### 2016

### M.Sc.

# 2nd Semester Examination

#### **CHEMISTRY**

PAPER-CEM-201

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)

Answer four questions, taking one question from each group.

# Group-A

Answer any one of the following.

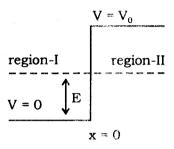
1. Show that in the n<sup>th</sup> eigen state of the Harmonic Oscillator, the average Kinetic energy, <T> is equal to the average potential energy, <V>.

5+5

(Turn Over)

2. (a) Consider a particle of mass m<sub>e</sub> moving in the positive x-direction under the potential field defined by

$$V = 0$$
 for  $x < 0$   
 $V = V_0$  for  $x > 0$ 



Find the transmission probability of the particle from region-I to region-II.

- (b) Draw the schematic potential energy diagram of the following:
  - (i) Umbrella inversion of ammonia
  - (ii)  $\alpha$ -particle decay from radioactive nucleus.

6+(2+2)

# Group—B

Answer any one of the following.

3. (a) Derive the equation for Lineweaver-Burk plot for enzyme catalysis reaction. State the consequences of this plot.

(b) Calculate the relaxation time for the reaction

$$H^+$$
 (aq) +  $C_6H_5COO^-$  (aq)  $\rightleftharpoons C_6H_5COOH$  (aq)

for a temperature jump experiment to a final temperature of 298K. The solution was initially prepared by adding 0.015 moles of benzoic acid to water such that a liter of total solution was made. Assume that both the forward and reverse reactions are first order in each of the reactants and the forward and backward rate constants are  $k_1 = 3.5 \times 10^{10} \, dm^3 \, mol^{-1} \, s^{-1}$  and

$$k_{-1} = 2.2 \times 10^6 \text{ s}^{-1}$$
 respectively. (5+2)+3

- 4. (a) Define oscillatory reaction with a suitable example.
  - (b) What is the principle of relaxation method to study the kinetics of fast reaction?
  - (c) Write down the basic criteria to occur a redox reaction through inner sphere mechanism.
  - (d) What is non-complementary electron transfer reaction? 3+2+3+2

#### Group-C

Answer any one of the following.

5. (a) Intensities of stokes and anti stokes lines are different in vibrational Raman spectra — why?

- (b) What do you mean by the term "CARS"? How is it advantageous over the conventional Raman spectroscopy?
- (c) N<sub>2</sub>O molecule shows the following peaks in IR and Raman spectra. Assign the peaks and predict the structure of N<sub>2</sub>O therefrom.

$\overline{v}$ (cm <sup>-1</sup> )	IR	Raman
580	m (temp. dependent)	m
589	s	v.w.
1167	m	¥. <b>S</b> .
1285	v.s.	V. <b>S</b> .
2223	v.s.	S

(s = strong, v.s. = very strong, m = medium, w = weak, v.w. = very weak)

- (d) Why are the maxima of vibrational energy levels (except the zeroth one) reside on the edges of the potential energy curves?

  2+(1+2)+3+2
- 6. (a) Symmetric stretching mode of vibration is Raman active for CO<sub>2</sub> while its bending mode and asymmetric vibrational modes are not — explain why.

- (b) Schematically show the different modes of vibration for H<sub>2</sub>O. Assign the peaks which are IR active and/or Raman active separately.
- (c) What are progressions and sequences in electronic spectroscopy?
- (d) Phenoic compounds are more basic in their ground states
  -- explain the reason.

  3+2+2+3

### Group-D

Answer any one of the following.

7. Consider a Harmonic Oscillator in the superposition state,

$$\psi(x, 0) = \frac{1}{\sqrt{2}} [\psi_0(x) + \psi_1(x)]$$

- (i) Find  $\psi(x, t)$
- (ii) Show that in the state  $\psi(x, t)$

$$\langle x \rangle = \sqrt{\frac{\hbar}{2mw}} Cos(wt)$$

where symbols have their usual significances.

- 8. (a) How does rate of a fast reaction is measured using plug flow technique?
  - (b) The presence of  $4.8 \times 10^{-6}$  mol dm<sup>-3</sup> of a competitive inhibitor decreases the initial rate of  $1.11 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$  by a factor of 3.7. Calculate K<sub>1</sub>, the equilibrium constant for the binding reaction between the enzyme and the inhibitor. Given turnover number =  $4.0 \times 10^7 \, \text{s}^{-1}$  $[E]_0 = 0.016 \times 10^{-6} \text{ mol dm}^{-3}$

 $K_m = 25 \times 10^{-3} \text{ mol dm}^{-3}$ 

 $[S]_0 = 4.32 \times 10^{-6} \text{ mol dm}^{-3}$