

M.Sc. 3rd Semester Examination, 2012

CHEMISTRY

PAPER—CEM-303

The figures in the right-hand margin indicate marks

(Organic Special)

[Marks : 40]

Time : 2 hours

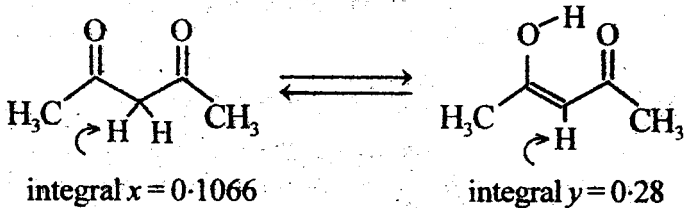
Answer any five questions

1. (a) Which nucleus will show NMR spectra ?
- (b) How does resonance occur in NMR ?
- (c) Show the ^1H -NMR spectra of $\text{CH}_3\text{—CH}_2\text{—OH}$ when it is (i) extra pure (in the absence of any acidic impurities), (ii) in the presence of traces of acidic impurities.

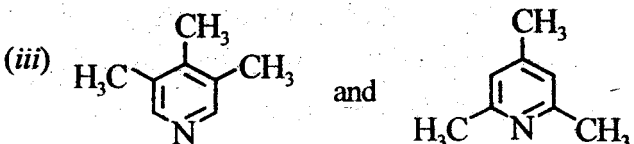
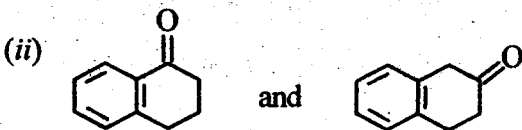
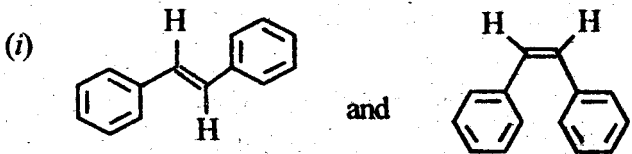
2 × 4

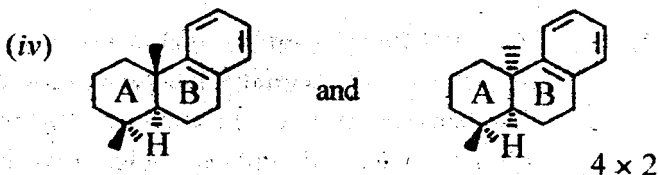
(Turn Over)

2. (a) Calculate the percentage of keto and enol forms of acetylacetone from the data given below :

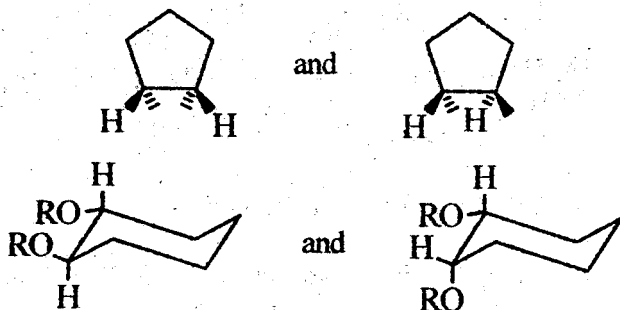


- (b) How would you distinguish between the following pairs of isomers from their proton chemical shifts? Indicate only the distinguishing feature(s) (any three) :





3. (a) What is Karplus equation? How this equation can be used to distinguish the following isomers:

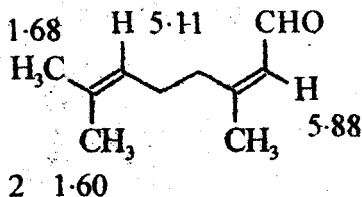
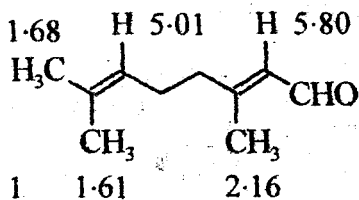


- (b) What is the relative order of J_{gem} , J_{cis} and J_{trans} in a monosubstituted olefin of the type $R-CH=CH_2$? Give reasons for your answer. 4 x 2

4. What is Nuclear Overhauser Effect? Explain the reason for this effect. The chemical shifts (in δ_{ppm}) of the vinylic methyls and the olefinic protons of citral-a(1) and citral-b(2) are shown on their

structural diagrams. How would you confirm their indicated stereochemistry and the assignments of the chemical shifts of the vinylic methyl protons at δ 1.68, 1.61 and 1.60 by Nuclear Overhauser Effect?

2 + 2 + 4



5. (a) What is metastable ion peak?

2

(b) Identify the compound $\text{C}_9\text{H}_{11}\text{NO}$ with the following spectral characteristics (with proper reasons):

UV : λ_{max} 235 (ϵ 8650) and 320 (ϵ 28300);
 IR : 2820, 2740, 1695, 1600(s), 1567, 1526,
 808, 720 cm^{-1} ; $^1\text{H-NMR}$: δ 9.72 (1H, s), 2.98
 (6H, s), 6.70 and 7.75 (each 2H, d, $J=9$ Hz);
 MS : m/z 149 (M^+), 148, 120.

6

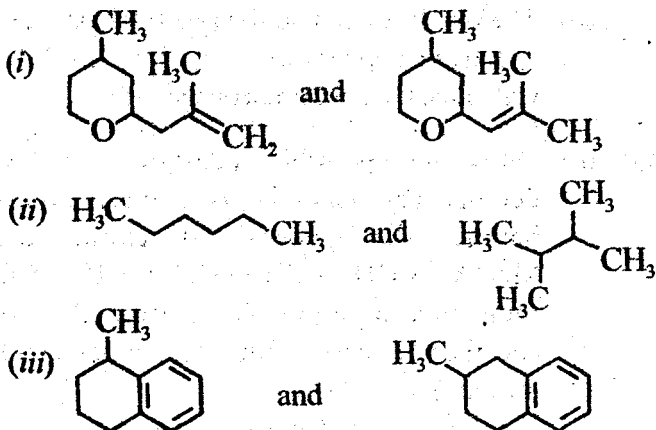
6. (a) What is McLafferty rearrangement in the mass spectral fragmentation of organic compounds?

Give direct evidence for the mechanism of this rearrangement using appropriate deuterium labeled compound.

4

(b) How would you distinguish between the following isomeric compounds from their mass spectral fragmentation?

4

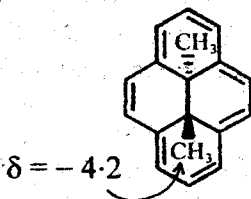


7. What are the full names of the terms COSY, HMQC and HMBC? What informations do they provide? Draw the COSY spectra of ethyl trans-crotonate having the following ^1H and ^{13}C NMR spectral data.

^1H NMR : δ 1.24(2H, t, $J = 7.0$ Hz), 1.88 (3H, dd, $J_1 = 6.8$ Hz, $J_2 = 1.7$ Hz), 4.13 (2H, q, $J = 7.0$ Hz),

5.81 (1H, *dq*, $J_1 = 16$ Hz and $J_2 = 1.7$ Hz) and 6.90 (1H, *dq*, $J_1 = 16$ Hz and $J_2 = 6.8$ Hz) ^{13}C NMR: δ_c 15.2 and 60.1 (OEt), 18.1 (Me-CH=), 124.5 (C-2), 145.3 (C-3) and 168.0 (C=O). 2 + 2 + 4

8. (a) What is used as a reference compound in D_2O as NMR solvent? 1
- (b) The two lines of a doublet in 400 MHz ^1H -NMR spectrum appears at 2.35 ppm and 2.38 ppm. Calculate the coupling constant (J). 1
- (c) Draw the possible configurations of the geometrical isomers of dimethylmuconate having the general structural formula $\text{MeO}_2\text{C} - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CO}_2\text{Me}$. Indicate how you would ascertain their stereochemistry from the chemical shifts of their olefinic protons? 4
- (d) Explain the unusual chemical shifts (ppm) of the indicated protons of the following compound: 2



(Inorganic Special)

[Marks : 40]

Time : 2 hours

Answer any *four* questions

1. (a) What is cyclic Voltammetry ? Why it is so called. 4
(b) State the application of cyclic voltammetry. 2
(c) Why is oxygen to be expelled from the polarographic cell before the experiment ? 4
2. (a) What is Retention Factor (R_F) and Retention Time (R_T) in GLC ? 4
(b) State the factors on which R_T depends. 3
(c) Name a few detectors used in HPLC. 3
3. Answer any *five* of the following : 2 × 5
(a) Differentiate quantum well and quantum wire.
(b) Name four different techniques of thin film synthesis.
(c) Why quantum effect is expected in nanomaterials ?

- (d) What is UHV ? Name different pump system to reach UHV.
- (e) What do you mean by e-lithography ?
- (f) Draw the density of state-energy diagram for OD and ID structure.
- (g) In nanomaterials surface to volume ratio increased from their bulk counterpart. True or false ? Justify.
- (h) What do you mean by PLD synthesis technique ?
4. (a) Justify the statement in the process of extraction, the extracting solvent should be used in parts instead of using the whole liquid in one lot. 3
- (b) How do you separate Copper and Lead in a solution by solvent extraction method ? 4
- (c) Calculate the amount of Fe^{+3} left unextracted from 100 ml of a solution containing 200 mg of Fe^{+3} after three extractions with 25 ml of ether each time. The value of distribution ratio in this case is 150 ? 3
5. (a) What is the basic difference in probe microscopy and electron microscopy ? 3
- (b) What is the working principle of AFM ? 2

- (c) What kind of information will come out from the following instruments? 3
- (i) NMR
- (ii) XRD
- (iii) FTIR.
- (d) What do you mean by luminescence? What is photo-luminescence? 2
6. (a) Determine the fraction of atoms in a given solid with the energy equal to 1.5 eV at room temperature and at 1000 K. What conclusion you can draw from these results? 3 + 1
- (b) Find an expression of dislocation energy in a solid containing screw dislocation? What is Burger vector? 5 + 1
7. (a) Explain what is the physical origin of band gap in a solid. 6
- (b) The E - K relation in CdS is given by $E = AK^2 + BK^3$, where A and B are positive constants. Find the effective mass of the electron at the bottom of conduction band. 3
- (c) What is meant by indirect band gap material? 1

(10)

(Physical Special)

[Marks : 40]

Time : 2 hours

Answer four questions taking one from each Group

GROUP – A

1. Probability of transition from state 'n' to 'k' under a perturbing field H' is given by

$$W_{n \rightarrow k} = |C_k^{(1)}|^2 = \frac{1}{\hbar^2} \left| \int_{t'=0}^{t'=t} e^{iW_{kn}t'} H'_{kn} dt' \right|^2$$

(Symbols have their usual significance)

Evaluate the transition probability using a perturbing field which is oscillating with time. Comment on your result.

6 + 4

2. What is meant by Homogeneous and Inhomogeneous broadening of spectral lines? What is Doppler broadening? Deduce the line shape function for Doppler broadening. How do you obtain the temperature of a gas from its Doppler line shape? 1 + 1 + 2 + 3 + 3

GROUP – B

3. Write down the characteristic features of LASER radiation. "Inversion of population can be achieved in a two level system." – Justify or criticize the statement. 3 + 7
4. (a) What is meant by Q-switching mode of LASER? How do you obtain giant LASER pulse using Q-switching mode? 2 + 4
- (b) Describe mode locking technique to obtain short LASER pulses. 4

GROUP – C

5. What is meant by *E*-type and *P*-type delayed emission? How do you obtain singlet-triplet energy gap (ΔE_{ST}) for a molecule showing *E*-type delayed emission? 2 + 2 + 6
6. (a) Deduce the following expression for unimolecular photophysical process.

$$\frac{\phi_p}{\phi_f} = \left(\frac{K_{ISC}}{K_f} \right) \left(\frac{K_p}{K_{ISC}^T + K_p} \right)$$

Where symbols have their usual significance. 6

- (b) State and explain the factors responsible for radiationless transition. 4

GROUP – D

7. (a) What is spin relaxation in NMR spectroscopy? Why is it so important to observe NMR transition?
- (b) “The net effect of spin lattice relaxation is to depopulate the higher level than to populate it.” – Explain. 2 + 2 + 6
8. (a) Deduce the selection rule for NMR transition. 4
- (b) Define chemical shift (δ_H) in NMR spectra. “Chemical shift of a given proton decreases with an increase in shielding constant.” – Explain. 2 + 4
-