

CHEMISTRY

Paper – I

Time Allowed : Three Hours

Maximum Marks : 200

Question Paper Specific Instructions

Please read each of the following instructions carefully before attempting questions :

*There are **ELEVEN** questions divided under **SIX** sections.*

*Candidate has to attempt **SIX** questions in all.*

*The **ONLY** question in Section A is compulsory.*

*Out of the remaining **TEN** questions, the candidate has to attempt **FIVE**, choosing **ONE** from each of the other Sections B, C, D, E and F.*

The number of marks carried by a question / part is indicated against it.

Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partly.

*Answers must be written in **ENGLISH** only.*

Neat sketches are to be drawn to illustrate answers, wherever required.

Unless otherwise mentioned, symbols and notations have their usual standard meanings.

Any page or portion of the page left blank in the Question-cum-Answer Booklet must be clearly struck off.

SECTION A

Q1. Answer all of the following :

5×10=50

- (a) Balance the following redox reaction in an acidic medium by the ion-electron method : 5
- $$\text{Cr}_2\text{O}_7^{2-} + \text{Fe}^{2+} \longrightarrow \text{Cr}^{3+} + \text{Fe}^{3+}$$
- (b) When a few Si atoms are replaced by P atoms in pure crystal of Si, what is the consequence in the physical property ? 5
- (c) The effective magnetic moment of $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is ~ 3.20 B.M. Is it higher or lower or equal to the $\mu_{\text{spin-only}}$ value ? Provide an explanation. 5
- (d) Identify the organometallic compound which obeys the 18 electron rule. 5
- (i) $[(\eta^7 - \text{C}_7\text{H}_7)\text{Mo}(\text{CO})_3]^+$
- (ii) $[(\eta^5 - \text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}]$
- (e) Why are nuclei having 'Magic Number' of nucleons exceptionally stable ? 5
- (f) Draw the structure of dimethyl beryllium and explain the bonding. 5
- (g) Nowadays CFC (Chlorofluorocarbon)-free refrigerators are promoted in the market. Why and what is the consequence upon release of CFCs to the atmosphere ? [Write only relevant reactions] 5
- (h) Compared to other actinides, why have the chemical properties of Th and U been extensively developed ? 5
- (i) Find the oxidation states of (i) Br in Br_3O_8 , and (ii) C in C_3O_2 . 5
- (j) The radii of Mo ($Z = 42$) and W ($Z = 74$) are 140 and 141 pm, respectively, despite the latter having many more electrons. Provide an explanation. 5

SECTION B

(Attempt any one question)

- Q2.** (a) Using a VSEPR model, arrive at and draw the shape of (i) XeO_2F_2 , and (ii) SO_2Cl_2 . 10
- (b) In going from left to right of the 1st transition series for bivalent ions, the Lewis acidity steadily increases. Justify your answer. 10
- (c) Iodine behaves differently in iodometric and iodimetric titrations. Provide an explanation. 10
- Q3.** (a) In the estimation of iron, copper and gold, three chemical methods are employed. Comment on these methods and explain with the chemical reactions involved in the extraction of these metals. 15
- (b) Write the product(s) formed from the following reactions and balance the equation : 15
- (i) $\text{NaBH}_4 + \text{I}_2 \longrightarrow$
- (ii) $\text{CaO} + \text{SiO}_2 \longrightarrow$
- (iii) $\text{Li} + \text{O}_2 \longrightarrow$
- (iv) $\text{PCl}_3 + \text{H}_2\text{O} \longrightarrow$
- (v) $\text{BF}_3 + \text{NH}_3 \longrightarrow$

SECTION C

(Attempt any one question)

- Q4.** (a) Draw the structures of *cis*-[Co(en)₂Cl₂] and *trans*-[Co(en)₂Cl₂].
(en = 1,2-diaminoethane) 10
- (b) Identify the presence or absence of Jahn-Teller distortion in [Fe(CN)₆]⁴⁻ and [Cu(H₂O)₆]²⁺. Justify your answer. 10
- (c) Determine the spectroscopic ground-states of [Co(H₂O)₆]³⁺ and [Fe(CN)₆]³⁻. 10
- Q5.** (a) When an aqueous solution of [Co(NH₃)₅Cl]⁺ is reacted with sodium nitrite and sodium thiocyanate separately, four new complexes could be isolated. Draw the structure of the new complexes. What is the nature of the incoming ligands? 10
- (b) Among the following complexes, which one assumes perfect octahedral geometry. Justify your answer. 10
- (i) [Cr(H₂O)₆]³⁺
- (ii) [VCl₆]²⁻
- (iii) [Fe(H₂O)₆]³⁺
- (c) From the following two complexes, identify the complex which is kinetically labile or kinetically inert : 10
- [Cr(H₂O)₆]³⁺ and [Mn(H₂O)₆]³⁺

SECTION D

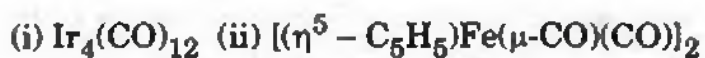
(Attempt any one question)

- Q6.** (a) Using MO diagrams, explain why B_2 is paramagnetic and C_2 is diamagnetic. 10
- (b) Write the balanced chemical reaction between (I) Br_2 , and (II) HCl with (i) benzene, and (ii) borazine. Comment on the reactivity pattern. 10
- (c) $B - Br$ bond of BBr_3 is a single bond; however, $B - F$ bond of BF_3 is between a single and a double bond. Rationalize the observation. 10
- Q7.** (a) B_2O_3 is acidic whereas Al_2O_3 is amphoteric. Rationalize your answer. 10
- (b) Draw the structures of P_4O_6 and P_4O_{10} . 10
- (c) (i) How is $(Me_2SiO)_n$ prepared starting from methyl chloride and silicon using copper as a catalyst? 5
- (ii) What are the applications of silicones? 5+5=10

SECTION E

(Attempt any one question)

Q8. (a) Predict the number of metal-metal bonds present in the following organometallic compounds : 15

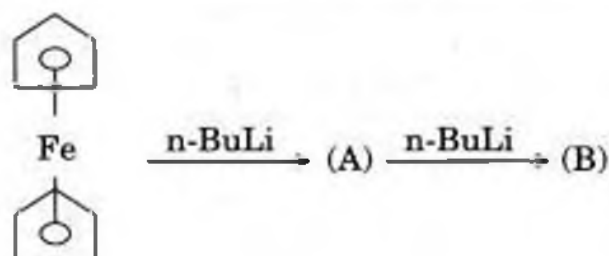


(b) What is Zeise's salt ? Explain its metal-ligand bonding interactions. 15

Q9. (a) While chromium hexacarbonyl exists as a monomer, manganese carbonyl forms a dimer. Rationalize your answer. 10

(b) The C – C distances in $[(\text{L})\text{Rh}(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)]$, L = acetylacetonate, are 201 – 202 pm ($\text{H}_2\text{C} = \text{CH}_2$) and 217 – 219 pm ($\text{F}_2\text{C} = \text{CF}_2$). Rationalize this observation. 10

(c) Predict the products [(A) and (B)] of the following nucleophilic addition : 10



SECTION F

(Attempt any one question)

- Q10.** (a) NaCl and NaOH cannot be used in place of NH_4Cl and NH_4OH for the precipitation of Group III A metal ions in qualitative group analysis. Provide an explanation. 10
- (b) Nuclear stability is associated with packing fraction. Provide an explanation. 10
- (c) Lanthanides typically display weak but sharp absorption bands. Explain. 10
- Q11.** (a) In qualitative inorganic analysis, H_2S is passed in acidic medium for Group II metal ions while for Group III B metal ions the same is passed in basic medium. Provide an explanation. 10
- (b) Aqueous solutions of potassium permanganate exhibit very intense electronic transition at ~ 530 nm. What is the nature of this transition? Justify your answer. 10
- (c) Write the ground state term symbols (LS coupling) for d^1 octahedral and d^9 octahedral. 10

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