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# UPSC CGS Exam

Mains Chemistry Paper I

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**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.*

*Neat sketches are to be drawn to illustrate answers, wherever required. These shall be drawn in the space provided for answering the question itself.*

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

*Assume suitable data, if necessary, and indicate the same clearly.*

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

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

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

## SECTION A

**Answer all of the following :**

**5×10=50**

- Q1.** (a) Explain why aluminophosphate forms quartz-like structure. 5
- (b) The stepwise formation constants for the complexes of  $\text{NH}_3$  with  $[\text{Cu}(\text{OH}_2)_6]^{2+}$  are  $\log K_{f1} = 4.15$ ,  $\log K_{f2} = 3.50$ ,  $\log K_{f3} = 2.89$ ,  $\log K_{f4} = 2.13$ , and  $\log K_{f5} = -0.52$ . Why is  $K_{f5}$  so different? 5
- (c) Both  $\text{H}^-$  and  $\text{P}(\text{C}_6\text{H}_5)_3$  are ligands of similar field strength, high in spectrochemical series. Discuss the orbital factors that account for the field strength of each ligand. 5
- (d) Why is methyl orange not a suitable indicator for titration of a strong base against a weak acid? 5
- (e) Explain how post-precipitation differs from co-precipitation. 5
- (f) Explain the role of  $\text{HgCl}_2$  in the volumetric determination of iron using potassium dichromate. 5
- (g) Explain the role of chelating agents in complexometric titrations. 5
- (h) Arrange the following metal carbonyls in the increasing order of their increasing C – O bond strength giving reason : 5
- $[\text{Cr}(\text{CO})_6]$   
 $[\text{Mn}(\text{CO})_6]^+$   
 $[\text{V}(\text{CO})_6]^-$
- (i) Complete the following nuclear reactions by giving the value of X : 5
- (i)  ${}^{14}_7\text{N} + {}^4_2\text{He} \longrightarrow \text{X} + {}^1_1\text{H}$
- (ii)  $\text{X} + {}^4_2\text{He} \longrightarrow {}^{30}_{15}\text{P} + {}^1_0\text{n}$
- (iii)  ${}^{23}_{11}\text{Na} + \text{X} \longrightarrow {}^{23}_{12}\text{Mg} + {}^1_0\text{n}$
- (iv)  ${}^{113}_{48}\text{Cd} + \text{X} \longrightarrow {}^{114}_{48}\text{Cd} + \text{energy}$
- (v)  $\text{X} \longrightarrow {}^0_{-1}\text{e} + {}^{232}_{91}\text{Pa}$
- (j) Why does the  $\mu_{\text{eff}}$  value for transition metal ions with ground state term S agree well with  $\mu_{\text{s.o.}}$  value while it differs with metal ions having ground state term as D or F? Explain with reason. 5

## SECTION B

Attempt any *one* question :

- Q2.** (a) Sketch the unit cell of  $\text{ReO}_3$  and determine (i) the coordination number of Re and O, and (ii) the identity of the structure type that would be generated if a cation is inserted in the centre of each  $\text{ReO}_3$  unit cell. 10
- (b) Would gallium arsenide be a suitable compound for a semiconductor? How could n- and p-type semiconductors be designed from it? 10
- (c) (i) The compound  $\text{Fe}_x\text{O}$  generally has  $x < 1$ . Describe the probable metal ion defect that leads to  $x$  being less than 1. 5
- (ii) Identify the product of the following : 5
- (I)  $\text{BaCO}_3(\text{s}) + \text{TiO}_2(\text{s}) \xrightarrow{1000^\circ\text{C}}$
- (II)  $\text{ZrO}_2(\text{s}) + 2\text{H}_3\text{PO}_4(\text{l}) \longrightarrow$
- (III)  $3\text{KF}(\text{aq}) + \text{MnBr}_2(\text{aq}) \longrightarrow$
- Q3.** (a) Explain the magnetic properties of the following coordination compounds using Crystal Field Theory : 5
- (i)  $[\text{Co}(\text{NH}_3)_6]^{3+}$
- (ii)  $[\text{Co}(\text{en})_3]^{3+}$
- (iii)  $[\text{Co}(\text{NO}_2)_6]^{3-}$
- (iv)  $[\text{CoF}_6]^{3-}$
- (v)  $[\text{Co}(\text{H}_2\text{O})_3\text{F}_3]^{3-}$
- (b) Why are the chemical properties of d-block elements seemingly erratic and irregular as compared to homogeneous chemical properties of lanthanides? 10
- (c) Why are the electronic spectra of lanthanides sharper as compared to transition metal complexes? Explain by giving suitable reason(s). 15

## SECTION C

Attempt any *one* question :

- Q4.** (a) An approximately 'octahedral' complex of Co(III) with ammine and chlorido ligands gives two bands with  $\epsilon_{\max}$  between 60 and 80  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ , one weak peak with  $\epsilon_{\max} = 2 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  and a strong band at higher energy with  $\epsilon_{\max} = 2 \times 10^4 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ . What do you suggest for the origin of these transitions ? 15
- (b) (i) Given that only the split between the top two energy levels of a square planar field can give rise to high and low-spin states, what number of d electrons,  $d^n$ , would have both possibilities ? Explain your answer. 10
- (ii) Consider the following cyanide complexes :  
 $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $[\text{Mn}(\text{CN})_6]^{3-}$ ,  $[\text{Cr}(\text{CN})_6]^{3-}$   
 Write the order of their lability. Justify your answer. 5
- Q5.** (a) Bearing in mind the Jahn-Teller effect, predict the structure of  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ . 10
- (b) Predict the product and explain its formation in the following reactions : 10
- (i)  $[\text{Pt}(\text{PR}_3)_4]^{2+} + 2\text{Cl}^- \longrightarrow$
- (ii)  $[\text{PtCl}_4]^{2-} + 2\text{PR}_3 \longrightarrow$
- (iii) *cis* -  $[\text{Pt}(\text{NH}_3)_2(\text{py})_2]^{2+} + 2\text{Cl}^- \longrightarrow$
- (c) The equilibrium constants for the successive reactions of 1,2-diaminoethane with  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  are as follows :
- $$[\text{M}(\text{OH}_2)_6]^{2+} + \text{en} \rightleftharpoons [\text{M}(\text{en})(\text{OH}_2)_4]^{2+} + 2\text{H}_2\text{O} \quad K_1$$
- $$[\text{M}(\text{en})(\text{OH}_2)_4]^{2+} + \text{en} \rightleftharpoons [\text{M}(\text{en})_2(\text{OH}_2)_2]^{2+} + 2\text{H}_2\text{O} \quad K_2$$
- $$[\text{M}(\text{en})_2(\text{OH}_2)_2]^{2+} + \text{en} \rightleftharpoons [\text{M}(\text{en})_3]^{2+} + 2\text{H}_2\text{O} \quad K_3$$
- | Ion              | $\log K_1$ | $\log K_2$ | $\log K_3$ |
|------------------|------------|------------|------------|
| $\text{Co}^{2+}$ | 5.89       | 4.83       | 3.10       |
| $\text{Ni}^{2+}$ | 7.52       | 6.28       | 4.26       |
| $\text{Cu}^{2+}$ | 10.72      | 9.31       | -1.0       |
- (i) What does the above data inform about successive formation constants ?
- (ii) How do you account for very low value of  $K_3$  for  $\text{Cu}^{2+}$  ? 10

## SECTION D

Attempt any one question :

- Q6.** (a) Find out the volume in mL of 0.1 N HCl solution required to react completely with 1.0 g of a mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  containing equimolar amounts of two components. 10
- (b) Methyl red has  $K_a = 10^{-5}$ . The acid form HIn is red and its conjugate base,  $\text{In}^-$  is yellow. Complete the following table : 10

pH	3	5	7
$[\text{In}^-] / [\text{HIn}]$	–	–	–
Colour	–	–	–

- (c) Sketch the general appearance of the curve for the titration of a weak diprotic base with strong acid. Explain different regions of the curve. 10
- Q7.** (a) What are redox titrations ? Explain the various types of redox titrations with examples. 15
- (b) Give reasons for the following : 15
- (i) Starch solution is added near the end point in iodometry titrations.
- (ii) Why is hot solution titrated against  $\text{KMnO}_4$  solution ?
- (iii) Potassium iodide is added in iodometric titration.

## SECTION E

Attempt any *one* question :

- Q8.** (a) Explain the complexometric titration curve for the titration of EDTA vs.  $M^{n+}$  ion solution. 15
- (b) Explain the principle in the determination of Mn-Mg-Zn mixture using complexometric titration. 15
- Q9.** (a) (i) What peculiarities does the Wilkinson's catalyst have that it behaves as a catalyst? 5
- (ii) Explain the mechanism for hydrogenation of alkene by Wilkinson's catalyst. 10
- (b) How would you account for metal-metal bonding in  $[Re_2Cl_8]^{2-}$  with the help of MO approach? 15

## SECTION F

Attempt any *one* question :

- Q10.** (a) What are the common possible nuclear fission reactions in case of  ${}_{92}^{235}\text{U}$  when a slow neutron enters the uranium nucleus ? 5
- (b) What is radioactive displacement law ? Illustrate the radioactive displacements by referring to the four radioactive decay series. 15
- (c) What do you understand by Alpha Decay ? Explain by giving suitable examples. 10
- Q11.** (a) Explain the general methods to avoid the supersaturation during precipitation in gravimetric estimation. 10
- (b) Explain the term peptisation with suitable example. 10
- (c) A very large excess of the precipitating agent is avoided in quantitative analysis. Justify. 5
- (d) Explain the effect of temperature on the solubility of a precipitate in gravimetric estimation. 5



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