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04/1

2005

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.

PART A

4×5=20

Each question carries 5 marks.

1. (a) Calculate the uncertainty in momentum of an electron (mass $9{\cdot}1 \times 10^{-31}$ kg) confined to a one dimensional box of length 10 nm.

(b) One mole of an ideal gas at 300 K undergoes expansion against a constant pressure of 1 atmosphere from an initial volume of 1 *l* to a final volume of 10 *l*. Calculate the work done by the gas in SI unit.

(c) Potassium crystallizes in body centered cubic lattice with a unit cell dimension of 5·34 Å. Calculate the perpendicular distance between (2 //) planes.

(d) The percentage transmittance of an aqueous solution of disodium fumarate at 250 nm is 19·2% for a 5×10^{-4} M solution in a 1 cm cell. Calculate the molar absorptivity.

PART B

10×10=100

Each question carries 10 marks.

1. (a) Write time independent Schrödinger wave equation. What would be the equation for a H atom.

   (b) Write molecular orbital configuration for O_2 and NO. Calculate the bond order of O_2 and NO.

2. Explain the need for second law of thermodynamics. State second law of thermodynamics.

3. What are point defects in crystals ? Write one example for each. How do defects modify properties of solids ? Explain.

4. What are the assumptions in collision theory of reaction rates ? Using collision theory derive an equation for the rate constant of a bimolecular reaction.

5. Define mean ionic activity coefficient. Using Debye Hückel theory, derive an equation for the mean ionic activity coefficient of an electrolyte.

6. What are the advantages of a fuel cell ? Write electrode reactions for $H_2 - O_2$ fuel cell. Indicate the sign of electrodes. What is the standard cell potential of $H_2 - O_2$ fuel cell ?

7. The photochemical reaction between H_2 and Br_2 is having a quantum yield of almost unity. But the quantum yield of $H_2 - Cl_2$ reaction is 10^6. Account for the observation.

8. How do d orbitals split in an octahedral crystal field ? Explain.

9. Give a brief account of the various oxidation states of lanthanides.

10. Explain briefly the advantages of liquid ammonia as a solvent for chemical reaction.

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PART C

6×15=90

Each question carries 15 marks.

1. (a) Explain the term 'activation energy' of a chemical reaction. Suggest a method to determine enthalpy of activation and entropy of activation of a chemical reaction.

(b) When the temperature was raised from 298 K to 308 K the rate of a reaction was doubled. Calculate the activation energy.

2. (a) Explain briefly moving boundary method to determine the transference number of an ion.

(b) Calculate the specific conductance of a 0·100 molar sodium chloride solution. The ionic mobilities of Na^+ and Cl^- are $4{\cdot}26 \times 10^{-8}$ and $6{\cdot}80 \times 10^{-8}$ $m^2v^{-1}s^{-1}$ respectively.

3. (a) Devise a concentration cell. Write Nernst equation for the emf of the cell.

(b) The emf of the cell Pt | H_2 1 atm | HCl 0·1 molal | AgCl (s) | Ag at 25° C is 0·3524 V. Calculate the mean ionic activity coefficient of 0·1 molal HCl. The standard electrode potential of Ag | AgCl (s) | Cl^- electrode is 0·2224 V.

4. Explain briefly bonding in metal carbonyls.

5. (a) Derive Gibbs Helmholtz equation. Explain its importance.

(b) How would you determine entropy of a gas using third law of thermodynamics ? Explain.

6. (a) How would you classify solids into seven crystal systems ? What are the Bravais lattices associated with cubic system ?

(b) Explain the term 'liquid crystal'. What are the various types of liquid crystals ? Explain with examples. Write two applications of liquid crystals.

PART D

3×30=90

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

1. Solve Schrödinger wave equation for a particle in one dimensional box. Find eigen values and eigen functions.

2. (a) Derive an equation for the free energy change of a chemical reaction in terms of standard free energy change and activities of reactants and products.

   (b) The standard free energy change of a chemical reaction is 150 kJ mol^{-1} at 500 K. Calculate the equilibrium constant of the reaction.

   (c) Explain the effect of pressure and temperature on the equilibrium of a chemical reaction.

3. (a) Derive an equation for the rate constant of a second order reaction $A + B \rightarrow C$.

   (b) The reaction $A + B \rightarrow C$ was carried out with initial concentration of A and B as 0·3 and 0·4 moles. After 30 minutes 0·2 moles of A remains. Find the rate constant.

4. Discuss briefly applications of emf measurements.

5. Discuss the magnetic properties and electronic spectra of transition metal complexes using crystal field theory.

Values of useful constants

R = 1·987 cals mol^{-1} K^{-1}

= 8·314 J mol^{-1} K^{-1}

= 08205 lit. atm mol^{-1} K^{-1}

Planck's constant h = $6·627 \times 10^{-34}$ Js

Faraday F = 96500 Coulombs

Mass of electron = $9·1 \times 10^{-31}$ kg

Velocity of light = 3×10^{8} ms^{-1}

1 eV = $1·602 \times 10^{-19}$ J

A (Debye Hückel equation) = 0·509

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2005

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.

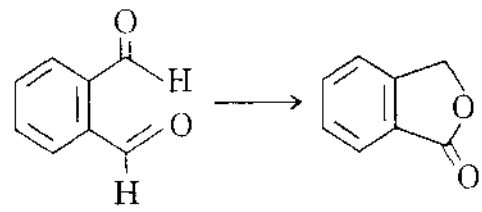
PART A

$4 \times 5 = 20$

Each question carries 5 marks.

1. (a) Predict the major mononitration product of chlorobenzene. Justify your answer.

(b) Give the mechanism of the following reaction leading to the formation of a lactone :



(c) Compare and contrast the reaction of borazine and benzene with HCl.

(d) Carbon dioxide is a linear molecule. Show the different stretching vibrational modes available to this molecule. Which of these are IR and Raman active ?

PART B

10×10=100

Each question carries 10 marks.

1. Anionic polymerization of styrene leads to a polymer whose structure is dominated by head to tail (HT) linkages. Account for this observation.

2. Explain the chemistry behind Skell procedure (based on stereochemistry of insertion to double bonds) for differentiating between singlet and triplet carbenes.

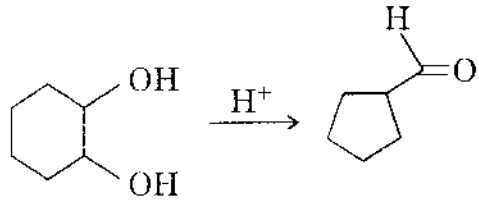
3. Using illustrative examples, explain how the following factors contribute towards the stability of carbocations : (a) inductive effects, (b) mesomeric effects (conjugation and hyperconjugation)

4. Based on Woodward-Hoffmann selection rules, predict whether the isomerization of 1-butene to 2-butene is thermally allowed or not.

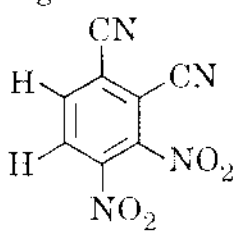
5. How will you convert adipic acid (hexanedioic acid) to cyclopentanone ?

6. Give the mechanism of ethylene polymerization to give high density polyethylene using a Ziegler-Natta catalyst prepared from triethylaluminum and titanium tetrachloride. Give the structure of the active catalyst.

7. How will you bring about the following transformation ?



8. What aspects of ^1H NMR spectroscopy (peak intensity, coupling constants and chemical shift positions) will enable you to differentiate between the following molecules ?



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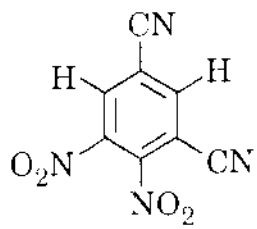

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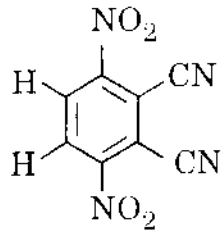

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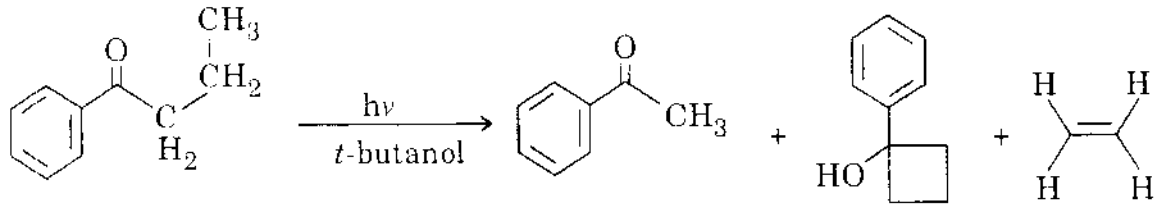
9. Predict the form of the ESR spectrum of benzene radical anion and NH_2 radical (NH_2) based on the following information : for ^{14}N, $I = 1$.

10. Indicate the steps involved in the following triplet-mediated photochemical reaction :



PART C

6×15=90

Each question carries 15 marks.

1. Using suitable examples, explain the S_NAr and benzyne mechanisms of aromatic nucleophilic substitution reactions.

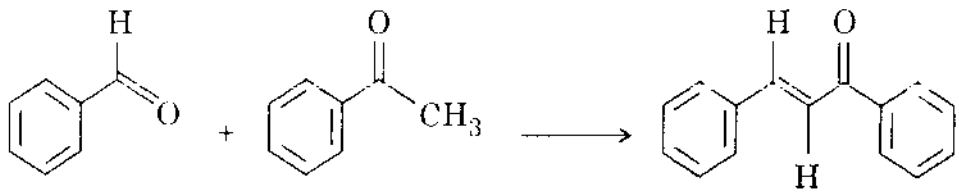
2. Give one example each of : (a) a thermally allowed cyclo addition reaction, and (b) a photochemically allowed electrocyclic reaction. Justify your answer.

3. Indicate the steps involved in the industrial manufacture of nylon-6 (starting from phenol). Explain how ammonium sulphate is obtained as a major byproduct in the manufacture of nylon-6.

4. Give the steps involved in the photoreduction of water to hydrogen and oxygen using the $[Ru(bpy)]^{3+}$ — MV^{2+} — TEOA system in the presence of colloidal platinum (MV stands for methylviologen, TEOA stands for triethanolamine).

5. Three consecutive lines in the rotational spectrum of isotopically pure HBr are observed at 84·544, 101·355, and 118·112 cm^{-1}. Assign the lines to their appropriate $J'' \rightarrow J'$ transitions, then deduce the values for B and hence evaluate the bond length of the molecule.

6. Give the mechanism of acid and base catalyzed aldol condensation reaction as illustrated below :



PART D

$3 \times 30 = 9$

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

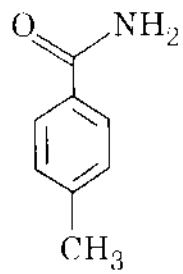
1. Write a detailed account on the effect of the following factors on the rate of S_N1 and S_N2 substitution reaction : (a) nature of leaving groups, (b) nature of incoming group, (c) medium, and (d) presence of electron withdrawing groups on α-carbon.

2. Determine the structure of the compound (a sweet smelling, volatile liquid) based on its spectral data as given below. The spectral data should be adequately interpreted. UV (cyclohexane) : transparent above 220 nm; IR (thin film) : 2994, 2870. 1745, and 1105 cm^{-1}; ^1H NMR ($CDCl_3$) : chemical shift δ 1·7 (triplet, coupling constant J = 7 Hz, 3 protons), 2·1 (singlet, 3 protons), and 4,2 (quartet, J = 7 Hz, 2 protons); MS : m/z (relative intensity) 88 (23), 73 (8), 60 (90), 43 (100), and 15 (35).

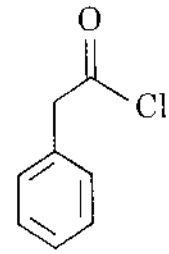
3. Write a detailed account on the determination of molecular weight of polymers using : (a) end group analysis, (b) osmometry, (c) light scattering, and (d) sedimentation equilibrium techniques. Which of these methods will give a more precise estimate of weight average molecular wights ?

4. Predict the major elimination product obtained when 2-Bromo3-methylbutane is subjected to elimination under E_1, E_2 and E_1cB conditions. Justify your answer and explain the observed regioselectivity in each case.

5. Reaction of toluene with phenylacetyl chloride in the presence of anhydrous aluminium chloride gave **A** ($C_{15}H_{14}O$) as the major product. Reduction of **A** using sodium borohydride gave **B** ($C_{15}H_{16}O$). Elimination of a molecule of water from **B** under appropriate conditions gave **C** ($C_{15}H_{14}$). Oxidation of **C** using osmium tetroxide gave **D** ($C_{15}H_{16}O_2$). Reaction of **D** with aqueous HIO_4 gave an equimolar mixture of two aldehydes : **E** (C_8H_8O) and benzaldehyde. Treatment of **E** with hydroxylamine under appropriate conditions gave a new product **F** (C_8H_9NO). Upon treatment with concentrated sulfuric acid, **F** gave 4-methylbenzamide as the only product. Identify compounds **A** to **F**.



4-Methylbenzamide



Phenylacetyl chloride

[Useful constants : h = $6{\cdot}626 \times 10^{-23}$ JK^{-1}; c = $2{\cdot}998 \times 10^{8}$ ms^{-1}; atomic masses : ^{79}Br = $131{\cdot}03 \times 10^{-27}$ kg; ^{1}H = $1{\cdot}673 \times 10^{-27}$ kg]