This question paper contains **16** printed pages]

HPAS (Main)—2012

CHEMISTRY

Paper I

Time : 3 *Hours* *Maximum Marks :* 150

Note :— Question No. **1** is compulsory and attempt any other *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*) The wavefunctions for hydrogen 1*s*- and 2*s*-atomic orbitals are given as :

$$\psi_{1s} = Ne^{-r/a_0} \text{ and}$$

$$\psi_{2s} = N\left\{1 - \frac{1}{2}\left(\frac{r}{a_0}\right)\right\}e^{-r/2a_0}$$

where :

$$a_0 = \frac{\varepsilon_0 h^2}{r m_e e_2}$$

P.T.O.

which is Bohr radius. Sketch the form for two wavefunctions, and find the location of the node in the 2*s*-orbital in terms of a_0.

(*b*) What is the most probable distance (expressed in terms of a_0) of a 1*s*-electron from the nucleus in a hydrogen atom ?

(*c*) Draw labelled molecular orbital scheme for B_2, noting that the molecule contains two unpaired electrons.

(*d*) The well-known Clausius-Clapeyron equation :

$$\ln p_A = \frac{-\Delta H^\circ_{vap}}{RT} + \text{constant}$$

tells us that a plot of $\ln p_A$ against 1/T should be :

(*i*) non-linear with a slope of $\left(-\Delta H^\circ_{vap}/R\right)$

(*ii*) linear with a slope of $\left(-\Delta H^{\circ}_{vap}/R\right)$

(*iii*) linear with a slope of $\left(+\Delta H^{\circ}_{vap}/R\right)$

(*iv*) non-linear with a slope of $\left(+\Delta H^{\circ}_{vap}/R\right)$.

(*e*) The gas phase reaction between CO and Cl_2 produces phosgene :

$$CO(g) + Cl_2(g) \rightarrow COCl_2(g).$$

Write the order of the reaction with respect to Cl_2 and to CO ?

(*f*) The H_2O_2 behave as ..... with respect to Fe^{3+}/Fe^{2+} at standard concentrations.

(*i*) oxidant

(*ii*) reductant

(*iii*) both, oxidant and reductant

(*iv*) remains non-reactive, inert.

(*g*) Write down the spectrochemical series of ligands with respect to their power in splitting *d*-orbitals of a particular metal ion.

(*h*) Construct a molecular orbital diagram of an octahedral complex (depicting bonding, antibonding and non-bonding molecular orbitals between metal ion and ligands).

(*i*) Complete the reactions :

(*a*) $2UO_2SO_4(aq) + 6NH_3(aq) + 3H_2O(l) \rightarrow \underline{?} + \underline{?}$

(*b*) $8C(\text{graphite}) + K^+_{(NH_3)} + e^-_{(NH_3)} \rightarrow \underline{?}$

(*j*) Sketch Jablonski Diagram and properly label it.

10×3=30

2. (*a*) The ionisation energies of hydrogen (13.6 eV) and of oxygen (13.5 eV) are approximately the same. Why ?

(*b*) Explain what is meant by the radial distribution function (rdf) of an electron, and sketch the form of the rdf for the 1*s* and 2*s*-orbitals of hydrogen described as :

$$\psi_{1s} = Ne^{-r/a_0} \text{ and}$$

$$\psi_{2s} = N\left\{1 - \frac{1}{2}\left(\frac{r}{a_0}\right)\right\}e^{-r/2a_0}$$

where :

$$a_0 = \frac{\varepsilon_0 h^2}{\pi m_e e_2}.$$

(*c*) The densities of diamond and ice are 3.5 and 0.94 g cm^{-3} respectively. Both solids adopt analogous structures. In diamond the C—C bond length is 0.155 nm, whereas in water the O—O distances are close to 0.276 nm. Comment.

(*d*) Balance the following redox reaction in acidic medium :

$$K_2Cr_2O_7 + NaI + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + I_2 + H_2O + Na_2SO_4 + K_2SO_4$$

(*e*) Calculate the root mean square velocity of H_2 at 0°C. 5×6=30

3. (*a*) (*i*) Explain how and why the rate of a bimolecular reaction in the gas phase depends on the temperature.

(*ii*) Justify, for the case of a gas phase reaction, the form of the Arrhenius equation, $k = A \exp(-E_a/RT)$.

(*b*) (*i*) What is ΔG° at 25°C for the following reactions ?

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g).$$

(*ii*) What is ΔG at 25°C under conditions where the partial pressures of H_2, CO_2, H_2O and CO are 10, 20, 0.02 and 0.01 atm, respectively ?

(c) (i) What is overpotential ? Explain.

(ii) Distinguish between physisorption and chemisorption. 3×10=30

4. (a) Calculate $\Delta S_{universe}$ for iron oxidation at 25°C involving $\Delta S_{surrounding}$ = +5510 J/K/mol :

$S_{Fe_2O_3}$ = 87.4 J/K/mol;

S_{Fe} = 27.3 J/K/mol;

S_{O_2} = 205 J/K/mol.

(b) Explain the observations that the bond length in N_2^+ is 2 pm greater than in N_2, while the bond length in NO^+ is 9 pm less than in NO.

(c) What are the characteristics of different types of molecular orbitals ?

(*d*) Differentiate between heterogeneous and homogeneous catalysis.

(*e*) The stoichiometric equation for the iodination of propane in an aqueous solution of sulphuric acid is :

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3ICOCH_3(aq) + H^+(aq) + I^-(aq)$$

Draw a reaction profile. 5×6=30

5. (*a*) Draw a molecular orbital energy level diagram for CO. How does it differ from that for N_2 ? The bond dissociation enthalpy of N_2 is 942 kJ/mol and that for CO is 1072 kJ/mol. Explain this observation.

(*b*) The (Tl^+/Tl) couple was prepared by saturating 0.1 M KBr with TlBr and allowing the Tl^+ from the relatively insoluble bromide to equilibrate. This couple was observed to have a potential of –0.443 V with respect to a (Pb^{2+}/Pb) couple in which Pb^{+2} was 0.1 molar. What is the solubility product of TlBr ?

(*c*) Hydrocarbon oxidation by dissolved oxygen is thought to occur via the following free-radical mechanism :

$$RH + O_2 \xrightarrow{k_1} R^{\cdot} + {}^{\cdot}O_2H$$

$$R^{\cdot} + O_2 \xrightarrow{k_2} RO_2^{\cdot}$$

$$RO_2^{\cdot} + RH \xrightarrow{k_3} RO_2H + R^{\cdot}$$

$$2R^{\cdot} \xrightarrow{k_4} R_2$$

Use the steady state approximation applied to $RO_2^{\bullet}$ to find an expression relating k_2 and k_3.

3×10=30

6. (*a*) Calculate the stabilization energies for the following complexes :

(*i*) $\left[Cr(H_2O)_6\right]^{3+}$

(*ii*) $\left[Fe(CN)_6\right]^{4-}$

(*iii*) $\left[Mn(CN)_6\right]^{3-}$.

(*b*) (*i*) Which effective method should be used for other Lanthanide ions separation from monazite ore ?

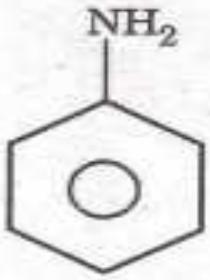
(*ii*) Why most of the compounds containing Ce^{3+} are colourless, even though *f-f* transition exists in the Ce^{3+} ion ?

(*c*) Complete the following chemical equations :

(*i*) $N_2O + 2K \xrightarrow{2NH_3}$

(*ii*) $\left[Pt(NH_3)_4\right]Br_2 \xrightarrow{K/NH_3}$

(*iii*) $H_3CCOOH + H_2SO_4 \longrightarrow$

(*iv*)  $+ H_2SO_4 \longrightarrow$

(*v*) $MnO_4^- + 5HF \longrightarrow$

(*vi*) $BaI_2 + Zn(CNS)_2 \xrightarrow{SO_2}$

(*d*) Both $\left[Fe(CN)_6\right]^{4-}$ and $\left[Fe(H_2O)_6\right]^{2+}$ appear colourless in dilute solutions. The former ion is low-spin and the latter is high-spin. Find out the number of unpaired electrons in each of these ions and also explain the colourless property of these ions.

(*e*) (*i*) How many structural and geometrical isomers can be written for the following without counting ring compounds :

(I) C_3H_5Cl

(II) $C_3H_4Cl_2$.

(*ii*) Explain the term hapticity citing suitable examples. 5×6=30

7. (*a*) (*i*) How are fluxional molecules identified ?

(*ii*) What are π-acid ligands ? Give examples.

(*iii*) Sketch the *two* isomeric forms of :

$$\left[\left(\eta^5 - C_5H_5\right)_2 Fe_2(CO)_4\right].$$

(*b*) (*i*) For a square coplanar complex :

$$\left[Pt(NH_3)(NH_2OH)\,Py(NO_2)\right]^+,$$

how many geometric isomers are possible ? Draw them.

(*ii*) Hexaaquairon (III) ion is practically colourless. Its solution become red when NCS^- is added. Explain, why ?

(c) (i) In each case indicate which liquid will have the higher boiling point and explain why ?

(I) CO_2 *or* SO_2

(II) Cl_2 *or* Br_2.

(ii) Write a note on auto-ionization of SO_2.

(d) (i) Write electronic configuration of the following rare earths :

(I) Eu

(II) Gd

(III) Ce^{3+}

(IV) Th^{+4}.

(*ii*) Why are the colour of lanthanides not affected by ligands ?

(*iii*) Draw molecular orbital diagram of $\left[Mn(CN)_6\right]^{3-}$ ion and also predict its geometry.

(*e*) What is Jahn-Teller effect ? Explain by drawing molecular orbital diagrams for $\left[Cu(H_2O)_6\right]^{2+}$ and $\left[CuF_6\right]^{4-}$ ions. 5×6=30