

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  $\text{ZnS}$  precipitates on  $\text{CuS}$  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

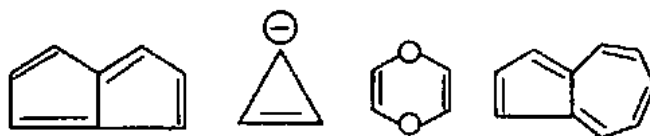
- (b) List the ores of aluminium and their composition.  
How do you determine 'Al' in Bauxite ? 5
- (c) How do you determine 'Pb' in samples of Petrol  
and Diesel ? 5
6. (a) How do you prepare 100 ppm of sodium chloride  
and sodium cation in 250 ml volumetric flask  
separately ? 5
- (b) Calculate 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

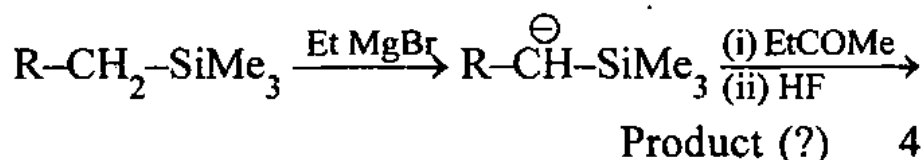
- (b) What do you understand by anti-aromaticity ?  
Which of the following compounds is aromatic and why ? 4



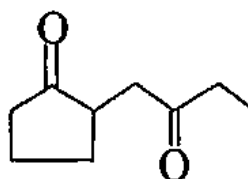
- (c) How will you make sure whether the two signals separated by 10 Hz in the  $^1\text{H}$  NMR spectrum are two singlets or a doublet ? 4
- (d) Give the basis for distinction between cis-2-butene and trans-2-butene using UV-visible spectroscopy. 4
- (e) How will you determine the molecular weight 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 :



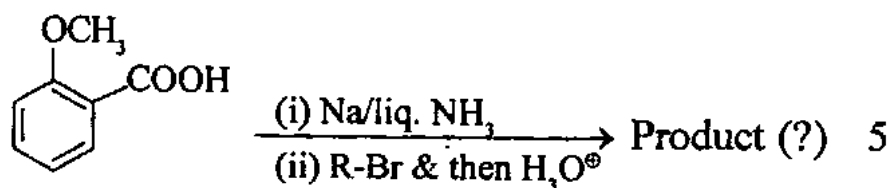
- (i) Write the main product of reaction between o-dichlorobenzene and sodamide. 4
- (j) Explain why anti-Markonikoff addition is not exhibited by HCl or HI when reacted with  $\text{CH}_2 = \text{CH}-\text{CH}_2-\text{CH}_3$  ? 4
8. (a) What is the major product formed when the following compound is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



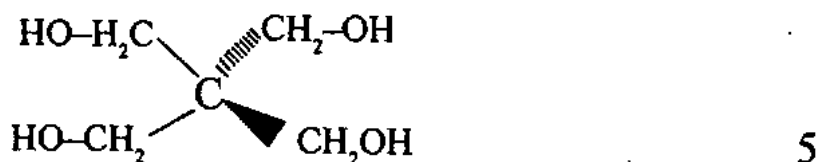
- (b) Explain the concept of thermodynamic and kinetic control of a reaction using the example of the reaction of an unsymmetrical ketone with a base. 5
- (c) How will you convert cyclohexanone to nylon (6) ? Give mechanism of the reactions involved. 5
9. (a) Suggest any two methods for the syntheses 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 :  

$$\text{Ph}-\text{C}\equiv\text{CH} \xrightarrow[\text{at } (-) 20^\circ\text{C}]{\begin{matrix} \text{(i) RMgBr + CuBr} \\ \text{(ii) MeI in THF} \end{matrix}} \text{Product (?)}$$
 5
- (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