UNIT - 2072b

9. (a) Define the term ***(any two)*** :

(i) Resolution (R_s)

(ii) Capacity factor (k')

(iii) selectivity (α) 3

(b) How would you separate and estimate Cl^- and Br^- in a mixture by anion exchange chromatography ? 3

c) For a solute with D = 25.0, show by calcutation which is more effective : extraction of 10 ml of an aqueous solution with 10 ml organic solvent or extraction with two separate 5.0 ml portions of organic solvent. $3\frac{1}{2}$

d) 20 ml of an aqueous solution of 0.10M butyric acid was shaken with 10 ml ether. After the layers are separated, it was determined by titration that 0.50 mmol butyric acid remains in aqueous layer. Calculate D and E. 3

M. Sc. Chemistry Examination, 2018

(2nd Semester)

Inorganic Chemistry

Paper - VII

Time : Two hours Full Marks : 50

(25 marks for each Unit)

Use a separate answerscript for Unit 2071 and Unit 2072

UNIT - 2071a

Answer ***any one*** question of the following :

1. a) Sm^{3+} is yellow while Sm^{2+} is red in acidified solution. Using Russell-Saunders Ground multiplets of Sm^{3+} and Sm^{2+} (Z=62) explain the difference. Calculate μ_s and μ_{L+s} ; compare with μ_{obs} , 1.4–1.7 BM. Explain line like spectrum of Sm^{3+} complexes. $3+3+1\frac{1}{2}$

b) Write short account on ***(any two)*** : $2\frac{1}{2}\times 2$

i) Lanthanide NMR-Shift Reagents,

ii) Luminescent properties of Eu(III)-β diketonato complexes,

iii) Organometallic chemistry of Lanthanides,

2. a) $La_xM_yCuO_4$(x = 1.2 to 1.8; M = Ba, Sr; y = 0.1 to 0.3) shows superconductivity. Explain the role of individual element. 3

b) "Gd(III)-N, O chelators are useful magnetic imaging complexes." Explain the role of the metal ion. 3

c) Account on the hazardous aspects of actinides. 2

d) "Early actinides are chemically closer to transition metals, while late actinides are lanthanide like." Support or contradict with reasoning. $2\frac{1}{2}$

e) Which Actinides were the first to be discovered ? Which Actinides were discovered in nature ? 1+1

UNIT - 2072a

5. Comment on the expected esr spectral features of the following : $1\frac{1}{2} \times 3$

   a) naphthyl radical

   b) Pyrazine anion radical

   c) $[VO(N–O)_2]$, where N–O depicts a mono-anionic N,O-donor chelating ligand.

6. What is TEMPO ? Describe its esr spectum and application. 1+2

7. A d^2 metal ion may or may not show esr spectrum, but a d^3 metal ion is always found to be esr-active. Explain. 3

8. What kind of X-ray is required for diffraction studies ? Cite one specific example. 1+1

UNIT - 2071b

Answer ***any one*** of the following questions :

3. a) Compute total valence electron count (TEC) and assign probable structural category to which $Os_5C(CO)_5$ and $Ir_4(CO)_{12}$ belong. 3

   b) OsO_4 is treated with sodium hydroxide solution in ethanol medium followed by the addition of pyridine. Write reaction and draw the structure of the product(s). $2\frac{1}{2}$

   c) What happens when liquid Br_2 is added at cold condition to the solution of $K_2[Pt(CN)_4]$ in dry THF ? Comment on the structure and properities of the compound so formed. $2\frac{1}{2}$

   d) Using trans effect, synthesise *cis*-$Pt(NH_3)_2Cl_2$ from $Pt(NH_3)_4]Cl_2$. Why cisplatin is serving as anticancer drug ? 2

   e) To an alcoholic solution of $RuCl_3$ under reflux pyrazine is added followed by the addition of excess ammonia. Draw the structure of the major complex ; comment on the spectrum and magnetic property of the complex. Classify the complex according to Robiss Day classification. $2\frac{1}{2}$

4. a) $RhCl_3$ is refluxed in 2-methoxy ethanol solution with large excess of PPh_3. A crystalline product (A) is isolated. The complex A is embedded on alumina surface and the

mixture of dry H_2 and l-propene is passed over it. What is the product ? Refer plausible mechanistic scheme of the reaction. 3

b) Carbon monoxide (CO) is passed separately to (i) a solution of $PtCl_2$ in thionyl chloride and the mixture is refluxed; (ii) $Na_2[PtCl_6]$ solution in acetonitrile solution and refluxed. Evaluate the chemical reachions, structure of the complexes and their importance. $2\frac{1}{2}$

c) An ethanol solution of $Na_2[PdCl_4]$ is reacted with azobenzene at room temperature. A dark shining crystalline product (D) is isolated. D is then suspended in THF and dry Cl_2 gas is passed. Write down the reactions and draw the structures. $2\frac{1}{2}$

d) N, N-Dimethylformamide solution of $IrCl_3$ is refluxed in presence of excess of PPh_3. Infrared spectrum of the isolated product (E) shows intense stretch at 1967 cm^{-1}. Characterise the product E. What will happen to this vibrational band upon reaction of E with MeI. Explain your anser. $2\frac{1}{2}$

e) Write a short note on Ruthenium Acticancer Drug. 2