

Chemical Science
Paper III

Time Allowed : $2\frac{1}{2}$ Hours]

[Maximum Marks : 200

- Note : (1) Attempt Question No. 1 and *Fourteen* other questions.
(2) Log table is enclosed.

1. Attempt any *three* of the following : (6 each)

A) Deduce the structure of a compound based on the following data :

Molecular formula : $C_{10}H_{18}O_4$

UV : 209 nm (ϵ 110)

IR (V_{max}) 1735, 1250, 1200 cm^{-1}

PMR (δ) : 0.93 (3 H, *t*, J = 7 Hz); 1.24 (6 H, *t*, J = 6.5 Hz); 1.38 (2 H, sextet, J = 7 Hz); 1.86 (2 H, *q*, J = 7 Hz); 3.35 (1 H, *t*, J = 7 Hz); 4.22 (4 H, *q*, J = 6.5 Hz)

Mass (m/z) : 29, 43, 129, 160, 174, 202 (m^+)

B) Assign structure to the compound based on the following data :

Molecular formula : $C_{11}H_{14}O_2$

UV. : weak bands between 250 to 270 nm

IR (V_{max}) : 3250 - 2800 (broad), 1710, 1602, 830 cm^{-1} .

PMR (δ) : 1.3 (3 H, *d*, J = 7 Hz); 2.34 (3 H, *s*); 2.6 (2 H, *d*, J = 7 Hz); 3.24 (1 H, sextet, J = 7 Hz); 7.15 (2H, *d*, J=8 Hz), 7.28 (2H, *d*, J = 7Hz); 10.8 (1H, bs, exchangeable with D_2O).

Mass (m/z) : 119, 133, 161, 163, 178 (m^+).

C) (i) Define the following terms in epr spectroscopy

Fine splitting, hyperfine splitting, superhyperfine splitting.

(ii) Explain epr spectrum of NH_2 radical.

Given : I (for ^{14}N) = 1

$$I (\text{for } ^1H) = \frac{1}{2}$$

D) Comment on the following observations in Mossbauer spectra of iron compounds :

	Compound	ΔE_Q , mm/S	δ , mm/S
(i)	$Na_3[Fe(CN)_5NH_3]$	0.6	-0.05
(ii)	$K_2[Fe(CN)_5NO]$	1.85	-0.27

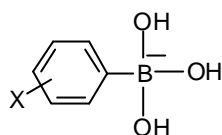
E) State the Franck-Condon principle. State how it explains observation of large vibrational structure in the electronic absorption bands.

F) What molecular terms would result if two atoms, each in a $3p$ term, combined to form a homonuclear diatomic molecule?

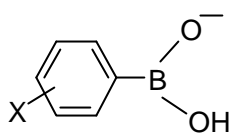
2. A) Interpret the ρ values for the ionization reactions of the following compounds : 4

	ρ		ρ
(i) Ar - OH	21	(ii) Ar-COOH	1.0
(iii) Ar-CH ₂ -CH ₂ -COOH	0.212	(iv) Ar-CH=CH-COOH	0.46

B) In the ionization of phenyl boronic acid two possible reaction sites are I & II :



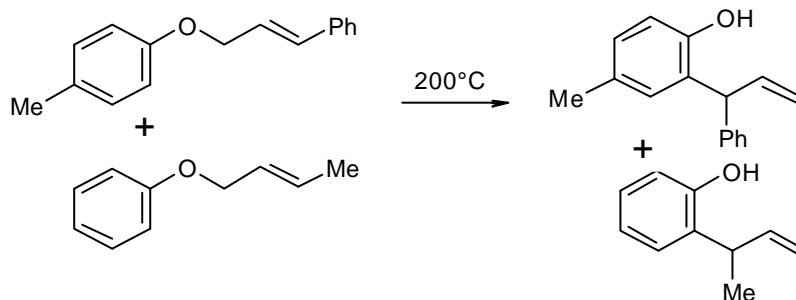
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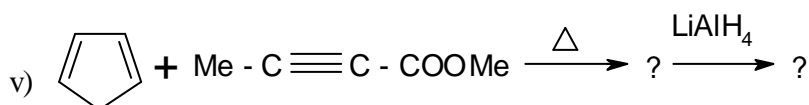
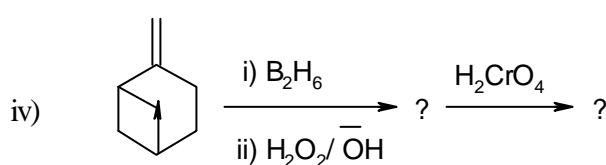
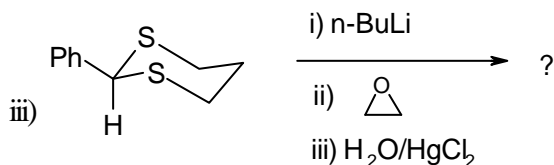
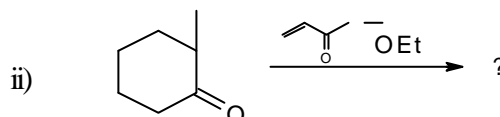
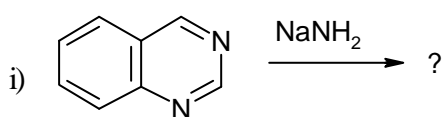
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The ρ value of the reaction is 2.57. Indicate the correct reaction site. 4

C) From the following observation, regarding Claisen rearrangement, what conclusion can be drawn about its mechanism? 5

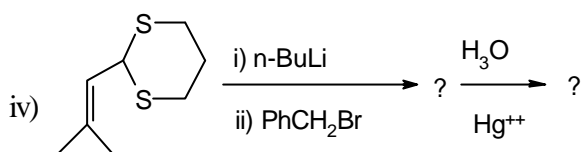
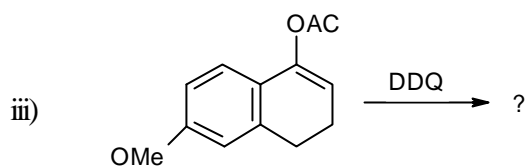
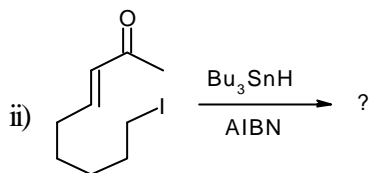
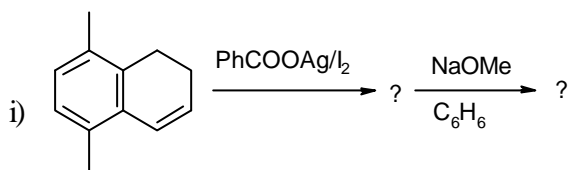


3. For each of the following, predict the product and name the reaction involved : 13



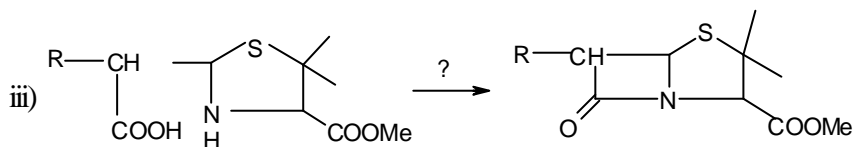
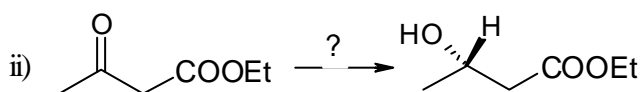
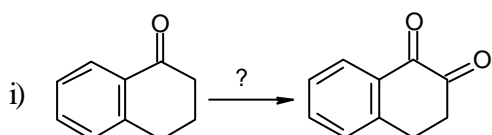
4. A) Predict the products of the following reactions :

8



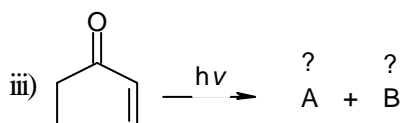
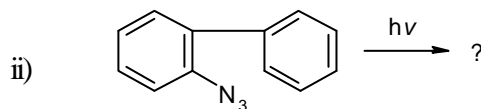
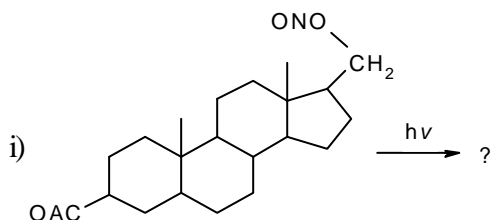
B) Indicate the reagents for the following conversions :

5



5. A) Predict the product and indicate the type of reaction for each of the following :

7

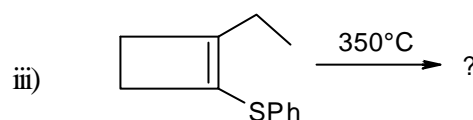
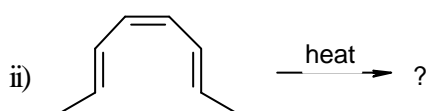
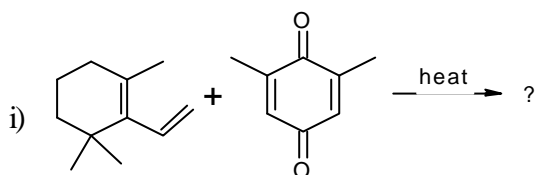


B) Compare naphthalene with the following with respect to (i) structure (ii) stability (iii) Aromaticity. 6

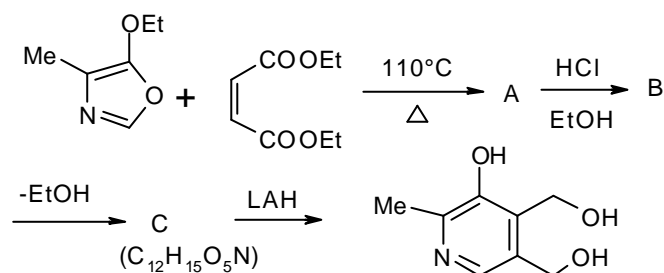
- (a) [14] annulene (b) 1,6-methanocyclodecapentaene.

6. A) Cyclopentadiene is present in its dimer form at room temperature.
- 1) Draw the structure of the dimer of cyclopentadiene 1
 - 2) How is cyclopentadiene obtained from the dimer? 1
 - 3) On reaction with chlorine, cyclopentadiene forms compound 'A' (C_5Cl_6). Compound 'A' on reaction with maleic anhydride forms compound 'B'. Draw the structures of 'A' and 'B' and name both the reactions. 3
 - 4) Explain the stereochemical outcome of the above reaction. 2

B) Predict the product and name and type of each of the following reactions : 6

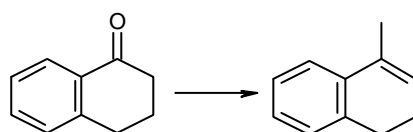


7. A) The following reaction sequence is used for the synthesis of pyridoxine. Complete the sequence indicating the intermediates A to C and identify the reactions involved : 6



B) Answer the following : 7

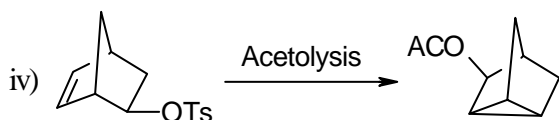
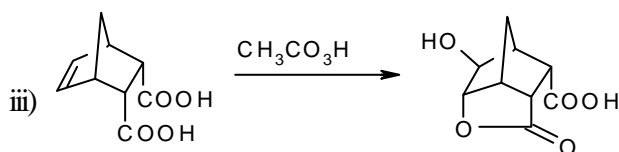
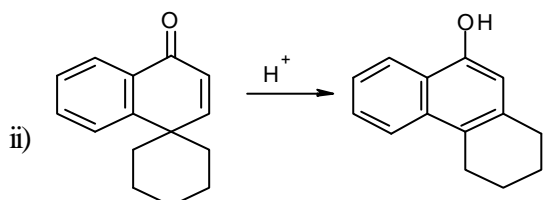
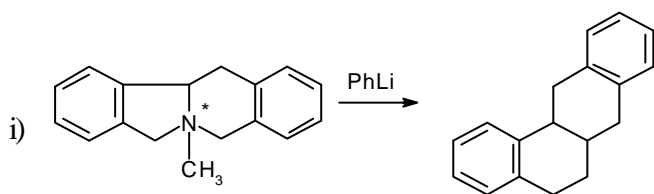
- (i) Outline a synthesis of p-bromonitrobenzene from benzene
- (ii) Write the sequence of reactions for the following conversion using Grignard reaction :



- (iii) Cis, 4-hydroxycyclohexane carboxylic acid lactonises easily while the trans isomer does not. Explain.

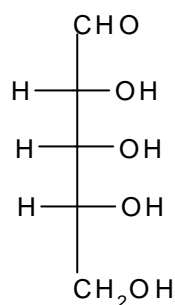
8. i) Pyrrole is a five-membered heterocycle with one nitrogen atom. Give its IUPAC name and draw its resonance structures. 3
- ii) In the $^1\text{H-NMR}$ spectrum of pyrrole three signals are observed at δ , 6, 12, 6.52 and 7.53. The signal at 7.53 disappears on D_2O exchange. Assign the peaks to the protons in pyrrole and give reasons. 3
- iii) Which positions in pyrrole undergo an electrophilic substitution faster? Why? 2
- iv) Draw the structures of the C- and N- protonated pyrrole species. 2
- v) Draw the structures of compounds containing a benzene ring fused to pyrrole ring and give their IUPAC names. 3

9. Propose mechanisms for the following reactions : 13



10. A) 1) Draw the structures of the polymers of the following : 3
- Vinyl chloride
 - Glycerol + Dimethyl terephthalate
 - Styrene + 1, 3-Butadiene.
- 2) Draw the structures of the isotactic, syndiotactic and atactic forms of the polymer obtained from vinyl chloride. 3

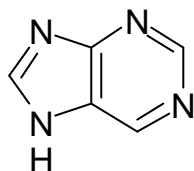
B) 1) D-Ribose (I) has the following structure :



I

Draw the furanose structures of D-ribose.

2) In a nucleoside along with D-ribose base II is present. The base is linked to the β -form of D-ribose through the N_1 of the base. Draw the structure of the nucleoside. 3



II

3) In DNA adenine is associated with thymine, and guanine with cytosine. In a DNA 30% of the total bases is found to be thymine. What will be the percentage of guanine ? 2

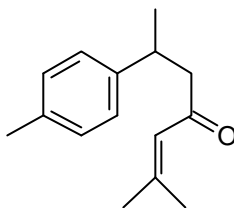
11. Write the reaction sequence using the following information : 13

Compound A ($C_9H_{12}O$) gives colouration with $FeCl_3$ and shows three singlets in its 1H NMR spectrum at 2.3, 7.1, 9.8 δ . It was reacted with allyl bromide in the presence of sodium methoxide in benzene to give B ($C_{12}H_{16}O$) which gave a peak in IR spectrum in the region 1650-1690. When B was reacted with diborane in THF at $0^\circ C$ followed by H_2O_2 in alkaline solution at $0^\circ C$, compound C was obtained. Further C was reacted with chromium trioxide and sulfuric acid in acetone to obtain D ($C_{12}H_{16}O_2$). D was in turn treated with bromine in water containing KBr to get E ($C_{12}H_{14}O_2Br_2$). E gives two peaks at 1732 and 1651 cm^{-1} in its IR spectrum.

- Complete the reaction sequence.
- Write structures of A to E.
- Explain the test and 1H NMR data given for A.
- Comment on the regioselectivity in the formation of B.
- Give the mechanism of B to C and D to E

12. A sesquiterpene has been assigned the structure

13



Answer the following :

- Write the structure of the product of hydrogenation with Pd-C
- What product will be formed when it is reacted with strong aq. NaOH ?
- Calculate the λ_{\max} (UV)
- Write the product of reaction with NH_2NH_2 .
- Using umpolung how will you prepare the above compound from $\text{CH}_2=\text{CHCHO}$?
- Suggest biogenetic pathway for the molecule.
- How many methyl signals will be observed in PMR ?

13. A) Deduce the structure of a compound based on the following data :

6

Molecular formula : $\text{C}_8\text{H}_6\text{O}_3$

U.V. : 275 (ϵ 6300), 315 nm (ϵ 10,000)

I. R. : 2720, 1695, 1600, 1480 cm^{-1}

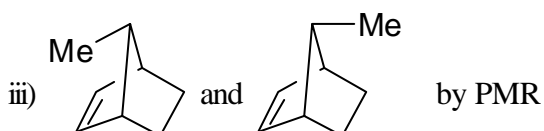
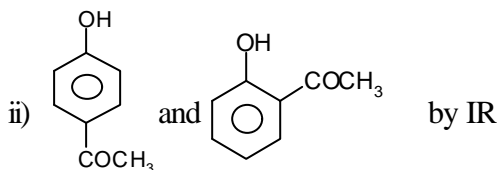
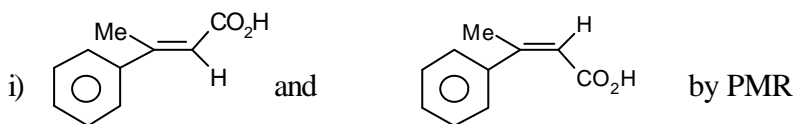
PMR (δ) : 6.04 (10 mm, S), 6.8 (5 mm, *d*, $J = 8$ Hz), 7.2 (5 mm, *d*, $J = 2$ Hz),
7.40 (5 mm, *dd*, $J = 2$ and 8 Hz), 9.75 (5 mm, S)

M. S. (m/z) : 150, 149 (base peak), 121

B) The peak positions of a triplet in the NMR spectrum are given below. The spectrum was recorded on 300 MHz instrument. Calculate the coupling constant in Hz. Peak positions (δ) 1.02, 1.04, 1.06. 2

C) Distinguish the compounds in the following pairs by the indicated spectral method :

5



14. A) Match the entries in column 'A' from those given below : 8

Column 'A'	Column 'B'
(Molecule)	(Symmetry)
1, 3, 5 tribromobenzene	
thiophene	
diborane	
CNFCIBr	
CCl ₄	
trans-dichloroethylene	
staggerd ethane	
SF ₆	
Entries for column 'B'	
C ₄	T _d
C _{3h}	C ₁
D _{3d}	D _{3h}
C _{2h}	C _{2v}
O _h	D _{4h}
T	D _{2h}

B) The Maxwell distribution of speeds is given by 5

$$F(v) dv = 4\pi v^2 \left[\frac{m}{2\pi kT} \right]^{3/2} \times \exp\left[-mv^2 / (2kT) \right] dv.$$

Show that the average speed, \bar{v} equals $(8kT/\pi m)^{1/2}$

$$\left\| \text{Use: } \int_0^\infty x^3 \cdot e^{-ax^2} dx = 1/2(2\alpha^2) \right\|$$

15. A) Make qualitative sketches of 7

$$\psi_{2s}, \Psi_{2s}^2 \text{ and } 4\pi r^2 \Psi_{2s}^2$$

$$\Psi_{2s}^2 = (2 - r) e^{-r/2}.$$

B) What are $\langle \hat{L}_z \rangle$, $\langle \hat{L}^2 \rangle$ and $\langle \hat{L}_x^2 + \hat{L}_y^2 \rangle$ values for $2p_z$ and $3d_{z^2}$ orbitals? 6

16. A) Plot a qualitative contour diagram of electron density of HeH⁺ ion. 6

B) The bonding MO energies for hexatriene are 7

$$\alpha + 1.80\beta, \alpha + 1.25\beta \text{ and } \alpha + 0.45\beta.$$

- i) Calculate the corresponding antibonding MO energies.
- ii) What is the delocalization energy of hexatriene ?
- iii) Evaluate $\pi \rightarrow \pi^*$ transition energy for this molecule.

17. The character table for C_{3v} point group is partly reproduced below. Identify the missing entries and provide your justification. 13
How will you justify the existence of only 3 irreducible representations ?

C_{3v}	E	$2C_3$	X
A_1	1	1	Z
A_2	1	1	W
Y	2	U	O

18. A) The Debye - Huckel limiting law may be written as 8

$$\log r_{\pm} = -AZ + Z - \sqrt{\mu}$$

State what each term represents. State the condition(s) under which it is valid. What is the value of A for aqueous solutions from the experiment plot for verification of the law. How can A be evaluated?

- B) Calculate the ionic strength of a solution which is 0.1 molal in KCl and 0.2 molal in K_2SO_4 . 5

19. A) What happens to the molecular energies due to Stokes and anti-Stokes transitions ? 5

- B) How the results of (a) show up in the Raman spectra ? 5

- C) What will happen to the vibrational frequency of the -OH group if it is replaced with -OD group. Give reasons. 3

20. A) i) Define packing fraction. 3
ii) How does packing fraction throw light on the stability of the nuclei ? 2
iii) In the nuclear fission of ^{235}U isotopes which elements occur as their isotopes with maximum yield. 2

- B) i) How is the radius of a nucleus related to mass number ? 2
ii) What are isobars and isotones ? 4

21. A) Define the number average (\bar{M}_n) and weight average (\bar{M}_w) molecular weights of polymers.

From the following techniques :

- i) Sedimentation rate
ii) Viscosity
iii) Osmotic pressure and
iv) Light scatter

Which molecular weight, \bar{m}_n or \bar{m}_w you obtain ? 8

- B) Show that if n_i is the number of molecules having masses.

$$\bar{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

From the above result what do you conclude about the relative values of \bar{M}_n and \bar{M}_w . 5

22. A) Write the expression for the total volume and estimate it when 100 ml of ethanol is added to 100 ml of water. The partial molar volumes of ethanol and water are 53.6 ml/mol and 18.0 ml/mol respectively. The densities of ethanol and water are 0.785 g/ml and 1.00 g/ml respectively. (M.W. water = 18.02 g/mol and M.W. ethanol = 46.07 g/mol). 7
- B) Aqueous HCl is added to an excess of aqueous NaOH. State the number of components in the system and the number of degrees of freedom. 6
23. A) Write expression for the rate constant according to the Transition - State - Theory in terms of partition functions for the reaction
- $$A + B - C \quad (A - B - C)^\ddagger \rightarrow \text{products}$$
- Assume that the partition functions corresponding to translation, rotation and vibration are f_t , f_r and f_v and barrier height is E_0 . 8
- B) One mole of an ideal gas A at 1 atm is mixed with four moles of another ideal gas B at 1 atm under isothermal conditions. Calculate the maximum work available from this process if the temperature is 298 K. Assume $R = 8.0 \text{ JK}^{-1} \text{ mol}^{-1}$. 5
24. Two hydrogen electrodes are each immersed in a solution of an aqueous acid. The two solutions are separated by a salt-bridge. The potential difference between the two electrodes is 0.118V. The pH of one of the solutions is 7. Estimate the pH of the other solution if the electrode immersed in it is at the higher potential. Assume $2.303 RT/F = 0.059 \text{ V}$. 13
25. A) Draw a BCC unit cell and show the (111) Miller plane. 5
- B) Draw a unit cell of NaCl and estimate the number of NaCl molecules in it. 8
26. A) Discuss the following :
- Structures of spinels and inverse spinels. 4
 - Defects in non-stoichiometric compounds with metal deficiency and consequences of such defects. 5
- B) ZnS occurs in nature as Wurtzite and zinc blende. How do they differ structurally? 4
27. A) Compare the spectral and magnetic properties of *f*-block elements with those of *d*-block elements. 7
- B) Give the ground state spectroscopic symbols for the following lanthanide ions : -
- Gd^{3+}
 - Pr^{3+}

- Given : Atomic number Gd = 64; Pr = 59. 4
- C) What are transuranic elements ? 2
28. A) What is intercalation ? Discuss the intercalation reactions of graphite and potassium.
Why can sodium undergo such reactions ? 6
- B) What is the structure of Silicon carbide ? 3
- C) Discuss the bonding in Fullerenes. 4
29. A) Discuss the structure of boric acid. Why is boric acid soft to touch ? 4
- B) Discuss structure, bonding, properties and uses of boron nitride. 6
- C) What are alumino-silicates ? Which are the alumino-silicates that give molecular sieve properties ? 3
30. A) What are interhalogen compounds ? Why are they more reactive than the halogens ? 5
- B) Draw the structures of : 4
- (i) IF_7 (ii) Cl_2O_7
- C) What are clathrate compounds ? Give example of clathrate compounds of noble gases. 4
31. A) Why is it that the second and third transition series metal ions give more low spin complexes than the first transition series metal ions? 3
- B) Explain the following observations :
- | Complex | μ_{eff} B.M. |
|---|-------------------------|
| i) $\text{K}_2[\text{ReOCl}_5]$ | 0 |
| ii) $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{FeCl}_4]$ | 5.4 |
| iii) $[\text{Ag}(\text{bipyridyl})_3][\text{ClO}_4]_2$ | 1.9 |
| iv) $\text{VO}(\text{acac})_2$ | 1.7 |
| v) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}\text{SO}_4$ | 3.23 |
- Atomic Nos. Re = 75; Fe = 26; Ag = 47; V = 23; Ni = 28 10
32. A) Give the structures of iron carbonyls. How will you distinguish between bridging and terminal carbonyl groups ? 5

- B) Explain the following observations : 8
- Addition of ammonium thiocyanate solution to nearly colourless ferric salt solution gives rise to intense red colour.
 - Addition of potassium ferrocyanide solution to ferric salt solution gives rise to dark blue precipitate.
 - Addition of conc. HCl to cobaltous chloride solution develops dark blue colour.
 - Addition of o-phenanthroline solution to ferrous salt solution develops dark orange red colour.
33. A) The rate of outer sphere electron exchange for $[\text{Ru}(\text{NH}_3)_6]^{2+} \rightarrow [\text{Ru}(\text{NH}_3)_6]^{3+}$ is $4 \times 10^4 \text{ m}^{-1}\text{s}^{-1}$ at 25°C , while that for $[\text{Co}(\text{NH}_3)_6]^{2+} \rightarrow [\text{Co}(\text{NH}_3)_6]^{3+}$ is $10^{-4} \text{ m}^{-1}\text{s}^{-1}$ at the same temperature. Rationalise this observation. 5
- B) Describe the tetragonal distortion of an octahedral d^9 system by elongation or compression along z-axis, with the help of a suitable orbital energy level diagram. 4
- C) What are metal clusters ? Give classification of metal clusters. 4
34. A) Give the reactions of ferrocene based on the central metal ion and the cyclopentadienyl rings, illustrating the answer with one example of each. 5
- B) What is 18-electron rule? Explain its application to metal carbonyls. Give an example of a molecule which does not obey this rule. 4
- C) Discuss the use of organometallic compounds as catalyst in hydroformylation reaction. 3
35. A) Discuss the thermogram of a mixture of CaCO_3 and MgCO_3 recorded in air 5
- B) The thermal curve of 125.7 mg sample which contained a mixture of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (mol. wt. = 146.12) and a thermally stable salt showed a mass loss Δm of 6.98 mg at an onset temperature of about 140°C corresponding to vapourization of water. Determine the percentage (w/w) of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ in the sample. 5
- C) What do you understand by the term Polarogram ? 3
36. A) Discuss any *two* interferences in atomic absorption spectroscopy. 4

B) A 0.1 mg/mL stock solution of Ca^{2+} was prepared. Different volumes of this solution, as shown in the following table, were diluted to 50 mL with distilled water. 5.0 mL of natural water was also diluted to 50 mL. The absorbances recorded on an atomic absorption spectrophotometer are shown in the table

Calculate the concentration of calcium in the natural water. 5

Volume of Stock Solutions (mL)	Absorbance
1.00	0.224
2.00	0.447
3.00	0.675
4.00	9.00
5.00	1.124
5.00 (natural water)	0.475

C) How is lead separated from blood by solvent extraction method ? 4

37. A) What are the different light reaction paths in photosynthesis ? What is the difference between them? 5

B) Draw the structure of pyridine cobaloxime, a model of vitamin B_{12} . 3

C) Give a brief account of "ion pumps". 5