

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. THIRD SEMESTER EXAMINATION, DECEMBER 2018

SECOND YEAR [BATCH 2017-20]

CHEMISTRY [Honours]

Paper : III [Gr-B]

Date : 17/12/2018

Time : 11 am – 1 pm

Full Marks : 35

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

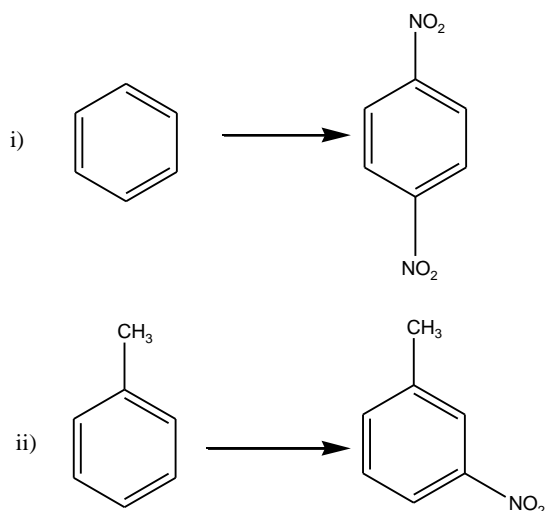
(Attempt one question from each Unit)

Unit I

[10 marks]

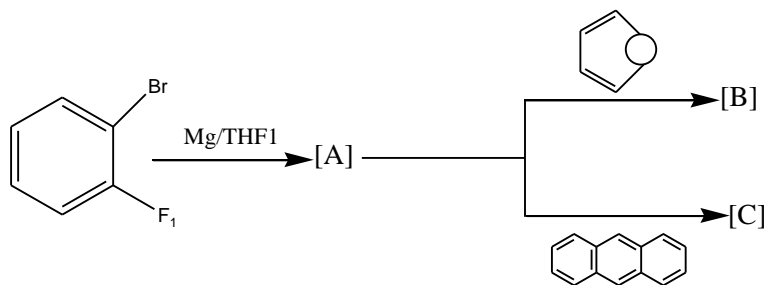
1. a) Carry out the following conversions:

1.5×2



b) Identify [A] [B] and [C] in the following reaction sequence.

2

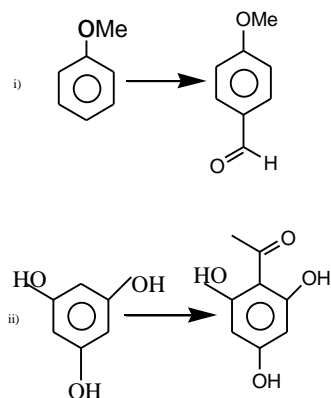


c) Both Phenol and Salicylic acid give identical product upon bromination-explain.

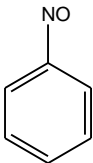
2

d) Carry out the following transformations.(Mechanism is not necessary).

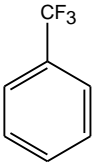
1.5×2

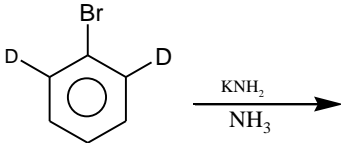


2. a) Account for the following observations: 1.5×2
 i) Nitrobenzene is used as solvent in Friedel-Crafts reaction.
 ii) 2,6-dimethyl acetophenone undergoes decarbonylation when treated with concentrated H_2SO_4
- b) Predict the favoured portion of electrophilic substitution of the following compound and justify your answer in each case. 2
- i)

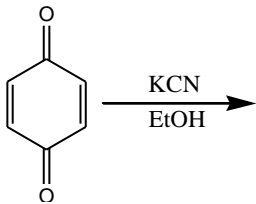


ii)


- c) Predict the product(s) of the following reactions. Give mechanism. 1.5×2
- i)



ii)


- d) Convert: Phenol → Paracetamol 2

Unit II

[8 marks]

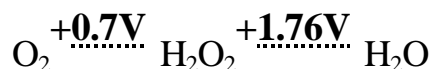
3. a) A pink solid has the empirical formula $\text{CoCl}_3 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$. An aqueous solution of this salt is also pink and rapidly gives 3 mol AgCl per mol salt when treated with excess AgNO_3 solution. When this pink solid is heated, it loses one mole of water per mole salt to give a purple solid with the same ratio of $\text{NH}_3:\text{Cl}:\text{Co}$. Deduce the structure of two complexes. 2
 b) Find out the pH of 10^{-8} M HCl solution. 2
 c) Me_3P can act as a stronger base than Me_3N towards B_2H_6 . Explain. 2
 d) Give one example of chelating ligand (with structure) applied in each of the qualitative and quantitative inorganic analysis. 1
 e) Write the IUPAC name of the complex: $[\text{Cr}(\text{NCS})_4(\text{NH}_3)_2]$ 1
4. a) Write the name of the complex according to IUPAC rules: $\text{Fe}(\text{C}_5\text{H}_5)_2$ 1
 b) State the essential characteristics of a ligand to form an inner metallic complex of first order with example. Describe an use of such complexes from analytical view point. 1+2
 c) State and explain the effect on acidity in the following cases?
 i) Addition of BiN to liquid NH_3 ii) Addition of CuSO_4 to aqueous $(\text{NH}_4)_2\text{SO}_4$ 2
 d) AgClO_4 is significantly more soluble in benzene than in n-hexane. Explain. 2

Unit III

[8 marks]

5. a) What will be the effect on the potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ system on adding (i) NH_4HF_2 (ii) 1,10-phenanthroline. 1.5+1.5
 b) Why $\text{Cu}(\text{II})$ readily liberates iodine from iodide but in presence of ethylenediamine it does not? 2
 [Given $E^\circ_{\text{Cu}(\text{II})/\text{Cu}(\text{I})} = +0.15\text{V}$; $E^\circ_{\frac{1}{2}\text{I}_2/\text{I}^-} = +0.54\text{V}$, $E^\circ_{\text{Cu}(\text{II})/\text{CuI}} = 0.87\text{V}$]

- c) Predict thermodynamic redox stability of H_2O_2 with the help of free energy calculation and also construct the Frost diagram from the following data:



6. a) Give the name and structure of a redox indicator. Show its mode of action with equation. 2
 b) prove that disproportionation reaction in aqueous solution is thermodynamically favourable for the system given below:

$$2\text{Cu}^+_{(\text{aq})} \rightleftharpoons \text{Cu}^0 + \text{Cu}^{2+}_{(\text{aq})}$$

 Given : $E^0_{\text{Cu}^{2+}_{(\text{aq})}/\text{Cu}^+_{(\text{aq})}} = +0.153\text{V}$, $E^0_{\text{Cu}^{2+}_{(\text{aq})}/\text{Cu}^0} = +0.337\text{V}$ 2
 c) Calculate the pK for the reaction $\text{HFe}(\text{CN})_6^{3-} = \text{H}^+ + \text{Fe}(\text{CN})_6^{4-}$. [Given $E^0_{\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}} = +0.365\text{V}$; $E^0_{\text{Fe}(\text{CN})_6^{3-}/\text{HFe}(\text{CN})_6^{3-}} = +0.619\text{V}$]. 3
 d) Establish the Nernst equation for the following redox couple: $\text{BrO}_3^-/\text{Br}^-$ in alkaline medium. 1

Unit IV

[9 marks]

7. a) Assuming X-axis as sigma bonding axis, predict how many π -m.os would be formed by d-orbitals of combining atoms. Give the orbital overlap diagram in each case. 2
 b) Stating reason, indicate the expected changes in bond order and bond distances in the following ionization process:
 i) $\text{O}_2 \rightarrow \text{O}_2^+ + e$ ii) $\text{NO} + e \rightarrow \text{NO}^-$ 2
 c) Account for the photoconductivity of selenium. 2
 d) Although HF is a monoprotic acid still it forms bi-salts..... Explain. 1
 e) Explain why O_3 molecules has a dipole moment. 2
8. a) CO and N_2 molecules are isoelectronic but differ greatly in their donor properly. Explain. 2
 b) Bonding molecular orbitals are stabilised while antibonding molecular orbitals are destabilised than the uncombined atomic orbitals. Justify the statement. 2
 c) Between H_2SO_4 and H_3PO_4 , which one is more viscous and why? 2
 d) What are intrinsic and extrinsic semiconductors? Indicate the type of semiconductor (n or p) expected in the following: (i) As doped Ge ii) B doped Si 3

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