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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 : $-1 \times 7 = 7$
- (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 : 2×4=8

- (a) Write the mechanism of the following reaction :

$$[(\text{NH}_3)_5\text{CoCl}]^{2+} + \text{OH}^- \rightarrow [(\text{NH}_3)_5\text{Co}(\text{OH})]^{2+} + \text{Cl}^-$$
- (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 : $5 \times 3 = 15$

- (a) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ 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 : $10 \times 3 = 30$

(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 $[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}$ and $[\text{Cd}(\text{en})_2]^{2+}$, en=ethylenediamine, are given below :

Ligand	$\frac{\Delta H^\circ}{(\text{kJ mol}^{-1})}$	$\frac{\Delta S^\circ}{(\text{J / mol} \cdot \text{K})}$
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4 CH_3NH_2	-57.3	-67.3
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2en	-56.5	+14.1
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Ligand	$\frac{-T \cdot \Delta S^\circ}{(\text{kJ mol}^{-1})}$	$\frac{\Delta G^\circ}{(\text{kJ mol}^{-1})}$	$\log \beta$
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4 CH_3NH_2	+20.1	-37.2	6.52
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2en	-4.2	-60.7	10.6
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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 $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ is labile, but the low spin complex ion $[\text{Cr}(\text{CN})_6]^{4-}$ 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 $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ is faint pink but that of $[\text{CoCl}_4]^{2-}$ is intense blue. 5

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

(ii) The electronic spectrum of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ion shows bands at $14,900 \text{ cm}^{-1}$, $22,700 \text{ cm}^{-1}$ and $34,400 \text{ cm}^{-1}$. Interpret the spectrum using an appropriate energy level diagram. 4

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

