

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.

Answers should be clearly indicated, 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.

(Compulsory Section)

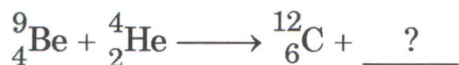
Answer **all** of the following :

5×10=50

- Q1.** (a) Which defect does silver chloride show and why ? 5
- (b) Which isomerism do $[(\text{NH}_3)_5\text{CoONO}]\text{Cl}_2$ and $[(\text{NH}_3)_5\text{CoNO}_2]\text{Cl}_2$ complexes show and why ? 5
- (c) Arrange the following metals in descending order of their trans-effect with proper justification : 5
 $\text{Ni}^{\text{II}}, \text{Pt}^{\text{II}}, \text{Pd}^{\text{II}}$
- (d) Phenolphthalein shows red colour in presence of dilute alkali. However, if treated with excess of concentrated alcoholic alkali, the red colour first produced disappears. Explain how. 5
- (e) Calculate the solubility product of silver chromate at a particular temperature, at which its solubility is 2.5×10^{-2} gram litre⁻¹. 5
[Given : The relative molecular mass of silver chromate is 331.728]
- (f) Determine the colour change interval for the indicator, diphenylamine, at 298 K. 5
[Given : E° for diphenylamine is + 0.756 V]
- (g) Why can Eriochrome Black T not be used to indicate the end point of a direct EDTA titration of calcium ? 5
- (h) Which metals of the following have the greatest tendency to form metal clusters ? Justify your answer. 5
- (i) V, Nb, Ta
- (ii) Zr, V, Nb
- (iii) Cr, Mo, Tc
- (iv) Nb, Mo, Tc

(i) Complete the following equations :

5



(j) Why is the first ionization enthalpy of 5d series elements higher than that of 3d and 4d series elements ?

5

SECTION B

Attempt any **one** question :

- Q2.** (a) How does BaTiO_3 show local ion displacement ? Also mention its electrical behaviour. 15
- (b) What should be the possible structure of binary hydrides and oxides of the following according to the composition ranges provided in brackets ? 10
- (i) LuH_x (1.85 – 2.23)
 - (ii) ErH_x (2.82 – 3.0)
 - (iii) TiO_x (0.7 – 1.25)
 - (iv) VO_x (0.9 – 1.20)
 - (v) TiO_x (1.9 – 2.0)
- (c) How will you synthesize $\text{YBa}_2\text{Cu}_3\text{O}_7$ quaternary oxide ? Explain with chemical reaction. 5

- Q3.** (a) 50 mL of 0.1 M phosphoric(V) acid is being titrated with 0.1 M potassium hydroxide solution at 25°C . Calculate the pH values at (i) the first equivalence point, (ii) the second equivalence point, and also at (iii) the third equivalence point.

Draw the titration curve. Suggest suitable indicator(s) in each stage of this titration. 15

[Given : K_1 = Primary dissociation constant of phosphoric (V)

$$\text{acid} = 7.5 \times 10^{-3}$$

K_2 = Secondary dissociation constant of phosphoric (V)

$$\text{acid} = 6.2 \times 10^{-8}$$

K_3 = Tertiary dissociation constant of phosphoric (V)

$$\text{acid} = 5.0 \times 10^{-13}$$

$$\text{Ionic product of water at } 25^\circ\text{C} = 1.1 \times 10^{-14}]$$

- (b) What is meant by salt hydrolysis ? Calculate (i) the hydrolysis constant, (ii) the degree of hydrolysis in %, and (iii) the pH of a 0.01 molar solution of sodium acetate at 25°C . 15

[Given : K_a for acetic acid = 1.8×10^{-5} and ionic product of water at $25^\circ\text{C} = 1.1 \times 10^{-14}$]

SECTION C

Attempt any **one** question :

- Q4.** (a) What is Wilkinson's catalyst ? Outline the catalytic cycle for the hydrogenation of alkene as catalysed by this catalyst. 15
- (b) What is 18-electron rule ? Confirm that the Cr centre in $[(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3]$ obeys the 18-electron rule, but the Rh in $[(\text{CO})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$ does not. 10
- (c) What are magic numbers ? $^{208}_{82}\text{Pb}$ is very stable. Explain why. 5
- Q5.** (a) What will be the structure and geometry of the given compounds ? 10
- (i) $[\text{CuCl}_5]^{3-}$
- (ii) $[\text{Ni}(\text{CN})_5]^{3-}$
- (iii) SF_6
- (iv) I_3^-
- (b) Arrange the following complexes based on their increasing ligand field strength with reason. 10
- $[\text{CrCl}_6]^{3-}$, $[\text{Cr}(\text{dtp})_3]$, $[\text{Cr}(\text{NH}_3)_6]^{3+}$ and $[\text{Cr}(\text{CN})_6]^{3-}$
- (where dtp = diethyldithiophosphate)
- (c) A small amount of a solution containing ^{24}Na ($t_{1/2} = 15$ hours) is injected into the bloodstream of a man. The initial activity is 2×10^3 counts second^{-1} . The activity of 1 cm^3 of blood sample taken from the man after 5 hours is 16 counts minute^{-1} . Find the total volume of blood of the man. 10

SECTION D

Attempt any **one** question :

Q6. (a) Consider the gravimetric estimation of sulphate as barium sulphate through filtering crucible method.

- (i) Mention the principle of this estimation with the requisite equation along with the ignition temperature of the precipitate.
- (ii) Find out the Gravimetric Factor (GF) of sulphate in barium sulphate.

[Given : Atomic weight of Barium = 137.33

Atomic weight of Sulphur = 32.064

Atomic weight of Oxygen = 15.999]

- (iii) How can the experimentally obtained results be lower or higher than the true value ? Suggest some measures in this respect so as to obtain a satisfactory result.

15

(b) Calculate the potential of a solution at the equivalence point in the titration of 25 mL of 0.1 N FeSO_4 solution with 0.1 N $\text{Cr}_2\text{O}_7^{2-}$ solution at 25°C.

15

The pH of the solution may be supposed buffered to pH 1.0 and also neglect the dilution effect.

[Given : $E^0_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V}$

$E^0_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.36 \text{ V}]$

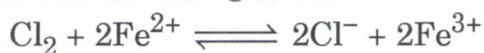
Q7. (a) Explain the thermodynamic and kinetic stability in $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Mn}(\text{CN})_6]^{3-}$ and $[\text{Cr}(\text{CN})_6]^{3-}$ complexes.

10

(b) What is the Jahn-Teller effect ? How does it affect the unsymmetrical electronic spectra of octahedral complexes of Ni (+III) ?

10

(c) Consider the following redox reaction :



Elucidate the fact that an iron (II) salt is almost completely oxidised by chlorine at 298 K.

10

[Given : $E^0_{\text{Cl}_2/2\text{Cl}^-} = 1.36 \text{ V}$

$E^0_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V}]$

SECTION E

Attempt any **one** question :

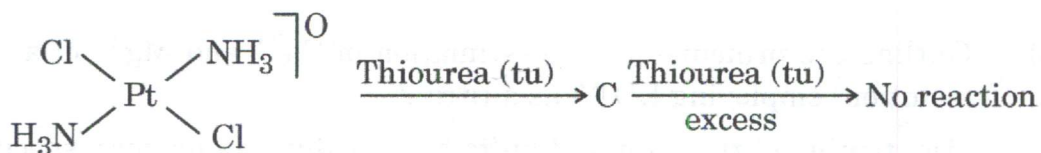
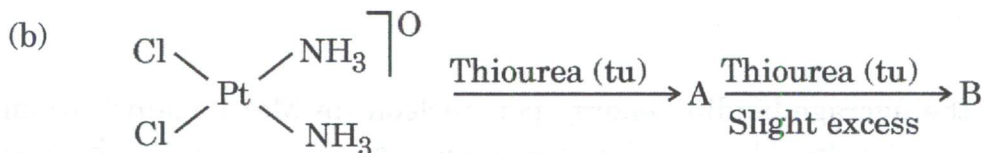
- Q8.** (a) What are redox indicators ? Mention the criteria of a suitable redox indicator. What is ferroin ? Draw the structures of ferroin in oxidised and reduced forms. Mention the colour(s) in these two forms. 15
- (b) On the basis of Lanthanide contraction, explain the following : 15
- (i) Nature of bonding in Lu_2O_3 and La_2O_3
 - (ii) Trends in the stability of Oxo salts of lanthanides from La to Lu
 - (iii) Stability of the complexes of Lanthanides
 - (iv) Radii of 4d and 5d block elements
 - (v) Trends in acidic character of Lanthanide oxide
- Q9.** (a) Draw the average binding energy per nucleon (in MeV) against atomic mass number plot. Mention the salient features of this plot. On the basis of this plot, how will you explain the chances of nuclear fusion and fission processes ? 15
- (b) Outline the principle for the estimation of Ca^{2+} and Mg^{2+} in a mixture (solution) employing EDTA as a titrant.
- [Mentioning of the names of buffers, pH values, indicators, specification of colour changes, basis of the calculations are required]
- Draw the structures of Ca^{2+} – EDTA and Mg^{2+} – EDTA complexes. 15

SECTION F

Attempt any **one** question :

- Q10.** (a) What are the metal-ion indicators ? Mention the requisites of a metal-ion indicator for use in the visual detection of end points. 10
- (b) Explain masking and demasking with a suitable example with particular reference to complexometric EDTA-based titration. 10
- (c) Write down the electronic configuration for La^{3+} , Gd^{3+} and Lu^{3+} and calculate the magnetic moment for those electronic configurations. 10

- Q11.** (a) What are the main components of Geiger-Muller counter ? How does a Geiger-Muller counter detect the presence of radiation ? 15



Identify A, B and C in the above reactions. Justify your answer. 5

- (c) Many octahedral complexes of Co^{2+} are pale pink in colour, while tetrahedral complexes of Co^{2+} are intensely blue in colour. Why ? 10