2018

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 used signify their usual meanings

1×7=7

1. Answer in brief :

(a) Find the eigenvalue for the operator $\frac{d^2}{dx^2}$ if the function is $\cos 4x$.

(b) An operator $\hat{O}$ is defined as $\hat{O}\psi = \lambda\psi$, where λ is a constant. Show whether the operator is linear or not.

(c) Show whether the function $\psi = e^{-x}$ is well-behaved or not within the interval $0 \leq x \leq \infty$.

(Turn Over)

Or

One of the conditions for a function to be well-behaved is that the function must be single-valued. State why the function has to be single-valued.

(d) Draw a diagram to show the orientations of the orbital angular momentum of magnitude $\sqrt{2}\,\hbar$ in presence of the applied magnetic field in the z-direction.

(e) Find the term symbol for an electron in the d-orbital.

(f) Write the value of the angular function for s-orbital.

Or

Define the shape of an orbital.

(g) For the ground-state H-atom, write the wave functions for the spin-orbital.

2. Answer the following questions : $2\times4=8$

(a) Find the operator for total energy of a particle with mass m having coordinate (x, y, z).

(Continued)

(b) Normalize the function $\sin\frac{n\pi x}{a}$ within the interval $0 \le x \le a$. Here $n = 1, 2, 3, \cdots$.

Or

Show that the functions $\sin\frac{\pi x}{a}$ and $\cos\frac{\pi x}{a}$ are orthogonal within the interval $0 \le x \le a$.

(c) Let ψ_1 and ψ_2 be the eigenfunctions of the linear operator $\hat{O}$, having the same eigenvalue λ. Show that the linear combination of ψ_1 and ψ_2 is also an eigenfunction of $\hat{O}$ having the same eigenvalue.

(d) Consider the following sets of quantum numbers :

(i) $n = 2,\ l = 0,\ m_l = 0$

(ii) $n = 2,\ l = 1,\ m_l = 0$

(iii) $n = 2,\ l = 1,\ m_l = +1$

(iv) $n = 2,\ l = 1,\ m_l = -1$

State which of these sets yield imaginary wave functions. State how real functions are obtained from these imaginary functions.

Or

Taking $2p_z$-orbital as example, write why the p-orbital is dumbbell in shape.

(Turn Over)

3. What do you mean by complete wave function? Using Pauli's anti-symmetry principle, prove that no two electrons of an atom can have all the four quantum numbers alike. 1+4=

Or

What do you mean by spin-orbit interaction? Write in brief about the Russell-Saunders scheme of coupling of angular momenta. Find the term symbols for the first excited state of He-atom. 1+2+2=

4. Answer any *two* questions : 5×2=1

(a) Write the time-independent Schrödinger equation for H_2^+. State Born-Oppenheimer approximation. Discuss how this approximation can be applied to separate the Schrödinger equation for H_2^+ into two equations—one for the nuclei and the other for the electron. 1+1+3=5

(b) Applying Hückel molecular orbital method, calculate the π-bond energy of ethene. Also find the expressions for the π-molecular orbitals. 3+2=5

(Continued)

(c) Write how the molecular orbitals of a homonuclear diatomic molecule can be classified as σ or π. Which of these two is doubly degenerate and why? What is the basis of classifying the MOs as *g* or *u*? 2+2+1=5

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

(a) A particle of mass *m* is moving within a box of lengths *a*, *b* and *c* along *x*-, *y*- and *z*-axes respectively. The potential energy within the box is considered to be zero; outside the box it is considered to be infinity. Solve the time-independent Schrödinger equation for the particle to get the values of the wave function and the energy. Use these results to explain degeneracy. 4+2=6

(b) Calculate the zero-point vibrational energy of HCl if its force constant is $516\ \mathrm{N\,m^{-1}}$. 4

Or

(c) State the experimental observation of the photoelectric effect. Discuss how Einstein explained the observation. 3+2=5

(Turn Over)

(d) A particle of mass m is moving in a one-dimensional box of length a, where potential energy is zero. Calculate the average kinetic energy of the particle. 3

(e) An electron is confined to a molecule of length 10^{-9} m. Considering the electron to be a particle in one-dimensional box, where $V = 0$, calculate its minimum energy. 2

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

(a) Define radial distribution function. Deduce an expression for the radial distribution function for non-s state. 1+3=4

(b) Explain what you mean by space quantization. 3

(c) Calculate the average value of potential energy of the electron of H-atom in the 1s state. 3

Or

(d) What do you mean by radial function? Give the plots of radial function against r for $n = 2$. State what information you can draw from these plots. 1+1+2=4

(Continued)

(e) State Hund's rule of maximum multiplicity. For the $2p^2$ electrons of the ground-state C-atom, the following terms are obtained :

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

Using Hund's rule, state which of these terms will be the lowest in energy. 2+1=3

(f) Show that the maximum probability of finding the electron of the ground-state H-like atom is at $r = a_0/z$. 3

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

(a) Write the energy expressions for the bonding and the anti-bonding molecular orbitals of H_2^+. Hence explain how the potential energy diagram is constructed. Write what information can be drawn from this diagram. 1+3+2=6

(b) Write the approximations of the Hückel molecular orbital theory. 4

Or

(c) Write the ground-state molecular orbital wave function of H_2. Hence explain the drawback of the molecular orbital theory in case of H_2. State how Heitler and London modified the wave function. 1+3+1=5

(Turn Over)

(d) Using LCAO-MO method, deduce the secular equations of H_2^+. Hence deduce the expressions for the MO wave functions and their energies. 5

Standard integration :

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

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2018

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) In a system, liquid water and water vapour are in equilibrium at a pressure of 1 atm. What is the number of degree of freedom for the system?

(b) The limiting partial molar volume of $MgSO_4$ in water is $-1{\cdot}4\ cm^3\ mol^{-1}$. If 60 g anhydrous $MgSO_4$ is added to 1 litre of distilled water, then what is the expected final volume of the solution?

(c) What is the exact difference between a transition state and an activated complex?

(Turn Over)

(d) What is the main difference between a photosensitizer and a catalyst?

(e) At 600 nm, *tris*-(2,2′-bipyridyl) ruthenium (II) complex shows fluorescence with an emission life-time of 6×10^{-7} s. On addition of a small amount of $9{\cdot}4\times10^{-4}$ mol dm^{-3} $[Fe(OH_2)_6^{3+}]$ solution, the emission lifetime of the complex decreases to $2{\cdot}17\times10^{-7}$ s. What is the role of Fe^{3+} solution in this case?

(f) Why does physisorption decrease with increase of temperature?

(g) Predict the effect of ionic strength on the rate constant of the reaction

$$[Pt(NH_3)_2Cl_2] + OH^- \rightarrow \text{Products}$$

2. Answer the following questions : $2\times4=8$

(a) "A mixture of HCl/H_2O (80% by mass of water) cannot be separated by distillation." Justify the statement.

(b) For a first-order reaction, the activation energy is 108·4 kJ mol^{-1}. What is the enthalpy of activation of the reaction at 130 °C?

(Continued)

(c) Both fluorescent and phosphorescent radiations are of shorter frequencies than the exiting light. Explain.

(d) A graph between $\log(x/m)$ and $\log P$ is a straight line at an angle of 45° with intercept on *Y*-axis equal to 0·3010. Calculate the amount of gas adsorbed per gram of the adsorbent when the pressure is 0·2 atm.

3. State the Stark-Einstein law of photochemical equivalence. What do you mean by one einstein of energy? When a sample of 4-heptanone was irradiated with 313 nm light with a power output of 50 W under conditions of total absorption for 100 s, it was found that $2{\cdot}8\times10^{-3}$ mole C_2H_4 was formed. What is the quantum yield for the formation of ethene? 1+1+3=5

Or

Draw energy profile diagrams for an exothermic and an endothermic reactions. Show that for a gaseous bimolecular reaction

$$A(g) + B(g) \rightarrow (AB)^{\dagger\dagger} \rightarrow \text{Product}$$

$E_a = \Delta H_m^{\dagger\dagger} + 2RT$, where the subscript m stands for molar. 1+1+3=5

(Turn Over)

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

(a) What do you mean by partial molar quantities? Explain with an example. The free energy change (ΔG) accompanying a given process is –85·77 kJ at 25 °C and –83·68 kJ at 35 °C. Calculate the change in enthalpy (ΔH) for the process at 30 °C. 2+3=5

(b) Draw and explain the phase diagram of a binary condensed phase system with the formation of an eutectic solid. Give an example of it. 4+1=5

(c) What do you mean by upper critical and lower critical solution temperatures? Give one example of each such system with appropriate phase diagram. Give an example of a system along with the phase diagram which shows both upper and lower critical temperatures. 1½+1½+2=5

(d) Derive Gibbs' phase rule. How is the number of component C calculated for systems involving ions and having some chemical reactions equilibrium among the constituents. Hence explain why KCl—NaCl—H_2O is a 4-component system whereas KCl—NaBr—H_2O is a 3-component system. 2+1½+1½=5

(Continued)

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

(a) What are the assumptions on which Langmuir isotherm is based? The following data were obtained for the adsorption of CO gas on 3·022 g of charcoal at 0 °C and 1 atm pressure. Verify that the data obey the Langmuir monolayer adsorption isotherm. Also determine the constant k and the volume corresponding to complete surface coverage : 2+3=5

P (torr)	100	200	300	400	500	600
V (cm^3)	10·2	18·6	25·5	31·4	36·9	41·6

(b) Derive BET equation for multilayer adsorption of an adsorbate on an adsorbent. 5

(c) Derive Langmuir adsorption isotherm. Show that for adsorption of a gas with dissociation ($X_2 \rightarrow 2X$) the Langmuir adsorption isotherm becomes

$$\theta = \frac{(kP)^{1/2}}{1+(kP)^{1/2}}$$ 3+2=5

(d) Write the expression for BET adsorption isotherm. Diagrammatically show how increasing value of the constant C changes the shape of BET isotherm. Derive Langmuir adsorption isotherm equation from the BET equation. 1+2+2=5

(Turn Over)

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

(a) For the elementary gaseous reaction $A + B \rightarrow$ Products, obtain an expression for the rate constant of the reaction on the basis of transition state theory. 5

(b) Write the mechanism of unimolecular reaction as proposed by Lindemann. Using this mechanism, deduce an expression for the rate of unimolecular reaction. 2+3=5

(c) Write an expression for the rate constant of a bimolecular gas-phase reaction on the basis of simple collision theory. What do you mean by steric requirement? Although the steric factor is normally found to be several orders of magnitude smaller than 1, for the reaction $K + Br_2 \rightarrow KBr + Br$, the experimental value of steric factor is found to be 4·8. Explain this observation. For the reaction $H_2 + C_2H_4 \rightarrow C_2H_6$, at 628 K, the experimental and theoretical values of the pre-exponential factor are $1{\cdot}24 \times 10^6$ L mol^{-1} s^{-1} and $7{\cdot}33 \times 10^{11}$ L mol^{-1} s^{-1} respectively. What is the value of steric factor for this reaction? 1+1+2+1=5

(Continued)

(d) What do you mean by kinetic salt effect? Derive Brönsted-Bjerrum equation. Predict with reasons the effect of increase in ionic strength of the following reactions : 1+1+1½+1½=5

(i) $H_2O_2 + H^+ + Br^- \rightarrow P$

(ii) $C_{12}H_{22}O_{11} + OH^- \rightarrow P$

7. Answer any *two* from the following : 5×2=10

(a) With the help of a Jablonski diagram, explain all the photophysical processes that an electronically excited molecule may undergo. Give two major differences between fluorescence and phosphorescence. 3+2=5

(b) The kinetics of decomposition of HI is given by the following mechanism :

(i) $HI + h\nu \xrightarrow{k_1} H + I$

(ii) $H + HI \xrightarrow{k_2} H_2 + I$

(iii) $I + I \xrightarrow{k_3} I_2$

Show that the value of quantum yield for the reaction is 2. As the reaction proceeds and iodine accumulates, the following thermal reaction occurs :

$$H + I_2 \xrightarrow{k_4} HI + I$$

(Turn Over)

Because of the occurrence of this thermal reaction, the quantum yield of the reaction decreases from its original value. Explain this observation.

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

(c) What do you mean by quenching of fluorescence? Derive Stern-Volmer equation. What is Stern-Volmer plot? Give an example of a quenching phenomena observed in plants. $1+3+1=5$

(d) Write the mechanism of the $H_2—Cl_2$ photochemical reaction. Prove that the rate of formation of HCl is directly proportional to the intensity of the absorbed radiation. $2+3=5$

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2018

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

(a) Write one reaction of Pd used as dehydrogenating agent.

(b) Define 'ketonic hydrolysis'.

(c) Write name and formula of an antidot compound.

(d) Write the structure of benzilic acid anion.

(e) What is Adam's catalyst?

(f) What is the limited importance of Lossen rearrangement reaction?

(Turn Over)

(g) Write the structure and name of a quinolinium salt.

(h) Fill in the blank of the following statement :

"Pericyclic reactions are _____."

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

(a) Give symmetry properties of π-orbitals of ethylene.

(b) What is Hinsberg's test?

(c) How can CH_3CH_2SH be prepared from thiourea? Write with reactions.

(d) How do you get adipic acid from diethyl malonate?

(e) Give one reaction each to distinguish acetonitrile and methyl isonitrile.

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

(a) How do the following reagents take part in reaction? 1×5=5

(i) Lead tetraacetate in oxidative decarboxylation

(Continued)

(ii) SeO_2 in oxidation of allylic C—H fragments

(iii) $LiAlH_4$ in hydride transfer

(iv) Pyridinium chloromate with 2° alcohol

(v) CrO_3 with aq. H_2SO_4 to cleave $\rangle C=C\langle$

(b) (i) What happens when $C_6H_5CH_2CON_3$ is heated? Give the mechanism of this reaction. 1+2=3

(ii) Identify *A* and *B* in the following reactions (give structure and name of each) : 2

(1) $C_2H_5-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{P_2O_5} A$

(2) $C_2H_5-I + AgCN \xrightarrow[\text{heat}]{\text{Aq. EtOH}} B$

(c) Write the mechanism of the following reaction

$$Ph_2C=N-OH \xrightarrow[2)\ H_2O^{18}]{1)\ PCl_5} PhCO^{18}NHPh$$

and establish that *(i)* original oxygen atom of oxime is lost, *(ii)* carbonium ion is formed as intermediate and *(iii)* it does not proceed by intramolecular exchange. 2+1+1+1=5

(Turn Over)

(d) What is Woodward-Hoffmann rule of an electrocyclic reaction? Explain the rule with orbital symmetry of 1,3-butadiene. 5

(e) What is a keto-quarternary ammonium salt? How does it react with strong base? Write the reaction and its mechanism. 5

4. Answer the following questions :

Either

(a) (i) Discuss relative reactivity of pyridine, thiophene, pyrrole and furan towards Friedel-Crafts acylation reaction reflected in the Lewis acid catalyst. 5

(ii) Write desulphurization reaction of $CH_3—S—CH_3$ takes part by Raney Ni. 1

(iii) "Birch reduction is regioselective." Justify with appropriate example. 3

(iv) How can thiophene be obtained from *n*-butane? 1

Or

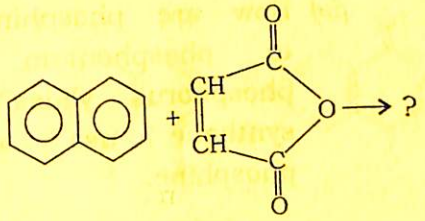
(b) (i) How can nitrobutane be converted to butanal? Give the reaction and write the mechanism. 3

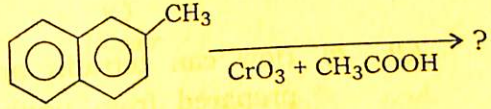
(Continued)

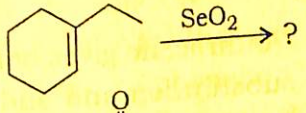
(ii) With the help of a reaction, prove that pyridine ring is present in quinoline. 1

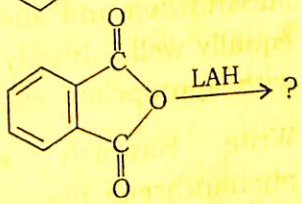
(iii) Prepare sulphone from thioether. 1

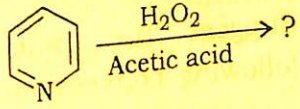
(iv) Give the product in each of the following reactions (give formula and name of each product) : 1×5=5

(1) 

(2) 

(3) 

(4) 

(5) 

Either

(c) (i) How is cyanoacetic ester prepared? 1

(Turn Over)

(ii) How do α-diazoketones undergo rearrangement with elimination of N_2? Give the reaction with mechanism. 1+2=3

(iii) Why does pyrrole give electrophilic substitution reaction with mild reagent? 1

(iv) How are phosphines converted to phosphonium salts and phosphorus ylides? Show one synthetic use of triphenyl-phosphine. 5

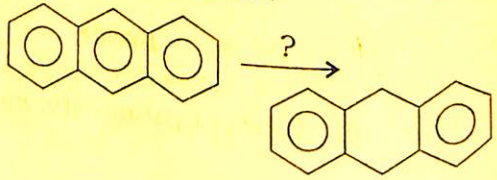
Or

(d) (i) How can tetralin and decalin be prepared from naphthalene? Give reaction. 2

(ii) "Anthracene gives both electrophilic substitution and addition reactions equally well." Justify the statement with appropriate example. 1½+1½=3

(iii) Write Haworth synthesis for phenanthrene preparation. 3

(iv) Suggest the reagents for the following conversions : ½×4=2

(1) 

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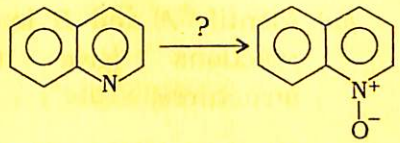
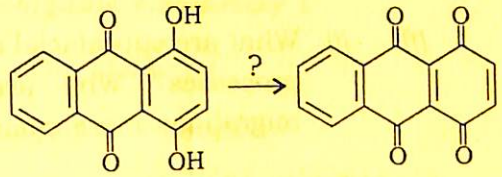
(2) 

(3) $CH_3CH_2CH_2NO_2 \xrightarrow{?} CH_3CH{=}CH_2 + HNO_2$

(4) 

Either

(e) (i) Discuss about kinetically and thermodynamically controlled product of naphthalene, when it undergoes sulphonation reaction with conc. H_2SO_4 at 80 °C and 160 °C. 3

(ii) Show that indole undergoes electrophilic substitution reaction at C-3 regioselectively. 3

(iii) How can 'yellow oil' be prepared from $CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{N}}H$? Give reaction. 2

(Turn Over)

(iv) Identify *A* and *B* in the following reactions (give names and structures) : $1\times2=2$

(1) $C_2H_5ONO_2 + H_2O \xrightarrow{H^+} A$

(2) $CH_3NO_2 + 3Cl_2 + 3NaOH \longrightarrow B$

Or

(f) *(i)* What are suprafacial and antafacial processes? Why are suprafacial migrations more common? $(1+1)+2=4$

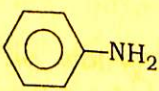
(ii) Prepare pentanone from acetoacetic ester. 2

(iii) Identify *A*, *B*, *C* and *D* in the following reactions (give structure and name of each) : $1\times4=4$

(1) $C_2H_5SH + HgO \longrightarrow A$

(2)  $\xrightarrow{HCN,\ HCl} B$

(3)  $\xrightarrow[Al_2O_3]{NH_3,\ steam} C$

(4) 

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2018

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 option of the following : 1×7=7

(a) The point-group symmetry for boric acid $B(OH)_3$ is

(i) D_3h

(ii) C_3

(iii) C_3h

(iv) C_{3v}

(b) Three-fold axes of symmetry are present in

(i) octahedron

(ii) tetrahedron

(iii) pentagonal bipyramid

(iv) square planar

(c) Which of the following complexes has the shortest C—O bond?

(i) $[V(CO)_6]^-$

(ii) $[Cr(CO)_6]$

(iii) $[Mn(CO)_6]^+$

(iv) $[Ti(CO)_6]^{2-}$

(d) The metalloprotein which is involved in the storage of iron in living system is

(i) ferredoxin

(ii) haemoglobin

(iii) myoglobin

(iv) ferritin

(e) The crystal field stabilization energy for a d^6-ion in a weak octahedral filed is

(i) $0 \cdot 4\Delta_o$

(ii) $0 \cdot 6\Delta_o$

(iii) $0 \cdot 8\Delta_o$

(iv) $1 \cdot 2\Delta_o$

(Continued)

(f) In biological system, the metal ion present in the enzyme carbonic anhydrase is

(i) Co^{2+}

(ii) Zn^{2+}

(iii) Fe^{3+}

(iv) Mn^{2+}

(g) Which of the following is the correct order of ligand strength?

(i) $H_2O < OX < NH_3 < NCS^-$

(ii) $NCS^- < H_2O < OX < NH_3$

(iii) $OX < H_2O < NCS^- < NH_3$

(iv) $NCS^- < NH_3 < H_2O < OX$

2. Write the following very short answer-type questions : $2 \times 4 = 8$

(a) Taking suitable example, show that

$$S_4^2 = C_2$$

(Turn Over)

(b) Formulate neutral 18-electron complexes of chromium which contain only cyclopentadienyl and nitrosyl ligands.

(c) The tetrahedral crystal field splitting Δ_t is roughly half $\left(\frac{4}{9}\Delta_o\right)$ of the octahedral splitting Δ_o. Explain.

(d) Show by means of a diagram, how the pattern of *d*-orbital splitting changes as an octahedral complex undergoes tetragonal distortion and eventually becomes a square planar complex.

3. Write the following short answer-type questions (any *three*) : 5×3=15

(a) What are symmetry elements and symmetry operations? A molecule is assigned with the point group D_4h. Taking appropriate example, show all the symmetry elements present in it.

(b) Discuss different modes of coordination of allyl ligands. How are allyl organometallics prepared? Draw the structure and verify the 18-electron rule for the allyl complex $[Mn(C_3H_5)(CO)_4]$.

(Continued)

(c) What is crystal field stabilization energy ? For each of the following pairs of complexes, identify the one that has the largest CFSE :

(i) $[Cr(H_2O)_6]^{2+}$ or $[Mn(H_2O)_6]^{2+}$

(ii) $[Fe(CN)_6]^{3-}$ or $[Ru(CN)_6]^{3-}$

(d) Write briefly about Na/K pump in biology. Why is saline solution (e.g., ORS) prescribed to patient suffering from diarrhoea?

(e) In the crystal structure of CuF_2, the Cu^{2+} ion is six coordinates with four $F^{(-)}$ at a distance of 1·93 Å and two $F^{(-)}$ at 2·27 Å. Explain the reason for this.

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

(a) (i) Discuss the conditions under which a group of symmetry elements forms a group.

(ii) Find the symmetry elements and respective point groups for the following molecules :

(1) CO_2

(2) $[PtCl_4]^{2-}$ 4+6=10

(3) NH_3

(Turn Over)

(b) Taking the general formula $M^{II}[M^{III}]O_4$, discuss normal and inverse spinels (where M^{II} is the group IIA elements or transition metal in +2 oxidation state and M^{III} is the group IIIA metal or transition metal in +3 oxidation state). With the help of CFSE calculation, verify the spinel nature of Fe_3O_4 and Mn_3O_4. 4+6=10

(c) (i) Discuss the functions of haemoglobin and myoglobin. Explain the terms 'cooperative effect' and 'Bohr effect'.

(ii) Give an account of toxicity arising from dioxygen in the living system. 6+4=10

(d) (i) What do you mean by hydroformylation reaction? Discuss the main features and the mechanism by taking a suitable example.

(ii) Explain the preparation, structure and bonding in Zeise salt. The IR stretching frequency of the C=C bond in metal ethylene complex is found to be 1576 cm^{-1} whereas the corresponding frequency for free C_2H_4 is 1625 cm^{-1}. Explain. 5+5=10

(Continued)

(e) The M—M bond lengths for the complexes $V_2(CO)_4Ph_2P(Bu)_2$ and $MO_2(CH_2Ph)_6$ are 2·92 and 2·17 Å respectively. Write what you know about M—M bonding and give the reason for this trend. Discuss the formation of a quadruple bond between Re atoms in $[ReCl_8]^{2-}$ showing overlap between orbitals involved in M—M bonding. 2+8=10

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