

UNIT - 2072b

9. a) Write a short note on Size-exclusion Chromatography (SEC). 3
- b) Define the term (any two): $1\frac{1}{2} \times 2$
- i) Retardation Factor (R_f) in case of paper chromatography.
- ii) Distribution Coefficient in case of solvent extraction
- iii) Total ion exchange capacity of a cation exchange resin
- c) Calculate the weight of Fe(III) left unextracted from 100 ml of a solution having 400 mg of Fe^{3+} ion in 6M HCl after two extractions with 25ml of diethyl ether each. [Given : $D=150$]. 3
- d) Citing suitable example explain Batch extraction. 2
- e) Distinguish between absolute stability constant and apparent stability constant. $1\frac{1}{2}$

M. SC. CHEMISTRY EXAMINATION, 2019

(2nd Semester)

INORGANIC CHEMISTRY**PAPER - VII**

Time : Two hours

Full Marks : 50

(25 marks for each Unit)

Use one answerscript for Unit 2071a and Unit 2071b and one answerscript for units 2072a and 2072b.

Unit 2071aAnswer *any one* question of the following :

1. a) Calculate Russell-Saunders Ground Term of Nd^{3+} ($Z=60$) and also derive all J states and arrange qualitatively according to their energy. Explain the f-f transition spectral features. 4
- b) Calculate μ_s (spin only) μ_j and of Eu^{3+} . The observed magnetic moment of Eu^{3+} complexes lies between 3.3 and 3.5 BM. Compare the results and give explanation. $3\frac{1}{2}$
- c) Write short account on (any two): $2\frac{1}{2} \times 2$
- i) Use of Lanthanum compounds as NMR Shift reagents.
- ii) Luminescent properties of Lanthanum complexes,
- iii) Gd (III) based magnetic imaging complexes

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2. a) Radius of La^{3+} (1.17 \AA) is larger by 0.16 \AA than Yb^{3+} (1.01 \AA). Why it happens? 2
- b) $\text{La}_x\text{M}_y\text{CuO}_4$ ($x=1.2$ to 1.8 ; $M=\text{Ba, Sr}$; $y=0.1$ to 0.3) compounds show superconductivity. Explain the role of individual element. 3
- c) Give outline of extraction and isolation of fuel active U from Pitchblende. 3
- d) Define hypersensitive transitions. Compare the spectra correspond to hypersensitivity and normal f-f transitions. $2\frac{1}{2}$
- e) Write a note on (any one) 2
- (i) Line like absorption spectra of lanthanide complexes
- (ii) Pre-Americium show variable valence states while post-Americium elements are lanthanide like.

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- e) Write a short note on (any two) $1\frac{1}{2} \times 2$
- (i) Water -Gas Shift reaction
- (ii) Use of Rh-CO complex in industrial acetic acid synthesis.
- (iii) Application of Pd-compounds in C-C coupling reaction.

UNIT - 2072a

5. What is dpph? Why is it used as a standard in esr studies? 2
6. Comment on the expected esr spectral features of the following: $1\frac{1}{2} \times 3$
- i) $\dot{\text{C}}\text{H}_3$
- ii) naphthalene anion radical
- iii) $[\text{Cu}^{11}(\text{N-O})_2]$, where N-O represents a mono-anionic bidentate chelating ligand.
7. Octahedral Ni^{2+} complexes, though paramagnetic, usually do not show esr signal on a X-band ESR spectrometer, but often show esr spectra on a Q-band machine. Explain. 3
8. What is electron diffraction? Mention its application. Find out the wavelength of electron-wave generated in a 200 kV electron microscope. 3

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intense IR stretching at 1865 cm^{-1} . Identify the structure of the complex, B. Mention synthetic application of B. $2\frac{1}{2}$

- e) Write a short note on (any two) $1\frac{1}{2}\times 2$
- i) High valent Os=O complexes; (ii) Creutz-Taube complex; (iii) Hydroformylation reaction
4. a) Synthesize Wilkinson catalyst and give mechanism, (*any one*) of its catalytic reaction. $2\frac{1}{2}$
- b) Using PSEPT compute the structures (*any two*) of $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$, $[\text{Rh}_6\text{C}(\text{CO})_{17}]$, $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$. 2
- c) To an ethanol solution of IrCl_3 a stream of CO is passed followed by the addition of PPh_3 (in excess) and refluxed. A shining compound, C, is crystallized. The compound, B is suspended in ethanol and excess of CO is passed followed by the addition of NaBH_4 . A new compound D is formed. Write the reactions, draw the structures of C and D. Explain the stability of D. $2\frac{1}{2}$
- d) RuO_4 is added in strongly alkaline medium ($\text{pH} > 10$) followed by the neutralization by adding HCl (Conc). The solution colour gradually changes from purple, brown to yellow. To this yellow solution H_2 (g) stream is passed and an inky blue solution of compound E is formed. Upon addition of Sodium acetate and acetic acid mixture a green salt, F, is crystallized. Draw the structures of E and F. Explain the origin of colour. $2\frac{1}{2}$

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UNIT - 2071b

Answer *any one* question :

3. a) Synthesize cisplatin from $\text{K}_2[\text{PtCl}_4]$. Why does cisplatin serve as anticancer drug? Give plausible mechanism of activity. Explain its toxicity in human health. $2\frac{1}{2}$
- b) Complete the following reactions (any two): 2
- i) $[(\text{C}_6\text{H}_5)_2\text{Pt}(\text{PPh}_3)_2] \xrightarrow{\Delta} ?$
- ii) $\text{K}[\text{Rh}(\text{CO})_2\text{I}_2] + \text{CH}_3\text{I} + \text{CO} + \text{H}_2\text{O} \rightarrow ?$
- iii) $(\text{C}_6\text{H}_5)\text{B}(\text{OH})_2 + \text{p-Me-C}_6\text{H}_4\text{-Br} \xrightarrow{?} \text{p-Me-C}_6\text{H}_4\text{-C}_6\text{H}_5$
- iv) $\text{Na}_2[\text{PdCl}_4] + \text{C}_6\text{H}_5\text{-N=N-C}_6\text{H}_5 \xrightarrow{\text{EtOH, Stir}} ?$
- c) To an aqueous solution of RuCl_3 ammonia is added intermittently and left in air for several days. An intense red solution is obtained. A solution of $\text{Ba}(\text{NO}_3)_2$ is added to isolate red crystalline salt. Draw the structure of red salt, A, and explain the origin of the colour. What will happen if you add few drops of Ceric ammonium sulfate to this red solution? $2\frac{1}{2}$
- d) Solid NaNO_2 is added to RuCl_3 in HCl (Conc) solution followed by the neutralization with liq, NH_3 A dark coloured complex, B, is separated and shows high

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