

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

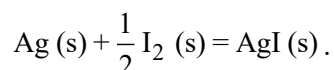
[Inorganic Chemistry]

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  $E^\circ$  for the disproportionation of  $\text{Cu}^+$  (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  $\text{pK}_a$  value of  $\text{HClO}_4$ .
- (e) What is magic acid and why is it called so?
- (f) Express  $\psi$  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)  $\text{Cu}^{2+}$  will oxidise  $\text{I}^-$  to  $\text{I}_2$  during iodometric estimation of  $\text{Cu}^{2+}$ . 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)  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  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  $\text{Mg}^{2+}$ . Justify the statement.
- (b) Comment on change of acidity in HF on addition of  $\text{SbF}_5$ . 3+2
5. (a) State Pauli's exclusion principle and apply this to predict the maximum capacity of  $2p$  subshell for accommodating electrons.
- (b)  $\text{I}_2$  is violet in trichloromethane but is brown in ethanol.— Explain. 3+2
6. (a) State the role of  $\text{MnSO}_4$  and phosphoric acid (of a Zimmerman-Reinhardt solution) in redox titrimetric estimation of  $\text{Fe}^{2+}$  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  $25^\circ\text{C}$  for the conversion of  $\text{MnO}_4^-$  to  $\text{MnO}_2(\text{s})$  in aqueous solutions at  $\text{pH} = 9.0$  and  $1\text{M MnO}_4^- (\text{aq})$ , given that  $E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\circ} = 1.69 \text{ V}$ .
- (b) Explain :
- (i) Acid strength of  $\text{BF}_3$  is lower than  $\text{BCl}_3$ .
- (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  $\text{BF}_3$  and  $E = 2.78$  and  $C = 7.98$  for  $\text{NH}_3$ )
- (b) The solubility of  $\text{Sb}_2\text{S}_3$  in water is  $1.0 \times 10^{-5} \text{ mol/L}$  at  $298 \text{ K}$ . 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?

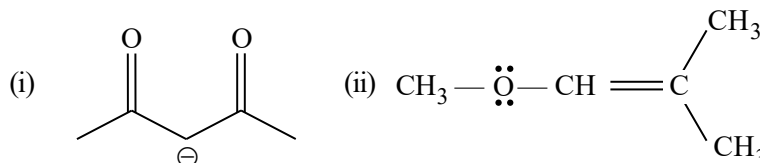
*n*-butane and *iso*-butane

- (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

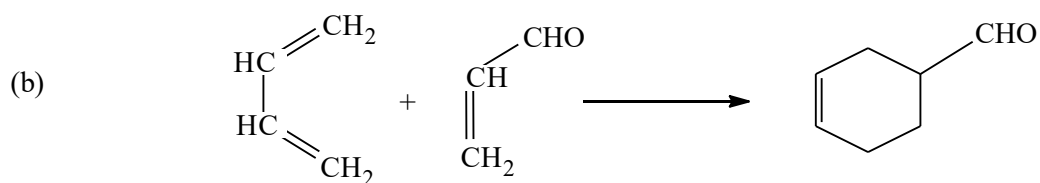
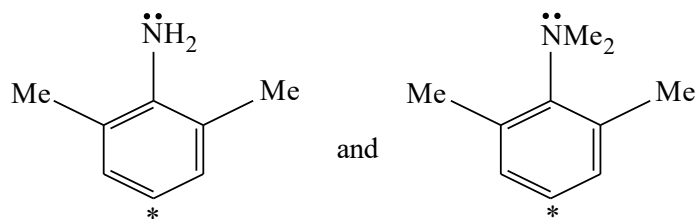
14. (a) Draw the resonating structures of the following molecules and designate the most contributory resonating structure with explanation.



- (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

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