

CHEMISTRY

PAPER—III

Time Allowed : Three Hours

Maximum Marks : 200

QUESTION PAPER SPECIFIC INSTRUCTIONS

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

There are TEN questions divided under TWO Sections.

Candidate has to attempt SIX questions in all.

Question No. 1 in Section—A and Question No. 6 in Section—B are compulsory. Of the remaining questions, candidates have to answer FOUR questions, choosing TWO from each Section.

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

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

Unless otherwise mentioned, symbols and notations have their usual standard meanings.

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

Attempts of questions shall be counted in sequential 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 Question-Cum-Answer Booklet must be clearly struck off.

Answers must be written in ENGLISH only.

SECTION—A

1. Answer **all** of the following questions :

5×8=40

- (a) Rewrite the following statement(s) if you find it/them incorrect :
Over the ionic strength range 0–0.1 M—
- (i) activity coefficients increase with increasing ionic strength;
 - (ii) activity coefficients increase with increasing ionic charge.
- (b) The molarity of $C_{29}H_{60}$ in winter rainwater is 5.6 nM. Find its concentration in parts per billion (ppb).
- (c) You have been asked to prepare a buffer solution with an alkaline pH by mixing ammonium chloride and aqueous ammonia from the following sets of solutions :
- (i) 50 ml solutions of 0.001 molar NH_4Cl and 0.003 molar aqueous ammonia
 - (ii) 50 ml solutions of 0.1 molar NH_4Cl and 0.3 molar aqueous ammonia
- Will both of them work? If not, which one will work efficiently and why?
- (d) During an acid-base titration experiment, a student noticed some drops of acid on the inside of the neck of the conical flask. The student decided to wash the drops into the main solution using distilled water. Briefly explain whether the action will have any consequences on the outcome of the titration.
- (e) In flame photometry, the analysis of analyte is carried out only in an interzonal region of the flame but not in the outer cone or primary combustion zone of the flame. Justify.
- (f) Explain the proximate analysis of coal.
- (g) How do you estimate manganese present in a steel sample volumetrically?
- (h) What is a gradient elution development in chromatography?

2. (a) Calculate the degree of hydrolysis and pH of 0.01 M Na_2CO_3 solution. Given, $K_1 = 4.31 \times 10^{-7}$ and $K_2 = 5.61 \times 10^{-11}$.

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(b) The equilibrium constant established between the salt and its corresponding ions in a given solvent is defined as solubility product. Taking a suitable example, explain how you will convert a salt with high solubility product into a solution.

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(c) In a direct titration of Cu^{2+} , Ni^{2+} , Co^{2+} , Cr^{3+} , Fe^{3+} and Al^{3+} with EDTA, Eriochrome Black T cannot be used as an indicator. Why?

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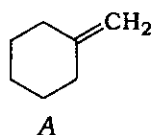
- (d) Numerous analytical procedures are based on titrations involving iodine. Starch is the indicator of choice for these experiments. What can be the sources of error in these procedures and how can it be avoided? 5
3. (a) Fluoride contamination is often encountered during purification of water. In order to ensure the permissible limits, concentration of fluoride needs to be determined. How will you determine it potentiometrically? 10
- (b) Differentiate between isoelectric and isoionic points by considering the example of a diprotic amino acid, alanine. 5
- (c) Which of the following equations represents redox reaction? After identification, balance the reaction and indicate the oxidizing and reducing agents : 5
- (i) $\text{BaCl}_2(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + 2\text{HCl}(\text{aq})$
- (ii) $\text{ClO}_3^-(\text{aq}) + \text{Zn}(\text{s}) + \text{H}^+(\text{aq}) \rightarrow \text{Cl}^-(\text{aq}) + \text{Zn}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- (d) Explain the concept of positive and negative errors during a co-precipitation process. 5
- (e) Hydrated oxides of iron(III) and aluminum have very high tendencies to adsorb the hydroxides of heavy metal cations such as zinc, cadmium and manganese. Suggest a solution to minimize this adsorption. 5
4. (a) A chloride of sulphur was found to have a relative molecular mass of 135. 5.4 g of the same sample was found to contain 2.84 g of chlorine. What is the molecular formula of the chloride? 5
- (b) Calculate the absorbance and transmittance of a $6.02 \times 10^{-5} \text{ M}$ solution of bis (1,10-phenanthroline) copper(I) complex at 435 nm. (The molar absorptivity of the complex is $7 \times 10^3 \text{ L cm}^{-1} \text{ mol}^{-1}$ and path length is 1 cm) 5
- (c) What is the real limitation of Beer's law? Explain the reasons for deviations from Beer's law. 5
- (d) In atomic spectroscopy, hollow cathode lamp is used as a radiation source. However, continuous radiation cannot be used as a radiation source in atomic spectroscopy. Justify. 5

- (e) Explain how two-line correction, background correction and Zeeman correction methods are employed to counter matrix interferences in atomic spectroscopy. 5
- (f) Thermal conductivity detector in GC responds to all analytes except the carrier gas. The flame ionization detector in GC is not universal. Justify. 5
5. (a) Write the basic theory of energy dispersive X-ray fluorescence spectroscopy (XRF). What is matrix effect in XRF? 10+5=15
- (b) What are isobaric interferences in ICP-MS? How are they eliminated? 5
- (c) How do you estimate Al_2O_3 in bauxite and copper in brass? 10

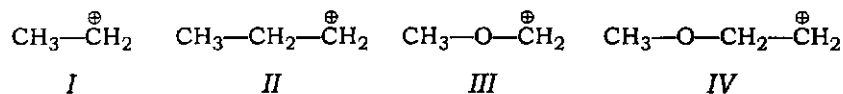
SECTION—B

6. Answer **all** of the following questions : 4×10=40

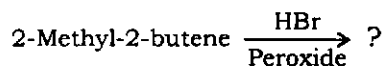
- (a) Give the product(s) expected from treatment of A with O_3 followed by Me_2S :



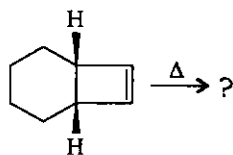
- (b) Arrange the following species in order of their decreasing stability :



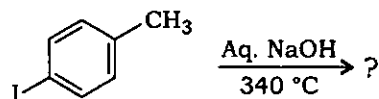
- (c) Involving the concept of stereoselectivity, write the acid-catalyzed dehydration product(s) of 2-pentanol.
- (d) Complete the following reaction showing the structure of the product(s) formed :



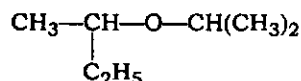
- (e) Indicating the process involved, write the product in the following transformation :



(f) Give the structure(s) of the product(s) in the following reaction :

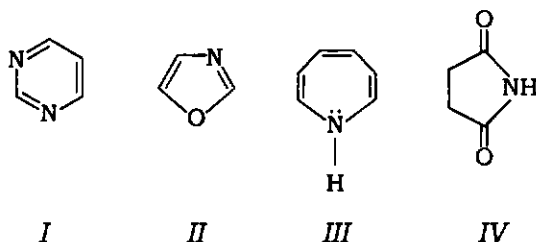


(g) Using the concept of inductive cleavage, predict the major peak in the mass spectrum of the following compound :

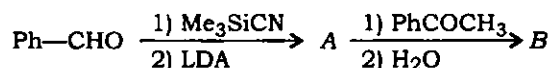


(h) Write the product of the reaction of cinnamic acid with hydrazoic acid (equimolar ratio) in presence of a strong mineral acid. Also give the name of the reaction involved.

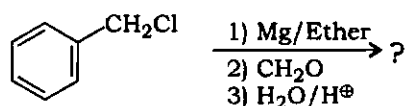
(i) Classify the following compounds as aromatic, anti-aromatic or non-aromatic :



(j) Identify A and B in the following sequence of reactions :



7. (a) Identify the intermediates and the final product in the following sequence of reactions giving mechanism of the last two steps : 10



(b) Arrange the following alkanes in decreasing order of their melting points giving proper explanation : 5

(i) Pentane

(ii) Neopentane

(iii) Isopentane

(c) How is the amino acid proline synthesized using the services of potassium salt of phthalimide? 10

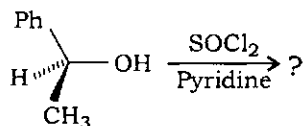
(d) Comment whether the following compounds are IR active or inactive in terms of C=C stretching absorption :

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- (i) 1-Octene
- (ii) 2-Methyl-1-heptene
- (iii) Cis-3-hexene
- (iv) Trans-3-hexene

8. (a) What is the product formed in the following reaction? Outline its mechanism explaining the stereochemistry :

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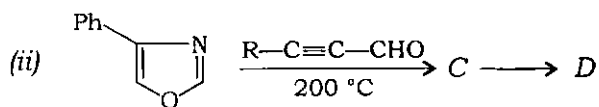
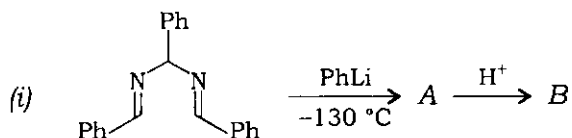


(b) What happens when trimethylacetyl chloride is treated with (i) benzene and (ii) anisole, in presence of AlCl_3 ? Explain giving plausible mechanism.

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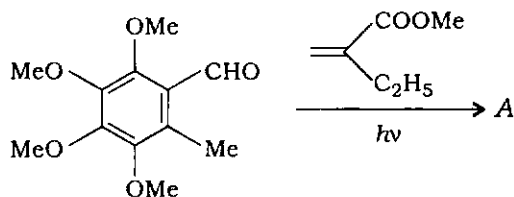
(c) Predict the products A, B, C and D in the following reactions :

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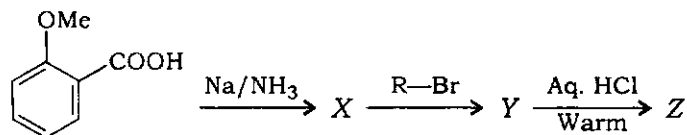


9. (a) Write the product A in the following reaction. Explain its formation mechanistically :

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(b) Consider the following reaction sequence :



Identify X, Y and Z. Explain the mechanism of their formation.

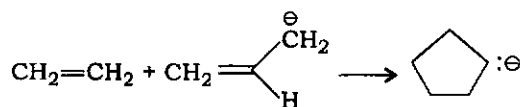
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(c) Comment upon the base-catalyzed elimination reaction of menthyl chloride and neomenthyl chloride while emphasizing on the stereoselectivity and stereospecificity.

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(d) Use the Woodward-Hoffmann rules to predict whether the following reaction would occur thermally or photochemically :

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10. (a) Deduce the structure of the organic compound showing the following spectral data :

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IR (cm^{-1}) = 3030, 1510, 1380, 930

EIMS = 210 (10%), 208 (30%), 173 (50%), 57 (100%)

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz, ppm) = δ 7.2–7.4 (*m*, 5H), 6.5 (*d*, $J=20.0$ Hz, 1H),
6.3 (*dd*, $J=20.0$ Hz and 6.0 Hz, 1H),
4.3 (*d*, $J=6.0$ Hz, 1H), 1.2 (*s*, 9H)

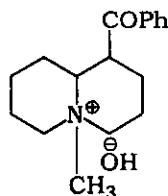
$^{13}\text{C-NMR}$ (proton decoupled) = 28, 37, 74, 126, 127, 128, 129, 132, 135

(b) Predict the $^1\text{H-NMR}$ spectrum of acetylacetone indicating the approximate δ -values of various peaks.

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(c) Supporting your answer with suitable mechanism, predict the product(s) when the following compound is heated :

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(d) Using Frost circle diagram, show why cyclooctatetraene is not aromatic while cyclopropenyl cation is aromatic.

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