

This question paper contains 8+4 printed pages]

HPAS (M)—2015

CHEMISTRY

Paper I

Time : 3 Hours

Maximum Marks : 150

Note :— Question No. 1 is compulsory and attempt any four questions out of the remaining six questions. i.e. attempt five questions in all. All parts of a question must be attempted in continuation at one place.

1. (a) All lanthanide metals form stable compounds with the metal in +3 oxidation state. However, Ce and Eu respectively form highly stable compounds with the metal in +4 and +2 oxidation states. Explain.
- (b) The effective magnetic moment of copper acetate monohydrate is 1.4 B.M. per copper atom at 300 K and this value decreases further with lowering of the temperature. Explain.

P.T.O.

- (c) If iodine is dissolved in an aqueous solution of potassium iodide (KI), an intense yellow colored species is formed. Discuss the reaction and the structure of intense yellow colored species.
- (d)  $[\text{Ni}(\text{en})_3]^{2+}$ , where en = ethylenediamine, is nearly  $10^{10}$  times more stable than  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ . Explain.
- (e) Why is  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  blue coloured while anhydrous  $\text{CuSO}_4$  is nearly colourless ?
- (f) Which of the following species has higher bond order and higher bond energy  $\text{N}_2$ ,  $\text{N}_2^+$ ,  $\text{N}_2^-$  ? Explain.
- (g) Calculate the ionic strength of an aqueous solution containing 0.004 M NaCl + 0.002 M  $\text{CaCl}_2$ .
- (h) How many crystal systems are known and what are they ?
- (i) In writing thermochemical equations, why is it important that the physical state of the reacting substances and products be indicated ?

- (i) What is the change in the rotational constant  $B$  when hydrogen is replaced by deuterium in the hydrogen molecule ? 10×3=30

2. (a) The paramagnetism of  $O_2$  molecule can very well be explained by the molecular orbital theory. Explain by drawing molecular orbital diagram of  $O_2$  molecule and identify the orbitals which contain the unpaired electrons.

- (b) Arrange the following metal-carbonyl complexes in the decreasing order of the carbonyl stretching frequency :

$[Ni(CO)_4]$ ,  $[Co(CO)_4]^-$ , and  $[Fe(CO)_4]^{2-}$ . Justify your answer.

P.T.O.

- (c) Identify the acceptable wave functions among the following :

$$\psi = x^2$$

$$\psi = \sin x$$

$$\psi = e^x$$

$$\psi = \tan x$$

$$\psi = e^{-x^2}$$

- (d) Define Mutual exclusion principle and comment on the IR and Raman activities of the normal vibrations of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  molecules (corresponding to symmetric stretching, symmetric bending and asymmetric stretching).

- (e) Calculate the nuclear partition function of ortho  $\text{H}_2$  and ortho  $\text{D}_2$  molecules.

5×6=30



3. (a) When CO is ionized to give  $\text{CO}^+$  ion by the removal of one electron, the bond length decreases from 1.28 Å in CO to 1.115 Å in  $\text{CO}^+$ . Explain this reaction with the help of molecular orbital diagram.
- (b) Discuss the d-orbital splitting for  $[\text{V}(\text{O})(\text{H}_2\text{O})_5]^{2+}$ , given that V = O bond distances is very short.
- (c) A certain metal (A) is boiled in dilute nitric acid to give a salt (B) and an oxide of nitrogen (C). An aqueous solution of B with brine gives a precipitate (D) which is insoluble in ammonium hydroxide. On adding aqueous solution of B to hypo ( $\text{Na}_2\text{S}_2\text{O}_3$ ) solution, a white precipitate (E) is obtained. E on standing turns to a black compound (F). Identify A, B, C, D, E and F.

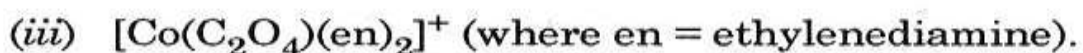
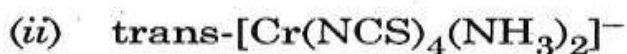
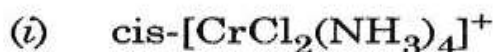
(d) One mole of an ideal gas is confined in a cylinder by a piston at  $27^{\circ}\text{C}$  and at a pressure of 1 atm. The external force on the piston is suddenly decreased by 20%. Assuming that isothermal conditions are maintained and the final state attained is also an equilibrium state, calculate (a) the change in internal energy (b) the external work done ( $R = 8.313 \text{ JK}^{-1} \text{ mol}^{-1}$ ).

(e) Highlight the merits of van der Waals' equation. 5×6=30

4. (a) Account for the fact that in  $\text{KCuF}_3$  two Cu ..... F distances are shorter ( $1.96 \text{ \AA}$ ) whereas four Cu ..... F distances are longer ( $2.07 \text{ \AA}$ ).

(b) How do you explain qualitatively the position of  $\text{I}^-$  and CO at the opposite ends of the spectrochemical series from crystal field/ligand field theories ?

(c) Name the following compounds according to IUPAC rules :



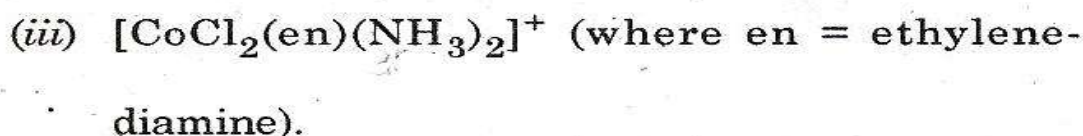
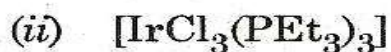
(d) What is Clausius-Clapeyron equation ? How do you determine the molar heat of vaporization using the Clausius-Clapeyron equation ?

(e) At a given temperature, the equivalent conductivity of 0.1 N solution of a weak acid HA is  $4.48 \text{ ohm}^{-1} \text{ cm}^2$  and the ionic conductivities of  $\text{H}^+$  and  $\text{A}^-$  ions at infinite dilutions are 418 and  $30 \text{ ohm}^{-1} \text{ cm}^2$ , respectively. Calculate the dissociation constant of the acid.

$$5 \times 6 = 30$$

P.T.O.

5. (a) Draw all possible isomers of :



(b) The absorbance of a 0.1 M aqueous solution of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  was found to be 0.56 when measured in a 1 cm cuvette. A distorted absorption band was centered at  $20,300 \text{ cm}^{-1}$ . Account for the spectrum and calculate the molar absorbance ( $\epsilon$ ). What would be the absorbance of the same solution in a 2 cm cuvette ?

(c) What are fast reactions ? How do you study the reaction rate using stopped flow technique ? What are the advantages of stopped flow method ?

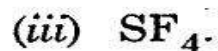
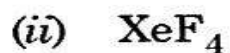
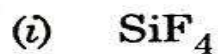


(d) One kilogram of a mixture contains equal parts by weight of benzene and toluene. Calculate the mole fractions of each component. How many grams of toluene should be added to make each mole fraction = 0.5 ?

(e) An excited atom has a mean life of  $\sim 10^{-8}$  s and radiates a photon while coming down to the ground state. Calculate the inherent uncertainty in the frequency of the photon ( $h = 1.054 \times 10^{-34}$  Js).

5×6=30

6. (a) Which of the following molecule will have a permanent dipole moment ? Justify your answer :



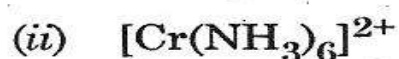
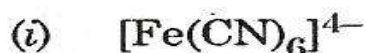
P.T.O.

- (b) When deep-red  $\text{PtF}_6$  vapour is mixed with an equal amount of Xe gas, the gases react immediately at room temperature to produce a yellow solid. Explain the reaction and identify the product.
- (c) If two heat reservoirs at temperatures  $T_1$  and  $T_2$  ( $T_1 > T_2$ ) are connected, heat will flow from high temperature to lower temperature. Let "q" be the amount of heat transferred from higher temperature to lower temperature. Calculate  $\Delta S$  of the two reservoirs.
- (d) Explain briefly the following with necessary diagrams :
- (i) Fluorescence
  - (ii) Phosphorescence.
- (e) Show that for a first order reaction, the time required for 99.9% of the reaction to take place is nearly 10 times that required for one-half of the reaction. ( $\log 2 = 0.3010$ ).

5×6=30

7. (a) Which single spectroscopic method out of mass, UV-vis, NMR, IR and Raman spectroscopy would be best suited to verify the oxidation state of the  $O_2$  ligand in oxyhemoglobin ? Justify your answer.

(b) Predict the number of unpaired electrons and calculate the spin-only magnetic moments at  $25^\circ\text{C}$  for each of the following :



(c) At a  $\text{Cys}_2\text{His}_2$  site,  $\text{Zn}(\text{II})$  ion binds approximately two orders of magnitude more tightly than does  $\text{Cd}(\text{II})$  ion; however, at a  $\text{Cys}_4$  site,  $\text{Cd}(\text{II})$  ion binds two to three orders of magnitude more tightly. Explain. [Cys = Cysteine; His = Histidine].

(d) Explain briefly :

(i) Surfactants and how do you classify the surfactants ?

(ii) Micelles

(iii) Critical Micelle Concentration.

(e) A solution containing 3.00 gms of an organic solute per 100 gms of  $\text{CCl}_4$  boils at  $77.3^\circ\text{C}$  at 1 atm. pressure. Calculate the molecular weight of the solute, assuming the normal boiling point of  $\text{CCl}_4$  to be  $76.8^\circ\text{C}$ .  $K_b$  for  $\text{CCl}_4 = 5.0 \text{ Kmol}^{-1}$ .  $5 \times 6 = 30$