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* quesions. 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*) $[Ni(en)_3]^{2+}$, where en = ethylenediamine, is nearly 10^{10} times more stable than $[Ni(NH_3)_6]^{2+}$. Explain.

(*e*) Why is $CuSO_4.5H_2O$ blue coloured while anhydrous $CuSO_4$ is nearly colourless ?

(*f*) Which of the following species has higher bond order and higher bond energy N_2, N_2^+, N_2^- ? Explain.

(*g*) Calculate the ionic strength of an aqueous solution containing 0.004 M NaCl + 0.002 M $CaCl_2$.

(*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 ?

(*j*) 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.

(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 CO_2 and H_2O molecules (corresponding to symmetric stretching, symmetric bending and asymmetric stretching).

(e) Calculate the nuclear partition function of ortho H_2 and ortho D_2 molecules. 5×6=30

3. (*a*) When CO is ionized to give CO^+ ion by the removal of one electron, the bond length decreases from 1.28 Å in CO to 1.115 Å in CO^+. Explain this reaction with the help of molecular orbital diagram.

(*b*) Discuss the d-orbital splitting for $[V(O)(H_2O)_5]^{2+}$, 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 ($Na_2S_2O_3$) 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°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 JK^{-1} mol^{-1}).

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

4. (*a*) Account for the fact that in $KCuF_3$ two Cu ..... F distances are shorter (1.96 Å) whereas four Cu ..... F distances are longer (2.07Å).

(*b*) How do you explain qualitatively the position of 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 :

(*i*) cis-$[CrCl_2(NH_3)_4]^+$

(*ii*) trans-$[Cr(NCS)_4(NH_3)_2]^-$

(*iii*) $[Co(C_2O_4)(en)_2]^+$ (where en = ethylenediamine).

(*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 ohm^{-1} cm^2 and the ionic conductivities of H^+ and A^- ions at infinite dilutions are 418 and 30 ohm^{-1} cm^2, respectively. Calculate the dissociation constant of the acid. 5×6=30

5. (*a*) Draw all possible isomers of :

(*i*) $[RuCl_2(NH_3)_4]$

(*ii*) $[IrCl_3(PEt_3)_3]$

(*iii*) $[CoCl_2(en)(NH_3)_2]^+$ (where en = ethylene-diamine).

(*b*) The absorbance of a 0.1 M aqueous solution of $[Ti(H_2O)_6]^{3+}$ was found to be 0.56 when measured in a 1 cm cuvette. A distorted absorption band was centered at 20,300 cm^{-1}. Account for the spectrum and calculate the molar absorbance (ε). 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 ~ 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 × 10^{-34} Js). 5×6=30

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

(*i*) SiF_4

(*ii*) XeF_4

(*iii*) SF_4.

(*b*) When deep-red 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 ΔS 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°C for each of the following :

(*i*) $[Fe(CN)_6]^{4-}$

(*ii*) $[Cr(NH_3)_6]^{2+}$

(*iii*) $[EuCl_6]^{4-}$.

(*c*) At a Cys_2His_2 site, Zn(II) ion binds approximately two orders of magnitude more tightly than does Cd(II) ion; however, at a Cys_4 site, Cd(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 CCl_4 boils at 77.3°C at 1 atm. pressure. Calculate the molecular weight of the solute, assuming the normal boiling point of CCl_4 to be 76.8°C. K_b for CCl_4 = 5.0 $Kmol^{-1}$. 5×6=30