M.Sc. 3rd Semester Examination, 2011
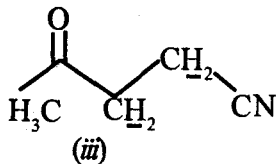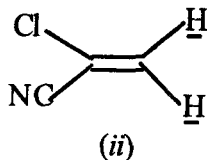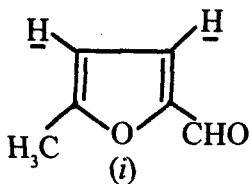
CHEMISTRY ·

PAPER — CEM- 303

Full Marks : 40

Time : 2 hours

The figures in the right hand margin indicate marks

(*Organic Special*)

Answer any **five** questions taking
at least **two** from each Group

GROUP — A

1. (*a*) Identify the spin systems (Pople notation) constituted by the protons underlined (H̲) in the following compounds (any *two*) : 2 + 2
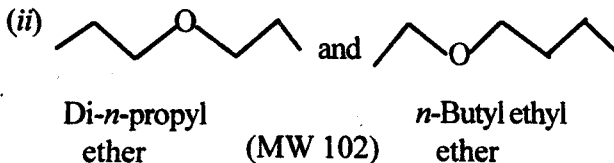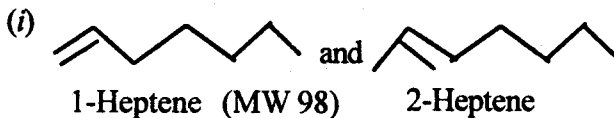
(b) What is a non-first order (^{1}H)NMR spectrum ? What are the three ways of getting information about δ and $\underline{J}$ values in such cases ? $1 + 3$

2. (a) What is the main disadvantage(s) of CW NMR ? How has this problem been solved ? $2 + 2$

(b) What chemical environments do the following $\underline{J}$ values correspond to ? 1×4

(i) 2-3 Hz

(ii) 7-8 Hz

(iii) 10-12 Hz

(iv) 16 -18 Hz .

3. (a) Write down the general structure of Lanthanide Shift reagents . If the lanthanide is europium and both the alkyl groups are CF_3 groups, what is the short name of this reagent ? $2 + 2$

(b) What is NOE ? Briefly explain your answer with a suitable example.   4

(Continued)

4. (a) Calculate the ^{13}C chemical shifts of the carbons marked with asterisks in the following compounds. Show the break-ups only. $2 + 2$

(i)

(ii)
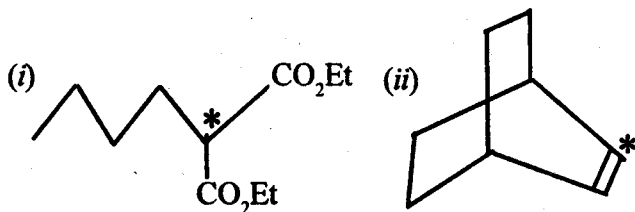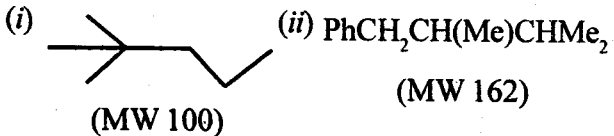

(b) Calculate S_{1_H}/S_{13_C}, i.e. the ratio of receptivities (strength of NMR signal) of ^1H and ^{13}C nuclei. Given, $\gamma_{1_H}/\gamma_{13_C} = 4$. 4

5. (a) Distinguish between the following structural isomers by EI-MS : $2 + 2$

(i)

1-Heptene (MW 98)   2-Heptene

(ii)

Di-*n*-propyl ether   (MW 102)   *n*-Butyl ethyl ether

(b) Show one important mass fragmentation of each of these compounds :   2 + 2

(i) [structure] (MW 100)   (ii) $PhCH_2CH(Me)CHMe_2$ (MW 162)

GROUP—B

6. Answer any *four* of the following :   2 x 4

   (i) State the number of molecular ion-peaks and their relative intensities to be observed in the El-MS of 1, 3, 5-tribromobenzene.

   (ii) Depict the formation of the peak of m/z 119 observed in the El-MS of anthranilic acid (MW 137).

   (iii) Show the genesis of the peak at m/z 72 observed in the El-MS of 3-heptanone (MW 114).

   (iv) Fatty acid methyl esters exhibit a strong peak at m/z 74 in their El-MS. Show the fragmentation.

   (v) Name a matrix used in FAB-MS or MALDI-TOF-MS. What is the full form of TOF ?

(*Continued*)

7. Find out the structures of the following *two* compounds from their data furnished below : 4 x 2

   (a) Compound 'A', $C_4H_8O_2$; UV : λ_{max} 206 nm ($\in$ 50); IR : 1736 cm^{-1} ; 1445 cm^{-1} ; ^{1}H NMR : δ 0·95 (3H, t, J = 7 Hz), 1·67 (2H, sextet, J = 7 Hz ; 4·12 (2H, t, J = 7 Hz), 8·07 (1H, s) ; MS : m/z 88 (M$^+$), 43.

   (b) Compound 'B', C_9H_{12} ; UV : λ_{max} 268 nm ($\in$ 480) ; IR : 1608, 1473 cm^{-1} ; ^{1}H NMR : δ 6·79(1H,s) , 2·26 (3H, s) ; MS : m/z 120 (M$^+$), 119.

8. (a) How would you differentiate the following pairs by mass spectrometry (any *two*) : 3 x 2

   (i)

   (ii)

   (iii)
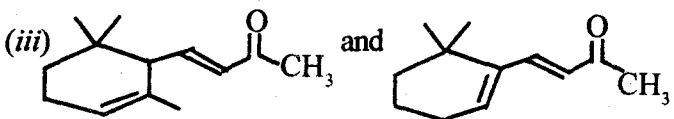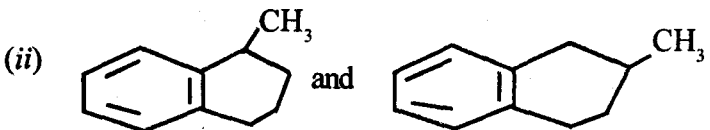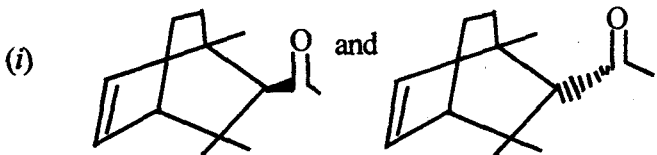
(b) What do you mean by metastable ion and peak ? Give an example. 2

9. (a) Write a short note about McLafferty Rearrangement. 3

(b) Show several fragmentation pattern of the following compound. 2
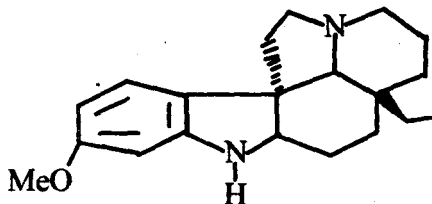
(c) Give some important features of the parent ion or peak. 3

10. (a) Distinguish between the following compounds with the help of mass spectrum (any *two*) : 2 x 2

(i) *n*-Butanol and 2-methyl propanol

(ii) and

(iii) $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$

and $CH_3 - \underset{\underset{CH_3}{|}}{CH} - \overset{\overset{CH_3}{|}}{CH} - CH_3$

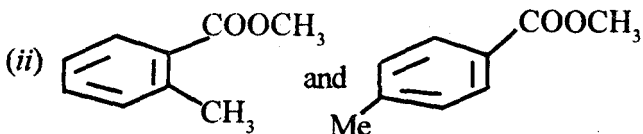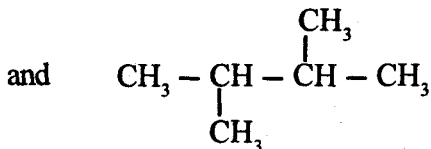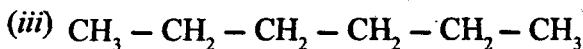(b) What is mass spectrum ?   1

(c) Why is accelerating voltage or magnetic field strength varried in mass spectro meter ?   3

(*Inorganic Special*)

Answer any **four** questions

1. Define Limiting Current and Half wave potential in polarography. How are these useful in analytical chemistry ?   10

2. (a) Lattice defects are inevitable in solid. Explain. $2\frac{1}{2}$

   (b) Explain with a neat diagram why lower stress is required to deform a solid which contain dislocation. $2\frac{1}{2}$

   (c) Find an expression for equilibrium concentration of Frenkel defect in an ionic crystal.   5

3. How does HPLC differ from GLC ? Name a few HPLC detectors. What are the characteristics of HPLC detectors ? 10

4. (a) Explain Kronig Penny model and find the E-k relation according to extended zone scheme and reduced zone scheme. 7

   (b) Distinguish metal, insulator and semiconductor according to Band theory. 3

5. (a) What is the difference between Distribution co-efficient and Distribution ratio ? 5

   (b) If distribution ratio for a certain solute in water-chloroform system is 10, calculate the percent of solute extracted from 50 ml of aqueous solution by 100 ml of chloroform where

      (i) 100 ml $CHCl_3$ is used in a single extraction.

      (ii) 100 ml $CHCl_3$ is divided in to five 20 ml portions which are used for extraction one after another ? 5

6. Answer any *five* questions from the following : 2 x 5

   (*i*) Why nano materials are much reactive than their bulk counterpart ?

   (*ii*) Name two chemical routes and two physical routes of nano material synthesis.

   (*iii*) State the basic principle of MOCVD.

   (*iv*) Give examples of one dimensional and two dimensional nano materials.

   (*v*) Give the basic difference between electron microscopy and probe microscopy.

   (*vi*) State distinct features of SEM.

   (*vii*) Draw the basic structure of atomic force microscope.

7. (*a*) What do you mean by Crystal engineering ? 2

   (*b*) Show the formation of hexagonal sheets by benzene -1, 3, 5-tricarboxylic acid via hydrogen bonding. 2

   (*c*) What is 'techton' ? 2

(*d*) What do you mean by the term 'network' in Crystal engineering ? Predict the Well's symbol for the following 2 D net : (2 + 2)
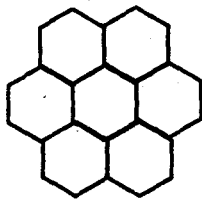
(*Physical special*)

GROUP – A

Answer any **one** question of the following

1. Use 1st order perturbation theory for a very weak perturbing potential (χH^1) and hence show that the transition probability from state '*n*' to '*k*' is given by

$$W_{n \to k} = \frac{1}{\hbar^2} \left| \int_{t'=0}^{t'=t} e^{i W_{kn} t'} H'_{kn} dt' \right|^2$$

where the terms have usual meaning. How does a perturbation constant with time effect on the transition probability ? Comment on your result. 6 + 4

2. What do you mean by prolate and oblate symmetric top ? Give one example for each. Show that for a rigid diatomic molecule, Rotational transition taken place between consecutive rotational level. Also justify that molecule must have permanent dipole moment to show IR activity. Given, Identity relation for associated Legendre polynomials. $\qquad$ $6 + 2 + 2$

$$(2J + 1)x\, P_J^{|M|}(x) = (J - |M| + 1)\, P_{J+1}^{|M|}(x) + (J - |M|)P_{J-1}^{|M|}(x)$$

GROUP – B

Answer any **one** question of the following

3. (a) Lasing action is a non-equilibrium phenomenon. Justify. "Inversion of population can be achieved for a three level system" — Comment. $\qquad$ $3 + 5$

   (b) Write down the characteristic features of LASER radiation. $\qquad$ 2

4. (a) Deduce the relation between Einstein co-efficient of induced emission and spontaneous emission for a two level system. $\qquad$ 5

(b) Write short notes (any *two*) of the following : $2\frac{1}{2} \times 2$

   (i) Dye Laser

   (ii) Semiconductor Laser

   (iii) Mode locking in Laser.

GROUP – C

Answer any **one** question of the following

5. (a) What do you mean by static and dynamic quenching of a fluorophore ?   2

   (b) How do you obtain the static and dynamic quenching constant for a fluorophore when both the quenching take place simultaneously ?   8

6. Write down the steps involved and the rate of each step for Unimolecular photophysical processes. Deduce the following relation,

$$K_{ISC} = \frac{1}{\tau_f^\circ}\left(\frac{1-\phi_f}{\phi_f}\right)$$

where symbols have their usual significances.

(Assume $\phi_f + \phi_p + \phi_{ISC}^T \cong 1$) $2+8$

GROUP – D

Answer any **one** question of the following

7. (a) Write down the magnetic interaction Hamiltonian for an isolated proton. Obtain the expression of its energy as well as frequency of transition between its states. 6

    (b) What do you understand by 1st order and 2nd order NMR spectrum. 2

    (c) Write a note on spin temperature. 2

8. Write down the magnetic interaction Hamiltonian and spin wave functions for A_2-X system. Obtain the zero order as well as 1st order correction to energy and hence show the frequency of all possible transitions. $2 + 6 + 2$