2015

M.Sc. 3rd Seme. Examination

CHEMISTRY

PAPER—CEM-303

Full Marks : 40

Time : 2 Hours

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

(Physical Special)

Answer any *five* questions, taking at least *two* from each group.

Group—A

1. Deduce the following form of Fermi-Golden rule for a system undergoing transition from state $|\psi_n\rangle$ to $|\psi_K\rangle$ under the weak perturbing field, H'

$$\frac{dw}{dt} = \frac{2\pi}{\hbar} |H'_{kn}|^2 P(E_K)$$

Where $H'_{kn} = \langle \psi_k | H' | \psi_n \rangle$, $P(E_k)$ is the density of state $|\psi_k\rangle$.

Transition probability from state $|\psi_n\rangle$ to $|\psi_k\rangle$ in given below,

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

8

2. Deduce the selection rule for rotational transition and also show that the presence of permanent dipole moment is one of the essential criteria for a molecule to show rotational transition.

Given below the recursion formula for Associated Legendre function.

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

8

3. What is meant by homogeneous and inhomogeneous broadening of spectral lines? Assume that the natural braodening of spectral line is due to damping of radiation and then obtain an experssion to compute the damping constant from the spectral lineshape.

2+6

(Continued)

4. (a) What is meant by Surface Plasmon Resonance (SPR) of metal nanoparticles. Write down the expression of extinction co-efficient (C_{ext}) for metal nanoparticles based on Mie's scattering theory.

(b) Explain the appearence of colour of Ag/Au nanoparticles in the visible region using the above expression.

(c) "Rod shaped silver nanoparticles shows two distinct absorption band in the visible region" — Explain.

$$(2+2)+2+2$$

Group—B

5. Write down the magnetic interaction Hamiltonian and spin wave function for A – X system. Obtain upto first order correction to energy and hence show the frequency of all possible transitions.   2+4+2

6. (a) What is meant by (i) 1st order and (ii) 2nd order NMR spectra.

How do you obtain 1st order NMR transition for a two spin system, showing 2nd order NMR transition in a 60 MHz NMR spectro-photometer ?

(b) Explain the ^1H NMR splitting pattern and their relative

intensity ratio of the equivalent protons of chloroethane.

$$(2+2)+(2+2)$$

7. (a) Deduce the expression of precissional frequency of a proton in presence of an applied magnetic field, B_0.

   (b) How does spin-lattice relaxation help to observe NMR transition ? 3+5

8. (a) Describe one method of each for the synthesis of (i) Spherical and (ii) Anisotropic gold nanoparticle.

   (b) Define the term Dispersion (F) for nanomaterials. Deduce the following expression of Dispersion (F) for a cubic nanocrystal having 'N' number of atoms.

$$F \simeq \frac{6}{N^{1/3}}$$

   (c) "Melting temperature of a nanocrystal decreases as its size decreases" — Explain. 3+3+2

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(Continued)

(Organic Special)

Answer any *five* questions.

1. Answer any eight of the following :   1×8

   (a) NMR is an absorption spectroscopy : True or False ?

   (b) What is spin-spin coupling ?

   (c) What are the full forms of HMQC and DEPT ?

   (d) What is the temperature at which the magnet of a high field (e.g., 400 MHz) NMR is kept ?

   (e) Give examples of two NMR active and two NMR inactive nuclei and explain why.

   (f) What is a proton decoupled spectrum in ^{13}C NMR?

   (g) What is spin-spin relaxation ?

   (h) What is the difference between a base peak and a molecular ion peak in Mass spectroscopy ?

   (i) What is NMR shift reagent ?

   (j) Which reference compound is used for NMR in D_2O ? Write its structure.

(Turn Over)

2. (a) One isomer of dimethoxy benzoic acid (A) has the ^{1}H NMR spectrum : δ : 3.85 (s, 6H), 6.63 (t, 2Hz, 1H), 7.17 (d, 2Hz, 2H) and one isomer of coumalic acid (B) has the ^{1}H NMR spectrum : δ 6.14 (d, 10Hz, 1H), 7.82 (dd, 10HZ 2Hz, 1H), 8.51 (d, 2Hz, 1H). Deduce the structure compounds in each case.   4

(b) Deduce the structure of the compound C_9H_8O which exhibited the following spectral data :

IR-v (cm^{-1}) 3090, 2820, 2750, 1685, 1610, 970, 745

COOH

[A]   [B]
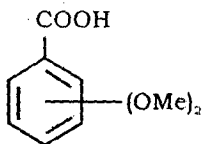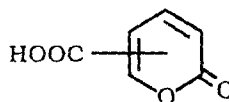
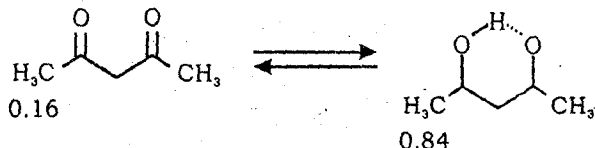NMR-δ 6.62 (dd, 16 & 7Hz, 1H), 7.41 (d, 1H), 7.49 (m, 5H), 9.66 (d, 1H).   4

3. (a) Identify the compound with molecular formula C_3H_7NO IR-v 3428, 1681 cm^{-1}

NMR-δ 1.87 (s, 1H), 7.30 (s, 3H), 8.1 (s, 3H).   3

(Continued)

(b) An organic compound with a molecular mass 120 absorbs in UV spectrum at 268 nm shows the following data in IR spectrum absorption bands are found at 3068-2907 cm-1 & 1608 cm-1 & 1473 cm^{-1}. The NMR spectrum 3.21 (9H, s) 7.74 (3H, s). Write down the structure of the compound. 3

(c) A certain compound has molecular formula C_2H_3N, compound exhibit a single peak in its ^{1}H-NMR spectrum at δ 2.15 ppm. Propose the structure of the molecule and explain its chemical shift. 2

4. (a) What is molecular ion peak and base peak? 2

(b) Ortho, meta & para xylenes all are give identical mass spectrum giving highly intense peak at m/z = 91 instead of m/z = 105 — Explain. 2

(c) Distinguish between the following compounds by mass spectroscopy. 2×2=4

(i) and

(ii) and
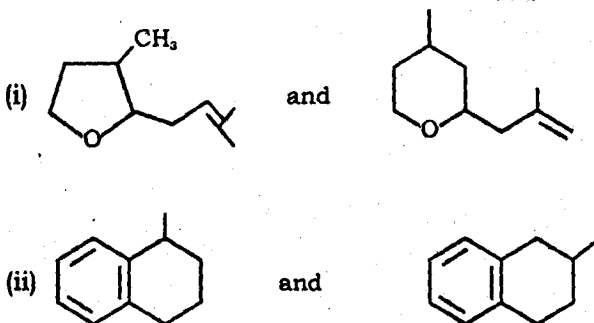
5. (a) Two lines of a doublet in 400 MHz ^{1}H-NMR spectrum appear at 2.32 and 2.36 ppm. Calculate the coupling constant.

(b) What will be the separation (in ppm) between the two lines in 200 MHz and 800 MHz ^{1}H-NMR ?

(c) Show qualitatively how a complex NMR spectrum recorded in a lower magnetic field can be simplified in a higher magnetic field.

(d) What are NMR shift reagents ? Give examples and write the mechanism of their activity.   2+1+2+3=8

6. (a) What is chemical exchange ?

(b) Calculate the percentage of keto and enol forms of acetyl acetone from the integral data given below ?

(c) A compound $C_9H_{10}O_2$ compound has strong infrared absorption at 1695 cm^{-1}. The ^{1}H NMR spectrum has five sets of line : a triplet at δ 1.3 (3H), a quartet at δ 4.1 (2H), a doublet at δ 7.0 (2H), a doublet at δ 7.8 (2H) and a singlet at δ 9.8 (1H) ppm. Suggest a structure for this compound.

O   O
H₃C   CH₃   ⇌   (keto-enol structures)
0.16   H₃C   CH₃
                       0.84

$$\underset{0.16}{\underset{H_3C}{\overset{O\quad O}{\diagdown}}CH_3} \;\rightleftharpoons\; \underset{0.84}{\underset{H_3C}{\diagdown}CH_3}$$

2+2+4

7. (a) Compound A, $C_8H_8O_3$, shows the following spectral data.

UV : λ_{max} (EtOH) 215, 235, 285 and 320 nm ; λ_{max} (EtOH-NaOH) 260, 303 and 355 nm.

^{1}H-NMR (δ) : 9.80 (s, 1H), 7.40 (m, 2H), 7.10 (s, 1H, disappeared on deuterium exchange), 7.0 (1H, d, $J = 8$ Hz), 3.95 (s, 3H)

MS (m/z) : 152 (M$^+$, 100%), 151 (96%) and 123 (8%).

Suggest a probable structure for the compound.

(b) Suggest a probable structure of the compound B, $C_9H_{11}NO$, showing the following spectral data.

UV : λ_{max} 235 (ε 8650) and 320 (ε 28300)

FTIR (cm^{-1}) : 1695, 1600 (s), 1567, 1526, 808, 720 and bands immediately above and below 3000 cm^{-1}, well-defined doublets at 2820 and 2740 cm^{-1}.

^{1}H-NMR (d) : 9.72 (s, 1H), 7.75 (d, 2H, $J = 9$ Hz), 6.70 (d, 2H, $J = 9$ Hz), 2.98 (s, 6H)

MS (m/z) : 149 (M$^+$), 148 (base peak) and 120.

4+4

(Turn Over)

(*Inorganic Special*)

Answer any *five* questions, taking at least *two* from each group.

Group—A

1. (a) Generally the photo-excitation of metal carboxyl compounds increases the weakness of metal-CO bond. How can you justify that the increase of the weakness of metal-CO bond is due to population of electron in σ-antibonding orbitals rather than depopulation of electron in π-bonding orbitals. 3

   (b) How can you distinguish between the static and dynamic quenching of fluorescence? 3

   (c) Write down the criterias to be fulfilled by a compound for functioning as a good photosensitizer. 2

2. (a) Explain the wavelength dependence for the quantum efficiency (ϕ) of $[M(CO)_5(pyridine)]$ to $[M(CO)_4(pyridine)_2]$ conversion. 4

Central	Solvent	$\phi_{366\ nm}$	$\phi_{436\ nm}$
Cr	THF	0.28	0.17
M_0	THF	0.35	0.22
W	THF	0.06	0.02

(b) Write short notes on :

(i) Resonance energy transfer

(ii) Exchange energy transfer. 2+2

3. (a) What is polarographic maxima? Write down character-istics of supporting electrolyte in polarography. 2+2

(b) Discuss about the application of thermogravimetry. 4

4. (a) What kind of information will come out from the follow-ing instruments

(i) SEM

(ii) TEM 2

(b) What is "top-down" approach of nanoscience? Give an example. 2

(c) Why the nanomaterials are different from their bulk coun-terpart? 2

(d) What is the working principles of probe microscope?

2

Group—B

5. (a) Discuss the thermodynamic and kinetic limitations on the photochemical conversion and storage of sunlight,

3

(b) How the photochemical reactions differ from the thermal reactions?

(c) The parity selection rule for radiationless transitions is precisely opposite to the selection rule for radiative transitions. Explain. 2

(d) What do you mean by "Einstein transition probability" of absorption? 2

6. (a) What is Ilkovic equation? What is half wave potential? 2+2

(b) Give a diagram for a Modern DSC instrumentation. 4

7. (a) Write down the application of thermometric titration. 4

(b) How can you get information about the oxidation of phenylene diamine by using cyclic voltametry? 4

8. (a) Why O_2 removal is very essential before pharographic experiment? 2

(b) Write short note on pH effect on polarograms. 2

(c) Give a diagram for a modern themobalance? Define tharmal methods. 3+1

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