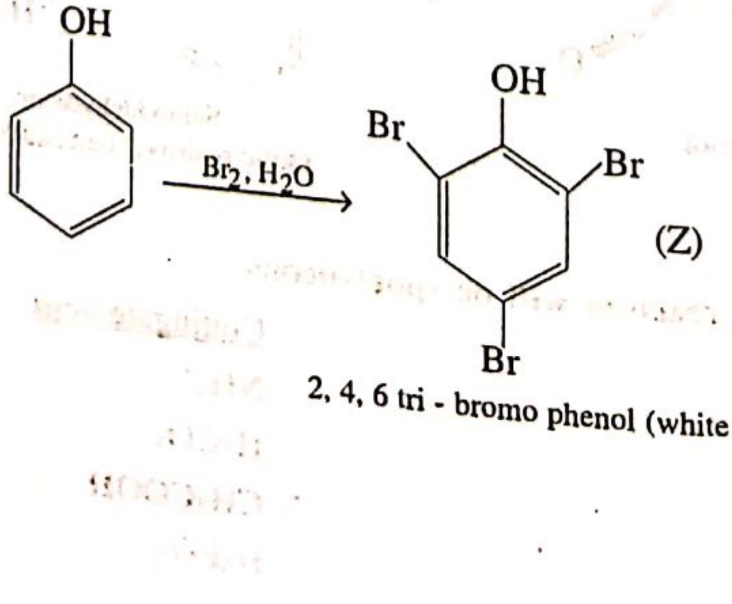
When light corresponding to the energy of the yellow - green region is absorbed by the complex, this would excite the electron from t_{2g} level to the e_g level $\left(t_{2g}^{1}e_g^{0} \rightarrow t_{2g}^{0}e_g^{1}\right)$. Thus the complex is violet in colour. On heating, water molecules are removed from the complex. Therefore, in the absence of ligands there is no crystal field splitting and substance become colourless as in case of $[\mathrm{Ti}(H_2O)_6]Cl_3$ when water molecules are removed it becomes colourless.

GROUP - C
(Long Answer Type Questions)

7. (a)

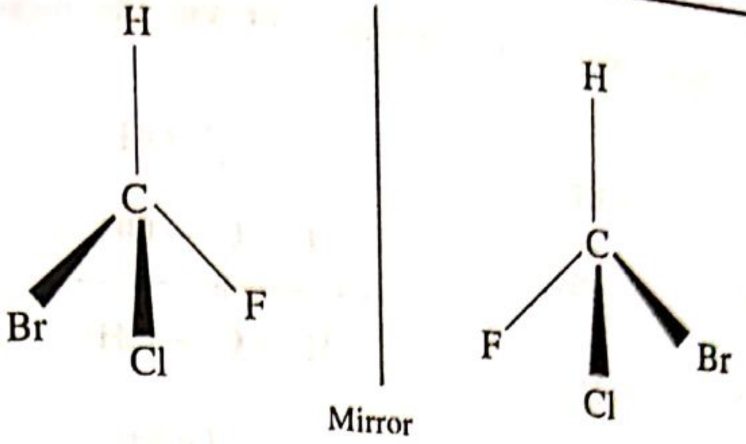


[Isomeric mono bromo phenols]



2, 4, 6 tri - bromo phenol (white ppt.)

(b)



Enantiomeric forms of fluorochlorobromomethane

Enantiomerism : It is evident from the picture that, these mirror images cannot be superimposed. The original compound (left one) and its mirror image (right one) are having different spatial arrangement of atoms around the central carbon atom and should be considered as stereoisomers. These stereoisomers which are non - superimposable mirror images of each other are known as enantiomers.

Therefore, we must remember that chirality is the most fundamental condition of enantiomerism.

Characteristics of Enantiomers

Enantiomers do exhibit the following characteristics—

(i) Enantiomers have similarities in their physical properties such as melting and boiling points, solubilities, refractive indices etc although they have difference in their optical properties like direction of rotation of plane polarized light.

(ii) They have identical chemical properties except the rate of reaction at which two enantiomers react with same other optically active compound.

(iii) Enantiomers differ in their biological properties. For example, animal metabolism is assisted by (+) sugar and (–) sugar is not metabolized at all.

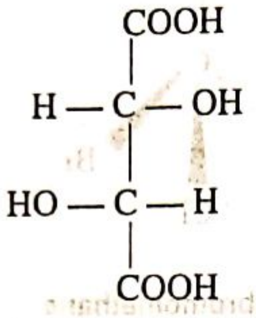
(iv) Although enantiomers are optically active when they exist in one particular form (+) or (–) but after mixing them in equal amount, the racemic mixture is formed which becomes optically inactive.

As an example (+) and (–) lactic acid are individually optically active but the reacemic mixture (±) lactic acid is optically inactive.

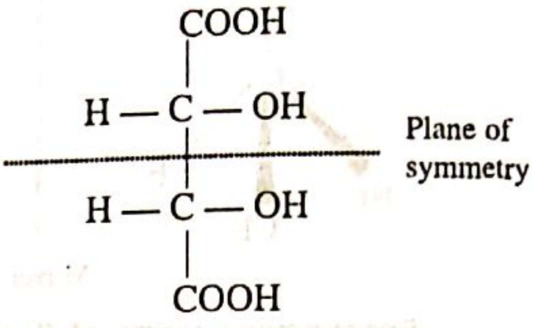
Diastereomerism : Stereoisomers of a compound which are neither mirror images of each other nor superimposable are known as diastereomers and the phenomenon is called diastereoisomerism.

Diastereomers differ in their configuration. One of them possess chirality but the other does not. Therefore, one of the diastereoisomers is optically active but the other is optically inactive.

Example : d - tartaric acid or l - tartaric acid and the meso form tartaric acid are diastereomers.



d - tartaric acid (Chiral)



Meso - tartaric acid (Achiral)

Characteristics of Diastereomers : As the diastereomers have different configuration, they may possess different physical as well as chemical properties, such as —

(i) Diastereomers have different physical properties like melting point, solubility, density, specific rotation etc.

(ii) Diastereomers possess similar chemical properties although the rate at which they react with other optically - active substances may vary.

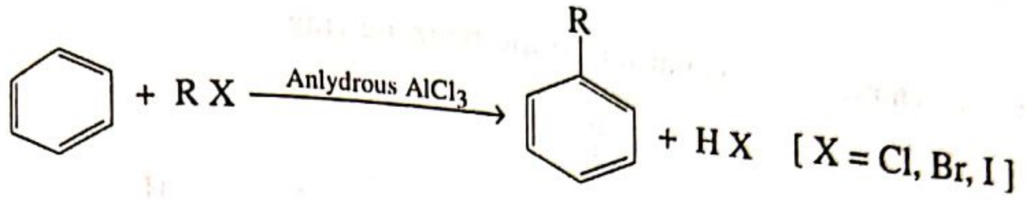
(iii) Stereoscopic characterization, specially the NMR and mass spectra of diastereomers may have difference.

Comparison of Enantiomers and Diastereomers

Enantiomers	Diastereomers
1. Enantiomers have mirror image relationship.	1. Diastereomers do not have any mirror image relationship.
2. They have similarities in physical properties	2. They possess difference in physical properties.
3. Enantiomers can show optical rotation to the same extent but in opposite direction.	3. Diastereomers may show optical rotation in the same or opposite directions but to the same extent.
4. These cannot be separated by the methods like fractional distillation, absorption chromatography etc.	4. These can be separated by these methods.
5. Enantiomers have identical chemical properties but they behave differently towards other optically active substances.	5. Diastereomers possess identical chemical properties but show difference in the rate of reaction with other optically active compounds.

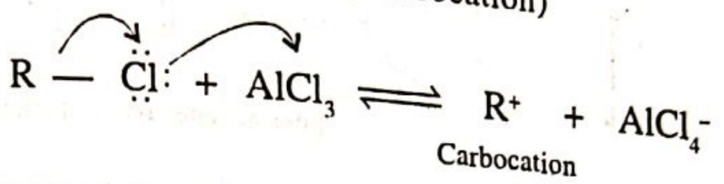
(c) **Frediel - Crafts Reaction :** Frediel - Crafts reactions are of two types, Alkylation and Acylation. Alkylation is done by treating benzene with an alkyl halide in presence of a Lewis acid. Acylation is carried out by treating benzene with an acid halide in presence of a Lewis acid.

Alkylation : The electrophile involved in this reaction is a carbocation (R^+) which is produced by the reaction between the Lewis acid $AlCl_3$ with a 2° or 3° alkyl halide. 1° alkyl halide is not considered as a reactant as it does not produce the required carbocation while reacting with Lewis acid $AlCl_3$.

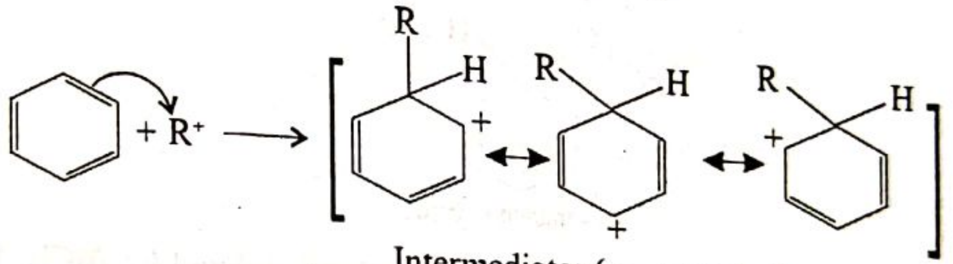


Mechanism

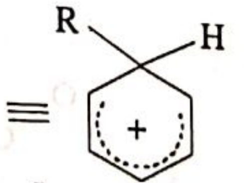
Step I : Formation of Electrophile R^+ (Carbocation)



Step II : Attachment of the carbocation to benzene ring

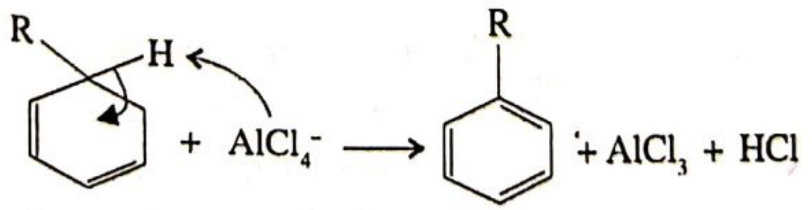


Intermediates (σ - complex)

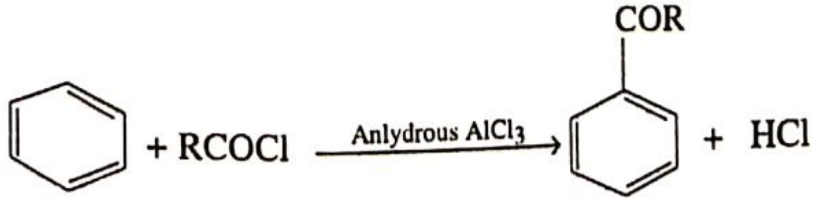


Resonance hybrid

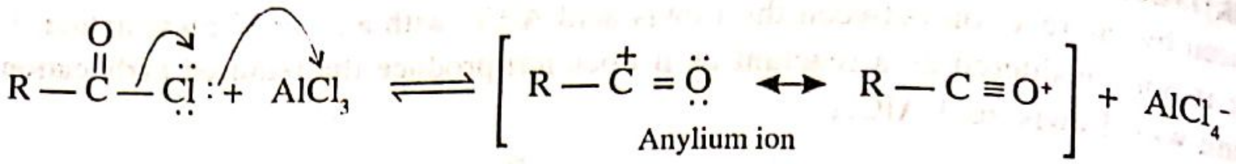
Step III : Elimination of proton from the intermediate. This process is assisted by $AlCl_4^-$ ion helping the intermediate to regain its aromaticity.



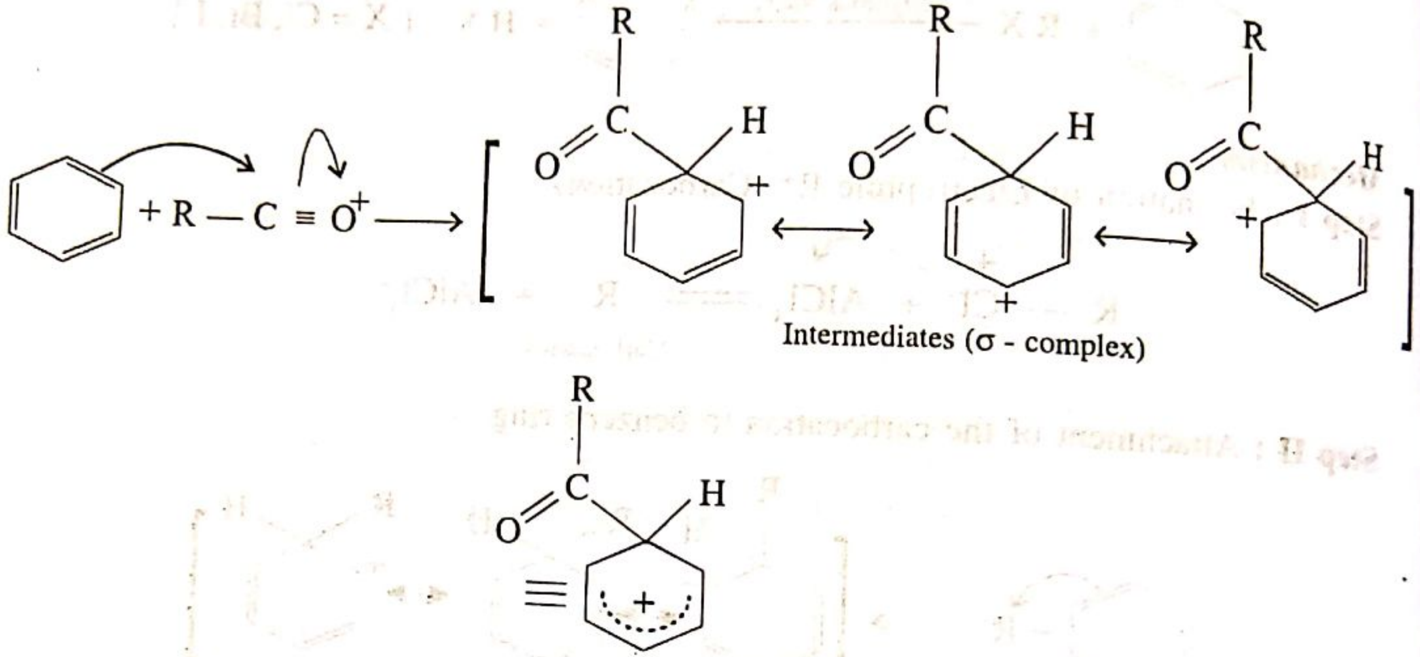
Acylation : The electrophile involved in this process is an Acylium ion (RCO^+) which is generated by the reaction between an Acyl halide and Lewis acis ($AlCl_3$).



Step I : Formation of Electrophile RCO⁺ (Acylium ion)

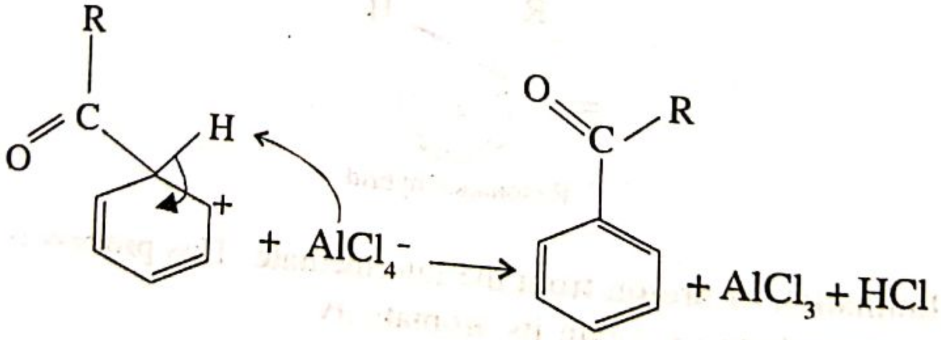


Step II : Attachment of Acylium ion to the benzene ring.


Intermediates (σ - complex)

Resonance hybrid

Step III : Elimination of proton from the intermediate assisted by $AlCl_4^-$ ion helping the intermediate to regain the aromaticity.



(d) (i) $H_3C-CH=CH_2 \xrightarrow[HBr]{(PH-CO-O)_2} H_3C-CH_2-CH_2Br$

(major product) 80%

+

$H_3C-CHBr-CH_3$

(minor product) 20%

In presence of organic peroxide, anti - markonikov's addition will be the major product.

(ii)

$$H_3C-CH=CH_2 \xrightarrow{\text{HBr}} H_3C-CHBr-CH_3$$

(major product) 80%

+

$$H_3C-CH_2-CH_2Br$$

(minor product) 20%

In absence of organic peroxides, markonikov's product will be the major product.

(e) Aromaticity

There are several organic compounds which possess similar chemical behaviour as Benzene which are quite different from those of aliphatic and alicyclic compounds. Some of the important characteristic features of aromatic compounds are as follows—

(i) Usually aromatic compounds have cyclic structures.

(ii) X-ray structure and electron diffraction method reveals that these compounds are mostly planar.

(iii) These have unusual stability, i.e.,thay are resistant to oxidation, hydrogenation and low heat of combustion.

(iv) Instead of being unsaturated, they do not undergo addition and substitution reactions easily.

(v) Carbon atoms present in the aromatic structures are sp^2 hybridized. Alternate single and double bonds are present in the structure and π -electrons are delocalized.

The above characteristic properties collectively called aromaticity and the class of compounds possessing these characteristics are termed as aromatic compounds.

8. a) Fundamental vibration frequency (ν) of HCl is related to force constant (k) by equation

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

where μ is reduced mass of HCl. (Frequency is in Hz = s^{-1})

Reduced mass of HCl is given by $\mu = \dfrac{m_H m_{Cl}}{m_H + m_{Cl}}$

where m_H and m_{Cl} are masses of one atom of H and Cl respectively.

Mass of one atom of $H = \dfrac{1gm}{N_A} = \dfrac{1gm}{6.023\times10^{23}} = 1.66\times10^{-24}\, gm$

Mass of one atom of $Cl = \dfrac{35.5gm}{N_A} = \dfrac{35.5gm}{6.023\times10^{23}} = 58.94\times10^{-24}\, gm$

So, reduced mass of $HCl = \dfrac{(1.66\times10^{-24}\,gm)(58.94\times10^{-24}\,gm)}{(1.66+58.94)\times10^{-24}\,gm}$

$$= \frac{97.84\times10^{-48}\,gm^2}{60.6\times10^{-24}\,gm} = 1.614\times10^{-24}\,gm$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{1.614\times10^{-24}\,g}}$$

$$\nu^2 = \frac{1}{4\pi^2}\times\frac{k}{1.614\times10^{-24}\,g}$$

$$k = (4\pi^2\nu^2)\times(1.614\times10^{-24}\,g)$$

$= 4 \times (3.14)^2 \times (8.667 \times 10^{13}\ s^{-1})^2 \times (1.614 \times 10^{-24}\ g)$
$= 4 \times (3.14)^2 \times (75.12 \times 10^{26}\ s^{-2}) \times (1.614 \times 10^{-24}\ g)$
$= 4781.6 \times 10^2\ g\ s^{-2}$
$= 4.7816 \times 10^5\ g\ s^{-2}$

$= 4.78\times10^5\,gs^{-2}$

$= 4.78 \times 10^5$ dyn cm^{-1} (since 1 dyn = 1 g cm s^{-2})

We can express force constant (k) in SI unit, that is in Nm^{-1}

$k = (4.78 \times 10^5) \times (10^{-5}$ N$) \times (10^2$ m$^{-1})$ since 10^5 dyn = 1N
and 10^2 cm = 1m

$= 478$ N m^{-1}

(b) Energy of one photon, $\varepsilon = h\nu$

$$= h\frac{c}{\lambda} \qquad \text{since } c = \nu\lambda$$

If h, c and λ all are taken in SI unit then energy $\in$ will be obtained in joule (J) which is SI unit of energy.

$h = 6.626\times10^{-34}\,Js$, $c = 2.998\times10^8\,ms^{-1}$

$\lambda = 2450\,\text{Å} = 2450 \times 10^{-8}$ cm $= (2450 \times 10^{-8} \times 10^{-2})$m $= 2450 \times 10^{-10}$ m

$$\in = (6.626\times10^{-34}\,Js)\times\frac{(2.998\times10^8\,ms^{-1})}{(2450\times10^{-10}\,m)}$$

$\in = 8.108\times10^{-19}\,J$

Energy of one mole photon, $E = N_A \in$ where N_A is Avogadro number

$$= \left(6.023\times10^{23}\right)\times\left(8.108\times10^{-19} J\right)$$
$$= 48.83 \times 10^4 \text{ J}$$
$$= 488.3 \text{ k J}$$
$$\simeq 488 k J$$

Bond energy of diatomic molecule = 95 kcal / mol.

$$= (95 \times 4.184) \text{ kJ/mol}$$
$$= 397.48 \text{ kJ/mol}$$
$$\simeq 397 k J / mol.$$

To break one mole of diatomic molecule 397 kJ energy is required whereas one mole of photon can supply 488 kJ energy. So the radiation of wavelength 2450Å will not be able to dissociate the diatomic molecule.

(c) From first law of thermodynamics $\Delta U = Q + W$ where W is negative for expansion process following IUPAC convention. In every diabatic process Q = 0. So, for adiabatic process $\Delta U = W$. In reversible expansion appreciable work is produced and ΔU is negative for a adiabatic reversible expansion since W is negative in expansion process. Expansion of solids or liquids need not be considered because volume increase of solids and liquid is neglible. For ideal gas internal energy (U) depends only on temperature and $\Delta U = C_v \Delta T$. Since in adiabatic reversible expansion ΔU is negative it is seen that for this process ΔT is negative (because C_v is always positive) $\Delta T = T_{final} - T_{initial}$. For adiabatic reversible expansion of ideal gas T_{final} is less than $T_{initial}$ ($T_f < T_i$). So, in adiabatic reversible expansion there occurs a fall of temperature. (For real gases volume increase has negligible effect on ΔU and there is cooling effect in adiabatic reversible expansion in all cases).

9. (a) Screening constant : In multi-electron atoms, the nuclear charge realized by the outer orbital electrons become less due to the shielding or screening of the inner orbital electrons. This is called shielding or screening effect. The actual amount of nuclear charge felt by an electron is termed as effective nuclear charge. The effective nuclear charge (Z_{eff} or Z^*) is—

$$Z^* = Z - \sigma$$

where Z is the actual nuclear charge and σ is the screening or shielding constant.

The magnitude of screening depends on the number of inner orbital electrons. Greater the number of inner electrons, higher would be the screening effect and consequently the effective nuclear charge felt by the outer orbital electrons will decrease. Hence, we can conclude that with decreasing effective nuclear charge, ionization energy decreases.

Cu (29) has ground state electronic configuration :

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$$

Effective nuclear charge for one (4s) electron is calculated as follows —

No other electron in the same group (4s) = 0

18 electrons in (n – 1) groups, (3s, 3p) and 3d : 0.85 each : 0.85 × 18 = 15.3

10 electrons in groups further left, i.e., $\le (n-2)$

1.0 each : 1.0 × 10 = 10.00

Total (σ) = 25.30

Thus, $Z_{eff} = 29.00 - 25.30$

$= 03.70$

K (19) has ground state electronic configuration

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

∴ No. of electron in the same group (4s) = 0

8 electrons in (n – 1) groups, (3s, 3p) :

0.85 each : 0.85 × 8 = 6.80

10 electrons in groups further left, i.e., $\le (n-2)$

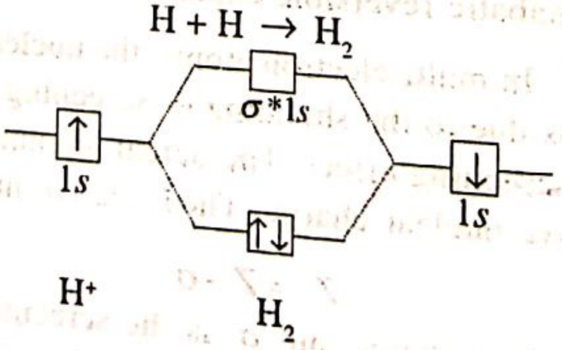
1.0 each : 1.0 × 10 = 10.00

Total (σ) = 16.80

Thus, $Z_{eff} = 19.00 - 16.80$

$= 02.20$

(b) (i) *Hydrogen molecule, H_2* : Hydrogen molecule (H_2) is formed by the overlap of 1s atomic orbitals of two hydrogen atoms having one electron each. From the overlap of these atomic orbitals, two molecular orbitals viz. bonding and antibonding are generated. In a hydrogen molecule we have total of two electrons which are accomodated in lower energy, bonding (σ_{1s}) molecular orbital (according to Pauli's exclusion principle these two electrons have opposite spins).



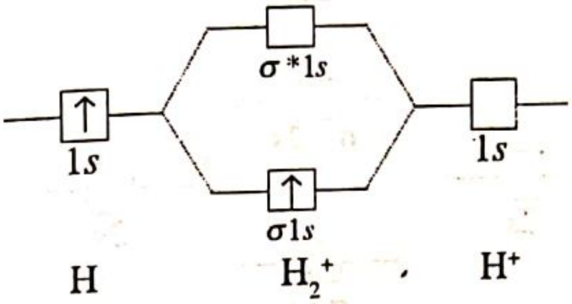
Molecular orbital energy level diagram for H_2 molecule.

Hence, molecular orbital electronic configuration of H_2 molecule = $\sigma_{1s}{}^2$ and Bond order $= \frac{1}{2}(N_b - N_a) = \frac{1}{2}(2-0) = 1$

As the bond order is greater than zero, hence H_2molecule is stable and it exists. H_2 molecule is diamagnetic in nature as both the electrons are paired.

Hydrogen molecule ion H_2^+ : It has only one electron in bonding σ_{1s} orbital. Therefore, the electronic configuration of H_2^+ is thus $\sigma_{1s}{}^2$. The bond order $=\frac{1}{2}(N_b-N_a)=\frac{1}{2}(1-0)=\frac{1}{2}$.

The positive value of the bond order indicates that the hydrogen molecular ion is stable. H_2^+ ion is paramagnetic due to the presence of a single electron.



Molecular orbital energy level diagram for H_2^+ ion.

Hydrogen molecule ion H_2^- : This is formed when a hydrogen atom having one electron in 1s atomic orbital combines with a hydride ion H^- having two electrons. Therefore, H_2^- ion possess total 3 electrons. The electronic configuration of H_2^- ion can be represented as —

$$H_2^- = \left(\sigma_{1s}{}^2\right)\left(\sigma_{1s}{}^{*1}\right)$$

The bond order $=\frac{1}{2}(N_b-N_a)=\frac{1}{2}(2-1)=\frac{1}{2}$

The positive value of bond order indicates that the hydrogen molecule ion H_2^- is stable. It is paramagnetic due to the presence of unpaired electron in antibonding MO.

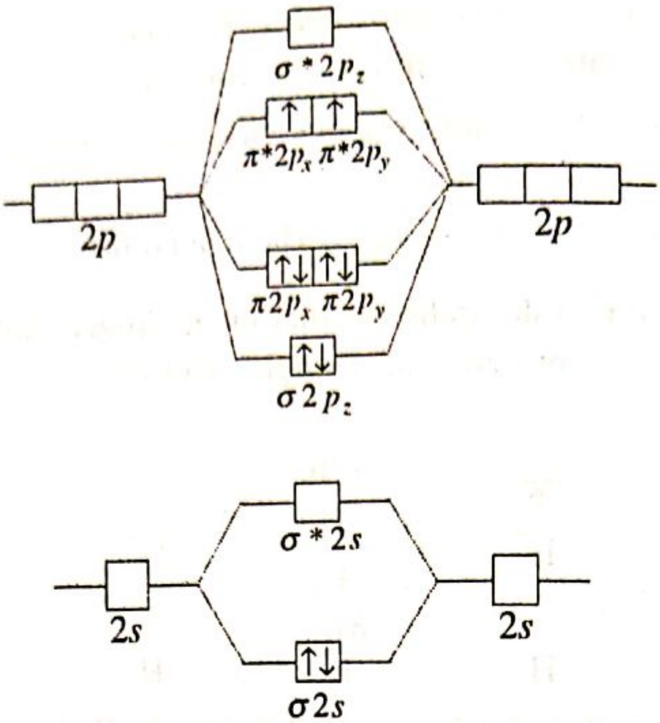
(ii) Oxygen molecule (O_2) : Each oxygen atom has electronic configuration $1s^2\ 2s^2\ 2p^4$. So, each oxygen atom contains 8 electrons and total 16 electrons are there in O_2 molecule. The arrangement of these 16 electrons are as follows —

$$\left(\sigma_{1s}{}^2\right)\left(\sigma_{1s}{}^{*2}\right)\left(\sigma_{2s}{}^2\right)\left(\sigma_{2s}{}^{*2}\right)\left(\pi_{2p_z}{}^2\right)\left(\pi_{2p_x}{}^2\right)\left(\pi_{2p_y}{}^2\right)\left(\pi^*_{2p_x}{}^1\right)\left(\pi^*_{2p_y}{}^1\right)$$

Therefore, the bond order $=\frac{1}{2}(N_b-N_a)=\frac{1}{2}(8-4)=2$

[Electron present in σ_{1s} and $\sigma_{1s}{}^*$ are not taken into consideration]

The positive value of bond order means the molecule O_2 is stable . It is paramagnetic in nature due to the presence of two unpaired electrons in $\pi_{2p_x}{}^*$ and $\pi_{2p_y}{}^*$ orbitals.



Molecular orbital energy level diagram for O_2

A comparison between O_2, O_2^+, O_2^- and O_2^{2-} is given below ——

Species	*Total no. of electron*	*Molecular orbital configuration*	**Bond order**	*Magnetic character*
O_2	16	$KK(\sigma_{2s}^{2})(\sigma^{*}_{2s})^{2}(\sigma^{2}_{2p_z})(\pi_{2p_x}^{2})(\pi_{2p_y}^{2})(\sigma^{*}_{2p_y})^{1}(\sigma^{*}_{2p_x}{}^{1})$	2	Paramagnetic
O_2^+	15	$KK(\sigma_{2s}^{2})(\sigma^{*}_{2s})^{2}(\sigma^{2}_{2p_z})(\pi_{2p_x}^{2})(\pi_{2p_y}^{2})(\sigma^{*}_{2p_y})^{1}$	2.5	Paramagnetic
O_2^-	17	$KK(\sigma_{2s}^{2})(\sigma^{*}_{2s})^{2}(\sigma_{2p_z}^{2})(\pi_{2p_x}^{2})(\pi_{2p_y}^{2})(\sigma^{*}_{2p_x}{}^{2})(\sigma^{*}_{2p_y})^{1}$	1.5	Paramagnetic
O_2^{2-}	18	$KK(\sigma_{2s}^{2})(\sigma^{*}_{2s})^{2}(\sigma_{2p_z}^{2})(\pi_{2p_x}^{2})(\pi_{2p_y}^{2})(\sigma^{*}_{2p_x}{}^{2})(\sigma^{*}_{2p_y})^{2}$	1	Diamagnetic

All the above species are stable as bond orders are positive for them.

Bond order for O_2^+ is highest and O_2^{2-} is lowest. Thus O_2^{2-} is the most stable species and in order of decreasing stability is $O_2^+ > O_2 > O_2^- > O_2^{2-}$.

O_2, O_2^+ and O_2^{2-} are paramagnetic due to the presence of unpaired electrons while O_2^{2-} ion is diamagnetic because of having all paired electrons.

(c) In p-block elements last electron (valence electron) enters the p-orbitals. In p-block elements some are metals, some are non-metals and some are metalloids.

Metals — Al, Ga, Tl, Bi

Nonmetals — B, C, N, S

Metalloids — As, Sb, Si, Ge

Types of Oxides of p-block elements are described below and two examples each of different types are also given.

Basic oxides — Bi_2O_3 , Tl_eO_3

The basic oxides react with acids to form salts

$$Bi_2O_3 + 6HCl \rightarrow 2BiCl_3 + 3H_2O$$

$$Tl_2O_3 + 3H_2SO_4 \rightarrow Tl_2(SO_4)_3 + 3H_2O$$

Acidic Oxides — CO_2 , SO_2

These oxides are said to be acidic oxides because they react with water to form acid.

$$CO_2 + H_2O \rightarrow H_2CO_3 \text{ (carbonic acid)}$$

$$SO_2 + H_2O \rightarrow H_2SO_3 \text{ (sulphurous acid)}$$

Amphoteric Oxides — Al_2O_3 , PbO

These oxides have both basic and acidic properties. These oxides react with both strong acids and strong bases.

$$Al_2O_3 + 6HCl \rightarrow 2Al^{3+} + 6Cl^- + 3H_2O$$

$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na^+ + 2\left[Al(OH)_4\right]^-$$

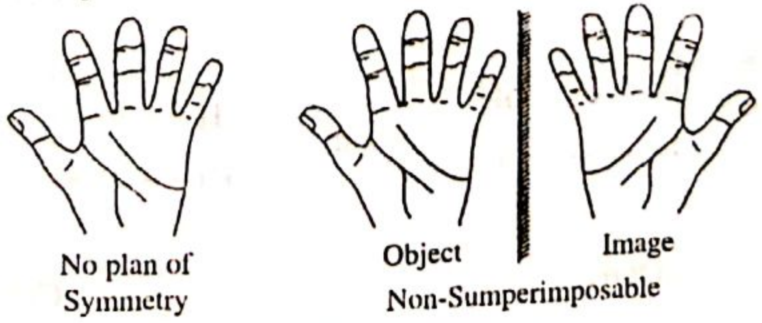
$$PbO + 2HNO_3 \rightarrow Pb^{2+} + 2NO_3^- + H_2O$$

$$PbO + NaOH \rightarrow Na^+ + [PbO \cdot OH]^-$$

Note : N_2O, NO, CO have no acidic or basic properties. These oxides are called neutral oxides.

10. (a) There are many organic and inorganic compounds available having similar chemical as well as physical properties but they differ in their behaviour towards the action of plane polarised light. Such compounds are known as optically active compounds and this phenomenon is called optical activity. Compounds, which can rotate the plane polarized light in right or clock-wise direction are called dextro-rotatory and are represented as d or (+) form ; whereas the compounds which can rotate it towards left or anti-clockwise direction are said to be levo-rotatory and represented as l or (–) form. Those isomers can exhibit optical isomerism. In this regard, let us discuss something about plane polarized light and optical activity.

Chial structures : An object or a structure becomes chiral (or disymmetric) if it possess no element of symmetry and if it is not superimposable to its mirrot image. For example, human hand is a chiral object as it has no plane of symmetry or other elements of symmetry and it cannot be superimposed on its mirror image as shown in the figure

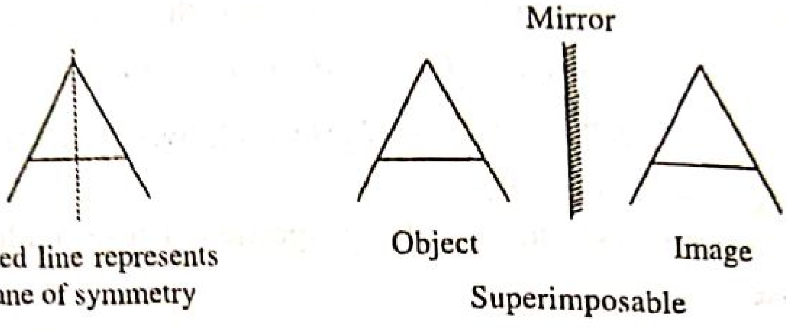


Chiral structure

Therefore a pair of hands or a pair of gloves are example of chiral objects. Few alphabets like E, F, P etc. are also common example of chiral objects.

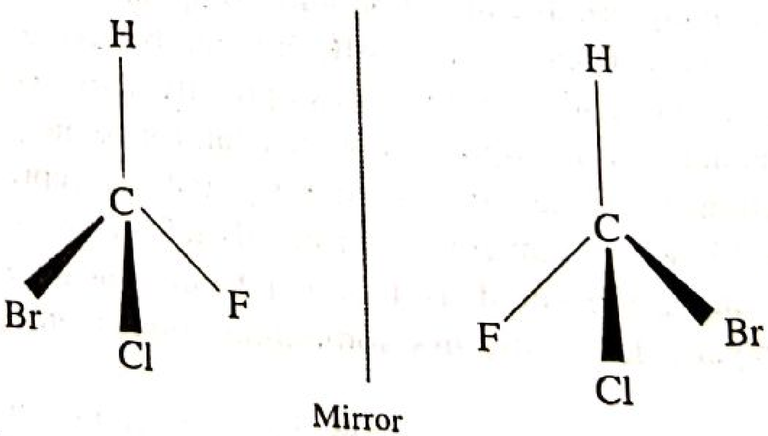
The origin of the term 'chiral' is coming from Greek word cheir (means hand), i.e., the relationship that exists between the left and right hands.

In recent time, we use the term disymmetric and dissymmetry in place of chiral are normally optically active.



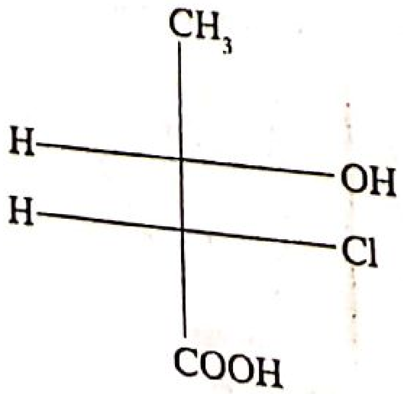
Achiral structure

Origin of Chirality in organic compounds : An organic compound consisting of carbon atoms become chiral when all four different atoms or group of atoms are attached to a hybridized carbon . Such a carbon atom was previously known as asymmetric carbon. This carbon centre is called chiral carbon and the molecule obtained is a chiral molecule possessing chirality or dissymmetry. As an example, we can consider a molecule containing sp^3 hybridized carbon atom which is attached to four different atoms, e.g. Cl, F, Br and H. Therefore, this molecule becomes chiral and dissymmetric

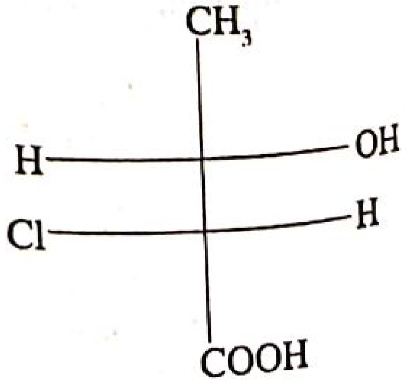


Enantiomeric forms of fluorochlorobromomethane

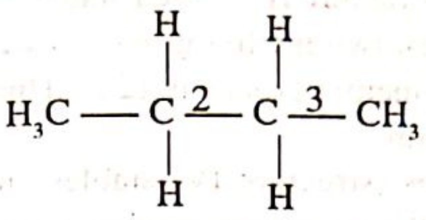
(b)



and



(c) Conformations of n - Butane :



$H_3C-\overset{H}{\underset{H}{C}}\overset{2}{-}\overset{H}{\underset{H}{C}}\overset{3}{-}CH_3$

The $C_2 - C_3$ bond of n-butane is quite similar to ethane molecule with one hydrogen atom of each carbon is replaced by a methyl group. It has a number of conformations due to the relative orientation of two methyl groups with respect to each other.

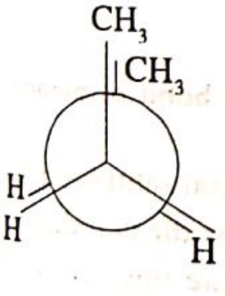
The most possible conformations of n-butane are—

(i) **Fully eclipsed :** In this conformation, the methyl groups and hydrogen atoms attached to C_2 and C_3 carbon atoms are completely eclipsed to each other (Structure I). This is the conformation in which the dihedral angle between the methyl groups is zero degree (0°).

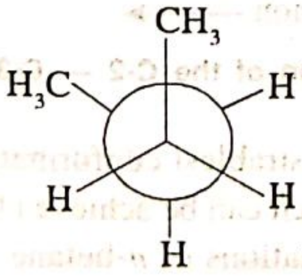
(ii) **Gauche :** On rotating $C_2 - C_3$ single bond by 60°, the conformation we get is a staggered form where methyl groups are apart from each other with an dihedral angle of 60° (Structure II). This staggered conformation is also called Gauche conformation. Two such Gauche conformations are possible.

(iii) **Eclipsed :** On rotating $C_2 - C_3$ bond by further 60° from Gauche conformation, we get Eclipsed conformation in which methyl group attached to one carbon is eclipsed with hydrogen atom attached with back carbon (Structure III). The dihedral angle between two methyl groups in 120°.

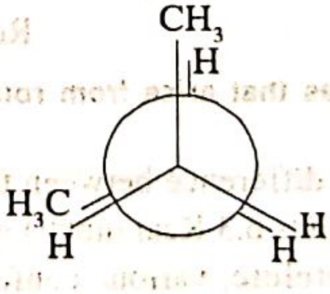
(iv) **Anti :** Rotating the $C_2 - C_3$ single bond by further 60° from eclipsed conformation we reach a conformation in which the two methyl groups are farthest from one another with an dihedral angle of 180°. (Structure IV).



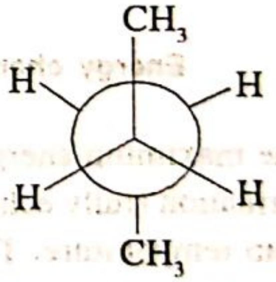
I



II



III



IV

Stability order of conformations of n-butane

The stability order of conformations of n-butane follows the order—

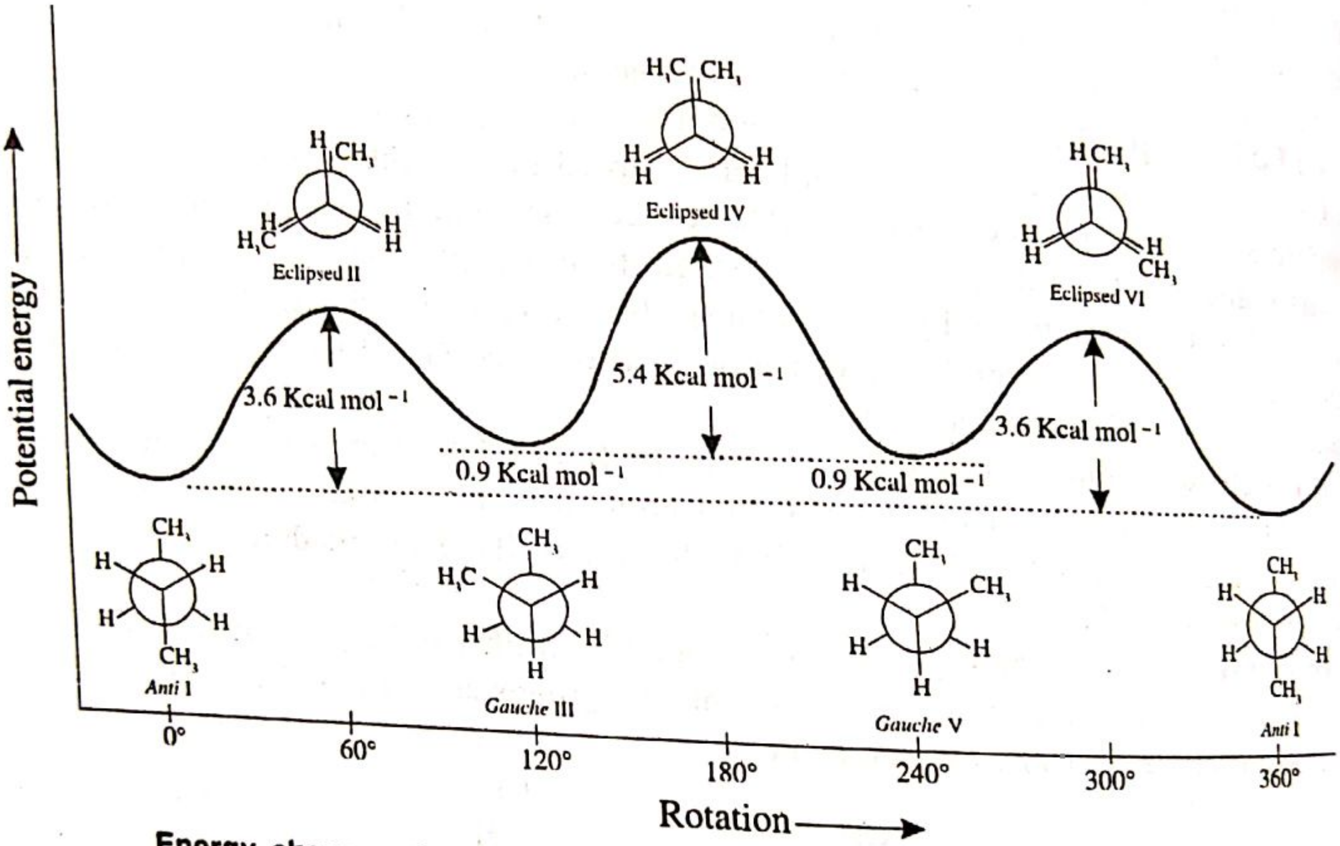
Anti ⟩ Gauche ⟩ Eclipsed ⟩ Fully eclipsed

(i) The fully eclipsed form (structure I) is least stable with highest potential energy as the two bulky methyl groups are closest to each other in this conformation. Due to the presence of torsional and steric strain, this conformation has highest energy and minimum stability.

(ii) The eclipsed conformation (Structure III) is stabler than fully eclipsed form because the distance between two methyl groups is greater in this conformation (dihedral angle 60°) compared to fully eclipsed conformation (dihedral angle 60°).

(iii) Gauche conformation (Structure II) is even stabler than eclipsed conformations because the repulsive interaction between two methyl groups is weaker than eclipsed conformation as the dihedral angle between two methyl groups is 120°. This conformation contains slight steric strain but free of torsional strain.

(iv) The anti conformation is (structure IV) stablest among all as the two methyl groups are farthest (dihedral angle 180°) from one another resulting least steric repulsion between each other. This form is free of torsional as well as steric strain.



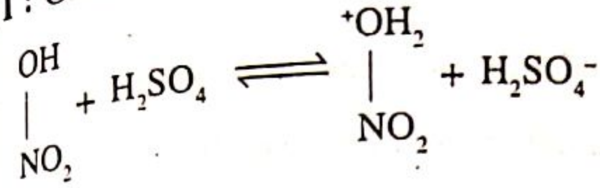
Energy changes that arise from rotation of the C-2 — C-3 bond of butane.

The maximum energy difference between the strablest conformation (anti) and least stable conformation (fully ecliped is 6.3 Kcal mol^{-1}) which can be achieved by the colliding molecules at room temperature. Therefore, various conformations of *n*-butane are inter-convertable and cannot be isolated. At any moment, *n*-butane remains in the mixture of all possible conformations which exist in dynamic equilibrium to each other. Although the percentage of anti conformation (stablest) will be highest and fully eclipsed (least stable) will be lowest in the mixture.

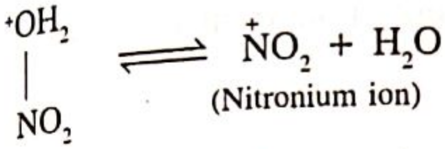
11. (a) **Nitration Reaction :** For nitration reaction in the aromatic system, the mixture of concentrated nitric acid (HNO_3) and concentrated sulphuric acid (H_2SO_4) is used which is also known as mixed acid is used as reagents. The mixed acid very rapidly generates highly reactive nitronium cation (NO_2^+) which acts as an electrophile in this reaction. The widely used and common mechanism is as follows —

Mechanism

Step I : Generation of Electrophile (Nitronium cation, NO_2^+)

(i) 

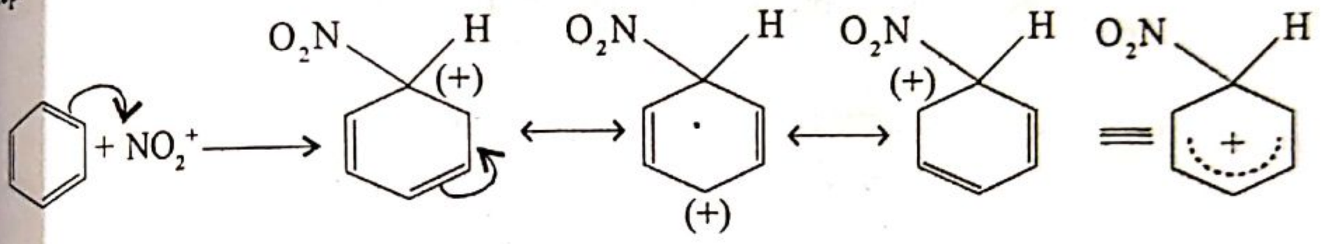
$$HO{-}NO_2 + H_2SO_4 \rightleftharpoons {}^{+}OH_2{-}NO_2 + HSO_4^-$$

(ii) 

$$^{+}OH_2{-}NO_2 \rightleftharpoons \overset{+}{N}O_2 + H_2O$$

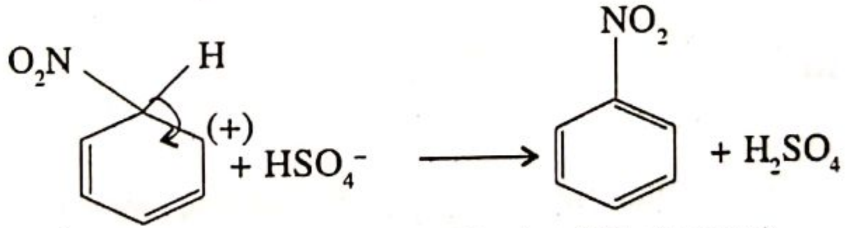
(Nitronium ion)

Step II : Attack by the electrophile nitronium ion (NO_2^+) to the aromatic ring resulting the formation of intermediate arenium ion. This is the slower step and known to be rate determining step.



This arenium ion intermediate is stabilized by the resonance effect.

Step III : Elimination of protons from the arenium intermediate.



Product (Nitro benzene)

This process is assisted by the HSO_4^- ion and the final product regains its aromaticity. This process is also called aromatization.

(b) Condition of spontaneity in terms of entropy for isolated system $\Delta S > 0$

Condition of spontaneity in terms of entropy for non-isolated system $\Delta S_{total} > 0$

ΔS_{total} is called $\Delta S_{universe}$. $\Delta S_{total} = \Delta S + \Delta S_{surrounding}$ where ΔS is entropy change of the system.

Condition of spontaneity in a constant T, P process is $\Delta G_{T,P} < 0$. (This has been derived in Chapter 4, section 4.30)

Condition of spontaneity in a constant T, V process is $\Delta A_{T,P} < 0$ (This has been derived in Chapter 4, section 4.29)

Comparing $\Delta G_{T,P} < 0$ and $\Delta G_{x,y} < 0$ we see x = T and y = P and comparing $\Delta A_{T,V} < 0$ and $\Delta A_{p,r} < 0$ we see p = T and r = V.

(c) <u>Pressure</u> is an intensive property, <u>Concentration</u> is an intensive property, <u>Entropy</u> is an extensive property, <u>Viscosity</u> is an intensive property, <u>Temperature</u> is an intensive property.

12. a) Let the strong acid is HCl. This is fully ionized.

For pH = 5 the concentration of HCl is 10^{-5}(M). When this HCl solution is diluted 100 times the concentration of HCl becomes 10^{-7}(M). So we have to find out pH of 10^{-7}(M) HCl. However in this 10^{-7}(M) HCl solution one should consider the dissociation of water (H_2O) to give some amount of H_3O^+. $C_{H_3O^+}$ is the solution will be given by

$C_{H_3O^+} = C_{HCl} + C_{OH^-}$ because hydronium ion concentration from dissociation of water (H_2O) will be same as the C_{OH^-}.

Since $K_w = C_{OH^-} \times C_{H_3O^+}$ we have

$C_{OH^-} = K_w / C_{H_3O^+}$ (K_w is ionic product of water = 10^{-14} at 25°C)

Therefore, $C_{H_3O^+} = C_{HCl} + \dfrac{K_w}{C_{H_3O^+}}$

$$C_{H_3O^+} = 10^{-7} + \frac{K_w}{C_{H_3O^+}}$$

$$C_{H_3O^+} = 10^{-7} + \frac{10^{-14}}{C_{H_3O^+}}$$

In this equation only unknown quantity is $C_{H_3O^+}$. By solving we can find out the value of $C_{H_3O^+}$. It can be seen that $C_{H_3O^+} = 1.618 \times 10^{-7}\,(M)$

So, $pH = -\log_{10} C_{H_3O^+}$

$$= -\log_{10}\left(1.618 \times 10^{-7}\right)$$

$$= 6.79$$

If we did not consider the H_3O^+ from water dissociation pH would be 7. But for very dilute solution of HCl (of concentration 10^{-7} M) we must not ignore some amount of H_3O^+ form water dissociation.

(b) Daniel Cell is represented as $Zn(s)\left|Zn^{2+}(aq)\right|\left|Cu^{2+}(aq)\right|Cu(s)$

The cell reaction for 2F electricity drawn is

$$Zn(s) + Cu^{2+}(aq) = Zn^{2+}(aq) + Cu(s)$$

Nernst equation for the cell reaction is

$$E = E^0 - \frac{RT}{2F}\ln\frac{a_{Zn^{2+}}a_{Cu}}{a_{Zn(s)}a_{Cu^{2+}}}$$

$$= E^0 - \frac{RT}{2F}\ln\frac{C_{Zn^{2+}}}{C_{Cu^{2+}}}$$ assuming activity of ion equal to concentration of the ion and activity of solid = 1

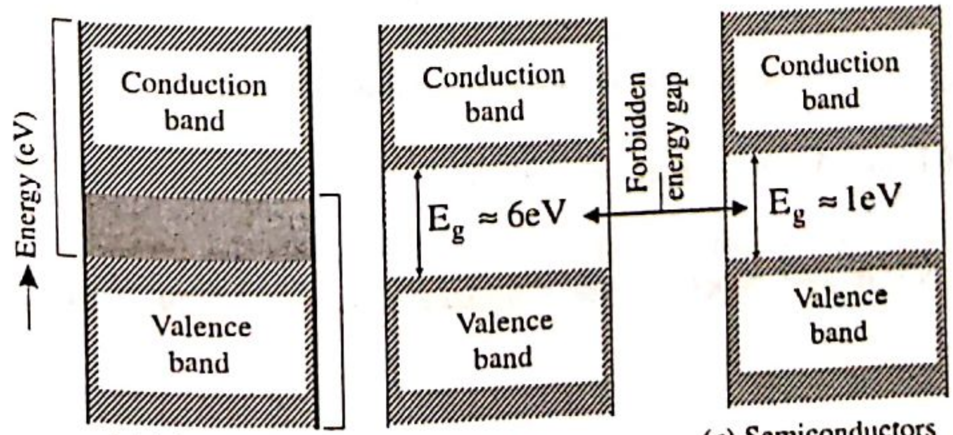
The Nernst equation shows that if concentration fo Zn^{2+} is increased cell potential E decreases. [$\Delta G_{T.P} = -nFE$. For spontaneous reaction E is positive and ΔG is negative. Decrease of E with increase of concentration of Zn^{2+} makes ΔG less negative. The tendency of forward reaction is diminished and this is an accord with Le-Chatelir principle that if a product species is added the reaction is shifted to the left side.]

(c) Based on band structure, solids can be classified into three different categories ——
(i) Metals, (ii) Insulators, (iii) Semiconductors

We know in a crystalline solids, large number of molecules are arranged in a definite pattern. Each electron of an atom in a molecule has a definite energy level. These energy levels can further split into a large number of energy levels due to the influence made by adjacent nucleii of other atoms. Hence, the original energy level of an electron splits into closely spaced energy level of small difference in energy to produce an energy band.

When a part of the band is occupied by the valence electrons, it is called valence band, the next energy level is called conduction band which is either completely vacant or partially filled up by electrons. The energy gap between conduction band and valence band is called "Forbidden" energy gap.

(i) Metals : The conduction shown by metals is due to the presence of free electrons. For metals, there is no forbidden energy gap between valence band and conduction band. The valence band and conduction band actually overlap with each other and possess same energy. Therefore electrons can travel from valence band to conduction band without assistance of any external energy such as heat or light. Therefore, a metal contains large number of free electrons in the conduction band as can act as a good conductor.

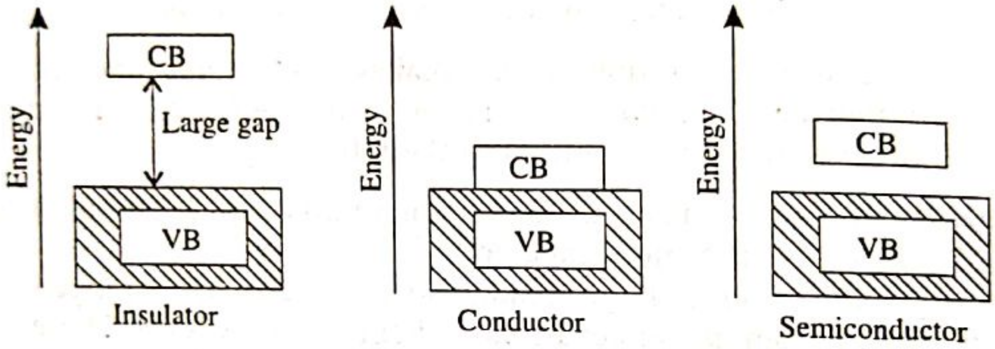


(a) Metals (conductors) (b) Insulators (c) Semiconductors

Energy band diagram.

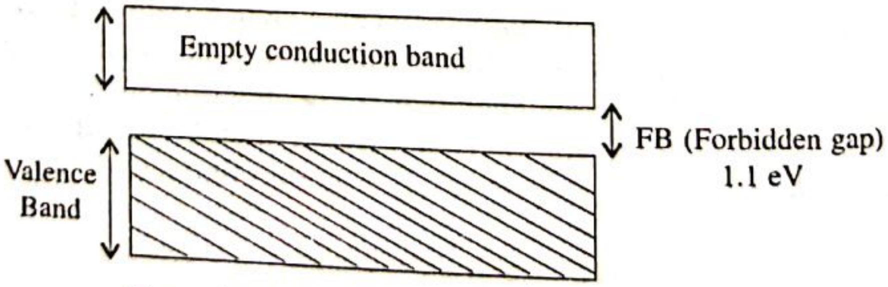
(ii) Insulators : Insulators are having very poor electrical conductivity. For insulators the forbidden energy gap very wide. Therefore, a large amount of energy is required to promote electrons from valence band to conduction band. Hence, it is almost impossible to find any electron in the conduction band and as a consequence no current flows through such materials and behaves like insulators.

(iii) Semiconductors : In case of semiconductors, the energy gap between valence band and conduction band is narrow (gap is smaller than insulators) and hence the electrons can be promoted from valence band (VB) to conduction band (CB) by applying some amount of thermal energy or by some other means.



Band gap diagrams for Insulators, Conductors and Semiconductors

Semiconductors are solids which have low conductivity at normal temperature but the conductivity increases with temperature. Conductivity of semiconductors belongs in between conductors and insulators. The forbidden energy gap between valence band (VB) and conduction band (CB) is much narrower than the insulators. The value of forbidden energy is 1.1 eV for Silicon and 0.7 eV for Germanium.



Energy band for pure silicon (Semiconductors)

(d) See 7(C) of Long Answer Type questions

(e) See chaper 2 for principle, section 2.21
Application of NMR and MRI — See Chapter 2, section 2.29, 2.29.1

MAULANA ABUL KALAM AZAD UNIVERSITY OF TECHNOLOGY, WEST BENGAL

Paper Code : BS-CH-101

PUID : 01034 (To be mentioned in the main answer script)

CHEMISTRY – I

Time Allotted : 3 Hours

Full Marks : 70

The figures in the margin indicate full marks.
Candidates are required to give their answers in thier own words as fas as practicable.

Group - A
(Multiple Choice Type Questions)

1. Choose the correct alternatives for any *ten* of the following : $10 \times 1 = 10$

(i) Energy required to remove an electron from outermost shell of an isolated gaseous atom is called

(a) potential energy
(b) kinetic energy
(c) electron affinity
(d) ionization energy.

(ii) At inversion temperature Joule-Thomson coefficient is

(a) zero
(b) positive
(c) negative
(d) none of these.

(iii) If uncertainty in position and momentum are equal, the uncertainty in velocity is

(a) $\sqrt{h/\pi}$
(b) $\frac{1}{2m}\sqrt{h/\pi}$
(c) $\sqrt{h/2\pi}$
(d) none of these.

(iv) For transition metal octahedral complexes, the choice between high spin and low spin electronic configuration arises only for

(a) d^1 to d^3 complexes
(b) d^4 to d^7 complexes
(c) d^8 to d^9 complexes
(d) d^1, d^2 and d^8 complexes.

(v) Which one of the following correctly represents the formation of bonding molecular orbital from the atomic orbitals having wave functions ψ_A and ψ_B ?

(a) $\psi_A \times \psi_B$
(b) ψ_A / ψ_B
(c) $\psi_A + \psi_B$
(d) $\psi_A - \psi_B$.

(vi) IR spectra detects

(a) functional group (b) unsaturation

(c) number of protons (d) nature of nuclei

(vii) What is the fingerprint region range in IR ?

(a) 4000 – 400 cm^{-1} (b) 4000 – 1600 cm^{-1}

(c) 1600 – 400 cm^{-1} (d) No range.

(viii) During the motion, if the centre of gravity of molecule changes, the molecule possesses

(a) Electronic energy (b) rotational energy

(c) Translational energy (d) Vibrational energy.

(ix) The strength of van der Waals forces depends upon

(a) size of the molecule

(b) molecular structure

(c) number of electrons present in the molecule

(d) all of these.

(x) In which of the following reactions is $\Delta H = \Delta U$?

(a) $H_2(g)+I_2(g)\rightarrow 2HI(g)$

(b) $KI(aq)+I_2(s)\rightarrow KI_3(aq)$

(c) $6NaOH(aq)+3Cl_2(g)\rightarrow 5NaCl(aq)+$

(d) $NaClO_3(aq)+3H_2O(l)$

d) $N_2O_4(g)\rightarrow 2NO_2(g)$.

(xi) Water at 4°C, under pressure of 1 atm, $(C_p - C_v)$ is

(a) positive (b) negative

(c) zero (d) R.

(xii) In which of the following processes does the entropy decrease ?

(a) The dissolving of NaCl in water

(b) The evaporation of water

(c) The conversion of $CO_2(g)$ into dry ice

(d) When one dozen marbles are taken out of a small bag and dropped on the ground.

GROUP - B

(Short Answer Type Questions)

Answer any *three* of the following. 3 × 5 = 15

2. Explain the following reactions with a suitable example :

(a) Wolff-Kishner reduction

(b) Cannizzaro reaction. 3 + 2

3\. (a) State the reason for the presence of only one electron in the 4*s* subshell of chromium?

(b) Which of the following has larger size and why?

(i) Mg^{2+} (ii) N^{3-}.

2 + 3

4\. (a) Give molecular orbital energy level diagram of CO. Write its electronic configuration, magnetic behaviour and bond order.

(b) Discuss types and conditions for hydrogen bonding.

3 + 2

5\. (a) For a reaction both ΔH and ΔS are positive. Under what conditions will the reaction be spontaneous ?

(b) What will be the conjugate acids for the following Bronsted bases ? NH_3., HCO_3^-, CH_3COO^-, $H_2PO_2^-$.

1 + 4

6\. Why violet coloured $[Ti(H_2O)_6]Cl_3$ becomes colourless when heated ?

GROUP - C

(Long Answer Type Questions)

Answer any *three* of the following. 3 × 15 = 45

7\. (a) Phenol on treatment with Br_2 in CS_2 at low temperature gives two isomeric monobromophenols *X* and *Y*. But phenol on treatment with bromine water gives a white precipitate Z. Identify the products *X*, *Y* and *Z* with chemical reactions. 6

(b) What do you mean by enantiomer and diastereomer ? Differentiate them with examples. 4

(c) Give one example of each of Friedel-Crafts' alkylation and acylation reaction. 2

(d) Predict the major product(s) of the following reactions and explain their formation: 2

(i) $H_3C-CH=CH_2 \xrightarrow[\text{HBr}]{(PH-CO-O)_2}$

(ii) $H_3C-CH=CH_2 \xrightarrow{\text{HBr}}$

(e) Write down the criteria for aromaticity. 1

8\. (a) Calculate the force constant for the bond in HCl from the fact that the fundamental vibration frequency is $8.667 \times 10^{13}\ s^{-1}$.

(b) Calculate the energy of one photon of light of wavelength 2450Å. Will it be able to dissociate a bond in diatomic molecule which absorbs this photon and has a bond energy equal to 95 kcal per mole ?

(c) "All adiabatic reversible expansions lead to a fall of temperature."—Comment or justify. 4 + (3 + 3) + 5

9\. (a) What is screening constant ? Calculate the effective nuclear charge (Z_{eff}) of one 4s electron of the following :

Cu (Z = 29) and K (Z = 19)

(b) Determine the bond order of each member of the following groups, and determine which member of each group is predicted by the molecular orbital model to have the strongest bond :

(i) H_2 , H_2^+, H_2^-

(ii) O_2 , O_2^{2+}, O_2^{2-}

(c) p-block elements form acidic, basic and amphoteric oxides. Explain each property by giving two examples and also write the reactions of these oxides with water.

5+4+6

10. (a) What is the necessary and sufficient condition to exhibit optical activity ?

(b) Draw all the stereo-isomers for the following :

$CH_3CH\ (OH) - CH\ (Cl)\ COOH$

(c) Arrange the different conformations of n-butane in terms of their stability. 5+5+5

11. (a) Nitration is also in absence of H_2SO_4 yet H_2SO_4 has no effect on benzene under the conditions employed. Show the mechanism of nitration of benzene.

(b) What is the condition of spontaneity in terms of entropy ? The condition of spontaneity :

$$\Delta G_{x,y} < 0\ ;\ \Delta A_{p,r} < 0,$$

where G is the Gibbs free energy and A is the Helmholtz free energy. Identify x, y, p and r.

(c) State whether the following properties are extensive or intensive properties : Pressure, Concentration, Entropy, Viscosity, Temperature.

4+(2+4)+5

12. (a) pH of a solution of a strong acid is 5. What will be the pH of the solution obtained after diluting the given solution 100 times ?

(b) Write the Nernst equation for the cell deaction in the Daniel cell. How will the E_{cell} effected when the concentration of Zn^{2+} is increased ?

(c) Draw and explain the energy level diagrams for conductor, semiconductor and insulator.

(d) Explain enantiomers and diastereoisomers with examples.

(e) Write the principle and application of NMR and MRI.

3+3+3+2+4