

CCE(M)/CHM-I/10/2024

CHEMISTRY

(PAPER—I)

Time : 3 hours]

[Full Marks : 250

Please read each of the following instructions carefully before attempting the questions :

- (i) There are **eight** questions divided in **two Sections**.
- (ii) Candidate has to attempt **five** questions in all.
- (iii) Question Nos. **1** and **5** are compulsory and out of the remaining, **three** are to be attempted choosing at least **one** question from each Section.
- (iv) The number of marks carried by a question/part is indicated against it.
- (v) Word limit in questions, wherever specified, should be adhered to.
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SECTION—A

1. Answer *any five* of the following questions :

10×5=50

- (a) Explain Heisenberg's uncertainty principle with its mathematical expression. Calculate the uncertainty in the velocity of a wagon of mass 3000 kg whose position is known to an accuracy of ± 10 pm. (Planck's constant = 6.63×10^{-34} Js).
- (b) What is Linear Combination of Atomic Orbitals method to form bonding and non-bonding molecular orbitals? Compare the (i) bond energy, (ii) bond length and (iii) magnetic character of CN and CN⁻ species with the help of molecular orbital theory.
- (c) What are the different chemical thermodynamic processes? A gas expands isothermally against a constant external pressure of 1 atm from a volume of 10 dm³ to a volume of 20 dm³. In this process it absorbs 800 J of thermal energy from its surroundings. Calculate ΔU for the process in joules.
($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$)

(d) Answer any two of the following questions :

- (i) What is meant by a reference electrode? Describe the construction and working of a Calomel electrode.
- (ii) What are fuel cells? Describe the construction and working of hydrogen-oxygen fuel cell with chemical reactions involved.
- (iii) What is meant by electrochemical series? Describe briefly the various uses to which the series can be put. Explain why zinc reacts with H_2SO_4 to give H_2 gas but silver does not.
- (iv) Describe the construction and working of galvanic cell with Zn and Cu electrode. What are the uses of salt bridge?

(e) Define Joule-Thomson effect. Derive an expression for the Joule-Thomson coefficient. Show that the value of Joule-Thomson coefficient is zero for an ideal gas.

(f) Explain the term 'Order of a reaction'. Derive an integrated expression for the rate constant of first order reaction.

(g) Define the term heat capacity at constant pressure and constant volume. Show thermodynamically that $C_p - C_v = R$ where R is universal gas constant.

2. Answer the following questions :

(a) What is meant by quantum yield in a photochemical reaction? The quantum yield in the combination of H_2 and Br_2 to form HBr is only 0.01 whereas the quantum in the combination of H_2 and Cl_2 to form HCl is 10^5 . How would you explain it? 20

(b) How can the critical constants (T_c , P_c and $V_{m,c}$) of a real gas be determined in terms of van der Waals' constants using theoretical isotherms according to van der Waals' equation? 15

(c) Explain the terms (i) surface tension and (ii) surface energy. How are they related to each other? How can surface tension be measured by capillary rise method? 15

3. Answer the following questions :

(a) What are silicates? Discuss in details the structures of the following : 20

- (i) Pyrosilicates
- (ii) Chain silicates
- (iii) Cyclic silicates
- (iv) Sheet silicates

(b) Name the following coordination compounds using IUPAC system : 15

- (i) $[\text{Cr}(\text{en})_3]\text{Cl}_3$
- (ii) $\text{Na}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$
- (iii) $[\text{CoCl}(\text{en})_2(\text{ONO})]^+$
- (iv) $\text{Hg}[\text{Co}(\text{SCN})_4]^+$
- (v) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]_3[\text{Cr}(\text{CN})_6]$

(c) How do you prepare diborane in the laboratory? Discuss the Lewis acidity of diborane. 15

4. Answer the following questions : 20

(a) Explain the following giving suitable reason :

(i) $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic while $[\text{CoF}_6]^{3-}$ is paramagnetic.

(ii) $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic and square planar.

(b) Discuss briefly about silicates and silicones. What are the applications of silicates and silicones? 15

(c) Discuss the structures and shapes of the following molecules using VSEPR model : 15

- (i) XeF_4
- (ii) XeOF_4
- (iii) XeO_2F_2

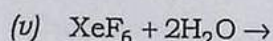
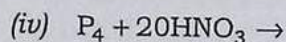
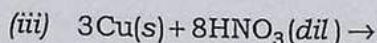
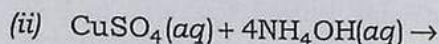
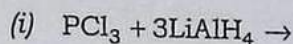
SECTION-B

5. Answer any five of the following questions : 10×5=50

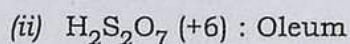
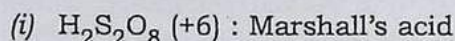
(a) Match the Column—A with Column—B in the following table :

Column—A	Column—B
(i) $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$	(m) Linkage isomerism
(ii) $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2(\text{py})_2]\text{NO}_3$ and $[\text{Co}(\text{NH}_3)_2(\text{ONO})_2(\text{py})_2]\text{NO}_3$	(n) Ionization isomerism
(iii) $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3$	(o) Coordination isomerism
(iv) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ and $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2\text{H}_2\text{O}$	(p) Geometrical/cis-trans isomerism
(v) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and $[\text{PtCl}_2(\text{NH}_3)_2]$	(q) Hydrate isomerism

(b) Complete any **two** of the following reactions with balancing factors :



(c) Explain the structure and shape of the following oxoacids of sulphur molecules using VSEPR theory :



(d) Derive Clapeyron-Clausius equation considering the two phases in equilibrium, liquid (L) and vapour (V) at the boiling point of the liquid.

(e) How the order of a reaction can be determined by the use of (i) differential rate expressions, (ii) half-life method?

(f) Compare between physisorption and chemisorption using any five highlighting points.

(g) An electrochemical cell is prepared by dipping a copper rod in 1M CuSO_4 solution and a nickel rod in 1M NiSO_4 solution. The standard electrode reduction potential of Cu-electrode and Ni-electrode at 25 °C are 0.34 V and -0.25 V respectively.

(i) Draw the cell diagram of the above electrochemical cell.

(ii) Write the electrodes and cell reactions and calculate EMF of the cell.

6. Answer the following questions :

(a) Discuss any five important general characteristics of catalytic reactions. Explain homogeneous and heterogeneous catalysis with suitable examples and theories. Discuss the function of a catalyst in terms of Gibb's free energy of activation with energy profile diagram.

20

(b) Calculate the EMF of zinc-silver cell at 25 °C when $[\text{Zn}^{2+}] = 0.10 \text{ M}$ and $[\text{Ag}^+] = 10 \text{ M}$. Given E°_{cell} at 25 °C = 1.56 volt.

15

(c) What is explosion reaction? Discuss under what conditions the first, second and third explosion limits are observed for gaseous $\text{H}_2 - \text{O}_2$ chain branching reaction.

15

7. Answer the following questions :

(a) Related to solid state, answer the following :

20

(i) In the mineral spinel, having the formula $MgAl_2O_4$, oxide ions are arranged in the cubic close packing (ccp). Mg^{2+} ions occupy the tetrahedral voids while Al^{3+} ions occupy the octahedral voids. What percentage of tetrahedral voids is occupied by Mg^{2+} ions? What percentage of octahedral voids is occupied by Al^{3+} ions?

(ii) Discuss the different types of stoichiometric defects found in crystals with diagrams and examples.

(b) What do you mean by an adsorption isotherm and an adsorption isobar? Explain Freundlich adsorption isotherm for the adsorption of gases on solids. Write its mathematical form and explain the different symbols used in the equation.

15

(c) In light of crystal field theory, explain diagrammatically :

15

(i) Splitting of d -orbital in an octahedral crystal field

(ii) Splitting of d -orbital in a square planar crystal field

(iii) Splitting of d -orbital in a tetrahedral crystal field

8. Answer the following questions :

(a) Describe the basic structure and biological role of (i) hemoglobin and (ii) chlorophyll.

20

(b) What are secondary cells? Describe the construction, chemical reactions involved and working of Lead Storage Battery.

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(c) What is lanthanide contraction? Discuss lanthanide contraction from the examples of variation of covalent and ionic radii.

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CHEMISTRY

(PAPER—II)

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SECTION—A

ESTD : 1988

1. Answer **any five** of the following questions :

10×5=50

(a) In light of Huckel rule of aromaticity, explain with suitable examples :

- (i) Aromatic
- (ii) Antiaromatic
- (iii) Nonaromatic

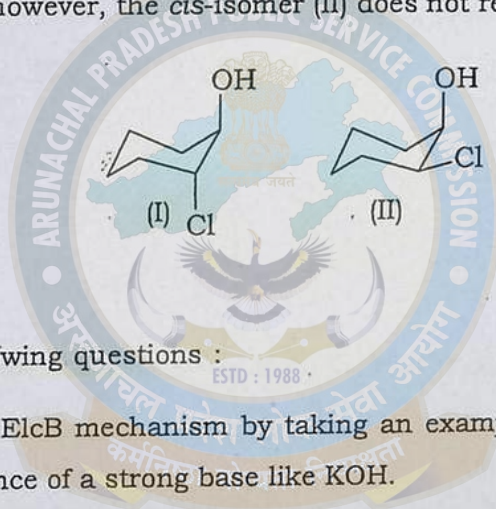
(b) Methyl radical is planar while the trifluoromethyl radical is pyramidal. Explain using VSEPR theory.

(c) Discuss the hybridization and orbital picture of (i) carbene and (ii) benzyne.

(d) Answer **any two** of the following questions :

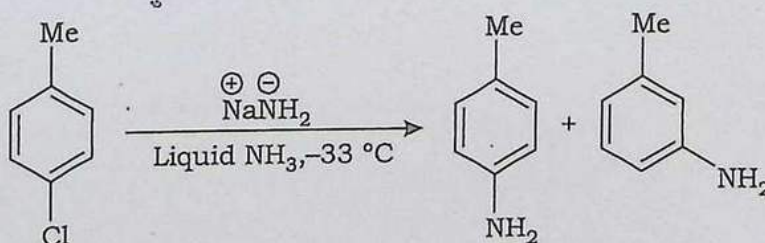
- (i) Discuss the kinetics and mechanism of S_N1 reaction taking an example of tert-butyl bromide as a reactant.

- (ii) Explain the energy profile diagram of an S_N1 reaction occurring between tert-butyl bromide and water.
- (iii) Explain the mechanism of an S_N2 reaction using any primary alkyl halide in presence of a strong base and give its energy profile diagram.
- (iv) Explain the difference between Saytzeff and Hofmann elimination reaction by using 2-chloropentane.
- (e) What is copolymerization? How can Buna-S be prepared?
- (f) "[2+2] Cycloaddition reactions are photochemically allowed processes." Justify the statement by using Frontier Molecular Orbital (FMO) approach using any suitable example.
- (g) *trans*-2-Chlorocyclohexanol (I) gives epoxycyclohexane in yield on reaction with NaOH however, the *cis*-isomer (II) does not react this way. Explain.



2. Answer the following questions :

- (a) Explain the $ElcB$ mechanism by taking an example of 4-hydroxyoctan-2-one in the presence of a strong base like KOH. 20
- (b) Explain the mechanism of the given aromatic nucleophilic substitution reaction : 15



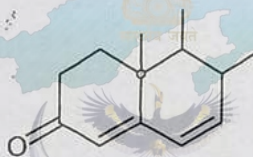
- (c) What is pinacol rearrangement? Explain the mechanism of pinacol-pinacolone rearrangement in the compound $Ph_2C(OH)-CH_2OH$ and predict the correct product with proper justification. 15

3. Answer the following questions :

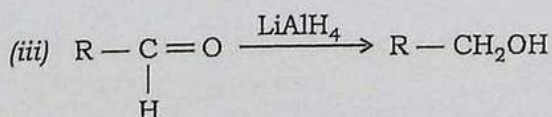
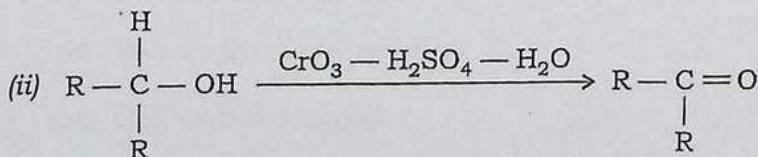
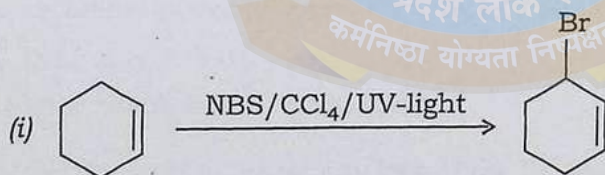
- (a) Explain the mechanism of Claisen condensation by taking an ester RCH_2-COOR in presence of sodium ethoxide to form a β -keto ester. 20
- (b) A [1,5] sigmatropic hydrogen shift is thermally allowed but [1,3] sigmatropic hydrogen shift is thermally forbidden. Explain by considering Frontier Molecular Orbital (FMO) symmetry diagram with appropriate example. 15
- (c) Describe the fate of the molecule in singlet and triplet states with the help of Jablonski diagram. 15

4. Answer the following questions :

- (a) What is photosensitization? Why can benzophenone be used as photosensitizer when buta-1,3-diene is irradiated? What is the difference observed in product formation from buta-1,3-diene in the absence of a photosensitizer? Explain with reason. 20
- (b) Calculate the λ_{max} (in alcohol) for the following compound using Woodward and Fieser rules : 15



- (c) Provide the plausible mechanism of the following reactions : 15

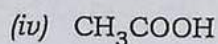
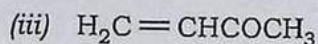
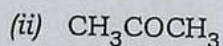
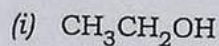


SECTION—B

5. Answer *any five* of the following questions :

10×5=50

(a) Give approximate positions of the characteristic infra-red (IR) bands in the following compounds :



(b) Discuss the secondary and tertiary structures of a protein molecule.

(c) Write a short note on Norrish type-II cleavage with an example of Hexan-2-one.

(d) What do you mean by the terms 'mer', 'monomer' and 'polymer'? Give the structures of the following polymers with their respective monomers :

(i) Polystyrene

(ii) Nylon 6 : 6

(e) Explain the Fischer-Indole synthesis with its step-wise formation.

(f) Discuss $\text{S}_{\text{N}}1$ reaction with suitable example.

(g) The E2 elimination can give a complex mixture of regioselective and stereoselective alkenes. Explain by taking 2-bromopentane as the substrate.

6. Answer the following questions :

(a) Write short notes on *any two* of the following name reactions :

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(i) Reformatsky reaction

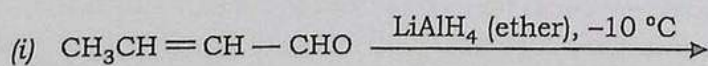
(ii) Reimer-Tiemann reaction

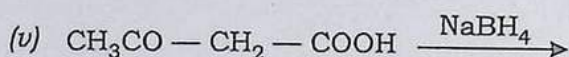
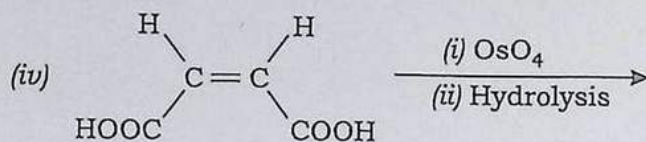
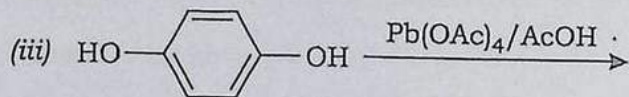
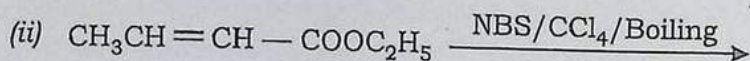
(iii) Cannizzaro reaction

(iv) Aldol condensation

(b) Predict the main product only and give its IUPAC or common name of the following reactions :

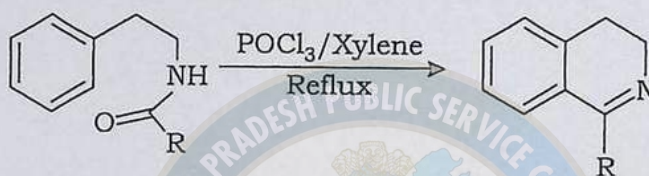
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(c) Give the steps of the following reaction :

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7. Answer the following questions :

- Discuss the Norrish type-1 (α -cleavage) of 2,2-dimethylcyclohexanone in its vapour phase and write all the possible products formation with mechanism. 20
- Explain *ortho*-Claisen and *para*-Claisen rearrangements with suitable examples. Why are they considered as [3,3] sigmatropic rearrangements? 15
- Explain the mechanistic basis of the Markovnikov addition of HBr to propene. 15

8. Answer the following questions :

- Answer the following related to spectroscopy : 20
 - Show different modes of vibrations that may occur in a triatomic molecule under the influence of IR radiation.
 - What do you mean by chromophore, auxochrome, bathochromic shift, hypochromic shift and hyperchromic shift used in UV spectroscopy?
 - Why is TMS used as a reference compound in NMR spectroscopy? Write the advantages of TMS being a reference compound in NMR spectroscopy.
 - Why is it called mass spectrometry, not mass spectroscopy? What are the ionization methods in mass spectrometry? Write in brief on the gas-phase ionization methods of mass spectrometry.

(b) What is the principle of rotational spectroscopy? Discuss in the context of a linear molecule. How does an isotopic substitution of an atom in a particular molecule affect the rotational spectra of molecule? 15

(c) Give the names and structures of different purine and pyrimidine bases present in DNA and RNA molecules. Draw the structures of any nucleoside and a nucleotide. 15

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