question paper contains 6 printed pages.

Your Roll No. .....

No. of Ques. Paper : 5071

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Ques. Paper Code : 217561

Name of Paper : CHPT-505 : Chemistry – V Chemistry of d Block Elements, Quantum Chemistry and Spectrascopy

Name of Course : B.Sc. Programme Life Science / Physical Science / Applied Life Science (Agrochemical & Pest Management) / Applied Physical Science (Analytical Chemistry / Industrial Chemistry)

Semester : V

Duration : 3 hours

Maximum Marks : 75

(Write your Roll No. on the top immediately on receipt of this question paper.)

Attempt three questions from Section A and three questions from Section B. Sections A and B are to be attempted in separate portions of the same answer sheet. Please indicate the Section you are attempting at the appropriate place and do not intermix the Sections. The questions should be numbered in accordance to the number in the question paper.

Calculators and log tables may be used.

SECTION A

Attempt any three questions.

1. (a) Give brief reasons for any *three* of the following:

(i) Cu(II) compounds are coloured while Cu(I) compounds are colourless.

(ii) Zinc, cadmium and mercury are softer than the transition metals.

(iii) Octahedral complexes of Co(III) may be of inner and outer orbital types but those of Cr(III) are only inner orbital.

(iv) Many transition metals and their compounds act as catalysts.

(v) The atomic radii of zirconium and hafnium are very similar.

(b) Define, using *two* examples, an ambidentate ligand. What specific type of isomerism is displayed in complexes containing such ligands? How does an ambidentate ligand differ from a bidentate ligand? 9,3½)

2. (a) Explain why a d^9 octahedral complex with six identical ligands is not expected to have identical bond lengths. Give the appropriate splitting diagram of such a case where the axial bonds are longer than the equatorial bonds.

(b) Give the IUPAC names of any *three* of the following:

(i) $K_2[OsCl_5N]$

(ii) $[Pt(NH_3)_4]\ [PtCl_3(NH_3)_3]_2$

(iii) $Na[Mn(CO)_5]$

(iv) $[(en)_2Co(NH_2)(OH)Co(en)_2](SO_4)_2$

(c) The magnetic moments of $[Fe(H_2O)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$ are 5.9 BM and 1.8 BM respectively. Explain on basis of

(f) Indicate which of these is an inner orbital complex and which is an outer orbital complex. 5.4

4. Write the formulae of any three of the following:

(i) Barium tetrafluorochromate(III)

(ii) Diammineselver(I) tetracyanoaurate(III)

(iii) Aquatris (triphenylphosphine) palladium(0)

(iv) Bis (ethylenediamine) copper(II) tetrahydroxocuprate(II)

(a) Calculate the CFSE in terms of Δ_t of the Co^{2+} ion placed in a tetrahedral field. Draw the splitting diagram and explain why the splitting pattern differs in tetrahedral and octahedral fields.

(c) Indicate the type of isomerism and the test to distinguish between the following:

(i) $[Co(NH_3)_5]SO_4$ and $[Co(SO_4)(NH_3)_5]$

(ii) $[Cr Cl(H_2O)_5]Cl_2$ and $[CrCl_2(H_2O)_4]Cl.H_2O$ 4½4.4

(d) Explain using CFT why an octahedral complex may be high spin or low spin but a tetrahedral complex is generally high spin.

(b) Indicate the appropriate choice and give brief reasons:

(i) Greater value of Δ_o $[Co(H_2O)_6]^{3+}$ or $[Co(H_2O)_6]^{2+}$

(ii) Good reducing agent Sn(II) or Ce(IV)

(iii) Optically active cis or trans $[CrCl_2(en)_2]^+$

Turn over

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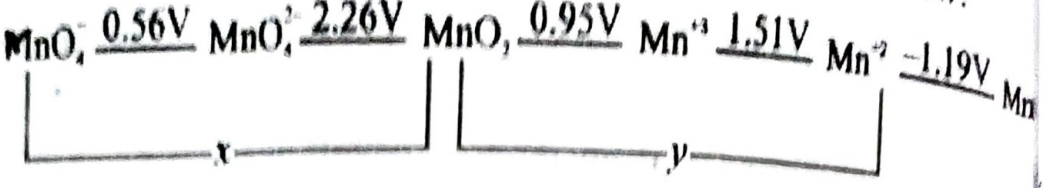
(c) The Latimer diagram of manganese is given below:



Calculate x and y and indicate by showing necessary calculations which species will be disproportionate.

Or

(c) Write short notes on any *two* of the following:

(i) Separation of lanthanides by ion exchange

(ii) Spectrochemical series

(iii) Variable oxidation states of 3*d* elements. 3,4½,5

Section B

Attempt any three questions.

Physical Constants

Planck's constant = 6.626×10^{-34} J s

Velocity of light = 3×10^{8} m s^{-1}

Avogadro's number = 6.023×10^{23} mol^{-1}

Atomic mass unit = 1.661×10^{-27} kg

Mass of electron = 9.109×10^{-31} kg

$\pi = 3.142$

5. (a) Write the mathematical expressions for the position operator x and the linear momentum operator p_x.

(b) Prove that the momentum and position operators do not commute with each other.

(c) Examine which of the following are acceptable wave functions:

(i) $\psi = x^2$ (ii) $\psi = e^x$

(iii) $\psi = e^{-x}$ (iv) $\psi = A \sin x$

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(a) Prove that the wave functions of a particle in one-dimensional box are normalized. 2,2½,4,4

(a) The fundamental vibration frequency of $N^{14}O^{16}$ is observed at 1870 cm^{-1}. Evaluate the zero point energy and the force constant of the molecule.

(b) A molecule AB is undergoing rotational motion under the rigid rotator approximation. What is this approximation? Write the mathematical expression for the Hamiltonian, Schrodinger's equation and the rotational energy E_{rot} associated with this system.

(c) Which of the following molecules can exhibit a pure microwave spectrum: Cl_2, NH_3, CO, C_2H_2? Explain briefly. 4,4½,4

(a) Explain the terms degeneracy and node using the particle in a box problem as an example.

(b) Predict the wave number of the lowest energy absorption band in the conjugated octatetraene molecule given that the average carbon-carbon bond distance is O.141 nm.

(c) For a photochemical reaction, $A \rightarrow B$, 1.08×10^{-5} moles of B are formed on absorption of 5.89 J at 360 nm. Calculate the quantum efficiency of the reaction. Explain why the quantum yield is quite high for certain reactions. 4,4,4½

Turn over

8. (a) Write a short notes on any *three* of the following:

(i) Fluorescence and Phosphorescence

(ii) Beer-Lambert's Law

(iii) Bathochromic and Hypsochromic shift

(iv) Bohr's correspondence principle.

(b) Define eigenfunction and eigenvalue. 3½,3,2