

2008
CHEMISTRY
Paper 1

Time : 3 Hours]

[Maximum Marks : 300

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.

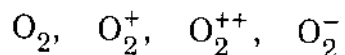
SEAL

PART A

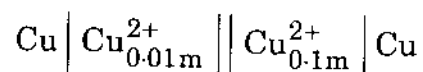
4×5=20

Each question carries 5 marks.

1. (a) Arrange the following species in the increasing order of stability. Justify your answer.



- (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 :



The standard electrode potential of $\text{Cu}^{2+} \mid \text{Cu}$ is 0.334 V.

PART B

10×10=100

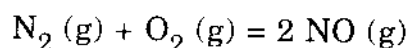
Each question carries 10 marks.

2. Explain the term 'well behaved functions'. Which of the following are well behaved functions ? Justify your answer.

$$e^{kx}, e^{-kx}, a \sin k\theta$$

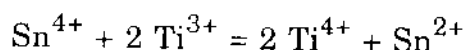
k is a constant, x varies from zero to infinity, θ varies from zero to 2π , a is a constant.

3. NO is produced from N_2 and O_2 according to the following equation :



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 3.60×10^{-3} .

4. List the seven crystal systems alongwith 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 cm^2 .
7. Calculate the equilibrium constant of the reaction



at 25° C. The standard electrode potentials of $Sn^{2+} | Sn$ and $Ti^{4+}, Ti^{3+} | Pt$ are -0.140 and 0.040 V respectively.

8. With the help of Jablonski diagram explain the various photochemical transitions.
9. Calculate the CFSE and spin only magnetic moment of $[CoF_6]^{3-}$.
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.

[Turn over

PART C

6×15=90

Each question carries 15 marks.

12. 1s (one s) 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 H_2 and Br_2 . Derive the rate law.
15. (a) An aqueous solution of 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 AgNO_3 was electrolysed between two Pt electrodes. A decrease in concentration of 5.124×10^{-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 Ag^+ and 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

3×30=90

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 H_2 ? 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 :

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{Faraday } F = 96500 \text{ Coulombs}$$

$$\text{Avogadro number} = 6.023 \times 10^{23}$$

2008
CHEMISTRY
Paper 2

Time : 3 Hours]

[Maximum Marks : 300

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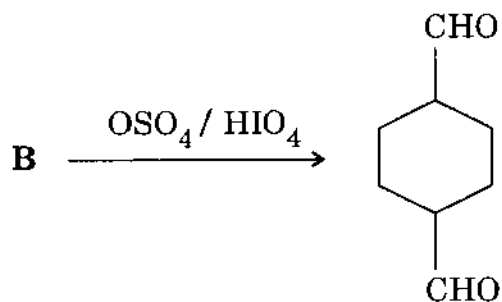
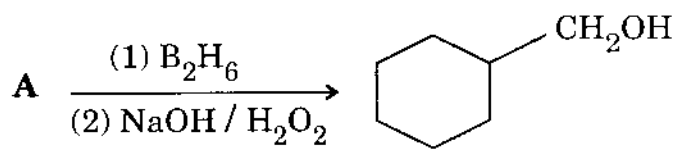
SEAL

PART A

4×5=20

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 :

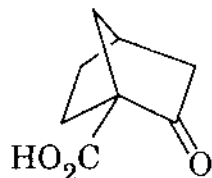


PART B

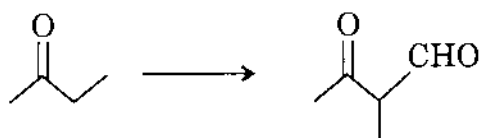
10×10=100

Each question carries 10 marks.

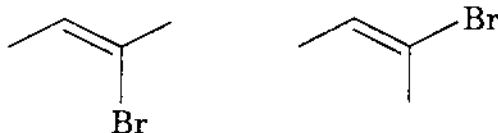
2. Simple β -ketoacids readily undergo decarboxylation on being heated, while the following compound is stable. Explain.



3. How will you effect the following conversion ?



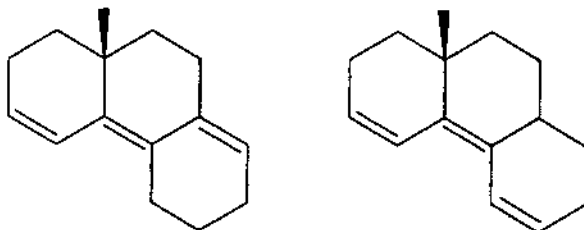
4. Which of the following bromoalkenes will give an alkyne on base catalysed elimination ? Why ? What is the product obtained in the case of the other bromoalkene ?



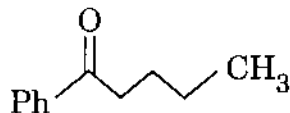
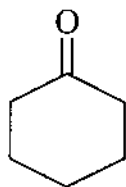
5. The treatment of *o*-bromoanisole with sodamide in liquid ammonia gives mainly *m*-aminoanisole. Account for this observation.
6. How will you account for the observation that, 2,4-dinitrobenzene-diazonium chloride couples with anisole, while benzenediazonium chloride does not undergo coupling reaction with anisole ?

[Turn over

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 :



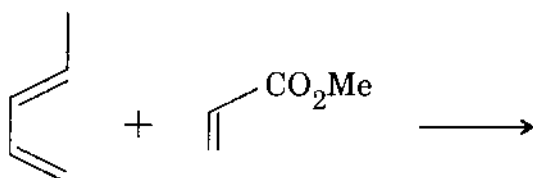
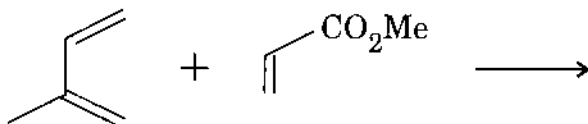
10. Give one method of determination of M_w of a polymer sample.
11. Give a brief account of the formation, structure, stability and fate of carbocations.

PART C

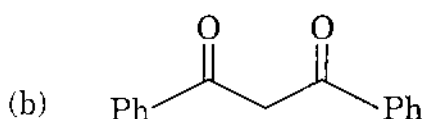
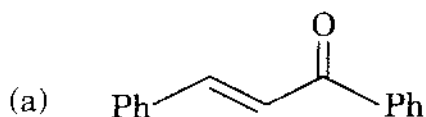
6×15=90

Each question carries 15 marks.

12. Cyanide ion catalyses the self condensation of benzaldehyde. Similar reaction is not given by OH^- . Explain.
13. Predict the product/s in the following reactions. Justify your answer.



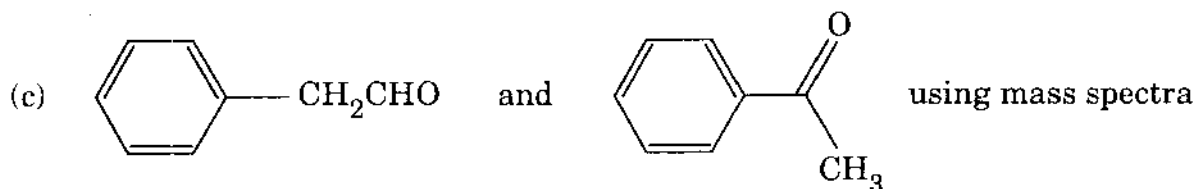
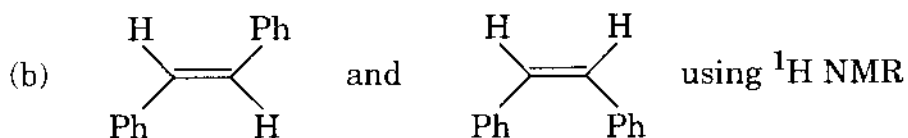
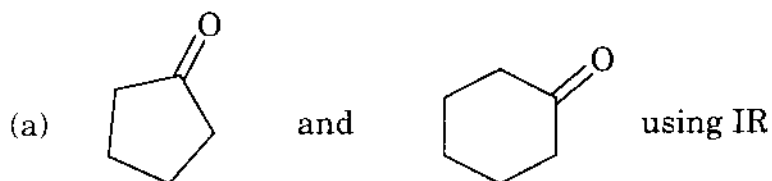
14. How would you employ base catalysed reactions in the synthesis of the following compounds ?



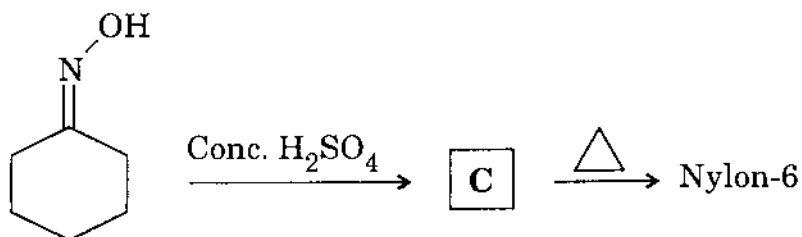
15. Aliphatic fluorides are less easily hydrolysed than the corresponding chlorides, whereas 2,4-dinitrofluorobenzene is more rapidly hydrolysed than 2,4-dinitrochlorobenzene. Explain.

[Turn over

16. How will you differentiate between the following compounds using the technique indicated against each pair ?



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



- Write down the structure of compound C.
- Indicate the mechanism involved in the formation of C.
- Give the structure of nylon-6 and nylon-6,6.
- Write down the structure of monomers that are involved in the preparation of nylon-6,6.

PART D

3×30=90

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 ($\text{H}_2\text{C} = \text{CH} - \text{CH} = \text{CH} - \text{CH}_2^+$) and pentadienyl anion ($\text{H}_2\text{C} = \text{CH} - \text{CH} = \text{CH} - \text{CH}_2^-$). 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 : $\text{C}_7\text{H}_{12}\text{O}_2$, 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 D_2O).
22. Discuss the influence of the following factors on $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ substitutions :
- (a) Nucleophile
 - (b) Leaving group
 - (c) α and β -branching on substrate
 - (d) Reaction medium