Total No. of Printed Pages—7

3 SEM TDC CHMH (CBCS) C 5

2022

(Nov/Dec)

CHEMISTRY

(Core)

Paper : C–5

(Inorganic Chemistry)

Full Marks : 53

Pass Marks : 21

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Choose the correct answer from the following : 1×5=5

(a) Which of the following acids results from better hard-hard combination?

(i) HCN

(ii) HI

(iii) HCl

(iv) HNO_2

(b) Which one of the following is the correct order of increasing basicity?

(i) $CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N < (CH_2CH_3)_3N$

(ii) $CH_3NH_2 < (CH_3)_2NH < (CH_2CH_3)_3N < (CH_3)_3N$

(iii) $CH_3NH_2 < (CH_2CH_3)_3N < (CH_3)_2NH < (CH_3)_3N$

(iv) $(CH_2CH_3)_3N < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$

(c) The type of hybridization for IF_5 is

(i) sp^3d

(ii) sp^3d^3

(iii) sp^3d^2

(iv) d^2sp^3

(d) The shape of $XeOF_4$ molecule with sp^3d^2 hybridization is

(i) pentagonal bipyramidal

(ii) octahedral

(iii) trigonal bipyramidal

(iv) square pyramidal

(e) In clathrates, the host-guest interaction is also known as

(i) covalent interaction

(ii) ionic interaction

(iii) coordination interaction

(iv) non-covalent interaction

2. Answer any *six* questions of the following : 2×6=12

(a) What are interhalogen compounds? Give examples.

(b) Compare the acid strength of $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{2+}$.

(c) Give two reactions to show resemblance of lithium with magnesium.

(d) Draw the structure of boric acid.

(e) Write a short note on hydrometallurgy.

(f) Why helium and neon do not form clathrates?

(g) XeF_6 cannot be stored in glass vessel. Explain with chemical reaction.

(h) Discuss the effect of dielectric constant of solvents in relative strength of acids and bases.

3. Answer any *four* questions of the following : 3×4=12

(a) What are *closo-*, *nido-* and *arachno-* boranes? Give one example of each.

(b) What are polyhalides? Among the halogens, iodine has the maximum tendency to form polyhalide anion. Explain the statement.

(c) What are silicones? Give the preparation of cross-linked silicones.

(d) Why is borazine called inorganic benzene? How is it prepared from diborane? Give a reaction to distinguish borazine from benzene.

(e) What are hydrides? Classify different types of hydrides with one example of each.

(f) Discuss the formation of 3c—2e bonds in diborane from molecular orbital theory. (Give the required MO diagrams)

4. Answer any *three* questions of the following : 4×3=12

(a) Mention the Wade's rules for determining the skeletal structure of boranes. Applying these rules, predict the structure of B_5H_{11} and $C_2B_4H_8$. 2+2=4

(b) Define acids and bases from solvent system theory. Discuss the acid-base behaviour of NH_4Cl and KNH_2 in liquid ammonia. 2+2=4

(c) Complete the following reactions : 1×4=4

(i) $H_3BO_3 + NaOH + H_2O \longrightarrow ?$

(ii) $BCl_3 + LiAlH_4 \longrightarrow ?$

(iii) $XeF_6 + SiO_2 \longrightarrow ?$

(iv) $NaNO_3 + H_2SO_4 \xrightarrow{150\,^\circ C - 200\,^\circ C} ?$

(d) What is meant by diagonal relationship of elements in the periodic table? Discuss the diagonal relationship between lithium and magnesium. 1+3=4

5. Answer any *three* questions of the following : 3×3=9

(a) What are phosphazines? Discuss the structure of hexachlorocyclotriphosphazine. 1+2=3

(b) State the HSAB principle. Explain why $[CoF_6]^{3-}$ is more stable than $[CoI_6]^{3-}$. 1+2=3

(c) What are the reasons for the anomalous behaviour of fluorine with its group members? Compare the variation of oxidation states of group 17 elements. 2+1=3

(d) Give the names of oxo-acids of chlorine. Compare the acid strength of oxo-acids of chlorine. 2+1=3

6. Answer *either (a) or (b)* from the following : 3

(a) Give the structures of—

(i) P_2O_5

(ii) $H_2S_2O_8$

(iii) $HClO_4$ 1+1+1=3

(b) Write short notes on any *two* of the following : 1½×2=3

(i) Zone refining

(ii) Fullerenes

(iii) Carbon reduction

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Total No. of Printed Pages—11

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(Nov/Dec)

CHEMISTRY

(Core)

Paper : C–6

(Organic Chemistry)

Full Marks : 53

Pass Marks : 21

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Choose the correct answer from the following : 1×5=5

(a) Addition of HBr to 2-methylpropene in the presence of benzoyl peroxide mainly forms

(i) 1-bromobutane

(ii) 2-bromopropane

(iii) 2-bromo-2-methylpropane

(iv) 1-bromo-2-methylpropane

(b) The intermediate in the acid-catalyzed dehydration of alcohol is

(i) carbene

(ii) carbanion

(iii) carbocation

(iv) free radical

(c) The electrophile involved in the Reimer-Tiemann reaction is

(i) $:CCl_2$

(ii) $\overset{\oplus}{C}HCl_2$

(iii) $\overset{\oplus}{C}HO$

(iv) $\overset{\ominus}{C}Cl_3$

(d) Malaprade reagent used to detect vicinal diol is

(i) OsO_4

(ii) H_5IO_6

(iii) $Pb(OAc)_4$

(iv) peracetic acid

(e) Which of the following compounds has the highest acid strength?

(i) C_6H_5OH

(ii) HCOOH

(iii) CH_3COOH

(iv) $ClCH_2COOH$

UNIT—I

2. Answer any *five* of the following questions : 2×5=10

(a) What is S_Ni mechanism? Explain with the help of an example.

(b) Discuss the benzyne mechanism for nucleophilic aromatic substitution reaction. Give evidences in support of the proposed mechanism.

(c) Synthesize the following : 1×2=2

(i) Ethyl bromide by Hunsdiecker reaction

(ii) Fluorobenzene through diazonium salt

(d) Using organometallic compound, how would you prepare a 3°-alcohol from an ethyl ester?

(e) Why are the aryl halides less reactive towards nucleophilic substitution reactions than alkyl halides?

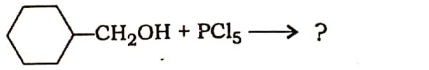
(f) Discuss the relative reactivity of alkyl, allyl and aryl halides towards nucleophilic substitution reactions.

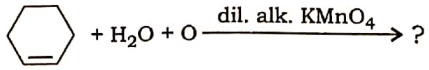
UNIT—II

3. Answer any *three* of the following questions : 2×3=6

(a) How will you distinguish between 1°-, 2°- and 3°-alcohols by Victor-Meyer method?

(b) Complete the following reactions :

(i) 

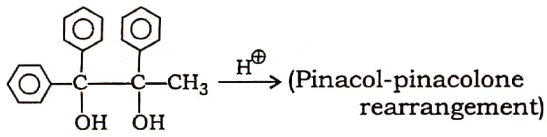
(ii) 

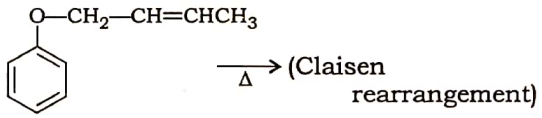
(c) How would you synthesize α,β-unsaturated alcohol and aldehyde from glycerol?

(d) Prepare acrolein from glycerol.

4. Answer any *two* of the following questions : 3×2=6

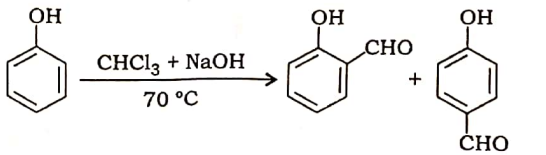
(a) Complete the following reactions with mechanisms :

(i) 

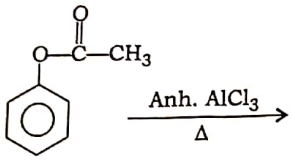
(ii) 

(b) (i) How can you prepare phenol from cumene? Give mechanism.

(ii) Give the mechanism of the following reaction :

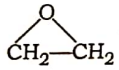


(c) (i) Complete the following rearrangement and suggest the mechanism :

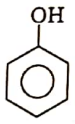


(Fries rearrangement)

(ii) Complete the following reactions :

(1)  + HCN ⟶ ?

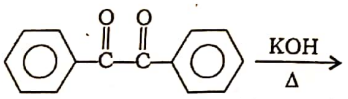
(2) $\begin{matrix} CH_2—OH \\ | \\ CH_2—OH \end{matrix}$ $\xrightarrow[AcOH]{Pb(OAc)_4}$?

(3)  + HCN + HCl $\xrightarrow[2)\ H_2O]{1)\ ZnCl_2}$?

UNIT—III

Answer *either* Q. No. **5** *or* Q. No. **6**

5. *(a)* Complete the following reactions and write down the mechanisms : 3×2=6

(i) 

(Benzil-benzilic acid rearrangement)

(Continued)

(ii)  + Ac_2O $\xrightarrow{AcONa}$ (Perkin reaction)

(b) Trichloroacetaldehyde is more reactive towards the nucleophilic addition reaction than acetaldehyde. Explain. 2

6. *(a)* Explain with example the mechanism involved in Wittig reaction. 3

(b) Write one synthetic application of each of the following reagents (any *three*) : 1×3=3

(i) $LiAlH_4$

(ii) $Pb(OAc)_4$

(iii) $NaBH_4$

(iv) PCC

(c) Write the Rosenmund's reaction for synthesis of acid chlorides. 2

(Turn Over)

7. Answer any *two* of the following questions : 2×2=4

(a) Synthesize the following (any *one*) : 2

(i) Methylvinyl ketone from acetone

(ii) Crotonaldehyde from acetaldehyde

(b) Write a short note on keto-enol tautomerism. 2

(c) What is Michael reaction? Explain with a suitable reaction. 2

8. How is barbituric acid prepared using malonic ester? 1

Or

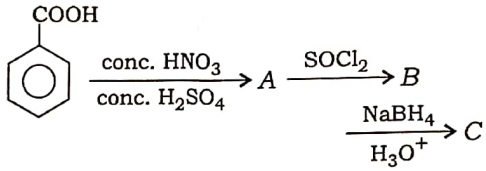
Write any one preparation method of acetoacetic ester.

UNIT—IV

Answer *either* Q. No. **9** *or* Q. No. **10**

9. *(a)* "Acetic acid is much weaker acid than formic acid." Explain. 2

(b) Identify *A*, *B* and *C* in the following reaction : 3



(c) Synthesize the following : 2×2=4

(i) Propanoic acid to ethanoic acid by Hoffmann degradation

(ii) Butanoyl chloride to propanoic acid by Curtius rearrangement

10. *(a)* Arrange the following acids in increasing order of their relative acid strength with proper explanation : 2

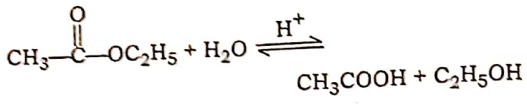
(i) $CH_3—CH_2—CH(Br)COOH$

(ii) $CH_3—CH(Br)—CH_2—COOH$

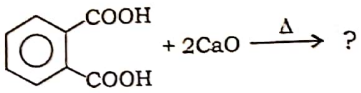
(iii) $CH_2(Br)—CH_2—CH_2—COOH$

(iv) $CH_3—CH_2—CH_2—COOH$

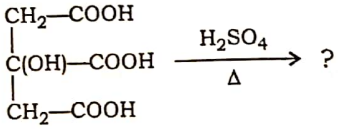
(b) Show the mechanistic steps of the following reaction : 3



(c) Complete the following reactions (any *two*) : 1×2=2

(i) 

(ii) 

(iii) 

(d) Account for the fact that maleic acid is a stronger acid than fumeric acid but maleate monoanion is a weaker acid than fumarate monoanion. 2

UNIT—V

Answer the following questions : 2×2=4

11. What are mercaptans? How will you prepare ethyl mercaptan from ethyl halide? 1+1=2

12. Give one method of preparation of thio-ether. What happens when a thiol reacts with an aldehyde in the presence of HCl? 1+1=2

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3 SEM TDC CHMH (CBCS) C 7

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CHEMISTRY

(Core)

Paper : C–7

(Physical Chemistry)

Full Marks : 53

Pass Marks : 21

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Choose the correct answer from the following : 1×5=5

(a) At a particular concentration, the $t_{½}$ of a reaction is 100 min. When the concentration of reactant becomes double half-life period becomes 25 min. The order of the reaction is

(i) 1

(ii) 2

(iii) 0

(iv) 3

(b) Number of components, number of phases and degrees of freedom of the system

$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$, $P_{NH_3} \neq P_{HCl}$

are

(i) 2, 2, 2

(ii) 2, 1, 1

(iii) 2, 1, 0

(iv) 1, 1, 1

(c) If two liquids *A* and *B* form minimum boiling azeotrope at some specific composition, then

(i) *A–B* interactions are stronger than those between *A–A* or *B–B*

(ii) vapour pressure of solution increases because more number of molecules of liquids *A* and *B* can escape from the solution

(iii) vapour pressure of solution decreases because less number of molecules of only one of the liquids escape from the solution

(iv) *A–B* interactions are weaker than those between *A–A* or *B–B*

(d) The condition which is not a favourable condition of physical adsorption is

(i) high pressure

(ii) negative ΔH

(iii) high critical temperature of adsorbate

(iv) high temperature

(e) A first-order reaction has a specific reaction rate of 10^{-2} s^{-1}. How much time will it take for 20 g of the reactant to reduce to 5 g?

(i) 238·6 seconds

(ii) 138·6 seconds

(iii) 346·5 seconds

(iv) 693·0 seconds

2. Answer any *five* questions from the following : 2×5=10

(a) The possibility of 4-phase equilibria in the sulphur system is ruled out. Explain.

(b) Describe the half-life method for determining the order of a reaction.

(c) "Azeotropes are mixtures." Comment on the statement with proper explanation.

(d) For the reaction $A(g)+3B(g) \rightarrow 2C(g)$, the rate of the reaction $\left\{\frac{-d[A]}{dt}\right\}$ is 3×10^{-3} mol L^{-1} min^{-1}. What is the value of $\frac{-d[B]}{dt}$ in mol L^{-1} min^{-1}?

(e) Explain any two factors upon which adsorption depends.

(f) What is shape-selective catalysis? Give one example of it.

3. Answer any *two* questions from the following : 6×2=12

(a) (i) Explain the effect of pressure on the transition temperature of rhombic sulphur and on the melting point of monoclinic sulphur with the help of Clapeyron equation. 2+2=4

(ii) What is the maximum number of phases that can coexist for a two-component system? Give reason. 2

(b) (i) Draw and explain the phase diagram of water system. 4

(ii) Explain why the fusion curve of ice has a negative slope whereas the sublimation curve has a positive slope in the phase diagram of water. 2

(c) (i) State Nernst distribution law. How is the law helpful in ascertaining the molecular complexity of the dissolved solute? 1+2=3

(ii) Prove that multi-step extraction is more economical than the single-step extraction. 3

4. Answer any *two* questions from the following : 6×2=12

(a) (i) Show that for a first-order reaction, the time required for 99·9% completion of the reaction is 10 times that required for 50% completion. 2

(ii) What are pseudounimolecular reaction? Give one example of this type of reaction. 2

(iii) Explain the effect of temperature on the rate of a chemical reaction. 2

(b) The following mechanism has been suggested for the decomposition of O_3 :

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$$

$$O_3 + O \xrightarrow{k_2} 2O_2$$

Assuming $k_{-1}[O_2] \geq k_2[O_3]$, show that the rate of the overall reaction is

$$\frac{-d[O_3]}{dt} = \frac{k[O_3]^2}{[O_2]}$$

What could be concluded from the appearance of $\frac{1}{[O_2]}$ in the rate equation? 5+1=6

(c) (i) For the reaction between gaseous chlorine and nitric oxide

$$2NO + Cl_2 \rightarrow 2NOCl$$

it is found that doubling the concentration of both reactants increases the rate 8 times but doubling the chlorine concentration alone doubles the rate. What is the order of the reaction with respect to nitric oxide and chlorine? Write the rate law of the reaction. 3+1=4

(ii) Show that for a second-order reaction, half-life period is inversely proportional to the initial concentration of the reactant. 2

(Continued)

5. Answer any *two* questions from the following : 4½×2=9

(a) What are enzyme-catalyzed reactions? Discuss the effects of concentration, temperature and pH on the rate of enzyme-catalyzed reaction. 1+3½=4½

(b) (i) Discuss any one mechanism of heterogeneous catalysis. 2½

(ii) What is autocatalysis? Give one example. 2

(c) (i) Discuss the use of nanoparticles as catalyst giving three examples. 3

(ii) What are catalytic poisons? Give one example. 1+½=1½

6. Answer any *one* question from the following : 5

(a) What are adsorption isotherms? Derive Langmuir adsorption isotherm and show that Freundlich isotherm is a special case of this isotherm. 1+3+1=5

(b) (i) Mention any four differences between physical adsorption and chemical adsorption. 2

(Turn Over)

(ii) Give reason why a finely divided substance is more effective as an adsorbent. 2

(iii) Write two important applications of adsorption in industry. 1

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