This question paper contains 8 printed pages.

5171A *Your Roll No*

B.Sc. Prog. / III J

CH–301— CHEMISTRY

[O.C.: Admissions of 2007 and before]

Time : 3 hours *Maximum Marks* : 75

(Write your Roll No on the top immediately on receipt of this question paper)

Use separate answer-sheets for Sections A and B

You are allowed to use any type of calculators except mobile calculators but you cannot share it. However log tables will be provided if asked for.

SECTION A Marks 50

(Inorganic Chemistry)

Attempt any four questions

Question No. 1 carries 14 marks
All other questions carry 12 marks each

1. (*a*) Explain the following:

(*i*) The metallic character of transition elements decreases almost regularly from Sc to Cr, remains constant upto Ni, and then decreases.

P T O.

(*ii*) Transition elements usually exhibit higher oxidation states in their fluorides than in carbon monoxide.

(*iii*) Lanthanides form fewer complexes as compared to transition elements, though their ions have high charge.

(*iv*) Although $[NiCl_4]^{2-}$ and $Ni(CO)_4$ are tetrahedral but they differ in magnetic behaviour.

(*v*) Low-spin tetrahedral complexes are not known. $2\times5=10$

(*b*) Given below is the Latimer diagram for Cobalt in acidic medium:

$$CoO_2 \xrightarrow{1\ 8} Co^{3+} \xrightarrow{1\ 82} Co^{2+} \xrightarrow{-0\ 28} Co$$

(*i*) Which is the stable oxidation state?

(*ii*) Do any species undergo disproportionation? 4

2. (*a*) Compound (*A*) when treated with Na_2CO_3 in the presence of excess O_2 gives a yellow coloured compound (*B*). *B* on treatment with H_2SO_4 and KCl gives an orange coloured compound (*C*). When (*C*) is heated with NH_4Cl it gives a green coloured compound (*D*). Identify *A* to *D* and also write the chemical reactions 4

(*b*) What happens when— (Give chemical equations.)

(*i*) Oxalic acid is added to acidic $KMnO_4$

(*ii*) Sodium nitroprusside is treated with Na_2S

(*iii*) $K_3[Fe(CN)_6]$ is added to the solution of $FeSO_4$

(*iv*) Cobalt nitrate in acetic acid is treated with $NaNO_2$? 2×4

3. (*a*) Explain hybridisation, structure and magnetic behaviour of the following complexes:

(*i*) $[MnBr_4]^{2-}$

(*ii*) $[Ni(Et_3P)_2Br_2]$

(*iii*) $[Cr(NH_3)_6]^{3+}$. 3×3

(*b*) Name the type of isomerism in the following pairs:

(*i*) $[Co(NH_3)_5I]SO_4$ and $[Co(NH_3)_5SO_4]I$

(*ii*) $[Cr(SCN)_4(H_2O)_2]^-$ and $[Cr(NCS)_4(H_2O)_2]^-$

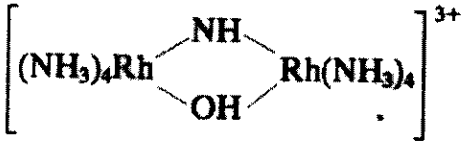
(*iii*) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

1×3

4. (*a*) Name the following complexes on the basis of IUPAC.

(*i*) $(CH_3)_4N[Co(NCS)_4(H_2O)_2]$

(*ii*) $[Cr(en)_2Cl_2]Cl$

(*iii*) 

(*iv*) $[Pt(NH_3)PyClBr]$

(*v*) $[Cu(NH_3)_4][CuCl_4]$

(*vi*) $Mn_2(CO)_{10}$ 1×6

(*b*) Complete the following reactions:

(*i*) $Cr(CO)_6 + 2PF_3 \longrightarrow$

(*ii*) $Ni(CO)_4 + 2NO \longrightarrow$

(*iii*) $Fe(CO)_5 \xrightarrow{\Delta}$

(*iv*) $Mn_2(CO)_{10} \xrightarrow{Li}$ 1×4

(*c*) Draw the structure of Zeiss salt 2

5. (*a*) Complexes of Co(III) like $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$ and $[Co(NO_2)_6]^{3-}$ are diamagnetic and yellow in colour whereas $[Co(H_2O)_6]^{3+}$ is paramagnetic and blue in colour, explain on the basis of CFT. 4

(*b*) Which of the following complexes show higher value of Δ_0 and why?

(*i*) $[Ni(H_2O)_6]^{2+}$ and $[NiCl_4]^{2-}$

(*ii*) $[CrCl_6]^{3-}$ and $[Cr(en)_3]^{3+}$ 2×2

(*c*) In terms of Crystal Field theory explain why a d^9 octahedral complex with six identical ligands is not expected to have all six metal donor distance identical. 4

6. (*a*) What do you mean by lanthanide contraction? What are its causes? How does it affect the chemistry of post-lanthanide elements? 4

(*b*) Work out the number of unpaired electrons in the following ions:

Eu^{3+} (At. No. 63), Er^{3+} (At. No. 68) 4

(*c*) (*i*) Higher oxidation states are more common for actinides than for lanthanides Why?

(*ii*) Actinides form oxocations but lanthanides do not Why? 2×2

Section B Marks 25

(*Physical Chemistry*)

Attempt any two questions.
All questions carry equal marks.

7. (*a*) What is meant by the term 'half-life period'? Show that the half-life period of a second order reaction is inversely proportional to the initial concentration of the reactants. The half-life period of a substance is 46 minutes at a certain concentration. When the concentration is reduced to one half of the initial concentration, the half-life period is 23 minutes. Find the order of the reaction. $1+2+2\frac{1}{2}$

(*b*) Explain why the hydrolysis of an ester in the presence of a dilute acid follows first order kinetics while that in the presence of a dilute alkali follows second order kinetics. 3

(*c*) In the following reaction scheme, write the differential rate equation for the removal of species A, B, C, and D:

$$A+B \xrightarrow{k_1} C+D$$

$$C+D \xrightarrow{k_2} A+B$$

$$C+B \xrightarrow{k_3} E+D$$

$$2D \xrightarrow{k_4} F$$

4

8. (*a*) Distinguish between Weiss Indices and Miller Indices. Compute Weiss Indices and Miller Indices for the faces with the following intercepts with the three axes perpendicular to each other:

(*i*) $2a, 3b, 2c$

(*ii*) $a, \frac{b}{3}, \frac{c}{2}$

(*iii*) $\frac{a}{2}, \frac{b}{4}, \infty$

(*iv*) ∞, b, ∞ 2+4

(*b*) Write short notes on the following:

(*i*) The Powder method

(*ii*) Packing efficiency in crystals

(*iii*) The law of constancy of interfacial angles. $2_{1/2}+2_{1/2}$

(*c*) Sketch (100), (110) and (111) planes. $1_{1/2}$

9. (*a*) Define 'Quantum yield" of a reaction. Why is it that in certain cases, quantum yield is lower than that expected from Einstein law of photochemical equivalence? Give suitable examples to validate your point. $2+2_{1/2}$

(*b*) Explain briefly fluorescence and chemiluminiscence. $2_{1/2}+2_{1/2}$

(*c*) The dissociation energy of hydrogen is 102900 cal mol^{-1}. If hydrogen is dissociated by illumination with radiation of wavelength 2537 Å, what

fraction of radiant energy will be converted into kinetic energy? 3

10. (*a*) What are enzymes? How do they differ from inorganic catalysts? 1½+2½

(*b*) Describe the factors that affect the enzyme catalysed reactions with suitable examples. 3½

(*c*) Write down the mechanism of enzyme catalysis suggested by Michaelis and Menten. What is the significance of Michaelis constant? 4+1

Values of some Physical Constants:

Planck constant $h = 6 \cdot 627 \times 10^{-34}$ Js

Boltzmann constant $k = 1 \cdot 38 \times 10^{-24}$ JK^{-1}

Avagardro Number $N = 6 \cdot 06 \times 10^{23}$