

Sl. No. 0010191

A-GSE-P-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 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 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 otherwise mentioned, symbols and notations have their usual standard meanings.

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

Section – A

1. Answer *all* of the following questions : $4 \times 10 = 40$

- (a) pH of an aqueous solution at 400°C is 6.76. What is the nature of the solution? (acidic/basic/neutral) {Given K_w at 400°C is 2.92×10^{-14} }. Justify your answer.
- (b) What are the alkaline error and the acid error of a glass membrane pH electrode?
- (c) What is solid phase extraction? Write down the main principle involved in it.
- (d) Silver forms ccp lattice and X-ray studies of its crystals show that the edge length of its unit cell is 408.6 pm. Calculate the density of silver (Atomic mass = 107.9^u).
- (e) State the purpose of an auxiliary complexing agent and taking an example, illustrate its use.
- (f) 20 ml of an aqueous solution of 0.10 M butyric acid was shaken with 10 ml ether. After the layers were separated, it was determined by titration that 0.5 mol of butyric acid remained in the aqueous layer. What is the distribution ratio and the per cent extracted?

- (g) 3% Ni in steel to be analyzed from 1.0 g of steel sample. What volume of 1% wt of DMG (dimethyl glyoxime) in alcohol to be used to provide a 50% excess of DMG for the analysis. The density of alcohol (0.79 g/ml). FM : Ni(58.69); DMG(116.12).
- (h) Write down the principles of High Performance Liquid Chromatography (HPLC) and Gas Liquid Chromatography (GLC).
- (i) In atomic absorption spectroscopy (AAS) what is the significance of background absorption and background correction.
- (j) Given,
 $\text{AgBr(s)} + e^- \rightleftharpoons \text{Ag(s)} + \text{Br}^-; E_+^0 = 0.071 \text{ V}$
 $\text{Ag}^+ + e^- \rightleftharpoons \text{Ag(s)}; E_-^0 = 0.799 \text{ V}$
 Compute the solubility product expressed as $\text{AgBr(s)} \rightleftharpoons \text{Ag}^+ + \text{Br}^-$.

2. (a) 25.00 ml liquid bleach was diluted to 1000 ml in a volumetric flask. An aliquot of 25 ml of this diluted sample was transferred to an Erlenmeyer flask and treated with excess KI. This gets oxidized to KI_3 and the bleach OCl^- to Cl^- . The liberated I_2 in the form of KI_3 required 8.96 ml of 0.09892 M $\text{Na}_2\text{S}_2\text{O}_3$ to titrate using starch as indicator. Find out the % W/V NaOCl in the bleach sample. 5
- (b) Lay down the procedure to separate and then estimate the constituents Cu, Zn, Sn, Pb and Fe of the Brass alloy. 5

(c) Consider a mixture of the two solids $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (FM : 244.26) and KCl (FM : 74.55). When the mixture is heated at 160°C for 1h, the water of crystallization is driven off. A sample originally weighing 1.783 g weighed 1.5623 g after heating. Calculate the weight % of Ba, K and Cl in the original sample. 5

3. (a) The amount of Fe in a 0.4891 g sample of an ore was determined by a redox titration with $\text{K}_2\text{Cr}_2\text{O}_7$. The sample was dissolved in HCl and the iron brought in to +2 oxidation state using Jones reductor. Titration using diphenylamine sulfonic acid as indicator, the end point required 36.92 ml of 0.02153 M of $\text{K}_2\text{Cr}_2\text{O}_7$. Report the iron content of the ore as % W/W Fe_2O_3 . 5

(b) Fill in the blanks :

- (i) When you double the frequency of electromagnetic radiation, you _____ the energy.
- (ii) When you double the wavelength, you _____ the energy.
- (iii) When you double the wave number, you _____ the energy.
- (iv) 10% transmittance equals _____ absorbance.
- (v) When you double the path length, you _____ absorbance. 5

- (c) Write down the equations in terms of the acid dissociation constants and $[H^+]$ for the highest alpha value for each of the following :
- (i) Tartrate
 - (ii) Acetate
 - (iii) Phosphate
 - (iv) Nitrilo acetic acid
 - (v) EDTA 5
4. (a) Calculate the H_3O^+ (hydronium ion) concentration for a buffer solution of 2 M phosphonic acid and 1.5 M potassium hydrogen phosphate [$K_{a_1}=7.11 \times 10^{-3}$; $K_{a_2}=6.32 \times 10^{-8}$]. 5
- (b) How many milligrams of CO_2 and H_2O will be produced from the combustion of 4.635 mg of benzoic acid ? 5
- (c) Define acid-base indicator. Suggest the transition pH-range with colour changes in methyl orange and phenolphthalein indicators. 5
5. (a) A solution of carbon in face centered cubic iron has a density of 8.105 g cm^{-3} and a unit cell edge of 3.589 \AA . Are the carbon atoms interstitial or do they substitute for iron atoms in the lattice? Calculate the weight % of carbon. 5

(b) A brown ore confused as red hematite or pyrolusite requires different tariff rates for transport. As analyst, you performed a fusion test of the ore using $\text{Na}_2\text{CO}_3\text{-Na}_2\text{O}_2$. You leached the mass once get cooled with water. The leached colour would either be brown-violet or green in colour. On acidification with cold dilute H_2SO_4 , the colour vanishes quickly or acquired a violet colour. Based on the observations, can you identify the brown ore. Explain the expected changes in colour if the ore was for an iron or for a manganese. 5

(c) Sketch photometric titration curves for the following conditions :

- | | | |
|------|-------------------------------|---------------|
| (i) | $\epsilon_S = \epsilon_P = 0$ | S – Substrate |
| | $\epsilon_T > 0$ | P – Product |
| | | T – Titrant |
| (ii) | $\epsilon_T > \epsilon_P > 0$ | |
| | $\epsilon_S = 0$ | |
- 5

6. (a) In a UV-visible spectrum, if you observe a negative absorbance, suggest the reasons that can be responsible for this and possible remedies. 5

(b) Plot a measured value of pipet against the percentage of measurements in an experiment to plot a histogram showing the distribution of say 50 results. Correlate this histogram with a Gaussian Curve bearing same mean and standard deviation.

[% in range : 6, 2, 14, 18, 26, 14, 10, 8, 2]

No. in range : 3, 1, 7, 9, 13, 7, 5, 4, 1]

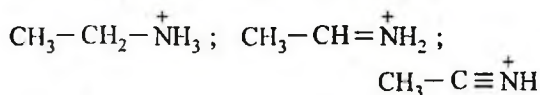
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- (c) 1.022 g of KIO_3 (FM : 214) was dissolved and made up to 500 ml in a standard measuring flask. When 50 ml of this solution was treated with excess KI (2g) and a mineral acid (10 ml of 0.5 M), I_3^- are produced. Find out the moles of I_3^- . 5

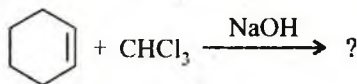
Section – B

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

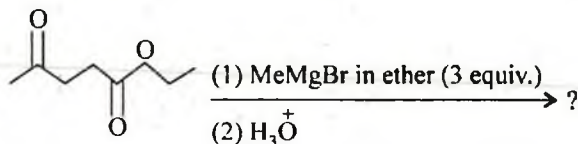
- (a) Arrange the following compounds in the order of decreasing acidity. Explain your answer.



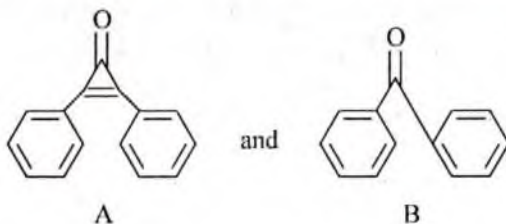
- (b) Predict the product of the following reaction and write the mechanism involved.



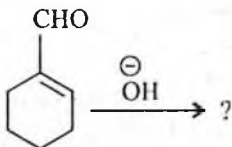
- (c) Complete the following reaction and propose a suitable mechanism for it.



- (d) Which of the following compounds A and B has the greater dipole moment? Explain.



- (e) Complete the following reaction and propose a suitable mechanism.

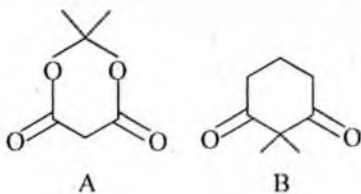


- (f) Sketch the following Π -molecular orbitals showing nodes:

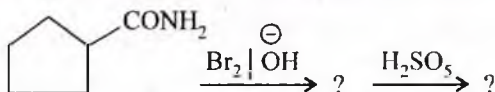
(i) HOMO for 1, 3-butadiene

(ii) LUMO for allyl cation

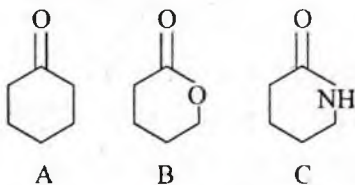
- (g) Explain why the compound A exists exclusively in the enol form and the compound B exists exclusively in the keto form.



- (h) Write the major product(s) of the following reaction sequence.

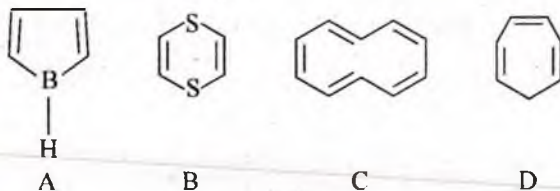


- (i) Arrange the compounds A, B and C in the order decreasing stretching frequency of $\text{C}=\text{O}$ in the IR spectrum. Justify your arrangements.



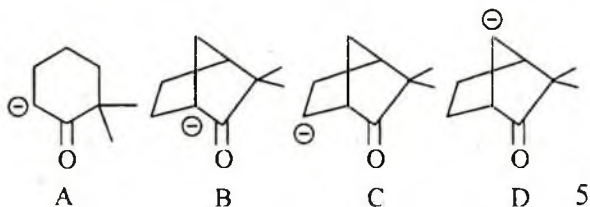
- (j) The mass spectrum of an unknown compound has a molecular ion peak with a relative intensity of 43.27% and an $M+1$ peak with a relative intensity of 3.81%. How many carbon atoms are present in the compound ?

8. (a) Classify the following compounds into aromatic, antiaromatic and non-aromatic. Explain your answer.



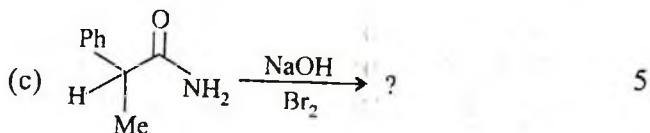
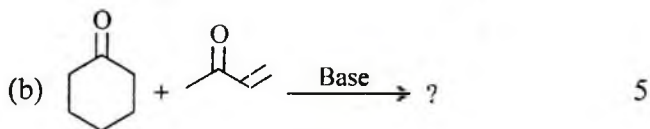
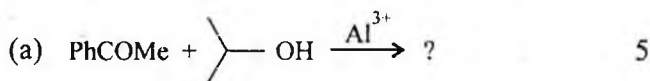
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- (b) Arrange the following Carbanions in their decreasing order of stability. Give reasons for the order given by you.

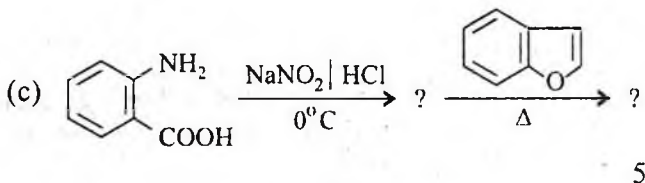
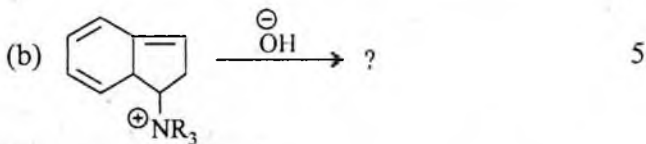
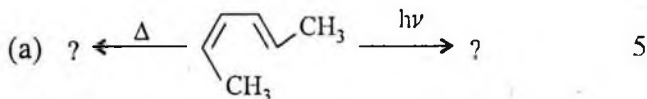


- (c) Describe Heinsberg's method of separation of amines. 5

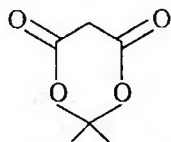
9. Give the main product of the following reactions and give plausible mechanisms involved for its formation.



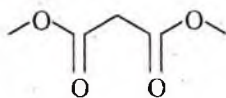
10. Predict the major product(s) in the following reactions. Suggest a suitable mechanism involved in each case.



11. (a) The cyclic compound A exhibits enhanced acidity when compared to acyclic compound B. Rationalize the observation.



A
 $\text{pK}_a = 7.42$



B
 $\text{pK}_a = 15.87$ 5

- (b) What are ylides? How the stabilized and unstabilized phosphorus ylides yield different products in the Wittig reaction with a cyclic ketone. 5

(c) Benzoin condensation fails or gives very low yields if the aldehyde contains electron donating or electron withdrawing groups. Explain. 5

12. (a) Why do polar solvents shift the $\Pi \rightarrow \Pi^*$ transition to a longer wavelength and $n \rightarrow \Pi^*$ transition to a shorter wavelength. 5

(b) A non-polar organic compound with molecular formula C_4H_6O does not show any significant UV absorption and has IR absorption at 3300–2900 and 2200 cm^{-1} . Its $^1\text{H-NMR}$ spectrum consists of three singlets at δ 3.0 (1H), 3.5 (3H) and 4.9 (2H). Elucidate the structure of the compound. 5

(c) An organic compound with molecular formula $C_8H_8O_3$ gives the following spectral data. Assign a suitable structure to the compound.

IR(cm^{-1}) : 2980(br), 1675(S), 1600(S), 1320(S), 1250(S), 1040(m), 940(br) and 835(S).

$^1\text{H-NMR}(\delta)$: 11.52 (1H, S), 6.8 – 8 (4H, m) and 3.85 (3H, S)

$^{13}\text{C-NMR}(\delta)$: 172, 167.2, 131.1, 122.9, 114, 56.

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