

2020

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.*

Group - A

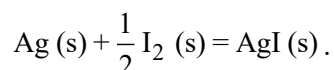
[Inorganic Chemistry]

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) Calculate E° for the disproportionation of Cu^+ (Given : $E^\circ_{\text{Cu}^{2+}/\text{Cu}^+} = 0.15\text{V}$, $E^\circ_{\text{Cu}^+/\text{Cu}} = 0.52\text{V}$).
- (b) Identify correct representation of hydrogen ion concentration of a slightly acidic solution :
 (i) $10^{-\text{pOH}}$ (ii) $10^{-(14-\text{pOH})}$
- (c) Find out the ground state term symbol of sodium atom.
- (d) Estimate using Pauling's rules the pK_a value of HClO_4 .
- (e) What is magic acid and why is it called so?
- (f) Express ψ for hydrogen-like atom in terms of radial and angular components.
- (g) Devise the cell in which the following reaction takes place :



- (h) What does $4\pi r^2 R(r)^2 = 0$ signify? (R and r have their usual significance).

2. (a) $R(2s) = \frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0} \right)^{3/2} \left(2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0}$

Based on the above, explain the plot of $R(r) \left(\frac{a_0}{Z} \right)^{3/2}$ vs. $\left(\frac{Zr}{a_0} \right)$ for H atom.

(R, r, a_0 and Z have their usual significance)

- (b) Find out the magnitude of orbital angular momentum of the electron in a d orbital.

3+2

Please Turn Over

3. (a) Cu^{2+} will oxidise I^- to I_2 during iodometric estimation of Cu^{2+} . Justify the statement from the relevant redox potential values given below.

$$E_{\text{Cu}^{2+}/\text{Cu}^+}^{\circ} = 0.15 \text{ V}$$

$$E_{\text{I}_2/\text{I}^-}^{\circ} = 0.54 \text{ V}$$

- (b) Calculate the pH of 0.01(M) acetic acid solution. (Given : $K_a = 1.75 \times 10^{-5}$) 3+2
4. (a) Ba^{2+} , Ca^{2+} , Sr^{2+} all can be precipitated as carbonate in $\text{NH}_4\text{Cl} - \text{NH}_4\text{OH}$ medium with $(\text{NH}_4)_2\text{CO}_3$ reagent, but not Mg^{2+} . Justify the statement.
- (b) Comment on change of acidity in HF on addition of SbF_5 . 3+2
5. (a) State Pauli's exclusion principle and apply this to predict the maximum capacity of $2p$ subshell for accommodating electrons.
- (b) I_2 is violet in trichloromethane but is brown in ethanol.— Explain. 3+2
6. (a) State the role of MnSO_4 and phosphoric acid (of a Zimmerman-Reinhardt solution) in redox titrimetric estimation of Fe^{2+} permanganometrically in presence of HCl.
- (Given : $E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\circ} = 1.51 \text{ V}$; $E_{\text{Cl}_2/\text{Cl}^-}^{\circ} = 1.36 \text{ V}$; $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = 0.77 \text{ V}$)
- (b) Balance by ion-electron method, the reaction of manganous sulphate and red lead in dilute nitric acid medium. 3+2
7. (a) Calculate the reduction potential at 25°C for the conversion of MnO_4^- to $\text{MnO}_2(\text{s})$ in aqueous solutions at pH = 9.0 and 1M MnO_4^- (aq), given that $E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\circ} = 1.69 \text{ V}$.
- (b) Explain :
- (i) Acid strength of BF_3 is lower than BCl_3 .
- (ii) Thionyl Chloride acts as an acid in sulphur dioxide solvent. 3+2
8. (a) Describe the neutralization curve of a weak base with a strong acid, indicating the choice of indicator.
- (b) Out of the following configurations, which will be more stable and why :
- (i) $(n-1)d^4ns^2$
- (ii) $(n-1)d^5ns^1$? 3+2
9. (a) For the reaction, $\text{BF}_3 + \text{NH}_3 \rightarrow \text{Products}$,
use the Drago-Wayland equation to predict the feasibility of the reaction.
(Given, $E = 21.2$ and $C = 3.31$ for BF_3 and $E = 2.78$ and $C = 7.98$ for NH_3)
- (b) The solubility of Sb_2S_3 in water is $1.0 \times 10^{-5} \text{ mol/L}$ at 298 K. What will be its solubility product? 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) Arrange the following groups in order of decreasing (-I) effect (No explanation needed) :



- (b) Calculate the DBE (double bond equivalent) of $\text{C}_8\text{H}_6\text{O}_4$. 1+1

11. (a) Give example of molecules or ions which corroborate the following facts :

- (i) A di-cation system having aromatic character.
- (ii) A non-benzenoid bicyclic hydrocarbon having aromatic character in ionic form.
- (iii) A molecule with $4n\pi$ electrons and anti-aromatic ($n = 1, 2, 3, \dots$).

- (b) Draw the orbital picture of the following compound indicating the hybridisation state of the key atoms.



12. (a) Which one of the following pair has higher boiling point and why?

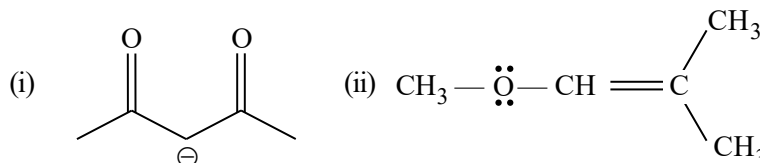
n-butane and *iso*-butane

- (b) Predict which one of the following pair of compounds has high resonance energy and justify your choice : cyclooctatetraene and styrene. 3+2

13. (a) Draw the M.O. diagram of ground state HOMO of 1, 3 pentadienyl free radical in *s-trans* form and *s-cis* form.

- (b) Draw the Frost Circle presentation of cyclopentadienyl anion. Comment on its nature. 3+2

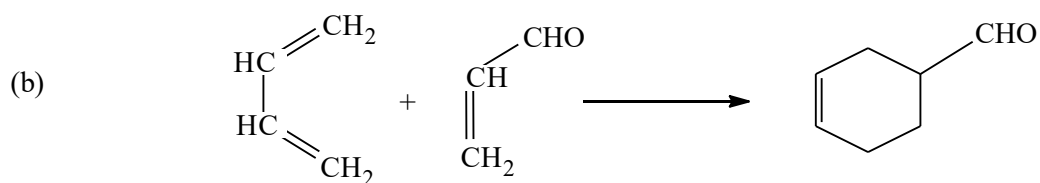
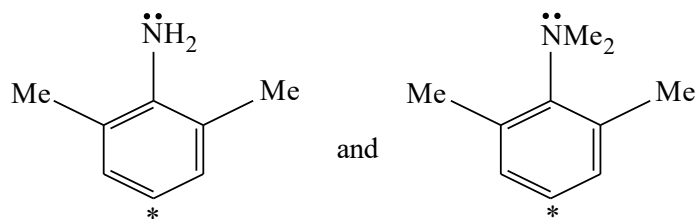
14. (a) Draw the resonating structures of the following molecules and designate the most contributory resonating structure with explanation.



- (b) Explain that ammonium chloride is insoluble in non-polar organic solvents, whereas tetramethylammonium chloride is appreciably soluble in these solvents. 3+2

Please Turn Over

15. (a) Which compound among the following pair will have a higher electron density at the marked C atom? Explain.



Classify the above reaction mechanism as ionic, radical or pericyclic and justify.

3+2
