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 in each section candidates have to answer **FOUR** questions choosing **TWO** from each section.*

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 Question-cum-Answer Booklet.

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.*

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.

SECTION A

Attempt any *three* questions including question no. 1 which is compulsory.

Q1. Answer all of the questions given below : *5×8=40*

(a) A mixture of CuO and Cu_2O with a mass of 10·50 g is reduced to give 8·66 g of pure Cu metal. What are the amounts of CuO and Cu_2O (in g) in the original mixture ? *5*

(b) To a mixture of Sr^{2+} and Ba^{2+} solution, Na_2SO_4 solution is added gradually. Which one of the two will be precipitated first ? *5*

Given :

$$S_{SrSO_4} = 2{\cdot}8 \times 10^{-7}$$

$$S_{BaSO_4} = 4{\cdot}2 \times 10^{-11}$$

(c) Aniline is a weak organic base in aqueous solutions. Suggest a solvent in which aniline can become a strong base with proper scientific reason. *5*

(d) Explain the scientific basis of functioning of fluoride ion selective electrode. *5*

(e) Discuss the effect of organic solvents in AAS measurement. *5*

(f) How does flame ionization detector work ? Name two compounds that cannot be measured by this detector. *4+1=5*

(g) Explain how proximity analysis of coal can be determined by thermogravimetric analyzer. *5*

(h) 0·1 g of dolomite ore was acid digested and a stock solution was prepared in a 25 mL volumetric flask using de-ionized water. An aliquot of 1 mL of the stock solution was pipetted into 100 mL volumetric flask and the volume was made up by de-ionized water. This solution was subjected to analysis of Fe content by ICP-MS. After suitable calibration, the output of ICP-MS analysis showed Fe concentration as 4 µg/L. Find the concentration of Fe in the dolomite ore in µg/g. *5*

Q2. (a) Arrange the following mixture of oxidant-fuel combination in the increasing order of flame temperature in AAS : *5*

air-acetylene; air-natural gas; nitrous oxide-acetylene; oxygen-acetylene

(b) Explain the Doppler broadening effect in AAS. *5*

(c) Explain the principle of XRF technique and comment how this technique is useful for qualitative and quantitative analysis. Arrange the K, L and M X-ray of Au in energy dispersive XRF. *6+4=10*

(d) A mineral corresponding to orthorhombic system was studied by XRD using X-rays of wavelength λ = 1·54 Å. The X-ray reflection planes from (100), (010) and (001) were observed at 2θ = 22·5°, 9·8° and 28·8° respectively. Find the dimension of the unit cell and the number of molecules of the mineral in the unit cell. *10*

Given :

Molecular weight of the mineral = 140 g/mol

Density of the mineral = 4·2 g/cm^3

Q3. (a) Compare the features of different types of detectors used in HPLC system. *10*

(b) What is correlation index in petroleum analysis ? How is it useful for classification of petroleum ? *5*

(c) Match the combinations for cellulose powder and sephadex gel as sorbents with the chromatographic mechanisms and applications listed below in columns A and B, respectively : *5*

Column A (Chromatographic Mechanism)	*Column B* (Applications)
• Exclusion principle	• Non-polar compound
• Stereo-adsorptive interaction	• Amino acids
• Modified partition	• Polymers
• Ion-exchange	• Mixture of enantiomers
• Partition	• Halides

(d) What is the principle involved in ICP-MS analysis ? Why should high salt content be avoided during sample preparation for ICP-MS analysis ? *10*

Q4. (a) A mixture of $KMnO_4$ and K_2CrO_4 weighing 0·24 g on being treated with acidic KI solution is found to liberate iodine (I_2) to react with 60 ml of 0·1 N $Na_2S_2O_3$. Find out the percentage of Cr and Mn in the mixture. *10*

(b) Calculate the concentration of Ni^{2+} in a solution that was prepared by mixing 50·0 mL of 0·0300 M Ni^{2+} with 50·0 mL of 0·0500 M EDTA. The mixture was buffered to a pH of 3·0. *10*

Given :

Formation constant of

Ni^{2+}- EDTA complex : $4{\cdot}2 \times 10^{18}$

α_4 for Ni^{2+}- EDTA

complex at pH = 3·0 : $2{\cdot}51 \times 10^{-11}$

(c) Explain the functions of

(i) Diphenylamine sulphonic acid

(ii) Methyl yellow

as indicators. *10*

Q5. (a) Write a balanced net ionic equation for the following reactions : *10*

$$IO_3^-(aq) + I^-(aq) \xrightarrow{\text{Acid}} I_3^-(aq)$$

$$P(s) + PO_4^{3-}(aq) \xrightarrow{\text{Base}} HPO_3^{2-}(aq)$$

(b) A compound X contains only carbon, hydrogen, nitrogen and chlorine. When 1·00 g of X is dissolved in water and allowed to react with excess $AgNO_3$, 1·95 g of AgCl is collected. When 1·00 g of X is subjected to complete combustion, 0·900 g of CO_2 and 0·735 g of H_2O are formed. What is the empirical formula of X ? *10*

(c) Are the equivalence point and end point the same ? Justify your answer. *5*

(d) Calculate the (i) molar concentration, and (ii) molality of a sulphuric acid solution of density 1·198 g/cm^3 containing 27% H_2SO_4 by weight. *5*

SECTION B

Attempt any *three* questions including question no. 6 which is compulsory.

Q6. Answer all the following : *5×8=40*

(a) Explain why p-nitrophenol is more acidic than m-nitrophenol. *5*

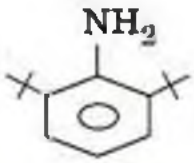
(b) Draw *pi* molecular orbital diagram of the following species : *5*

(I) (II)

(c) Explain why acetaldehyde is more reactive than benzaldehyde for nucleophilic addition reaction. *5*

(d) Arrange the given carbocations in their decreasing order of stability and give reasons for your answer. *5*

(I) (II) (III)

(e) Explain why  is more basic than aniline although both are aromatic primary amines. *5*

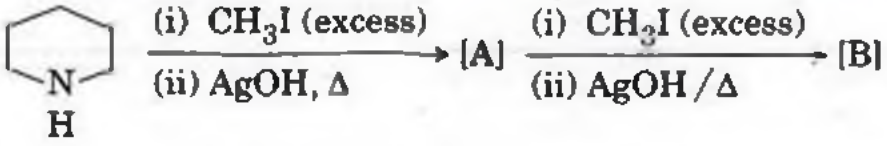
(f) Which one of the following compounds has higher dipole moment and why ? *5*

(I) (II)

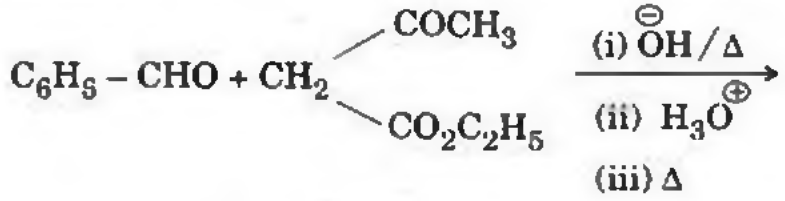
(g) Explain why one of the following compounds gives S_N1 reaction : *5*

(I) (II)

(h) Complete the following reaction and give the structure of the compounds [A] and [B] : 5



Q7. (a) Complete the following reactions and give their mechanisms : **5×2=10**

(i) 

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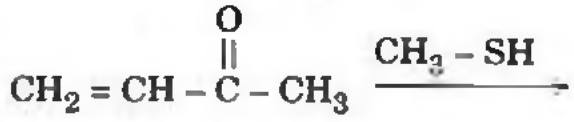
(ii) 

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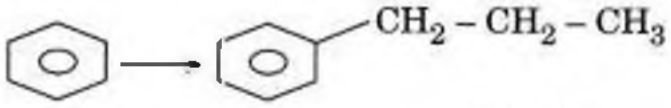
(b) How can the following conversions be achieved ? Provide suitable methods which give good yields. **5×2=10**

(i) 

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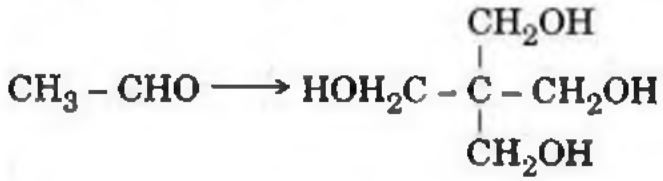
(ii) 

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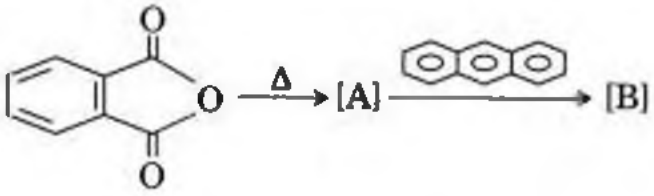
(c) Complete the following reaction and give the structure of [A] and [B] : 10



Q8. (a) Complete the following reactions and give the stereochemistry of the product(s) : **5×2=10**

(i) 

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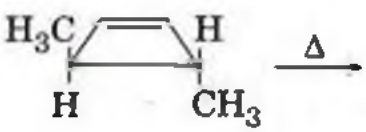
(ii) 

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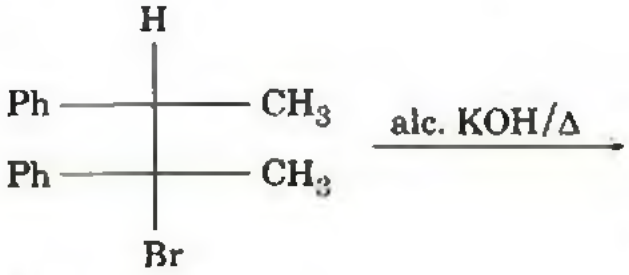
(b) Complete the following reactions and provide stereochemistry of the product : **5×2=10**

(i) 

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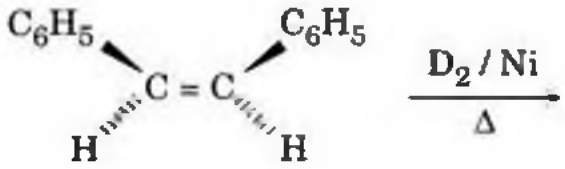
(ii) 

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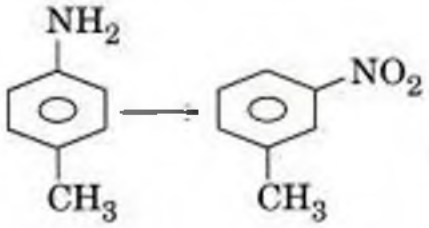
(c) How can the following conversions be achieved ? **5×2=10**

(i) 

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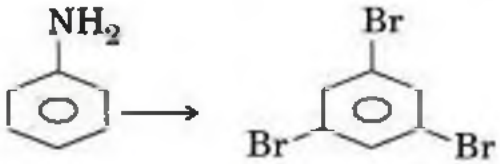
(ii) 

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Q9. (a) What are the characteristics of pericyclic reactions ? Give *pi* molecular orbital diagram of 1,3,5-hexatriene. Indicate

(i) Ground state HOMO and LUMO, and

(ii) Excited state HOMO and LUMO

of the system. *10*

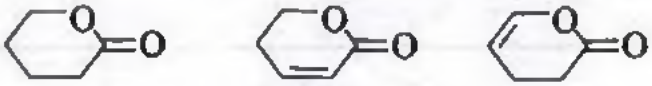
(b) Complete the following reactions : **5×2=10**

(i) $CH_3 - CH_2 - Cl \xrightarrow[\text{(ii) NaH}]{\text{(i) } Ph_3P}$  5

(ii) $C_6H_5CHO \xrightarrow[\text{(ii) } H_3O^{\oplus}]{\text{(i) } BrCH_2\overset{O}{\overset{\|}{C}} - OC_2H_5 / Zn}$ 5

(iii) Δ

(c) Arrange ν_{max} (C = O) of the following compounds in decreasing order. Give reasons in favour of your answer. *10*



(I) (II) (III)

Q10. (a) Give relative intensities of the parent cations of the compounds given below : *10*

CH_2Br_2 CH_2Cl_2

(I) (II)

(b) Indicate the number of PMR and CMR signals of the given compounds : *10*

(I) (II)

(c) An organic compound $C_6H_{12}O_2$ gave the following spectral data :

UV : λ_{max} 283 nm, ε_{max} 27

IR : Significant absorption bands at 3450, 2900 and 1705 cm^{-1}

PMR : δ 1·3 (6H, S); 2·2 (3H, S) and 3·8 (1H, S : exchangable with D_2O); 2·5 (S, 2H).

CMR (off-resonance decoupled) : Two singlets, one triplet and one quartet. One of the singlets is at 210 pm and the other at 70 ppm.

Mass : Prominent peaks at m/z 116, 58 and 43.

Deduce the structure of the compounds and explain the spectral data. *10*