

Time: 3 hours

Full Marks: 70

Use separate answer scripts for each half

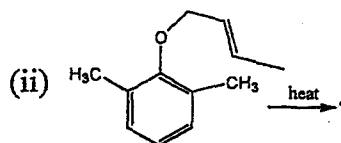
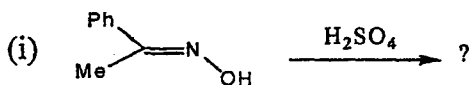
FIRST HALF

1. (a) What type of electronic transitions do you expect from each of the following compounds?

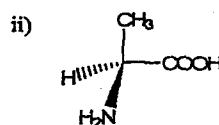
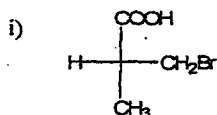
(i) Acetone, (ii) 1,3-Butadiene and (iii) *para*-nitroaniline

(b) Explain why aniline shows blue shift in acidic solution.

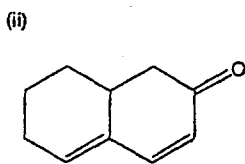
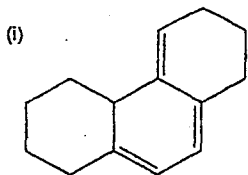
(c) Predict the product(s) in the following reactions and give the mechanism of product(s) formation in each case.



(d) Find out the absolute configuration of following compounds:



(e) Calculate λ_{\max} for the following compounds:



$$[3+2\frac{1}{2}+(2\frac{1}{2}\times 2)+(1\frac{1}{2}\times 2)+(2\times 2)]$$

OR

2. (a) Explain why:

- Vinyl chloride undergoes polymerization but ethyl chloride does not.
- Cyclopentadienyl anion is more stable than cyclopentadiene.
- Para*-nitrophenol shows red shift in alkaline medium.

(b) Distinguish between addition polymerization and condensation polymerization with examples.

(c) Write short notes on:

(i) Hofmann halo-amide reaction, (ii) Bakelite, and (iii) Plane of symmetry.

[(2×3)+4+(2½×3)]

3. (a) What are the essential elements of life? Show graphically the nature of the dependence of metabolic activity on the concentration of essential and toxic elements. Explain with example that essentiality also depends on the oxidation state of the element.

(b) Write down names and chemical structures of chelating antidote for removal of

(i) lead (ii) arsenic and (iii) mercury from living system.

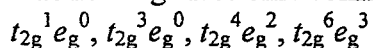
[2+5+3+(3×2½)]

OR

4. (a) Write down the names and structures of two platinum based anticancer drugs. Discuss the limitations of these drugs.

(b) What are the promising ruthenium based anticancer compounds? Give two examples.

(c) Which of the following electronic configurations exhibit Jahn-Teller distortion?



(d) Tetrahedral complexes show only high spin configuration – Explain.

[(2+2+2½)+(2½+2½)+3+3]

SECOND HALF

5.(a) Explain with suitable diagram, the variation of equivalent conductance with concentration for strong and weak electrolyte.

(b) The speed ratio of Ag^+ and NO_3^- in an aqueous solution is 0.92. Calculate transport number of these two ions

(c) Why is alternating current used in measuring solution conductance?

(d) A piece of iron is dipped into 1(M) NiSO_4 solution. Calculate E^0 and equilibrium constant for the system. [Given: $E^0 \text{Fe}^{2+}/\text{Fe} = -0.441\text{V}$ and $E^0 \text{Ni}^{2+}/\text{Ni} = -0.24\text{V}$].

(e) Show that for a very weak electrolyte, the degree of dissociation is directly proportional to square root of dissociation constant and inversely proportional to square root of concentration.

[4 + 3 + 2 + 4 + 4½]

OR

6. (a) Define ionic conductance, ionic mobility and transport number and obtain the relation between them.

(b) Find out the free energy change, under standard condition, for the reaction: $\text{Cd} + \text{Hg}_2\text{Cl}_2 \rightarrow \text{Cd}^{2+} + 2\text{Cl}^- + 2\text{Hg}$. Configure the cell and write down the half cell reactions. Given $E^0_{(\text{Cd}/\text{Cd}^{2+})} = 0.402\text{V}$ and $E^0_{\text{calomel}} = -0.2415\text{V}$

(c) Illustrate the working principle of a Li-ion battery during charging and discharging cycle.

[5½ + 6 + 6]

7. (a) For the reaction scheme, $\text{A} \rightarrow \text{B} \rightarrow \text{C}$ with successive first-order rate constants k_1 and k_2 derive the necessary equation describing the temporal behaviour of [C]. Hence, show that the rate of formation of C depends solely on the last-step of the reaction provided $k_1 \gg k_2$, where k_1 and k_2 are rate constants for the first and second steps respectively.

(b) As per Arrhenius equation plot $\ln k$ vs T . Rewrite Arrhenius activation energy in terms of E_1 as it appears in $k = B T^m \exp(-E_1 / RT)$?

(c) Draw the energy band spectrum of Lithium crystal, starting from its atomic levels.

(d) The energy band gap decreases in the given manner: Diamond > Silicon > Germanium. Explain the behaviour. Why is diamond an insulator at room temperature while it conducts around $T = 600\text{K}$.

[(3+2) + (1+3½)+3 + (3 + 2)]

OR

8. (a) Justify the Arrhenius equation of reaction rate by employing Van't Hoff equation or collision theory.

(b) Considering the rate law: $r = k_2 \left(\frac{k_1}{2k_4} \right)^{1/2} C_{\text{CH}_3\text{CHO}}^{3/2}$ for the thermal decomposition of acetaldehyde, show that the measured activation energy E is given by $E = E_2 + 1/2 (E_1 - E_4)$.

(c) The rate of decomposition of HI is given by $\frac{-dC_{\text{HI}}}{dt} = kC_{\text{HI}}^2$, with $k = 4 \times 10^{-6} \text{ l/mol/sec}$ at 327°C . How many molecules of HI would decompose per sec at atmospheric pressure?

(d) Define the terms: (i) Acceptor levels, and (ii) Recombination

(e) Describe the conducting behaviour of an n-type Silicon crystal using the band diagram.

[4+2+4+2+5½]