

Sub - Physical Chemistry

Unit I - Quantum Chemistry

Q-1) Short Answer - 1 Mark

i) State Pauli Exclusion principle - April 2018

ii) Eigen values associated with Hamilton operator - April 2018

iii) For a particle in a three dimensional box the state of system is characterized by three quantum numbers as n_x , n_y & n_z with energy of $\frac{14h^2}{8ma^2}$ what is

the degeneracy of the energy level represented by three quantum numbers

iv) Define Laplacian operator - April 2014, Oct 2015

v) Give the criteria of well behaved function
Nov - 2014
Oct - 2015

vi) Eigen values associated with Hamilton operator are always - Nov 2014, Oct 2015

vii) Mention the eigen values for angular momentum - April 2015

viii) What is the Hermitian operator? - April 2014

- ix) write the term symbols for $L=2, S=1$
- x) state selection of particle confi - April 2015
- x) state selection of particle confirmed in the box system - April 2014, oct 2015
- xi) Define Ladder operators - Nov 2014, oct 2015
- xii) state expectations value theorem - Nov 2014

Q-2) Short Note - 4 Mark

- i) Give the characteristics of well behaved function - April 2018
- ii) Born interception of wave function - April 2018
- iii) concept of particle in a box system for understanding electronic spectra - April 2014, oct 2015
- iv) Explain the eigen values of angular momentum - April 2015
- v) Degeneracy & its importance using particle in a cubic box system - Nov 2015 2014, April - 2015

Q-3) Long Answer - 5/6/8/10 Mark

- i) Explore the concept of commutating & non commutating operators with suitable examples - April 2018
- ii) For a cubical box, what will be the effect of stretching of the box along x-direction on degeneracy & energy, state represented by $\frac{6h^2}{8ma^2}$ - April 2018
- iii) State postulates for quantum mechanics & discuss the properties of operators
- iv) If ψ_1 & ψ_2 are eigen functions of Hermitian operator A with eigen values a_1 & a_2 respectively, then prove that ψ_1 & ψ_2 are orthogonal - April 2014
- v) Show that if two operators commute, they have simultaneous non degenerate eigen function - April 2015
- vi) Prove that eigen values associated with Hermitian operators are real - April 2015

II) Photochemistry

Physical

1) Fluorescence resonance energy transfer processes. - 4MK
April-2014.

2) Distinguish between excimer, dimer, photodimer and an exciplex. - 5MK

3) The fluorescence intensity of a fluorophore is quenched 80% by addition of 0.01 M quencher concentration. Calculate half quenching concentration - 5MK

4) Construct Jablonski diagram and discuss possible photophysical pathways of deactivation for the excited molecules. - 4MK

5) Distinguish between excimer, exciplex and excited dimer with respect to their spectral characteristics - 6MK

6) Photoisomerization reaction - 4MK

7) Photodimerization reactions - 4MK

1) What is delayed fluorescence?

2) State Einstein's law of photochemical equivalence.

3) Define Distinguish between singlet and triplet states.

4) Calculate the term symbols for ground state of He.

5) What is the basic criteria for fluorescence resonance energy transfer (FRET) between donor and acceptor.

6) "Exciplex emission observed only in heteroatom." State whether the statement is true or false.

7) Differentiate the nature of fluorescence spectrum of monomer emission and excimer emission.

8) Define the life time of electronically excited state

Electrochemistry

beats Question

- 1) What is electrophoretic effect? (2014)
- 2) Write the expression for the electrical density (ρ) for univalent electrolyte (Apr-2018)
- 3) $\text{Pt}(\text{H}_2)\text{g}/\text{H}^+$ is an example of first order or second order kind of electrode (Apr-2018)
- 4) Write the cell representation of third kind of electrode (Oct-2015), (Oct-2012)
- 5) The thickness of ionic atmosphere as the concentration of electrolyte increases (fill in the blank) (Oct-2015)
- 6) As the concentration of electrolyte increases the thickness of ionic atmosphere decreases. State whether this statement is true or false (2015) (Apr-2015), (Oct-2014)
- 7) Construct the electrochemical cell in which the reaction is

$$\text{Ag}^+ + \text{Cl}^- \longrightarrow \text{AgCl}$$
 (Apr-2015)
- 8) Name the liquid fuels used in fuel cell (Apr-2015)
- 9) Write the cell representation of first kind of electrode (Apr-2014)
- 10) When the salt bridge is removed, the potential

of the electrochemical cell - - - - -

(Apr - 2014), (Oct - 2014)

till the blank from following)

i) increases ii) decreases iii) remain constant iv) become zero

11) A catalyst increases the rate of chemical reaction by decreasing the activation energy. State whether this statement is true or false (Apr - 2014)

12) Write the cell representation of second kind of electrode (Oct - 2014)

13) The temperature coefficient for general reaction is $2-3$. True / False (Oct - 2012)

14) Represent alkaline storage battery (Oct - 2012)

15) Write equation for emf of a concentration cell with transference for HCl electrolyte (Oct - 2012)

16) In case of concentration cell with transference for HCl, if $a_2 > a_1$ then reaction is non-spontaneous. Whether the above statement is true or false? (Oct - 2012)

Long answer Question & Short answer

- (Q.1) a) Describe the method of determining activity coefficient of an electrolyte using Conc. cell with transference [Apr-2009] [5M]
- b) Describe in detail construction & working of acid storage battery [5M]
- c) For a conc. cell, $\text{Ag} / \text{AgCl}(s), \text{HCl}, \text{HCl}(a=1), \text{AgCl}(s) / \text{Ag}$ the emf obtained at 25°C is 194mV & transference no. of H^+ ion is 0.825 . Calculate the activity coefficient of unknown HCl soln [5M] (Apr-2014)
- 2) Describe construction & working of acid storage battery. (Apr-2014)
- 3) Derive the relationship betⁿ rational activity coefficient (f), practical activity coefficients ($f_\pm, f_m$) of an electrolyte soln [6M] (Apr-2018)
- 4) Calculate the ionic strength of 0.1M Copper chloride soln. [4M] (Apr-2018)
- 5) a) Derive Stern-Volmer relation for bimolecular collision fluorescence quenching (6M) (Apr-2015)
- b) Discuss EMF method of determination of activity coefficient of an electrolyte (6M) (Apr-2018), (Apr-2014)
- 6) EMF method for the determinatⁿ of instability constant [4M] (Apr-2018)

- 7) a) Describe in detail the emf method of determination of dissociation constant of weak acid [6M] (Oct-2014)
b) Obtain an expression for the potential ψ_i on the ion due to ionic atmosphere in dilute soln. (Apr-2014). [6M]
c) Calculate the ionic thickness of ionic atmosphere in 0.1M soln of 1:1 salt in nitrobenzene at 25°C ($D = 34.8$) [4M] (Apr-2018)
- 8) Acid storage battery (6M) (Oct-2015), (Apr-2015), (Oct-2012)
- 9) Determination of instability constant of silver-ammonia complex (4M) (Oct-2015), (Apr-2014), (Oct-2014), (Oct-2012)
- 10) Explain relaxation & electrophoretic effect (6M) (Apr-2015), (Oct-2014)
- 11) Describe in detail the accurate method of dissociation constant of weak acid by emf measurements (6M) (Apr-2014)
- 12) Alkaline storage battery (4M) (Apr-2014) (Oct-2014), (Oct-2012), (Apr-2009)
- 13) Give an account of dissociation constant of monobasic weak acid by approximate emf methods (Oct-2012)
- 14) How will you determine the activity coefficient by using the emf values of conc. cell without transference? (Oct-2012)

IV) Chemical Kinetics

Physical

● Short beats. [1M]

- 1) Write the eqⁿ for the rate of the reacⁿ,
 $2A + B \rightarrow \text{product}$ [April-18]
- 2) "presence of catalyst does not alter the equilibrium constant in a reversible reaction" state whether this statement is true or false. (April-18)
- 3) Give the name of eqⁿ which expresses variation of rate constant with temperature. (April-18)
- 4) 'A catalyst increases the rate of chemical reaction by increasing the activation energy' state whether this statement is true or false. (Oct-15)
- 5) What is positive & negative salt effect. (Oct-15, April-14.)
- 6) Mention the factors on which rate of reaction depends. (Oct-15)
- 7) 'A catalyst increase the rate of chemical reaction by decreasing the activation energy' state whether this statement is true or false. (April-14)
- 8) If for any reacⁿ, the rate is equal to the rate of the reacⁿ at all concentration, then what is the order of this reaction. (April-14)
- 9) What will be the order of reacⁿ when rate of reacⁿ doubles upon increasing the concentration of reactant four times. (Nov-14)
- 10) Mention the factors on which rate of enzyme catalyzed reactions depends. (Nov-14)

● Short answer questions - [6M]

- 1) What is steady state approximation? using this principle discuss kinetic's of decomposition of ozone. (April-14, 18)
- 2) Discuss EMF method of determination of activity coefficient of an electrolyte. (April-18)
- 3) Describe in detail the EMF method of determination dissociation constant of weak. (Oct-15)
- 4) Discuss kinetics of reaction betⁿ NO_2 & F_2 (NOV-14, OCT-15)
- 5) Discuss conductivity method of following kinetic's of reaction with suitable example. (OCT-15)
- 6) Discuss the factors affecting enzyme catalyzed reaction. (OCT-15)
- 7) Derive the rate law equation for the decomposition N_2O_5 . (April-15)
- 8) Discuss kinetics of enzyme catalyzed reactions. (April-14, 15)
- 9) Discuss kinetics of homogenous acid-base catalyzed reacⁿ with suitable example (NOV-14)

• Short Notes - [4 M]

- 1) From the following data show that the decomposition of N_2O_5 in CCl_4 solution at $48^\circ C$ is a first order rea^n .

Time in minute	10	15	20	∞
Vol of O_2 evolved.	6.30	8.95	11.40	34.35

- 2) Give a brief Comment on factor's affecting enzyme catalysis. (April-18)
- 3) primary salt effect (April-18)
- 4) EMF method for the determination of instability Constant. (April-18)
- 5) Consequences of ozone layer depletion (April-18)
- 6) primary & Secondary salt effect (April-14, Oct-15)
- 7) kinetics of acid base catalyzed rea^n . (Oct-15)
- 8) for given rea^n at temp, T , the velocity Const, k is expressed as, $k = A \cdot e^{-27000K'/T}$. Given, $R = 2 \text{ cal mol}^{-1} K^{-1}$, calculate the values of energy of activation (April-15)
- 9) The optical rotation of cane sugar in 0.5N lactic acid at $25^\circ C$ at various time intervals are given below.

Time in minute.	0	1435	11360	infinity
Angle of rotation.	34.50	31.10	13.98	-10.77

Show that rea^n is first order. (April-14)

- 10) The half period of the reaction, $\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2}\text{O}_2$ is 2.4 hours at 30°C . What time would be required to reduce 5×10^{10} molecules of N_2O_5 to 10^8 molecules? (Nov-14)
- 11) kinetics of decomposition of nitrogen pentoxide. (April-14)

• Long answer questions [10 M].

- 1) Discuss kinetics of thermal decomposition of N_2O_5 & derive rate law eqⁿ. (April-2009)