2022

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-1* (Group-A) and *Organic Chemistry-1A* (Group-B) questions in *separate answer books.*

Group - A

(Inorganic Chemistry - 1)

Answer **question no. 1** (compulsory) and **any five** questions from the rest (**question nos. 2 to 9**).
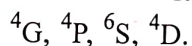
1. Answer the following questions :   1×8

   (a) Write down a set of quantum numbers that uniquely defines $4d_{z^2}$ when the external magnetic field is applied along z axis.

   (b) Predict the number of maxima when a curve is plotted between $4\pi r^2 R^2(r)$ vs. r for 5d orbital.

   (c) Predict the increasing order of energy among the following R-S terms :

 $$^4G, \ ^4P, \ ^6S, \ ^4D.$$

   (d) Identify the acid and base using suitable theory : $2HF + PF_5 \rightleftharpoons H_2F^+ + PF_6^-$

   (e) Indicate whether the pH of an aqueous solution of NaCN at 25°C is greater or lesser than 7.

   (f) Identify with reason whether the below-mentioned reaction is a double decomposition reaction or a redox reaction : $CuH + HCl = CuCl + H_2$.

   (g) Write the Nernst equation for the reduction of $Fe_2O_3(s)$:

   $$Fe_2O_3 \, (s) + 6H^+ \, (aq) + 6e^- \rightarrow 2Fe(s) + 3H_2O \, (l)$$
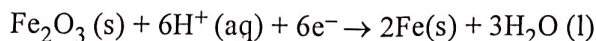
   (h) Predict the direction of the following equilibrium using HSAB concept :

   $$La_2(CO_3)_3 + Tl_2S_3 \rightleftharpoons La_2S_3 + Tl_2(CO_3)_3.$$
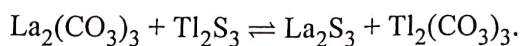
2. (a) Cu^{2+} ion readily liberates iodine from iodide ion in acid medium but not in presence of ethylene diamine.— Justify. $\left[E^{\circ}_{Cu^{2+}/Cu^+} = 0.15V, \ E^{\circ}_{Cu^{2+}/CuI} = 0.87V, \ E^{\circ}_{\frac{1}{2}I_2/I^-} = 0.54V \right]$

   (b) Discuss the physical significance of magnetic quantum number.   3+2

Please Turn Over

3. (a) Although $N(CH_3)_3$ is a stronger base than NH_3, the adduct of the latter is more stable than the former with $B(CH_3)_3$. Explain.

(b) Determine the ground state term symbol for Chromium (Atomic No. 24).   3+2

4. (a) How will you titrate an aqueous solution of acetic acid potentiometrically against an aqueous solution of NaOH? Show the expected titration curve for the neutralisation reaction.

(b) Predict and justify the correct order of basicity : CH_3^-, NH_2^-, F^-, OH^-.   3+2

5. (a) From the following Latimer diagram predict whether hypochlorous acid (HClO) will disproportionate or not in aqueous solution :

$$HClO_3 \xrightarrow{\text{1.43 V}} HClO \xrightarrow{\text{1.63 V}} Cl_2$$
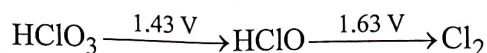
(b) Which member of the following pairs is the stronger acid? Give reason(s) for your choice.

(i) $[Al(H_2O)_6]^{3+}$ or $[Ga(H_2O)_6]^{3+}$

(ii) H_2CrO_4 or $HMnO_4$ 3+2

6. (a) Choose and justify :

(i) more basic : $[Fe(CN)_6]^{3-}$ or $[Fe(CN)_6]^{4-}$

(ii) more acidic in gas phase : PH_3 or NH_3

(iii) stronger acid : HSO_3F or $[SbF_5(\sim 14 \text{ mol } \%) + HSO_3F]$

(b) Electronic configuration of Cr is [Ar] $3d^5 4s^1$ rather than [Ar] $3d^4 4s^2$. Justify on the basis of exchange energy.   3+2

7. (a) Establish Nernst equation for MnO_4^-/Mn^{2+} system in acid medium and explain why Cl^- is oxidized by MnO_4^- only at low pH (< 6) and not in neutral medium.

$$\left[E^°_{MnO_4^-/Mn^{2+}} = 1.51 \text{V}; E^°_{\frac{1}{2}Cl_2/Cl^-} = 1.36 \text{V} \right]$$

(b) SiO_2 is added to a molten mixture of Fe + FeO. Predict the change in acidity.   3+2

8. (a) The 3s and 3p orbitals have identical energies in the hydrogen atom, but in the chlorine atom their energies are much different. Explain.

(b) Balance the following redox reaction by ion-electron method :

(i) $KMnO_4 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + CO_2 + K_2SO_4 + H_2O$

(ii) $MnO_4^- + H_2SO_3 \rightarrow Mn^{2+} + HSO_4^-$.   3+2

9. (a) The value of K_{sp} for AgCl is 1.77×10^{-10} (at 298 K). Compare the solubility of AgCl in water and in 0.0100 mol dm^{-3} hydrochloric acid.

(b) Why dilute hydrochloric acid is used for the precipitation of cations in analytical group 1? 3+2

Group - B

(Organic Chemistry - 1A)

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

10. (a) Calculate DBE (Double Bond Equivalent) for the molecular formula C_6H_7N.

(b) Draw the canonical forms of $\overset{(+)}{>}C-\overset{..}{\overset{..}{O}}Me$. Identify the most stable structure. 1+1
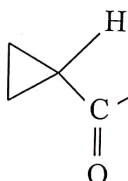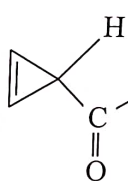
11. (a) Draw the orbital picture of $CH_2 = CH - CH\overset{..}{O}$, mentioning the hybridization of all the carbon and oxygen atoms present in the molecule.

(b) Arrange the following C – C bonds 'a', 'b' and 'c', in increasing order of bond length giving proper reasons. 3+2
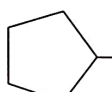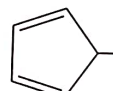
$$HC \equiv C \overset{'a'}{-\!\!-} CH = CH \overset{'b'}{-\!\!-} CH_2 \overset{'c'}{-\!\!-} CH_3$$
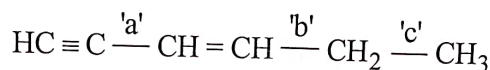
12. (a) Represent the π M.O. diagram of cyclobutadiene. How can you predict the antiaromatic nature of the molecule from the diagram?

(b) Compare the acidities of

and

and justify. 3+2

13. (a) When

—I is treated with silver perchlorate in propionic acid (solvent), the molecule is rapidly solvolysed but under same condition

—I undergoes no solvolysis at all. Explain the observation.

(b) Tertiary butanol is miscible in water in all proportions but *n*-butanol is partly miscible. Explain. 3+2

14. (a) 1,3-Butadiene is a conjugated diene whereas 2, 3-ditertiarybutyl–1, 3–butadiene behaves like a non-conjugated one. Explain.

(b) Explain why free rotation is possible about the double bond between rings of the following compound— 3+2
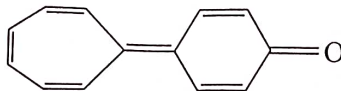
15. (a) Give one example of each type of the following reactions :

(i) Pericyclic reaction (ii) Substitution reaction (iii) Elimination reaction.

(b) Comment about the dipole moments of the following pair of molecules. 3+2