2019
CHEMISTRY
[HONOURS]
Paper : I

Full Marks : 50   Time : 2 Hours

The figures in the right-hand margin indicate marks.
Candidates are required to give their answers in
their own words as far as practicable.

1.   Answer any **five** questions: 2×5=10

   a)   Write down the Gutmann's rule.

   b)   Give example of one inorganic disproportionation reaction and one inorganic comproportionation reaction.

   c)   Define Schiff bases and synthesise one tridentate schiff base.

   d)   Which of two HBrO or HClO is stronger and why?

   e)   Define ionic potential.

   f)   Explain the difference between standard potential and formal potential.

   g)   Why does SbF_5 increases the acidity and conductivity of liquid HF but NaF reduces its acidity?

   h)   The first Bohr radius of hydrogen atom is $0.529\,\text{Å}$. Find the same for He^+ ion.

2.   Answer any **four** questions: 5×4=20

   a)   i)   Calculate lattice energy of sodium chloride (NaCl) with the help of following data:

   Electronic charge $= 4.8 \times 10^{-10}$ e.s.u.,
         Born exponent $= 9$
         Madelung constant for NaCl $= 1.748$,
         Ionic radius of $Na^+ = 0.95\,\text{Å}$ and ionic radius of $Cl^- = 1.81\,\text{Å}$.

         ii)   What is lattice energy?   4+1=5

   b)   i)   i)   From the following Latimer diagram, establish that H_2O_2 is unstable toward disproportionation:

         $$O_2 \xrightarrow{0.70\,V} H_2O_2 \xrightarrow{1.76\,V} H_2O$$

         ii)   Why is the bond energy of Li_2 less than that of H_2?   3+2=5

   c)   i)   Write at least three differences between VB and MO theory.

         ii)   All I−F bonds in IF_7 are not equivalent— Explain. $2\frac{1}{2}+2\frac{1}{2}=5$

d) i) Calculate the electronegativity of Arsenic atom $(z = 33)$ having covalent radius $1.21\,\text{Å}$.

ii) "$SnCl_2$ and $SnCl_4$ have melting points 246°C and -33°C respectively",— why?

$$3+2=5$$

e) i) Draw the structure of following species with the help of VSEPR theory:

a) NH_4^+

b) IOF_5.

ii) Write down the Pauling's rule for oxoacid strengths. Explain with suitable example. $(1\frac{1}{2}+1\frac{1}{2})+2=5$

f) i) The dipole moment of HF molecule is $1.91\,\text{D}$ and the bond distance is $0.92\,\text{Å}$. Calculate the fractional charge (δ) on H and F in the HF bond. (electronic charge $= 4.8 \times 10^{-10}$ e.s.u.)

ii) You are given $20\,\text{ml}$ of 0.2M HCl. How would you make solution of pH 7.0?
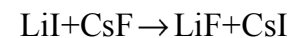
$$3+2=5$$

g) i) How many isomers are possible for the following compounds? Draw the structure:

A) $\left[Co(NH_3)_3 Cl_3\right]$
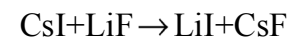
B) $\left[Cr(en)_2 (NCO)Br\right]^+$
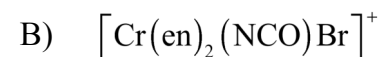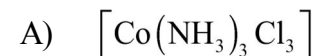
ii) Define Lux-Flood concept of acids and bases with example. $(1\frac{1}{2}+1\frac{1}{2})+2=5$
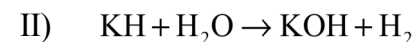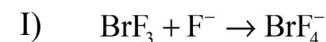
3. Answer any **two** questions: $10 \times 2 = 20$

a) i) Which of the following reaction actually takes place and why?

$$LiI + CsF \rightarrow LiF + CsI$$

OR

$$CsI + LiF \rightarrow LiI + CsF$$

ii) Identify the Lewis acids and bases in the reactions:

I) $BrF_3 + F^- \rightarrow BrF_4^-$

II) $KH + H_2O \rightarrow KOH + H_2$

iii) Arrange as per the increasing acidity:

$HClO,\ HClO_4,\ HClO_3\ \&\ HClO_2$

iv) Explain why hydrogen selenide is a stronger acid than hydrogen sulphide.

$$2+3+3+2=10$$

b) i) What are soft & hard acids and bases?

ii) Define auto-oxidation. Give two examples to explain it.

iii) "The value of radius of Bohr's orbit (a_0) agrees remarkably well with that obtained by wave mechanical treatment."— Elucidate.

iv) Compare chelating and innermetallic compounds.

v) "The equivalent weight of $KMnO_4$ is different in acid and alkaline medium."— Comment. $2 \times 5 = 10$

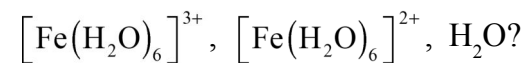c) i) Calculate the equilibrium constant for the following reaction:

$$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$$
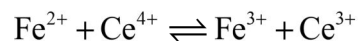
Given E^0 of $Fe^{3+}/Fe^{2+} = 0.77\,V$

and $E^0_{Ce^{4+}/Ce^{3+}} = 1.44\,V$ at $25^{\circ}C$.

ii) Calculate the pH of 10^{-8} M HCl.

iii) Which is the strongest protonic acid in the series:

$$\left[Fe(H_2O)_6\right]^{3+}, \left[Fe(H_2O)_6\right]^{2+}, H_2O?$$

iv) $ZnCl_2$ is soluble in organic solvents while $MgCl_2$ is insoluble— Explain.

$$3+2+3+2=10$$

d) i) Which is more polar and give reason:

$$NH_3 \text{ and } NF_3.$$
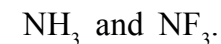
ii) F_2O_2 has a very short O–O bond $(1.217A^0)$ compared with that of H_2O_2 $(1.48A^0)$– Explain.

iii) Is $KMnO_4$ a primary standard? Reason out your answer.

iv) Arrange the following in the decreasing base strength:

Pyridine, 2-methyl pyridine, 4-methyl pyridine (towards $B(CH_3)_3$ as Lewis acid).

v) Differentiate between sp^3d^2 and d^2sp^3 hybrid orbitals. $2 \times 5 = 10$

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