**1(Sc)** 

UG-II/Chem.-IV(H)/21

## 2021

## **CHEMISTRY**

[HONOURS]

Paper: IV

Full Marks: 75

Time: 4 Hours

The figures in the right-hand margin indicate marks.

Candidates are required to give their answers in their own words as far as practicable.

## **GROUP-A**

[Marks:  $37\frac{1}{2}$ ]

- 1. Answer any **three** questions:
- $1 \times 3 = 3$
- a) Mention a chemical reaction where H<sub>2</sub>O behaves as a reductant.
- b) What is the shape of (H<sub>2</sub>Si)<sub>2</sub>N molecule?
- c) Write down the name and structure of a tetra dentate ligand.
- d) Give IUPAC name of the following:

$$\left[ \text{Co(CN)}_2 \left( \text{NO}_2 \right)_2 \left( \text{NH}_3 \right)_2 \right]^{-}$$

2. Answer any **three** questions:

- $2\times3=6$
- a) What do you mean by comproportionation reaction? Give example.
- b) Explain the term 'flexidentate ligand' with proper example.
- c) Two S-orbitals cannot form a 'pi' bond– Explain.
- d) Predict the shape of nitrosyl chloride.
- 3. Answer any **three** questions:  $6 \times 3 = 18$ 
  - a) Define the following with proper examples:
    - i) Linkage isomerism
    - ii) Ligand isomerism
    - ii) Coordination isomerism 2+2+2
  - b) Write a brief note on the factors that influence complex formation.
  - c) i) Chromium (III) under forcing condition forms [CrCl<sub>6</sub>]<sup>3-</sup> but the corresponding complexes are never found in Mn(III) and Fe(III)—Explain.
    - ii) Predict the shapes of the  $ICl_4$  and  $SOF_4$  molecules. 2+(2+2)
  - d) i) Predict the bond orders of  $O_2^+$ ,  $O_2$ ,  $O_2^-$  and  $O_2^{2-}$  using M.O. diagram.

- ii) The B-F bond energy in BF<sub>3</sub> is much higher than the N-F bond energy in NF<sub>3</sub>
   Explain.
- e) i) Discuss the applications of Latimer and Frost diagram in redox chemistry.
  - ii) The standard reduction potentials of the Ni<sup>2+</sup>/Ni and Co<sup>+2</sup>/Co are -0.25 V and -0.277 V respectively. Calculate the equilibrium constant of the reaction:

$$Ni^{+2} + Co \rightleftharpoons Ni + Co^{+2}$$
 4+2

- 4. Answer any **one** question:  $10 \times 1 = 10$ 
  - a) i) Establish the relation between overall and stepwise stability constant for a  $\mathrm{ML}_6$  complex.
    - ii) The equatorial OCIF bond angle in CIOF<sub>3</sub>
       molecule is substantially lower than 120°
       Justify the statement.
    - iii) BF<sub>3</sub> has no dipole moment whereas NF<sub>3</sub> has a dipole moment– Explain.
    - iv) KReO<sub>4</sub> is colourless whereas KMnO<sub>4</sub> is purple in colour– Give reason.

b) i) KMnO<sub>4</sub> can oxidize Cl<sup>-</sup> to Cl only at low pH– Explain.

$$MnO_4^-/Mn^{+2} = +1.51 \text{ V}$$

$$\frac{1}{2}Cl_2/Cl^- = +1.36 \text{ V}$$

- Both Fe<sup>3+</sup> abd Cu<sup>2+</sup> can liberate I<sub>2</sub> from I<sup>-</sup>, but in presence of F<sup>-</sup> only Cu<sup>2+</sup> can do so Give reason.
- iii) [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> is nearly colourless but upon the addition of KSCN a blood red colour develops— Explain.
- Define Bent's rule with proper example. 3+3+2+2

(General proficiency:  $\frac{1}{2}$ )

## **GROUP-B**

(Marks:  $37\frac{1}{2}$ )

5. Answer any **three** questions:  $1 \times 3=3$ 

- a) How many unpaired electrons are there in Tb<sup>3+</sup> ion?
- b) Give the name and chemical composition of an anion exchange resin.
- c) Name one important ore of Pu.
- d) Name the element with the ground state electronic configuration [Xe]4f<sup>5</sup>6s<sup>2</sup>.
- 6. Answer any **three** questions:  $2 \times 3 = 6$ 
  - a) Explain the effect of excess addition of NH<sub>4</sub>OH in gravimetric estimation of Ni as [Ni(DMG)<sub>2</sub>].
  - b) Name two factors that affect the selectivity of ion exchange resins.
  - c) Zr and Hf very often co-exist in nature and are chemically similar— Explain.
  - d) Give the principle of separation by column chromatography.
- 7. Answer any **three** questions:  $6 \times 3 = 18$ 
  - a) i) Define the terms 'co-precipitation' and 'post-precipitation'. Give examples.
    - ii) Write a brief account on the super heavy elements. 3+3

- b) i) Lanthanides exhibit +3 oxidation state in general whereas actinides show variable oxidation states— Explain.
  - ii) What do you mean by retention factor (Rf) in a chromatographic separation technique? 4+2
- c) i) Describe the principles for the gravimetric estimation of Mg as its phosphate compound.
  - ii) Give a brief outline of the ion-exchange method of separation of the lanthanide elements. 3+3
- d) i) Describe the principle and advantage of solvent extraction method.
  - ii) What do you mean by 'chromatogram'?

4+2

- e) i) Write the name of the organic reagent which is used in colorimetric analysis of Fe(II). Draw its structure.
  - ii) Why EDTA is the most suitable reagent in complexometric titration?
  - iii) Name one demasking agent. How does this work? 2+2+2

8. Answer any **one** question:

- $10 \times 1 = 10$
- a) i) Describe masking and demasking reagents with suitable examples.
  - ii) Why actinides show a somewhat wider range of oxidation states than lanthanides?
  - iii) Describe the method of determination of Al<sup>3+</sup> using an organic precipitant. What are the limitations of this method?
  - iv) Lanthanides in many respect resemblance the alkaline earths— Explain.

$$3+2+(2+1)+2$$

- b) i) Write a brief note on preparation, properties and uses of sodium nitropruside.
  - ii) Yttrium is more close to lanthanide than scandium– Explain.
  - iii) Discuss the principle of complexometric titration taking example for the determination of Mg with EDTA.
  - iv) Explain the anomalous magnetic properties of Sm<sup>3+</sup> and Eu<sup>3+</sup>. 3+2+3+2

(General proficiency :  $\frac{1}{2}$ )