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.

(Continued)

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

(d) The associated Le defined by

$$P_l^{|m|}(w) = \frac{1}{2^l\, l!}(1 - w^2)^{|m|}$$

The solution of the S for H-atom also in function $P_l^{|m|}(\cos\theta)$. the function when quantum number l

(e) A particle with mass dimensional box of potential energy is wavelength associat is $\frac{2a}{n}$.

3. (a) Write the quantum radial wave functio wave function of H Discuss what in obtained from the function and squar function.

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 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 blac 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

(Continued)

(e) Calculate the avera
potential energy of the
in ground state.

6. Answer *either (a)* and *(b)*

(a) Write the secular
benzene on the
molecular-orbital th
theory, explain how
π-electrons stabiliz
molecule.

(b) Write the basis
molecular orbitals a
molecular orbitals
diatomic molecule be
Answer stating re
between σ- and π-
using symmetry conc

Or

(c) State how the Coulon
resonance integrals
Hückel molecular orb
this theory, deduce
the energies and
π-molecular orbital
ethene.

(d) Consider that the
function of ground s
obtained from 1s orb
$2p_z$ orbital of F

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 :

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

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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 charge.

(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 kJ mol^{-1} and +328 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 : 2×4=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 $\phi_{F,0} = 0 \cdot 20$ and $\tau_0 = 2 \cdot 6$ ns respectively. Determine the fluorescence rate constant of this substance.

(c) The standard molar entropy of liquid water at 0 °C is 65 JK^{-1} mol^{-1} and that

(Continued)

of ice at that
43 JK^{-1} mol^{-1}. Calcu
for water by rise of
What is the effect
temperature by 1·0 K

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

3. Answer any *three* of the

(a) (i) Show that wh
adsorbs as atom
solid, the La
isotherms becor

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

where the symb
meanings.

(ii) Calculate the
1-aminobutanoi
0·10 mol dm^{-3}
20 °C. Given th

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

(b) If V is the volume of a gas (corrected to STP) absorbed 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 $155 \cdot 5\ cm^3\ g^{-1}$ of charcoal. If the area covered by one molecule of N_2 (g) is $6 \cdot 6 \times 10^{23}\ cm^2$, 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

(Continued)

presence of species M molecule such as an

$$A + M \xrightarrow{k_1} A$$

$$A^* + M \xrightarrow{k_{-1}}$$

$$A^* \xrightarrow{k_2} P \text{ (dec}$$

Using the steady st derive the rate law f the product.

(b) Discuss, how ionic the rate of a chemic ions.

(c) Predict with reasons in ionic strength on each of the following

(i) $H_2O_2 + H^+ + Br$

(ii) $[Co(NH_3)_5Br]^{2+}$

(iii) $C_{12}H_{22}O_{11} + OH$

(iv) $NO_2NC^{\ominus}O_2C_2H$

(d) The following mec proposed for enzyme

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

$$ES \xrightarrow{k_2}$$

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 $K_m >> [S]$. 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 :

$$A + h\nu \xrightarrow{k_1} A^* \text{ (activation)}$$

$$A^* + A \xrightarrow{k_2} A_2 \text{ (dimerization)}$$

$$A^* \xrightarrow{k_3} A + h\nu' \text{ (fluorescence)}$$

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

$$H_2\,(g) + Cl_2\,(g) \xrightarrow{h\nu} 2HCl\,(g)$$

is $1{\cdot}0 \times 10^6$ with a wavelength of 480 nm. Calculate the number of moles of HCl (g) produced per joules of radiant energy absorbed. 1+4=5

(Continued)

(c) Write the mechani photochemical react rate of formation proportional to th absorbed radiation.

(d) In a certain photoche 464 nm radiation, power was 16·0 W absorbed 75% of th quantum yield of the to be 0·15. How product were forme 100 S?

6. Answer *either (a), (b)* an

(a) What do you mean with congruent melt phase diagram of a two such compou diagram.

(b) NH_4Cl (s) is heated when the following

$$NH_4Cl\,(s) \rightleftharpoons NH_3$$

Find the number of and degrees of freed

(c) What is the maximu of phases that can component system?

(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

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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?

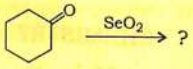
(b) What is 'reductive amination'?

(c) What happens when acetylene and H_2S are passed over alumina at 400 °C?

(d) Why does diethyl malonate undergo alkylation?

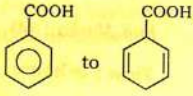
(e) Why is naphthalene less aromatic than benzene?

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



(g) Define 'conrotatory ring closure'.

(h) Write the appropriate reagent to convert

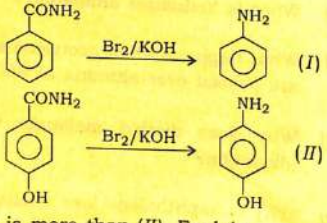


2. Answer the following questions (any *four*) : 2×4=8

(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.

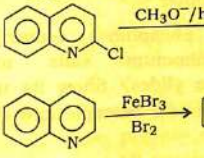
(Continued)

(d) Pyridine is basic. E

(e) Explain the acidic alkane.

3. Answer the following que (a) and (b) and *two* fron

(a) Write Skraup syn What is the role reaction? Explain quinoline with th reactions :



(b) Define pericyclic re electrocyclic reac specific, with appro

(c) Convert benzoph benzanilide in the p give equation with is the driving force this reaction?

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

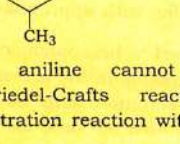
(e) Why do aliphatic nitrocompounds dissolve in aqueous alkali? How can CH_3CN and CH_3NC be prepared? What do you get when they are subjected to acid hydrolysis? 1+2+2=5

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

(Continued)

Or

(b) (i) Write products the products (wh the reactions giv

(1) $ROH + H_2S \rightarrow$

(2)  $+ NH_3$

(3)  SO Pyri

(4)  CH

(5) 

(ii) From ethyl acet you prepare (1 and (2) succini

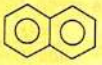
(iii) Why K_b of pyri that of pyrrole

Eithe

(c) (i) Identify *A*, *B*, following reac each product)

(1)

(2)  $\xrightarrow[\Delta]{Na + EtOH} B$

(3)  $\xrightarrow[CH_3COOH]{CrO_3} C$

(4)  $+ H_2 \xrightarrow[120\ °C–150\ °C]{Raney\ Ni} D$

(5) $C_6H_5CH{=}CH{-}CHO \xrightarrow{LAH} E$

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

(Continued)

Either

(e) *(i)* How can y reaction)—

(1) dimethyl a isocyanide;

(2) methyl pr acetoacetic

(3) acetic ac cyanide?

(ii) Write Hawor naphthalene.

(iii) How does hydri of propanone ta in alcohol? Why carboxylic grou

(iv) What is the re conversion rea of the reaction

$CH_3CH_2\underset{\underset{Cl}{|}}{C}{=}O$

Or

(f) *(i)* What happe reactions)—

(1) *m*-dinitrobe $(NH_4)_2S$;

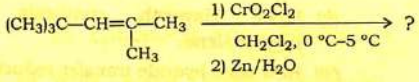
(2) N-methyl HONO;

(3) ethyl bron potassium

(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

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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 B_{12} contains

(a) Zn

(b) Fe

(c) Co

(d) Mo

4. Which of the following statements is true about the octahedral complexes of Ni^{2+}?

(a) Both strong- and weak-field complexes are diamagnetic

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

(Continued)

(c) The strong-fiel paramagnetic ar complex is diamag

(d) Both strong- and are paramagnetic

5. $[Fe_2(CO)_9]$ is diamagnet

(a) the presence of o ligand

(b) the metal-metal (molecule

(c) the presence of ligand

(d) the oxidation stat

Very short answer-type que

6. What are the symmetr eclipsed and staggere State which one betw the centre of inversi symmetry elements.

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

   (a) $[Fe(CO)_5]$

   (b) $[Cr(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]$

8. What is the Cr—Cr bond order in the compound $Cr_2(\mu\text{-}O_2CCH_3)_4(H_2O)_2$?

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

10. Predict the magnetic properties of the species $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$.

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

    Co_3O_4 and Fe_3O_4

(Continued)

12. What are organome
    Comment on the stabili
    in organometallic compo
    suitable examples.

13. Give the methods of p
    salt and discuss its st
    metal-ethylene complex
    frequency of the C=C
    1516 cm^{-1} whereas
    frequency for free C_2
    1625 cm^{-1}. Explain.

14. What is the nature of
    site in haemoglobin? H
    that the protein part o
    involved in the reversi

15. The spin-only magne
    $[NiCl_4]^{2-}$ and [Ni(CN)
    found to be 2·87 BM a
    Using the μ values, p
    the complex ions and
    hybridization of Ni^{2+}

Essay-type questions (any *three*) : 10×3=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 $[Ti(H_2O)_6]^{3+}$ and the magnetic moment of the species $[Co(SCN)_4]^{2-}$. 6+2+2=10

18. *(a)* Give the method of preparation for the binuclear species $[Re_2Cl_8]^{2-}$ and discuss its bonding giving an appropriate diagram. 5

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

(Continued)

19. Distinguish between heterogeneous catalys catalytic cycle of hydrof by a cobalt carbonyl ca CO partial pressure threshold decreases th catalyzed hydroformyl Suggest an interpretatio

20. Write short notes on an topics :

(a) Ziegler-Natta catal

(b) Molecular-orbital t chemistry

(c) Role of metal ions

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