2015

CHEMISTRY

(Major)

Paper : 5.1

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

(Symbols signify their usual meanings)

1. Answer in brief : 1×7=7

(a) Find the eigenvalue of the operator $-\frac{d^2}{dx^2}$ if the eigenfunction is $\cos 2x$.

(b) The H-like wavefunctions corresponding to $n = 2$, $l = 1$, $m_l = \pm 1$ are imaginary. But the orbitals cannot be imaginary. State how the orbitals are found out corresponding to these quantum numbers.

(c) The ground state electronic configuration of H_2^+ is $(1s\sigma_g)^1$. Write the term symbol.

(d) Show whether the operator $\hat{O}$ in the equation $\hat{O}\psi = \psi^2$ is linear or not.

(Turn Over)

(e) The normalization condition is $\int \psi^2 \, d\tau = 1$. State what this condition actually means.

(f) Show whether the function e^{-x} is well-behaved or not within the limit $-\infty \leq x \leq \infty$.

(g) If the state function of a system is ψ, write the expression for the expectation value of a physical quantity denoted by M.

2. Answer the following questions (any *four*) : 2×4=8

(a) Normalise the H-like function $\psi = e^{-n}$.

(b) Show that the functions $\sin \frac{\pi x}{a}$ and $\cos \frac{\pi x}{a}$ are orthogonal within the limit $0 \leq x \leq a$.

(c) For the two equivalent electrons $(2p^2)$ of ground state carbon atom, the terms are as follows :

$$^1D_2, \; ^3P_2, \; ^3P_1, \; ^3P_0, \; ^1S_0$$

Using Hund's rule, explain which will be the ground term.

(Continued)

(d) Show that the wavefunction for a particle in one-dimensional box of length a, where the potential energy is zero, is not an eigenfunction of the linear momentum operator in one dimension.

(e) It is required that the eigenfunction of an opeator representing a physical quantity should be single valued, continuous and quadratically integrable. State why the function should be single-valued and continuous.

3. Answer the following questions : 5×3=15

(a) State Pauli's antisymmetry principle. Using this principle, show that no two electrons of an atom can have all the four quantum numbers alike. 1+4=5

Or

What do you mean by complete wavefunction? Using the complete wavefunctions of the first excited He-atom, identify the singlet and triplet states. 1+4=5

(b) Write what you mean by radial distribution function. Find an expression for the radial distribution function. Give the plot of radial distribution function against the radial distance from the nucleus for 1s orbital. State how this plot differs from the plot of square of the radial function against the radial distance. 1+2+1+1=5

(Turn Over)

Or

Write the general expressions for the magnitude and z-component of angular momentum. Write what you mean by space quantisation of angular momentum. Discuss with diagram the orientations of angular momentum of magnitude $\sqrt{2}\hbar$ in presence of applied magnetic field in z-direction. 1+2+2=5

(c) Answer either *(i) or (ii)* and *(iii)* :

(i) Calculate the zero-point vibrational energy of CO molecule assuming it to be a harmonic oscillator if the force constant of the bond between the two atoms is 1840 Nm^{-1}. Find the energy difference between two consecutive vibrational levels taking the same assumption. 3+2=5

Or

(ii) Find the average value of the distance of the electron from the nucleus of the ground state H-atom. 3

(iii) According to Huckel theory, the energies of the six delocalized π molecular orbitals of benzene are $\alpha + 2\beta$, $\alpha + \beta$ (doubly degenerate), $\alpha - \beta$ (doubly degenerate) and $\alpha - 2\beta$ respectively. Find the energy of the π-electrons of the molecule. 2

4. Answer *either (a)* and *(b)* or *(c)* and *(d)* :

(a) Write in brief about the experimental observation of the photoelectric effect as observed by Lennard. State how classical physics fails to explain these results. Write how Einstein explained these. 3+2+2=7

(b) A cosmic ray photon with energy $h\nu$ is scattered through 90° by an electron initially at rest. The scattered photon has wavelength twice as that of the incident photon. Find the wavelength of the incident photon. 3

Or

(c) Show that the Compton shift, observed when a beam of monochromatic X-ray impinges on carbon block and gets scattered, depends on the angle through which scattered radiation is observed; but does not depend on the wavelength of the incident radiation. 6

(d) Show that the total energy of all the radiations emitted by a blackbody is proportional to the 4th power of the absolute temperature of the blackbody. 4

5. Answer *either (a)* and *(b)* or *(c)* and *(d)* :

(a) Using the MO wavefunction of H_2, discuss the drawback of the MO theory. Write how Heitler-London modified the wavefunction. Discuss about the correct form of the wavefunction for bonding in H_2 taking into account of resonance. 3+1+3=7

(b) Show that the maximum probability of finding the electron of H-like atom in the ground state is at a distance of a_0 / z from the nucleus. 3

Or

(c) Write the basic assumptions of Huckel molecular orbital theory. Using this theory, explain how the formation of π-molecular orbital stabilizes the ethene molecule. 2+5=7

(d) For a particle in a one-dimensional box of length a, find the probability of finding the particle in the region $0 \leq x \leq a/4$ in the ground state. 3

6. Answer *either (a), (b)* and *(c) or (d), (e)* and *(f)* :

(a) Let a cubic box of edge length 1 nm, within which potential energy is zero, contain 10 electrons. Considering ground state, explain with diagram how these electrons occupy the different states. 3

(Continued)

(b) Write the angular function for s-orbital and hence explain why s-orbital is spherically symmetric. 1+2=3

(c) Taking the example of H_2^+, explain how the potential energy diagram can be constructed. What information regarding characterization of a bond can be obtained from this diagram? 3+1=4

Or

(d) Taking $2p_z$ orbital as example, explain why p-orbital is dumbbell in shape. 3

(e) Find the operator for kinetic energy in x-dimension. Hence deduce an expression for the kinetic energy in the ground state of a particle in one-dimensional box with zero potential energy. 1+3=4

(f) Draw the molecular orbital energy-level diagram of HF. Write the molecular orbital wavefunctions involved. 1+2=3

Standard integrals :

$$\int_0^\infty x^n e^{-ax}\, dx = \frac{n!}{a^{n+1}}$$

$$\int_0^\infty \frac{x^3}{e^x - 1}\, dx = \frac{\pi^4}{15}$$

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CHEMISTRY

(Major)

Paper : 5.2

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer in brief : 1×7=7

(a) State what is meant by quantum yield for photochemical reactions.

(b) What would be the ratio (σ / A) of the collision cross-section σ of a spherical molecule B, undergoing B-B type collisions in gas phase and of its surface area $A = \pi r^2$, where r is the molecular radius?

(c) Under what condition would the Lindemann theory of unimolecular gaseous reactions show second-order kinetics?

(d) How does the rate of the ionic reaction

$$S_2O_8^{2-} + 2I^- \rightarrow \text{products}$$

performed in aq. NaCl solutions would change with the increasing concentration of NaCl in water? Explain.

(e) How is the glow of fireflies explained in chemistry?

(f) Find the degree of freedom for an equilibrium mixture of gaseous ammonium chloride, ammonia and hydrogen chloride at 200 °C (a temperature at which all these substances remain at gas phase), given that the ammonia and hydrogen chloride gases there formed only from decomposition of the ammonium chloride introduced into the system.

(g) What is the relation between the surface area S of the solid adsorbent, the number of adsorbate gas molecules N_m forming a completely occupied monolayer, and the surface area ($A = \pi r^2$) of each adsorbate gas molecule?

2. Answer the following questions : 2×4=8

(a) What is meant by a molecular beam? In what way is a molecular beam used?

(Continued)

(b) What is the relation between adsorption and heterogeneous catalysis caused by solid catalyst surfaces? Why does the catalytic activity of solid catalysts become more pronounced when they are powdered?

(c) Explain how one may calculate the surface area of an adsorbent, provided the monolayer volume V_m of the adsorbate gas was determined using either the BET or the Langmuir isotherm.

(d) Obtain an expression for the Gibbs free energy of mixing $\Delta_{mix}G$ for an ideal binary liquid solution in terms of the mole amounts n_1 and n_2 of the two liquids, the mole fractions x_1 and x_2 and the temperature T.

3. Answer any *three* of the following : 5×3=15

(a) Show that for bimolecular collision of structureless particles, the transition state theory reduces to the simple collision theory.

(b) On the basis of the postulates of Langmuir adsorption theory, deduce the Langmuir adsorption isotherm. How can the monolayer volume V_m be obtained from this isotherm?

(Turn Over)

(c) The decomposition of HI takes place by the following mechanism :

$$HI + h\nu \rightarrow \dot{H} + \dot{I}$$

$$\dot{H} + HI \rightarrow H_2 + \dot{I}$$

$$\dot{I} + \dot{I} \rightarrow I_2$$

Find an expression for the rate of the reaction. Also find the quantum efficiency of the reaction.

(d) Draw and interpret the phase diagram of a binary condensed-phase system with the formation of a eutectic solid. Mention a real-life example of such a system. Why is a eutectic mixture not considered as a compound?

4. Defining the number of phases, the number of components and the degree of freedom, derive the Gibbs phase rule relating them. How does the expression for the degree of freedom get altered for condensed systems for which pressure has a negligible effect? How is the number of components C calculated for systems in which some chemical reaction equilibria and some stoichiometric restrictions bind their concentrations? Hence show that for a solution of acetic acid in water, $C = 2$, even though there are four chemical species, namely H_2O, CH_3COOH, CH_3COO^- and H^+ present in the system.

5+1+2+2=10

(Continued)

Or

State the difference between solid compounds formed in binary condensed-phase systems with congruent and incongruent melting points. Draw the phase diagrams for both the cases and explain how the solid compound is formed from the melt and how the solid melts in each case. Give an example for each situation. 2+6+2=10

5. On the basis of hard sphere collision theory of reaction rates, obtain an expression for the rate constant of a bimolecular gaseous reaction. What is the physical significance of the steric factor P in the above expression? Estimate the steric factor P for the dimerisation of gas-phase methyl ($\cdot CH_3$) radicals at 300 K, given that their molecular diameter $d = 3 \cdot 1$ Å (related to the reactive collision cross-section as $\sigma = \pi d^2$) and that the experimental pre-exponential factor is $2 \cdot 4 \times 10^{10}$ dm^3 mol^{-1} s^{-1}. 5+1+4=10

Or

For the elementary gaseous reaction $A + B \rightarrow$ products, obtain an expression for the rate constant of the reaction as per the transition state theory in terms of the entropy of activation and the enthalpy of activation. The

(Turn Over

reaction $A^- + H^+ \rightarrow P$ has a rate constant given by the empirical expression

$$k_2 = 2 \cdot 06 \times 10^{13} \exp(-8670\, K / T)\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$$

(where T is the Kelvin temperature). Calculate the entropy, the energy and the enthalpy of activation at 300 K. 5+5=10

6. *(a)* Discuss the mechanism of the photochemical reaction between hydrogen and bromine and find the expressions for the reaction rate and the quantum yield for this reaction. 5

(b) Discuss the role of nitrogen oxides and chlorofluorocarbons in ozone layer depletion. 3

(c) Explain the phenomenon of fluorescence with the help of Jablonski diagram. 2

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CHEMISTRY

(Major)

Paper : 5.3

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer the following questions (any *seven*) : 1×7=7

(a) Give the product of the following reaction :

$$CH_3\text{—}CH{=}CH\text{—}COOH \xrightarrow[2)\ H_3O^+]{1)\ LiAlH_4,\ Ether}$$

(b) Which among furan, pyrrole and thiopene undergoes Diels-Alder reaction? Write the structure of the product formed by it with maleic anhydride.

(c) Why does electrophilic aromatic substitution of indole occur preferably at the 3-position?

(d) Which bond of phenanthrene is readily attacked by reagents?

(e) 2-methyl-2-nitropropane does not dissolve in alkali whereas 2-nitropropane dissolves. Why?

(f) Write the structure of the product when the following compound is treated with Na/Hg :

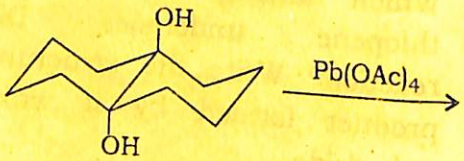
$$PhCH{=}CHCH_2\overset{\oplus}{N}(CH_3)_3I^{\ominus}$$

(g) Why does pyridine not undergo Friedel-Crafts reaction?

(h) Why is catalytic reduction of thiophene difficult?

2. Answer the following questions (any *four*) : 2×4=8

(a) Write the appropriate product for the following reactions :

(i) 

(ii) $CH_3CH_2C{\equiv}CCH_2CH_3 \xrightarrow[\text{Lindlar's catalyst}]{H_2}$

(Continued)

(b) Draw the tautomers of acetoacetic ester. Identify the stable form and explain why it is more stable than the other form.

(c) How will you use 1,3-dipolar reagents to synthesize five-membered heterocyclic compounds?

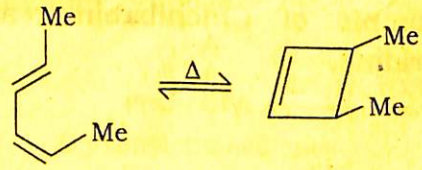
(d) Which one is more acidic—ethanethiol or ethanol and why? How can one distinguish ethanethiol from ethanol?

(e) Why is cope rearrangement called [3,3] sigmatropic shift?

3. Answer any *three* of the following questions [any *one* from *(a)* and *(b)*, any *two* from *(c)*, *(d)* and *(e)*] : 5×3=15

(a) How can you convert propanoic acid to ethanamine, using a reaction that involves isocyanate intermediate? Name the reaction. Write the mechanism of the reaction. 2+1+2=5

(b) Explain why (2*E*, 4*Z*) hexadiene thermally cyclizes to give *cis*-3,4-dimethyl cyclobutene.



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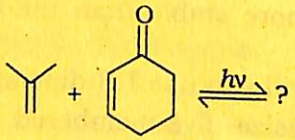
Write the product of the following reaction :



4+1=5

(c) How will you distinguish between 1°, 2° and 3°-nitroalkanes? What products are obtained when nitrobenzene is reduced in *(i)* acidic and *(ii)* alkaline media?

3+2=5

(d) Explain why methylene group in diethylmalonate is more reactive than methylene group in malonic acid. Starting from diethylmalonate, how can you synthesize *(i)* a dicarboxylic acid, *(ii)* a heterocyclic compound, *(iii)* an alicyclic compound and *(iv)* α, β-unsaturated acid? 1+1+1+1+1=5

(e) What are the IUPAC names of pyrrole, furan and pyridine? Write down the steps involved in the Bischler-Napieralski reaction leading to synthesis of isoquinoline. Give an example of Chichibabin reaction of pyridine.

1½+2+1½=5

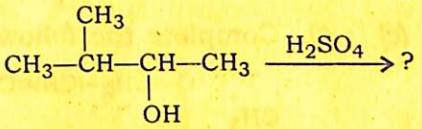
(Continued)

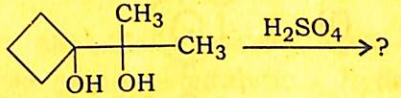
4. Answer the following questions :

Either

(a) (i) Predict the product in each case and write the mechanism for each :

2+3=5

(1) 

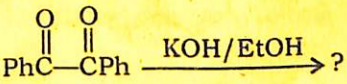
(2) 

(ii) (1) Explain why reaction of naphthalene with conc. H_2SO_4 at 40 °C yields naphthalene-1-sulphonic acid whereas at 160 °C naphthalene-2-sulphonic acid is the major product. 3

(2) Convert nitrobenzene to 1,3-dichlorobenzene (give equations). 2

Or

(b) (i) Give the product of the following reaction, name the rearrangement and propose a mechanism : 1+1+3=5



Diphenylethanedione

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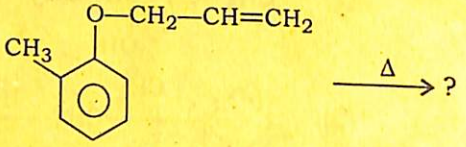
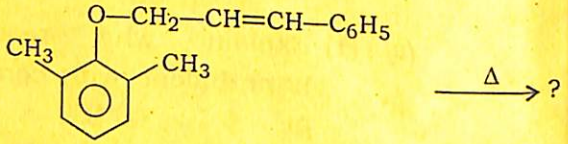
(ii) Show by symmetry correlation diagram approach that [2+2] cycloaddition is a photochemically allowed process. 5

Either

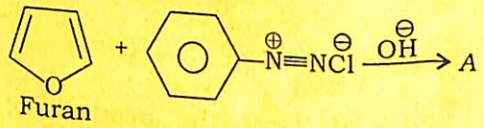
(c) (i) Complete the following reactions :

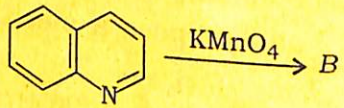
(1) 

(2) 

Account for the product obtained in each case. 2½+2½=5

(ii) Identify *A*, *B*, *C*, *D* and *E* in the following reactions : 1×5=5

(1) 

(2) 

(3) $CH_3NO_2 \xrightarrow{Cl_2/NaOH} C$

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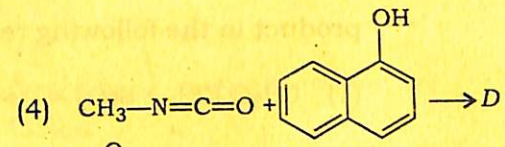
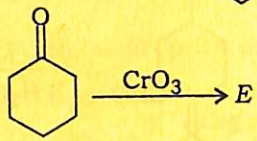
(4) 

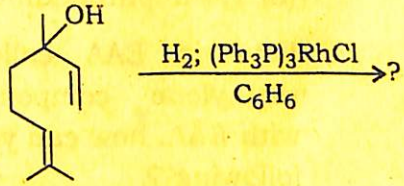
(5) 

Or

(d) (i) What are the disadvantages of heterogeneous catalytic hydrogenation? Predict the product in each of the following reactions : 2+1+1+1=5

(1) $PhCH{=}CHCO_2CH_2Ph \xrightarrow[H_2]{[Ph_3P]_3RhCl} ?$

(2) $PhCH_2OH \xrightarrow[25\ °C,\ 3\ atm]{H_2\text{-}Pd} ?$

(3) 

(ii) Describe the mechanism involved in the oxidation of 1,2-diols with lead tetraacetate. Identify the

(Turn Over

product in the following reactions : 3+1+1=5

(1). $CH_3COCH_3 + SeO_2 \longrightarrow ?$

(2)  $\xrightarrow[2)\ H_2O_2]{1)\ O_3,\ AcOH} ?$

Either

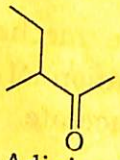
(e) *(i)* How many monosubstituted derivatives of naphthalene are possible? Which position is preferentially attacked in electrophilic substitution reactions of naphthalene? How can the following naphthalene derivatives be prepared? 1+1+3=5

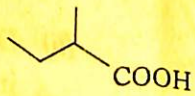
(1) 2-naphthylamine

(2) 1-naphthol

(3) 1,4-naphthaquinone

(ii) Why is EAA called an active methylene compound? Starting with EAA, how can you prepare the following ? 1+4=5

(1) 

(2) 

(3) Adipic acid

(4) 

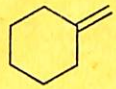
(No mechanism needed)

(Continued)

Or

(f) *(i)* Describe a method of synthesis of furan. 3

(ii) How can you prepare the following? 2

(1)  by Wittig reaction

(2) PhCOOMe by Baeyer-Villiger reaction

(iii) Why does Hofmann elimination of a quaternary ammonium salt give thermodynamically less stable alkene as the predominant product? 2

(iv) Write one general method of synthesis of thiols, RSH. How can RSH be converted to (1) RSSR and (2) RSR? 1+1+1=3

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