2018
CHEMISTRY – HONOURS

Paper : CC-1
Full Marks : 50

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

Write the answers to Inorganic Chemistry (Group-A) and Organic Chemistry (Group-B) questions in separate answer scripts.

Group-A

[Inorganic Chemistry]

Answer question no. 1 (compulsory) and any five questions from the rest (question nos. 2 to 9)

1. Answer the following questions : 1×8

(a) What is the significance of $\psi$ in Schrödinger equation.

(b) Predict the direction of the following equilibria

$$2\text{CH}_3\text{MgF} + \text{HgF}_2 \rightleftharpoons (\text{CH}_3)_2\text{Hg} + 2\text{MgF}_2$$

(c) Write the expression of formal potential of Cu$^{2+}$/Cu$^+$ couple in presence of I$^-$ in acid medium.

(d) What will be the values of $l$ and $m_l$ for $p_z$ and dz$^2$ orbitals?

(e) What is the nature of PbNH in liquid ammonia?

(f) The term symbols for V$^{3+}$ are: 3$^F$, 3$p$, 1$^D$, 1$^S$. Identify the ground state term.

(g) Why is NH$_4$Cl used in ammoniacal medium for the precipitation of Group III A metallic ions as hydroxides?

(h) From the given Latimer diagram which of the following species will be unstable in aqueous solution?

$$\text{Cu}^{2+} \xrightarrow{0.15\text{V}} \text{Cu}^+ \xrightarrow{0.52\text{V}} \text{Cu}^0$$

2. (a) Give diagrammatic representation of radial wave function and radial distribution function for 2s and 2p orbitals for Hydrogen atom with interpretations.

(b) Arrange the following compounds according to their increasing Lewis basicity towards BMe$_3$, Me$_2$N, Me$_2$O, MeF $^3+2$
3. (a) How do the shapes of s and p orbitals can be obtained from angular function for a hydrogen like system?
(b) Write the redox reaction involved in the titration of potassium permanganate with oxalic acid in acidic medium and balance by ion-electron method.  

4. (a) Acetic acid behaves as weak acid in water, strong acid in liquid ammonia but as a base in liquid HF. Justify with reactions.
(b) Which electronic configuration is energetically more favourable amongst the following and why?
\[ \text{[Ar]} 3d^48^2, \text{[Ar]} 3d^58^1 \]  

5. (a) Find out the pH at the equivalence point for the titration of 100 ml 0.1N acetic acid with 0.1N NaOH solution (Given pKa of CH₃COOH = 4.74). Indicate the choice of indicator for this titration.
(b) Write the conjugate acids or bases of the following:
\[ \text{HSO}_4^-, \text{HS}^-, \text{O}_2^-, \text{CH}_3\text{COOH} \]  

6. (a) Construct a Frost diagram for oxygen from the following Latimer diagram in acidic solution.
\[ \text{O}_2 \xrightarrow{+0.70V} \text{H}_2\text{O}_2 \xrightarrow{+1.76V} \text{H}_2\text{O} \]
(b) Using Pauli exclusion principle find out the maximum capacity of electrons for third quantum shell.  

7. (a) Cupric ions readily oxidise potassium iodide to iodine in acidic medium. Justify the statement using the following data.
\[ E^o_{\text{Cu}^{2+}/\text{Cu}^+} = 0.15V \]
\[ E^o_{\text{I}_2/\text{I}^-} = 0.54V \]
(b) Orbital angular momentum of an orbital is \( \frac{\sqrt{6}}{2\pi} \). Identify the orbital.  

8. (a) Explain the acidity order amongst H₃PO₄, H₃PO₃ and H₃PO₂.
(b) Calculate the standard potential of the copper-zinc cell from the following redox reactions:
\[ \text{Cu}^{2+} + 2e \rightleftharpoons \text{Cu(s)} \quad E^o = +0.34V \]
\[ \text{Zn}^{2+} + 2e \rightleftharpoons \text{Zn(s)} \quad E^o = -0.76V \]  

9. (a) Elucidate the basic principle for the potentiometric titration between 100ml 0.1N Fe²⁺ solution and 0.1N KMnO₄ solution at [H⁺] = 1M.
(b) Explain how Aufbau principle is violated in the process of electron filling in lanthanoides.
(3)

Group-B

[Organic Chemistry (1A)]

Answer question no. 10 (compulsory) and any three from the rest (question nos. 11 to 15)

10. (a) Classify the following species as electrophile or nucleophile:

\[ \text{CCl}_2, \text{OCH}_3, \text{NH}_3, \text{Me}_3\text{C} \]

(b) Classify the following molecules as aromatic or antiaromatic:

\[ \text{\begin{array}{c}
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\end{array}} \quad \text{\begin{array}{c}
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\end{array}} \quad \text{\begin{array}{c}
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\end{array}} \quad \text{\begin{array}{c}
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\end{array}} \]

11. (a) Cyclooctatetraene is non-planar whereas its dianion is planar. Explain.

\[ \text{\begin{array}{c}
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\end{array}} \quad \text{\begin{array}{c}
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\end{array}} \]

(b) Although N-F bonds are much polar than N-H bonds, NF\(_3\) (0.26 D) has a smaller dipole moment than NH\(_3\) (1.46 D). Explain.

12. (a) Draw the orbital picture of H\(_2\)C\(-\text{CH} = \text{C} = \text{O}\) and also mention the hybridisation of all the carbon atoms.

(b) The boiling point of carboxylic acids are higher than those of alcohols of comparable molecular weights. Explain.

13. (a) Heat of hydrogenation of the following molecules are as follows:

\[ \text{1-Butene} + \text{H}_2 \xrightarrow{\text{Pt}} \quad [\Delta H^o = -127 \text{ KJ/mol}] \]

\[ \text{cis-2-Butene} + \text{H}_2 \xrightarrow{\text{Pt}} \quad [\Delta H^o = -120 \text{ KJ/mol}] \]

\[ \text{trans-2-Butene} + \text{H}_2 \xrightarrow{\text{Pt}} \quad [\Delta H^o = -115 \text{ KJ/mol}] \]

What should be the order of stability of molecules? Explain why.

(b) Dipole moment of 2, 3, 5, 6—tetramethyl -4-nitroaniline is lower than that of 4-nitroaniline. Explain why.

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14. (a) Draw a properly labelled diagram representing the pi molecular orbitals of 1, 3-butadiene. Indicate the HOMO and LUMO of the molecule in the ground state.

(b) Arrange the following compounds in order of increasing rate of thermal decomposition to yield nitrogen and give your reasoning.

\[ H_3C - N = N - CH_3, \quad C_6H_5CH_2 - N = N - CH_2C_6H_5, \quad H_2C - CH_2 - N = N - CH_2 - CH_3 \]

15. (a) Define addition and substitution reactions with one example for each.

(b) Out of cis-1, 2-dibromoethene and trans-1, 2-dibromoethene which one has a higher melting point and why?