2018

CHEMISTRY (Major)

Paper: 4.2

Full Marks: 60

Time: 3 hours

The figures in the margin indicate full marks for the questions

- 1. Select the correct answer/Answer the following questions: 1×7=7
 - (a) Which one of the following is pseudohalide?
 - (i) ICl (ii) (iii) (iii)
 - (ii) IF₅
 - (iii) CN⁻
 - (iv) 1₃
 - (b) XeO₃ is prepared by the
 - (i) direct combination of Xe and O2
 - (ii) hydrolysis of XeF4
 - (iii) oxidation of XeO2
 - (iv) hydrolysis of XeF6

- (c) Which of the following compounds has a cage structure?
 - (i) Borazine
 - (ii) B₂H₆
 - (iii) P₄O₁₀
 - (iv) Phosphazine
- (d) Among the metals Mn, Fe, Co and Ni, the ones those would react in their native forms directly with CO giving metal carbonyl compounds are
 - (i) Co and Mn
 - (ii) Mn and Fe
 - (iii) Fe and Ni
 - (iv) Ni and Co
- (e) In which one of the following is a metal-metal bond present?
 - (i) Cupric chloride
 - (ii) Mercurous chloride
 - (iii) Stannous chloride
 - (iv) Mercuric chloride
- (f) Write the possible geometrical isomers for octahedral [Co(OX)(PMe₃)₂NH₃Cl].

(g) Give the IUPAC name of the following compound:

[Pt(NH₃)₄NO₂C1]SO₄

- **2.** Answer the following questions: 2×4=8
 - (a) Why transition metal exhibits highest oxidation state in oxides and fluorides?
 - (b) The reaction

 $Al + Cr_2O_3 \rightarrow Cr + Al_2O_3$ $\Delta G = -281 \text{ kJ/mol}$

is thermodynamically feasible but it does not take place at room temperature. Why?

- (c) Write the reaction for preparation of 1,7-B₁₀H₁₀C₂RR'.
- (d) Which is more stable—chloric acid or perchloric acid? Justify.
- **3.** Answer any three from the following questions: 5×3=15
 - (a) Discuss the nature of bonding in borazine. Justify why borazine does not show true aromatic character. 3+2=5
 - (b) Which special properties of Au make it so important in human civilization?

 How does gold occur in nature and how is it commercially extracted? 2+3=5

(c) Discuss the oxidation states of the elements of the first transition series. Indicate common oxidation states and their relative stability for the metals Cr—Cu.

(d) Briefly describe the preparation, structure and properties of xenon fluorides.

(e) Write the formula for the complex dichlorobis(ethane-1,2-diamine)cobalt(III) ion. Draw its geometrical and optical isomers. Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands with the central metal ion?

1+2+2=5

10

5

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- **4.** Answer any three from the following questions: $10 \times 3 = 30$
 - (a) Explain the different types of isomerism exhibited by coordination compounds in square planner, tetrahedral and octahedral geometry.

(b) (i) Transition metals show variable oxidation states. Give examples of two different oxidation states shown by Mn in its compounds. In each case, give the oxidation state,

and an example of a compound containing Mn in that oxidation state.

(ii) Transition metals and their compounds are frequently used as catalysts. Name the catalysts employed in the following processes:

Haber process for the manufacture of ammonia, hydrogenation of carbon-carbon double bonds and contact process for the manufacture of sulphuric acid.

(iii) Identify A, B, C and D in the following reactions:

$$\begin{array}{c} \mathbf{V_2O_5} \xrightarrow{\mathbf{OH^-(pH=14)}} A \xrightarrow{\mathbf{pH=12}} B \\ \xrightarrow{\mathbf{pH=10}} C \xrightarrow{\mathbf{pH=9}} D \end{array}$$

- (c) (i) Compare the magnetic behaviour of the oxides and mixed oxides of iron with those of Ruthenium and Osmium.
 - (ii) Give the method of preparation, properties and structure of S_4N_4 . 2+1+2=5

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(Continued)

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(Turn Over)

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(d) Explain the following:

2×5=10

- (i) Chromium is a typical metal while mercury is a liquid metal.
- (ii) Zn readily liberates H_2 from cold dil. H_2SO_4 but not from cold conc. H_2SO_4 .
- (iii) Transition elements and d-block elements.
- (iv) Cu⁺ ion has 3d¹⁰4s⁰ configuration and colourless but Cu₂O is red and Cu₂S is black.
- (v) Enthalpies of atomization of transition elements are higher than those of alkali and alkaline earth metals.
- (e) (i) Describe the stereochemistries of Zn and Cd compounds.
 - (ii) Will Hg_2^{2+} ion disproportionate in aqueous solution into Hg^{2+} and Hg^0 ? Given that

$$E_{\text{Hg}_{2}^{2+}/\text{Hg}_{0}}^{\circ}$$
, $E^{\circ} = 0.7960 \text{ V}$
 $E_{\text{Hg}_{2}^{2+}/\text{Hg}_{2}^{2+}}^{\circ}$, $E^{\circ} = 0.9110 \text{ V}$
 $E_{\text{Hg}_{2}^{2+}/\text{Hg}_{0}}^{\circ}$, $E^{\circ} = 0.8535 \text{ V}$

(f) (i) What are silicates? Draw the structure of four different types of silicates and give the name and formula of each type.

(ii) Draw and describe the structure of the compound formed by CH₃COO⁻ with chromium.

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