

B.Sc. 5th Semester (Honours) Examination, 2019 (CBCS)

Subject : Chemistry

Paper : CC-11

Time: 2 Hours

Full Marks: 40

*The figures in the margin indicate full marks.**Candidates are required to give their answers in their own words as far as practicable.*

1. Answer any five questions: 2×5=10
- Exemplify the terms: magnetically dilute and magnetically concentrated substances.
 - UO_2^{2+} ion predominates the chemistry of uranium (VI) — Why?
 - State the selection rules in electronic spectroscopy.
 - State the conditions for orbital contribution to the magnetic moment.
 - What do you mean by Spin Cross-Over (SCO)? Give an example of a co-ordination compound showing this bi-stability.
 - Why do 4d and 5d metals form square planar complexes but not tetrahedral complexes?
 - Identify the products:
 - $\text{Th}(\text{NO}_3)_4 \xrightarrow{\text{H}_2\text{C}_2\text{O}_4}$
 - $\text{U}_3\text{O}_8 \xrightarrow{\text{conc.HNO}_3}$
 - Pick up the ions from the following list that have same colours. Indicate the reason for such similarity. Pm^{3+} , Sm^{3+} , Ho^{3+} , Dy^{3+}
2. Answer any two questions: 5×2=10
- State the reason between the following:
 - * Gold being a metal forms auride (Au^-) ion.
 - * Osmium and iridium are the densest among metals.
 - “ Ce^{4+} is an oxidant whereas Sm^{3+} is a reductant” — Explain. (1.5+1.5)+2=5
 - Predict and explain the relative position of fluoride, iodide ions and water in the spectrochemical series and nephelauxetic series.
 - “Complexes of Cu^{2+} usually depart considerably from octahedral geometry”. Comment. 3+2=5
 - $\text{Sm}(\text{III})$ and $\text{Eu}(\text{III})$ shows exceptional magnetic behaviour with respect to other trivalent lanthanide cations. — Explain.
 - Molar susceptibility ($\chi_M^{\text{corrected}}$) value for a complex has been reported as $1.11 \times 10^{-2} \text{ cm}^3 \text{ mol}^{-1}$ at 293 K. Calculate the number of unpaired electrons in the corresponding metal ion. [Assume that $\mu_{\text{eff}} = \mu_{\text{spin}}$ only] 3+2=5
 - Both $[\text{Fe}(\text{bpy})_3]^{2+}$ and $[\text{FeO}_4]^{2-}$ ions are colour. State the origin of colour in these two ions.

- (ii) "X and Y are the two complexes of nickel (II) — one of which with tetrahedral and the other with octahedral structures. The intensity in colour of Y is greater than that of X". Guess the geometry of each one from such spectral findings. Measurement of which physicochemical property would exclude the possibility of either complex being square planar? 2+3=5

3. Answer any two questions: 10×2=20

- (a) (i) Comment on the stoichiometry, colour and magnetic behaviour of the products when anhydrous manganous iodide is treated with alkyl isocyanide in alcoholic medium.
- (ii) Work out the spin only magnetic moment values of $K_3[CoF_6]$ and $K_2[NiF_6]$.
- (iii) Note down the postulates of Crystal Field Theory on metal-ligand bonding.
- (iv) Depict the structure of Cr(II) acetate dihydrate. Also Comment on its magnetic moment. 3+2+3+2=10
- (b) (i) Write the concise account of the principles and ion exchange separation method of lanthanoid ions.
- (ii) Portray the Orgel combined energy level diagram for d^n (Octahedral and tetrahedral) configuration. ($n = 1, 4, 6, 9$). (2+2)+(1.5×4)=10
- (c) (i) State the SI units of the following:
- * magnetic pole strength
 - * magnetic moment
 - * magnetic permeability
 - * molar susceptibility
- (ii) Outline the preparatory procedure of the following (balanced equation is not required)
- * Millon's base
 - * Purple of Cassius
 - * Wolfram's red
- (iii) Cite an example of super-exchanged pathway with respect to a coordination molecule. What is the net effect? (1/2×4)+(2×3)+2=10
- (d) (i) Identify the following:
- * $K_2[PtCl_4] + H_2C = CH_2 \xrightarrow{dil.HCl} A$
 - * $NH_4VO_3 \xrightarrow{\Delta} B$
 - * $TiCl_4 \xrightarrow[THF]{NaC_5H_5 (excess)} C$
 - * $Na_2[Fe(CN)_5(NO)] \xrightarrow{NaOH} D$
- (ii) Show the pattern of splitting of d-orbitals in crystal field mention the relation of $10Dq$ in cubic crystal field with tetrahedral and octahedral crystal field.
- (iii) Write relevant chemical equations in connection with van Arkel-de Boer process. (1×4)+4+2=10