SD – 549

Total No. of Pages : 3

Seat No.	

M.Sc. (Part - I) (Semester - II) Examination, April - 2019

CHEMISTRY/APPLIED CHEMISTRY/INDUSTRIAL CHEMISTRY

Physical Chemistry - II (Paper - VII) (New) (CBCS)

Sub. Code : 71523

Day and Date :Friday, 05 - 04 - 2019 **Total Marks : 80**

Time : 11.00 a.m. to 02.00 p.m.

Instructions : 1) Attempt in all five questions.

2) Attempt any two questions from Section - I and any two from Section - II.

3) All qusestions carry equal marks.

4) Figures to right indicate full marks.

5) Neat and labeled diagrams should be drawn.

6) Use of calculator and log table is allowed.

Q1) Solve the following (one mark each) : **[16]**

a) Write equations for the raising and lowering ladder operators.

b) What is the Heisenberg uncertainty principle?

c) Write equation for the operator use to determine kinetic energy (T).

d) What is the physical significance of wave function?

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

f) "Exciplex emission observed only in heteroatom" state whether the statement is True or False.

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

h) Define the life time of electronically excited state.

i) Write the relationship between three forms of activity coefficients for dilute solution.

P.T.O.

j) Write the cell representation of 3rd kind of electrode.

k) The mobile phase in electroosmosis is _____.

l) Name the mechanism with which the abnormal conductance of hydrogen ion is explained.

m) The minimum amount of energy needed to bring about a non spontaneous change is the _____.

n) For a second order reaction the rate constant is $10 m^{-1}s^{-1}$. Calculate half life of the reaction if a = 1.0×10^{-2}M.

o) Name the method of following a reaction in which the diffusion current is measured.

p) The temperature of coefficient for general reaction is 2.3. True/False

SECTION - I

Q2) a) Derive an expression of wave function for three dimensional cubical box and draw the energy levels with degeneracy. **[8]**

b) Show that $[\hat{L}_x, \hat{L}_y] = i\hat{L}_z$. **[8]**

Q3) a) What is bimolecular fluorescence quenching? Derive Stern-Volmer relation for fluorescence quenching by nonfluoresence quencher. How the validity of this equation is tested experimentally? **[8]**

b) Distinguish between photodimer, excited photodimer, excited and exciplex species. **[8]**

Q4) a) Describe the methods used for determining instability constant of silver-ammonium complex ion. **[8]**

b) Derive the relationship between three forms an activity coefficient. Compare the activity coefficient fx, fc and fm in an aqueous solution containing 0.1 M phenol per litre, taking the density of solvent as 1.00 and that of solution as 1.005 gm/cc. **[8]**

SECTION - II

Q5) a) Describe the theory of homogeneous and heterogeneous catalysis. [6]

b) What is meant by the term catalyst? Give general characteristics of catalytic reactions. [6]

c) Explain the effect of ions on the zeta potential. [4]

Q6) a) Discuss the excitation energy transfer (EET) in host-guest organic systems. Illustrate the examples with their nature of fluorescence spectra in EET process. [6]

b) Discuss in detail Michaelis and Menten's enzyme mechanism to express the rate of reaction? [6]

c) What will be the uncertainty in its velocity, If a base ball (m = 200 g) is moving with a velocity of 3000 cm s^{-1}. If its position is located with an uncertainty of 500 nm (Given, $h = 6.62 \times 10^{-34}$ J.s). [4]

Q7) Write short notes on ***any three*** of the following : [16]

a) Electrical double layer.

b) Polarographic technique for chemical kinetic.

c) Postulates of quantum mechanics.

d) Enzyme catalysis.

Seat No.

SI-56

Total No. of Pages : 3

M.Sc. (Part - I) (Semester - II) (CBCS) Examination, December - 2016
CHEMISTRY / APPLIED CHEMISTRY
Physical Chemistry - II (Paper - VII)
Sub. Code : 61359/61377

Day and Date : Thursday, 08-12-2016

Time : 10.30 a.m. to 1.30 p.m. **Total Marks : 80**

Instructions :
1) **Attempt in all five questions.**
2) **Question No.1 is compulsory.**
3) **Attempt any two questions from Section - I and any two questions from Section - II.**
4) **All questions carry equal marks.**
5) **Use of log table and calculator is allowed.**

Q1) Solve the following: **[16]**

a) Write the expression for the constant B in Debye - Huckel - Onsager equation.

b) "In case of concentration cell with transference for HCl if $a_2 \geq a_1$ then reaction is non-spontaneous." State whether this statement is True or False.

c) Write the cell representation and equation of electrode potential of first kind of electrode.

d) Write the Debye - Huckel Limiting law for a single ion.

e) Which of the following atomic orbitals form σ - bonding and antibonding molecular orbitals?

i) s-orbitals ii) p-orbitals

iii) d-orbitals iv) f-orbitals

f) Time required for the electronic transition to occur in diatomic molecule is _____ second.

i) 10^{-15} ii) 10^{-13} iii) 10^{-11} iv) 10^{-8}

g) Give the relation between fluorescence life times and rate constant of fluorescence.

P.T.O.

h) Mention the criteria for efficient energy transfer from excited fluorescent donor to ground state acceptor.

i) What will be the value of temperature coefficient when rate of reaction doubles upon increasing the temperature by 10°C?

j) The SI unit of energy of activation is _____.

k) "Presence of catalyst does not alter the equilibrium concentration in a reversible reaction", state whether this statement is true or false.

l) What is the meaning of enzyme inhibition?

m) Define Hermition operators.

n) Give the selection rule for the electronic transitions in the frame work of particle in a box problem.

o) State average value theorem.

p) Define step up and step down operators for angular momentum.

SECTION - I

Q2) a) Write step wise mechanism of bimolecular collisional fluorescence quenching of molecules and derive Stern - Volmer equation. **[6]**

b) Give an account of selection rules in electronic transitions. **[6]**

c) The fluorescence of quinine sulphate is 60% quenched by 5×10^{-5} M sodium chloride solution. Calculate the half quenching concentration. **[4]**

Q3) a) Describe in detail the emf method used for determining instability constant of silver - ammonia complex ion. **[6]**

b) What do you mean by storage battery? Explain in detail the acid storage battery. **[6]**

c) Calculate the thickness of ionic atmosphere in 0.1 N solutions of 1:1 slat in nitrobenzene at 25°C (D = 34.8). **[4]**

Q4) a) Obtain an expression for operators used to represent physically observable properties such as linear momentum, kinetic energy and total energy. **[8]**

b) Prove that, $[L_x, L_y] = iL_z$. **[8]**

Q5) a) Derive rate law for the enzyme catalyzed reaction. Show that at low concentration it obey first order and zero order at high concentration of substrate. [6]

b) Applying steady state approximation derive the rate law for the decomposition of ozone. [6]

c) The kinetics of a reaction is followed at 25°C by measuring absorbance of the reactant at wavelength of maximum absorption. The plot of logarithm of Absorbance versus Time produces a straight line with slope value $-(0.3 \times 10^{-2})$. Calculate the rate constant. [4]

Q6) a) Explain the Franck - Condon principle of electronic transitions in a diatomic molecule and discuss photdissociation and predissociation in the electronic spectra of these molecules. [6]

b) Discuss with suitable example dilatometric method of determination of rate constant of a reaction. [6]

c) Explain the Bjerrum's ion association theory. [4]

Q7) Write notes on any four of the following: [16]

a) Primary salt effect.

b) Electrophoretic effect.

c) Delayed fluorescence.

d) Qualitative verification of Debye-Huckel equation of activity coefficients.

e) Green house effect.

f) Postulates of quantum mechanics.

SK-405

Total No. of Pages : 4

Seat No.

M.Sc. (Part - I) (Semester - II) (CBCS) Examination, April - 2017

CHEMISTRY / APPLIED CHEMISTRY

Physical Chemistry - II (Paper - VII)

Sub. Code: 61359/61377

Day and Date : Tuesday, 25-04-2017 **Total Marks : 80**

Time : 11.00 a.m. to 2.00 p.m.

Instructions :

1) **Attempt in all five questions.**
2) **Questions No. 1 is compulsory.**
3) **Attempt any two questions from Section - I and any two questions from Section - II.**
4) **All questions carry equal marks.**
5) **Use of log table and calculator is allowed.**

Q1) Solve the following: **[16]**

a) What is first postulate of Debye-Huckel theory of interionic attraction?

b) Write equation for the value of r_{min} according to Bjerrum's theory.

c) Write the cell representation of alkaline storage battery.

d) Write equation for emf of a concentration cell with transference in which HCl solution is at two different concentrations.

e) Define quantum efficiency fluorescence.

f) Time required for the electronic transition to occur in diatomic molecule is _____ second.

i) 10^{-15} ii) 10^{-13} iii) 10^{-11} iv) 10^{-8}

g) "All molecules excited to higher electronic state do not emit fluorescence". Give the reason.

h) State Hund's rule of maximum multiplicity.

P.T.O.

i) Define temperature coefficient of a reaction.

j) Which of the following properties of solution is measured when reaction is followed by polarographically?

i) Emf ii) conductance

iii) diffusion current iv) absorbance

k) "Presence of catalyst does not alter the equilibrium constant in a reversible reaction", state whether this statement is true or false.

l) What is the meaning of positive catalysis?

m) $[L^2L_z]$ = _____.

n) Give the selection rule for the electronic transitions in the frame work of particle in a box problem.

o) Eigen values associated with Hermition operators are always ____.

p) Define Laplacian operator.

SECTION - I

Q2) a) What is meant by fluorescence? Explain the mechanism of prompt fluorescence and delayed fluorescence. [6]

b) Give a brief account of green house effect. [6]

c) Define the term half quenching concentration. Show that half quenching concentration is reciprocal of the Stern-Volmer constant. [4]

Q3) a) Derive an expression for electrical work done in charging an ion at definite concentration and infinite dilution according to Debye-Huckel theory. [6]

b) Explain in detail the electrophoretic and relaxation effects with corresponding expressions and their effect on the conductance of an electrolyte solution. [6]

c) Calculate the ratio of activity coefficient f_x, f_c and f_m for 0.1 N KI (MW = 166) in ethyl alcohol at 25°C. The densities of pure solvent and solution are 0.7919 and 0.8014 respectively. [4]

Q4) a) Explain the concept of commuting and non-commuting operators with suitable examples. [6]

b) Prove that if ψ_1 and ψ_2 are eigen functions of Hermition operator A with eigen values a_1 and a_2 respectively, then ψ_1 and ψ_2 are orthogonal. [6]

c) Shwo that, [4]

$$L_z L_- = L_-(L_z - 1)$$

SECTION - II

Q5) a) What are heterogeneous catalysis reactions? Give some examples of such reactions and show that,

$$\theta = \frac{k1p}{k2 + k1p}$$ with usual notations. [6]

b) Applying steady state approximation derive the rate law for the decomposition of N_2O_5. [6]

c) Write the equation for rate of enzyme catalyzed reaction and give significance of the terms involved in it. Show that the concentration of the substrate at half of the maximum rate is equal to the Michalis-Menten constant. [4]

Q6) a) Sketch the Jablonski diagram and show the ways by means of which an electronically excited molecule losses its excitation energy.

Discuss various radiative and radiation less pathways. [6]

b) Discuss with suitable example polarography method of determination of rate constant of a reaction. [6]

c) Discuss validity of Debye-Huckel-Onsager equation and comment on the deviation from Onsager equation. [4]

Q7) Write notes on any four of the following: [16]

a) Secondary salt effect.

b) Bjerrum's ion pair association theory.

c) Formation and shapes of molecular orbitals.

d) Qualitative verification of Debye-Huckel equation of activity coefficients.

e) Excimer and exciplex emission.

f) Postulates of quantum mechanics.

SE-225

Total No. of Pages : 3

Seat No.

M.Sc. (Part - I) (Semester - II) (CBCS) Examination, November - 2017

CHEMISTRY / APPLIED CHEMISTRY

Physical Chemistry - II (Paper - VII)

Sub. Code : 61359 / 61377

Day and Date : Monday, 06 - 11 - 2017 **Total Marks : 80**

Time : 10.30 a.m. to 1.30 p.m.

Instructions :

1) **Attempt in all five questions.**
2) **Question No. 1 is compulsory.**
3) **Attempt any two questions from Section I and any two questions from Section II.**
4) **All questions carry equal marks.**
5) **Use of log-table and calculator is allowed.**

Q1) Solve the followings : **[16]**

a) What is the nature of graph when λ is plotted versus $\sqrt{C}$ according to Debye-Huckel-Onsagar equation?

b) Construct an electrochemical cell in which the reaction is,

$Ag^{+} + Cl^{-} \rightarrow AgCl$.

c) Give an example and write presentation of first kind of electrode.

d) How the thickness of ionic atmosphere varies with the concentration of electrolyte?

e) Give the equation which relates radiative life time and rate constant of fluorescence.

f) Which of the following is the value of time required for the electronic transitions to occur?

i) 10^{-13} second ii) 10^{-11} second

iii) 10^{-15} second iv) 10^{-9} second

g) "Phosphorescence is arising from the triplet states of molecule". State whether this statement is true or false.

h) State selection rule in terms of electron spin.

i) Write the rate law equation for the reaction, $2A + B \rightarrow$ product.

P.T.O.

j) Give the unit of frequency factor of chemical reaction.

k) State whether molybdenum acts as promoter or inhibitor in the Haber process of synthesis of ammonia by using Fe.

l) Write Arrehenius equation showing temperature dependence of rate constant of a chemical reaction.

m) $[L_y, L_z] =$ _____.

n) For a particle in three dimensional box, the state of system is characterized by three quantum numbers as n_x, n_y and n_z with energy of $\frac{14h^2}{8ma^2}$. What is the degeneracy of the energy level represented by three quantum numbers?

o) If A and B are commutating operators then, [A,B] = _____.

p) Eigen values associated with hermition operators are always _____.

SECTION - I

Q2) a) Explain mechanism of quenching of fluorescence of probe molecule A by quencher Q involving energy transfer and derive Stern-Volmer equation for this process. **[6]**

b) In the quenching of fluorescence of a substance A by a quencher Q, the fluorescence life time in absence of quencher is 2.5 ns. Using the data given below calculate quenching rate constant. **[6]**

Q (moles per dm^3)	0.01	0.032	0.067
$\frac{F^0}{F}$	1.32	2.02	3.14

c) "Ozone layer in the stratosphere is the Earth's Umbrella", justify the statement. **[4]**

Q3) a) Give an account of method of determination of activity coefficient of an electrolyte by emf measurement using concentration cell. **[6]**

b) Derive relationship between three different forms of activity coefficients. **[6]**

c) Calculate the ionic strength of 0.01 M Aluminum sulphate and magnesium phosphate solutions. **[4]**

Q4) a) For particle confined in a box system, derive the selection rule for the electronic transition through evaluation of transition dipole moment integral. Given : $\psi_n = \sqrt{a/2}\sin\frac{n\pi x}{a}$. [6]

b) Explain the concept of commuting and noncommuting operators with suitable examples. [6]

c) Discuss postulates of quantum mechanics. [4]

SECTION - II

Q5) a) Discuss spectrophotometric method used to follow kinetics of hydrolysis of ester with suitable example. [6]

b) What is steady state approximation? Using this principle discuss kinetics of reaction between NO_2 and F_2. [6]

c) From the following data for the decomposition of N_2O_5 in CCl_4. solution at 48°C, show that the reaction is first order. [4]

Time (minute)	10	15	20	∞
Volume of O_2 evolved	6.30	8.95	11.40	34.35

Q6) a) Discuss photodissociation and predissociation in diatomic molecule. [6]

b) Explain in detail primary and secondary salt effect. [6]

c) Give a brief comment on relaxation and electrophoretic effects. [4]

Q7) Write notes on any four of the following: [16]

a) Characteristics of enzyme catalysis reaction.

b) Heterogeneous catalysis.

c) Excimer and exciplex emission.

d) Instability constant of Ag-ammonia complex.

e) Franck-Condon principle.

f) Born interpretation of wave function.

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SD-10

Total No. of Pages : 3

Seat No.

M.Sc. (Part - I) (Semester - II) (CBCS) Examination, April - 2018

CHEMISTRY / APPLIED CHEMISTRY

Physical Chemistry - II (Paper - VII)

Sub. Code : 61359 / 61377

Day and Date : Tuesday, 10- 04 - 2018 Total Marks : 80

Time : 11.00 a.m. to 2.00 p.m.

Instructions :
1) Attempt in all five questions.
2) Question No. 1 is compulsory.
3) Attempt any two questions from Section - I and any two questions from Section - II.
4) All questions carry equal marks.
5) Use of log table and calculator is allowed.

Q1) Solve the following : [16]

a) Write the expression for the electrical density (ρ) for uni-univalent electrolyte.

b) Pt, $(H_2)_g/H^+$, is an example of first or second kind of electrode.

c) Give the relation between dissociation constant (K) and fraction of association (θ).

d) Write an expression for thickness of ionic atmosphere.

e) "Electronic transitions are more probable when nuclei are in their extreme position during vibration". This is the statement of _____ principle.

i) Pauli Exclusion.

ii) Avogadro's.

iii) Steady state.

iv) Franck-Condon.

f) State Teller's rule of non crossing of energy levels.

g) What should be the multiplicity of energy level of excited electronic state for a promoted electron with reversal of spin to accommodate?

h) "Fluorescence spectrum of excimer species is structureless broad band". State true or false.

i) Write the equation for the rate of the reaction, $2A + B \rightarrow$ product.

P.T.O.

j) "Presence of catalyst does not alter the equilibrium constant in a reversible reaction". State whether this statement is true or false.

k) Define turn over number.

l) Give the name of equation which expresses variation of rate constant with temperature.

m) State Pauli Exclusion Principle.

n) Eigen values associated with Hermition operators are _____.

o) $[L_y, L_z] =$ _____.

p) For a particle in three dimensional box, the state of system is characterized by three quantum numbers as n_x, n_y and n_z with energy of $\frac{14h^2}{8ma^2}$. What is the degeneracy of the energy level represented by these quantum numbers.

SECTION - I

Q2) a) Distinguish between excimer, exciplex and excited dimer with respect to their spectral characteristics. **[6]**

b) Discuss the photodissociation, photoabsorption and predissociation of diatomic molecules on the basis electronic spectra. **[6]**

c) Construct Jablonski Diagram and discuss possible photophysical pathways of deactivation for the excited molecules. **[4]**

Q3) a) Give an account on validity of Debye-Huckel-Onsager equation. **[6]**

b) Derive the relationship between rational activity coefficients (f_x) and practical activity coefficients (f_c, f_m) of an electrolyte solution. **[6]**

c) Calculate the ionic strength of 0.1 M copper chloride solution. **[4]**

Q4) a) Explore the concepts of commuting and noncommuting operators with suitable examples. **[6]**

b) For a cubical box, what will be the effect of stretching of the box along x-direction on degeneracy and energy of the state represented by $\frac{6h^2}{8ma^2}$. **[6]**

c) Give the characteristics of well behaved function. **[4]**

SECTION - II

Q5) a) Explain the spectroscopic method to follow the kinetics of hydrolysis of ester. [6]

b) What is steady state approximation? Using this principle discuss kinetics of decomposition of ozone. [6]

c) From the following data show that the decomposition of N_2O_5 in CCl_4 solution at 48°C is a first order reaction. [4]

Time in min	10	15	20	∞
Volume of O_2 evolved	6.30	8.95	11.40	34.35

Q6) a) Derive Stern-Volmer relation for bimolecular collision fluorescence quenching. [6]

b) Discuss EMF method of determination of activity coefficient of an electrolyte. [6]

c) Give a brief comment on factors affecting enzyme catalysis. [4]

Q7) Write notes on any four of the following : [16]

a) Postulates of Debye-Huckel theory.

b) Primary salt effect.

c) FRET approach in chemical analysis.

d) EMF method for the determination of instability constant.

e) Consequences of ozone layer depletion.

f) Born interpretation of wave function.

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