

2016

CHEMISTRY

(Major)

Paper : 5.1

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

(The symbols used signify their usual meanings)

1. Answer in brief (any seven) : 1×7=7

(a) Define eigenvalue and eigenfunction.

(b) State true or false with reason :

$\hat{O}[f(x) + g(x)]$ is always equal to $\hat{O}f(x) + \hat{O}g(x)$.

(c) Find the expression for the Hamiltonian operator for a particle of mass m in x -dimension.

(2)

- (d) For a particle in one-dimensional box of length a , where potential energy is zero, the wave function is

$$\psi = N \sin \frac{n\pi x}{a}, \quad N = \text{normalization constant}$$

State why the value of the quantum number n cannot be zero.

- (e) State what you mean by spin-orbital.
- (f) Find the value of the orbital angular momentum of an electron in d -orbital.
- (g) Write the term symbol for H_2 in ground state.
- (h) Give the schematic plots of ψ and $|\psi|^2$ against coordinate for $n=2$ state of a particle in one-dimensional box of length a where potential energy is zero.

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

- (a) What do you mean by eigenvalue equation? Write with example what the constant in the eigenvalue equation indicates.
- (b) Show that the average value of momentum of a particle described by the wave function e^{ikx} is $\hbar k$, where k is a constant.

(3)

- (c) Explain how many folds a particular energy level of the free axis rigid rotator is degenerate.

- (d) The associated Legendre function is defined by

$$P_l^{m|}(w) = \frac{1}{2^l l!} (1-w^2)^{|m|/2} \frac{d^{l+|m|}}{dw^{l+|m|}} (w^2-1)^l$$

The solution of the Schrödinger equation for H-atom also involves this type of function $P_l^{m|}(\cos\theta)$. Find the values of the function when the value of the quantum number l is 1.

- (e) A particle with mass m is moving in one-dimensional box of length a where the potential energy is zero. Show that the wavelength associated with the particle is $\frac{2a}{n}$.

3. (a) Write the quantum numbers on which radial wave function and the angular wave function of H-like atom depend. Discuss what information can be obtained from the plots of radial wave function and square of the radial wave function. 1+4=5

(4)

Or

Write in brief about Russell-Saunders coupling of angular momenta. Find the term symbols for the ground state and the first excited state of He atom. $2+1+2=5$

- (b) Write the general expression for the Hamiltonian of a molecule. Explain how Born-Oppenheimer approximation can be applied to separate the Schrödinger equation for a molecule into electronic and nuclear Schrödinger equations. $1+4=5$

Or

Write the MO wave functions and the corresponding energy values for the electron of hydrogen molecule ion. Using these, explain how the potential energy diagram is constructed. State what information can be obtained from this diagram. $1+3+1=5$

- (c) Solve the electronic Schrödinger equation of H_2^+ using LCAO-MO method to find the energies and the MO wave functions. 5

Or

Discuss how Heitler-London method is an improvement over the MO method for H_2 . 5

(5)

4. Answer either (a), (b) and (c) or (d), (e) and (f): 10

(a) Show graphically how energy is distributed among different wavelengths emitted by a blackbody at a definite temperature. Deduce Planck's radiation law which can explain the above experimental observation. $1+4=5$

(b) The work function for Na metal is 1.82 eV. Calculate its threshold frequency. 2

(c) Find the lowest kinetic energy of an electron in a three-dimensional box of lengths 1×10^{-13} cm, 2×10^{-13} cm and 3×10^{-13} cm assuming potential energy to be zero. 3

Or

(d) Consider a particle with mass m moving in a box of lengths a , b and c along x -, y - and z -axes respectively. Assume that the potential energy inside the box is zero, and outside it is infinity. Solve the time-independent Schrödinger equation for the particle to get the values of the wave function and the energy. 4

(e) It is found that the surface of the sun radiates as a blackbody with λ_{\max} of 480 nm. Calculate the surface temperature of the sun. 3

(f) Show that the wave function for the particle in one-dimensional box, where potential energy is zero, is not an eigenfunction of the momentum operator \hat{p}_x ; but it is an eigenfunction of \hat{p}_x^2 . 3

5. Answer either (a) and (b) or (c), (d) and (e) : 10

(a) Define radial distribution function. Find an expression for the radial distribution function for s-orbital. Prove that the maximum probability of finding the electron of H-atom is at a distance equal to the first Bohr radius of H-atom. $1+2+3=6$

(b) Consider an atom with two electrons, one in p-orbital and the other in d-orbital. Find the symbols for the terms arising out of the coupling between the angular momenta of the two electrons. 4

Or

(c) Write the approximate spatial function and the possible spin functions for the electrons of the ground state He-atom. Applying Pauli's antisymmetry principle, find the acceptable ground state complete wave function of the He-atom. $2+3=5$

(d) The wave function for the ground state H-atom is Ne^{-r/a_0} . Find the value of the normalization constant N. 2

(e) Calculate the average value of the potential energy of the electron of H-atom in ground state. 3

6. Answer either (a) and (b) or (c), (d) and (e) : 10

(a) Write the secular determinant for benzene on the basis of Hückel molecular-orbital theory. Using this theory, explain how delocalization of π -electrons stabilizes the benzene molecule. $1+5=6$

(b) Write the basis of classifying the molecular orbitals as g or u. Can the molecular orbitals of a heteronuclear diatomic molecule be assigned as g or u? Answer stating reason. Distinguish between σ - and π -molecular orbitals using symmetry concept. $1+1+2=4$

Or

(c) State how the Coulomb integrals and the resonance integrals are represented in Hückel molecular orbital method. Using this theory, deduce the expressions for the energies and the corresponding π -molecular orbital wave functions of ethene. $1+5=6$

(d) Consider that the valence-bond wave-function of ground state HF molecule is obtained from 1s orbital of H atom and $2p_z$ orbital of F atom. Write the

unnormalized valence-bond wave functions for the molecule considering it to be (i) purely covalent and (ii) purely ionic.

(e) Draw the molecular orbital energy-level diagram of CO. Find its bond order.

Standard integral :

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

2016

CHEMISTRY

(Major)

Paper : 5.3

Full Marks : 60

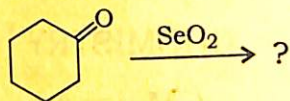
Time : 3 hours

The figures in the margin indicate full marks for the questions

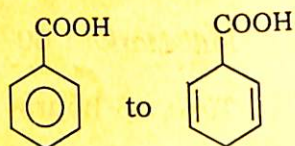
1. Answer the following questions (any seven) : 1×7=7
- (a) Why does colourless aniline on storage turn brown?
 - (b) What is 'reductive amination'?
 - (c) What happens when acetylene and H_2S are passed over alumina at $400\text{ }^\circ\text{C}$?
 - (d) Why does diethyl malonate undergo alkylation?
 - (e) Why is naphthalene less aromatic than benzene?

(2)

- (f) Give the product (with name) of the following reaction :

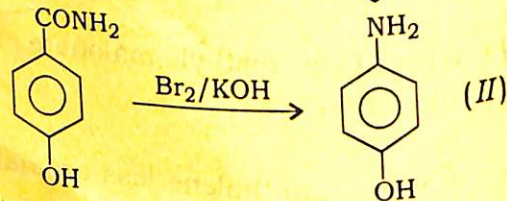
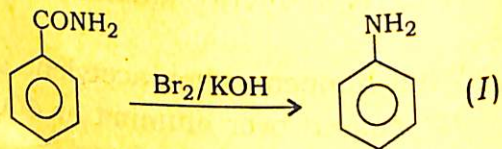


- (g) Define 'conrotatory ring closure'.
(h) Write the appropriate reagent to convert



2. Answer the following questions (any four) : $2 \times 4 = 8$

- (a) What is enolate anion and how can it be prepared?
(b) What happens to α -diazoketone when it is heated thermally in presence of Ag_2O ? Give the reaction.
(c) Reaction rate of



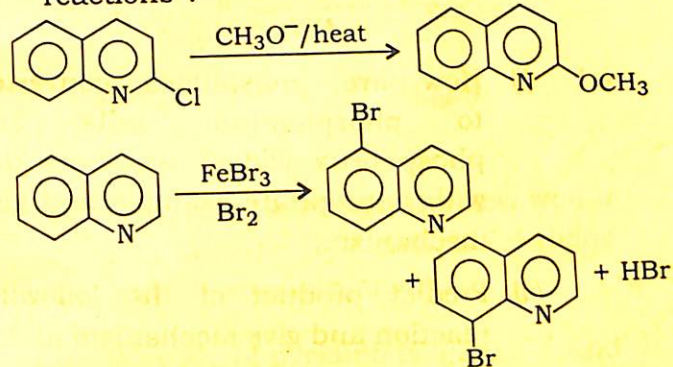
(I) is more than (II). Explain.

(3)

- (d) Pyridine is basic. Explain.
(e) Explain the acidic behaviour of nitro-alkane.

3. Answer the following questions [any one from (a) and (b) and two from (c), (d) and (e)] :
 $5 + (5 \times 2) = 15$

- (a) Write Skraup synthesis of quinoline. What is the role of FeSO_4 in this reaction? Explain the reactivity of quinoline with the help of following reactions : $2\frac{1}{2} + \frac{1}{2} + 2 = 5$



- (b) Define pericyclic reaction. Explain, why electrocyclic reactions are stereospecific, with appropriate examples. $1 + 4 = 5$
(c) Convert benzophenone oxime to benzanilide in the presence of PCl_5 and give equation with mechanism. What is the driving force for the 1,2-shift in this reaction? $1 + 3 + 1 = 5$

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(Turn Over)

(4)

(d) Write Nakabayashi mechanism of Clemmensen reduction. Explain why in this reaction amalgamated zinc is used instead of pure zinc. $4+1=5$

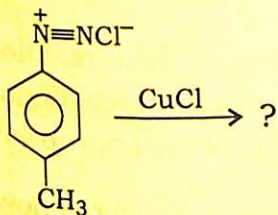
(e) Why do aliphatic nitrocompounds dissolve in aqueous alkali? How can CH_3CN and CH_3NC be prepared? What do you get when they are subjected to acid hydrolysis? $1+2+2=5$

4. Answer the following questions :

Either

(a) (i) How are phosphines converted to phosphonium salts and phosphorus ylides? Show its use with appropriate example and give mechanism. $3+2=5$

(ii) Predict product of the following reaction and give mechanism of it : 3



(iii) Why aniline cannot undergo
(1) Friedel-Crafts reaction and
(2) nitration reaction with HNO_3 ? $1+1=2$

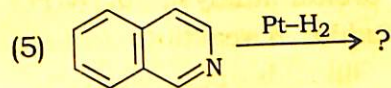
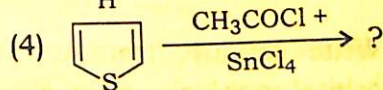
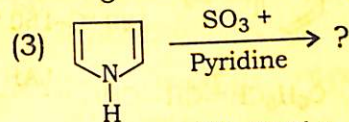
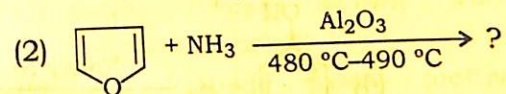
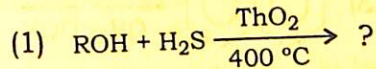
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(5)

Or

(b) (i) Write products and the names of the products (wherever possible) for the reactions given below : $1 \times 5 = 5$

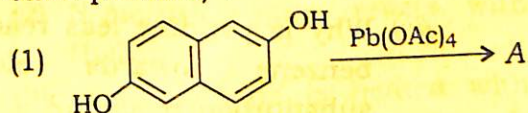


(ii) From ethyl acetoacetate, how would you prepare (1) pentane-2,4-dione and (2) succinic acid? $2+2=4$

(iii) Why K_b of pyridine is 2.3×10^{-9} and that of pyrrole is 2.5×10^{-4} ? 1

Either

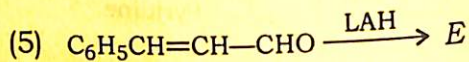
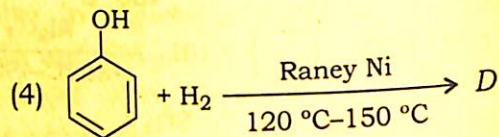
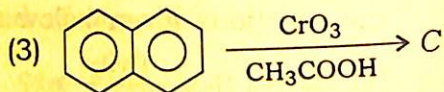
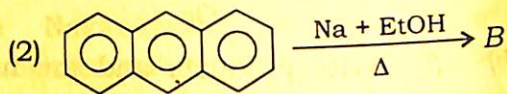
(c) (i) Identify A, B, C, D and E in the following reactions (write name of each product) : $1 \times 5 = 5$



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(6)



- (ii) Write about frontier molecular orbital analysis of a [4+2] cyclo-addition reaction.

Or

- (d) (i) Explain 'ion pair mechanism in a solvent cage' with appropriate example of a rearrangement reaction.

- (ii) How can you obtain butanoic acid from diethyl malonate? Write the reaction.

- (iii) How can benzene be converted to anthracene with phthalic anhydride? Give reaction.

- (iv) Why is pyridine less reactive than benzene towards electrophilic substitution reaction?

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(7)

Either

- (e) (i) How can you obtain (give reaction)—

(1) dimethyl amine from methyl isocyanide;

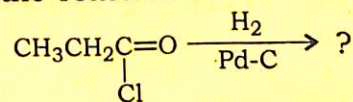
(2) methyl propyl ketone from acetoacetic ester;

(3) acetic acid from methyl cyanide? $1 \times 3 = 3$

- (ii) Write Haworth synthesis of naphthalene. 2

- (iii) How does hydride transfer reduction of propanone take place with NaBH₄ in alcohol? Why is hydride transfer of carboxylic group difficult? $2+1=3$

- (iv) What is the role of C in following conversion reaction? Give product of the reaction



2

Or

- (f) (i) What happens when (give reactions)—

(1) *m*-dinitrobenzene reacts with (NH₄)₂S;

(2) *N*-methyl aniline reacts with HONO;

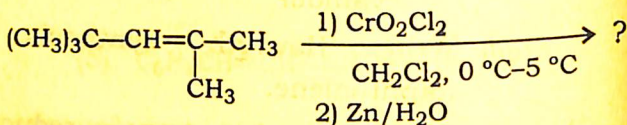
(3) ethyl bromide is heated with potassium sulphide? $1 \times 3 = 3$

(Turn Over)

(ii) Give an example to show the application of benzilic acid rearrangement. 2

(iii) How is primary amine diazotized? Show the mechanism with aniline. 1+2=3

(iv) Complete the following reaction : 1



(v) How is the strong acidity of the reagent, pcc, generally controlled? 1

2016

CHEMISTRY

(Major)

Paper : 5.4

(Inorganic Chemistry)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

Objective-type questions (choose the correct option) : 1×5=5

1. The point-group symmetry of $P(C_6H_5)_3$ is

(a) D_{3h}

(b) C_3

(c) D_3

(d) C_{3v}

2. TEL is an/a

- (a) ionic organometallic compound
- (b) sigma-bonded organometallic compound
- (c) electron-deficient organometallic compound
- (d) None of the above

3. Vitamin B₁₂ contains

- (a) Zn
- (b) Fe
- (c) Co
- (d) Mo

4. Which of the following statements is true about the octahedral complexes of Ni²⁺?

- (a) Both strong- and weak-field complexes are diamagnetic
- (b) The strong-field complex is diamagnetic and the weak-field complex is paramagnetic

(c) The strong-field complex is paramagnetic and the weak-field complex is diamagnetic

(d) Both strong- and weak-field complexes are paramagnetic

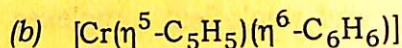
5. [Fe₂(CO)₉] is diamagnetic, because of

- (a) the presence of one CO as a bridging ligand
- (b) the metal-metal (Fe—Fe) bond in the molecule
- (c) the presence of a monodentate CO ligand
- (d) the oxidation state of iron is zero

Very short answer-type questions : 2×5=10

6. What are the symmetry point groups for the eclipsed and staggered forms of ferrocene? State which one between the two will have the centre of inversion (i) as one of the symmetry elements.

7. Do the following organometallic species obey the 18-electron rule?



8. What is the Cr—Cr bond order in the compound $\text{Cr}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$?

9. Iron(II) salts undergo oxidation in air but the cobalt(II) salts do not. Explain.

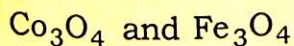
10. Predict the magnetic properties of the species $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$.

Short answer-type questions (any three) :

5×3=15

11. What are spinels? Why do some AB_2O_4 compounds having transition elements as A and/or B prefer the inverse spinel structure and some others the normal spinel structure? Predict the structure of the following spinels :

1+2+2=5



(Continued)

12. What are organometallic compounds? Comment on the stability of the M—C bond in organometallic compounds. Explain giving suitable examples.

2+3=5

13. Give the methods of preparation of Zeise's salt and discuss its structure. For a given metal-ethylene complex, the IR stretching frequency of the C=C bond is found to be 1516 cm^{-1} whereas the corresponding frequency for free C_2H_4 is observed at 1625 cm^{-1} . Explain.

3+2=5

14. What is the nature of the dioxygen binding site in haemoglobin? How do you conclude that the protein part of haemoglobin is also involved in the reversible binding of O_2 ?

5

15. The spin-only magnetic moments (μ) for $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ ions have been found to be 2.87 BM and 0 BM respectively. Using the μ values, predict the geometry of the complex ions and also comment on the hybridization of Ni^{2+} ion in each case.

3+2=5

Essay-type questions (any three) : $10 \times 3 = 30$

16. What are symmetry elements and symmetry operations? Illustrate the improper rotation operation S_4 with the help of a diagram. Discuss how both tetrahedral and octahedral geometries may be stated to have cubic symmetry. Take help of diagrams as appropriate. $3+2+5=10$

17. Discuss the importance and shortcomings of crystal-field theory. Does this theory address the formation of metal-ligand bonds? Use crystal-field theory to predict the electronic spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ and the magnetic moment of the species $[\text{Co}(\text{SCN})_4]^{2-}$. $6+2+2=10$

18. (a) Give the method of preparation for the binuclear species $[\text{Re}_2\text{Cl}_8]^{2-}$ and discuss its bonding giving an appropriate diagram. 5

(b) Comment on the organometallic compounds of Sn and describe their utilities. 5

19. Distinguish between homogeneous and heterogeneous catalyses. Discuss the catalytic cycle of hydroformylation of alkenes by a cobalt carbonyl catalyst. An increase in CO partial pressure above a certain threshold decreases the rate of the cobalt-catalyzed hydroformylation of 1-pentene. Suggest an interpretation of this observation. $1+6+3=10$

20. Write short notes on any two of the following topics : $5 \times 2 = 10$

- Ziegler-Natta catalysts
- Molecular-orbital theory in coordination chemistry
- Role of metal ions in biology
