

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.

- (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.

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(Continued)

- (c) Explain how many energy level of the f is degenerate.

- (d) The associated Legendre function defined by

$$P_l^{m_l}(w) = \frac{1}{2^l l!} (1-w^2)^{l/2} \dots$$

The solution of the Schrödinger equation for H-atom also in terms of associated Legendre function $P_l^{m_l}(\cos\theta)$, where l is the quantum number l .

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

3. (a) Write the quantum number for the radial wave function of H-atom. Discuss what information is obtained from the radial wave function and square of the radial wave function.

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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

4. Answer either (a), (b) and (

(a) Show graphically distributed among di emitted by a black temperature. Deduce law which can e experimental observa

(b) The work function 1.82 eV. Calcula frequency.

(c) Find the lowest ki electron in a three-lengths 1×10^{-13} cm 3×10^{-13} cm assumi to be zero.

Or

(d) Consider a particle v in a box of lengths a and z -axes respectiv potential energy ins and outside it is time-independent S for the particle to g wave function and t

(e) It is found that the radiates as a black 480 nm. Calcula temperature of the

- (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

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(Continued)

- (e) Calculate the average potential energy of the electron in ground state.

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

- (a) Write the secular determinant for benzene on the basis of molecular-orbital theory, explain how π -electrons stabilize benzene molecule.

- (b) Write the basis functions for molecular orbitals of a diatomic molecule. Answer stating the difference between σ - and π -molecular orbitals using symmetry considerations. Or

- (c) State how the Coulomb and resonance integrals are calculated in Hückel molecular orbital theory, deduce the energies and wave functions of π -molecular orbitals of ethene.

- (d) Consider that the wave function of ground state of a diatomic molecule is obtained from 1s orbital of one atom and $2p_z$ orbital of another atom.

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unnormalized valence-bond wave functions for the molecule considering it to be (i) purely covalent and (ii) purely ionic. 2

(e) Draw the molecular orbital energy-level diagram of CO. Find its bond order. 2

Standard integral :

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

2016

CHEMISTRY

(Major)

Paper : 5.2

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer the following in brief : 1×7=7

- (a) Write whether the values of enthalpy of adsorption and entropy of adsorption are negative or positive.
- (b) Write the difference between chemical reaction and photochemical reaction in terms of Gibbs free energy change.
- (c) In photosynthesis, CO_2 reacts with water in presence of chlorophyll and other plant pigments to produce starch. State the role of chlorophyll and the other pigments in the reaction.

- (d) The standard Gibbs energies of formation of HN_3 at 298 K are $+327 \text{ kJ mol}^{-1}$ and $+328 \text{ kJ mol}^{-1}$ for the liquid and gas phases respectively. Which phase of hydrogen azide is the more stable at that temperature and 1 bar?
- (e) In case of many reaction, the entropy of activation is negative. State the reason.
- (f) Why are powdered substances more effective absorbents than their crystalline forms?
- (g) An iceberg is floating in the lake. If one considers the lake, iceberg and atmosphere as a one system, what are the number of phases?

2. Answer the following questions : $2 \times 4 = 8$

- (a) Express Eyring equation regarding activated complex theory in terms of entropy and enthalpy of activation.
- (b) The fluorescence quantum yield and observed fluorescence lifetime of tryptophan in water are $\phi_{F,0} = 0.20$ and $\tau_0 = 2.6 \text{ ns}$ respectively. Determine the fluorescence rate constant of this substance.
- (c) The standard molar entropy of liquid water at 0°C is $65 \text{ JK}^{-1} \text{ mol}^{-1}$ and that

of ice at that $43 \text{ JK}^{-1} \text{ mol}^{-1}$. Calculate ΔS_{fusion} for water by rise of T . What is the effect of ΔS_{fusion} on temperature by 1.0 K rise?

- (d) Write the Clapeyron solid-liquid boundary diagram. How does temperature on this

3. Answer any three of the

- (a) (i) Show that when a gas adsorbs as atoms on a solid, the Langmuir isotherms become

$$\theta = \frac{(KP)^{1/2}}{1 + (KP)^{1/2}}$$

where the symbols have their usual meanings.

- (ii) Calculate the standard molar entropy of 1-aminobutanol at 20°C . Given that

$$\left(\frac{d\eta}{d \ln C} \right)_T$$

(b) If V is the volume of a gas (corrected to STP) adsorbed on the surface of a solid, then show that a plot of P/V versus P , where P is the gas pressure in the Langmuir adsorption isotherm, gives a straight line. Also show that for small surface coverages, a plot of $\ln(\theta/P)$ versus θ gives a straight line. 3+2=5

(c) Deduce BET equation of adsorption. 5

(d) (i) Discuss the mechanism of hydrogenation of ethene using metal catalyst. 3

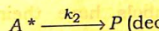
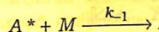
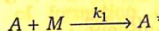
(ii) At 0°C and 1 atm pressure, the volume of N_2 (g) required to form a monolayer on a sample of charcoal is $155.5 \text{ cm}^3 \text{ g}^{-1}$ of charcoal. If the area covered by one molecule of N_2 (g) is $6.6 \times 10^{23} \text{ cm}^2$, then calculate the surface area per gram of charcoal. 2

(e) Derive thermodynamically the Gibbs adsorption isotherm for the adsorption of a solute on the surface of a liquid. 5

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

(a) Consider the following Lindemann mechanism for the unimolecular decomposition of a molecule A in the

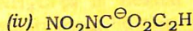
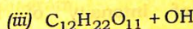
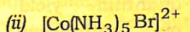
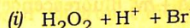
presence of species M molecule such as an



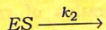
Using the steady state approximation, derive the rate law for the formation of the product.

(b) Discuss, how ionic strength affects the rate of a chemical reaction involving ions.

(c) Predict with reasons the effect of ionic strength on the rate of each of the following reactions:



(d) The following mechanism is proposed for enzyme catalyzed reaction:



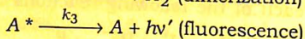
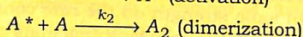
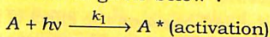
Using steady state approximation for $[ES]$, show that the reaction rate is given by

$$r = \frac{K_2[E]_0[S]}{K_m + [S]}$$

where the symbols have their usual meanings. Discuss the rate when $K_m \gg [S]$. 3+1=4

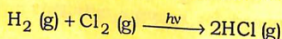
5. Answer either (a) and (b) or (c) and (d) :

- (a) What is the role of photosensitizer in the photochemical reaction? The mechanism of photochemical dimerization of an anthracene is given below :



Show that quantum yield for dimerization of anthracene is independence of intensity of light absorbed. 1+4=5

- (b) What is quenching? The quantum efficiency for the photochemical reaction



is 1.0×10^6 with a wavelength of 480 nm.

Calculate the number of moles of HCl (g) produced per joules of radiant energy absorbed. 1+4=5

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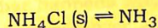
- (c) Write the mechanism of photochemical reaction of formation of product proportional to the absorbed radiation.

- (d) In a certain photochemical reaction, 464 nm radiation, power was 16.0 W absorbed 75% of the quantum yield of the product to be 0.15. How much product were formed in 100 S?

6. Answer either (a), (b) and (c)

- (a) What do you mean by congruent melting? Draw phase diagram of a system with two such components.

- (b) $NH_4Cl(s)$ is heated when the following equilibrium is established.



Find the number of degrees of freedom and degrees of freedom.

- (c) What is the maximum number of phases that can co-exist in a component system?

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(d) Draw the phase diagram of water and explain what the different curves signify. Using Clapeyron equation, predict the slope of each curve. $3+3=6$

(e) Show that the free energy of mixing of three gases has a minimum value with respect to each gas only when the mole fraction of the components are equal. Consider ideal behaviour. 4

2016

CHEMISTRY

(Major)

Paper : 5.3

Full Marks : 60

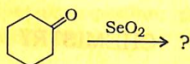
Time : 3 hours

The figures in the margin indicate full marks for the questions

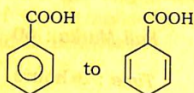
1. Answer the following questions (any seven) : 1×7=7

- (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 $400\text{ }^\circ C$?
- (d) Why does diethyl malonate undergo alkylation?
- (e) Why is naphthalene less aromatic than benzene?

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



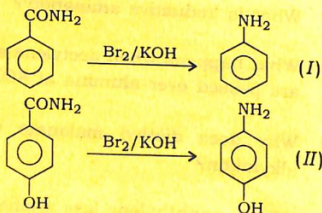
- (g) Define 'conrotatory ring closure'.
 (h) Write the appropriate reagent to convert



2. Answer the following questions (any four) :

2×4=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.

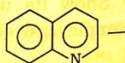
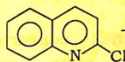
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(Continued)

- (d) Pyridine is basic. Explain.
 (e) Explain the acidic character of alkanes.

3. Answer the following questions (any two) :

- (a) Write Skraup synthesis of quinoline. What is the role of $\text{CH}_3\text{O}^-/\text{H}^+$ in the reaction?



- (b) Define pericyclic reaction. Give an example of electrocyclic reaction which is stereospecific, with appropriate reagents.
 (c) Convert benzophenone to benzamide. Give the equation with reagents. What is the driving force in this reaction?

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

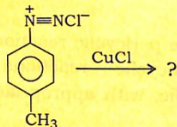
(e) Why do aliphatic nitrocompounds dissolve in aqueous alkali? How can CH_3CN and CH_3NC be prepared? What do you get when they are subjected to acid hydrolysis? $1+2+2=5$

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

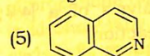
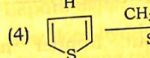
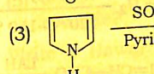
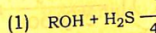


(iii) Why aniline cannot undergo
(1) Friedel-Crafts reaction and
(2) nitration reaction with HNO_3 ?

$1+1=2$

Or

(b) (i) Write products the products (with the reactions given)

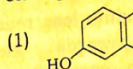


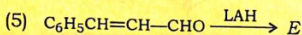
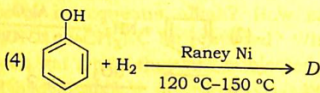
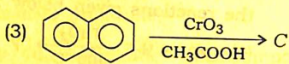
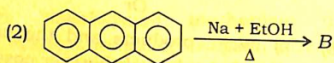
(ii) From ethyl acetate you prepare (1) and (2) succinimide

(iii) Why K_b of pyridine that of pyrrole

Either

(c) (i) Identify A, B, following reaction each product)





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

5

Or

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

5

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

2

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

2

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

1

Ether

- (e) (i) How can you (write the reaction) —

(1) dimethyl acetoacetic isocyanide,

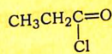
(2) methyl acetoacetic isocyanide,

(3) acetic acetoacetic isocyanide?

- (ii) Write Haworth projection of naphthalene.

- (iii) How does hydration of propanone take place in alcohol? Why does it form a carboxylic group?

- (iv) What is the mechanism of the conversion reaction of the reaction



Or

- (f) (i) What happens in the following reactions —

(1) *m*-dinitrobenzene + (NH₄)₂S;

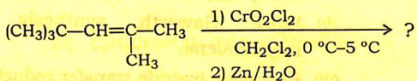
(2) N-methylacetamide + HONO;

(3) ethyl bromide + potassium cyanide

(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
- ionic organometallic compound
 - sigma-bonded organometallic compound
 - electron-deficient organometallic compound
 - None of the above
3. Vitamin B₁₂ contains
- Zn
 - Fe
 - Co
 - Mo
4. Which of the following statements is true about the octahedral complexes of Ni²⁺?
- Both strong- and weak-field complexes are diamagnetic
 - The strong-field complex is diamagnetic and the weak-field complex is paramagnetic

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(Continued)

- The strong-field paramagnetic and complex is diamagnetic
 - Both strong- and weak-field complexes are paramagnetic
5. [Fe₂(CO)₉] is diamagnetic
- the presence of only one terminal ligand
 - the metal-metal bond in the molecule
 - the presence of only one terminal ligand
 - the oxidation state of iron

Very short answer-type question

6. What are the symmetry elements in eclipsed and staggered ethane? State which one between them is the centre of inversion and which one is the axis of symmetry elements.

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7. Do the following organometallic species obey the 18-electron rule?
- (a) $[\text{Fe}(\text{CO})_5]$
- (b) $[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-C}_6\text{H}_6)]$
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) : $5 \times 3 = 15$

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 :
- $1+2+2=5$
- Co_3O_4 and Fe_3O_4

12. What are organometallic complexes? Comment on the stability of organometallic complexes. Give suitable examples.
13. Give the methods of preparation of metal-ethylene complexes and discuss its structure. The frequency of the $\text{C}=\text{C}$ stretching vibration is 1516 cm^{-1} in the complex whereas the frequency for free C_2H_4 is 1625 cm^{-1} . Explain.
14. What is the nature of the binding site in haemoglobin? How does the protein part of the heme group involved in the reversible binding of O_2 ?
15. The spin-only magnetic moment of $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ is found to be 2.87 BM and 0 BM respectively. Using the μ values, predict the geometry of the complex ions and the hybridization of Ni^{2+} .

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 heterogeneous catalytic cycle of hydroformylation by a cobalt carbonyl catalyst. How does the CO partial pressure threshold decrease as the catalyst is changed to a rhodium catalyzed hydroformylation? Suggest an interpretation.

20. Write short notes on any two of the following topics :

(a) Ziegler-Natta catalysis

(b) Molecular-orbital theory in transition metal chemistry

(c) Role of metal ions in biological systems