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

(a) Exemplify the terms: magnetically dilute and magnetically concentrated substances.

(b) UO_2^{2+} ion predominates the chemistry of uranium (VI) — Why?

(c) State the selection rules in electronic spectroscopy.

(d) State the conditions for orbital contribution to the magnetic moment.

(e) What do you mean by Spin Cross-Over (SCO)? Give an example of a co-ordination compound showing this bi-stability.

(f) Why do 4*d* and 5*d* metals form square planar complexes but not tetrahedral complexes?

(g) Identify the products:

(i) $Th(NO_3)_4 \xrightarrow{H_2C_2O_4}$

(ii) $U_3O_8 \xrightarrow{conc.HNO_3}$

(h) 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

(a) (i) State the reason between the following:

* Gold being a metal forms auride (Au^-) ion.

* Osmium and iridium are the densiest among metals.

(ii) "Ce^{4+} is an oxidant whereas Sm^{3+} is a reductant" — Explain. (1·5+1·5)+2=5

(b) (i) Predict and explain the relative position of fluoride, iodide ions and water in the spectrochemical series and nephelauxetic series.

(ii) "Complexes of Cu^{2+} usually depart considerably from octahedral geometry". Comment. 3+2=5

(c) (i) Sm (III) and Eu (III) shows exceptional magnetic behaviour with respect to other trivalent lanthanide cations. — Explain.

(ii) Molar susceptibility $\left(\chi_M^{corrected}\right)$ value for a complex has been reported as $1{\cdot}11 \times 10^{-2}$ cm^3 mol^{-1} at 293 K. Calculate the number of unpaired electrons in the corresponding metal ion. [Assume that $\mu_{eff} = \mu_{spin}$ only] 3+2=5

(d) (i) Both $[Fe(bpy)_3]^{2+}$ and $[FeO_4]^{2-}$ 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 $K_3[CoF_6]$ adn $K_2[NiF_6]$.

(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? (½×4)+(2×3)+2=10

(d) (i) Identify the following:

* $K_2[PtCl_4] + H_2C = CH_2 \xrightarrow{\text{dil.HCl}} A$
* $NH_4VO_3 \xrightarrow{\Delta} B$
* $TiCl_4 \xrightarrow[THF]{NaC_5H_5\ (excess)} C$
* $Na_2[Fe(CN)_5(NO)] \xrightarrow{NaOH} D$

(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