

CHEMISTRY PAPER - III

Time Allowed : 2 1/2 Hours

Maximum Marks : 200

Note : Attempt question one and fourteen other questions.

1. a) d-d electronic transition bands of transition elements are usually weak. Explain. 6
- b) The absorbance of 0.1 M solution of $K_2Cr_2O_7$ is 0.2 at 450 nm and with 1 cm pathlength. Calculate the value of the molar extinction coefficient. What will be its value if both the pathlength and the concentration were simultaneously doubled ? 6
- c) Predict the structure of the compound C_8H_{10} which shows ^1H-NMR signals at δ 0.9 (t, 2H); 2.3 (q, 2H) 7 : (s, 5H). Assign the NMR signals. 6
- d) The mass spectrum of a compound $C_5H_{12}O$ has ions at m/z 88,43,29. Derive its structure and suggest plausible structures for the ions. 6
- e) How will you distinguish between thiophenol (Ph-SH) styrene (Ph-CH=CH₂) and phenylacetylene by IR spectroscopy ? 6
2. State the Boltzmann distribution law (BDL). Use BDL to calculate the ratio of population at 300 K for energy levels separated by
 i) 1000 cm^{-1} ii) 10 $kJ mol^{-1}$ 13
3. Which of the species given below has higher prescribed property ? Explain your answer with a qualitative MO diagram. 13
- | Species | Property |
|----------------------------|---------------------------------|
| (i) O_2, O_2^-, O_2^+ | bond order |
| (ii) N_2, O_2, F_2 | number of bonding electrons |
| (iii) O_2^{2-}, N_2^{2-} | number of antibonding electrons |
| (iv) NO, CO | first ionization energy |
| (v) F_2, F_2^+, F_2^{++} | bond energy |
4. a) Show that the wave functions for H atom. 6

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} e^{-r}$$

and

$$\Psi_{2s} = \frac{1}{4\sqrt{2\pi}}(2-r)e^{-r/2}$$

are orthonormal

Hint : Use $\int_0^{\infty} r^n e^{-\alpha r} dr = \frac{n}{\alpha^{n+1}}$

- b) Calculate the values of r where $4\pi r^2 \Psi_{1s}^2$ and $4\pi r^2 \Psi_{2s}^2$ attain maxima 7
5. a) Homonuclear diatomic molecules do not exhibit rotational spectra, whereas heteronuclear diatomics do. Explain. 5
- b) Write down expressions for moment of inertia (I) for a diatomic molecule and also for frequency separation (2B) of the rotation lines. 8
6. a) The rotational spectra of CO and HF show a series of lines separated by $3,842\text{cm}^{-1}$ and 419cm^{-1} respectively. Account for the difference. 5
- b) Define C_p and C_v . 4
- c) Show that for an ideal gas. 4
- $$C_p - C_v = P \left(\frac{\partial V}{\partial T} \right)_P$$
7. a) Write the cell reactions, calculate the standard e.m.f. of the following cells. Indicate anode and cathode. 8
- i) $\text{Ag} | \text{Ag}^+, \text{Br}^- (a=1) | \text{AgBr} (s) | \text{Ag}$ $E^\circ (\text{Ag}^+, \text{Ag}) = + 0.799 \text{ V}$
 $E^\circ (\text{AgBr}, \text{Br}^-) = + 0.095 \text{ V}$
- ii) $\text{Pt} | \text{Hg} | \text{Hg}_2\text{Cl}_2 | \text{Cl}^-, \text{H}^+ (a=1) | \text{H}_2 | \text{Pt}$ $E^\circ (\text{Hg}^+, \text{Hg}) = +0.268 \text{ V}$
- b) Illustrate graphically the variation of mean ionic activity coefficient for HCl and $\text{Ca} (\text{NO}_3)_2$ as a function of \sqrt{c} . When c is concentration. How would the activity coefficient of urea vary with c? 5
8. a) Calculate the translational partition function for H_2 (g) at 2000 K and 1 atom. 8
- b) What is Born–Oppenheimer approximation ? 2
- c) The plot electronic energy vs internuclear distance for H_2 is called potential energy diagram. Explain. 3
9. a) Write down the expression for radioactive decay of a single radionuclide 2

- b) Show that for radioactive decay, the half life is independent of initial concentration. 4
- c) What is pair production ? What is the minimum energy requirement for pair production ? 4
- d) State why (d, p) reaction is more favoured than (d, n) reaction. 3
10. a) Consider a particle of mass m in a cubic box with length l . What is the degeneracy of the eigenstate with energy $= 51h^2/(8 ml^2)$? 8
- b) Given the wavefunctions for ethylene within Huckel theory.
- $$\Psi_{\pm} = \frac{1}{\sqrt{2}}(\phi_1 \pm \phi_2)$$
- calculate the bond order p_{12} and atomic charge q_1 . 5
11. a) Write down the Arrhenius equation for activation energy. Relate frequency factor to probability factor and collision number. 6
- b) How does collision number vary with temperature ? How is K^* related to ΔG^* , ΔH^* and ΔS^* , the respective thermodynamic quantities for the activated complex ? 7
12. Explain briefly the following terms with an example / figure / equation if necessary
- a) homogeneous catalysis 3
- b) partial molal volume 3
- c) first-order perturbation theory 4
- d) activity coefficient 3
13. a) Give IUPAC nomenclature for the following complexes :
- i) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$ ii) $[\text{Co}(\text{en})\text{Cl}_3(\text{H}_2\text{O})]$
- iii) $[\text{Co}(\text{NH}_3)_5\text{CO}_3]_2$ iv) $\text{Fe}[\text{PtCl}_4]$ 8
- b) Both $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ appear colourless even though there is a significant difference in their Δ values. Why ? 5
14. a) What is effective atomic number ? Calculate EAN of Fe in $\text{Fe}(\text{NO})_2(\text{CO})_2$ and in $\text{Fe}(\text{C}_5\text{H}_5)_2$ 7

- b) Using valence bond model, predict geometries and spin state in (Bohr magnetons) of the following ions :
- | | | |
|--------------------------------------|-------------------------------------|---|
| i) $[\text{Ag}(\text{CN})_2]^-$ | ii) $[\text{Cu}(\text{CN})_4]^{2-}$ | |
| iii) $[\text{Fe}(\text{CN})_6]^{3-}$ | iv) $[\text{Zn}(\text{CN})_4]^{2-}$ | 6 |
15. a) Cerium shows +3 and +4 oxidation states in the compounds while europium exhibits +2 and +4 oxidation states. Explain. 7
- b) Draw the shapes of the following molecules, indicating position of lone pairs(s) of electrons (if any)
- | | | |
|--------------------|----------------------------------|---|
| i) XeF_2 | ii) ICl_5 | |
| iii) SF_6 | iv) $\text{Si}_2\text{O}_7^{6-}$ | 6 |
16. a) With the help of an energy level diagram show relative d orbital splitting for an octahedral, tetrahedral and square planar complexes. 7
- b) With the help of balanced chemical equations, explain in brief the extraction of silver using sodium cyanide. 6
17. a) Outline the steps in the synthesis of borazine ($\text{B}_3\text{N}_3\text{H}_6$) from diborane and ammonia. 6
- b) Explain with the help of chemical equations dehydrating and oxidising behaviour of sulphuric acid. 7
18. a) Explain why Schottky defects are predominant in alkali halides, while Frenkel defects prevail in silver halides. 4
- b) State one experimental method for determining the nature of defects present in crystals. 2
- c) Draw schematic band diagram of intrinsic semiconductor. Label valence and conduction bands. Show the Fermi level and forbidden energy gap. 7
19. a) Name any two π -acid ligands and state the nature of the acceptor orbitals for each. 6
- b) Write a brief account of nitrogenase 7
20. a) Hydrated calcium oxalate is thermally decomposed to the oxide in an inert atmosphere in the temperature range $20^\circ - 700^\circ\text{C}$. Draw a schematic DTA curve. Label the various DTA peaks. 4

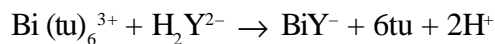
b) Draw the shapes of the polarographic waves for Cd^{2+} ion.

i) without the addition of maximum suppressor and

ii) with the addition of maximum suppressor.

Comment on the difference in shapes of these curves.

21. a) Explain briefly the principle of photometric titrations. Ethylene diamine tetraacetic acid abstracts bismuth (III) from its thiourea complex



Draw the shape of the photometric titration curve based on the above reaction, given that the Bi(III)-thiourea complex is the only species in the system which absorbs at 465 nm. Locate the equivalence point on the curve. 7

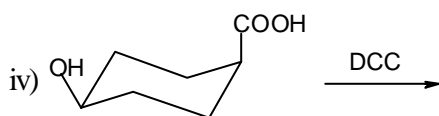
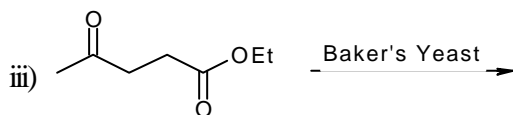
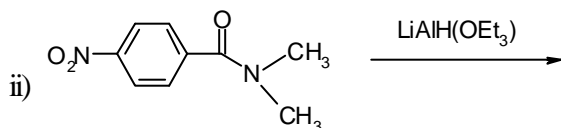
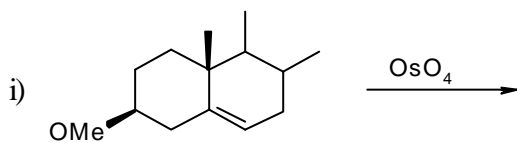
b) Draw schematic acid-base conductometric titration curves for the titration of

(i) HCl with NaOH and ii) CH_3COOH with NaOH

Locate the equivalence point on the curves. 6

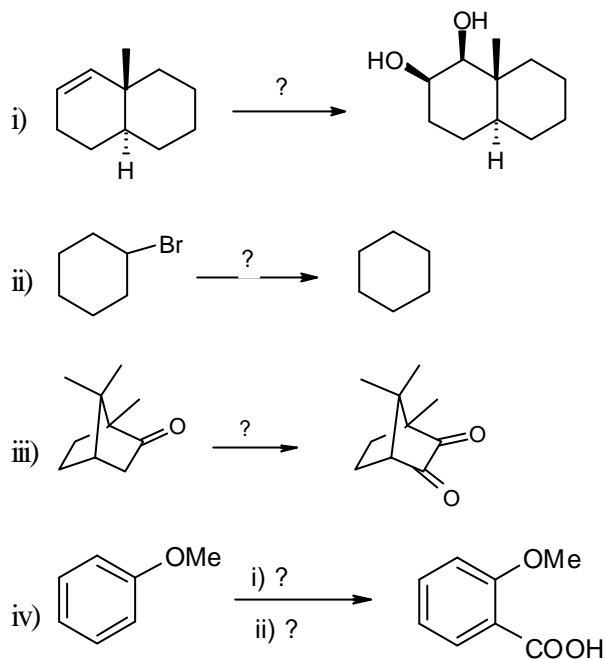
22. Give the products of the following reactions :

13

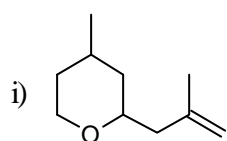


23. Indicate the reagents required for the following conversion :

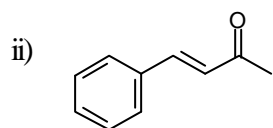
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24. a) Match the following



a) IR : 2200 cm^{-1}



b) $^1\text{Hnmr}$: 6.7, 1H, J = 16 Hz
 CDCl_3 , δ : 7.48, 1H, J = 16 Hz

iii) Ph - $\text{C}\equiv\text{N}$

c) MS : m/z 55; 99 (100%)

a)

b)

c)

6

b) Based on the spectral data given below deduce the structure of the hydrocarbon Assign the signals.

IR : $3030, 1600, 1500, 700\text{ cm}^{-1}$ and a characteristic strong band at 2210 cm^{-1} .

$^1\text{Hnmr}$: 3.1 (1H, s); 7.4 (5H, s)

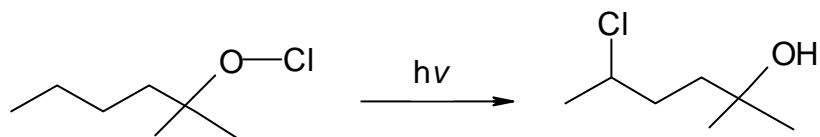
CDCl_3 , δ

Mass : m/z 102 (M^+)

7

25. a) Propose a mechanism for the reaction given below :

7



b) Complete the following :

6

