INSTRUCTIONS

Candidates should attempt all the questions in Parts A, B & C. However, they have to choose only three questions in Part D.

Answers must be written in the medium opted (i.e. English or Kannada).

This paper has four parts:

- A 20 marks
- B 100 marks
- C 90 marks
- D 90 marks

Marks allotted to each question are indicated in each part.
PART A

Each question carries 5 marks.

1. (a) Arrange the following species in the increasing order of stability. Justify your answer.
   \[ \text{O}_2, \text{O}_2^+, \text{O}_2^{++}, \text{O}_2^- \]

(b) One mole of an ideal gas undergoes expansion from 22.4 l to 44.8 l at 273 K against a constant pressure of 5 atmospheres. Calculate the work done and also the enthalpy change.

(c) The rate constant of a first order reaction increases from \[ 2 \times 10^{-5} \text{ s}^{-1} \] to \[ 2 \times 10^{-4} \text{ s}^{-1} \] when the temperature is increased from 27° C to 47° C. Calculate the activation energy of the reaction.

(d) Calculate the potential of the following cell at 300 K:
   \[ \text{Cu} | \text{Cu}^{2+}_{0.01m} | \text{Cu}^{2+}_{0.1m} | \text{Cu} \]

The standard electrode potential of \[ \text{Cu}^{2+} | \text{Cu} \] is 0.334 V.
PART B

Each question carries 10 marks.

2. Explain the term 'well behaved functions'. Which of the following are well behaved functions? Justify your answer.
   \[ e^{kx}, \ e^{-kx}, \ \sin k\theta \]
   
   \( k \) is a constant, \( x \) varies from zero to infinity, \( \theta \) varies from zero to 2\( \pi \), \( a \)
   is a constant.

3. NO is produced from \( N_2 \) and \( O_2 \) according to the following equation:
   \[ N_2 (g) + O_2 (g) = 2 \text{ NO} (g) \]
   Calculate the free energy change when NO is produced at a pressure of 1 atmosphere from \( N_2 \) and \( O_2 \) each at a pressure of 0.5 atmosphere. The reaction temperature is 2500 K. The equilibrium constant for the reaction at 2500 K is 3.60 \times 10^{-3}.

4. List the seven crystal systems along with relationship between unit cell dimensions.

5. Define collision cross-section. How does rate of bimolecular reaction depend on collision cross-section? Derive the relationship.

6. The resistance of 0.5 M electrolyte in a cell was found to be 1000 ohms. Calculate the molar conductance of the solution. The electrodes were kept 2 cm apart and have an area of 5 cm².

7. Calculate the equilibrium constant of the reaction
   \[ \text{Sn}^{4+} + 2 \text{Ti}^{3+} = 2 \text{Ti}^{4+} + \text{Sn}^{2+} \]
   at 25°C. The standard electrode potentials of \( \text{Sn}^{2+} | \text{Sn} \) and \( \text{Ti}^{4+}, \text{Ti}^{3+} | \text{Pt} \) are -0.140 and 0.040 V respectively.

8. With the help of Jablonski diagram explain the various photochemical transitions.

9. Calculate the CSFE and spin only magnetic moment of \([\text{CoF}_6]^{3-}\).

10. What are the main sources of Thorium and Uranium? How are they extracted? Explain.

11. One mole of He is mixed with 0.5 moles of Ne at 300 K keeping the pressure constant. Calculate the entropy change and free energy change.
Each question carries 15 marks.

12. The 1s wave function of H atom is given by \( \psi_{1s} = \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{3/2} e^{-r/a_0} \)

\( a_0 = \) Bohr radius, \( r = \) distance from the nucleus.

Draw the radial distribution curve for 1s atomic orbital. Show that the radial probability distribution is maximum at \( r = a_0 \).

13. Lithium (\( M = 6.941 \text{ g mol}^{-1} \)) crystallises in b.c.c. The separation between 100 planes of the metal is 350 picometer. Calculate the density of lithium.

14. State the essential steps in the photochemical reaction between \( \text{H}_2 \) and \( \text{Br}_2 \). Derive the rate law.

15. (a) An aqueous solution of \( \text{CuSO}_4 \) is electrolysed between (i) two Cu electrodes, (ii) two Pt electrodes. Predict the products at cathode and anode. Justify your answer.

(b) A decinormal solution of \( \text{AgNO}_3 \) was electrolysed between two Pt electrodes. A decrease in concentration of \( 5.124 \times 10^{-4} \) gram equivalents occurred in the anode compartment. The amount of Cu deposited in the copper coulometer connected in series was 0.03879 g. Calculate the transference number of \( \text{Ag}^+ \) and \( \text{NO}_3^- \).

(Atomic weight of Cu = 63.6 g mol\(^{-1}\))

16. Briefly explain the principle of potentiometric titration. What are the methods to detect the end point in a potentiometric titration? Explain.

17. Discuss the bonding in olefin complexes.
PART D

Answer any three of the following questions. Each question carries 30 marks.

18. Compare Valence Bond and Molecular Orbital method of chemical bonding. Which of these do you find better in H₂? Justify your answer.

19. What are the assumptions in Absolute Rate Theory? Using Absolute Rate Theory derive an equation for the rate constant of a bimolecular reaction.

20. Define mean ionic activity coefficient. How would you evaluate mean ionic activity coefficient of a strong electrolyte using Debye Hückel theory?

21. What are the factors that influence reactions in non-aqueous media? Compare reactions in non-aqueous media with those in aqueous media taking a specific example.

22. What is meant by liquid crystal? What are the different types of liquid crystals? How are they classified? Write a brief account of the applications of liquid crystals.

Values of useful constants:

\[ R = 8.314 \text{ JK}^{-1}\text{ mol}^{-1} \]

Faraday \( F = 96500 \text{ Coulombs} \)

Avogadro number = \( 6.023 \times 10^{23} \)
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PART A

Each question carries 5 marks.

1. (a) How can IR spectroscopy be used to distinguish between intramolecular and intermolecular hydrogen bonding?

(b) Alkaline hydrolysis of ethylbromide is catalysed by iodide ion. Explain.

(c) How can mass spectroscopy be used for detecting the presence of Br in an organic compound?

(d) Write the structure of substrates A and B in the following conversions:

\[
A \xrightarrow{(1) B_2H_6} \xrightarrow{(2) NaOH / H_2O_2} \]

\[
B \xrightarrow{OSO_4 / HIO_4} \]

\[
\text{CHO} \quad \text{CHO} \]
PART B

Each question carries 10 marks.

2. Simple β-ketoacids readily undergo decarboxylation on being heated, while the following compound is stable. Explain.

![Chemical structure]

3. How will you effect the following conversion?

![Chemical structure conversion]

4. Which of the following bromoalkenes will give an alkyne on base catalysed elimination? Why? What is the product obtained in the case of the other bromoalkene?

![Chemical structures]

5. The treatment of o-bromoanisole with sodamide in liquid ammonia gives mainly m-aminoanisole. Account for this observation.

6. How will you account for the observation that, 2,4-dinitrobenzene-diazonium chloride couples with anisole, while benzenediazonium chloride does not undergo coupling reaction with anisole?
7. How will you distinguish between the following compounds using UV-Vis spectroscopy?

8. What are the common methods for generating carbenes? With the help of an example, suggest a suitable reaction that can be used for distinguishing between a singlet and a triplet carbene.

9. Discuss the reactions given by the following compounds, on photoexcitation of the carbonyl groups:

10. Give one method of determination of $M_w$ of a polymer sample.

11. Give a brief account of the formation, structure, stability and fate of carbocations.
12. Cyanide ion catalyses the self condensation of benzaldehyde. Similar reaction is not given by OH\textsuperscript{−}. Explain.

13. Predict the product/s in the following reactions. Justify your answer.

\[ \text{\begin{align*} 
\text{CH}_2=CH\text{CH}=CH_2 + \text{CH}_2=CH\text{CO}_2\text{Me} & \rightarrow \\
\text{CH}_2=CH\text{CH}=CH_2 + \text{CH}_3=CH\text{CO}_2\text{Me} & \rightarrow 
\end{align*}} \]

14. How would you employ base catalysed reactions in the synthesis of the following compounds?

(a) \[ \text{Ph}\text{CH}=\text{CHCO}_2\text{Ph} \]

(b) \[ \text{PhCOCOPh} \]

15. Aliphatic fluorides are less easily hydrolysed than the corresponding chlorides, whereas 2,4-dinitrofluorobenzene is more rapidly hydrolysed than 2,4-dinitrochlorobenzene. Explain.
16. How will you differentiate between the following compounds using the technique indicated against each pair?

(a) \[
\begin{align*}
\text{O} & \quad \text{and} \quad \text{O} \\
\end{align*}
\]
using IR

(b) \[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]
and \[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\end{align*}
\]
using \text{^1H NMR}

(c) \[
\begin{align*}
\text{CH}_2\text{CHO} \\
\end{align*}
\]
and \[
\begin{align*}
\text{CH}_3 \\
\end{align*}
\]
using mass spectra

17. Answer the following questions based on the following scheme which indicates a practical route to nylon-6:

\[
\begin{align*}
\text{N} & \quad \text{OH} \\
\xrightarrow{\text{Conc. H}_2\text{SO}_4} & \quad \text{C} \\
\triangle & \quad \text{Nylon-6} \\
\end{align*}
\]

(a) Write down the structure of compound C.

(b) Indicate the mechanism involved in the formation of C.

(c) Give the structure of nylon-6 and nylon-6,6.

(d) Write down the structure of monomers that are involved in the preparation of nylon-6,6.
PART D

Answer any three of the following questions. Each question carries 30 marks.

18. Base catalysed condensation of an ester and a ketone to get β-diketones. Illustrate the limitations of this procedure, using the condensation reaction of 3-pentanone and ethyl acetate.

19. With suitable examples, illustrate the application of Ziegler–Natta catalysts in the synthesis of stereoregular polymers.

20. Sketch the HOMO for the pentadienyl cation (H₂C = CH–CH = CH–CH₂⁺) and pentadienyl anion (H₂C = CH–CH = CH–CH₂⁻). Determine whether these undergo conrotatory or disrotatory ring closure under thermal conditions. Verify that the stereochemical course of these reactions are consistent with Woodward–Hoffmann rules.

21. Given the following data, assign the structure of the organic compound:

   Molecular formula: C₇H₁₂O₂, IR (br., 1720, 1640 cm⁻¹),
   1H NMR (δ) 1.7 (6H, s), 2.0 (2H, m), 2.36 (2H, t), 5.1 (1H, t),
   10.5 (1H, exchanged with D₂O).

22. Discuss the influence of the following factors on S_N1 and S_N2 substitutions:

   (a) Nucleophile
   (b) Leaving group
   (c) α and β-branching on substrate
   (d) Reaction medium