CHEMICAL SCIENCES

Paper – III

SECTION – I

Note : i) Answer all questions.

ii) Each question carries twenty marks.

iii) Each answer should be given in 500 words ($2\frac{1}{2}$ – 3 pages).

$2 \times 20 = 40$

1. Answer either *(a)* or *(b)* or *(c)* or *(d)* :

(a) Discuss the major differences between valence bond and molecular orbital theories with special reference to H_2 molecule.

OR

(b) R_3B can act as a Lewis acid to initiate a reaction with CO or CN^- acting as a Lewis base. Use this concept for synthesis of (i) RCH_2OH, (ii) R_3COH and (iii) $R_2C=O$. Indicate the steps with proper reaction conditions and mechanisms where deemed important.

OR

(c) Outline the quantitative methods of analysis of the following :

(i) SO_2 in air

(ii) Phenol in industrial waste

(iii) Fluoride in ground water

(iv) Mercury in river soil.

Write down chemical equations where possible.

OR

(d) Discuss the mechanism of biological nitrogen fixation, mentioning the necessary requirements for the process and explaining the functioning of the enzyme involved and the roles of the metal ion(s) therein.

2. Answer either *(a)* or *(b)* or *(c)* or *(d)* :

(a) In the light of *mo* concept (pictorial approach) discuss the metal-ligand bonding in *oh* complexes of transition metal ions with sigma-basic only, sigma-basic pi-basic and sigma-basic pi-acidic ligands with the aid of approximate energy level diagrams and giving one example of each type.

OR

(b) Indicate the basic differences between the following pairs of techniques :

(i) Gas liquid chromatography and gas solid chromatography

(ii) Atomic emission and atomic absorption spectroscopy.

OR

(c) Benzaldehyde condenses with acetone in the presence of base to give compound *A*, whose mass spectrum showed the molecular ion at *m/z* 146 and two other intense peaks at *m/z* 131 and 103. *A* showed following spectral data :

$1R : \nu_m$ 1650 cm^{-1}

^{1}H-NMR : δ 6·7 (1H, *d*, J 16 Hz), 7·4 (5 H, m), 7·5 (1H, *d*, *J* = 16)

OR

(d) Write a note on the meaning of molecular weight of a polymer referring to at least three methods of determination (principles only).

SECTION – II

Note : i) Answer all questions.

ii) Each question carries fifteen marks.

iii) Each answer should be given in 300 words (1 – $1\frac{1}{2}$ pages).

$3 \times 15 = 45$

3. Answer either *(a)* or *(b)* or *(c)* or *(d)*

(a) Find the number of different types of bonds in the boron hydride, $B_{10}H_{14}$ and arrive at a reasonable structure for this compound using topological approach.

OR

(b) Explain when angular momentum is useful, with a brief survey of the operators involved, their representations in Cartesian coordinates, commutation relations and role in defining states of the H atom.

OR

(c) Ozone depletion mainly occurs in the stratosphere over the Antarctica. This phenomenon is relatively less important in the Arctic and equatorial regions. Explain.

OR

(d) An aliphatic hydrocarbon *A* (M.F. C_3H_4) on thermal catalyic trimerization, affords *B*, which in its ^1H NMR spectrum gives two singlets in the intensity ratio 1 : 3. *A* undergoes methylation with CH_3I in liq. $NH_3/NaNH_2$ to produce *C* which gives a singlet at $\delta \sim 2{\cdot}1$ in its ^1H NMR spectrum. *C* undergoes hydration reaction with dil. H_2SO_4 containing Hg^{2+} ion to produce *D* (M.F. C_4H_8O) which shows in its ^1H NMR spectrum a singlet, a triplet and a quartet. Write the structures of *A*, *B*, *C* and *D* and rationalise your answer.

4. Answer either *(a)* or *(b)* or *(c)* or *(d)* :

(a) State and prove the upper bound property of variationally determined functions and explain how it can be extended to states of lowest energy of a given symmetry, but not to higher energy states.

OR

(b) For polarographic study, the dissolved O_2 is to be removed by purging N_2 gas. Why ? Why do we use supporting electrolyte in polarographic study ?

OR

(c) Electronic spectrum of an octahedral cobalt (II) complex shows three bands at 7,200, 15,200 and 19,200 cm^{-1}. Indicate the transitions on an Orgel diagram giving the corresponding expressions for the transition energies. Find the values of 10 Dq and β. (Given : *B* for gaseous cobalt (II) ion is 970 cm^{-1}.]

(The terms have their usual meanings).

OR

(d) Define H/D primary kinetic isotope effect (pK_i). In terms of H/D-pK_i effect, explain the more rapid loss of HI from CH_3CH_2I than from CD_3CH_2I when a strong base is used.

5. Answer either *(a)* or *(b)* or *(c)* or *(d)* :

(a) How can you generate nuclear fuels from ^{232}Th and ^{239}Pu ?

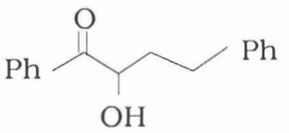
OR

(b) Comment critically on the statement, "unattainability of absolute zero".

OR

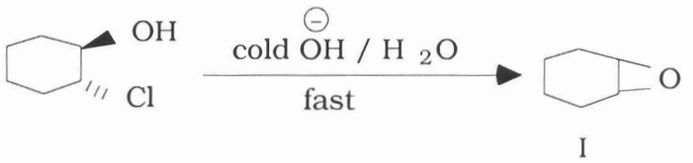
(c) (i) Write the structures of the products (*A* – *C*) with proper stereochemical assignments and designate (*R*/*S*) to *C*.

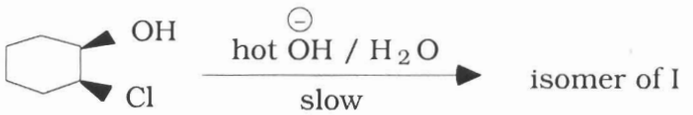
S-(–)-Cyclohex-2-enol $\xrightarrow{Zn/CH_2I_2}$ *A* $\xrightarrow{CrO_3}$ *B* $\xrightarrow{Li/NH_3}$ *C* . 7

(ii) Outline a synthetic route for the formation of 

5

(iii) Account for the different reactivities between the following isomeric 2-chlorohydrins : 3

x) 

y) 

OR

(d) Stability of 3d (M^{2+}) ion complexes with ethylenediamine (*en*) follows the Irving-Williams order for the $[M(en)^{2+}]$ and $[M(en)_2^{2+}]$ complexes, but the order breaks down for the $[M(en)_3^{2+}]$ complexes at $[Cu(en)_3^{2+}]$, which is unexpectedly much less stable. Give a reasonable explanation.

SECTION – III

Note : i) Answer all questions.

ii) Each question carries ten marks.

iii) Each answer should be given in 50 words ($\frac{1}{2}$ – 1 page). $9 \times 10 = 90$

6. Calculate the μ_S and μ_{L+S} values of Fe^{II} ion.

7. For a solid-liquid equilibrium, obtain Clapeyron's equation. Why is it useful ? Explain.

8. (a) Reaction of *para*-cresol with $CHCl_3$ and KOH yields, as one of the products, a compound with molecular formula $C_8H_8OCl_2$. Write the structure of the product and explain why chlorine removal does not occur from this product under the strong alkaline condition of the reaction. 5

(b) *Ortho*-fluoroanisole reacts with two moles of phenyl lithium in THF. On working up the reaction mixture, the product is found to have a molecular formula $C_{13}H_{12}O$. Write the structure of the product and explain its formation. 5

9. Calculate the probability that particle in a one-dimensional box of length a is found to be between 0 and $a/2$.

10. In what way magnetic properties of lanthanides are different from those of the transition elements ?

11. Mention appropriate reagents for the following transformations :

(i)

(ii)

(iii) 

Major (> 90%)

(iv) 

(v) 

12. Write down the expression for one-particle translational (3 – d) partition function of an ideal gas. Use standard relations to estimate the pressure and average energy for N particles.

13. N – O stretching frequency in NO molecule is much lower than that in $NO^+ \left[ClO_4^- \right]$. Why is it so ?

14. When heated progressively to high temperature, calcium oxalate monohydrate loses weight successively as given below :

Temperature (C°)	*Weight loss %*
100 – 250	12·32
400 – 500	19·18
620 – 860	30·14

Using these data, work out the thermal decomposition steps of the compound.

SECTION – IV

Note : i) Answer all questions.

ii) Each question carries five marks.

iii) Each answer should be given in 30 words ($\frac{1}{4} - \frac{1}{2}$ page). $5 \times 5 = 25$

15. Find out the Mo – Mo bond order in $\left[\left(\eta^5 - C_5H_5 \right) Mo \left(CO \right)_3 \right]_2$. Draw the possible isomers.

16. Predict the pKa values of ortho-phosphoric acid using Pauling's rules.

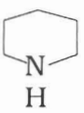
17. Show that the average value $< x >$ of a set of data $\{ x_i \}$ obeys the inequality

$< x^2 > \geq < x >^2$.

18. Write the structure of the compound which will yield two moles of malondialdehyde on ozonolysis.

19. Arrange the following organic compounds in the order of increasing basicity. Briefly explain :

(i) 

(ii) 

(iii)