

GG552

B. Sc. (Hons.)-M. Sc. Dual Degree EXAMINATION, 2021

(Seventh Semester)

(B Scheme) (Main Only)

CHEMISTRY

DCH403

Inorganic Chemistry-VII

Time : 2½ Hours]

[Maximum Marks : 75

Before answering the question-paper candidates should ensure that they have been supplied to correct and complete question-paper. No complaint, in this regard, will be entertained after the examination.

Note : Attempt *Four* questions in all. All questions carry equal marks.

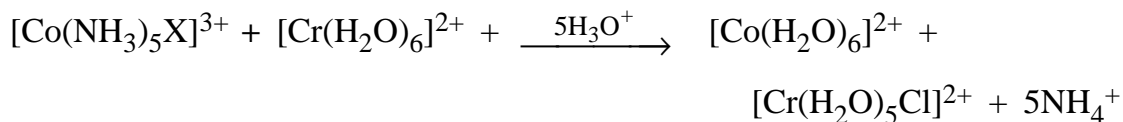
1. (a) What is the magnetic moment of $[\text{RhF}_6]^{3-}$ in B.M. ?
- (b) Draw the plot of χT versus T (where χ is molar magnetic susceptibility and T is the temperature) for a paramagnetic complex, which strictly follows Curie equation.
- (c) Which two among $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{FeF}_6]^{3-}$, $[\text{Cu}(\text{bpy})_2]^{2+}$ and $[\text{Mn}(\text{acac})_3]$ (acac = acetyl acetonate anion) show the same spin-only magnetic moment ?
- (d) Describe Kurnakov test.
- (e) Give the reason for intense blue colour of Prussian blue.
- (f) The complex $[\text{TiCl}_6]^{3-}$ absorbs at 13000 cm^{-1} . What is the value of Δ_0 ?
- (g) What product is formed when oxalic acid reacts with $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$?
- (h) Predict the number of unpaired electron in $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{4-}$. Calculate CFSE for the same.

- (i) Among $(\text{CH}_3)_3\text{P}$, NO^+ , CN^- and I_3^- ligands, which one is not a π -acceptor ligand ?
- (j) In the trigonal bipyramidal crystal field, which d -orbital exhibit the highest energy ?
2. (a) What is the effect of π -donor and π -acceptor ligands on Δ_0 ? Explain on the basis of ligand field theory.
- (b) Pt (II) makes square planar complexes almost exclusively. Explain with the help of crystal field theory.
- (c) Draw the crystal field splitting diagram for $[\text{CoCl}_4]^{2-}$ and calculate CFSE.
3. (a) Tetrahedral complexes are high spin. Explain with examples.
- (b) Define Jahn-Teller theorem. Giving reason, explain in which case this effect would be observed.
- $$t_{2g}^3 e_g^1 \text{ or } t_{2g}^6 e_g^2$$
- (c) Which complex in each of the following pairs will have greater crystal field splitting and why ?
- (i) $[\text{Co}(\text{en})_3]^{3+}$ or $[\text{Rh}(\text{en})_3]^{3+}$
- (ii) $[\text{Cr}(\text{CN})_6]^{3-}$ or $[\text{Cr}(\text{NH}_3)_6]^{3+}$
- (iii) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ or $[\text{Fe}(\text{CN})_6]^{3-}$
- (iv) $[\text{Co}(\text{NO}_2)_6]^{3-}$ or $[\text{Co}(\text{ONO})_6]^{3-}$
4. (a) The three absorption bands for $[\text{CrF}_6]^{3-}$ are observed in an electronic spectrum at 14900 cm^{-1} , 22700 cm^{-1} and 34400 cm^{-1} . Determine the values of B' and Δ_0 .

- (b) Characterize the origin of electronic transitions in the following and indicate the intensity of the complexes :
- MnO_4^- , $[\text{MnBr}_4]^{2-}$, $[\text{CoCl}_4]^{2-}$, $[\text{Fe}(\text{bipy})_3]^{2+}$, $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, $\text{Cr}_2\text{O}_7^{2-}$, $\text{Ni}(\text{CO})_4$ and $\text{KFe}[\text{Fe}(\text{CN})_6]$.
5. (a) The single absorption bands for $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Ti}(\text{NCS})_6]$ occur in their absorption spectra at 470 nm and 544 nm respectively (i) Calculate crystal field splitting energies for these complex ions in kJ mol^{-1} , (ii) Also predict the colours of these complex ions.
- (b) High spin octahedral complexes of Mn^{2+} ion are colourless. Explain.
6. (a) Using crystal field theory, explain the structure and magnetic properties of $[\text{NiCl}_4]^{2-}$, $[\text{NiCN}_4]^{2-}$ and $[\text{Ni}(\text{CO})_4]$.
- (b) Using the crystal field theory, calculate the magnetic moments in terms of B.M. of the following complexes :
- $[\text{CoF}_6]^{3-}$
 - $[\text{MnBr}_4]^{2-}$
 - $[\text{Co}(\text{NH}_3)_6]^{2+}$
 - $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
 - $[\text{Ni}(\text{CO})_4]$
 - $[\text{Ru}(\text{NH}_3)_6]^{3+}$
 - $[\text{RhF}_6]^{3-}$
7. (a) The magnetic moment of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ varies with temperature. The magnetic moments at 200 K and 50 K are 4.9 B.M. and 0 B.M. respectively. Write the *d*-electron configurations of Fe at both temperatures and give reason for the observed change in the magnetic moment. (phen = 1, 10 pheanthroline)

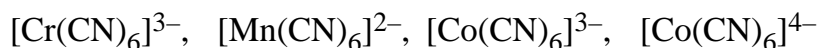
- (b) What change in magnetic properties (if any) can be expected when NO_2^- ligands in $[\text{Co}(\text{NO}_2)_6]^{3-}$ are replaced by Cl^- ligands ?

8. (a) For the following general reaction : 8

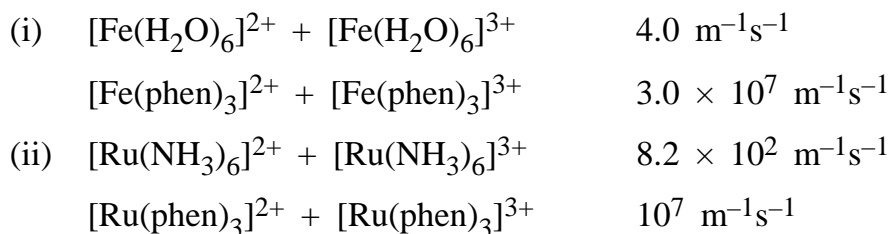


Rate constant increases in the order $\text{X}^- = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-$. Explain it and also give the mechanism of above reaction.

- (b) Arrange the following complexes in the increasing order of inertness :



9. (a) Explain the rate enhancement for the following reaction pairs :



- (b) What is trans effect ? What product is obtained when $[\text{Pt}(\text{Cl})_4]^{2-}$ is treated with :

- (i) NH_3 followed by R_3P
 (ii) R_3P followed by NH_3 ?