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# 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 $[RhF_6]^{3-}$ in B.M. ?

(b) Draw the plot of $\chi$T *versus* T (where $\chi$ is molar magnetic susceptibility and T is the temperature) for a paramagnetic complex, which strictly follows Curie equation.

(c) Which two among $[Fe(CN)_6]^{3-}$, $[FeF_6]^{3-}$, $[Cu(bpy)_2]^{2+}$ and $[Mn(acac)_3]$ (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 $[TiCl_6]^{3-}$ absorbs at 13000 $cm^{-1}$. What is the value of $\Delta_0$ ?

(g) What product is formed when oxalic acid reacts with $[Pt(NH_3)_2Cl_2]$ ?

(h) Predict the number of unpaired electron in $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$. Calculate CFSE for the same.

(i) Among $(CH_3)_3P$, $NO^+$, $CN^-$ and $I_3^-$ ligands, which one is not a $\pi$-acceptor ligand ?

(j) In the trigonal bipyramidal crystal field, which *d*-orbital exhibit the highest energy ?

**2.** (a) What is the effect of $\pi$-donor and $\pi$-acceptor ligands on $\Delta_0$ ? 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 $[CoCl_4]^{2-}$ 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) $[Co(en)_3]^{3+}$ or $[Rh(en)_3]^{3+}$

(ii) $[Cr(CN)_6]^{3-}$ or $[Cr(NH_3)_6]^{3+}$

(iii) $[Fe(H_2O)_6]^{3+}$ or $[Fe(CN)_6]^{3-}$

(iv) $[Co(NO_2)_6]^{3-}$ or $[Co(ONO)_6]^{3-}$

**4.** (a) The three absorption bands for $[CrF_6]^{3-}$ are observed in an electronic spectrum at 14900 $cm^{-1}$, 22700 $cm^{-1}$ and 34400 $cm^{-1}$. Determine the values of B' and $\Delta_0$.

(b) Characterize the origin of electronic transitions in the following and indicate the intensity of the complexes :

$MnO_4^-$, $[MnBr_4]^{2-}$, $[CoCl_4]^{2-}$, $[Fe(bipy)_3]^{2+}$, $[Mn(H_2O)_6]^{2+}$, $Cr_2O_7^{2-}$, $Ni(CO)_4$ and $KFe[Fe(CN)_6]$.

**5.** (a) The single absorption bands for $[Ti(H_2O)_6]^{3+}$ and $[Ti(NCS)_6]$ 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 $[NiCl_4]^{2-}$, $[NiCN_4]^{2-}$ and $[Ni(CO)_4]$.

(b) Using the crystal field theory, calculate the magnetic moments in terms of B.M. of the following complexes :

(i) $[CoF_6]^{3-}$

(ii) $[MnBr_4]^{2-}$

(iii) $[Co(NH_3)_6]^{2+}$

(iv) $[Co(H_2O)_6]^{3+}$

(v) $[Ni(CO)_4]$

(vi) $[Ru(NH_3)_6]^{3+}$

(vii) $[RhF_6]^{3-}$

**7.** (a) The magnetic moment of $[Fe(phen)_2(NCS)_2]$ 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 $[Co(NO_2)_6]^{3-}$ are replaced by $Cl^-$ ligands ?

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

$$[Co(NH_3)_5X]^{3+} + [Cr(H_2O)_6]^{2+} + \xrightarrow{5H_3O^+} [Co(H_2O)_6]^{2+} + [Cr(H_2O)_5Cl]^{2+} + 5NH_4^+$$

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

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

$[Cr(CN)_6]^{3-}$, $[Mn(CN)_6]^{2-}$, $[Co(CN)_6]^{3-}$, $[Co(CN)_6]^{4-}$

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

(i) $[Fe(H_2O)_6]^{2+} + [Fe(H_2O)_6]^{3+}$ $\quad$ $4.0\ m^{-1}s^{-1}$

$[Fe(phen)_3]^{2+} + [Fe(phen)_3]^{3+}$ $\quad$ $3.0 \times 10^7\ m^{-1}s^{-1}$

(ii) $[Ru(NH_3)_6]^{2+} + [Ru(NH_3)_6]^{3+}$ $\quad$ $8.2 \times 10^2\ m^{-1}s^{-1}$

$[Ru(phen)_3]^{2+} + [Ru(phen)_3]^{3+}$ $\quad$ $10^7\ m^{-1}s^{-1}$

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

(i) $NH_3$ followed by $R_3P$

(ii) $R_3P$ followed by $NH_3$ ?