Total No. of printed pages = 8

2015

CHEMISTRY

(Major)

Theory Paper : M-4.1

Full Marks – 60

Time – 2½ hours

The figures in the margin indicate full marks
for the questions.

1. Answer the following :   7×1=7

   (a) Why the stability of MX_4 tetrahalides of group 14 elements of the periodic table decreases from CCl_4 to $PbCl_4$ and from CF_4 to Cl_4.

   (b) Why carbon show much greater tendency for catenation in comparison to Si ?

   (c) Which of the two compounds, $MgCO_3$ and $CaCO_3$ is expected to have a higher decomposition temperature and why?

[Turn over

(d) The melting point of AgCl is only 445°C while that of KCl is 776°C though the crystal radii of Ag^+ and K^+ ions are almost the same. Give reason.

(e) Draw the structures of pentoxides of nitrogen and phosphorous.

(f) Write the valence shell electronic configurations of each element of group 15 of the periodic table.

(g) Why does sulfur in the vapour state exhibits paramagnetic behaviour ?

2. Answer the following :   4×2=8

(a) Arrange the Oxoacids of phosphorous, H_3PO_2, H_3PO_3 and H_3PO_4 in order of decreasing acid strength. How will you explain this trend by considering the structures of the Oxoacids?

(b) Draw structures of a Closo- and a nido-polyhedral borane.

(c) The reaction
$Et_3SiI + AgBr \rightarrow Et_3SiBr + AgI$,
(where Et = $-C_2H_5$) is irreversible. Explain giving appropriate reasons.

(d) Comment on the colour and magnetic properties of alkali metals in pure liquid ammonia at different concentrations. Give appropriate reasons.

3. Answer any *three* of the following :   5×3=15

(a) (i) Fluorine is more electronegative than Cl, although its electron gain enthalpy is less than that of Cl. Explain the statement giving reasons.   2

    (ii) Write about the mechanism of formation and depletion of ozone layer in the stratosphere.   3

(b) (i) Using Slater's rules, calculate Z* for a 3d electron in Mn.   2

    (ii) Write about the use of liquid HF as a solvent in terms of acid-base, precipitation and solvolysis reactions. 3

(c) (i) Potassium dichromate is a common oxidizing agent in acidic medium for the titration of $Fe^{2+}(aq)$. Is there any harm if the solution contains a large quantity of Cl^- ions ? Explain giving appropriate reasons.
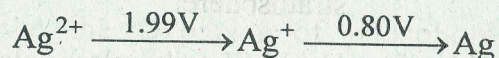
Given $E^0_{Cr_2O_7|Cr^{3+}} = 1.38V$

$E^0_{Fe^{3+}|Fe^{2+}} = 0.77V$

$E^0_{Cl_2|Cl^-} = 1.36V$ 2

(ii) Write about the various allotropic forms of sulfur in solid, liquid and gaseous states.   3

(d) (i) Draw a Frost diagram from the following Latimer diagram of Ag : 3

$$Ag^{2+} \xrightarrow{1.99V} Ag^+ \xrightarrow{0.80V} Ag$$

(ii) Write about the preparation and structure of hydrazine.   2

(e) (i) Draw the molecular structures of Peroxodisulphuric acid and Peroxomonosulphuric acid.   2

(ii) Write about the Clathrate compounds with reference to stability, inert gas clathrates and clathrate hydrates.   3

4. Answer any *three* of the following :   10×3=30

(a) (i) Compare qualitatively the first ionization energies of Ca and Zn both having $4S^2$ configuration of their valence shell. 3

(ii) Explain which compound of each of the following pairs is more covalent. Give appropriate reasons :   3
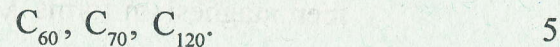
CuO or CuS, $AlCl_3$ or

$GaCl_3$, AgCl or NaCl.

(iii) Define group electronegativity. Explain the differences in the nucleophilic attack for the following reactions :   1+3=4

$CH_3I + OH^- \rightarrow CH_3OH + I^-$

$CF_3I + OH^- \rightarrow CF_3H + IO^-$
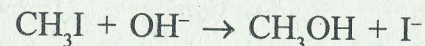
(b) (i) What are fullerenes ? How fullerenes are prepared ? Write about the structure and properties of the following :

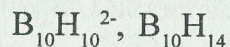$C_{60}, C_{70}, C_{120}.$ 5

(ii) "Trisilylamines such as $(H_3Si)_3N$ differ from $(H_3C_3)N$ in being planar rather than pyramidal and in being very weak Lewis bases."
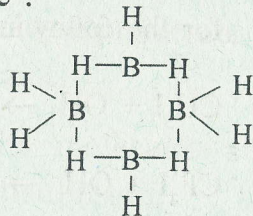
Explain the statement giving appropriate reasons.   3

(iii) Write one use each of NO and N_2O. 2

e) (i) Use Wade's rule to classify the following into closo-, nido- or arachno and name them as per rules :

$$B_{10}H_{10}{}^{2-}, B_{10}H_{14}$$

Write the stix number for the following structure :   4+1=5

(ii) Second ionization energy of Mg is approximately twice its first ionization energy. Also, the second electron gain enthalpy of oxygen is positive. Why then magnesium forms $Mg^{2+}O^{2-}$ rather than Mg^+O^- ?   2

(iii) Cesium iodide (CsI) is nearly ten times more soluble in water than sodium fluoride (NaF) but it is much less soluble than CsF. Explain giving appropriate reasons.   3

(d) (i) The reaction $HgI_2 + 2KOH \rightleftharpoons Hg(OH)_2 + 2KI$ does not show any strong tendency to proceed to one side or other and has an equilibrium constant close to 1. Explain giving appropriate reasons.   3

(ii) Explain the preparation, structure properties and uses of hydrazine.   5

(iii) What are superacids? Write how magic acid is prepared which can protonate even hydrocarbons.   2
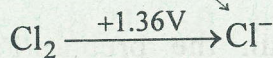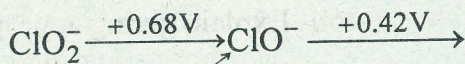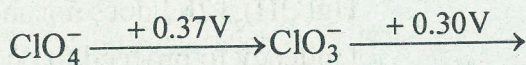
(e) (i) Will Cu^+ ion disproportionate in aqueous solution into Cu^{2+} and Cu^0 ? Explain :   3

Given $E^0{}_{Cu^+|Cu} = +0.52V$

$E^0{}_{Cu^{2+}|Cu^+} = +0.153V$

(ii) What are super oxides ? Write about the preparation and properties of super oxides. Give necessary equations. 4

(iii) The Latimer diagram of chlorine in basic medium ($P^H = 14$) is

$$ClO_4^- \xrightarrow{+0.37V} ClO_3^- \xrightarrow{+0.30V}$$

$$ClO_2^- \xrightarrow{+0.68V} ClO^- \xrightarrow{+0.42V}$$

$$Cl_2 \xrightarrow{+1.36V} Cl^-$$

Calculate E^0 for the couple $ClO^- - Cl^-$.

3