2021

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* (Group-B) questions in separate answer-book.

Group - A

[Inorganic Chemistry - 1]

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

1. Answer the following questions:

 1×8

- (a) What is the lowest value of principal quantum number that allows 'g' orbital to exist?
- (b) Predict the Lewis acid and base in the reaction : $I_2 + \Gamma \rightarrow I_3^-$.
- (c) Identify the orbital with one radial node and two angular nodes.
- (d) One mole of ferrous sulphate requires how many moles of KMnO₄ to get oxidized completely in an acidic medium?
- (e) Write Nernst equation for the following half-cell at 25°C

$$O_{2_{(a)}} + 4H^{+}_{(aq)} + 4e \rightarrow 2H_{2}O_{(l)}; E^{\circ} = 1.23V$$

- (f) Calculate the exchange energy for a f^5 system.
- (g) Whether the pH will increase or decrease, if Al(OH)3 is added to a NaOH solution?
- (h) Of the substances, Ni, Ni²⁺, Zn and Zn²⁺ which one is the strongest oxidant?

$$E_{Zn^{2+}/Zn}^{\circ} = -0.76V; E_{Ni^{2+}/Ni}^{\circ} = -0.26V$$

- **2.** (a) What are 'radial functions' and 'radial distribution functions' of an orbital? Interpret the relative penetrations of 2s and 2p orbitals from their radial distribution plots.
 - (b) Find out the 'ground state term' for a free ion with 3d⁷ configuration.

3+2

- 3. (a) Order of strength of strong acids: $H_2SO_4 > HCl > HNO_3$ in acetic acid medium but they exhibit comparable strength in water.— Explain.
 - (b) Explain why the d⁵ electronic configuration is more stable than the d⁶ electronic configuration.

3+2

- **4.** (a) The formal potential of Fe³⁺/Fe²⁺ couple becomes less than its standard reduction potential in presence of F⁻ ions, but opposite phenomenon occurs in case of Cu²⁺/Cu⁺ couple in presence of excess Γ ions. Explain.
 - (b) The solubility product (K_{sp}) of MgF₂ is 7×10^{-4} . Find its solubility in 0.01M aqueous NaF solution. 3+2
- **5.** (a) What is Aufbau principle? Explain any two of its exceptions with respect to the electron filling in Lanthanoids.
 - (b) Arrange the following in the order of acid strength:

$$H_2SeO_3$$
, H_3AsO_3 , $HClO_4$, H_2SO_4 .

- **6.** (a) Write complete, balanced equations for the following and indicate the nature of change on the acidity of the solution (*if any*):
 - (i) Trimethylamine is added to water.
 - (ii) Small amount of HCl is added to a mixture of acetic acid and sodium acetate.
 - (iii) Ammonium nitrate is added to water.
 - (b) NaCl and NaOH cannot be used instead of NH₄Cl and NH₄OH to precipitate the M(OH)₃ [M = Fe^{III}, Al^{III}, Cr^{III}] of Group IIIA in qualitative analysis.— Justify. 3+2
- 7. (a) Addition of H₃PO₄ is essential in the estimation of Fe²⁺ by K₂Cr₂O₇ using BDS (Barium-diphenylamine Sulphonate) as indicator.— Explain the statement.

Given:
$$E_{\frac{1}{2}Cr_2O_7^{2-}/Cr^{3+}}^{\circ} = 1.33V$$
, $E_{Fe^{3+}/Fe^{2+}}^{\circ} = 0.77V$, $E_{Ind(ox)/Ind(red)}^{\circ} = 0.76V$.

(b) Calculate the overall formation constant for $[Fe(CN)_6]^{3-}$, given that the overall formation constant for $[Fe(CN)_6]^{4-}$ is $\approx 10^{32}$.

Given:
$$E_{Fe^{3+}/Fe^{2+}}^{\circ} = +0.77 \text{ V}; E_{Fe(CN)_6^{3-}/Fe(CN)_6^{4-}}^{\circ} = +0.36 \text{ V}$$
 3+2

8. (a) Construct the Frost diagram using following Latimer diagram of manganese in acid medium:

$$MnO_4^- \xrightarrow{0.89 \text{ V}} MnO_4^{2-} \xrightarrow{2.09 \text{ V}} MnO_2$$

and justify whether MnO₄²⁻ would disproportionate in solution.

(b) Predict the direction of the following equilibrium and give reasons.

$$[SnCl3]^- + (CO)5MnCl \rightleftharpoons (CO)5MnSnCl3 + Cl^-$$
3+2

- 9. (a) Draw a conductometric titration curve for dilute H₂SO₄ vs. NH₄OH and comment on the nature of the curve.
 - (b) A buffer solution is prepared by mixing 8 mL of 0.1(M) acetic acid with 4.0 mL 0.1(M) NaOH solutions. Find out the pH of the solution. (pK_a of acetic acid = 4.75).

Group - B

[Organic Chemistry (1A)]

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

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

- (b) Write the structure of an organic compound that contains sp, sp² and sp³ hybridised carbon (at least one of each) atoms.
- 11. (a) Which one in each of the following pair of molecules should have greater dipole moment and why?

- (ii) CHCl₃ and CH₂Cl₂
- (b) Arrange the following anions in order of decreasing nucleophilicity. Give reasons for your answer.

$$R\overset{\odot}{\text{O}}$$
:, $R_2\overset{\odot}{\text{N}}$:, $R_3\overset{\odot}{\text{C}}$:

- 12. (a) Draw the M.O. diagram of allyl anion. Indicate the HOMO and LUMO in its ground state.
 - (b) The reaction (i) shown below takes place readily to form a pale yellow precipitate of silver bromide but the reaction (ii) does not take place at all. Explain the observation.
 - (i) Cycloheptatrienyl bromide $\xrightarrow{\text{AgNO}_3}$ A nitrate salt + AgBr \downarrow (Pale yellow)
 - (ii) Cyclopentadienyl bromide $\xrightarrow{\text{AgNO}_3}$ No reaction. 3+2
- 13. (a) Draw s-cis and s-trans geometry for 1, 3-butadiene. Comment on their relative stabilities.
 - (b) Arrange the following compounds in increasing order of their boiling points. (No explanation needed) CH₃CH₂CH₂CH; CH₃CH₂CH₂CH₂CH; CH₃CH₂CH₂CH; CH₃CH₂CH₂CH; CH₃CH₂CH₂CH; CH₃CH₂CH₂CH; CH₃CH₂CH; CH₃CH₂CH; CH₃CH; CH
- 14. (a) Use the appropriate curly arrows to show the movement of electrons in each of the following chemical equations shown below. Indicate, with reason, the type of bond breaking in each case.
 - (i) $R OH_2 \rightarrow R^{\oplus} + H_2O$
 - (ii) $CH_3 H + C\dot{l} \rightarrow H_3\dot{C} + H Cl$
 - (b) Classify the following molecules as aromatic, antiaromatic and homoaromatic with reason. (any two)



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15. (a) Classify the following reaction mechanisms as ionic or radical or pericyclic in nature. (No explanation needed)

(i)
$$CH_3$$
 CH_2CI $+ CI_2 \xrightarrow{hv}$ $+ HCI$ CH_3 CH_3 $+ CI_2 \xrightarrow{FeCI_3}$ $+ CI_2 \xrightarrow{CH_3}$ $+ CI_2 \xrightarrow{CO_2Et}$ $+ CO_2Et$ $+ CO_2Et$

(b) Allyl cation is more stable than a secondary carbocation. Explain the observation on the basis of resonance. 3+2