

Signature of Invigilators

Roll No.

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1. ....

## CHEMICAL SCIENCES

(In figures as in Admit Card)

2. ....

### Paper III

Roll No. ....

**D-0302**

(In words)

Name of Areas/Section (if any) .....

Time Allowed ; 2½ Hours]

[Maximum Marks : 200

#### Instructions for the Candidates

1. Write your Roll number in the space provided on the top of this page.
2. Write name of your Elective/Section if any.
3. Answer to short answer/essay type questions are to be written in the space provided below each question or after the questions in test booklet itself. No additional sheets are to be used.
4. Read instructions given inside carefully.
5. Last page is attached at the end of the test booklet for rough work.
6. If you write your name or put any special mark on any part of the test booklet which may disclose in any way your identity, you will render yourself liable to disqualification.
7. Use of calculator or any other Electronics Devices are prohibited.
8. There is no negative marking.
9. You should return the test booklet to the invigilator at the end of the examination and should not carry any paper outside the examination hall.

પરીક્ષાર્થીઓ માટે સૂચનાઓ :

૧. આ પૃષ્ઠના ઉપલા ભાગે આપેલી જગ્યામાં તમારી ક્રમાંક સંખ્યા (રોલ નંબર) લખો.
૨. તમે જે વિકલ્પનો ઉત્તર આપો તેનો સ્પષ્ટ નિર્દેશ કરો.
૩. ટૂંક નોંધ કે નિબંધ પ્રકારના પ્રશ્નોના ઉત્તર દરેક પ્રશ્નની નીચે આપેલી જગ્યામાં જ લખો. વધારાના કોઈ કાગળનો ઉપયોગ કરશો નહીં.
૪. અંદર આપેલી સૂચનાઓ ધ્યાનથી વાંચો.
૫. આ ઉત્તરપોથીને અંતે આપેલું પૃષ્ઠ કાચા કામ માટે છે.
૬. આ ઉત્તરપોથીમાં ક્યાંય પણ તમારી ઓળખ કરાવી દે એવી રીતે તમારું નામ કે કોઈ ચોક્કસ નિશાની કરી હશે તો તમે આ પરીક્ષા માટે ગેરલાયક સાબીત થશો.
૭. કેલક્યુલેટર અથવા ઈલેક્ટ્રોનિક્સ સાધનો જેવા ઉપયોગ કરવો નહીં.
૮. નકારાત્મક ગુણાંક પદ્ધતિ નથી.
૯. પ્રશ્નપત્ર લખાઈ રહે એટલે આ ઉત્તરપોથી તમારા નિરીક્ષકને આપી દેવી. પરીક્ષાખંડની બહાર કોઈપણ પ્રશ્નપત્ર લઈ જવું નહીં.

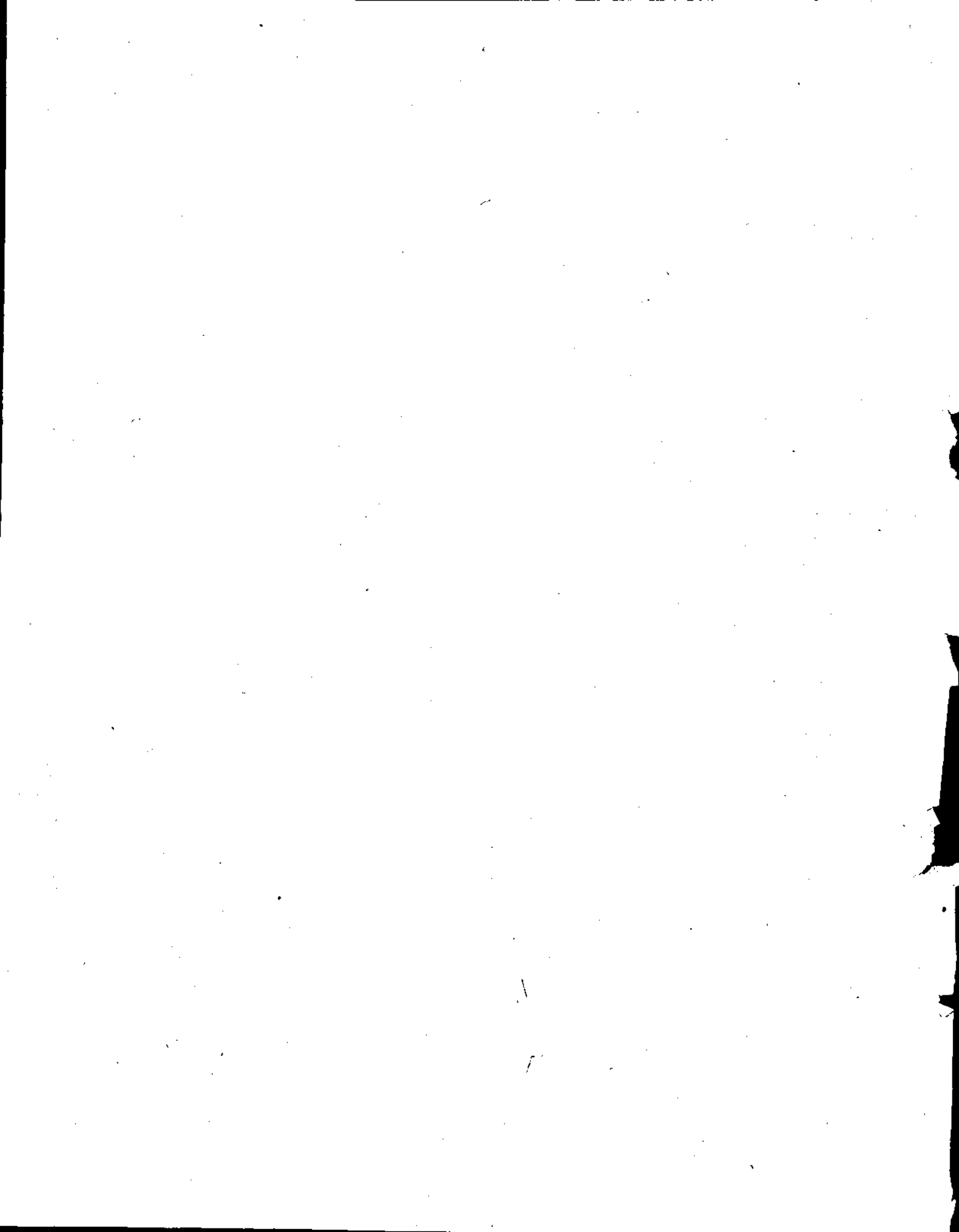
#### FOR OFFICE USE ONLY Marks Obtained

Question Number	Marks Obtained	Question Number	Marks Obtained	Question Number	Marks Obtained
1		26			
2		27			
3		28			
4		29			
5		30			
6		31			
7		32			
8		33			
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Total Marks Obtained.....

Signature of the co-ordinator.....  
(Evaluation)

SEAL





LOGARITHMS

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70	0060	0103	0146	0188	0230	0272	0314	0356	0398	0440	0482	0524	0566	0608	0650	0692	0734	0776	0818	0860	0902
80	0070	0113	0156	0198	0240	0282	0324	0366	0408	0450	0492	0534	0576	0618	0660	0702	0744	0786	0828	0870	0912
90	0080	0123	0166	0208	0250	0292	0334	0376	0418	0460	0502	0544	0586	0628	0670	0712	0754	0796	0838	0880	0922

LOGARITHMS

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## CHEMICAL SCIENCES

### Paper III

Note :—(i) Question No. 1 is compulsory (40 marks). Answer it in 800 words (8 pages.)

(ii) Attempt any ten questions out of the remaining 35 questions (16 marks each). Answer each question in 300 words (3 pages).

General Physical Constants :—

Speed of light  $C = 2.998 \times 10^8 \text{ ms}^{-1}$

Avogadro constant  $N = 6.023 \times 10^{23} \text{ mol}^{-1}$

Faraday  $F = 96500 \text{ coulombs mol}^{-1}$

Planck constant  $h = 6.626 \times 10^{-34} \text{ Js}$

Boltzmann constant  $k = 1.381 \times 10^{-23} \text{ JK}^{-1}$

Gas constant  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$  or  $1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$

1. Attempt any four of the following :

(a) (i) A solution containing 4.48 ppm  $\text{KMnO}_4$  has a transmittance of 0.309 in a 1.00 cm cell at 520 nm. Calculate the molar absorptivity of  $\text{KMnO}_4$  (M. Wt. of  $\text{KMnO}_4$  is 158).

(ii) Why are spectral bands sharper in i.r. than in visible spectrum? 10

(b) Calculate the relative no. of protons in the higher and lower magnetic states when a sample is placed in 4.69 T at 20°C.

( $\gamma$  : magnetogyric ratio =  $2.68 \times 10^8$ ) 10

(c) (i) How are Auger electrons generated?

(ii) Explain only the signal development in non-dispersive i.r. 10

(d) Describe the variation of  $g$  values in ESR spectroscopy. 10

(e) Deduce the structural formulas that are consistent with the data given for the following compounds :

(i) Mol. formula :  $\text{C}_8\text{H}_8\text{O}_3$

IR : 3400, 2900, 1740, 1600, 820  $\text{cm}^{-1}$

NMR : 3.9 $\delta$  (3H, s); 7.1 $\delta$  (2H, d,  $J = 8 \text{ Hz}$ ); 6.1 $\delta$  (2H, d,

$J = 8 \text{ Hz}$ ); 4.5 $\delta$  (1H, s).

(ii) Mol. formula :  $C_3H_5ON$

UV : NO  $\lambda_{max}$  above 200 nm

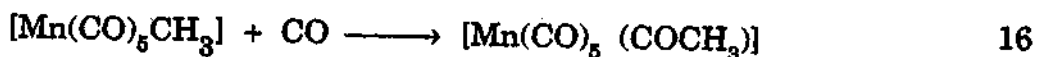
IR : 2941 - 2857, 2247, 1460  $cm^{-1}$

NMR : 4.8 $\delta$  (3H, s); 3.5 $\delta$  (2H, s)

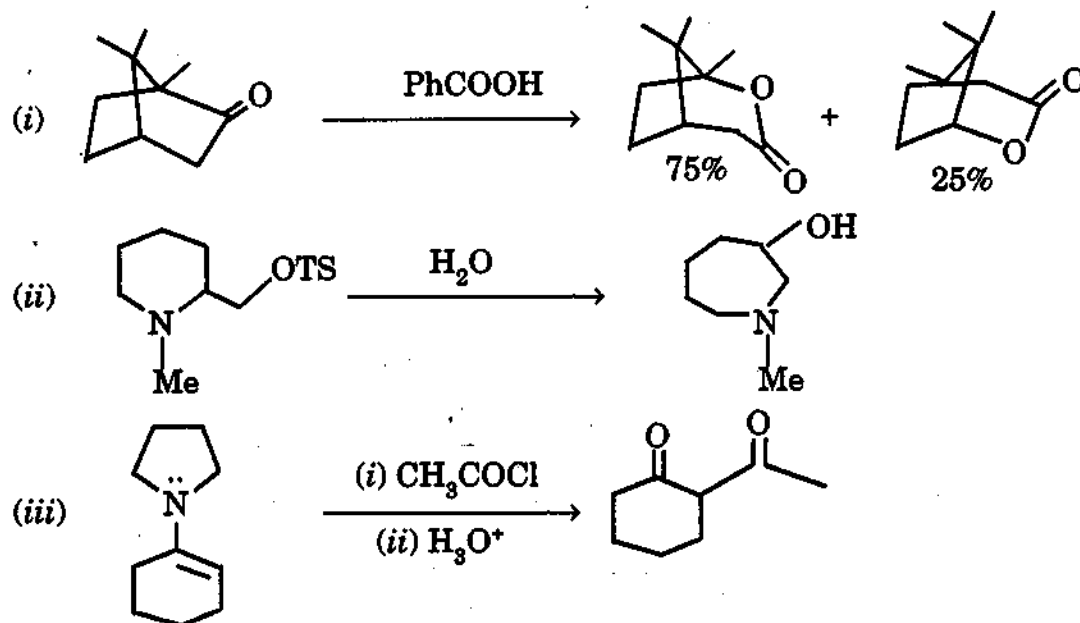
10

- (f) The spacing between the successive lines of pure rotational spectrum of HCl is 20.6  $cm^{-1}$ . Evaluate the H—Cl bond length. 10
2. (a) After one extraction 90% zinc is extracted with trioctylamine in xylene and only 5% of cadmium in xylene phase. Calculate the separation factor for zinc and cadmium assuming the volume ratio to be unity.
- (b) What is the difference between liquid-liquid partition chromatography and reversed phase partition chromatography ? 16
3. (a) Calculate the total number of theoretical plates and the height equivalent of theoretical plate in a column with 30 cm length if the distance from the stationary point is 5 cm and the width of the elution curve at base is 0.05 cm.
- (b) Why is it necessary to use hydride generator in analysis of arsenic, selenium or tellurium by atomic absorption spectrometer ? 16
4. (a) What is Ilkovic equation ? Explain the significance of each term involved in this equation.
- (b) In coulometric titration of potassium dichromate with iron (III) solution state whether platinum electrode serves as the cathode or anode ? 16
- (c) What do you understand by living polymerisation ?
5. (a) What is Liquid-junction potential ? State how it is overcome in the potentiometric titrations.
- (b) Explain the working of specific ion electrode for the fluoride anion estimation. 16

6. (a) What is the basic difference in principles as well as in instrumentation in nephelometry and turbidimetry ?
- (b) Why is it essential to modify Boltzmann equation when used in atomic absorption and atomic emission spectroscopy ?
- (c) Depict the shape of the amperometric titration curve when both titrant and substance undergo reversible redox reaction. 16
7. (a) Why is  $\text{BeCl}_2$  soluble in organic solvents ?
- (b) Why does  $\text{C}^{4+}$  ion not exist ? 16
8. (a) Describe the bonding in  $\text{B}_2\text{H}_6$ .
- (b) Sketch the structure of  $\text{S}_4\text{N}_4$  molecule. 16
9. (a) Describe any two synthetic methods for the preparation of borazine  $\text{B}_3\text{N}_3\text{H}_6$ .
- (b) Suggest synthesis for  $\text{XeO}_4$ . 16
10. (a) Assign the following complexes to their appropriate point group :
- (i)  $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2$
- (ii)  $\text{Fe}(\text{CO})_5$
- (iii)  $[\text{PtCl}_4]^{2-}$
- (iv)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$
- (b) Why does  $\text{SF}_4$  have  $\text{C}_{2v}$  symmetry rather than  $\text{C}_{4v}$  ? 16
11. (a) How is the  $18 e^-$  rule satisfied in  $\text{Co}_4(\text{CO})_{12}$  ?
- (b) How does ethylene bind with metal ion in metal- $\eta^2$ -ethylene complexes ? 16
12. (a) Illustrate homogeneous hydrogenation of ethylene with Wilkinson's catalyst.
- (b) What is the driving force for the following carbonyl insertion reaction :

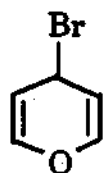
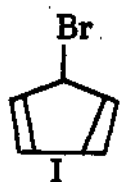


13. (a) The stability of Fe (II) state in the  $[\text{Fe}(\text{II})(\text{L})_6]^{n+}$  complex increases with increase in  $\pi$ -acceptor ability of L. Explain.
- (b) Differentiate the outersphere and innersphere electron transfer mechanism using an example. 16
14. (a) In  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  complex, all the six Cu—O bond distances are not identical. Explain.
- (b) Why are the intensities of  $d-d$  transitions much lower than the metal-ligand charge-transfer transitions ? 16
15. (a) Assign the electronic transition frequencies at 14900, 22700 and 34400  $\text{cm}^{-1}$  for  $[\text{CrF}_6]^{3-}$ . Determine the values of 10 Dq and B parameters.
- (b) Crystal field theory cannot justify the spectrochemical series. Explain. 16
16. (a) Why is metal-ligand bonding in case of lanthanide (III) ions predominantly ionic in nature ?
- (b) Why is color of the lanthanide (III) complexes less intense compared to that of the transition metal complexes ? 16
17. (a) Propose reasonable mechanisms for the following conversions : 12



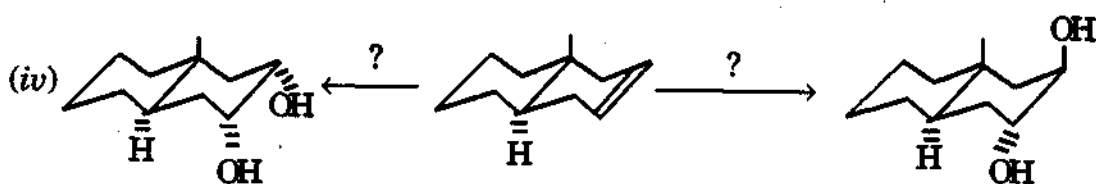
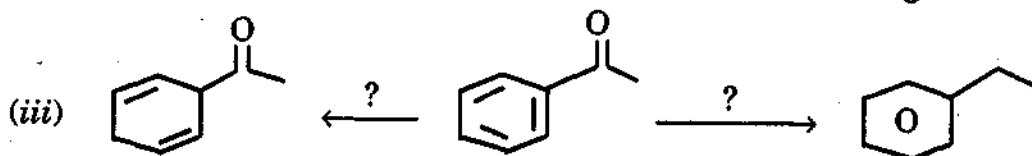
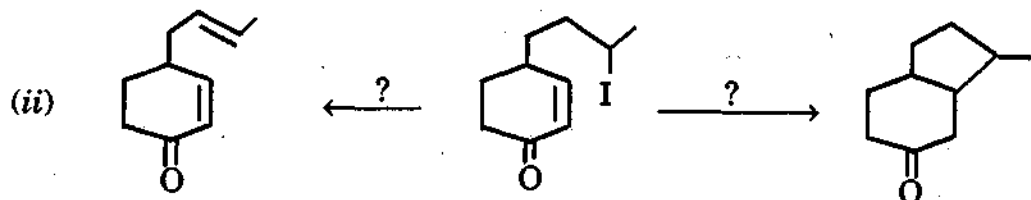
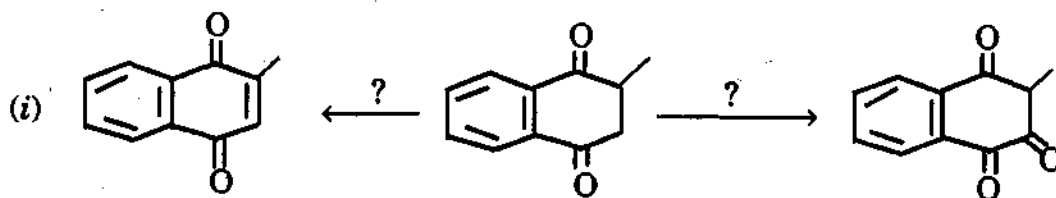


- (b) Which one of the following bromides will undergo facile solvolysis ? 4  
Justify.



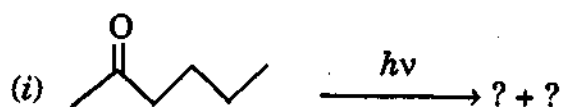
18. Indicate the reagents for the following transformations :

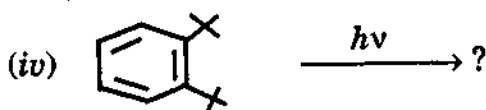
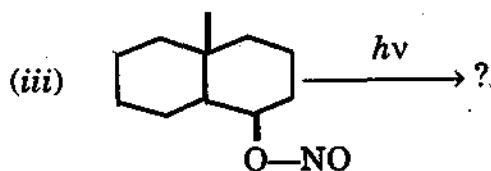
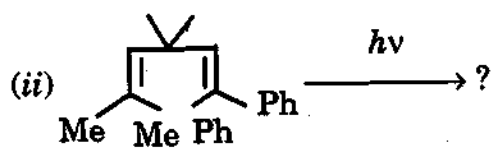
16



19. Identify the product(s) in the following photochemical reactions and specify their stereochemistry, if any :

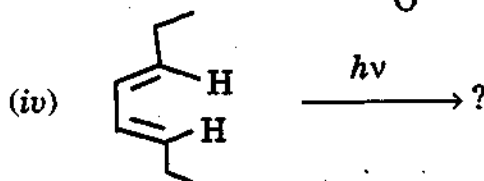
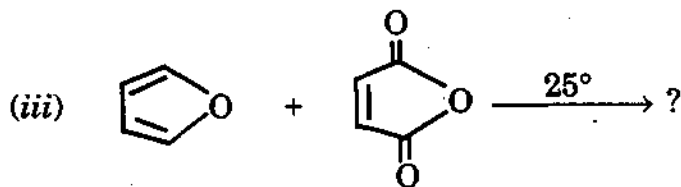
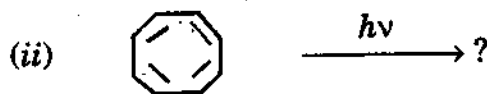
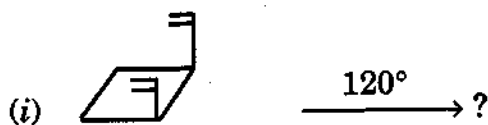
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20. Predict the product(s) and its stereochemistry; name the reaction type and quote selection rule for the following :

16



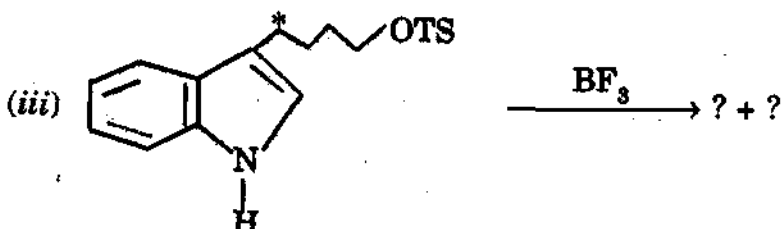
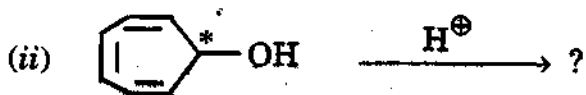
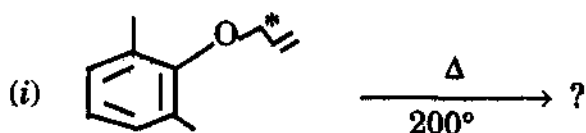
21. (a) Match the rho ( $\rho$ ) values with appropriate reactions :

7

<i>Reactions</i>	$\rho$
(i) ionization of substituted phenols	(a) -6.0
(ii) ionization of substituted phenyl acetic acids	(b) -1.5
(iii) ionization of substituted anilinium ions	(c) 2.1
(iv) formylation of substituted anilines	(d) 2.89
(v) nitration of benzenes	(e) 0.49
(vi) ionization of benzoic acids in 100% EtOH	(f) -0.483
(vii) acid hydrolysis of benzamides	(g) 1.9
(i)..... (ii)..... (iii)..... (iv).....	
(v)..... (vi)..... (vii).....	

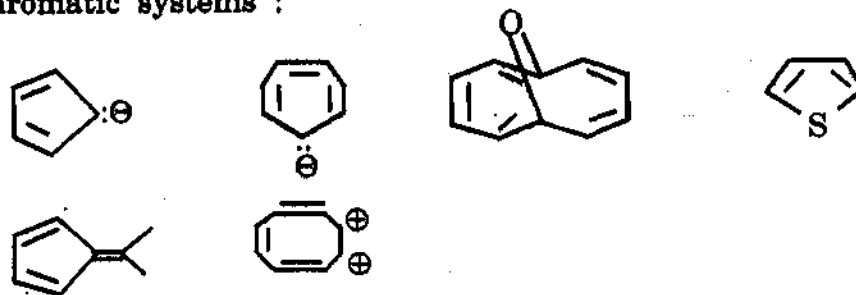
(b) Name the reaction, predict the product(s) and indicate the position of label for the following :

9



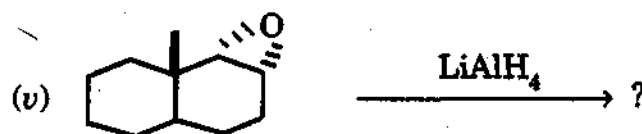
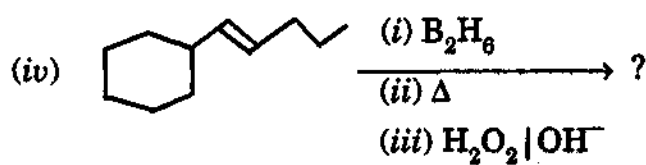
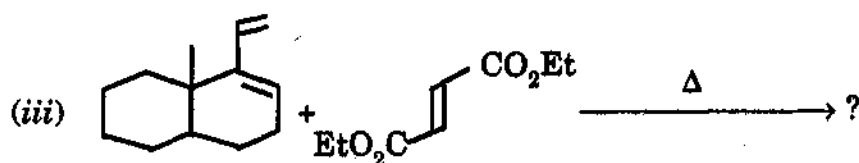
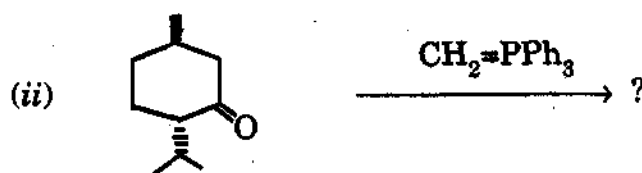
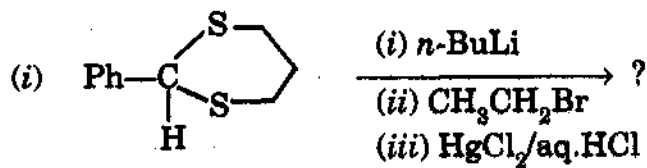
22. (a) Classify the following molecules into aromatic, non-aromatic and anti-aromatic systems :

6



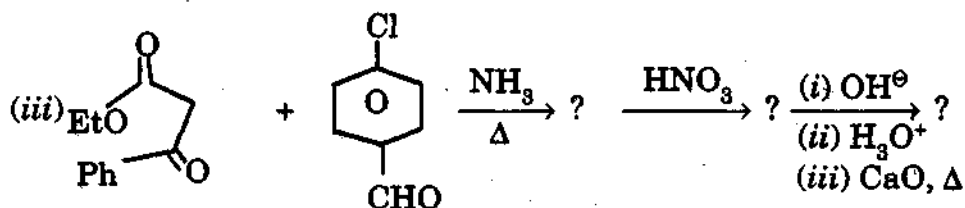
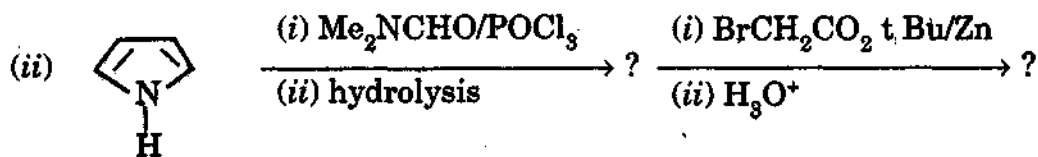
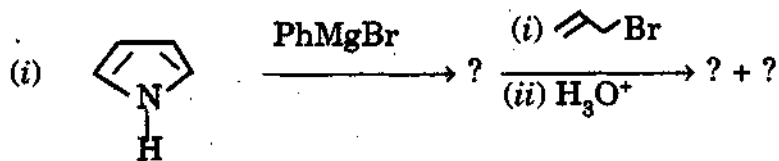
(b) Predict the product and identify the reaction :

10



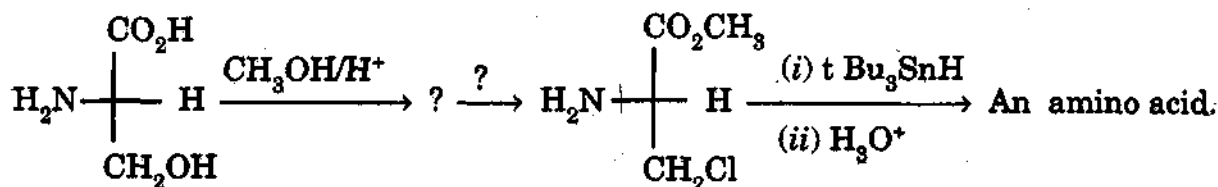
23. Complete the following reaction sequences by identifying the product(s) :

16



24. (a) Identify the missing link in the following reaction sequence and assign the configuration of the resultant amino acid :

8



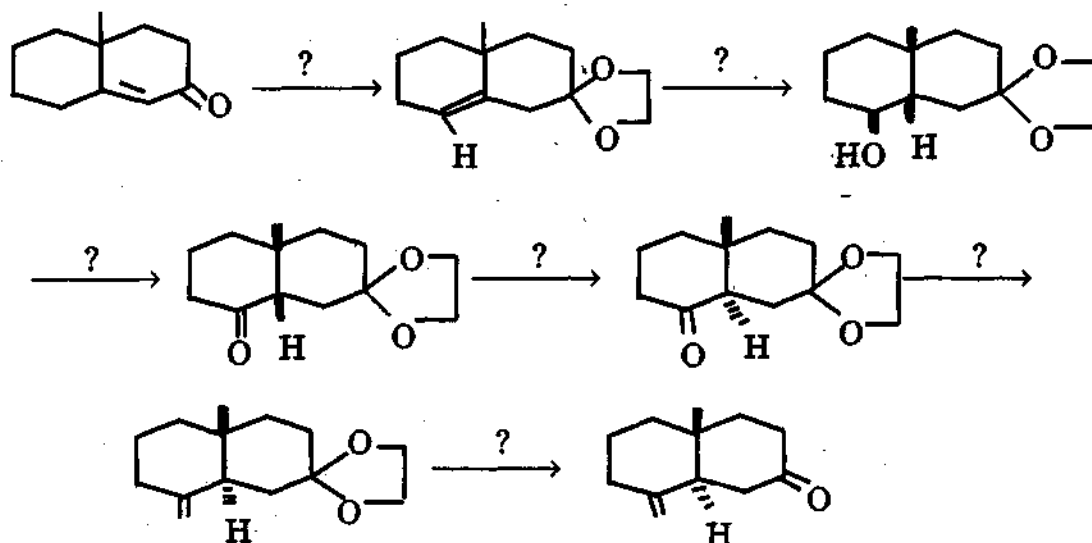
(b) Match the following :

8

- |  |                           |
|--|---------------------------|
| (i) $\text{PhCH}_2\text{-N}^\oplus\text{Et}_3$   | (a) vision                |
| (ii) amino acids                                 | (b) iron                  |
| (iii) c-terminal analysis                        | (c) hydrolysis of peptide |
| (iv) Guanine                                     | (d) electrophoresis       |
| (v) Haemoglobin                                  | (e) DNA                   |
| (vi) Chymotrypsin                                | (f) cytosine              |
| (vii) Genetic code                               | (g) PTC                   |
| (viii) Rhodopsin                                 | (h) pancrease             |
| (i)..... (ii)..... (iii)..... (iv)..... (v)..... |                           |
| (vi)..... (vii)..... (viii).....                 |                           |

25. (a) In the following synthesis provide the required reagents :

12



(b) Identify the isoprene units in the following molecules :

4



26. (a) Deduce the structure that is consistent with the data given :

8

M.W. : 120

UV :  $\lambda_{\text{max}}$  268 nm,  $\epsilon$  480

IR : 3067 – 2907, 1608, 1473, 880  $\text{cm}^{-1}$

NMR : Two singlets at 7.2 and 2.8  $\delta$  having intensity ratio 1 : 3

(b) Write feasible structures for the molecules having given fragment ions and i.r. band :

8

(i)  $m/z$  : 134, 119, 92, 91, 65, 51, 43

IR : 1715  $\text{cm}^{-1}$

(ii)  $m/z$  : 45, 43, 55, 73

IR : 3500  $\text{cm}^{-1}$

27. Identify the various symbols and briefly indicate the physical meaning of the following equations : 16

(i)  $F = C - P + 2$

(ii)  $\frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau} \geq \epsilon_0$

(iii)  $W = \frac{N \cdot \prod_i g_i^{n_i}}{\prod_i n_i}$

(iv)  $\Delta S_{mix} = -R(x_A \ln x_A + x_B \ln x_B)$

(v)  $\frac{-d[S]}{dt} = \frac{k_2[E_0][S]}{K_m + [S]}$

(vi)  $Z_{AB} = \left( \frac{N_A N_B}{V^2} \right) \cdot \pi d_{AB}^2 \cdot \bar{c}_{AB}$

(vii)  $\sum_R \chi_i^*(R) \chi_j(R) = g \cdot \delta_{ij}$

(viii)  $\mu = \frac{1}{2} \sum_i c_i Z_i^2$

28. (a) The energy of an eigenstate of particle in a 3D cubic box of length  $a$  is :

$$\frac{27h^2}{8ma^2}$$

Identify the degeneracy and list the corresponding quantum numbers  $n_x$ ,  $n_y$  and  $n_z$ . 8

(b) Generate the term symbols for a  $3p^2$  electronic configuration and identify the ground state. 8

29. The ground state of F atom has a degeneracy of 4. The first excited state has a degeneracy of 2 and is  $404 \text{ cm}^{-1}$  above the ground state. What fraction of F atoms will be in the first excited state at 1000 K ?

(Assume only one low-lying excited state exists).

16

30. (a) The VB wave function for  $H_2$  molecule is given by

$$\psi(1, 2) = \{\varphi_a(1) \varphi_b(2) + \varphi_a(2) \varphi_b(1)\}.$$

(Assume  $\varphi_a, \varphi_b$  to be real).

(i) Normalize the wave function. 4

(ii) Calculate the one-electron density

$$\rho(1) = 2 \int \psi^2(1, 2) d\tau_2. \quad 8$$

(b) Match the following : 4

(i) SCF theory

(a) Bohr

(ii) Nuclear atom model

(b) Hartree

(iii) H-atom line spectrum

(c) Heisenberg

(iv) Uncertainty principle

(d) Rutherford

(i)..... (ii)..... (iii)..... (iv).....

31. (a) Give a brief account of flash photolysis.

(b) Calculate the ionic strength and activity coefficient for 0.1 M NaCl solution.  $A = 0.509$ . 16

32. (a) What is meant by partition functions ?

Derive the equation for translational partition function.

(b) Calculate the translational partition function of oxygen molecule confined to a 200 ml. vessel at 298 K (mass of oxygen molecule =  $16 \times 3.348 \times 10^{-27}$  kg). 16

33. (a) A dead sea scroll gives 12.6 dpmpg. Similar living sample gives 15.3 dpmpg. If the half-life period of carbon-14 is 5720 years, what will be the age of the sea scroll ?

[dpmpg : disintegrations per minute per gram]

8



(b) Match A with B :

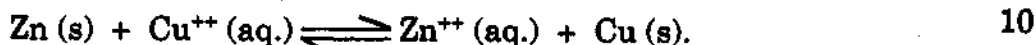
8

A

B

- |                                     |                          |
|-------------------------------------|--------------------------|
| (i) Radioactivity                   | (a) Seaborg              |
| (ii) Photoelectric effect           | (b) Heitler-London       |
| (iii) Laws of electrolysis          | (c) Ernst                |
| (iv) Chemical kinetics              | (d) Einstein             |
| (v) FT NMR spectroscopy             | (e) Faraday              |
| (vi) Valence bond theory            | (f) Becquerel            |
| (vii) Theory of strong electrolytes | (g) Eyring               |
| (viii) Transuranic elements         | (h) Debye-Hückel-Onsager |
| (i).....                            | (ii).....                |
| (iii).....                          | (iv).....                |
| (v).....                            | (vi).....                |
| (vii).....                          | (viii).....              |

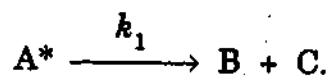
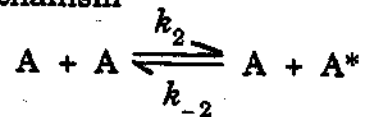
34. (a) Explain with schematic diagrams Schottky and Frenkel defects. 6
- (b) The values of standard reduction potentials of Zn/Zn<sup>2+</sup> and Cu/Cu<sup>2+</sup> half cells are -0.76 V and +0.34 V respectively at 25°C. Calculate the values of free energy change and the equilibrium constant for the reaction at 25°C :



35. (a) Identify the entries X, Y, Z and W in the character table of point symmetry group, D<sub>3h</sub>. Provide brief reasoning : 8

D <sub>3h</sub>	E	2C <sub>3</sub>	3C <sub>2</sub>	X	S <sub>6</sub>	3Y
A <sub>1</sub> '	1	1	1	1	1	1
A <sub>2</sub> '	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
A <sub>1</sub> ''	1	1	1	-1	-1	-1
A <sub>2</sub> ''	1	1	-1	-1	-1	1
Z	2	-1	0	-2	1	W

(b) Consider the mechanism



Obtain an expression for  $\frac{d[B]}{dt}$  invoking steady state approximation.

What would be the result for  $\frac{d[B]}{dt}$  for  $k_{-2} [A] \gg k_1$  ? 8

36. (a) Illustrate the structures of atactic, syndiotactic and isotactic polypropylene. 6

(b) Explain the use of Ziegler-Natta catalyst in the synthesis of co-ordination polymers. 10