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. These shall be drawn in the space provided for answering the question itself.

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

Q1. (a) The following values were obtained for the determination of cadmium in a sample of dust :

$$4 \cdot 3, \ 4 \cdot 1, \ 4 \cdot 0 \ \text{and} \ 3 \cdot 2 \ \mu g \ g^{-1}$$

Applying the Q-test, decide whether the last value, $3 \cdot 2$, should be rejected or not. [Given : Q critical for a sample size of four is $0 \cdot 831$]   5

(b) What is the ultimate analysis of coal ?   5

(c) A solution of concentration 1×10^{-3} M shows 60% transmittance where the cell thickness is 1 cm. Calculate the molar absorptivity of the sample solution. [Given : $\log_{10}(0 \cdot 60) = -0 \cdot 2218$]   5

(d) How will you estimate Zn in brass gravimetrically ?   5

(e) Mention the requisite conditions of the extracting solvent to be fit for solvent extraction.   5

(f) "Inductively Coupled Plasma (ICP) source is important as an atomisation source for emission spectroscopy." Explain why.   5

(g) Mention the function of Hollow Cathode Lamp (HCL). How does it function ?   5

(h) "X-ray powder diffraction methods are well-suited for solid state qualitative identification." Explain why.   5

Q2. (a) What do you mean by R_f (retardation factor) as used in Thin Layer Chromatography (TLC) ? What is the unit of R_f ? On which factor(s) does this R_f value depend(s) ? What is the utility of this factor ?   *4+1+3+2=10*

(b) $2 \cdot 5$ gm sample of brass is dissolved in acid and the volume is made up to 250 mL to prepare a stock solution. 25 mL of this stock solution is pipetted out and is titrated iodometrically with $0 \cdot 1010$ N standard $Na_2S_2O_3$ solution to have 16 mL titre value. Calculate the % Cu in the brass sample. [Atomic weight of Cu = $63 \cdot 54$]   5

(c) What is the main infrared (IR) region of interest for analytical purposes ? Write down the main sources of IR radiation as used in IR spectrophotometers. Which is the main means of monochromation in the IR region and why ? Mention the detectors as used in the detection of IR signal.   *1+6+5+3=15*

Q3. (a) Why is background correction required in Flame Atomic Absorption (FAA) and in Flame Atomic Emission (FAE) spectrometry ? Discuss about the various methods for such background correction. *2+13=15*

(b) How will you estimate $CaCO_3$ and $MgCO_3$ in a sample of dolomite titrimetrically ? *15*

[Sequential steps for the dissolution of dolomite, outlines of necessary titrations and the basis of calculations need to be mentioned].

Q4. (a) Briefly discuss about the theoretical basis of X-Ray Fluorescence (XRF) method. "XRF gives information about the bulk sample, not just the surface atoms as in Auger work." Explain why. *10+5=15*

(b) Mention the essential components of a UV-visible spectrophotometer along with their functions. *10*

(c) Distinguish between the scanning mode and isothermal mode of thermogravimetry (TG). Mention the principal components of a thermobalance. *3+2=5*

Q5. (a) A substance was known to contain $49 \cdot 10 \pm 0 \cdot 02\%$ of a constituent, 'A'. Two analysts attempted to determine 'A' using the same substance and the same analytical method. The results obtained by them were as follows :

First Analyst : % A $49 \cdot 01, 49 \cdot 25, 49 \cdot 08$ and $49 \cdot 14$

Second Analyst : % A $49 \cdot 40, 49 \cdot 44, 49 \cdot 42$ and $49 \cdot 42$

Compare their accuracies and precisions. Identify the types of errors associated with their analyses. *10*

(b) How will you extract Pb^{2+} ions from its aqueous solution through extraction by chelation technique ? *5*

(c) The TG curve of $2 \cdot 9$ mg of a sample containing $MgSO_4 . 7H_2O$ (molecular weight is 246) exhibited a weight loss of $0 \cdot 6$ mg at a temperature of $105°C$. Calculate the % of $MgSO_4 . 7H_2O$ in the sample. *5*

(d) Mention the utility of peristaltic pump in Inductively Coupled Plasma (ICP) spectroscopy. *5*

(e) $0 \cdot 55$ gm sample of an alloy steel was dissolved and its manganese content was oxidized to permanganate ion. The volume of the solution was diluted to 100 mL in a volumetric flask. The solution shows an absorbance of $0 \cdot 42$ at 530 nm due to MnO_4^- ion. Calculate the % of Mn in the alloy steel if path length is 1 cm and molar absorptivity for MnO_4^- ion is $4 \cdot 2 \times 10^3$ lit mole^{-1} cm^{-1}. [Atomic weight of Mn = 55]. *5*

SECTION B

Q6. **(a)** Arrange the following alkenes in increasing order of reactivity toward electrophilic addition reactions. Also give justification for the answer. **4**
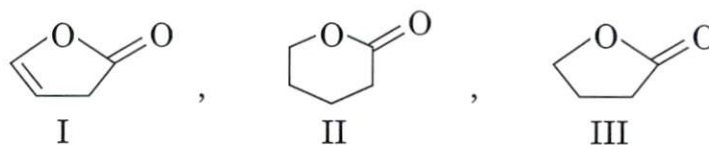
$CH_3CH = CH_2$, $CCl_3CH = CH_2$, $ClCH_2CH = CH_2$, $Cl_2CHCH = CH_2$

(b) Predict the product and propose a suitable mechanism for the following reaction : **4**
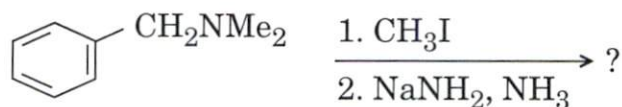
**(c)** Arrange the following compounds in order of increasing λ_{max}. Provide λ_{max} values also. **4**

| I | II | III |
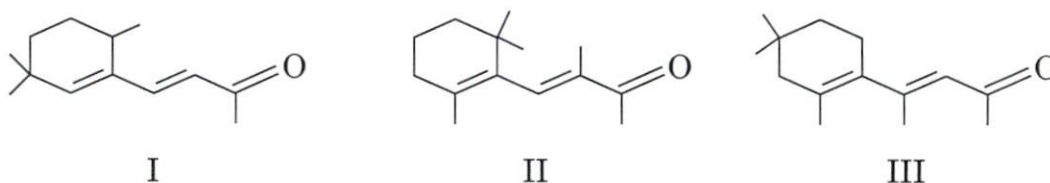
(d) Arrange the following compounds in descending order of the carbonyl stretching absorptions : **4**

| I | II | III |

(e) Predict the product in the following reaction. Provide a suitable justification to your answer. **4**

m-chloroperbenzoic acid, $\triangle$
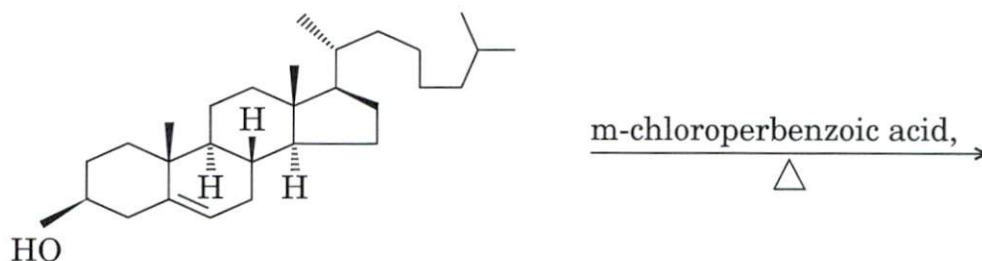
(f) Providing suitable mechanism, write down the product(s) in the following reaction :
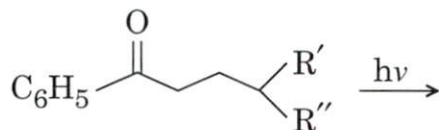
Compare the product(s) pattern formation when

(i) $R' = R'' = H$

(ii) $R' = R'' = CH_3$ **6**
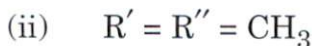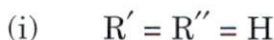
(g) Three isomeric compounds A, B and C have molecular formula $C_4H_8O_2$. All of these show a strong absorption at 1730 cm^{-1} in their IR spectra. Their ^{1}H NMR spectra are as follows :

A : δ 1·2 (3H, t); 2·35 (2H, q); 3·7 (3H, s)

B : δ 1·2 (3H, t); 2·0 (3H, s); 4·1 (2H, q)

C : δ 1·0 (3H, t); 1·65 (2H, m); 4·1 (2H, t); 8·0 (1H, s)

Assign suitable structures to A, B and C. 6

(h) Explain the peculiar fragmentation pattern(s) observed in the mass spectrum of the following : 6

(i) 2-heptanone
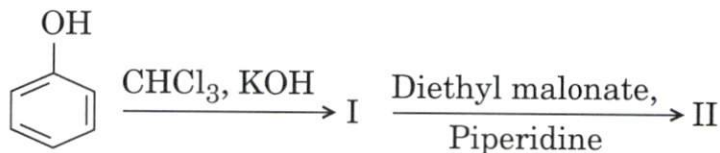
(ii) Hexanoic acid

(iii) Methyl hexanoate

(i) Arrange giving reasons, the following bonds in order of their decreasing vibrational frequencies : 2
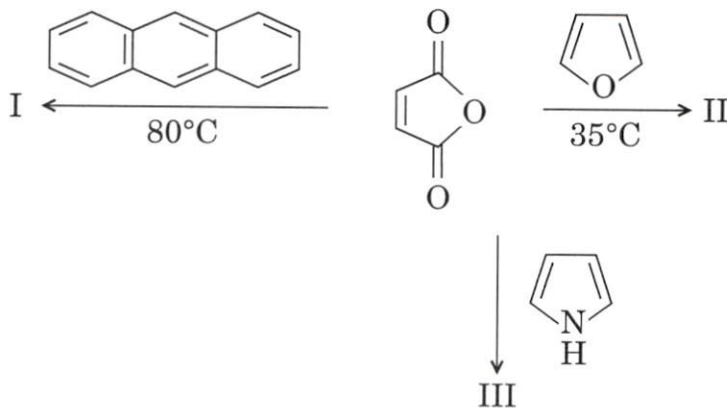
C – Cl, C – Br, C – C, C – O, C – H, C – I

Q7. (a) Complete the following reaction while sketching the suitable mechanism : 5+5=10

(b) Predict the products I, II and III in the following reactions with maleic anhydride. Propose mechanisms. 4+4+4=12

(c) 2,2-Dimethylcyclopropanone undergoes ring opening when attacked by methoxide ion, the product obtained possesses the following spectral properties :
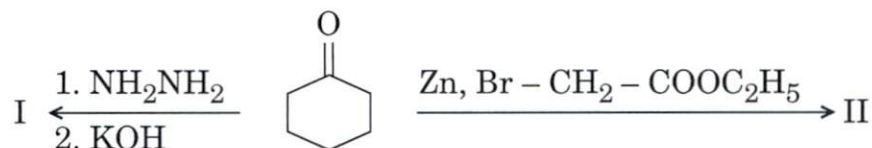
IR (v cm^{-1}) : 1740, 1160

^{1}H NMR (δ) : 3·6 (3H, s), 1·2 (9H, s)

Mass (m/z) : 116, 85, 59, 31

Deduce the structure of the product and explain its formation. Also write the structure of the other possible product.　　　　*8*

Q8. (a) Cyclohexanone gives different product(s) under the given reaction conditions. With the help of mechanism(s), explain the product(s) formation.
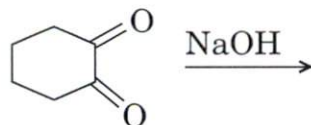

$$I \xleftarrow[\text{2. KOH}]{\text{1. NH}_2\text{NH}_2} \quad\bigcirc\!\!\!\!=\!\!O\quad \xrightarrow{\text{Zn, Br}-\text{CH}_2-\text{COOC}_2\text{H}_5} II$$

Also provide distinguishable IR spectral peaks of compound II.　　*5+5=10*

(b) Predict the product of the following reactant under given conditions. Suggest a suitable mechanism.　　　　*8*
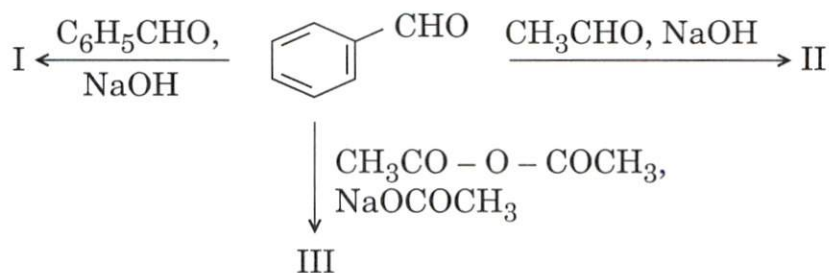

$$\xrightarrow{h\nu} ?$$
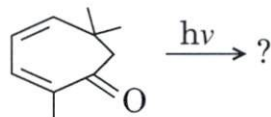
(c) While proposing a suitable mechanism, write down the product(s) obtained in the following dicarbonyl compound on treatment with base :　*4*

$$\xrightarrow{\text{NaOH}}$$

(d) Out of *cis*-2-butene or *trans*-2-butene, which one will give racemic-2,3-dibromobutane or meso-butan-2,3-diol on treatment with $Br_2 \,|\, CCl_4$ and $KMnO_4$, respectively ? Justify your answer.　　*4+4=8*
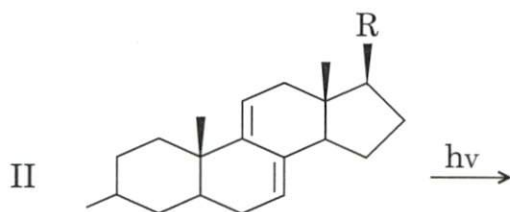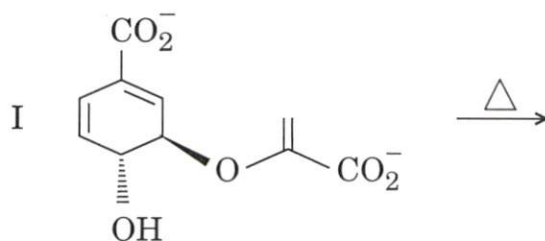
Q9. (a) Predict the product(s) when benzaldehyde is allowed to react with different reactants under given conditions.

$$I \xleftarrow[\text{NaOH}]{C_6H_5CHO,} \quad \text{[benzaldehyde: } C_6H_5\text{-CHO]} \quad \xrightarrow{CH_3CHO,\ NaOH} II$$

$$\Bigg\downarrow \begin{array}{l} CH_3CO - O - COCH_3, \\ NaOCOCH_3 \end{array}$$

III

Also provide suitable mechanism. *12*

(b) Giving justification, write down the reagents used and draw the mechanistic scheme for the synthesis of 1-methylcyclopentanol and 2-methylcyclopentanol from 1-methylcyclopentene. *8*

(c) Predict the products in the following reactions under given reaction conditions. Give justification. *10*

I [cyclohexadiene bearing CO_2^-, OH and $O\text{-}CO\text{-}CO_2^-$ ester substituents] $\xrightarrow{\triangle}$

II [steroid skeleton with R group] $\xrightarrow{h\nu}$

Q10. (a) Giving proper explanation, deduce the structure of the organic compound with molecular formula $C_{12}H_{14}O_4$ with the following spectral data : *10*

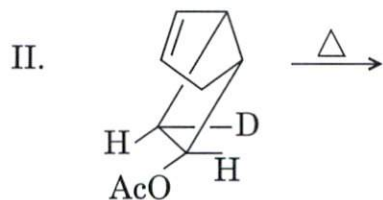UV, λ_{max} nm : 230 (ε-10,000)

IR, ν cm^{-1} : 3040 (w), 2980 (w), 2880 (w), 1715 (s), 1600 (m), 1580 (m), 1450 (m), 1375 (m), 1280 (s), 1070 (s), 740 (s)

^{1}H NMR, δ : 1·31 (t, J = 7 Hz, 6H), 4·4 (q, J = 7 Hz, 4H), 7·64 – 7·98 (m, 4H)

MS [m/z] : 222, 177, 149, 121

(b) Write down the products in the following reactions and provide a suitable explanation : 4+6=10

I.   2 $\xrightarrow{\text{Room temp.}}$

II. $\xrightarrow{\Delta}$

(c) Sketch the route for the synthesis of the following from benzoic acid involving common intermediate(s) : 10

(i) $C_6H_5NHCONHCH_3$

(ii) $C_6H_5NH_2$

(iii) $C_6H_5NHCOOC_2H_5$