2021

Full Marks - 60

Time - 3 hours

The figures in the right-hand margin indicate marks

Answer *all* questions

Part-I

1. Answer the following : 1 × 8

   a) Name one element which is purified by zone refining.

   b) Which out of Li^+ and Ag^+ is a soft acid ?

   c) Write any two allotropic forms of Sulphur.

   d) Ti^{3+} is better oxidant than In^{3+} due to ___

   e) The molecular formula of metaboric acid is ___.

   f) What are boranes ?

   g) Which noble gas is radioactive ?

   h) Sillicons have high thermal stability due to ___ chains.

[Turn Over

Part-II

2. Answer any *eight* of the following : $1\frac{1}{2} \times 8$

a)   Is a reaction having a large negative value of ΔG possible or not ?

b)   Classify into acids and bases -$AlCl_3$, RNH_2, BF_3.

c)   What are conugate acid and bases ? Give one example.

d)   What is the structure of $[BeF_4]^{2-}$.

e)   Define catenation. Give an example.

f)   Which out of NH_3 and $(CH_3) N$ is more basic and why ?

g)   Which out F_2 and I_2 has basic properties ?

h)   What are interhalogen compond ?

i)   What is the hybrid state of Xe in XeF_6.

j)   Give two uses of helium.

Part-III

3. Answer any *eight* of the following : 2×8

a)   What is hydrometallurgy ?

b)   Explain the Bronsted-Lowry concept of acid and bases with two examples.

c) What are solvated protons ? Give one example.

d) What is the structural difference between red and yellow phosphorus ?

e) Why helium does not form clathrates ?

f) Define hydrides. Describe briefly ionic or covalent hydrides with example.

g) What are different allotropic forms of carbon ?

h) What are polyhalide ions ? Give two examples of polyhalides.

i) What are silicates ?

j) Why noble gases are inert in nature ?

Part-IV

4. a) What are Ellingham Diagrams ? Explain its use by using carbon as reductant.   6

OR

b) What is HSAB principle and its application.   6

[Turn Over

5. a) What is diagonal relationship ? Which elements show diagonal relationship and why ?   6

OR

b) Write notes on the following :   3 + 3

i) Complex formation tendency of s and p-block elements

ii) Inert pair effect.

6. a) Discuss preparation, properties and structure of boric acid.   6

OR

b) Write notes on the following :   3 + 3

i) Oxoacids of chlorine

ii) Carboranes.

7. a) Describe any two methods of preparation of XeF_4. Explain its structure.   6

OR

b) Give a comparison between organic and inorganic polymers.   6

2021

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Answer *all* questions

Part-I

1. Answer the following :   1 × 8

   a) When HBr is added to But-2-ene, Markowikoff's
       rule ___.

   b) R–Cl + KI ⟶ R–I + KCl. It is called ___
       reaction.

   c) What is the order of SN^1 reaction ?

   d) Why formaldehyde does not undergo Aldol
       condensation reaction ?

   e) An SN^2 reaction at an asymmetric carbon of a
       compound always gives which products ?

f) What is the hybridisation of carbonyl carbon

$$\overset{O}{\underset{\|}{(-C-)}} ?$$
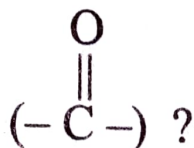
g) Clemenson reductions convert ketones to alcohol or alkane.

h) Methyl chloride reacts with silver acetate to formed ___ .

Part-II

2. Answer any *eight* of the following : 1½ × 8

   a) Arrange the following in order of their increasing reactivity towards nucleophilic substitution reactions CH_3F, CH_3Cl, CH_3I, CH_3Br.
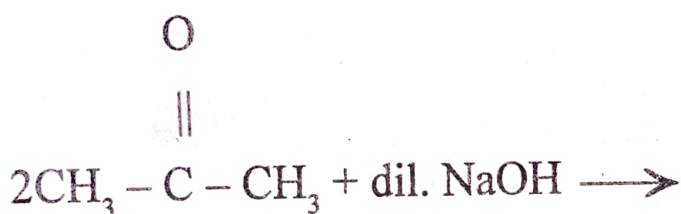
   b) Vinyl chloride is less reactive than CH_3Cl. Explain.

c) What happens Chlrobenzene reacts with KNH$_2$/NH$_3$.

d) How is phenol obtained from cumene ?

e) What is Lucas reagent ? Find out the order of reactivity of alcohols in Lucas test.
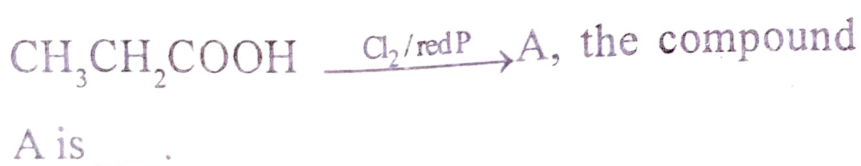
f) Complete the reaction

$$2CH_3 - \overset{\overset{\displaystyle O}{\displaystyle \|}}{C} - CH_3 + dil. \ NaOH \longrightarrow$$

g) Complete the reaction :

$$C_6H_5CHO + BrCH_2COOC_2H_5 \xrightarrow{\text{i) Zn/ii) H}_2\text{O}} ?$$

h) Acetic acid on reduction with LiAlH$_4$ yields.

i) In the reaction :

$$CH_3CH_2COOH \xrightarrow{Cl_2/redP} A, \text{ the compound}$$

A is ___.

Part-III

3. Answer any *eight* of the following : $\quad\quad 2 \times 8$

a) What is Grignards reagent ? Explain with one example.

b) Give an example of Wurtz-Fitting reaction with example.

c) Write any two preparation of alkylhalide.

d) Give an example of Pinacole-Pinacolone rearrangement.

e) Give an example of Reimer-Tiemann reaction.

f) What is Backmann rearrangement reaction ?

g) What is Michael addition reaction with one example ?

h) What is Rosenmunds reaction ?

i) What is Hofmann bromamide reaction ?

j) Arrange the following in decreasing order of reactivity towards nucleophilic addition $HCHO, CH_3CHO, CH_3CH_2CHO$.

Part-IV

4. a) Discuss the mechanism of SN^1 and SN^2 reaction. What is the effect of the solvent and concentration of nucleophilic reagent on two reactions ?   6

OR

b) Describe the elimination addition mechanism of nucleophilic aromatic substitution reaction. Give evidence in support of the mechanism.

5. a) How can you prepare three types of alcohols by using Grignard's reagent ?   6

OR

b) Write notes on the following :　　　　　　　　3 + 3

　　i) Give the electrophilic substitution reaction of phenol

　　ii) Fries rearrangement reaction.

6. a) How is malonic ester prepared ? How will you obtain the following from it ?　　　　2 + 2 + 2

　　i) Succinic acid

　　ii) Cinnamic acid.

OR

b) Write notes on the following :　　　　　　　　3 + 3

　　i) Bayer Villiger Oxidation Reaction

　　ii) Clemmensen Reduction Reaction.

7. a) Discuss the mechanism of acidic and basic hydrolysis of ester.

　　　　　　　　　　　　　　　　　　　　　6

OR

b) Write notes on the following :   3 + 3

   i) Reformatsky reaction

   ii) Claisen condensation reaction.

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Answer *all* questions

Part-I

1. Answer the following :   1 × 8

   a) The Gibb's phase rule for general system is ____.

   b) The point at which all phases can exist in equilibrium is called ____.

   c) What is the unit of rate constant in zero order reaction ____ .

   d) Calculate the number of component of the following reaction

      $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

   e) What is the effect of increasing pressure on a system having UCST as well as LCST ?

   f) Calculate the order of reaction in the following equation when $r = [A]^{3/2}[B]^{1/2}$.

   g) What is the main role of catalyst in a chemical reaction ?

   h) What is homogeneous catalyst ?

[Turn Over

Part-II

2. Answer any *eight* of the following : 1½ × 8

a) What is meant by metastable equilibrium ?

b) What is degree of freedom and give equation as well as their meaning ?

c) Why the mixture of two immiscible liquids boils at a lower temperature ?

d) Write Duhem-Margule equation only.

e) Define the term activation energy.

f) The half life period of first order chemical reaction is 6.93 minutes. Calculate the time required for the completion of 99% of chemical reaction.

g) What is rate law and rate constant ?

h) Write a note on heterogeneous catalyst.

i) Why all adsorptions are exothermic in nature ?

j) Give the derivation of Nernst distribution law.

Part-III

3. Answer any *eight* of the following : 2 × 8

a) How is supercooled water an example of metastable equilibrium.

b) What is the form of the Gibbs phase rule for two component system ?

c) What is an azeotrope ?

d) What are ideals and non ideal solution ?

e) State distribution law. How is the law derived from thermodynamic considerations ?

f) Discuss the Arrhenius equation for the temperature dependence of reaction rate.

g) What is activation energy ? Explain graphically.

h) Write a note on adsorption isotherm and its significane.

i) Distiguish between physical and chemical adsorption.

j) How nanoparticles act as catalyst more efficiently ?

Part-IV

4. a) Discuss the appilication of phase rule to the equilibrium met in case of sulphur system. 6

OR

b) Derive Clausis-Clapeyron equation for the equilibrium liquid = vapour. How will you obtain the heat of vapourisation using this equation ?

[Turn Over

5. a) Write a note on three component system water-chloroform-acetic acid.   6

OR

b) Write notes on the following :   3 + 3

i) Write a few lines on minimum boiling azeotrope.

ii) Phenol-water binary system (upper critical solution type)

6. a) Derive an expression for the rate constant of a first order reaction. Define half life period first order reaction.   6

OR

b) Write notes on the following :   3 + 3

i) Parallel raction

ii) Consecutive reactions.

7. a) What is Langmuir adsorption ? Derive and explain Langmuir adsorption isotherms.   6

OR

b) Derive the Michaells-Menten equation in enzyme catalysis of following reaction
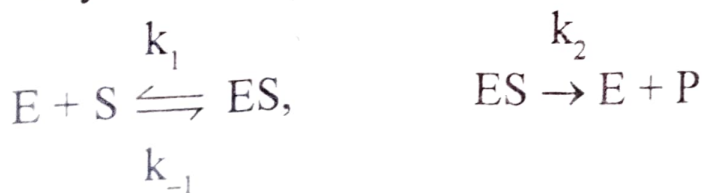
$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES, \qquad ES \xrightarrow{k_2} E + P$$

□□

2021

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Answer *all* questions

Part-I

1. Answer the following : 1×8

   a) Write the electronic configuration of Cu^{+1} is ___.

   b) What is the shape of d-orbital ___.

   c) Calculate the number of radial node in 5f-orbital.

   d) What is the increasing order of hydrogen bonding of NH_3, H_2O and HF.

   e) Give the order of reactivity of hydrogen halides with alkene (Hl, HBr, HCl).

   f) Write the structural formula of 1-Bromo-2-methyl propane.

   g) Write the correct structure of-
      (R) 2-Bromo-2-ethyl pentane.

   h) What is the product (A) of the following reaction
      $R - MgX + H_2O \rightarrow A + Mg(OH)X$

[Turn Over

Part-II

2. Answer any *eight* of the following :   1½×8

a) What is the expression for de-Broglie wavelength ?

b) Write the possible quantum numbers of an electron in 4d-orbital.

c) Write the shape and hybridisation of NH_3.

d) Define electrovalency. Write electrovalency of calcium.

e) What is Pauli's exclusion principle ?

f) Define Electrophile and give one example.

g) What are the intermediates formed during Homolytic and Heterolytic cleavage of a bond ?

h) Complete the reaction :

$$CH \equiv CH + H_2O \xrightarrow{H_2OSO_4/HgSO_4} ?$$

i) Draw the stucture of z-pent-2-ene.

j) Complete the reaction :

$$CH_3 - CH = CH - CH_3 \xrightarrow{O_3/H_2O/Zn} ?$$

Part-III

3. Answer any *eight* of the following : 2×8

   a) Give the signaificance of ψ and ψ^2.

   b) Calculate the momentum of a particle which has a de-Broglie wave length of 0.1nm.

   c) State Hund's rule.

   d) Write down the limitation of VBT.

   e) Explain why BaO has higher melting point than MgO.

   f) What is the bond order of CO molecule ?

   g) What is carbanion ? Give one example.

   h) Explain Wurtz reaction with examples.

   i) Explain the term chirality.

   j) State Huckel's rule.

Part-IV

4. a) What are quantum numbers ? Discuss about all quantum numbers with their significance.   6

   OR

   b) What is Heisenberg Uncertainty principle ? Explain it.

5. a) Define lattice energy. How lattice energy of NaCl is calculated by Born-Haber Cycle ? 6

OR

b) What is hybridization ? Discuss the shape CH_4, BCl_3 and PCl_5 molecules on the basis of hybridization.
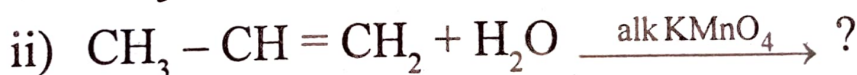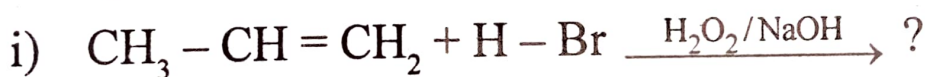
6. a) Draw the Newmann projections of Cyclohexane. 6

OR

b) Write notes on the following : 3 +3

i) Inductive effect

ii) Hyperconjugation.

7. a) Complete the reaction : 2 + 2 + 2

i) $CH_3 - CH = CH_2 + H - Br \xrightarrow{H_2O_2/NaOH}$?

ii) $CH_3 - CH = CH_2 + H_2O \xrightarrow{alk\,KMnO_4}$?

iii) $CH_3 - CH = CH_2 + H_2 \xrightarrow{Ni}$?

OR

b) Write notes on the following : 2 + 2 + 2

i) Birch reduction

ii) Kolbe's synthesis

iii) Markownikoff's rule.

2018

Full Marks - 60

Time - 3 hours

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Answer *all* questions

1. a) Derive an expression for Gibb's free energy of mixing (ΔG_{mix}) for an ideal solution. Show that for an ideal solution the volume of mixing is zero where as the entropy change of mixing is always positive. 9

   b) Explain the application of Nernst distribution law of study the complex ion. 3

   c) Determine the number of components, numbers of phases and degrees of freedom for the following system with justification. 3
   $$CaCO_{3(S)} \rightleftharpoons CaO_{(S)} + CO_{2(g)}$$

OR

d) Draw and discuss the formation of compounds with congruent melting points, taking $FeCl_3$-H_2O system into consideration. 9

e) A mixture of two immiscible liquids A and B is distilled under equilibrium conditions at 1 atm pressure. Assuming ideal gas behaviour, Calculate the mole fraction of A in the distillate if the vapour pressure of pure B is 425 Torr. 3

f) What is triple point ? Explain the same for one component H_2O system. 3

2. a) Describe Hittort's theoretical device to show although most of the ions differ largely in their mobility's, their equivalent amounts are discharged, on electrolysis at appropriate electrodes. Explain Hittort's method for determination of transport number. 9

b) At $25^\circ C$ the specific conductance of distilled water is $58.0 \times 10^{-7} s \ m^{-1}$ and λ_m^0 values for H^+ and H^- ions are 349.8×10^{-4} and $198.5 \times 10^{-4} \ s \ m^2 mol^{-1}$ respectively. Assuming that Λ_m and Λ_{m^0} differs slightly, calculate the ionic product of H_2O at $25^\circ C$. 3

c) With neat diagram explain the working of a hydrogen electrode. 3

OR

d) Discuss the principle underlying potentiometric titrations. Explain how would you carry out potentiometric titration of a solution of HCl against a standard solution of NaOH. 9

e) What are specific conductance, equivalent conductance and molar conductance ? Make relations among them. 3

f) Calculate the potential of an electrode consisting of zinc metal in zinc sulphate solution, in which $[Zn^{2+}] = 0.01M$, for the reaction

3

$$Zn^{2+}_{(aq)} + 2e \rightarrow Zn_{(s)}. E^0 = -0.76V.$$
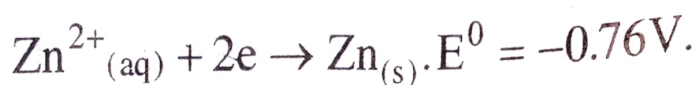
3. a) Write the mechanism for the acid-catalysed trans esterification of ethyl acetate and tert.-butyl acetate with methanol.

9

b) Explain Reformatsky reaction with suitable example.

3

c) Predict the product with mechanism.

3

$$Cl + H_2O \rightarrow ?$$

OR
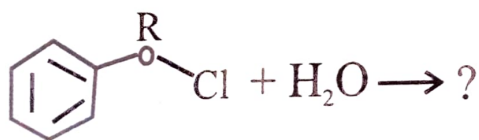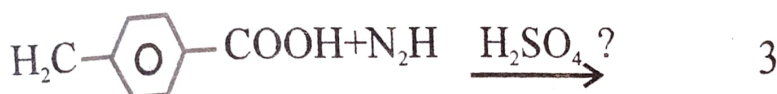
d) Explain the following reaction with mechanism.

   i) Perkin condensation 9

   ii) Hofmann bromide reaction.

e) Predict the product with suitable mechanism. 3

$$H_3C-\langle O \rangle-COOH+N_2H \xrightarrow{\ H_2SO_4\ } ?$$ 3

f) Predict the product with suitable mechanism. 3

$$+2\ CH_2NH_2 \longrightarrow ?$$
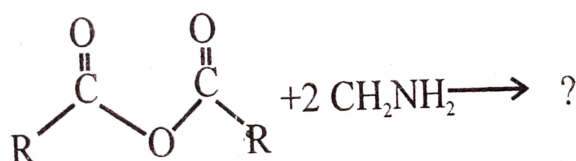
4. a) Explain the structure of protein. 9

   b) Explain why amino acids, unlike most amines and carboxylic acids are insoluble in diethyl ether ? 3
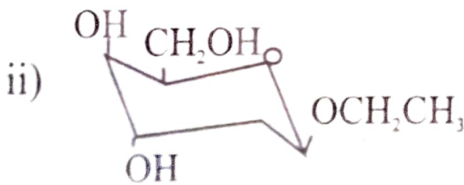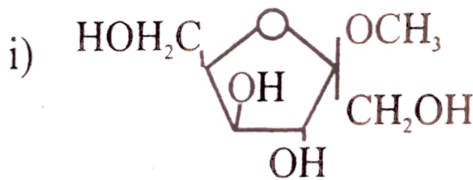
[6]

c) Name the epimers of D-glucose.   3

OR

d) The reaction of D-ribose with one equivalent of
methanol plus HCl forms four products. Draw
the products with mechanisms.   9

e) Explain the difference in the Pka values of the
carboxylic groups of alanine, serine and
cystein.   3

f) Name the following compounds.   3

i) HOH₂C $\overset{}{\underset{OH}{\bigvee}}$ O, OCH₃, CH₂OH, OH

ii) OH, CH₂OH, OCH₂CH₃, OH

[7]

iii)

OH CH$_2$OH

OH

OCH$_3$