OLD

2015

Part-I 3-Tier

CHEMISTRY

PAPER—I

(Honours)

Full Marks : 90

Time : 4 Hours

The figures in the margin indicate full marks.

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

Illustrate the answers wherever necessary.

Use separate answer scripts for Group–A and B

Group—A

(Organic)

[Marks : 45]

Group—A (a)

Answer any *one* question : 1×15

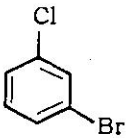
1. (a) Draw orbital picture for the following species indicating state of hybridization of the non-hydrogen atoms :

(i) Acrylonitrile ;

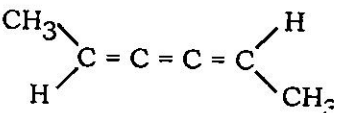
(ii) Allyl radical. 2

(b) Of the following compounds, which can function as a hydrogen bond donor and hydrogen bond acceptor with itself in a non-polar solvent like hexane CH_3COOH, CH_3COCH_3, CH_3CONH_2, $CH_3 - O - CH_3$. 2

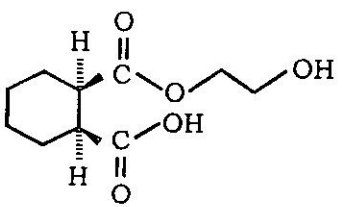
(c) Identify the elements of symmetry (if any) in the following molecules as shown (any two) : 2

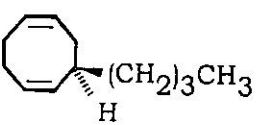
(a) 

(b) $C(CH_3)_4$

(c) 

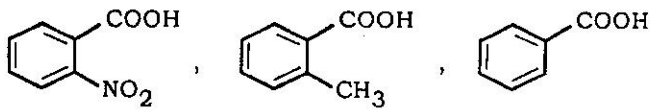
(d) Using CIP Nomenclature specify the absolute configuration of each of the chiral centres of the following molecules 3

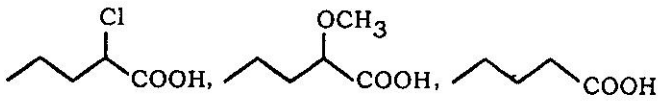
(a) 

(b) 

(Continued)

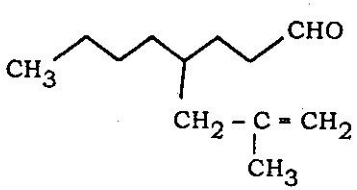
(e) Arrange each of the following sets of compounds in order of decreasing acidity with reason — 2+2

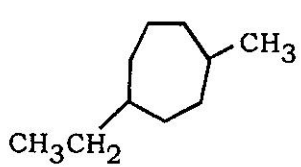
(a) 

(b) 

(f) Cis – 4 – hydroxycyclohexane carboxylic acid readily forms a lactone but trans-isomer can not — justify. 2

2. (a) Give IUPAC name of the following compounds : 2

(i) 

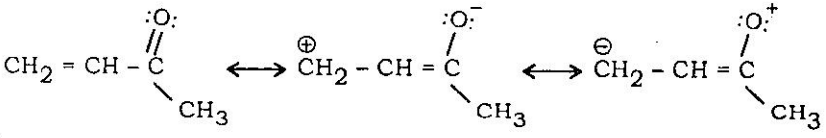
(ii) 

(b) The boiling point of acetic acid is nearer to that of octane than it is to that of butane — justify. 2

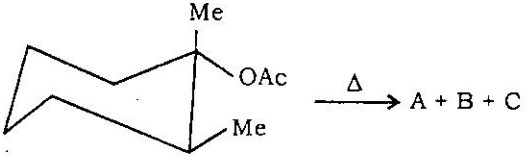
(c) Predict the expected uv spectral change on addition of one drop of 5% NaOH solution to a solution of p-cresol in spectral ethanol with justification. 3

(d) Compound $C_5H_{10}O$ had a band at 1715 cm^{-1} in its IR spectroscopy and showed two signals — a triplet and a quartet in its ^1H NMR spectrum. Establish the structure of the compound. 3

(e) For each of the following resonance structures, rank each structure in order of its relative importance in contributing to the resonance hybrid with reason — 2



(f) The following acetate on pyrolysis gives three products. Identify those products with possible mechanism — 3



Group—A (b)

Answer any *two* questions : 2×10

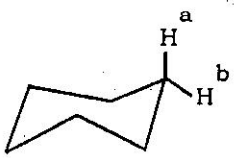
3. (a) Write one example of an organic molecule having the following characteristics —

(i) One having a chirotopic but non-stereogenic centre (give reasons).

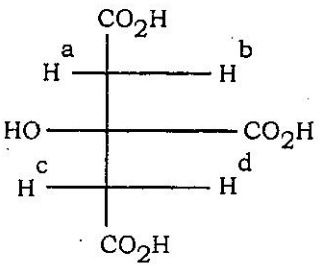
(ii) One having a C_2-axis but optically active (show the axis). 2

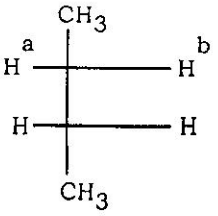
(b) Classify the atoms / groups indicated by superscripts a, b, etc. as homotopic, enantiotopic or diastereotopic for each of the following molecules — 3

(i)

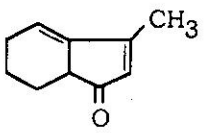


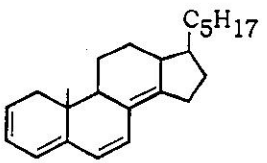
(ii)



(iii) 

(c) Calculate the λ_{max} value for the following compounds — 3

(a) 

(b) 

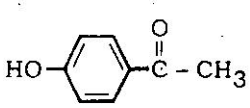
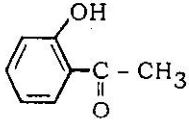
(d) Draw the most stable conformation of 1-phenylpropane with respect to the $C_1 - C_2$ bond, showing both Newmanh and Sawhorse projections. 2

4. (a) Account for the following fact :

Of the 1, 2 - dimethylcyclopentanes, the trans-isomer is more stable than cis-isomer whereas of 1, 3 - dimethylcyclopentane, the cis-isomer is more stable than the trans. 3

(b) Distinguish the following pairs by IR spectroscopy — 3

(i)  and

(ii)  and 

(c) Draw the possible staggered conformations in Newmann projection of the threo-form (about C - 2 / C - 3 bond) of 3 - amino pentan - 2 - ol and comment on their relative stabilities. 3

(d) Justify whether the following statement is true or false :

Alkylation adjacent to carbonyl group causes C = 0 stretching to absorbs at higher frequency. 1

5. (a) Give the structure of the compounds named

(i) (2E, 4Z) - Hepta - 2, 4 - dienoic acid

(ii) [2(5)E, 6E] octa - 2, 3, 4, 6 - tetraene. 2

(b) Of the following compounds, which one would you expect to have the highest solubility in water? Explain briefly.

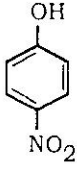
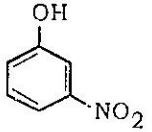
$CH_3COCH_2CH_2CH_3$, $H_2N - COCH_2CH_2CH_3$,

$CH_3CH_2OCH_2CH_2CH_3$. 3

(c) Isomeric 3, 3 - dimethylcyclohexanols undergo CrO_3 oxidation at different rates to give the same product — explain. 3

(d) Give the resolution of (±) alanine by means of chemical method. 3

6. (a) Explain how polarity of solvent affects absorption maxima in UV spectroscopy? 3

(b) Distinguish  and  at pH 8.5 from UV spectroscopy. 2

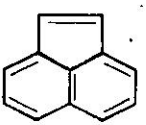
(c) Define the term chemical shift. What differences in chemical shift values are expected for the protons of CH_3F, CH_3Cl, CH_3Br and why? 1+2

(d) Arrange the following amines in oder of increasing basicity in aqueous medium with reason.
Me_2NH, Me_3N, $MeNH_2$. 2

Group—A (c)

7. Answer any *five* questions : 5×2

(a) State with reason, whether the following compound is aromatic or not.



(b) Define the term homoaromaticity with one example.

(c) Explain the extreme instability of [10]– annulene though it has Huckel's no. of π-electrons.

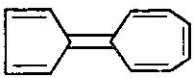
(d) O – H is always absorbed at higher frequency than C – C. Is this statement true? Explain with reason.

(e) Fill up the blanks :

(i) Alkyne hydrogens are more shielded than alkene due to _____ .

(ii) When the IR transition occurs from a ground state (V = 0) to the first excited state (V = 1) it generates _____ bands.

(f) The compound 'A' has high dipole moment — explain.



(A)

(g) Define with examples chromophore and auxochrome.

(h) Draw ^{1}H NMR spectrum of ethyl chloride. Explain the relative chemical shifts of different protons and splitting pattern.

(i) The order of polarisability of C – X bond is C – I > C – Br > C – Cl though the bond polarity order is exactly the reverse — explain.

Group—B

(Inorganic)

Group—B (a)

Answer any *one* question : 1×15

8. (a) Define electron affinity. 2

(b) How does it differ from electronegativity ? 2

(c) Explain the trends of variation of electron affinity along the second period and Gr. 17 of modern periodic table. 4

(d) Me_2S can form a stable adduct with BH_3 but Me_2O can not — explain. 2

(e) Arrange the elements : N, O, F and Cl in increasing order of electron affinity with justification. 2

(f) Addition of SbF_5 enhances the acidity of pure HF while the addition of NaF reduces acidity. Explain. 2

9. (a) Describe Frenkel and Schottky defects. Discuss the kind of crystal defect observed when ZnO is heated.

State the detectable change. $1+1+1\frac{1}{2}+\frac{1}{2}$

(b) Draw the MO energy level diagram for H_2O. Hence comment on the angular structure of H_2O molecule and compare with the structure of BeH_2. 4+2

(c) Discuss the magnetic properties of B_2 and C_2 with reference to MO theory. 3

(d) Compared to Me_3N, $(SiH_3)_3N$ has got almost no basicity. Explain. 2

Group—B (b)

Answer any *two* questions : 2×10

10. (a) Explain the structure and bonding of diborane. 4

(b) How will you prepare Lithium Aluminium hydride ? Give two examples of its application in organic synthesis. 1+1

(c) $SnCl_2$ is reducing while $PbCl_2$ is neither reducing nor oxidising. — Explain. 2

(d) LiF and NaI possess very low melting point though both of them crystallise like NaCl structure. Explain. 2

11. (a) Draw the Born-Haber cycle for the formation of Potassium hydride, hence find the electron affinity of hydrogen atom using the following data given in (kJ/mol) :

Heat of sublimation of Potassium metal = 83

First ionisation Potential of Potassium = 417

Bond dissociation energy of hydrogen molecule = 436

Lattice energy of Potassium hydride = – 742

Heat of formation of Potassium hydride = – 59

1+2

(b) H_2S is passed through a 0.01(M) solution of $ZnCl_2$. Calculate the lowest pH at which ZnS can be precipitated.

Given :

Solubility product of ZnS = 1×10^{-23} (mol $l^{-1})^2$. 3

(c) Write down the IUPAC name of the elements having atomic numbers 108 and 112. What would be their symbol ? 2

(d) AlF_3 gets dissolved in HF in the presence of NaF but it again gets precipitated on passing BF_3 gas through the solution — justify the statement. 2

12. (a) Using MO theory, explain the observations that the bond length in N_2^+ is 0.02Å greater than that in N_2. While the bond length in NO^+ is 0.09Å less than that in NO. 2+2

(b) Explain why ozone molecule has a dipole moment. 2

(c) Among Cu, Ag and Au, the +2 and +1 oxidation states are well documented for Cu while +1 and +3 states are well known for Au ; and Ag is best characterised in +1 state. Explain. 2

(d) Draw the possible resonance structures of nitrate ion and indicate with reasons the greatest contributing structure. 1+1

13. (a) Predict which way the following reaction will go in gas phase with explanation. 1

$CF_3H + CH_3F = CF_4 + CH_4$ 1

(b) In the light of solvent system theory, justify the nature of BiN in liq. NH_3 and of CaO in water. 1

(c) Compare and contrast the characteristics of C, Si, Ge, Sn and Pb with respect to their

(i) hydrides

(ii) halides

(iii) oxides 3×2

(d) formation of O^{2-} is energetically unfavourable, but MgO is formed and it is ionic — explain. 2

Group—B (c)

14. Answer any *five* questions : 5×2

(a) Which of Na_2CO_3 and $NaHCO_3$ is less soluble in water and why ? Explain.

(b) In water, potasium bicarbonate is less stable than potassium carbonate, but it is more stable than sodium bicarbonate. — Explain.

(c) $\angle F-P-F$ bond angle in PF_3 is 104° but $\angle H-P-H$ bond angle in PH_3 is 93.3°. Why ?

(d) Observe trends of solubility in water are

(i) $MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$

(ii) $MgF_2 < CaF_2 < SrF_2 < BaF_2$ — Explain

(e) Borazine is more reactive than benzene towards addition of HX. (X = halide) — Explain.

(f) MgO is harder and has higher melting point than NaF although Mg^{2+}, O^{2-}, Na^+ and F^- ions are isoelectronic. Explain.

(g) Electrical conductivity of Ge increases many folds if traces of As is incorporated into it. Why is it so?

(h) What happen when $NiSO_4$ is treated with dimethyl glyoxime in presence of excess ammonia. Write down the structure of the compound and state the nature of the compound.

(i) The interionic distance in chlorine molecule is 1·98Å. Calculate the Allred Rochow electronegativity using Slater's rule.
