

Total No. of printed pages = 8

3 (Sem 4) CHM M1

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, H₃PO₂, H₃PO₃ and H₃PO₄ 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
$$\text{Et}_3\text{SiI} + \text{AgBr} \rightarrow \text{Et}_3\text{SiBr} + \text{AgI},$$

(where Et = -C₂H₅) 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 : $5 \times 3 = 15$

(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 $\text{Fe}^{2+}(\text{aq})$. Is there any harm if the solution contains a large quantity of Cl^- ions? Explain giving appropriate reasons.

Given $E^0_{\text{Cr}_2\text{O}_7|\text{Cr}^{3+}} = 1.38\text{V}$

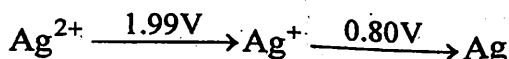
$$E^0_{\text{Fe}^{3+}|\text{Fe}^{2+}} = 0.77\text{V}$$

$$E^0_{\text{Cl}_2|\text{Cl}^-} = 1.36\text{V}$$

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



(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 : $10 \times 3 = 30$

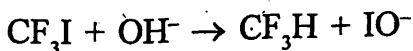
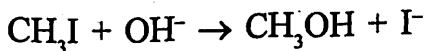
(a) (i) Compare qualitatively the first ionization energies of Ca and Zn both having $4s^2$ configuration of their valence shell. 3

(ii) Explain which compound of each of the following pairs is more covalent. Give appropriate reasons : 3

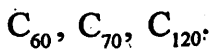
CuO or CuS, $AlCl_3$ or

$GaCl_3$, AgCl or NaCl.

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



(b) (i) What are fullerenes ? How fullerenes are prepared ? Write about the structure and properties of the following :



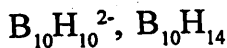
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- (ii) "Trisilylamines such as $(\text{H}_3\text{Si})_3\text{N}$ differ from $(\text{H}_3\text{C})_3\text{N}$ in being planar rather than pyramidal and in being very weak Lewis bases."

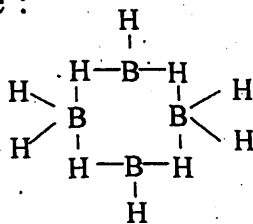
Explain the statement giving appropriate reasons. 3

- (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 :



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 $\text{Mg}^{2+}\text{O}^{2-}$ 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 $\text{HgI}_2 + 2\text{KOH} \rightleftharpoons \text{Hg(OH)}_2 + 2\text{KI}$ 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

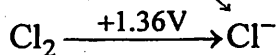
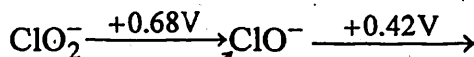
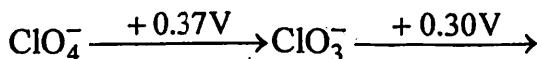
(e) (i) Will Cu^+ ion disproportionate in aqueous solution into Cu^{2+} and Cu^0 ? Explain : 3

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

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

(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 ($\text{pH} = 14$) is



Calculate E^0 for the couple $\text{ClO}^- - \text{Cl}^-$.

3