3 SEM TDC CHM M 1 (N/O)

2019

(November)

CHEMISTRY

(Major)

Course: 301

(Inorganic Chemistry-I)

(New Course)

Full Marks: 48
Pass Marks: 14

Time: 2 hours

The figures in the margin indicate full marks for the questions

1. Select the correct answer:

1×5=5

- (a) The spectroscopic free ion ground term for d^2 configuration is
 - (i) 1S
 - (ii) ³ P
 - (iii) 2D
 - (iv) 3F

- (b) The complex ion which obeys the EAN rule is
 - (i) [Fe(CN)₆]³⁻
 - (ii) [Cr(NH₃)₆]³⁺
 - (iii) [Fe(CN)6]4-
 - (iv) [Pt(NH3)4]2+
- (c) The CFSE for the d^3 -ion in strong crystal field is
 - (i) 4 Dq
 - (ii) 8 Dq
 - (iii) 12 Dq
 - (iv) 16 Dq
- (d) Which of the following is not a member of actinoids?
 - (i) Nobelium
 - (ii) Uranium
 - (iii) Californium
 - (iv) Europium

- (e) Which of the following is least labile?
 - (i) [Ba(H₂O)₆]²⁺
 - (ii) [Mg(H2O)6]2+
 - (iii) [Sr(H2O)6]2+
 - (iv) [Ca(H2O)6]2+
- 2. Answer any five of the following questions:

3×5=15

- (a) Give IUPAC names of the following: 1×3=3
 - (i) [Co(NH₃)₆] [CuCl₄]

(ii)
$$\left[(NH_3)_4 Cr < \frac{NH_2}{NO_2} > Fe(H_2O)_4 \right] Cl_4$$

- (iii) [Cr(PPh3)(Co)5]
- (b) Write down the formulae of the following complexes: 1×3=3
 - (i) Tetrahydroxonickelate(II)
 - (ii) Ammonium tetrathiocyanato-

5 chromate(II)

- (iii) μ-amidodecamminedicobalt (III)
- (c) Write down the conditions required to determine the ground term of a configuration. Find out the free ion ground term for d^7 configuration. 2+1=3

- (d) What is EAN? Find the EAN for $[Co_4(Co)_{12}]$. Write down the limitations of EAN rule (any two). 1+1+1=3
- (e) What is Irving-William series? Discuss briefly. 1+2=3
- (f) Give reasons of the following: 1½×2=3

 (i) Ti⁴⁺ ion is more stable than Ti³⁺
 ion.
 - (ii) D-block elements show variable oxidation state.

3. Answer the following questions:

- (a) What is CFSE in octahedral complexes?

 Calculate CFSE for the following: 1+1+1=3

 (i) [FeF₆]³⁻ ion

 (ii) [Fe(CN)₆]³⁻ ion
- (b) Explain the Orgel diagram of a metal complex with d^9 configuration.
- (c) Draw the splitting and energy level diagrams of metal d-orbitals in octahedral, tetragonal and square planar complexes. Why is crystal field splitting Δ_{sp} greater than Δ_0 ? 3+1=4

3

| 4. | (a) | Explain the mechanism of the reaction in terms of S_N 1-CB mechanism: | 5 |
|----|-----|---|---|
| | [Co | $(NH_3)_5Cl]^{2+} + OH^{\Theta} \rightarrow [Co(NH_3)_5OH]^{2+} + Cl^{\Theta}$ |) |
| | (b) | Give an account of 'trans-effect'. | 2 |
| 5. | (a) | Discuss the stereoisomerism exhibited by the complex [Cr(gly) ₃]. | 2 |
| | (b) | Define macrocylic ligands. Give the meaning of the numbers 18 and 6 in the complex [Na(18-crown-6)] ⁺ . | 2 |
| | (c) | A solution containing $2.674 \mathrm{g}$ of $\mathrm{CoCl}_3 \cdot 6 \mathrm{NH}_3$ was passed through a cation exchanger. The solution obtained gave $4.305 \mathrm{g}$ of AgCl precipitate with AgNO ₃ solution. Determine the formula of the complex. (Given, molar masses of $\mathrm{CoCl}_3 \cdot 6 \mathrm{NH}_3 = 267.4$ | |
| | | and AgCl = 143 · 45) | 4 |
| 6. | Ans | wer any <i>one</i> question : | 3 |
| | (a) | Explain the fact that the most common oxidation state of the three elements La (57), Gd (64) and Ln (71) is +3. | |
| | (b) | What are the consequences of | |

(Old Course)

Full Marks: 48
Pass Marks: 19

Time: 3 hours

The figures in the margin indicate full marks for the questions

1. Select the correct answer:

 $1 \times 5 = 5$

- (a) Which of the following complexes obeys EAN rule?
 - (i) [Fe(CN)₆]³⁻
 - (ii) [Co(CN)₆]⁴⁻
 - (iii) [Fe(CN)6]4-
 - (iv) [Ni(NH3)6]2+
- (b) The high-spin configuration of Cr(II) ion is octahedral. Crystal field is
 - (i) $t_{2g}^4 e_g^0$
 - (ii) $t_{2g}^{3}e_{g}^{1}$
 - (iii) $t_{2g}^3 e_g^2$
 - (iv) $t_{2g}^4 e_g^1$

| (c) | The spectroscopic free ion ground term |
|-----|--|
| | for d ¹ configuration is |

- (i) ⁵D
 - (ii) 4 F
- (iii) 2D
- (iv) 3 F

(d) Which of the following has the minimum trans-effect?

- (i) NO2
- (ii) C2H4
- (iii) Br
- (iv) NH3

(e) Common oxidation state of lanthanides is

- (i) +2
- (ii) +3
- (iii) +4
- (iv) None of the above

2. Answer any five of the following questions:

 $2 \times 5 = 10$

- (a) What is ambidentate ligand? Give an example.
- (b) What are the L and S values of ³F, ¹D, ³P and ²G?
- (c) What are inert and labile complexes?
- (d) Draw the structures of all possible stereo-isomers of [Co(en)₂Cl₂]⁺.
- (e) Give the electronic configurations of europium and neodymium.
- (f) What do you mean by diamagnetism and paramagnetism?
- (g) Write down the chemical formulae of the following compounds:
 - (i) Chloronitro bis(ethylenediamine) cobalt(III) ion
 - (ii) Decaamine-μ-hydroxodichromium(III) bromide

3. Answer any three of the following questions:

 $3 \times 3 = 9$

(a) Write the IUPAC names of the following compounds:

(i) [Pt(NH₃)₄][PtCl₄]

(ii) LiAlH4

(iii) [(NH₃)₅Co—NH₂—Co(NH₃)₅]Cl₅

- (b) What is chelation? Why are chelate complexes highly stable?
- (c) On the basis of crystal field theory, explain that [CoF₆]³⁻ is paramagnetic but [Co(NH₃)₆]³⁺ is diamagnetic.
- (d) Draw and explain Orgel diagram of a metal complex with d^1 configuration.
- (e) On the basis of valence bond theory, discuss the structures of [Ni(CO)₄] and [Ni(CN)₄]²⁻.

4. Answer any three of the following questions:

4×3=12

(a) Discuss briefly the splitting and energy level diagrams of metal d-orbitals in octahedral and tetrahedral complexes. Why is crystal field splitting Δ_t less than Δ_o ? 3+1=4

- (b) Calculate the number of unpaired electrons (n), spin only magnetic moments (μ_s) and CFSE in terms of Δ_o for the complex $[Cr(H_2O)_6]^{2+}$. $1+(1\frac{1}{2}\times 2)=4$
- (c) Write short notes on the following: 2×2=4(i) Colour of complexes in the light of crystal field theory
 - (ii) Nephelauxetic effect
- (d) What is spectro-chemical series? Write the spectro-chemical series of the common ligands. Calculate CFSE for an octahedral complex with d⁷ metal ion under strong and weak field conditions.
- 5. Answer any *three* of the following questions: $3\times 3=9$
 - (a) Explain the associative and dissociative mechanisms in ligand substitution reaction.
 - (b) Discuss the kinetics of acid hydrolysis of Co(III) compounds with suitable example.
 - (c) What is trans-effect? Starting from [PtCl₄]²⁻ and other ligands, outline the synthesis of cis- and trans-[PtCl₂(NH₃)(NO₂)]. 1+2=3

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(d) Discuss inert and labile complexes with examples. Which one of the following is more labile? 1½×2=3

 $[Mg(H_2O)_6]^{2+}$ and $[Al(H_2O)_6]^{3+}$

6. Answer either (a) or (b):

3

- (a) Give three points of differences between lanthanides and actinides.
- (b) What do you mean by lanthanide contraction? What are the causes of lanthanide contraction?

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