

2006
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. The number of marks carried by each question is indicated at the end of the question.*

Answers must be written in English.

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.

Simple Scientific non-programmable type calculators are permitted.

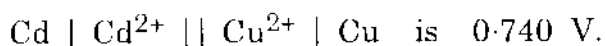
SEAL

PART A

4×5=20

Each question carries 5 marks.

1. (a) Calculate the zero point energy of an electron confined to a one-dimensional box of length 10 nm.
- (b) A first order reaction is 30% complete in one hour. Find the rate constant.
- (c) The standard emf of the cell



Write the cell reaction.

Calculate the equilibrium constant of the cell reaction at 300 K.

- (d) An iron complex gives electronic spectrum with a wavelength maximum at 540 nm. Calculate the energy of the radiation in kJ mol^{-1} .

PART B

10×10=100

Each question carries 10 marks.

2. Define radial distribution function. Draw radial distribution functions for 3s, 3p and 3d atomic orbitals. Explain the nature of the curves.
3. "Decrease in Gibbs free energy is a measure of the maximum amount of work other than pressure–volume work that can be obtained from a thermodynamic system." Justify the statement using thermodynamic equations.
4. Copper crystallizes in cubic phase. XRD of copper is taken using X-rays of wavelength 1.541 Å. Reflections are found at $\Theta = 21.65^\circ, 25.21^\circ, 37.06^\circ, 44.96^\circ, 47.58^\circ$ and higher angles. Calculate the length of the side of the unit cell and also predict the lattice type.
5. The second order reaction $A + B \rightarrow \text{Products}$ is having a rate constant 39.1 litres $\text{mol}^{-1} \text{minute}^{-1}$. A solution is made with 0.004 molar in A and 0.005 in B. How long will it take 90% of A to react ?
6. Calculate the mean ionic activity coefficient of 0.01 molal CaCl_2 in water at 25° C. The value of 'A' in Debye Hückel equation is 0.509.
7. Define liquid function potential. Explain one method to determine liquid function potential.
8. Photobromination of cinnamic acid was carried out using light of wavelength 435.8 nm. A light intensity of $1.4 \times 10^{-3} \text{ Js}^{-1}$ produced a decrease of 0.075 milli moles of bromine during an exposure of 1105 sec. The solution absorbed 80.1% of the light passing through it. Calculate the quantum yield.
9. Calculate the CFSE of Ni^{2+} (At. No. 28) in octahedral and tetrahedral field for strong and weak ligands. Neglect pairing energy. Predict the most stable complex.
10. Give a brief account of magnetic properties of lanthanides.
11. What are the advantages of non-aqueous titrimetry ? Explain.

[Turn over

PART C

6×15=90

Each question carries 15 marks.

12. Define lattice energy. Describe one method to determine lattice energy.
13. (a) State the third law of thermodynamics. Using the third law of thermodynamics show that absolute zero of temperature is unattainable.
(b) How would you determine the absolute entropy of a gas from the third law of thermodynamics ? Explain.
14. A second order reaction has an activation energy of 45.5 kcal mol⁻¹. The molecular diameter is 5 Å. Calculate the rate constant of the reaction at 500 K using Collision theory. The molecular weight of A is 100 g per mole.
15. Describe Onsager modification of Debye Hückel theory to understand conductance behaviour of electrolytes.
16. How would you determine the mean ionic activity coefficient of an electrolyte like HCl from emf measurements ? Explain.
17. Discuss the synthesis, structure and properties of ferrocene.

PART D

3×30=90

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

18. Discuss briefly the molecular orbital theory of bonding. Write molecular orbital configuration of the following molecules/ions. Predict the bond order.
- (a) CO
 - (b) NO
 - (c) CN^{\ominus}
19. Discuss briefly the kinetics of polymerization choosing one method of polymerization.
20. (a) Derive Bragg's Law for X-ray diffraction.
- (b) Explain single crystal method of X-ray diffraction analysis.
 - (c) State law of constancy of interfacial angles. What are the consequences of the law ? Discuss.
21. What are the advantages of fuel cells over other sources of energy ? Discuss the construction, working and applications of hydrogen-oxygen fuel cell.

! Turn over

22. Derive the following relations :

(a) $\bar{C}_p - \bar{C}_v = R$ for an ideal gas

(b) $\left(\frac{\partial u}{\partial v}\right)_T = 0$ for an ideal gas

(c) Kirchoff equation

(d) $\left(\frac{\partial \mu}{\partial p}\right)_T = \bar{V}$

(e) $\Delta S_{\text{mix.}} = -R [n_1 \ln x_1 + n_2 \ln x_2]$

$[\bar{C}_p, \bar{C}_v]$ — heat capacities at constant pressure and constant volume

u — internal energy

v — volume

\bar{V} — molar volume

μ — chemical potential

$\Delta S_{\text{mix.}}$ — entropy of mixing

n_1 and n_2 — number of moles

x_1 and x_2 — mole fractions of components 1 and 2 |

Values of useful constants

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

$$\text{Planck's constant } h = 6.627 \times 10^{-34} \text{ Js}$$

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

$$\text{Mass of electron} = 9.1 \times 10^{-31} \text{ kg}$$

$$\text{Velocity of light} = 3 \times 10^8 \text{ ms}^{-1}$$

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

$$A \text{ (Debye Hückel equation)} = 0.509$$

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

SEAL

2006
CHEMISTRY
Paper 2

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. The number of marks carried by each question is indicated at the end of the question.*

Answers must be written in English.

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.

Simple Scientific non-programmable type calculators are permitted.

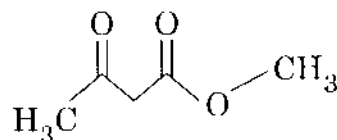
SEAL

PART A

4×5=20

Each question carries 5 marks.

1. (a) Fluoride can be easily displaced in an aromatic substitution reaction, while in aliphatic substitution reactions fluoride is the most difficult of the halides to be displaced. Explain.
- (b) How many signals are expected in the ^1H NMR spectrum of the following compound? Predict the chemical shift values. Justify.



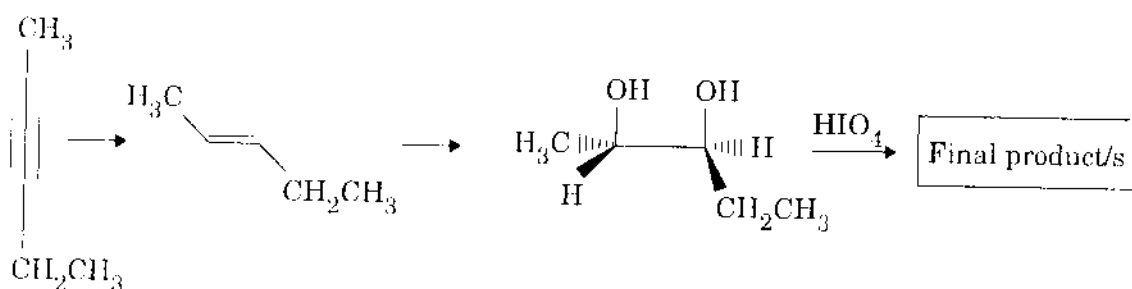
- (c) Treatment of anisole (methoxy benzene) with Na/liquid NH_3 in t-butanol gives 1-methoxy-1,4-cyclohexadiene and not 3-methoxy-1,4-cyclohexadiene. Why?
- (d) Give a method of determination of N-terminal amino acid of a polypeptide.

PART B

10×10=100

Each question carries 10 marks.

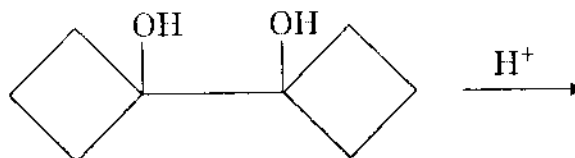
- Briefly discuss the main pathways of formation of carbocations. Explain why p-methoxybenzyl cation is more stable than benzyl cation.
- Suggest suitable reagent/s for the first two steps in the following conversion and indicate the structure of the final product :



- Discuss the advantages of Friedel-Crafts acylation over Friedel-Crafts alkylation.
- Draw a reaction coordinate diagram with the following criteria :
 - exergonic 3-step reaction
 - the first step is the rate determining step
 - the second intermediate is more stable than the first intermediate
 - the third step of the reaction is faster than the reverse of the second step
- What is step-growth polymerisation ? Write down the reactions involved in the formation of polyamide by step growth polymerisation.
- Write down the major product of nitration ($\text{H}_2\text{SO}_4/\text{HNO}_3$) of aniline and acetanilide. Explain the directing effects observed.
- Write down the structure of the major product obtained in the sodium catalysed mixed condensation between ethyl benzoate and ethyl acetate. Indicate the mechanism and justify the answer.

[Turn over

9. Explain how you would use ^1H NMR spectroscopy to distinguish between ethyl acetate and methyl propanoate and IR spectroscopy to distinguish between butanoic acid and methyl propanoate.
10. Predict the product and indicate the mechanism for the following reaction :



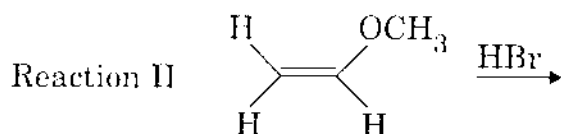
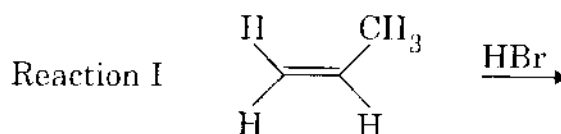
11. How can viscometry be used for determination of molecular weight of a polymer ?

PART C

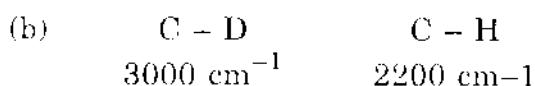
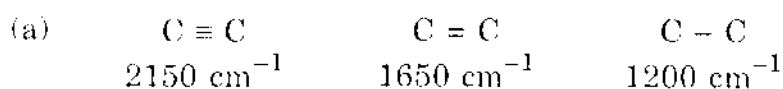
6×15=90

Each question carries 15 marks.

12. Write down the structure of the product in Reaction I and Reaction II. Which of these reactions is expected to proceed faster (Reaction I or II)? Justify the answer by indicating the mechanism and reaction coordinate diagrams.

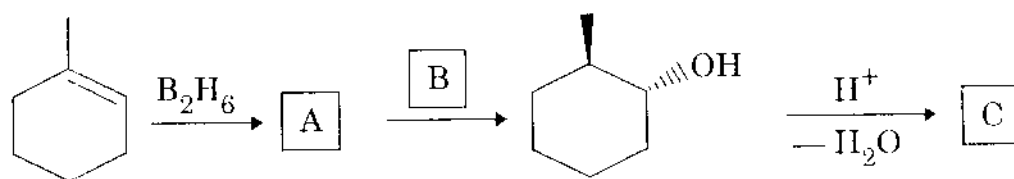


13. Predict the major product in the acetylation of furan with acetic anhydride and a Lewis acid. Write down the mechanism involved and justify your reasoning.
14. (a) Write down the equation showing the formation of PVC by a free radical chain reaction.
 (b) Briefly discuss the reaction used for preparation of crystalline polystyrene.
15. Briefly discuss the photochemical reactions of carbonyl compounds.
16. Account for the observed values for vibration stretch for the following bonds :



[Turn over

17. Supply missing reagent B and indicate the structure of the intermediate product A and the final product C. Justify the formation of C mechanistically.

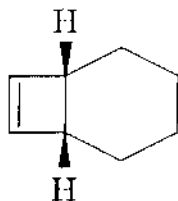


PART D

3×30=90

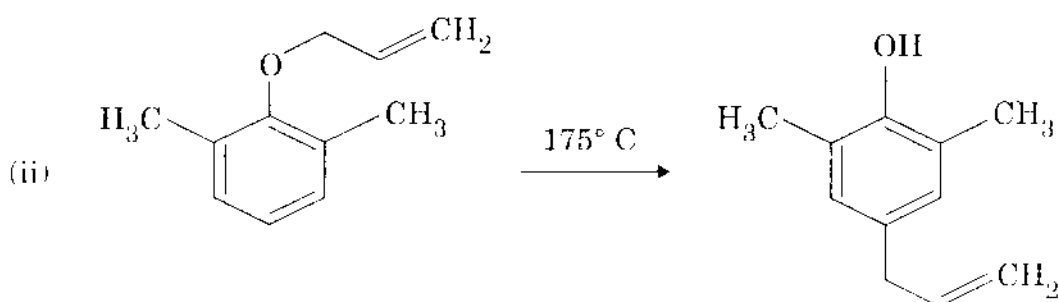
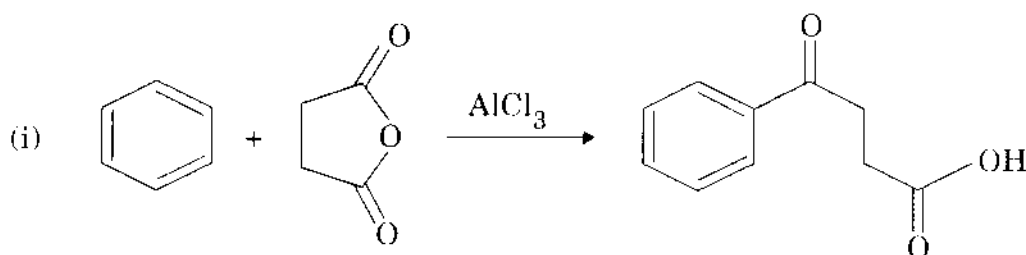
Answer any **three** of the following questions. Each question carries 30 marks.

18. (a) When (1Z, 3E)-1,3-cyclooctadiene is heated, bicyclo[4.2.0]oct-7-ene (structure given below) is obtained. (1Z, 3Z)-1,3-cyclooctadiene undergoes a photochemical ring closure to give the same compound. But (1Z, 3Z)-1,3-cyclooctadiene does not give a cyclobutene product when heated. Account for these observations.



bicyclo[4.2.0]oct-7-ene

- (b) When bicyclo[4.2.0]oct-7-ene is heated above 300° C (1Z, 3Z)-1,3-cyclooctadiene is obtained. Is this a concerted process?
19. (a) Indicate a mechanism for the following reactions :



[Turn over

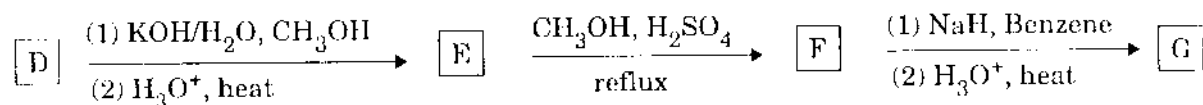
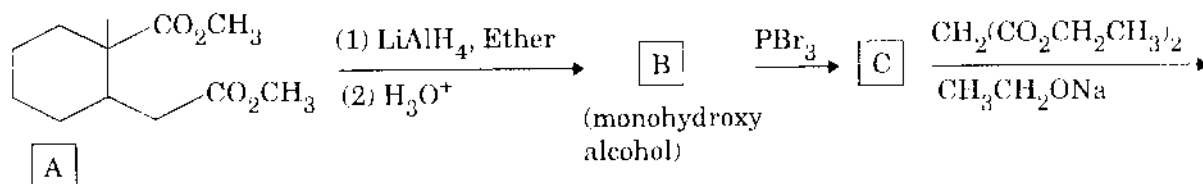
(b) How will you effect the following transformation ?



20. (a) Give a detailed account of the effects of the strength of the base on E1 vs. E2 vs. E1cB reactions.

(b) Explain the role of medium in deciding the rate of SN1 and SN2 substitutions.

21. Write down the structures corresponding to the letters B to G in the following reaction sequence :



22. An organic compound $\text{C}_5\text{H}_{12}\text{O}$ has the following IR and ^1H NMR spectral data. Deduce the structure of the compound. Explain the data.

IR : 3350, 3000, 1460, 1120 cm^{-1}

NMR (δ) : 0.9 (6H, triplet, $J = 6$ Hz), 1.3 (4H, quintet, $J = 6$ Hz),

3.3 (1H, quintet, $J = 6$ Hz), 3.6 (1H, singlet).

SEAL