Combined Geo-Scientist (Main) Examination, 2024

SGSE–P–CMS

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 (QCA) Booklet must be clearly struck off.

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

SECTION—A

(Compulsory Section)

Answer **all** of the following : 5×10=50

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

(i)	Dolomite	1.	Alumina
(ii)	Corundum	2.	$MgCO_3 \cdot CaCO_3$
(iii)	Sphalerite	3.	$CuFeS_2$
(iv)	Silicon	4.	ZnS
(v)	Chalcopyrite	5.	Semiconductor

(b) The observed magnetic moment for $K_3[TiF_6]$ is $1{\cdot}70\ \mu_B$.

(i) Calculate μ (spin only) for this complex.

(ii) Why is there a difference between calculated and observed values? 5

(c) Match the following : 5

Titrations involving

	A		*B*
(i)	Strong acid vs. Weak base	1.	Methylene blue ($pK_a = 3{\cdot}8$)
(ii)	Weak acid vs. Strong base	2.	Bromothymol blue ($pK_a = 7{\cdot}2$)
(iii)	Strong acid vs. Strong base	3.	No indicator
(iv)	Weak acid vs. Weak base	4.	Phenolphthalein ($pK_a = 9{\cdot}3$)
(v)	Redox reactions	5.	Methyl orange ($pK_a = 3{\cdot}5$)

(d) A sample of slag from a blast furnace is analyzed for SiO_2 by decomposing a 0·5003 g sample with HCl leaving a residue with a mass of 0·1414 g. After treating with HF and H_2SO_4, and evaporating the volatile SiF_4, a residue with a mass of 0·0183 g remains. Determine the % w/w SiO_2 in the sample. 5

(e) Given that the standard electrode potentials for the reactions

$$2Fe^{2+}(aq) \rightleftharpoons 2Fe^{3+}(aq) + 2e^- \quad \text{(i)}$$

$$H_2O_2 + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O \quad \text{(ii)}$$

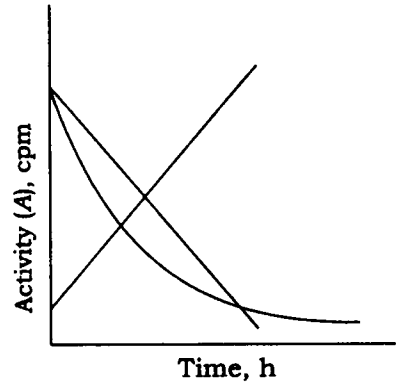
are $-0{\cdot}77$ V and $1{\cdot}77$ V respectively. Determine whether the oxidation of Fe^{2+} to Fe^{3+} is spontaneous or not. 5

(f) MnO_4^- is a stronger oxidizing agent than ReO_4^-. Explain and relate the oxidizing abilities of these ions with the relative positions of their charge-transfer absorptions. 5

(g) What pH is better for the effective use of CN^- as a masking agent? Explain the reason for this pH dependency. 5

(h) The complex $[Fe_2(Cp)_2(CO)_4]$ has one strong IR band at 1800 cm^{-1} and other bands appeared at ~ 1980 cm^{-1} and 2020 cm^{-1} for CO. Account for each band with proper reason. 5

(i) Which of the curves represent nuclear decay? Justify your answer with mathematical logic : 5



(j) Explain why stable and readily isolable carbonyl complexes are unknown for the lanthanoids. 5

SECTION—B

Attempt *any* **one** question

2. (a) (i) Differentiate between fluorite and antifluorite.

(ii) Differentiate between Schottky defect and Frenkel defect.

(iii) Differentiate between spinel and inverse spinel. 5+5+5=15

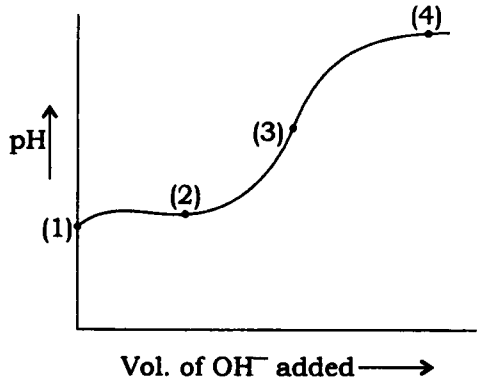
(b) Discuss each of the following observations : 10

(i) The $[CoCl_4]^{2-}$ ion is a regular tetrahedron but $[CuCl_4]^{2-}$ has a flattened tetrahedral structure.

(ii) The electronic spectrum of $[CoF_6]^{3-}$ contains two bands with maxima at 11500 cm^{-1} and 14500 cm^{-1}.

(c) What is polymorphism in crystals? Give an example. 5

3. *(a)* The titration curve for a weak acid vs. strong base (NaOH) has the following shape :



(i) Identify the weak acid :

I. CH_3COOH ($K_a = 1{\cdot}69 \times 10^{-5}$)

II. HCN ($K_a = 5 \times 10^{-10}$)

III. Benzoic acid ($K_a = 6{\cdot}3 \times 10^{-5}$)

IV. Pyridinium ion ($K_a = 5{\cdot}9 \times 10^{-6}$)

(ii) Explain the process and species involved in the regions marked as (1), (2), (3) and (4) that contribute to the pH at near regions. 15

(b) What are the general criteria of choosing a suitable indicator for a given volumetric titration? 5

(c) Give the salient features of estimation of sodium carbonate and bicarbonate mixtures by acidimetry. Which two acid-base indicators are used and why? 10

SECTION—C

Attempt *any* **one** question

4. *(a)* Oxyhemoglobin is bright red, whereas deoxyhemoglobin is purple. Explain the difference in colour qualitatively. 10

(b) Given the reactants PPh_3, NH_3 and $[PtCl_4]^{2-}$, propose efficient routes to both *cis* and *trans* $[PtCl_2(NH_3)(PPh_3)]$. 10

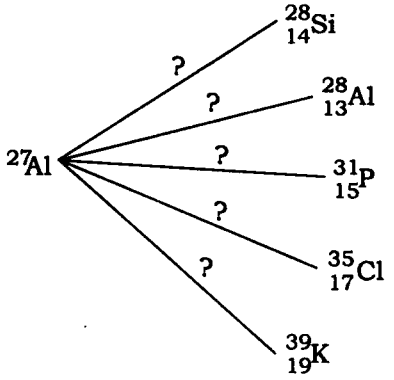
(c) Iron(II) oxide, FeO crystal has a cubic structure and each edge of the unit cell is 5·0 Å. Taking density of the oxide as 4·0 $g\,cm^{-3}$, calculate the number of Fe^{2+} and O^{2-} ions present in each unit cell. 10

5. *(a)* The compound $[Ni_3(C_2H_5)_3(CO)_2]$ has a single CO stretching absorption at 1761 cm^{-1}. The IR data indicate that all C_5H_5 ligands are pentahapto and probably in identical environments.

(i) On the basis of these data, propose a structure.

(ii) Does the electron count for each metal in the structure agree with the $18e^-$ rule? 10

(b) Identify the required particles to produce the listed product nuclei : 10



(c) An ore containing magnetite, Fe_3O_4 was analyzed by dissolving a 1·500 g sample in conc. HCl giving a mixture of Fe^{2+} and Fe^{3+}. After adding HNO_3 to oxidize any Fe^{2+} to Fe^{3+}, the resulting solution was diluted with water and Fe^{3+} precipitated as $Fe(OH)_3$ by adding NH_3. After filtering and rinsing, the residue was ignited giving 0·8525 g of pure Fe_2O_3. Calculate the % w/w Fe_3O_4 in the solution. [Given : FW of Fe_2O_3 = 159·69 g/mol and FW of Fe_3O_4 = 231·54 g/mol] 10

SECTION—D

Attempt *any* **one** question

6. *(a)* A thermogram was recorded for calcium oxalate monohydrate, $CaC_2O_4 \cdot H_2O$. The original sample weighed 24·60 mg and was heated from room temperature to 1000 °C at a rate of 5 °C/min. The following changes in mass and corresponding temperature ranges were observed :

Loss of 3·03 mg from 100–250 °C

Loss of 4·72 mg from 400–500 °C

Loss of 7·41 mg from 700–850 °C

Determine the solid residue at each step of the thermal decomposition. 15

(b) Match the following : 5

(i)	Cupferron	1.	Co^{2+}
(ii)	Cupron	2.	Ni^{2+}
(iii)	1-Nitroso-2-naphthol	3.	Al^{3+}
(iv)	Dimethylglyoxime	4.	Cu^{2+}
(v)	8-Hydroxyquinoline	5.	Fe^{3+}
		6.	Pb^{2+}
		7.	Cr^{3+}

(c) Discuss the following observations : 10

(i) ΔH° for the formation of $[Ln(EDTA)(OH_2)_x]^-$ ($x = 2$ or 3) in aqueous solution is nearly constant for all Ln and is almost zero.

(ii) Many actinoid oxides are non-stoichiometric but few lanthanoid oxides are.

7. (a) Explain the terms oxidative addition and reductive elimination in the hydrogenation reactions and how the coordination numbers of the metal atom alter with an example. 10

(b) (i) Draw the two isomeric forms of $Co_2(CO)_8$.

(ii) Show the cluster structure of $Ir_4(CO)_{12}$ metal-metal bonds. 10

(c) Ordinary bottle glass appears nearly colourless when viewed through the wall of the bottle but visibly coloured (green) when viewed from the end so that light has a long path through the glass. The colour is associated with the presence of Fe^{3+} in the silicate matrix. Explain this observation. 10

SECTION—E

Attempt *any* **one** question

8. (a) Complete the following by giving the missing part on the right or left hand side of the equations and also identify their applications in daily life or industry : 15

(i) $\underline{??} \longrightarrow PbSO_4 + 2e^-$

(ii) $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow \underline{??}$

(iii) $6CO_2 + 6H_2O \xrightarrow{h\nu} \underline{??}$

(iv) $\underline{??} \longrightarrow Cu$

(b) Following are the standard redox potentials for the reactions in aqueous media :

$$Ag^{2+} + e^- \rightleftharpoons Ag^+ \quad +1{\cdot}98\ V$$
$$Mg^{2+} + 2e^- \rightleftharpoons Mg \quad -2{\cdot}37\ V$$
$$Li^+ + e^- \rightleftharpoons Li \quad -3{\cdot}04\ V$$
$$Ca^{2+} + 2e^- \rightleftharpoons Ca \quad -2{\cdot}87\ V$$
$$Na^+ + e^- \rightleftharpoons Na \quad -2{\cdot}71\ V$$

Arrange the above metals in the order of their increasing reducing power. 5

(c) Establish that the end point in a redox reaction occurs when

$$E = E^{\circ}_{(In_{ox}/In_{red})} - \frac{0{\cdot}05916}{n}$$ 10

9. (a) Calculate the activity (in dpy) due to ^{14}C in 1·00 kg of carbon found in a living specimen. The abundance of ^{14}C in a carbon sample present-day specimen is $1{\cdot}3 \times 10^{-12}$ ($t_{1/2}$ of ^{14}C is 5730 y, $N_A = 6{\cdot}023 \times 10^{23}$ atoms/mole, At. mass of carbon = 12·011 u). 10

(b) Identify the missing part in the following nuclear reactions : 5

$$^{7}_{3}Li + \underline{\ ?\ } \longrightarrow {}^{10}_{5}B + {}^{1}_{0}n$$

$$^{12}_{6}C + {}^{1}_{1}H \longrightarrow \underline{\ ?\ } + \gamma$$

$$^{12}_{6}C + \underline{\ ?\ } \longrightarrow {}^{8}_{4}Be + {}^{4}_{2}He$$

$$^{41}_{19}K + {}^{1}_{0}n \longrightarrow {}^{40}_{19}K + \underline{\ ?\ }$$

$$^{27}_{13}Al + {}^{2}_{1}d \longrightarrow \underline{\ ?\ } + {}^{1}_{0}n$$

(c) Explain the relation between elementary separation factor, α and enrichment factor, ε in terms of abundance of a particular isotope in a mixture during the separation. 10

(d) A sample of radioactive isotope with $t_{1/2}$ of 1600 y has an activity of 20 mCi (Ci = curie). How long it would take the activity to be reduced to almost 1 mCi (≈ 1·25 mCi)? 5

SECTION—F

Attempt *any* **one** question

10. *(a)* The EDTA titration of mixtures of Ca^{2+} and Mg^{2+} can be followed thermometrically. Sketch the thermometric titration curve for a mixture of $5{\cdot}00\times10^{-3}$ *M* Ca^{2+} with $5{\cdot}00\times10^{-3}$ *M* Mg^{2+} with 0·0100 *M* EDTA. The heats of formation for CaY^{2-} and MgY^{2-} are respectively –23·9 kJ/mol and –23·0 kJ/mol. (Given : $\log K_1$ for Ca^{2+}-EDTA complex = 10·69 and $\log K_1$ for Mg^{2+}-EDTA complex = 8·79) 10

(b) Show that F^- is an effective masking agent in preventing a reaction of Al^{3+} with EDTA. Assume that only significant forms of fluoride and EDTA are F^- and Y^{4-}.

(Given : *(i)* $\log K_1 = 6{\cdot}11$, $\log K_2 = 5{\cdot}01$, $\log K_3 = 3{\cdot}88$, $\log K_4 = 3{\cdot}00$, $\log K_5 = 1{\cdot}4$, $\log K_6 = 0{\cdot}4$ for the complexes between Al^{3+} and F^- and *(ii)* $\log K$ for the complex between EDTA and Al^{3+} = 16·3) 10

(c) *(i)* Write the following ligand-exchange reactions :

1. $[Co(H_2O)_6]^{3+} + 6NH_3 \rightarrow$
2. $[Co(H_2O)_6]^{3+} + 3en \rightarrow$

(ii) Which of the reactions should have a larger $\Delta S°$?

(iii) Given that Co — N bond length is approximately same in both complexes. Which reaction will have a larger equilibrium constant? Explain your choice. 10

11. *(a)* Calcium in powdered milk is determined by ashing a 1·50 g sample and then titrating calcium with EDTA solution, 12·1 mL being required. EDTA was standardized by titrating 10·0 mL of a zinc solution prepared by dissolving 0·632 g zinc metal in acid and diluting to 1 L (10·8 mL EDTA is required for titration). What is the concentration of calcium in the powdered milk in parts per million? 10

(b) Give the trends in the stability of higher oxidation states in the first row *d*-block metal compounds. 10

(c) *(i)* Explain why isostructural HfO_2 and ZrO_2 have densities of 9·68 g cm^{-3} and 5·73 g cm^{-3} respectively.

(ii) Why are high coordination numbers not usual for first row *d*-block elements? 10

★ ★ ★