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3 SEM TDC CHM M 1

2015

(November)

CHEMISTRY

(Major)

Course : 301

(Inorganic Chemistry—I)

Full Marks : 48

Pass Marks : 19 (Backlog) / 14 (2014 onwards)

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^{10} configuration is

(i) 1S

(ii) 2S

(iii) 2D

(iv) 3F

(b) The complex which does not obey EAN rule is

- (i) $[\text{Cu}(\text{CN})_4]^{2-}$
- (ii) $[\text{Fe}(\text{CN})_6]^{4-}$
- (iii) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ +
- (iv) $[\text{Ag}(\text{NH}_3)_4]^+$

(c) Which of the following methods can be used to differentiate between *cis*- and *trans*-isomer?

- (i) Dipole moment measurement
- (ii) Infrared spectroscopic technique
- (iii) Optical activity measurement
- (iv) All of the above

(d) Which of the following reacts most rapidly?

- (i) $[\text{Co}(\text{CN})_6]^{3-}$
- (ii) $[\text{Ni}(\text{CN})_4]^{2-}$
- (iii) $[\text{Cr}(\text{CN})_6]^{3-}$
- (iv) $[\text{Mn}(\text{CN})_6]^{4-}$

(e) Which of the following elements has electronic configuration $[\text{Xe}] 4f^6 5d^1 6s^2$?

- (i) Americium
- (ii) Californium
- (iii) Europium
- (iv) Fermium

2. Answer the following questions : 2×5=10

(a) Write the formula of the following compounds :

- (i) *Tris*-(trimethyl phosphine) copper(I) perchlorate
- (ii) Decammine- μ -amido dicobalt(II) ion

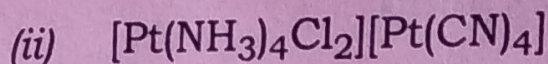
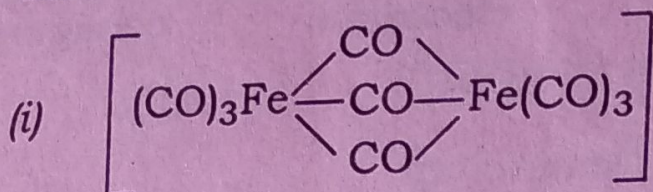
(b) Define effective atomic number (EAN). Calculate EAN for the central atom in the complex $[\text{Co}(\text{NH}_3)_4 \text{Cl}_2] \text{Br}$.

(c) What do you mean by diamagnetism and paramagnetism?

(d) Explain inert and labile complexes with example.

(e) Discuss the causes of lanthanide contraction.

3. (a) Give the IUPAC names of the following : 2



(b) Define macrocyclic ligand. Give the meaning of the numbers 18 and 6 in the complex $[\text{Na} (18\text{-crown-}6)]^+$. 2

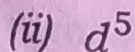
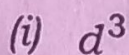
(c) How will you distinguish between $[\text{FeBr}(\text{NH}_3)_5]\text{SO}_4$ and $[\text{FeSO}_4(\text{NH}_3)_5]\text{Br}$? 1

4. Answer any four questions :

4×4=16

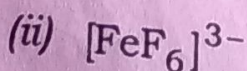
(a) What do you mean by the term in spectroscopy? Write the spectroscopic free ion ground terms for the following :

$$1 + (1\frac{1}{2} \times 2) = 4$$



(b) On the basis of valence bond theory, explain the shape and magnetic behaviour of the following :

$$2 + 2 = 4$$



(c) Using crystal field theory and spin only formula, calculate the magnetic moments of $[\text{Co}(\text{NH}_3)_6]^{2+}$ and $[\text{MnCl}_4]^{2-}$. 2+2=4

(d) Discuss the splitting of d -orbitals in an octahedral field. 4

(e) For the complex ions $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Fe}(\text{CN})_6]^{4-}$, the electron pairing energies (P) are found to be $25,500 \text{ cm}^{-1}$ and $17,600 \text{ cm}^{-1}$ respectively. The magnitudes of Δ_0 are 7800 cm^{-1} and $33,000 \text{ cm}^{-1}$ respectively. Calculate crystal field stabilization energy for the complex ions. 2+2=4

(f) (i) Write a note on spectrochemical series. 2

(ii) Tetrahedral complexes are generally high spin. Explain. 2

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

(a) (i) Explain associative and dissociative mechanisms in ligand substitution reactions in octahedral complexes. 4

(ii) What do you mean by acid hydrolysis? Discuss the effect of the following factors on the rate of acid hydrolysis of a hexacoordinated complex : 1+4=5

- (1) Charge on the complex
- (2) Strength of metal-leaving group

(b) (i) What is base hydrolysis? Discuss the mechanism of base hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$. 1+4=5

(ii) Hydrolysis of $[\text{Fe}(\text{CN})_5(\text{NH}_3)]^{3-}$ does not proceed through $\text{S}_{\text{N}}1(\text{cB})$ mechanism. Why? 1

(iii) What is *trans*-effect? Starting from $[\text{PtCl}_4]^{2-}$, outline the preparation of *cis*- and *trans*- $[\text{Pt}(\text{NH}_3)(\text{C}_2\text{H}_4)\text{Cl}_2]$. 1+2=3

6. Answer any one question :

(a) Explain the fact that the most common oxidation state of the three elements La (57), Gd (64) and Lu (71) is +3. 3

(b) What are the consequences of lanthanide contraction? 3
