Total No. of printed pages = 6

3 (Sem 6) CHM M4

2015

CHEMISTRY

(Major)

Theory Paper : M-6.4

(Inorganic Chemistry)

Full Marks – 60

Time – Three hours

The figures in the margin indicate full marks for the questions.

1. Answer the following questions : 1×7=7

   (a) What is the ground state term for the high spin d^5 configuration in O_h symmetry ?

   (b) Why are transition metals such as Mn, Fe, Co and Cu needed in photosynthesis and respiration rather than metals such as Zn, Ga or Ca ?

   (c) What are exoergic and endoergic nuclear reactions ?

[Turn over

(d) Why do many square planar complexes have two-term rate laws for ligand replacement reactions ?

(e) Why is +3 oxidation state the characteristic oxidation state of lanthanides though the atoms in the series contain only two electrons in the outermost shell ($6s^2$) ?

(f) What is hole formalism ?

(g) What is the principal function of nitrogenase ?

2. Answer the following : $2\times4=8$

(a) Write the mechanism of the following reaction :

$$[(NH_3)_5CoCl]^{2+} + OH^- \rightarrow [(NH_3)_5Co(OH)]^{2+} + Cl^-$$

(b) Classify the following configurations as A, E, T in complexes having O_h symmetry $t_{2g}^4 e_g^2$, t_{2g}^6.

(c) What are the observations in connection with beta-emission that lead to the neutrino hypothesis ? How are neutrinos detected ?

(d) What are the effects of increase of nitrate and nitrite ion concentration in drinking water ?

3. Answer any *three* of the following : 5×3=15

(a) $[Fe(H_2O)_6]^{2+}$ has a two-humped absorption peak near 1000 nm. By using the appropriate diagram account for the most likely origin of this absorption. Then, account for the splitting of the absorption band.

(b) Write briefly about photosynthesis in chloroplast membrane clearly describing the electron transfer chains and the role played by PS-I and PS-II.

(c) Determine the possible microstates for an s^1p^1 configuration and use them to prepare a microstate table.

(d) Explain what do you mean by radioactive equilibrium and state the conditions under which such equilibrium is established. What do you mean by secular and transient equilibrium ? Give necessary expressions and decay curves.

(e) Give an account of the magnetic properties of actinide elements and compare them with transition elements (d-block).

4. Answer any *three* from the following : 10×3=30

(a) (i) Using the theory of redox titrations show the problems associated with the estimation of Fe^{2+} by standardized $KMnO_4$ solution in hydrochloric acid medium. Explain suggesting appropriate reasons, how you would overcome this problem. 5

(ii) Write very briefly about the role of metal salts in diet, diagnosis, chemotherapy and medicine. 5

(b) (i) The thermodynamic parameters for Cd^{2+} complexes $[Cd(CH_3NH_2)_4]^{2+}$ and $[Cd(en)_2]2^+$, en=ethylenediamine, are given below :

Ligand	ΔH° $\left(kJmol^{-1}\right)$	ΔS° $(J/mol\cdot K)$
$4CH_3NH_2$	–57.3	–67.3
2en	–56.5	+14.1

Ligand	$-T.\Delta S^\circ$ $\left(kJ\ mol^{-1}\right)$	ΔG° $\left(kJ\ mol^{-1}\right)$	$\log\beta$
$4CH_3NH_2$	+20.1	–37.2	6.52
2en	–4.2	–60.7	10.6

Explain the above data giving appropriate reasons. 5

(ii) Briefly discuss the advantages and limitations of nuclear fission and fusion processes as probable alternatives to fossil fuels as energy sources. 5

(c) (i) Explain the terms packing fraction and mass defect. How is mass defect related to nuclear binding energy ? Show the variation of packing fraction against mass number.

What do you mean by positive and negative packing fraction ? 5

(ii) Define kinetically labile and inert complexes. The high spin complex ion $[Cr(H_2O)_6]^{2+}$ is labile, but the low spin complex ion $[Cr(CN)_6]^{4-}$ is inert. Explain giving reasons. 2+3=5

(d) (i) Describe the methods of separation of isotopes. What is the best method of separation of isotopes of uranium ? 5

(ii) Write the Laporte and spin selection rules for electronic transitions in coordination complexes. Explain why an aqueous solution of $COCl_2.6H_2O$ is faint pink but that of $[COCl_4]^{2-}$ is intense blue. 5

(e) (i) Explain how mercury compounds act as poison in biological systems. 4

(ii) The electronic spectrum of $[Cr(H_2O)_6]^{3+}$ ion shows bands at 14,900 cm^{-1}, 22,700 cm^{-1} and 34,400 cm^{-1}. Interpret the spectrum using an appropriate energy level diagram. 4

(iii) Write the structures of the products of the following reactions : 2

$[Pt(NH_3)_4]^{2+} + 2Cl \rightarrow$

$[PtCl_4]^{2-} + 2NH_3 \rightarrow$