## 2008

## **CHEMISTRY**

PAPER — CH - 1103

Full Marks: 40

Time: 2 hours

Answer four questions taking at least two from each Group

The figures in the right-hand margin indicate marks

Candidates are required to give their answers in their own words as far as practicable

Illustrate the answers wherever necessary

## GROUP-A

- 1. (a) What do you mean by 'Trigger mechanism'?
  - (b) Discuss Hill's equation.
    - (c) Write a note on ' $N_2$ -fixation'.
    - (d) What is "Hemosiderin".

2 + 3 + 3 + 2

- 2. (a) How will you synthesize "ruthenates"?
  - (b) Write down the synthesis and structure of "Osminate"?
  - (c) What happen, when
    - (i) RuO<sub>4</sub> is treated with aq. HCl in presence of KCl.
    - (ii) OsF<sub>6</sub> is treated with CO in presence of SbF<sub>5</sub>.
  - (d) Write short note on  $K_2$  [Pt (CN)<sub>4</sub>]  $3H_2O$ .
  - (e) How will you synthesize anh. VOSO<sub>4</sub>?
  - (f) Write down the structure of NbOCl<sub>3</sub>. 1+2+3+2+1+1
- 3. (a) Identify the core structure of the following species on the basis of Wade's rules:

$$CB_{10}H_{11}^{-}$$
,  $(\eta^{5} - C_{5}H_{5})$  Co  $(C_{2}B_{9}H_{11})$ .

(b) A borane molecule whose styx number is 4012, find out its formula and predict how many electron pair bonds are there.

(c) Carryout the following transformation:

1, 
$$2 - C_2 B_{10} H_{12} \rightarrow (HOOC)_2 C_2 B_{10} H_{12}$$
.

- (d) Justify that  $C_2B_9H_{11}^{2-}$  is more effective as a ligand than  $C_5H_5^-$ .
- (e) Complete the following reaction:

$$C_2B_9H_{11}^{2-} + Mo(CO)_6 \xrightarrow{h v}$$

$$(2+2)+2+1+2+1$$

- 4. (a) Derive the transformation matrix for rotation by an angle  $\phi$  about the y-axis of a point in xz plane.
  - (b) Chromium (II) fluoride and manganese (II) fluoride both have a central metal ion surrounded by six fluoride ligands. All the Mn-F bond distances are equivalent but all Cr-F bond distances are not equivalent. Provide an explanation.
  - (c) Discuss the role of the perfluoro chemicals (PFCs) as synthetic oxygen carriers.

- (d) What are the "Picket-fence" porphyrins and why they are used in model studies of oxygen binding to hemoglobin and myoglobin?
- (e) What is Creutz Taube cation? 3+2+2+2+1

## GROUP-B

- 5. (a) Prove that the vectors whose components are the characters of two different irreducible representations are orthogonal.
  - (b) Considering P—O bond along z-axis, derive the matrix representation of vertical planes in POCl<sub>3</sub> molecule.
  - (c) Identify the point group for each of the following molecules:
    - (i) Be(CH<sub>3</sub>COCHCOCH<sub>3</sub>)<sub>2</sub>(ignore H atoms)
    - (ii)  $ClF_2^+$
    - (iii) Staggered Cr(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>
    - (iv)  $AsF_4^-$ .

3 + 5 + 2

- 6. (a) Prove that if a C<sub>4</sub> axis and one plane containing this axis exists then there must be a second plane which contain C<sub>4</sub> axis and at an angle of 45° to the first one.
  - (b) Explain why the ligand field (d-d) bands are shifted only slightly for [CoX (NH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup> ions (X<sup>-</sup>=F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>), but charge-transfer bands are shifted greatly for the series?
  - (c) Prove that each element in a group has a unique inverse.
  - (d) Classify the following Oxides as normal or inverse spinel with explanation:

3 + 3 + 1 + 3

7. (a) Using "Great Orthogonality Theorem" prove that the sum of the squares of the characters in any irreducible representation equals to the order of the group.

- (b) From the reaction of NiBr<sub>2</sub> and Ph<sub>2</sub>Et P, it is possible to isolate green crystals of [Ni(Ph<sub>2</sub>Et P) Br<sub>2</sub>], which have a magnetic moment of 3.20 B.M. and red crystals of [Ni(Ph<sub>2</sub>Et P) Br<sub>2</sub>], which have a magnetic moment of zero. When either of these is dissolved in dichloromethane at 40°C, the resulting solution has a magnetic moment of 2.69 B.M. Suggest structures for the green and red crystals and offer an explanation for the solution magnetic moment.
- (c) The ligand to metal charge transfer bands increases in energy in the series:

  [Co I<sub>4</sub>]<sup>-</sup> < [Co Br<sub>4</sub>]<sup>-</sup> < [Co Cl<sub>4</sub>]<sup>-</sup>. Explain.
- (d) Explain why the electronic spectral bands due to d-d transitions in a transition metal complex are broad. 3+3+2+2
- 8. (a) Write notes on:
  - (i) Molybdenum blue
  - (ii) Ruthenium red.

- (b) What are electron transport protein? Give examples.
- (c) Discuss the origin of red colour of Rubredoxin.  $(3 \times 2) + 2 + 2$