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# UPSC CGS Exam

Chemistry (Paper III)

Simplifying  
Government Exams

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**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<sub>2</sub>O 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<sub>2</sub>O (in g) in the original mixture ? 5
- (b) To a mixture of Sr<sup>2+</sup> and Ba<sup>2+</sup> solution, Na<sub>2</sub>SO<sub>4</sub> solution is added gradually. Which one of the two will be precipitated first ? 5

Given :

$$S_{SrSO_4} = 2.8 \times 10^{-7}$$

$$S_{BaSO_4} = 4.2 \times 10^{-11}$$

- (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  $\lambda = 1.54 \text{ \AA}$ . The X-ray reflection planes from (100), (010) and (001) were observed at  $2\theta = 22.5^\circ$ ,  $9.8^\circ$  and  $28.8^\circ$  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 =  $4.2 \text{ g/cm}^3$

- 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

<i>Column A</i>	<i>Column B</i>
(Chromatographic Mechanism)	(Applications)
<ul style="list-style-type: none"> <li>• Exclusion principle</li> <li>• Stereo-adsorptive interaction</li> <li>• Modified partition</li> <li>• Ion-exchange</li> <li>• Partition</li> </ul>	<ul style="list-style-type: none"> <li>• Non-polar compound</li> <li>• Amino acids</li> <li>• Polymers</li> <li>• Mixture of enantiomers</li> <li>• Halides</li> </ul>

- (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  $\text{KMnO}_4$  and  $\text{K}_2\text{CrO}_4$  weighing 0.24 g on being treated with acidic KI solution is found to liberate iodine ( $\text{I}_2$ ) to react with 60 ml of 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$ . Find out the percentage of Cr and Mn in the mixture. 10

- (b) Calculate the concentration of  $\text{Ni}^{2+}$  in a solution that was prepared by mixing 50.0 mL of 0.0300 M  $\text{Ni}^{2+}$  with 50.0 mL of 0.0500 M EDTA. The mixture was buffered to a pH of 3.0. 10

Given :

Formation constant of

$\text{Ni}^{2+}$ - EDTA complex :  $4.2 \times 10^{18}$

$\alpha_4$  for  $\text{Ni}^{2+}$ - EDTA

complex at pH = 3.0 :  $2.51 \times 10^{-11}$

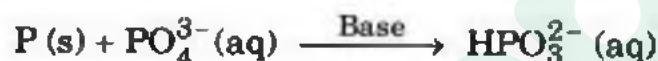
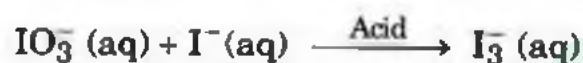
- (c) Explain the functions of

(i) Diphenylamine sulphonic acid

(ii) Methyl yellow

as indicators. 10

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



- (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  $\text{AgNO}_3$ , 1.95 g of  $\text{AgCl}$  is collected. When 1.00 g of X is subjected to complete combustion, 0.900 g of  $\text{CO}_2$  and 0.735 g of  $\text{H}_2\text{O}$  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  $1.198 \text{ g/cm}^3$  containing 27%  $\text{H}_2\text{SO}_4$  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

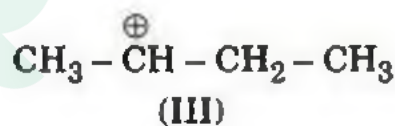
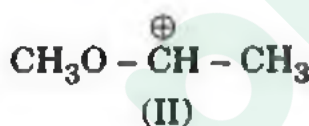
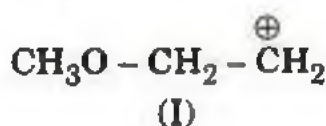


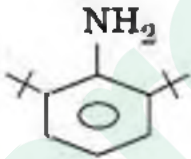
(I)



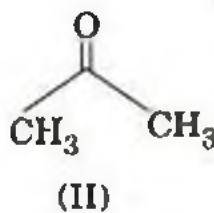
(II)

- (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

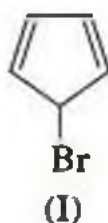


- (e) Explain why  is more basic than aniline although both are aromatic primary amines. 5

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

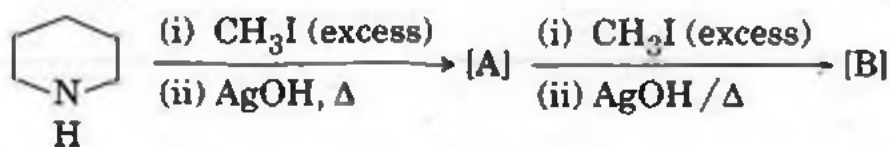


- (g) Explain why one of the following compounds gives  $\text{S}_{\text{N}}1$  reaction : 5



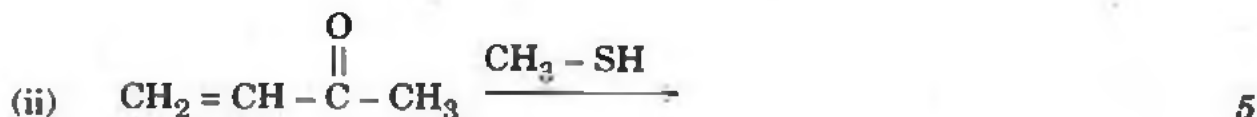
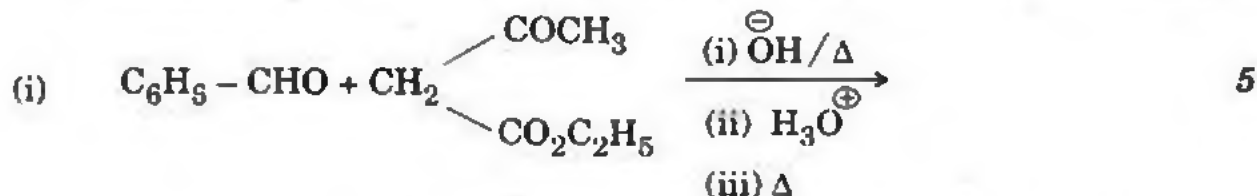
- (h) Complete the following reaction and give the structure of the compounds [A] and [B] :

5



- Q7. (a) Complete the following reactions and give their mechanisms :

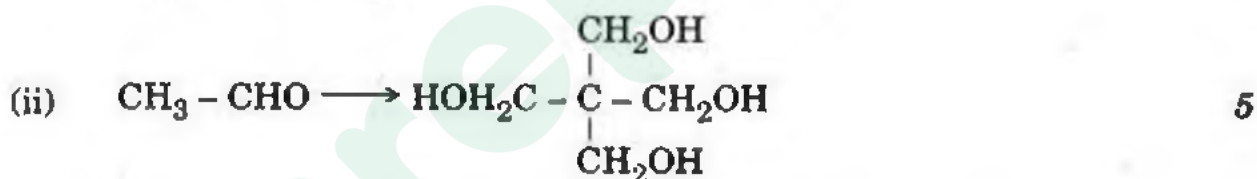
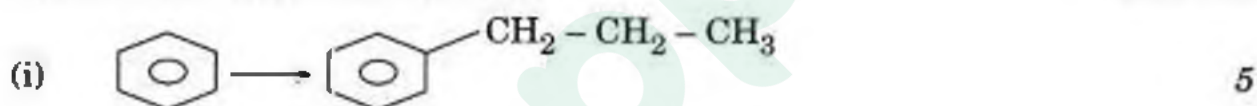
5×2=10



5

- (b) How can the following conversions be achieved ? Provide suitable methods which give good yields.

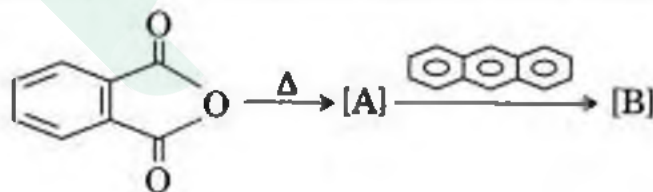
5×2=10



5

- (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

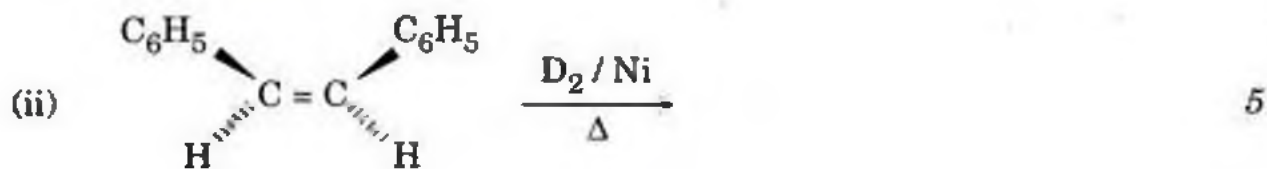
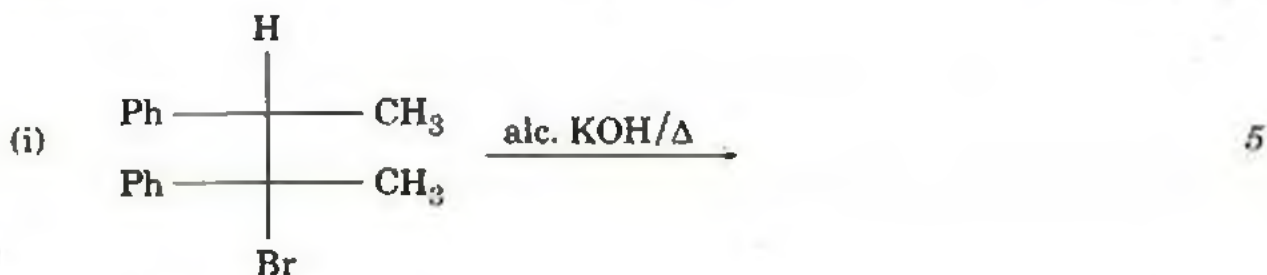


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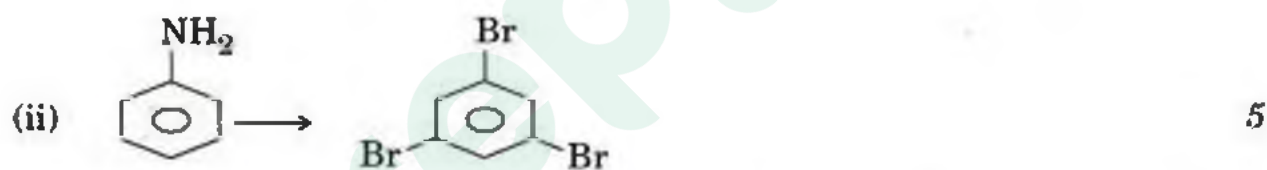


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- (b) Complete the following reactions and provide stereochemistry of the product : 5×2=10



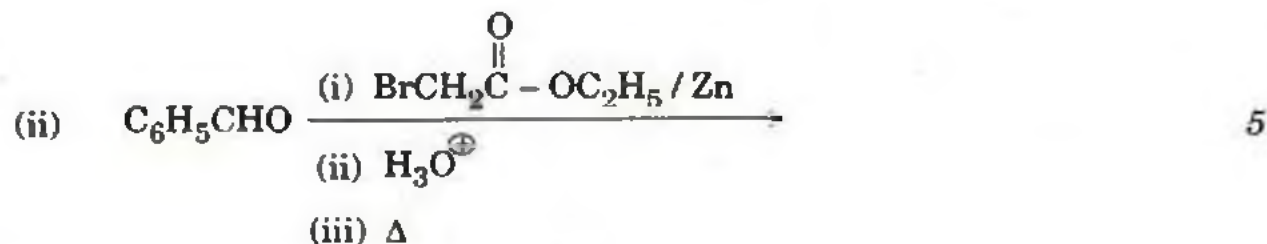
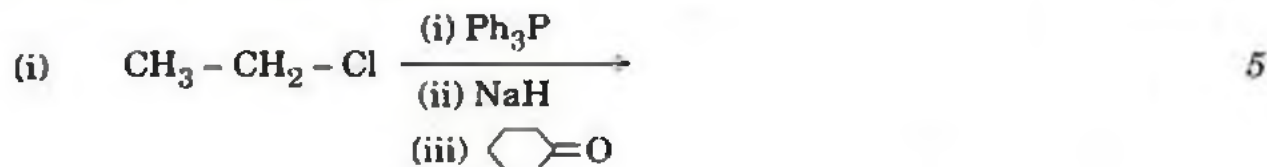
- (c) How can the following conversions be achieved ? 5×2=10



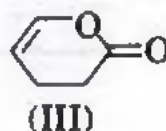
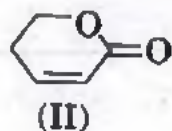
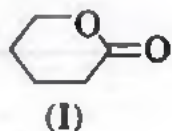
- Q9. (a) What are the characteristics of pericyclic reactions ? Give  $\pi$  molecular orbital diagram of 1,3,5-hexatriene. Indicate
- Ground state HOMO and LUMO, and
  - Excited state HOMO and LUMO of the system.

10

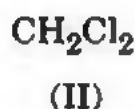
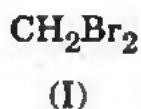
- (b) Complete the following reactions : 5×2=10



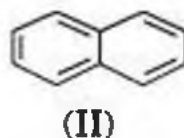
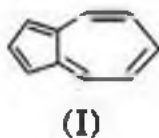
- (c) Arrange  $\nu_{\max}$  (C = O) of the following compounds in decreasing order. Give reasons in favour of your answer. 10



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



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



- (c) An organic compound  $\text{C}_6\text{H}_{12}\text{O}_2$  gave the following spectral data :

UV :  $\lambda_{\max}$  283 nm,  $\epsilon_{\max}$  27

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

PMR :  $\delta$  1.3 (6H, S); 2.2 (3H, S) and 3.8 (1H, S : exchangeable with  $\text{D}_2\text{O}$ ); 2.5 (S, 2H).

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



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