2022

M.Sc.

2nd Semester Examination

CHEMISTRY

PAPER—CEM-201

PHYSICAL CHEMISTRY-II

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.

Group—A

Answer any *four* questions. 4×2

1. If 'H' is the time independent Hamiltonian and 'A' is the operator corresponding to any observable of a quantum mechanical system described by the wave function ψ, then evaluate the integral :
   $< \psi | [H, A] | \psi >$.

2. In a one electron system with $l = 0$ and $m = 0$, the function $N_0 e^{-\sigma}$ and $N_1(2 - \sigma)e^{-\sigma/2}$ refer the ground (E_0) and first excited state (E_1) energy levels respectively. If a trial wave function $Ae^{-a\sigma}$ ('α' is the variational paremeter and 'A' is the normalized constant) yields an average energy, $<E>$, then which of the following is correct ? (Justify your answer)

(i) $<E> \geq 0$ (ii) $<E> \geq E_0$

(iii) $E_0 \leq E_1 \leq <E>$ (iv) $0 \leq <E> \leq E_0$

3. Define relaxation time of a kinetic reaction.

4. Define autocatalysis with a suitable example.

5. "Smaller water drops evaporate faster" — criticize or justify.

6. Between dipole moment and polarizability, which one must change for a mode to be Raman active and why ?

Group—B

Answer any *four* questions. 4×4

7. Consider a particle of mass 'M' is constrained to move on a rigid frictionless string of radius 'a' with its centre at the origin in xy plane. Write down the expression of its (i) Hamiltonian, (ii) wave function and (iii) energy eigen value.

8. A particle in a simple Harmonic potential is described by the following wave function :

$$\psi(x, 0) = A[\psi_0(x) + 2\psi_n(x)] \; ;$$

where $\psi_0(x)$ and $\psi_n(x)$ are normalized eigen states. Evaluate the average energy ($<E>$) of the particle.

9. (a) What is inhibition in enzyme catalysis ?

(b) The path of mixed enzyme inhibition is more effective inhibition than competitive inhibition path in a kinetic reaction — Explain. 1+3

10. The equilibrium constant for the reaction

$$D^+ \text{(aq)} + OD^- \text{(aq)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} D_2O \text{(liq.)}$$
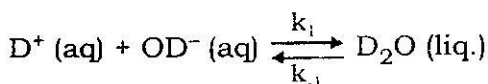
at 25°C is $K_c = 4.08 \times 10^{16} \text{ mol}^{-1} \text{ dm}^3$. The rate constant k_{-1} is independently found to be 2.52×10^{-6} sec^{-1}. What can you predict for the observed relaxation time for a temperature jump experiment to a final temperature of 25°C ? The density of D_2O is 1.104 gcm^{-3} at 25°C.

11. Write down the salient features of Rayleigh scattering and explain with mathematical expression.

12. How does a Langmuir adsorption pattern vary with temperature ?

Group—C

Answer any *one* question.   1×8

13. (a) Discuss the kinetics of reaction taking place in flow system involving plug flow technique.

   (b) The following reaction occurs in aqueous solution

$$[Co(NH_3)_5 Br]^{2+} + HO^- \longrightarrow [Co(NH_3)_5 HO]^{2+} + Br^-$$

Explain qualitatively the followings :

    (i) The effect on the rate of decreasing dielectric constant.

    (ii) The effect on the rate of decreasing ionic strength.

    (iii) The sign of entropy of activation.   5+3

14. How does the environment surrounding of a molecule affect the absorption and emission spectra ? Why phenolic compounds have lower pK_a value in the excited state compared to the ground state ?   4+4

Group—D

Answer any *one* question.   1×8

15. Use linear variational principle to obtain the energies and wave functions of π-MO of Allyl radical system. (Use Huckel approximations)

16. Deduce the selection rule for a rigid rotator undergoing transition from (J, M) to (J', M') quantum level. Given below the recursion relation of Associated Legendre polynomials,

$$(2J + 1)xP_J^M(x) = (J - |M| + 1)P_{J+1}^M(x) + (J + |M|)P_{J-1}^M(x)$$