

A-FDN/RB-N-DIC

## CHEMISTRY

### Paper—III

Time Allowed : Three Hours

Maximum Marks : 200

### INSTRUCTIONS

*Please read each of the following instructions carefully before attempting questions :*

*There are TWELVE questions divided under TWO Sections. Candidate has to attempt TEN questions in all.*

*Attempt any FIVE questions from each of the TWO Sections A and B including question no. 1 (Section A) and question no. 7 (Section B) which are compulsory.*

*The number of marks carried by a question / part is indicated against it.*

*All parts and sub-parts of a question are to be attempted together in the answer book.*

*Attempts of questions shall be counted in chronological order. Unless struck off, attempt of a question shall be counted even if attempted partly.*

*Any page or portion of the page left blank in the answer book must be clearly struck off.*

*Answers must be written in ENGLISH only.*

*Neat sketches are to be drawn to illustrate answers, wherever required.*

*Unless other-wise mentioned, symbols and notations have their usual standard meanings.*

*Assume suitable data, if necessary and indicate the same clearly.*

## SECTION—A

(Attempt any FIVE questions including question no. 1 which is compulsory.)

1. Answer ALL of the following : 4×10=40
- (a) (i) Calculate the pH of  $1 \times 10^{-8}$  M  $\text{H}_2\text{SO}_4$  solution. 2
- (ii) Explain the behaviour of  $\text{NH}_4\text{Cl}$  in liquid ammonia solution. 2
- (b) Explain why ZnS precipitates on CuS from an acidic solution containing both copper and zinc on passing  $\text{H}_2\text{S}$  ? 4
- (c)  $\text{SO}_2$  and  $\text{NO}_2$  in atmosphere are to be analyzed. How do you collect the sample for analysis ? 4
- (d) Iodometry and Iodimetry are two different volumetric methods. Explain the difference between them with suitable examples and how they are useful ? 4
- (e) A mixture of hydrocarbons are analyzed using Gas chromatography with flame ionization detector. The peaks are sharp.

$R_T$  values and the corresponding intensities are as follows :

S.No.	Name of the compound	$R_T$ Value in mins	Signal Intensity
(i)	A	20.7	25
(ii)	B	2.9	500
(iii)	C	14.5	100
(iv)	D	8.0	300
(v)	E	16.3	50
(vi)	F	12.2	150

Draw the corresponding chromatogram. 4

- (f) Explain why absorption bands are broad in UV-visible spectra of a coloured organic compound. 4
- (g) Discuss the difference between Emission and Absorption spectra taking Flame Photometer and Atomic Absorption Spectrometer. 4
- (h) X-ray fluorescence (XRF) is used in the analysis of ores and minerals. What parameters in XRF are used? What are the interferences in the analytical method? What steps one should take to overcome them? 4
- (i) What is the difference between thermal coal, coking coal and metallurgical coke? What is their composition? How is calorific value of a coal sample determined? 4
- (j) What are different types of interferences in the quantitative analysis using ICP-MS? What methods one should use to overcome them? Explain with suitable examples. 4
2. (a) The solubility product constant of  $\text{CaF}_2$  in water at  $25^\circ\text{C}$  is  $K_{\text{sp}} = 4 \times 10^{-12}$ . Calculate the solubility of  $\text{Ca}^{2+}$  at equilibrium condition and in 0.01 M NaF solution. 5
- (b) What are the different sampling methods available for collecting an iron ore gross sample from 100 rakes train? What are the different techniques used to bring the gross iron ore sample collected to laboratory sample? 5
- (c) What are the criteria in the selection of a substance as acid-base indicator? How do you select

- indicators for strong acid-strong base titrations and strong acid-weak base titrations ? What is the difference between equivalence point and end point in a volumetric titration ? 5
3. (a) Explain the principles of Gas Chromatography, High Performance Liquid Chromatography and Ion Exchange Chromatography. What type of substances can be analyzed using the above ? 5
- (b) Explain how TLC is superior over Column Chromatography. 5
- (c) In a water sample pH and  $F^-$  are to be determined. What instrument do you use for the analysis of both the parameters ? What precautions one should take in the analysis ? 5
4. (a) What are the different modes of Atomic Absorption Spectroscopy ? What is difference among them ? Explain the function of Hollow cathode lamps. 5
- (b) How can you perform the analysis of an XRD of a mineral given to you ? Explain the same with Bauxite ore sample. 5
- (c) A sample of water is given for analysis of trace metals in ppb concentration. Which method do you choose and what precaution do you take while performing the analysis ? 5
5. (a) What are the different parameters in Proximate analysis of coal ? Describe the methods briefly. 5

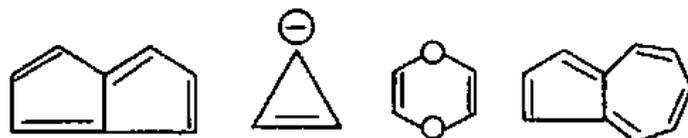
- (b) List the ores of aluminium and their composition.  
How do you determine 'Al' in Bauxite ? 5
- (c) How do you determine 'Pb' in samples of Petrol  
and Diesel ? 5
6. (a) How do you prepare 100 ppm of sodium chloride  
and sodium cation in 250 ml volumetric flask  
separately ? 5
- (b) Calculate the concentration of an indicator which  
has an absorption of 0.85 at 460 nm. The spectrum  
is taken in 0.5 cm thickness quartz cell. The molar  
extinction co-efficient of the indicator at 460 nm  
is  $5 \times 10^5 \text{ l.mole}^{-1}.\text{cm}^{-1}$ . 5
- (c) If 30 ml of 0.1 N  $\text{FeSO}_4$  was diluted to 100 ml  
and titrated with 0.1 N ceric sulphate with calomel  
as reference electrode. What was the 'emf' of the  
cell when 20 ml of  $\text{Ce}(\text{SO}_4)_2$  solution was added ?  
(Given  $E^\circ_{\text{Fe}} = +0.771$ ,  $E^\circ_{\text{SCE}} = +0.286$ ). 5

### SECTION—B

(Attempt any FIVE questions including  
question no. 7 which is compulsory.)

7. Answer ALL of the following :  $4 \times 10 = 40$
- (a) Write the structure of the compound with molecular  
formula  $\text{C}_9\text{H}_{18}$  which has only primary hydrogens. 4

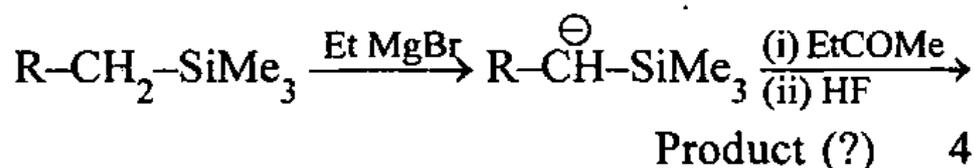
- (b) What do you understand by anti-aromaticity ?  
Which of the following compounds is aromatic and why ? 4



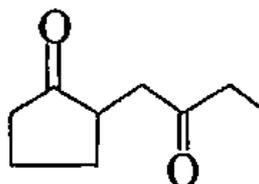
- (c) How will you make sure whether the two signals separated by 10 Hz in the  $^1\text{H}$  NMR spectrum are two singlets or a doublet ? 4
- (d) Give the basis for distinction between cis-2-butene and trans-2-butene using UV-visible spectroscopy. 4
- (e) How will you determine the molecular weight of a compound which does not show molecular ion in its mass spectrum ? 4
- (f) How will you distinguish between p-hydroxybenzaldehyde and salicylaldehyde using IR spectroscopy ? 4
- (g) Explain the relative rate of solvolysis of the following tertiary chlorides :

Compound	Relative Rate	
$\text{Me}_3\text{CCl}$	33	
$\text{Me}_2\text{EtCl}$	55	
$\text{Et}_3\text{CCl}$	99	
$\text{Me}(\text{i-Pr})_2\text{CCl}$	450	4

- (h) Write the stereochemical structure of the major product of the following reaction sequence :

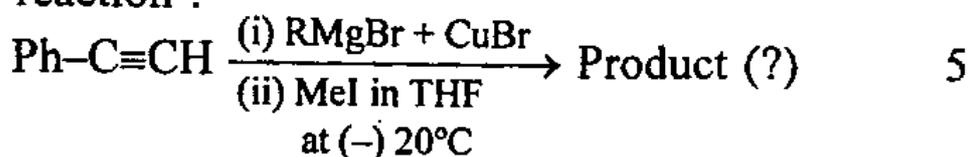


- (i) Write the main product of reaction between o-dichlorobenzene and sodamide. 4
- (j) Explain why anti-Markonikoff addition is not exhibited by HCl or HI when reacted with  $\text{CH}_2 = \text{CH}-\text{CH}_2-\text{CH}_3$ ? 4
8. (a) What is the major product formed when the following compound is treated with a strong base? Give reasons for your answer. 5

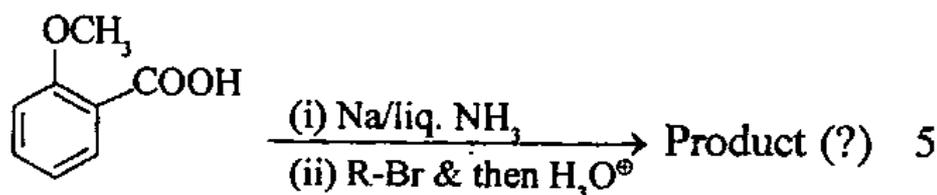


- (b) Explain the concept of thermodynamic and kinetic control of a reaction using the example of the reaction of an unsymmetrical ketone with a base. 5
- (c) How will you convert cyclohexanone to nylon (6)? Give mechanism of the reactions involved. 5
9. (a) Suggest any two methods for the syntheses of polyvinyl alcohol giving reasons for the better of the two. 5
- (b) Explain why 2 + 2 cycloadditions are thermally not favoured while photochemically they are preferred? 5
- (c) Claisen rearrangement is believed to involve a concerted pericyclic [3, 3] sigmatropic rearrangement. Explain this reaction by taking phenyl- $\alpha$ -methylallylic ether as an example. 5
10. (a) Draw the stereostructure of the most stable isomer of benzenehexachloride and explain why it persists in the soil for a long period? 5

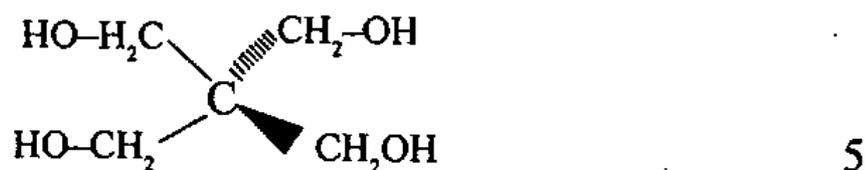
- (b) How will you convert cyclohexanone to cyclopentanone in good yield? Give mechanism for the reaction chosen by you. 5
- (c) Illustrate the use of boron hydrides for the transformation of isopropanol to n-propanol. 5
11. (a) Explain why 1, 8-(N, N-dimethylamino)-naphthalene is a much stronger base than N, N-dimethylaminobenzene? 5
- (b) Give the stereochemical outcome of the following reaction :



- (c) Explain the structure of the product formed in the following reactions :



12. (a) How will you synthesise A from carbonyl compounds containing one or two carbon atoms :



- (b) The mass spectrum of methyl salicylate shows a strong peak at  $m/z$  120. Explain its origin. 5
- (c) A compound having molecular formula  $\text{C}_8\text{H}_8\text{O}_2$  showed IR absorption at  $1680 \text{ cm}^{-1}$  as a strong sharp peak and prominent signals in its  $^1\text{H}$  NMR at  $\delta$  3.9 (s, 3H), 7.0 (d, 2H,  $J = 8.1 \text{ Hz}$ ), 7.8 (d, 2H,  $J = 8.1 \text{ Hz}$ ), 9.3 (s, 1H). Identify the compound. 5