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Reg. No. : .....

Name : .....

**First Semester M.Sc. Degree Examination, January 2017**  
**Branch : Chemistry**  
**CH/CL/CA/CM 213 : PHYSICAL CHEMISTRY – I**  
**(2016 Admission)**

Time : 3 Hours

Max. Marks : 75

## SECTION – A

Answer **any two** from **a, b, c** of **each** question. **Each** sub-question carries **2** marks.

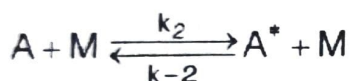
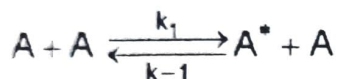
**(10×2=20 Marks)**

1. a) What is meant by the term degeneracy ?  
b) State the significance of Term symbols.  
c) What is an eigen function ?
2. a) What is the uniqueness of enzyme catalysis ?  
b) Give the mathematical expression for Freundlich isotherm.  
c) Name the different types of surfaces.
3. a) State the condition for spontaneity of a process.  
b) What is the significance of Vant Hoff isochore ?  
c) Give the mathematical expression of Lewis Randall law.
4. a) Give the statement of steady state principle.  
b) What is a consecutive reaction ? Give one example.  
c) State the Stark-Einstein's law of photochemistry.
5. a) Define surface tension of a liquid.  
b) Calculate the various degrees of freedom in  $H_2O$ .  
c) For oxygen at  $25^\circ C$ , calculate the mean free path at 1 ohm pressure.

P.T.O.

Answer **either a or b** of **each** question. **Each** question carries **5** marks. (5×5=25 Marks)

6. a) Discuss the algebra of operators.  
b) Write a note on spin orbit coupling.
7. a) What is surface potential ? Explain how it is measured.  
b) Bringout the similarities and differences between physisorption and chemisorption.
8. a) Derive the expression for any two Maxwell's relation. State its significance.  
b) Explain the determination of activity and activity coefficient of electrolytes.
9. a) With a neat Jablonski diagram, explain all photophysical processes.  
b) Consider the following Lindemann mechanism for the unimolecular decomposition of a molecule A in the presence of an inert gas molecule M.



Applying steady state approximation to  $A^*$ , derive the rate law for the formation of the product.

10. a) Derive the expression for average velocity of molecules.  
b) Write a note on inter molecular forces.

## SECTION - C

Answer **any three** questions. **Each** question carries **10** marks.

(3×10=30 Marks)

11. Derive the expression for the energy of a particle in 1 - D box.
12. Derive the expression for Langmuir adsorption isotherm, thermodynamically and statistically.
13. Derive the Gibbs Helmholtz equation and discuss its applications.
14. Derive the expression for Eyring equation. State its importance.
15. Explain the procedure involved in the determination of surface tension of a liquid.



Reg. No. : .....

Name : .....

First Semester M.Sc. Degree Examination, February 2015

Branch : Chemistry

CH 213 : PHYSICAL CHEMISTRY – I

(2013 Admission Onwards)

(Common for CH/CL/CA/CM 213)

Max. Marks : 75

Time : 3 Hours

## SECTION – A

Answer **any two** among **a, b** and **c** of **each** question. **Each** sub-question carries **2** marks. **(10×2=20 Marks)**

1. a) Calculate the uncertainty in momentum for an electron confined to one dimensional box of length  $1\text{Å}$ .  
 b) Write spectroscopic term symbol for the ground state (i) O atom (ii)  $d^3$  system.  
 c) Define spin orbital. Write one example.
2. a) Write Schoenflies symbol of point group for (i)  $\text{CH}_2\text{Cl}_2$  (ii) Staggered ethane.  
 b) The essential criteria for chirality is the absence of  $S_n$ . Justify the statement.  
 c) Generate matrix for  $S_3$ .
3. a) Show that  $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ .  
 b) What is residual entropy? Write two examples.  
 c) State and explain Lewis-Randall rule of fugacity.
4. a) For the reaction  $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ , find the steady state concentration of B.  
 b) Explain the term 'adiabaticity' with reference to reaction dynamics.  
 c) How is NMR spectroscopy made use of in the study of fast reactions? Explain.

5. a) What is the effect of temperature on the distribution of molecular velocities of a gas? Explain.
- b) What type of information would you get from XRD of liquids? Explain.
- c) Distinguish between smectic and nematic crystals with examples.

## SECTION - B

Answer either **a** or **b** of each question. Each question carries 5 marks. (5×5=25 Marks)

6. a) Write kinetic energy operator. Show that it is a Hermitian operator.
- b) Find the commutator of  $\hat{L}_x$  and  $\hat{L}_y$ .

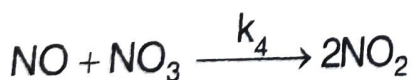
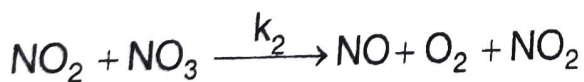
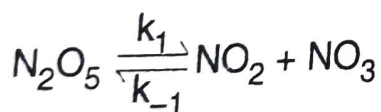
7. a) Using Great Orthogonality theorem, derive reduction formula.
- b) Derive  $C_{3v}$  character table.

8. a) Use third law of thermodynamics to show that absolute zero of temperature is unattainable.

- ✓ b) Define fugacity. How would you determine fugacity of a gas?

9. a) Show that for a rigid sphere model of bimolecular reaction Absolute Rate Theory agrees with Simple Collision Theory.

- b) Decomposition of  $N_2O_5$  takes place according to the following mechanism. Derive the rate law.



10. a) Calculate the viscosity of  $O_2$  at  $25^\circ C$ . The molecular diameter is  $3.6 \text{ \AA}$ .

- b) How would you determine the vapor pressure of a volatile solid? Discuss.

## SECTION - C

Answer **any three** questions. **Each** question carries **ten** marks.

(3×10=30 Marks)

11. Apply Schrodinger wave equation for a simple harmonic oscillator. Find eigen functions and eigen values.
12. Find hybridized orbitals of B in  $\text{BF}_3$ . Use  $D_{3h}$  character table.
13. a) Define excess thermodynamic function. Discuss their importance in the properties of binary solutions.  
b) Write a brief account of the methods for the determination of activity coefficient of nonelectrolytes.
14. Briefly discuss Somenoff Herishelwood theory of branching chain reactions.
15. Derive Maxwell's distribution of molecular velocities for a 3 dimensional gas

$D_{3h}$	E	$2C_3$	$3C_2$	$\sigma_h$	$3\sigma_v$	$2S_3$		
$A'_1$	1	1	1	1	1	1		$z^2, x^2 + y^2$
$A'_2$	1	1	-1	1	-1	1	Rz	
$E'$	2	-1	0	2	0	-1	(x, y)	(xy, $x^2 - y^2$ )
$A''_1$	1	1	1	-1	-1	-1		
$A''_2$	1	1	-1	-1	1	-1	z	
$E''$	2	1	0	-2	0	1	(xz, yz)	(Rx, Ry)



Reg. No. : .....

Name : .....

First Semester M.Sc. Degree Examination, March 2018

Branch : CHEMISTRY

CH/CL/CM/CA 213 - Physical Chemistry - I

(2016 Admission Onwards)

Time 3 Hours

Max Marks 75

## SECTION - A

Answer any two from a, b, c of each question. Each sub-question carries 2 marks.

- Calculate the uncertainty product for a moving electron of mass  $9.109 \times 10^{-28}$  g.
  - Show that  $\Psi = \sin(k_1x) \cdot \sin(k_2y) \cdot \sin(k_3z)$  is an eigen function of  $\nabla^2$  operator. What is the eigen value?
  - State the eigen value postulate of quantum mechanics.
- Write Gibbs adsorption isotherm and explain the terms.
  - Distinguish between physisorption and chemisorption.
  - Outline the principle of X-ray photoelectron spectroscopy.
- Explain the term fugacity.
  - Calculate the entropy change when an ideal gas expands reversibly and isothermally from an initial volume of  $10 \text{ dm}^3$  to final volume  $100 \text{ dm}^3$  at  $27^\circ\text{C}$ .
  - Explain the significance of Duhem Margules equation.
- What is secondary salt effect?
  - Explain the term 'potential energy surface'.
  - What are E-type and P-type phosphorescence?
- Write Virial equation of state and explain the terms.
  - Find the relation between root mean square velocity and most probable velocity of a gas at a definite temperature.
  - Write equation of state for liquids and explain the terms. (10×2=20 Marks)

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SECTION – B

Answer either **a** or **b** of **each** question. **Each** question carries **5** marks.

6. a) What are Hermitian operators? Prove that "the eigen functions of a Hermitian operator that correspond to different eigen values are orthogonal".  
b) Write a note on quantum mechanical tunneling.
7. a) Provide the statistical derivation of Langmuir adsorption isotherm.  
b) Explain Langmuir Hinshelwood model of bimolecular surface catalysis.
8. a) Explain chemical potential. Predict the influence of temperature and pressure on chemical potential.  
b) What are excess functions? Derive expressions for excess free energy and excess entropy.
9. a) Briefly explain the relaxation method of studying fast reactions.  
b) Explain various photophysical phenomena using Jablonski diagram.
10. a) Illustrate a typical radial distribution curve of a liquid and explain the structure.  
b) Explain any one method for determining the surface tension of a liquid.

(5×5=25 Marks)

SECTION – C

Answer **any three** questions. **Each** question carries **10** marks.

11. Solve the time independent Schrödinger equation of a 1-D simple harmonic oscillator and obtain expressions for the wave function and energy of the system.
12. Derive expression for BET adsorption isotherm.
13. Explain any two methods of determining partial molar properties.
14. Discuss absolute reaction rate theory.
15. Write notes on :
  - i) intermolecular forces and
  - ii) relative viscosity determination by Ostwald method.

(3×10=30 Marks)



Reg. No. : .....

Name : .....

**First Semester M.Sc. Degree Examination, February 2019**  
**Branch : Chemistry/Polymer Chemistry**  
**CH/CL/CM/CA/PC 213 – PHYSICAL CHEMISTRY – I**  
**(Common for Chemistry) (2016 Admission Onwards) and**  
**Polymer Chemistry (2018 Admission)**

Time : 3 Hours

Max. Marks : 75

## SECTION – A

Answer **any two** from **a, b, c** of **each** question. **Each** subquestion carries **2** marks. **(10×2=20 Marks)**

1. a) State uncertainty principle and comment on its significance.  
b) Derive the operator for momentum.  
c) What is spin-orbit coupling ?
2. a) Explain the difference between physisorption and chemisorption.  
b) Explain the principles of ESCA.  
c) Briefly explain enzyme catalysis.
3. a) Explain Euler's relation.  
b) State Lewis Randall rule.  
c) How fugacity and pressure are related ?
4. a) What is collision theory ?  
b) What is the principle of flash photolysis ?  
c) State laws of photochemistry.
5. a) Explain Chapman equation.  
b) What are different types of molecular velocities ?  
c) How dipole-dipole interactions differ from hydrogen bond interactions ?



P.T.O.





## SECTION - B

Answer either **a** or **b** of **each** question. **Each** question carries **5** marks. **(5×5=25 Marks)**

6. a) Derive equation of state for real gases.  
b) Explain the barometric method of determination of vapor pressure.
7. a) Explain fluorescence and its quenching.  
b) Explain Lindmann theory of unimolecular reactions.
8. a) How do we determine the activity and activity coefficients of electrolytes ?  
b) Explain the effect of temperature and pressure on chemical equilibrium.
9. a) Explain BET theory.  
b) Explain diffraction method of characterization of catalysts.
10. a) Explain quantum mechanical tunneling with examples.  
b) Explain postulates of quantum mechanics.

## SECTION - C

Answer **any three** questions. **Each** question carries **10** marks. **(3×10=30 Marks)**

11. Determine the eigenvalues and eigenfunctions of simple harmonic oscillator.
  12. Explain any two methods for determining the surface area of solids.
  13. Explain Maxwell relations and its significances.
  14. Explain the kinetics of  $H_2-Br_2$  reaction.
  15. Explain the method of determination of diameter of a molecule.
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**First Semester M.Sc. Degree Examination – Model question paper**  
**Branch III – Chemistry/ Branch IV – Analytical Chemistry**  
**CH/CL 213: PHYSICAL CHEMISTRY – I**  
(2020 Admission Onwards)

Time: 3 Hrs

Max. Marks: 75

**SECTION A**

Answer **two** among (a), (b) and (c) from each. Each sub question carries 2 marks

1. (a) Check whether the function  $e^{-x^2}$  is an eigen function for kinetic energy operator. If so what is the eigen value?  
(b) Show that the momentum of particle in 1D box is quantised.  
(c) Write the general expression for Hermite polynomial. Deduce first two polynomials.
2. (a) Distinguish between associative and dissociative chemisorption.  
(b) Under what condition can multilayer adsorption become more important than monolayer adsorption?  
(c) Explain one method of determination of surface pressure.
3. (a) Calculate  $\Delta S$  of mixing when 2 moles of  $H_2$ , 3 moles of He and 2 moles of  $O_2$  are mixed at fixed temperature assuming ideal behaviour and no chemical change.  
(b) Write any two Maxwell's relations and give their significance.  
(c) State 'Konowaloff's' rule.
4. (a) Give two reasons to show that conventional techniques are not suitable for the study of kinetics of fast reactions.  
(b) Explain steady state principle?  
(c) How volume of activation affects the reaction rate?
5. (a) Identify the symmetry elements present in the following and assign the point group  
(i)  $H_2$                       (ii) HCl  
(b) Explain improper axis of symmetry.  
(c) Cyclic groups are abelian. Explain.

[2 × 10 = 20]

**SECTION B**

Answer either (a) or (b) from each question. Each sub question carries 5 marks

6. (a) For a particle in 3D box with  $L_x = L_y = \frac{L_z}{2}$ , what would be the energy when  $n_x = 1$ ,  $n_y = 2$  and  $n_z = 2$  and when  $n_x = 1$ ,  $n_y = 1$  and  $n_z = 4$ . Use the calculations to explain the meaning of the term accidental degeneracy.

- (b)  $H(x)$  is written as a power series in  $x$  as  $H(x) = \sum_{j=0}^n a_j x^j$ . Derive recursion formula.
7. (a) Write any two methods for the determination of surface area of a solid.  
 (b) Explain Langmuir-Hinshelwood mechanism of surface catalyzed reactions.
8. (a) Derive Van't Hoff isotherm. How is this useful in the study of chemical equilibria?  
 (b) Derive Gibbs-Duhem equation.
9. (a) Compare the rate constant as given by Arrhenius equation and collision theory and show that  $E_a = E_0 + \frac{RT}{2}$   
 (b) Derive the rate law for the decomposition of  $N_2O_5$ .
10. (a) Construct the group multiplication table for the symmetry operations of  $NH_3$  molecule.  
 (b) Determine the number of active IR and Raman lines in the vibrational spectrum of  $POCl_3$ .

[5 × 5 = 25]

### SECTION C

Answer any **three** questions. Each question carries 10 marks

11. Set up the Schrodinger wave equation for a simple harmonic oscillator. Find the eigen functions and eigen values.
12. Explain any two instrumental techniques used for surface characterization.
13. Write a brief account of the methods for the determination of activity coefficient of electrolytes and non-electrolytes.
14. Explain chain reactions. Discuss Semionoff Henshelwood theory of branching chain reactions
15. a) Explain the hybridization scheme in  $BF_3$  molecule using group theory.  
 b) Show that the four elements of  $C_{2v}$  point groups forms 4 classes?

$D_{3h}$	$E$	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$		
$A_1'$	1	1	1	1	1	1		$x^2 + y^2, z^2$
$A_2'$	1	1	-1	1	1	-1	$R_z$	
$E'$	2	-1	0	2	-1	0	$(x, y)$	$(x^2 - y^2, xy)$
$A_1''$	1	1	1	-1	-1	-1		
$A_2''$	1	1	-1	-1	-1	1	$z$	
$E''$	2	-1	0	-2	1	0	$(R_x, R_y)$	$(xz, yz)$

[10 × 3 = 30]