

2020
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 : 37½]**

1. Answer any **three** questions: 1×3=3
- a) Write down the name and structure of a tetra dentate ligand.
- b) Give IUPAC name of the following:
- $$\left[\text{Co}(\text{CN})_2(\text{NO}_2)_2(\text{NH}_3)_2 \right]^-$$
- c) Mention a chemical reaction where H₂O behaves as a reductant.
- d) What is the shape of (H₃Si)₃N molecule?

2. Answer any **three** questions: 2×3=6
- a) Two S-orbitals cannot form a 'pi' bond– Explain.
- b) Predict the shape of nitrosyl chloride.
- c) What do you mean by comproportionation reaction? Give example.
- d) Explain the term 'flexidentate ligand' with proper example.
3. Answer any **three** questions: 6×3=18
- a) i) Predict the bond orders of O₂⁺, O₂, O₂⁻ and O₂²⁻ using M.O. diagram.
- ii) The B–F bond energy in BF₃ is much higher than the N–F bond energy in NF₃ – Explain. 4+2
- b) i) Discuss the applications of Latimer and Frost diagram in redox chemistry.
- ii) The standard reduction potentials of the Ni²⁺/Ni and Co⁺²/Co are –0.25 V and –0.277 V respectively. Calculate the equilibrium constant of the reaction:
- $$\text{Ni}^{+2} + \text{Co} \rightleftharpoons \text{Ni} + \text{Co}^{+2} \quad 4+2$$
- c) Define the following with proper examples:
- i) Linkage isomerism
- ii) Ligand isomerism
- iii) Coordination isomerism 2+2+2

[Turn over]

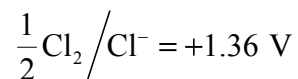
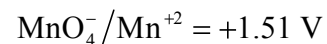
d) Write a brief note on the factors that influence complex formation. 6

e) i) Chromium (III) under forcing condition forms $[\text{CrCl}_6]^{3-}$ 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)

4. Answer any **one** question: 10×1=10

a) i) KMnO_4 can oxidize Cl^- to Cl_2 only at low pH– Explain.



ii) Both Fe^{3+} and Cu^{2+} can liberate I_2 from I^- , but in presence of F^- only Cu^{2+} can do so – Give reason.

iii) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is nearly colourless but upon the addition of KSCN a blood red colour develops– Explain.

iv) Define Bent's rule with proper example. 3+3+2+2

b) i) Establish the relation between overall and stepwise stability constant for a ML_6 complex.

ii) The equatorial OCIF bond angle in ClOF_3 molecule is substantially lower than 120° – Justify the statement.

iii) BF_3 has no dipole moment whereas NF_3 has a dipole moment– Explain.

iv) KReO_4 is colourless whereas KMnO_4 is purple in colour– Give reason.

4+2+2+2

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

GROUP-B

(Marks : 37½)

5. Answer any **three** questions: $1 \times 3 = 3$
- Name one important ore of Pu.
 - Name the element with the ground state electronic configuration $[\text{Xe}]4f^5 6s^2$.
 - How many unpaired electrons are there in Tb^{3+} ion?
 - Give the name and chemical composition of an anion exchange resin.
6. Answer any **three** questions: $2 \times 3 = 6$
- Zr and Hf very often co-exist in nature and are chemically similar– Explain.
 - Give the principle of separation by column chromatography.
 - Explain the effect of excess addition of NH_4OH in gravimetric estimation of Ni as $[\text{Ni}(\text{DMG})_2]$.
 - Name two factors that affect the selectivity of ion exchange resins.
7. Answer any **three** questions: $6 \times 3 = 18$
- Define the terms 'co-precipitation' and 'post-precipitation'. Give examples.
 - Write a brief account on the super heavy elements. $3+3$

- Lanthanides exhibit +3 oxidation state in general whereas actinides show variable oxidation states– Explain.
 - What do you mean by retention factor (R_f) in a chromatographic separation technique? $4+2$
- Describe the principles for the gravimetric estimation of Mg as its phosphate compound.
 - Give a brief outline of the ion-exchange method of separation of the lanthanide elements. $3+3$
- Describe the principle and advantage of solvent extraction method.
 - What do you mean by 'chromatogram'? $4+2$
- Write the name of the organic reagent which is used in colorimetric analysis of Fe(II). Draw its structure.
 - Why EDTA is the most suitable reagent in complexometric titration?
 - Name one demasking agent. How does this work? $2+2+2$

8. Answer any **one** question: $10 \times 1 = 10$

- a) 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^{3+} and Eu^{3+} . $3+2+3+2$
- b) 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^{3+} using an organic precipitant. What are the limitations of this method?
- iv) Lanthanides in many respect resemblance the alkaline earths– Explain.

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

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