SL No of QP :7024
Unique Paper Code : 2172514701
Name of the Paper : Chemistry of d- and f- block elements, Advanced Organic Spectroscopy and Quantum Chemistry
Name of the Course : B.Sc (Prog.) Physical Sciences
Semester : VII
Duration : 3 hours
Maximum Marks : 90

Instructions for candidates

- *There Write your roll number on the top on receipt of this question paper.*
- *This question paper comprises of three sections, each of 30 marks.*
  ***Section A**- Inorganic, **Section B**- Organic and **Section C** - Physical Chemistry*
- *Attempt each section in a separate answer sheet MARKING as **Section A/B/C** respectively ON the TOP OF THE SHEET for the respective sections.*
- *Attempt six questions in all (**Two** questions from each section).*
- *Scientific Calculator is allowed.*

Section A

(Inorganic Chemistry: Chemistry of d and f block elements)

(***Attempt any two questions***) (***Max Marks:30***)

Q1. **(5, 5, 5).**

(A) (i) Give the electronic configuration of Molybdenum (atomic number 42) and Palladium (atomic number 46), and discuss their anomaly.

(ii) Explain why the aqueous solution of Cr (VI) is highly oxidizing in nature ?

(B) Explain the following :

(i) Compounds of transition metals in higher oxidation states are more covalent in nature than those in lower oxidation states.

(ii) The aqueous solution of Mn^{2+} is faint pink while $KMnO_4$ solution is intense violet in color.

(C) Complex of a certain metal ion has magnetic moment value of 4.9 BM. Another complex of the same metal in the same oxidation state has zero magnetic moment. The central metal ion could be Cr(III), Mn(II), Fe(III) or Co(III) . Justify your answer.

Q2. **(5,5, 5).**

(A) (i)Explain why Ce^{4+} acts as a strong oxidizing agent while Eu^{2+} acts as a strong reducing agent?

(ii)Explain why the absorption spectra of lanthanides show little effect with the change of ligands?

(B) (i) Why aqueous solutions of Yb^{3+} is colourless, while Sm^{2+} is blood red in color?

(ii) Lanthanides have poor tendency to form complexes. Why ?

(C) Although lanthanides are identical in +3 oxidation state, they are effectively separated by ion exchange method. Explain.

Q 3 (A). Attempt **ANY THREE** from the following : **(3 x 5).**

a. Discuss the role of transition elements and their compounds as catalyst. Give two examples.

b. What is lanthanide contraction? Give its causes and consequences.

c. How do *d* block elements differ from *f* block elements?

d. Construct Frost diagram using the following reduction potential data of Chromium in acidic medium. Also, give reason which is the most stable oxidation state of chromium.

$$E^oCr_2O_7^{2-}/Cr^{3+} = 1.33$$

$$E^oCr^{3+}/Cr^{2+} = -0.41$$

$$E^oCr^{2+}/Cr = -0.91$$

Section: B

(Organic Chemistry :Advanced Organic spectroscopy)

(Attempt any two questions) ***(Max Marks:30).***

Q 1. Attempt **ANY FIVE** : **(5x3).**

(i) Differentiate cyclohexanol and Phenol using IR spectroscopy.

(ii) If G is an electronegative atom or functional group, discuss the influence of G on the proton chemical shift of G-C- **H** in ^{1}H NMR(considering G as sp^3,sp^2, sp hybridized carbon too besides mentioning other functional groups).

(iii) Identify C_3H_9N having a single peak in both ^{1}H NMR and ^{13}C NMR and explain.

(iv) How will you differentiate using ^{13}C NMR of 1,3,5-Trimethyl benzene and 1,2,3-Trimethyl benzene? Explain.

(v) Explain genesis of m/z 121 by fragmentation of 2-nitroaniline. Give other fragments too.

(vi) Draw ESR spectrum of methyl radical and explain.

Q2. **(9, 3, 3).**

(A) ^{13}CNMR spectra of 1-chloro-2-propanol gives peaks at δ (ppm) : 20, 51, 67 .

(i) Assign peaks.

(ii) Explain the concept of off-resonance decoupling and draw spectra.

(iii) Draw its DEPT spectrum for each carbon and give this technique's importance. Give full form of DEPT.

(B) Write a short note on 2D NMR COSY spectrum of 2-Nitropropane.

OR

(B) Write a short note on metastable ions taking example of para-nitro anisole (4-methoxy nitrobenzene). Calculate position of metastable peak in MS.

(C) Explain why ^{1}HNMR spectra of N,N-dimethylformamide (DMF) exhibits 3 peaks:

δ 2.8 (s,3H); δ3.1 (s, 3H) and at δ8.1 (s, 1H). .

Q3. **(5, 5, 5).**

(A) A compound shows M^+ peak at 142 (100 %) and M + 2 peak 144 (131 %), M + 4 peak 146 (30 %). It shows two signal in the ^{1}H NMR at 3.2 and 2.9 ppm of equal intensity. Identify the compound with structure and draw the spectra.

(B) Write a short note on McLafferty Rearrangement using example of *n*-Butylphenylketone giving peaks at (m/z): 162, 120, 105 and 85.

(C) Assign the peaks and deduce the structure of a compound with molecular formula C_3H_6O exhibiting following spectral data: [Calculate DBE and then proceed]

UV(EtOH): λmax: 210nm, intensity very low;

IR (KBr) in cm^{-1}: 3300(s), 3050, 1650(m), 995and 900(s), 1050(s)

MS :(m/z) =57(Base peak)

^{13}**C NMR** (CDCl$_3$) in δ (ppm) : 115, 140, 65

Section: C

(Physical Chemistry: Quantum Chemistry)

(*Attempt any two questions*) (*Max Marks:30*)

Q 1. **(5,5,5).**

(A) For the ground state of simple harmonic oscillator (SHO), evaluate, $\langle x \rangle$ & $\langle x^2 \rangle$ and thereby, derive the uncertainty relation for position and momentum.

$$\Delta x \cdot \Delta p_x \geq \frac{h}{4\pi} \left(\text{Given:} \Delta p_x = \frac{h\sqrt{\alpha}}{2\sqrt{2\pi}}\right)$$

(B) Determine the energy required for a transition from the $n_x = n_y = n_z = 1$ to $n_x = n_y = n_z = 2$ state for an argon atom (molar mass = 39.95 g mol^{-1}) in a cubic container with a 1.0 cm side.

(C) What is turn-over rule? Prove that the Eigen values of a Hermitian Operator are orthogonal to each other.

Q 2. **(5,5,5).**

(A) (i). Show that the function $e^{-\beta x^2}$ is an Eigen function of the differential operator, (d/dx).

(ii). Find the value of commutator $[p_x^2, x]$.

(B) Calculate the probability that an electron described by a hydrogen atomic 1s wave function will be found within one Bohr's radius of a nucleus.

(C) (i) What is Born Oppenheimer Approximation?

(ii) Set up a Schrodinger equation for many electron atom & outline the factors which prevent the direct solution of this equation.

Q: 3 **(5,5,5).**

(A) Write the trial wave function for H_2^+ molecule ion Valence Bond theory & discuss its solutions briefly.

(B) Explain time independent first order perturbation theory for non-degenerate states.

(C) Explain, what you understand by Pauli's exclusion principle. Discuss the statement using total acceptable wave functions for a two-electron system.