

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. THIRD SEMESTER EXAMINATION, DECEMBER 2017

SECOND YEAR [BATCH 2016-19]

CHEMISTRY [Honours]

Paper : III [Gr-B]

Date : 14/12/2017

Time : 11 am – 1 pm

Full Marks : 35

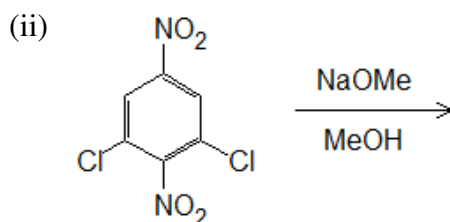
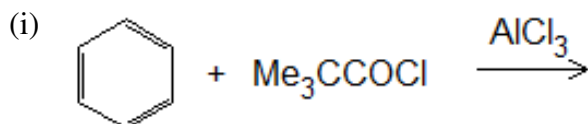
[Use one Answer Book for Unit I and another Answer Book for Unit II, III & IV]

(Attempt one question from each Unit)

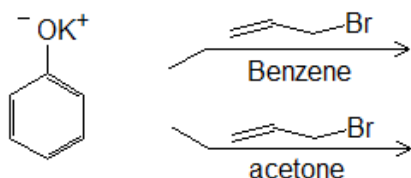
Unit I

[10 marks]

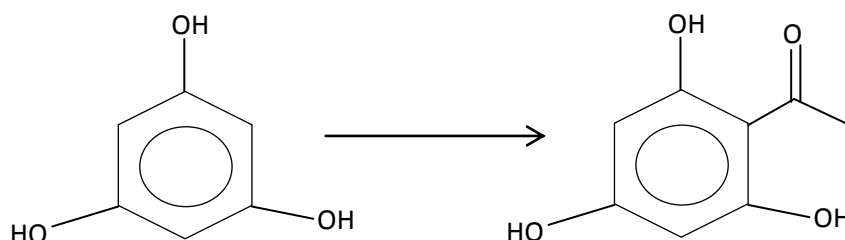
1. a) When treated with $\text{Br}_2\text{-H}_2\text{O}$, phenol gives 2,4,6-tribromophenol, however, when treated with $\text{Br}_2\text{-CS}_2$, it gives 2- and 4-bromo phenol – Justify. [2]
b) Identify the products of the following reactions and explain their formation: [2+2]
(i) 2,4,6-trinitroanisole $\xrightarrow{\text{EtOK/EtOH}}$
(ii) 2,6-dideuterobromobenzene $\xrightarrow{\text{KNH}_2/\text{NH}_3}$
c) Predict the course of the following reactions with appropriate mechanism: [2+2]



2. a) For the synthesis of salicylic acid, Kolbe-Schmidt reaction of sodium phenolate is useful and not potassium phenolate. Explain. [2]
b) Carry out the following conversions: aniline to 2,6-dichloroaniline [2]
c) Predict the products for the following reactions with proper explanation: [2]

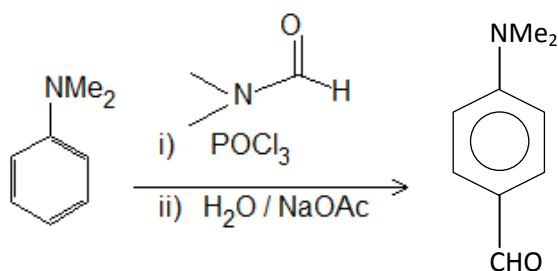


- d) Carryout the following conversion with mechanism. [2]



e) Rationalise the following reaction with plausible mechanism.

[2]



Unit II

[9 marks]

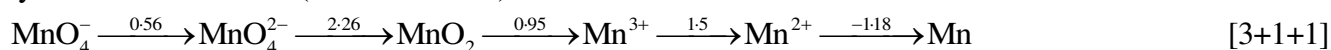
3. a) Illustrate with suitable example the phenomenon of 'symbiosis'. [2]
- b) A solution containing 0.319 g of a coordination compound of molecular formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was passed through a cation exchange resin in acidic form and the acid so liberated was neutralised with 19ml of 0.125(N) NaOH. Identify the compound. (Molecular weight of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O} = 266.5$) [2]
- c) 20ml of a weak acid HX of strength 0.02 N is titrated with 20ml of a strong base YOH of strength 0.02N. Calculate the pH when (i) 19.9 ml of YOH is added and (ii) at the equivalent point. (Given : $\text{pK}_{\text{HX}} = 4.7$). Also draw the respective titration curves (qualitative). [2]
- d) Write the IUPAC name of the complex : $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$. [1]
- e) Complexes of acetone are less stable than those of acetylacetone —Justify or contradict. [2]
4. a) Trisilylamine and trimethyl amine differ completely in their reactions with HCl —explain giving equations. [2]
- b) Arrange the following complexes with explanation in order of their molar conductance values in aqueous solution. $\text{Pt}(\text{NH}_3)_6\text{Cl}_4$, $\text{Pt}(\text{NH}_3)_3\text{Cl}_4$, K_2PtCl_6 , $\text{Co}(\text{NH}_3)_5(\text{NO}_2)\text{Cl}_2$, $\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$. [2]
- c) Careful addition of NH_4I to the solution of Zn^{2+} in excess KNH_2 solution produces white precipitate which dissolves if excess NH_4I is added. Explain the observation with reaction. [2]
- d) Mention one application of chelate complex in each of the qualitative and quantitative inorganic analysis. [2]
- e) Give the corresponding conjugate acids and bases of the species : NH_4^+ , HS^- , HCO_3^- , H_2O . [1]

Unit III

[8 marks]

5. a) Explain Cu^{+2} ion readily liberates I_2 from $\text{I}^{(-)}(\text{aq})$ but in presence of ethylene diamine (en) it does not. [2]
- b) Complete and balance by ion-electron method : $\text{NaNO}_3 + \text{NaOH} + \text{Al} \rightarrow$. [2]
- c) Establish Nernst equations for the following redox couples : (i) $\text{Cr}_2\text{O}_7^{2-} / \text{Cr}^{3+}$ in acid medium (ii) $\text{BrO}_3^- / \text{Br}^-$ in alkaline medium. [2]
- d) Reinhardt solution is used in the titration of Fe^{2+} with KMnO_4 solution in HCl medium —Explain. [2]
6. a) Indicate the directions in which the following reactions proceed spontaneously and assign them with scientifically appropriate names : (i) $\text{Cu}^+ + \text{Cu}^+ \rightleftharpoons \text{Cu}^{+2} + \text{Cu}^0$; (ii) $\text{Ag}^+ + \text{Ag}^+ \rightleftharpoons \text{Ag}^{+2} + \text{Ag}^0$.
Given : $E^\circ_{\text{Cu}^{+2}/\text{Cu}^+} = +0.16\text{v}$; $E^\circ_{\text{Cu}^+/\text{Cu}} = +0.52\text{v}$; $E^\circ_{\text{Ag}^{+2}/\text{Ag}^+} = +1.98\text{v}$; $E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80\text{v}$. [3]

- b) From the following Latimer diagram draw the corresponding Frost diagram for the manganese redox system in acid medium (E^0 value in volt).



Then answer the following question :

- From redox perspective, which is the most thermodynamically stable species?
- Which species would potentially disproportionate?

Unit IV

[8 marks]

- Rationalise the following facts in the light of molecular orbital concept :
 - Bond dissociation energy of NO is less than that of N_2 . [2]
 - B_2 but not C_2 is paramagnetic. [2]
 - Assuming x-axis as the bonding axis, predict how many π -MOs would be formed by d-orbitals of two combining atoms. Give the overlap diagram in each case. [2]
 - Between H_2SO_4 and H_3PO_4 which one is more viscous and why? [2]
- Differentiate between : $2c - 2e$ and $3c - 2e$ bonds with examples. [2]
 - The conductivity of Ge is enhanced many folds when trace amount of As is added to it. —Explain. [2]
 - Construct the M.O. diagram of CN^- ion and hence comment on its pi-acidity. [3]
 - Although HF is a monoprotic acid still it forms bi-salts. —Explain. [1]

————— x —————