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^o for the disproportionation of Cu^+ $\left(\text{Given}: E^o_{Cu^{2+}/Cu^+} = 0{\cdot}15V, E^o_{Cu^+/Cu} = 0{\cdot}52V\right)$.

(b) Identify correct representation of hydrogen ion concentration of a slightly acidic solution :
(i) 10^{-pOH} (ii) $10^{-(14-pOH)}$

(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 :

$$Ag(s) + \frac{1}{2} I_2(s) = AgI(s).$$

(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 $R(r)\left(\frac{a_o}{Z}\right)^{3/2}$ vs. $\left(Zr/a_o\right)$ for H atom.

(R, r, a_o 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.

$$E^o_{Cu^{2+}/Cu^+} = 0{\cdot}15\ V$$

$$E^o_{I_2/I^-} = 0{\cdot}54\ V$$

(b) Calculate the pH of 0·01(M) acetic acid solution. (Given : $K_a = 1{\cdot}75 \times 10^{-5}$) 3+2

4. (a) Ba^{2+}, Ca^{2+}, Sr^{2+} all can be precipitated as carbonate in $NH_4Cl - NH_4OH$ medium with $(NH_4)_2CO_3$ 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 2*p* 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.

$\left(\text{Given : } E^o_{MnO_4^-/Mn^{2+}} = 1.51\ V;\ E^o_{Cl_2/Cl^-} = 1{\cdot}36\ V;\ E^o_{Fe^{3+}/Fe^{2+}} = 0{\cdot}77\ V\right)$

(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 25ºC for the conversion of MnO_4^- to $MnO_2(s)$ in aqueous solutions at pH = 9·0 and 1M MnO_4^- (aq), given that $E^o_{MnO_4^-/Mn^{2+}} = 1{\cdot}69\ V$.

(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, $BF_3 + NH_3 \rightarrow$ 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 $1{\cdot}0\times10^{-5}$ 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) :

$$-NO_2,\ \overset{\oplus}{N}Me_3,\ F$$

(b) Calculate the DBE (double bond equivalent) of $C_8H_6O_4$. 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 ($n = 1, 2, 3,...$).

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

$$CH_3–CH=C=CHCl.$$ 3+2

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

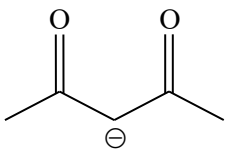
n-butane and *iso*-butane

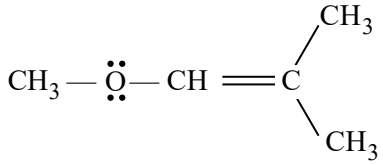
(b) Predict which one of the following pair of compounds has high resonance energy and justify your choice : cyclooctatetraene and styrene. 3+2

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

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

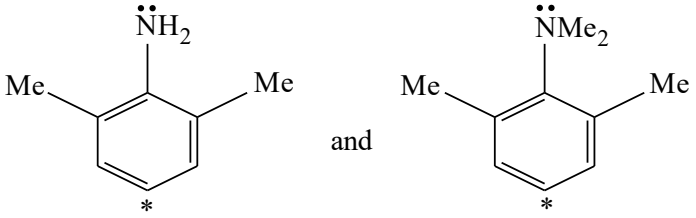
14. (a) Draw the resonating structures of the following molecules and designate the most contributory resonating structure with explanation.

(i) 

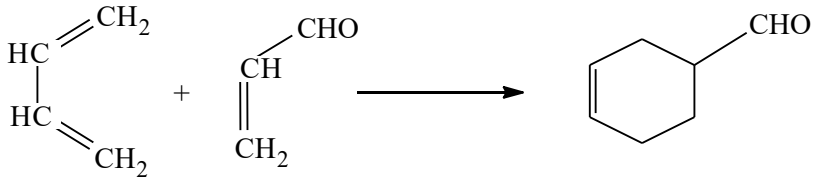
(ii) 

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

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



(b)



Classify the above reaction mechanism as ionic, radical or pericyclic and justify. 3+2
