M.Sc. 2nd Semester Examination, 2012

CHEMISTRY

(*Physical*)

PAPER – CEM- 201

Full Marks : 40

Time : 2 hours

Answer any **five** questions taking
one from each Group

The figures in the right hand margin indicate marks

GROUP – A

1. Find out the solution of a free particle problem. Show with reasons why the general solution of the problem is not acceptable. 8

2. State and explain the theorem concerning the acceptance of a ladder operator. Verify the same for $\overline{H}$ and r_+ operator, the terms having usual meaning. 8

Or

Explain what are meant by Ladder operators and show that these are the step up and step down operators with respect to the eigenvalue of the angular momentum operator $\hat{L}_z$. 8

GROUP – B

Answer any *one* of the following :

3. (*a*) Define an oscillating reaction with a suitable example.

(*b*) The presence of $4{\cdot}8 \times 10^{-6}$ mol dm^{-3} of a competitive inhibitor factor of 3·6. Calculate K_I, the equilibrium constant for the binding reaction between the enzyme and the inhibitor. Given $\gamma_{max} = 0{\cdot}64$ mol dm^{-3} s^{-1} and $K_m = 25 \times 10^{-3}$ dm^{-3}. 3 + 5

4. (*a*) What is an enzyme catalysis process ? Give one live example. 1 + 1

(*b*) What is line Weaver-Burk plot ? Can you determine the Michaelis constant from this plot ? 1 + 1

(*c*) The protein catalase catalyzes the reaction

$$2H_2O_2\,(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

and has a Michaelis constant of $K_m = 25 \times 10^{-3}$ mol dm^{-3} and a turn over number of $4{\cdot}0 \times 10^7\ s^{-1}$. Calculate the initial rate of this reaction if the total enzyme concentration is $0{\cdot}016 \times 10^{-6}$ mol dm^{-3} and the initial substrate concentration is $4{\cdot}32 \times 10^{-6}$ mol dm^{-3}. Calculate γ_{max} for this enzyme. Catalase has a single active site. 4

GROUP – C

Answer any *one* of the following :

5. (*a*) What do you mean by asymmetry effect ? Compute electrophoretic component of velocity of a moving ion. 1 + 2

(*b*) What do you mean by surface excess of a substance ? Derive Gibbs adsorption equation and indicate when an electrolyte accumulates at the surface of a liquid. 1 + 3 + 1

6. (*a*) When does the concentration overpotential arise ? Derive an equation relating concentration overpotential and limiting current density. 1 + 3

(*b*) Deduce the following polarographic wave equation :

$E = E1/2 + (\cdot 0591/n)\log (id\text{-}i)/i$ at 250C, where the terms have their usual significance. 4

GROUP – D

Answer any *one* of the following :

7. Write down the Secular equation for Butadiene. Hence obtain the energy states and possible combination of atomic orbitals (AO) to form π-molecular orbitals (π-MO). 2 + 4 + 2

8. Write, without derivation, Maxwell's expression for the speed distribution in three dimensions and starting from this expression obtain the expression for the fraction of the total number of molecules having an energy higher than a specified minimum value ϵ'. Explain its significance. 1 + 5 + 2

GROUP – E

Answer any *one* of the following :

9. Show that, the potential energy (V) of interaction between two dipoles (μ_1 and μ_2) at a distance (centre to centre) 'r' is given by 8

$$V = \frac{1}{4\pi \epsilon_0}\left[\frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{r^3} - \frac{3(\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r})}{r^5}\right]$$

10. (*a*) Write down Lennard Jones (12, 6) potential for two interacting molecules. Schematically draw the potential energy curve as a function of distance (r) between the two molecules and hence obtain the distance of closest approach.

(*b*) Write a short note on London dispersion interaction. 8