M.Sc. 2nd Semester Examination, 2023

CHEMISTRY

PAPER — CEM-201

Full Marks : 40

Time : 2 hours

The figures in the right hand margin indicate marks

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

GROUP—A

Answer any **four** of the following questions : 2×4

1. The reaction between $K_2S_2O_8$ and KI is carried out separately in presence of 0.1 (M) KNO_3 and 0.5(M) KNO_3 at the same temperature and same solvent. In which case the rate of the reaction will be higher and why ?

2. The reaction

$$Cr(H_2O)_6^{3+} CNS^- \rightarrow Cr(H_2O)_5 CNS^{2+} + H_2O$$

occurs in aqueous solution. Deduce qualitatively

   (*i*) The effect of increasing dielectric constant on the rate of the reaction.

   (*ii*) The sign of entropy of activation.

3. Consider a model system of five non-interacting Fermions in a single 3-dimensional Harmonic Oscillator and hence obtain the ground state energy of the system.

4. Find the first order correction to energy for the nth state of a simple Harmonic Oscillator perturb by the following function '

   $H' = bx^3$ (where '*b*' is a constant)

5. How do you differentiate fluorescence from Raman Signal ?

6. How do you measure micellar aggregation number using fluorescence technique ?
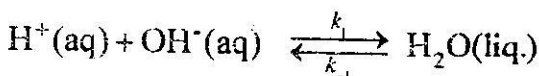
GROUP—B

Answer any **four** questions of the following : 4×4

7. Use time independent non-degenerate perturbation theory to show that the first order correction to energy is the expectation value of the perturbing potential with respect to the zero order wavefunction.

8. Show that in the nth eigen state of a linear Harmonic Oscillator, the average kinetic energy ($< T >$) is equal to the average potential energy ($< V >$). Comment on your result.

9. How do the CMC of
   (*a*) nonionic and
   (*b*) ionic surfactant vary with temperature ? Explain.

10. What are the advantages of studying biological samples by Raman spectroscopy ? What is Resonance Raman spectroscopy ?

11. Derive the expression for determining relaxation time of the fast reaction given below :

$$D^+(aq) + OD^-(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} D_2O(liq.)$$
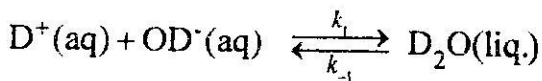
12. The eqn. constant for the reaction.

$$H^+(aq) + OH^-(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O(liq.)$$

at $25°C$ is $K_C = 4.08 \times 10^{16} \, mol^{-1}dm^3$. The rate constant k^{-1} is independently found to be $2.52 \times 10^{-6} \, sec^{-1}$. What can you predict for the observed relaxation time for a temperature jump experiment to a final temperature of $25°C$? The density of H_2O is $1.009 \, gcm^{-3}$ at $25°C$.

GROUP—C

Answer any **two** questions of the following : 8×2

13. The trial wave function for the ground state of a Simple Harmonic Oscillator is given by,

$$\phi = Ae^{-\alpha r^2}$$

where 'A' is the normalization constant and 'α' is the variational parameter. Find the normalization constant. Use variational method to obtain the ground state energy of the oscillator.   8

14. Deduce the selection rule for vibrational transition. Show that there must be some fluctuation of dipole moment during molecular vibration for a molecule to be IR active

Given below the identity relation of Hermite Polynomial

$$\xi H_v(\xi) = vH_{v-1}(\xi) + \frac{1}{2}H_{v+1}(\xi)$$

Here symbols have their usual significance.   8

15. What is Enzyme inhibition reaction ? Explain with proper mechanism three different types of enzyme inhibition.   2 + 6

16. Describe the mechanism of a redox reaction occuring via inner sphere mechanism.   8