Ex/M.Sc/CH/2/2071A+B/102/2017

M. Sc. Chemistry Examination, 2017

(2nd Semester)

INORGANIC CHEMISTRY

PAPER - VII

Time: Two hours Full Marks: 50

 $(12\frac{1}{2} \text{ marks for each unit})$

Use a separate answerscript for each unit.

UNIT - 2071A

Answer any one question

- 1. a) Derive ground state electronic configuration and ground term of Eu³⁺. Calculate its magnetic moment and comment on the observed data. $3\frac{1}{2}$
 - b) How do the colour of Ln³⁺ ions in aqueous solution related to their electronic configurations? What are the characteristics of absorption spectra of Ln³⁺ in aqueous media compared with 3d transition metal ions? Explain Hypersensitivity in the electronic transitions of Ln³⁺ complexes.
 - c) "Pro-Americium actinides are transition metal-like and post-Americium elements are lanthanide-like." Explain.

2. a) Difference in radius between La^{3+} and Lu^{3+} is 0.17 $\overset{\circ}{A}$, although they appear in a single position in Periodic Table. Explain.

[Turn over

- b) Account on the luminescence properties of lanthanideacetylacetonato complexes and their mixed ligand complexes. 3
- c) Write notes on organometallic complexes of f-block 3 elements.
- d) Give detail synthesis and applications of Ammonium Ceric (IV) nitrate. 2
- e) Comment on the high temperature superconductivity of lanthanide barium copper oxides. $2\frac{1}{2}$

UNIT - 2071B

Answer any one question

- a) Compute total valence electron count (TEC) and assign $4\frac{1}{2}$ probable structural category to
 - i) $\left[\operatorname{Os}_8(\operatorname{CO})_{22} \right]^{2-}$ ii) $\operatorname{Fe}_5\operatorname{C}(\operatorname{CO})_5$
 - iii) $\left[Os_{10}C(CO)_{24} \right]^{2-}$
 - b) Ethylene gas is passed through OsO₄ suspension in dry benzene. Write down the reaction and draw the structure of the product(s). Establish the plausible mechanism of the reaction. 3

ii)
$$M^{2+}$$
 + Phen $\stackrel{K_1}{\longleftarrow} [M(Phen)]^{2+}$

$$[M(Phen)]^{2+}$$
 + Phen $\stackrel{K_2}{\longleftarrow} [M(Phen)_2]^{2+}$

$$[M(Phen)_2]^{2+}$$
 + Phen $\stackrel{K_3}{\longleftarrow} [M(Phen)_3]^{2+}$

When M = Co, the order of formation constants is $K_1>K_2< K_3$ but for M = Fe this order is $K_1>K_2< K_3$ -explain.

- c) What is $pH_{1/2}$? How is it related to % E? $3\frac{1}{2}$
- d) How would you separate and estimate Cd²⁺ and Hg²⁺ in a mixture by ion exchange chromatography? 3

OR

For
$$Pb_{a}^{2+} + 2HQ_{o} \xrightarrow{K_{ex}} PbQ_{2} + 2H_{a}^{+}$$

K_{ex} for distribution of PbQ₂ between water and CCl₄ is 2.0×10^4 . A 25 ml aliquot of an aqueous solution that is 5.0×10^{-4} M in Pb²⁺ and 0.50 M HClO₄ is extracted with two $10\,\text{ml}$ portions of CCl₄ that are $0.025\,\text{M}$ in HQ. Calculate % of unextracted Pb²⁺ in aqueous solution.

UNIT - 2072A

5. Deduce the equation

 $h\nu=g\beta H$

taking an electron as the paramagnetic sample.

- 6. Comment on the expected esr spectral features of the following:
 - i) $\dot{N}H_2$
 - ii) benzene anion radical

 $1\frac{1}{2}x3$

2

- iii) [VO(acac)₂]
- 7. What is dpph? Why is it used as a standard in esr studies?

2

 What is zero-field splitting? Explain its impact on the esr activity of a paramagnetic sample containing two unpaired electrons.

UNIT - 2072B

- 9. a) What do you mean by Plate Height (H) and Plate Number (N)? How would you experimentally determine N? 3
 - b) i) "Irving William series of stability constants is a consequence of enthalpy effect" explain. 3

c) What happens when CO (Carbon monoxide) is passed through strongly alkaline solution of $\left[\text{Rh} \left(\text{CO} \right)_2 \text{I}_2 \right]^-$ followed by the slow addition of CH₃I at low temperature; the solution is then acidified? Write down the reactions. Give plausible mechanism of the reaction.

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- 4. a) What happens when pyrazine is added to refluxing alcoholic solution of RuCl₃ followed by the addition of excess of ammonia? Comment on the structure, spectra and magnetic property of the complex. What is Robin-Day classification of mixed valence complexes?
 - b) Hydrogen gas is passed through 6N HCl solution of RuCl₃ in inert environment. An inky blue solution is formed. Comment on the colour and the structure of the complex. $2\frac{1}{2}$
 - c) Write a short note on Dihydrogen complexes of Ruthenium.
 - d) How do you synthesise *cis* platin from K₂PtCl₄? How does *cis* platin serve as an anticancer drug? Write notes on toxicity of *cis* platin during medication.