No 009802

B-JGT-K-DIA

CHEMISTRY

Paper I

| Time Allowed : Three Hours | Maximum Marks : 200 |

INSTRUCTIONS

Candidates should attempt questions 1 and 5 which are compulsory, and any THREE of the remaining questions, selecting at least ONE question from each Section.

All questions carry equal marks.
Marks allotted to parts of a question are indicated against each.

Assume suitable data, if considered necessary, and indicate the same clearly.

Answers must be written in ENGLISH only.

Unless otherwise indicated, symbols and notations have their usual meanings.

SECTION A

1. (a) Devise a Born – Haber cycle for the formation of Na_2O_2. 10

    (b) In a hexagonal close-packed system, how many octahedral and tetrahedral voids belong to each sphere ? Illustrate with the help of a diagram. 10

(c) Explain the equivalence of all Fe – CO bonds in trigonal bipyramidal $Fe(CO)_5$ using Berry's pseudorotation.   *10*

(d) Write the two possible resonance forms of laughing gas molecule.   *10*

2. (a) Write the Schrödinger equation for the hydrogen atom. What are the different quantum numbers required to specify the hydrogen atom wave functions ? What is the total orbital degeneracy for (i) the ground state (ii) the first excited state of the hydrogen atom ? Comment on the difference in the orbital angular momentum of the ground state in the wave mechanical model and the Bohr model.   *30*

(b) Superacid systems are necessarily non-aqueous. Explain.   *10*

3. (a) Formic acid has an acid dissociation constant $K_a = 1.8 \times 10^{-4}$ mole/litre at 25°C. You are to titrate about 2 N aqueous formic acid solution with 2 N aqueous NaOH solution with the help of pH-metric method of titration. What will be the pH of the solution at the equivalence point ?   *15*

(b) The Marsh test indicates the presence of arsenic in compounds such as H_3AsO_4 by reaction with metallic zinc in dilute H_2SO_4 to give AsH_3, $ZnSO_4$ and water.

What is the ratio of the stoichiometric coefficients of H_3AsO_4 and Zn in the balanced equation for the Marsh test ?   *15*

(c) With an appropriate example, discuss the difference between acidity and nucleophilicity.   *10*

4. (a) For the nitrogen fixation reaction, eight electrons are released though six electrons are needed to reduce one N_2 molecule. Account for the rest two electrons. What is the role of molybdenum in the larger protein of nitrogenase ?   *20*

(b) Name the complex $K[PtCl_3(C_2H_4)]$. Describe its geometry and bonding.   *20*

SECTION B

5. (a) Using modified crystal field theory explain :   *10*

     (i) $KMnO_4$ with d^0 electronic configuration is violet in colour.

     (ii) HgS (Vermilion) with d^{10} electronic configuration is red in colour.

     (iii) ZnS with d^{10} electronic configuration is colourless.

    (b) Explain the different modes of CO bonding in metal carbonyls, with specific examples.   *10*

    (c) The absorption bands of (M^{3+}) lanthanide ions in general are very sharp as compared to the absorption bands of transition metal ions.   *10*

    (d) Poisoning caused by mercuric ion can be treated with chelating agents for removal but the same is not effective while treating for poisoning caused by mercury alkyls.   *10*

6. (a) A polarogram was recorded for a deaerated aqueous solution of 5 mM $K_4Fe(CN)_6$ in 1 M K_2SO_4 using dropping mercury electrode and saturated calomel electrode as a working and reference electrode respectively. Discuss the nature of the current – voltage curve. Define half wave potential and diffusion current.   *20*

(b) Human body discharges about 960 g of CO_2 per day. If the cabin for an astronaut has a volume of 7600 L and the partial pressure of CO_2 must be maintained at no more than 4·1 torr at 27°C, what weight of CO_2 must be removed on the first day of the voyage ? (Assume that the initial partial pressure of CO_2 is zero)   *20*

7. (a) Explain the eclipsed configuration of the two halves of $\{Re_2Cl_8\}$ unit in $K_2[Re_2Cl_8]$ based on multiple metal bonding.   *20*

   (b) Show that both the reactions satisfy the conditions for oxidative addition reactions.

   (i) $SnCl_2 + Cl_2 \rightarrow SnCl_4$

   (ii) $[Ir(CO)(PPh_3)_2Cl] + H_2 \rightarrow$
   $$[Ir(CO)(H)_2(PPh_3)_2Cl]$$

   Do you anticipate the addition of hydrogen is a case of oxidation in reaction (ii) ?   *20*

8. (a) Explain in thermodynamic terms why crystallographic defects may be found in seemingly pure materials. Discuss based on a simple quantum mechanical model, the origin of colour in colour centre defects.   *20*

   (b) Paramagnetic $K_2[NiCl_4]$ on reaction with KCN produces diamagnetic $K_2[Ni(CN)_4]$. Find out the splitting of the d-orbitals in both cases to explain the magnetic behaviour by crystal field theory.   *20*