PG/IVS/CEM-403/15

M.Sc. 4th Semester Examination, 2015

CHEMISTRY

PAPER — CEM-403

Full Marks : 40

Time : 2 hours

The figures in the right hand margin indicate marks

(*Inorganic Special*)

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

GROUP —A

1. (*a*) A commercial EPR spectrometer use 7·79 mm microwave radiation. What magnetic field is needed to satisfy the resonance condition ?   2

   (*b*) Spin angular momentum of electron act just opposite in direction as spin magnetic moment explain.   2

(c) Explain the appearance of three lines in the ESR spectrum of naphalene diradical. 3

(d) What do you mean by "Zero field splitting" ? 1

2. (a) Write short notes on Meissner effect and edge dislocation. 3

(b) What is the average energy of an electron in a metal at $T = 0K$? 2

(c) Give the energy level expression of Sommerfeld model for a free electron in the metal. 3

3. (a) Explain why Mn (II) is EPR active but Cr(II) is EPR inactive. 2

(b) "The ESR signals are expected to be more intense than those of NMR signals" — Comment. 2

(c) Explain the ESR spectrum of $[NO(SO_3)_2]^{2-}$. 2

(d) Predict the number of lines in the ESR spectrum of the following radicals

$[^{13}CF_2H]^{\cdot}, [CF_2D]^{\cdot}$ $I(^{13}C) = \frac{1}{2}, I(^{19}F) = \frac{1}{2}, I(D) = 1.$ 2
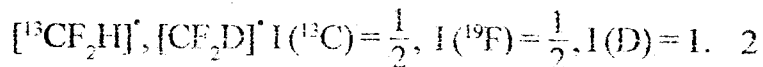
4. (a) The ESR spectrum of $[Fe(CN)_5(NO)]^{3-}$ ion consists of three lines with equal intensity. Explain. 2

(b) What do you mean by "X-band frequency" and "Q-band frequency" in ESR spectroscopy ? What are the advantages and limitations in using "Q-band frequency" ? 1 + 2

(c) The ESR Spectrum of
$[(NH_3)_5 Co-O-O-Co(NH_3)_5]^{5+}$
shows fifteen lines. Derive the structural information of this complex ion from this data. $[I_{Co} = 7/2]$ 3

GROUP —B

5. (a) Explain lanthanide luminescence spectra. 4

(4)

(b) Discuss the following applications of lanthanide :   2 + 2

    (i)   as shift reagent

    (ii)   as bio-probes.

6. (a) Calculate the equilibrium concentration of Schottky defect in an ionic crystal.   4

   (b) What is colour centre ? Describe the mechanism of formation of F-Centre.   2 + 2

7. (a) Draw a flow diagram for the extraction of lanthanoid metals from its monazite ore.   4

   (b) Write short notes on :   2 + 2

     (i)   Absorption spectra of lanthanoids

     (ii)   Cerium

     (iii) Chemistry.

8. (a) Mention the important characteristics of a superconductor.   5

   (b) Write short notes on point defect.   3

(Organic Special)

Answer any **five** questions

1. Elucidate the non-mevalonate pathway for the simultaneous formation of isopentenyl pyrophosphate (IPP) and dimethylallyl pyrophosphate (DMAPP). 8

2. Name the different types of folding patterns of 3(S)-oxidosqualene for biogenesis of lanosterol and lupeol. Outline the steps for the formation of either lanosterol or lupeol. 8

3. (a) Discuss the biosynthetic pathway for the formation of R-mevalonic acid from acetyl CoA indicating the enzymes involved in each of the steps.

   (b) Outline the synthesis of etorphine from thebaine. 4 + 4

4. "Changes in concentration of hydrochloric acid cause the formation of different products form thebaine." Justify the statement by identifying the products and explaining their formation.   4 + 4

5. (a) Discuss the mechanism for the formation of squalene from tail-to-tail combination of two units of farnesyl pyrophosphate with evidences, if any.
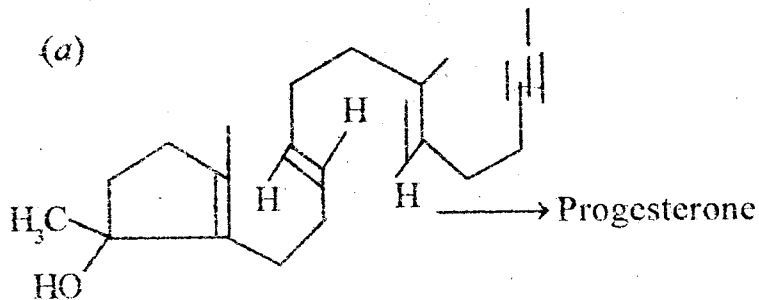
   (b) Predict the products of the following reactions with mechanisms.

      (i) Thebaine warmed with dil. HCl

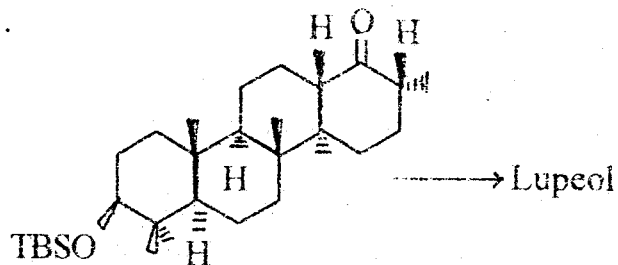   (ii) Quinine reacted with dil. acetic acid.
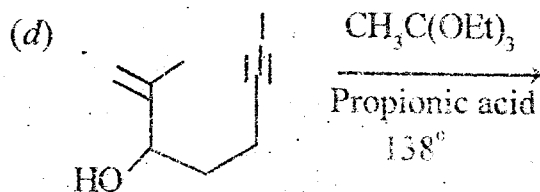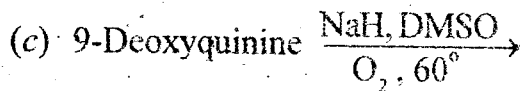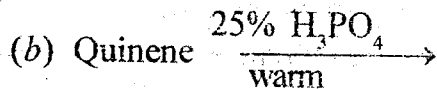   4 + 2 × 2

6. Carry out following transformations. Mention only the reagents and reaction conditions.   4 + 4

   (a)

H_3C— HO —→ Progesterone

(Continued)

(b)

------→ Lupeol

7. Discuss the retrosynthetic steps for the enantioselective synthesis of quinine carried out by professor G. Stork.　　　8

8. Write down the products of the following reactions and explain plausible mechanisms.

(a) Morphine $\xrightarrow[\text{warm}]{\text{Conc. HCl}}$　　2 + 2 + 2 + 2

(b) Quinene $\xrightarrow[\text{warm}]{25\% \ H_3PO_4}$

(c) 9-Deoxyquinine $\xrightarrow[O_2, 60°]{NaH, DMSO}$

(d)

$\xrightarrow[\substack{\text{Propionic acid} \\ 138°}]{CH_3C(OEt)_3}$

(Physical Special)

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

GROUP —A

Answer any **two** of the following

1. (*a*) What is LASER ? Inversion of population
   is the essential criteria of a system to show
   Lasing activity—Explain. $1 + 3$

   (*b*) Inversion of population can not be achieved
   for a two level system—Justify or criticize
   the statement. 6

2. (*a*) State the principle for the generation of
   second $(2\gamma_0)$ ands Third $(3\gamma_0)$ Harmonic
   frequency from a given frequency (γ_0) of
   radiation. 4

   (*b*) Write short notes on : 3×2

   (*i*) Q-Switching and

   (*ii*) Mode locking of Laser.

(Continued)

3. Write down the steps and the rate of each steps for Unimolecular photophysical processes in electronic spectroscopy. Assuming $\phi_p + \phi_f + \phi_{ISC}^T \cong 1$;
Deduce the following expression,

$$K_{ISC} = \frac{1}{T_f}\left(\frac{1-\phi_f}{\phi_f}\right)$$

Symbols have their usual significances.   3 + 7

4. What is meant by static and dynamic quenching of a fluorophore ? How do you obtain static and dynamic quenching constant when both the quenching processes take place simultaneously.

3 + 7

GROUP – B

Answer any **two** of the following

5. What is exciplex emission ? Write down the characteristic features of exciplex emission with one example. Explain the stability of exciplex formation using MO diagram of its constituent molecule.   2 + 3 + 1 + 4

6. How do you obtain the excited state acidity of an organic acid using Fröster cycle ? What is twisted intramolecular charge transfer (TICT) processes ? Write down the characteristic features of TICT emission with an example.

7 + 1 + 2

7. (a) Write down the magnetic interaction Hamiltonian and spin wave functions of Hydrogen atom. Obtain zero order energy and the frequency of all possible transition of hydrogen atom.

2 + 4

   (b) Draw the energy levels with possible M_I and M_S values for CH_3 radical and the possible ESR transitions.

4

8. (a) Define anisotropy of a fluorophore.

   (b) Why alignment of polarizer is necessary during anisotropy measurement ?

   (c) Show that anisotropy

$$r = \frac{3 < \cos^2 \theta > -1}{2}$$

   where symbols have their usual significances.

2 + 3 + 5