

- (c) Using the energy expressions, find the normalized MO wave functions of H_2^+ . Give the schematic plots of the square of the wave functions against internuclear distance. State what information can be drawn from these plots. 4+2=6

- (d) The energies of the π -MOs of benzene, according to Hückel method, are $\alpha + 2\beta$, $\alpha + \beta$, $\alpha - \beta$ and $\alpha - 2\beta$. Here each of the energy levels $\alpha + \beta$ and $\alpha - \beta$ is doubly degenerate. Using this result, explain how the formation of delocalized π -MOs stabilizes the molecule. 4

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

2019

CHEMISTRY

(Major)

Paper : 5.1

(Quantum Chemistry)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

Symbols signify their usual meanings

1. Answer any seven of the following in brief :

1×7=7

- (a) Write the postulate of quantum mechanics regarding the expectation value of a physical quantity of a system.
- (b) Find the expression for the Hamiltonian operator for a particle of mass m with potential energy V . Consider only x -dimension.

- (c) The state function Ψ takes on only real values. State True or False.
- (d) The normalization condition is $\int \psi^2 d\tau = 1$. State what this condition actually means.
- (e) Write the spin orbital for ground state H-atom.
- (f) State why the molecular orbitals of a heteronuclear diatomic molecule cannot be classified as g or u .
- (g) Write the term symbol for the ground state hydrogen molecule.
- (h) The energy of a free axis rigid rotator is given by $\frac{\hbar^2}{I}$. State how many folds this energy level will degenerate.
- (i) Give the schematic plot of ψ^2 against x of one-dimensional harmonic oscillator, if the value of the quantum number is zero.

2. Answer the following questions :

2×4=8

- (a) A function must be quadratically integrable in order to be well-behaved. State when a function is said to be quadratically integrable. Write why the function has to be quadratically integrable.
- (b) Show that e^{ikx} is an eigenfunction of the momentum operator, p_x .
- (c) Normalize the function $\cos \frac{\pi x}{a}$ over the interval $0 \leq x \leq a$.

Or

Out of $\frac{d}{dx}$ and taking square-root ($\sqrt{\quad}$), explain which is linear operator and which is not.

- (d) Write the expressions for the magnitude and the z -component of angular momentum. Find the magnitude of the orbital angular momentum of an electron in d -orbital.

Or

Find the magnitude of the spin angular momentum of an electron. Write how many orientations of the spin angular momentum will be observed in presence of a magnetic field applied in a particular direction.

3. (a) Write the approximate spatial function and the spin functions for the electrons of the ground state He-atom. State Pauli's antisymmetry principle and hence find the acceptable complete wave function of He-atom. $2+3=5$
- (b) Using Hückel method, find the π -bond energy of ethene. Hence explain how the formation of the π -molecular orbital stabilizes the molecule. $3+2=5$
- (c) Write the time-independent Schrödinger equation for H_2^+ . Indicate the kinetic energy terms and the potential energy terms present in the Hamiltonian of the equation. Using Born-Oppenheimer approximation, explain how the Schrödinger equation for H_2^+ can be separated into two equations. $1+1+3=5$

Or

Use the LCAO method to form the MO wave function of H_2^+ . Using this wave function, deduce the energy expressions for the bonding and the antibonding MOs. $1+4=5$

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

- (a) For a particle moving on a ring of radius r , the wave function is $\psi = Ne^{im\phi}$. Show that the possible values of m are $0, \pm 1, \pm 2, \dots$. 3
- (b) For a particle in a one-dimensional box of length a , where potential energy is zero, solve the time-independent Schrödinger equation to get the value of the wave function and energy. 4
- (c) The ground-state translational energy of a particle in a one-dimensional box of length 300 pm is 4 eV. Find the ground-state translational energy of the same particle, if it is moving in a cube of length 100 pm. 3
- (d) Deduce Planck's radiation law in terms of wavelength in case of blackbody radiation. 4

- (e) For a particle in one-dimensional box, where potential energy is zero, show that the average value of momentum is zero. 3
- (f) Assume $b \sin \frac{n\pi x}{a}$ to be the wave function for a particle in one-dimensional box of length a , where $V=0$. Verify whether it satisfies the eigenvalue equation, $H\psi = E\psi$, or not. 3

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

- (a) Mention the quantum numbers on which the radial function and the angular function of H-atom depend. Discuss what information can be drawn from the plots of the radial function and the square of the radial function against the radial distance. 1+3=4
- (b) Write in brief about the Russell-Saunders coupling of angular momentum. Write the term symbol for $3s^1$ electron. 2+1=3
- (c) Show that the maximum probability of finding the electron of the ground state H-atom is at $r = a_0$. 3

- (d) Write a short note on Stern-Gerlach experiment. 4
- (e) Deduce an expression for the radial distribution function for non-s state. 3
- (f) Calculate the average value of the radial distance of the electron from the nucleus of the H-atom in ground state. 3

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

- (a) Heitler and London used the following wave function for the bonding in H_2 :
- $$\psi = C_1 1s_A(1) 1s_B(2) + C_2 1s_A(2) 1s_B(1)$$
- Explain why this wave function is preferred to the MO wave function of H_2 . Write how this wave function is an improvement over the MO wave function of H_2 . 3+3=6
- (b) Using the energy expression of the bonding MO of H_2^+ , write how the potential energy diagram is constructed. Also write what information you can draw from this diagram. 2+2=4

2019

CHEMISTRY

(Major)

Paper : 5.2

(Physical Chemistry)

Full Marks : 60

Time : 3 hours

*The figures in the margin indicate full marks
for the questions*

1. Answer the following questions in brief : $1 \times 7 = 7$

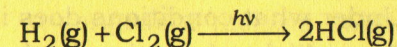
- (a) Give the degrees of freedom of a solution of acetic acid in water.
- (b) When 100 numbers of photons are absorbed by a reacting system, 10^5 numbers of molecules of a reactant are converted into products. What is the quantum yield of the reaction?

- (c) Ice and water-phase diagram has negative slope. Explain.
- (d) Give the signs of ΔH and ΔS in an adsorption process.
- (e) In many reactions, the entropy change of activation is negative. Explain the reason.
- (f) Draw the graph representing the variation of chemical potentials of ice and water with temperature.
- (g) State the Stark-Einstein law of photochemical equivalence.

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

- (a) Using the Clausius-Clapeyron equation, explain the nature of variation of vapour pressures with temperature.
- (b) Write down the Eyring equation and give the meanings of the terms involved in the equation.

- (c) 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 formed per joule of radiant energy absorbed.

- (d) The volume of nitrogen gas required to cover a sample of silica gel with monomolecular layer is 0.129 dm^3 per gm of the gel at 1 atm and 273 K. If each nitrogen molecule occupies $1.62 \times 10^{-19} \text{ m}^2$ area, calculate the surface area of the gel.

3. Answer any *three* of the following questions :

$5 \times 3 = 15$

- (a) Discuss the effect of ionic strength on the rate constant of an uncatalyzed ionic reaction. 5
- (b) Write the postulates of hard-sphere collision theory. Using this theory, deduce the expression of rate constant for a bimolecular gas-phase reaction.

$2 + 3 = 5$

- (c) Derive an expression for Langmuir unimolecular adsorption isotherm. Under what conditions does it reduce to Freundlich adsorption isotherm? 3+2=5

- (d) Define fugacity. For a mixture of ideal gases at constant temperature and pressure, show that

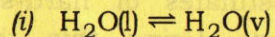
$$\Delta G_{\text{mix}} = nRT \sum x_i \ln x_i$$

where the terms have their usual meanings. 1+4=5

4. Answer any two of the following questions : 5×2=10

- (a) Write the mechanism of the $\text{H}_2\text{—Cl}_2$ photochemical reaction. Prove that the rate of formation of HCl is directly proportional to the intensity of the absorbed radiation. 2+3=5

- (b) Draw the phase diagram representing schematically each of the following :



- (ii) A temperature-composition phase diagram for binary system having a eutectic mixture

- (iii) A temperature-composition phase diagram for a binary system having a congruent melting point

Why a eutectic mixture cannot be separated by using simple distillation?

$$1+1\frac{1}{2}+1\frac{1}{2}+1=5$$

- (c) Write the Lindemann's mechanism of unimolecular reaction. Using this mechanism, deduce an expression for the rate of the unimolecular reaction.

$$2+3=5$$

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

$$5 \times 2 = 10$$

- (a) Define chemical potential and give its physical interpretation. How does chemical potential change with the change of compositions of a system?

$$2+3=5$$

- (b) In the photochemical decomposition of acetone using 313 nm radiation, 7.57×10^{-6} moles of CO is formed in 20 minutes. If the energy of radiation absorbed corresponds to $2.41 \times 10^{-3} \text{ J s}^{-1}$, calculate the quantum efficiency for the formation of CO.

5

(6)

(c) What is surface excess? Derive the Gibbs' equation of surface excess. 1+4=5

(d) Derive the BET equation. 5

6. Answer any *two* of the following questions :

5×2=10

(a) Discuss the mechanism of hydrogenation of ethene using Ni catalyst. Also discuss the effect of surface area on the rate of the above reaction. 3+2=5

(b) Using ACT, derive the thermodynamic formulation of rate constant for a bimolecular gas-phase reaction. 5

(c) What is potential energy surface? With the help of the potential energy surface, how can you explain the different paths of a chemical reaction? Explain with an example. 1+4=5

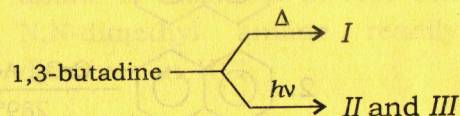
(d) (i) Using hard-sphere collision theory expression of rate constant of a bimolecular gas-phase reaction, deduce the Arrhenius factor.

(7)

(ii) The hard-sphere diameters of O_2 and CO molecules are found to be 3.6 Å and 3.7 Å. Calculate the hard-sphere collision theory frequency factor for the bimolecular gas phase reaction between O_2 and CO at 2700 K. 3+2=5

Or

- (f) (i) Predict the structures for compounds I, II and III : 3



- (ii) What is sigmatropic rearrangement? What do you mean by the order $[i, j]$ of a sigmatropic rearrangement? Give example. 1+1+1=3

- (iii) Discuss the FMO method of (4+2) cycloaddition reaction. 2

- (iv) Write down the Woodward-Hoffmann rules for electrocyclic reaction. 2

2019

CHEMISTRY

(Major)

Paper : 5.3

(Organic Chemistry)

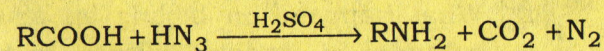
Full Marks : 60

Time : 3 hours

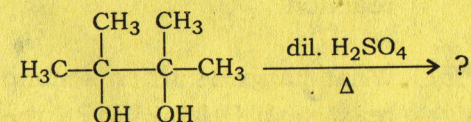
The figures in the margin indicate full marks for the questions

1. Answer any seven of the following : 1×7=7

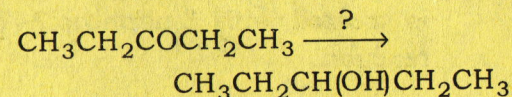
- (a) What is the name of the following reaction?



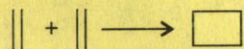
- (b) Complete the following reaction :



- (c) Complete the following reaction :



(d) Name the type of the following reaction :



(e) What is the full form of HOMO?

(f) Which one is more acidic RSH or ROH?

(g) Why is furan least aromatic than thiophene?

(h) Which position of pyridine undergoes electrophilic substitution reaction?

(i) Why is nitromethane acidic?

2. Answer any *four* of the following questions :

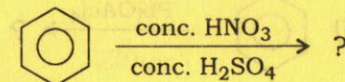
2×4=8

(a) What happens on boiling an aqueous solution of sodium nitrite with an α -halogen carboxylic acid? Write the reaction.

(b) What happens when secondary amines react with HNO_2 ? Write the reaction.

(c) What happens when aryldiazonium salt is treated with β -naphthol? Write the reaction.

(d) Complete the following reaction :



Give the mechanism.

(e) Draw the tautomers of acetoacetic ester. Which one is more stable and why?

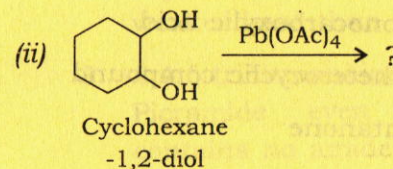
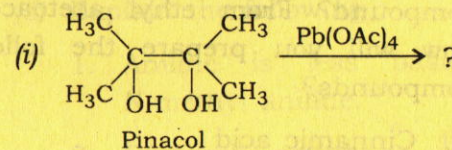
3. Answer any *three* of the following questions :

5×3=15

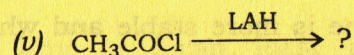
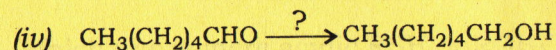
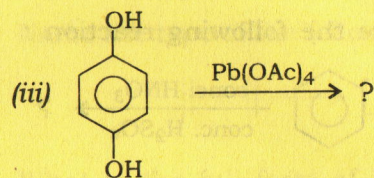
(a) How does phenyl acetate undergo intramolecular rearrangement reaction in the presence of AlCl_3 ? Give mechanism of this reaction. What are the factors on which relative amount of product depends?

1+3+1=5

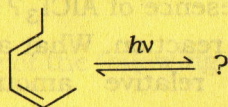
(b) Complete the following reactions : 1×5=5



(4)



- (c) Which cycloaddition reaction is known as Diels-Alder reaction? Write the product of the following reaction and justify the stereochemistry of the product using FMO method : $1+4=5$



- (d) What do you mean by active methylene compound? From ethyl acetoacetate, how will you prepare the following compounds? $1+4=5$

- Cinnamic acid
- Monocarboxylic acid
- A heterocyclic compound
- Butanone

(Continued)

(5)

4. Answer the following questions : $10 \times 3 = 30$

Either

- (a) (i) What happens when ethanal treated with nitroethane in the presence of a base? Write the reaction and give the mechanism. Write the Mannich reaction. $1+3+1=5$

- (ii) What are the different products you obtain when nitrobenzene undergoes reduction in alkaline medium? Write the reactions. 5

Or

- (b) (i) What is exhaustive methylation of amines and Hoffmann's elimination? Discuss with a suitable example. 5

- (ii) Explain the following : $1+1+1+2=5$

- Aniline is less basic than N-methyl aniline.
- Diphenyl amine is a much weaker base than aniline.
- 2,4,6-trinitroaniline is termed Picramide even though it contains no amide linkage.

(Turn Over)

4. Triphenyl amine and N,N-dimethyl aniline are both tertiary amines. Triphenyl amine is insoluble in HCl but N,N-dimethyl aniline readily dissolves in HCl.

Either

- (c) (i) Explain why the electrophilic substitution takes place preferably at α -position in furan, thiophene and pyrrole. 3

- (ii) Pyrrole is acidic in character like phenol. Explain. 2

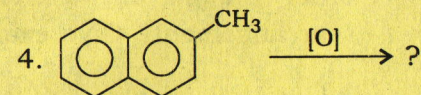
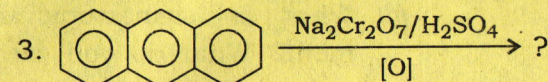
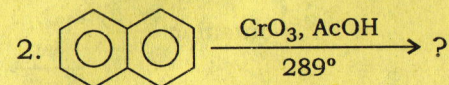
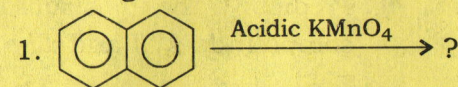
- (iii) Describe the mechanism of nitration of pyridine and justify that substitution takes place at position 3. 5

Or

- (d) (i) What are polynuclear hydrocarbons? What are the different types? 1+2=3

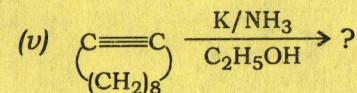
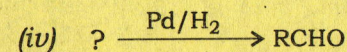
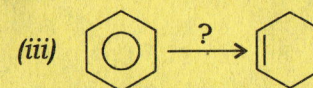
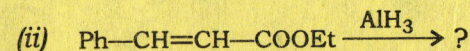
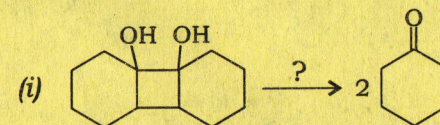
- (ii) Write the Haworth's synthesis of naphthalene. 3

- (iii) Give the product with name of the following : 1×4=4



Either

- (e) Complete the following, specifying the transformation as oxidation or reduction : 2×5=10



2019

CHEMISTRY

(Major)

Paper : 5.4

(Inorganic Chemistry)

Full Marks : 60

Time : 3 hours

*The figures in the margin indicate full marks
for the questions*

1. Choose the correct options for the following :

1×7=7

- (a) Each of the following contains a six-membered ring. Which molecule will have a six-fold (C_6) principal rotation axis?

- (i) Borazine
- (ii) Pyridine
- (iii) Benzene
- (iv) S_6 -molecule

(b) The correct C—O bond order in the complexes $[\text{Ni}(\text{CO})_4]$, $[\text{Co}(\text{CO})_4]^-$ and $[\text{Fe}(\text{CO})_4]^{2-}$ is

(i) $[\text{Ni}(\text{CO})_4] < [\text{Co}(\text{CO})_4]^- < [\text{Fe}(\text{CO})_4]^{2-}$

(ii) $[\text{Ni}(\text{CO})_4] > [\text{Co}(\text{CO})_4]^- > [\text{Fe}(\text{CO})_4]^{2-}$

(iii) $[\text{Co}(\text{CO})_4]^- > [\text{Fe}(\text{CO})_4]^{2-} > [\text{Ni}(\text{CO})_4]$

(iv) $[\text{Fe}(\text{CO})_4]^{2-} > [\text{Co}(\text{CO})_4]^- > [\text{Ni}(\text{CO})_4]$

(c) The crystal field splitting energies for octahedral and tetrahedral complexes are related as

(i) $\Delta_t = \frac{1}{2} \Delta_o$

(ii) $\Delta_t = \frac{4}{9} \Delta_o$

(iii) $\Delta_o = \frac{4}{9} \Delta_t$

(iv) $\Delta_t = \frac{2}{5} \Delta_o$

(d) If free heme in aqueous solution is exposed to dioxygen (O_2), it is converted almost immediately to a dimer

(i) ferritin

(ii) ferryl complex

(iii) hematin

(iv) oxyhaemoglobin

(e) The correct Cr—Cr bond order in the complex $[\text{Cr}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{OH}_2)_2]$ is

(i) 2

(ii) 4

(iii) 3

(iv) 2.5

(f) Which of the following will have a centre of symmetry?

(i) $[\text{PtCl}_4]^{2-}$

(ii) $[\text{CoCl}_4]^{2-}$

(iii) $[\text{BF}_4]^-$

(iv) $[\text{Ni}(\text{CO})_4]$

(g) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ has a magnetic moment of 3.83 BM. The correct distribution of 3d-electron in the chromium of the complex is

(i) $(3d_{xy})^1(3d_{x^2-y^2})^1(3d_{yz})^1$

(ii) $(3d_{xy})^1(3d_{z^2})^1(3d_{yz})^1$

(iii) $(3d_{xy})^1(3d_{yz})^1(3d_{xz})^1$

(iv) $(3d_{x^2-y^2})^1(3d_{z^2})^1(3d_{xy})^1$

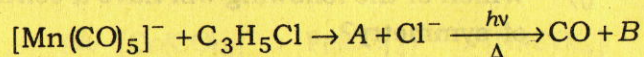
2. Answer the following very briefly :

2×4=8

(a) Based on crystal field theory, show the d-orbital splitting pattern in square planar and trigonal bipyramidal geometry.

(b) Explain, why BF_3 molecule possesses an S_3 axis of improper rotation but NF_3 does not.

(c) Identify the products A and B in the following reaction :



(d) For Mn^{3+} ions, the electron pairing energy P is 28000 cm^{-1} . Δ_o values for complexes $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Mn}(\text{CN})_6]^{3-}$ are 15800 cm^{-1} and 38500 cm^{-1} respectively. Write the electronic arrangement of Mn^{3+} in terms of t_{2g}^x and e_g^y .

3. Answer any *three* of the following short answer-type questions : 5×3=15

(a) What are symmetry elements and symmetry operations? Assign the symmetry elements present in
(i) a $d_{x^2-y^2}$ orbital, (ii) $\text{trans-N}_2\text{F}_2$ and
(iii) $\text{F}_2\text{C}=\text{O}$. 5

(b) Discuss the Dewar-Chatt-Duncanson theory of bonding in metal olefin complexes. 5

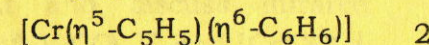
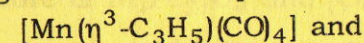
(c) (i) Discuss the factors which influence the magnitude of orbital splitting energy Δ in a complex. 3

(ii) Write the electronic arrangement in terms of e^x and t_2^y for tetrahedral complex $[\text{FeCl}_4]^{2-}$. Also find the spin only magnetic moment value. 2

(d) Discuss the mechanism of formation of hematin a μ -oxodimer, when free heme in aqueous medium is exposed to dioxygen. 5

(e) (i) Explain the basis of 18-electron rule for octahedral organic complexes. 3

(ii) Verify the EAN rule for the organometallic compounds



4. Answer any *three* of the following essay-type questions : 10×3=30

(a) (i) CH_4 molecule does not have a four-fold axis of rotation (C_4) but it does have an S_4 axis of improper rotation. Discuss the statement with a proper diagram. 3

- (ii) What symmetry elements do BCl_3 and PCl_3 have in common? Also mention the point groups to which these molecules belong. 5
- (iii) N_2 has molecular orbital rather similar to those of CO. Would you expect N_2 to be a stronger or weaker π -acceptor than CO? Explain. 2
- (b) Discuss the catalytic cycle of hydroformylation reaction of alkenes by cobalt carbonyl catalyst. An increase in carbon monoxide (CO) partial pressure decreases the rate of cobalt catalyzed hydroformylation of 1-pentene. Suggest an interpretation of this observation. 6+4=10
- (c) Give a brief description of molecular orbital theory as applied to coordination compounds. Construct a molecular orbital energy level diagram for an octahedral complex involving metal-ligand sigma (σ) bonds only. Write the molecular electronic configuration of the complex $[\text{Co}(\text{NH}_3)_6]^{3+}$. 5+4+1=10

- (d) (i) Discuss the physiology of haemoglobin and myoglobin. What do you mean by cooperativity binding of dioxygen with Hb? 5
- (ii) How can you predict z-out and z-in distortion in an octahedral complex? 1
- (iii) Why are transition metal aryls more stable than transition metal alkyls? 2
- (iv) Write the IUPAC names for $[(\text{Co})_3(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-C}_5\text{H}_5)\text{W}]$ and $[\text{Ni}(\eta^3\text{-C}_3\text{H}_5)_2]$. 2
- (e) (i) What do you mean by normal and inverse spinels? With the help of CFSE calculation, verify the spinel nature of $\text{Ni}[\text{Fe}_2]\text{O}_4$ and $[\text{Co}_3]\text{O}_4$. 5
- (ii) Comment and discuss infrared spectra of $[\text{V}(\text{CO})_6]^-$ and $[\text{Cr}(\text{CO})_6]$. Show absorptions at 1859 cm^{-1} and 1981 cm^{-1} respectively assigned to ν_{CO} and 460 cm^{-1} and 441 cm^{-1} assigned to ν_{MC} . 5

★ ★ ★