# CHEMISTRY

## Paper – I

*Time Allowed : **Three** Hours*

*Maximum Marks : **200***

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### 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 (QCA) Booklet must be clearly struck off.*

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

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## SECTION A
## (Compulsory Section)

*Answer **all** of the following :* $5 \times 10 = 50$

**Q1.** (a) Match the following : 5

| | | | |
|---|---|---|---|
| (i) | Frenkel defect | (A) | $Al_2O_3$ |
| (ii) | Perovskite | (B) | $MgAl_2O_4$ |
| (iii) | Spinel | (C) | $FeTiO_3$ |
| (iv) | Ilmenite | (D) | $CaTiO_3$ |
| (v) | Corundum | (E) | AgCl |

(b) What are labile and inert complexes ? Explain with examples. 5

(c) Calculate the effective atomic number of the following complex ions : 5

(i) $[Co(NH_3)_6]^{3+}$ (ii) $[Pt(NH_3)_6]^{4+}$

(d) Phenolphthalein indicator is colourless at pH < 8·0 but pink at pH > 9·6. Explain why. 5

(e) The solubility product of lead phosphate at a particular temperature is found to be $1{\cdot}5 \times 10^{-32}$. Determine its solubility in gm/litre at that temperature. 5

[Given : Atomic weight of Pb = 207·19

Atomic weight of P = 30·974

Atomic weight of O = 15·999]

(f) Distinguish between iodometry and iodimetry. 5

(g) Citing a suitable example, explain displacement type of EDTA titration. 5

(h) A radioactive substance has a half-life of 250 years. How many years will it take to retain 74% of its original amount ? 5

(i) Justify why the carbonyl stretching frequency for $Mo(CO)_6$ is about 2000 $cm^{-1}$ whereas it is about 1760 $cm^{-1}$ for $Mo(dien)(CO)_3$. 5

(j) Show that $V^{3+}$ is paramagnetic whereas $V^{5+}$ is diamagnetic. 5

## SECTION B

*Attempt any **one** question :*

**Q2.** (a) $[PtCl_4]^{2-} \xrightarrow{NH_3} A \xrightarrow{NH_3} B$

$[Pt(NH_3)_4]^{2+} \xrightarrow{Cl^-} C \xrightarrow{Cl^-} D$

Identify A, B, C and D. Justify your answer. *10*

(b) Explain one chemical method to distinguish between *cis* and *trans* isomers of complexes of the type, $[PtA_2X_2]$, where A = amine and X = halide. *10*

(c) How does Jahn – Teller effect explain the unsymmetrical electronic spectra of octahedral complexes of $Ti^{3+}$ ? *10*

**Q3.** (a) Give an example for spinel solid and explain the charge distribution of $AB_2O_4$ system.

Mention the structural changes in the case of inverse spinel. *15*

(b) A sample of Wustite $Fe_xO$ contains one Fe(III) for every three Fe(II). Find the value of 'x'. *10*

(c) Write a brief note on point defect. *5*

## SECTION C

*Attempt any **one** question :*

**Q4.** (a) Enumerate the important assumptions of Crystal Field Theory. Draw crystal field splitting of d-orbitals in different geometries (Octahedral, Tetrahedral and Square-planar). *20*

(b) Differentiate between spectrochemical series and nephelauxetic series. *10*

**Q5.** (a) 50 mL of 0·1 N sodium carbonate is titrated with 0·1 N HCl at 298 K. Explain the course of titration with necessary equations. Calculate the pH values at the equivalence points. Suggest appropriate indicators. *15*

[Given : $K_1$ for $H_2CO_3 = 4{\cdot}3 \times 10^{-7}$ and $K_2$ for $H_2CO_3 = 5{\cdot}6 \times 10^{-11}$]

(b) 100 mL of 0·1 M acetic acid ($K_a = 1{\cdot}82 \times 10^{-5}$) is neutralised with 0·1 M sodium hydroxide solution at 25°C.

Calculate the pH at (i) the initial point; (ii) when 50 mL of alkali has been added; (iii) at the equivalence point, and also (iv) when 100·1 mL of alkali has been added.

Show the titration curve. Suggest a suitable indicator. *15*

[Given : Ionic product of water ($K_w$) at 25°C = $1{\cdot}1 \times 10^{-14}$]

## SECTION D

*Attempt any **one** question :*

**Q6.** (a) (i) Explain co-precipitation and post-precipitation with suitable examples.

(ii) What is oxine ? Mentioning the pH of its formation, show the structure of aluminium-oxinate complex. *10+5*

(b) Mention the principle for the gravimetric estimation of nickel employing dimethylglyoxime. Write down the requisite chemical equation. Draw the structure of the complex. Find the Gravimetric Factor (GF) for nickel in the complex. *15*

[Given : Atomic weight of nickel = 58·693]

**Q7.** (a) If 25 mL of Mohr's salt solution requires 15·5 mL of 0·1 M $KMnO_4$ solution for titration, calculate the amount of Mohr's salt present in one litre of its solution. [Molar mass of Mohr's salt is 392 g/mol] *10*

(b) Mention the composition of Zimmermann – Reinhardt solution. Discuss specific function of each component present in it. In which case is it used as a "Preventive solution" ? *15*

(c) Mention the predominant converted form of $MnO_4^-$ ion when $KMnO_4$ is used in the following cases : *5*

(i) in acidic medium

(ii) in strongly alkaline medium

(iii) in moderately alkaline medium

## SECTION E

*Attempt any **one** question :*

**Q8.** (a) (i) Outline the underlying principle for the determination of cyanide with $Ag^+$ titrimetrically providing necessary equations. How can the end point be detected ?

(ii) EDTA is a hexaprotic system, designated as $H_6Y^{2+}$. At pH 6·00 and at a formal concentration of 0·10 M, the composition of an EDTA solution is found to be as follows :

$[H_6Y^{2+}] = 8{\cdot}4 \times 10^{-24}$ M; $[H_5Y^{+}] = 8{\cdot}4 \times 10^{-14}$ M;

$[H_4Y] = 2{\cdot}7 \times 10^{-9}$ M; $[H_3Y^{-}] = 2{\cdot}7 \times 10^{-5}$ M;

$[H_2Y^{2-}] = 0{\cdot}059$ M; and $[HY^{3-}] = 0{\cdot}041$ M and

$[Y^{4-}] = 2{\cdot}3 \times 10^{-6}$ M.

Find the fraction of EDTA in the form, $Y^{4-}$. *10+5*

(b) Enumerate the outline of the procedure for the estimation of total hardness of water using EDTA. *15*

**Q9.** (a) Verify whether the following metal carbonyl compounds satisfy the 18 $e^-$ rule or not : *15*

(i) $Fe(CO)_5$

(ii) $Cr(CO)_6$

(iii) $Mn_2(CO)_{10}$

(iv) $Co_2(CO)_8$

(v) $Ni(CO)_4$

(b) Explain the catalytic cycle of hydrogenation of olefins by Wilkinson catalyst. *10*

(c) Write a short note on preparation of Wilkinson catalyst. *5*

## SECTION F

*Attempt any **one** question :*

**Q10.** (a) Why does atomic radii of transition metals first decrease, remain constant and then increase as one moves from left to right along the 3d series ? *10*

(b) What is lanthanide contraction ? How does it account for higher basicity of $La(OH)_3$, compared to $Lu(OH)_3$ ? *10*

(c) How can lanthanides be separated by ion-exchange method ? Explain the principle involved in it. *10*

**Q11.** (a) Calculate the packing fraction, mass defect and binding energy of Fe atom, $^{56}_{26}Fe$. *15*

[Given : $^{56}_{26}Fe$ = 55·9375 a.m.u.

Mass of proton = 1·007825 a.m.u.

Mass of neutron = 1·008665 a.m.u.

1 a.m.u. = 931·5 MeV]

(b) A piece of wood sample has a disintegration rate which is 20% of the disintegrations as shown by an equal weight of a new piece of wood. Find the age of the wood sample. *10*

[Given : $t_{1/2}$ for $^{14}C$ = 5740 years]

(c) Write 'X' in the following equations : *5*

(i) $^{24}_{12}Mg + X \longrightarrow {}^{27}_{14}Si + {}^{1}_{0}n$

(ii) $^{14}_{7}N + X \longrightarrow {}^{12}_{6}C + {}^{3}_{1}H$

(iii) $^{9}_{4}Be + X \longrightarrow {}^{12}_{6}C + {}^{1}_{0}n$

(iv) $^{7}_{3}Li + X \longrightarrow {}^{8}_{4}B + \gamma$

(v) $^{27}_{13}Al + X \longrightarrow {}^{24}_{11}Na + {}^{4}_{2}He$