

Reg. No. : .....

Name : .....

**First Semester M.Sc. Degree Examination, August 2021**

**Chemistry/Analytical Chemistry/Polymer Chemistry**

**CH/CI/PC 213 : PHYSICAL CHEMISTRY – I**

**(2020 Admission)**

Time : 3 Hours

Max. Marks : 75

SECTION – A

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

1. (a) Determine the average value of linear momentum for particle in a one dimensional box.  
(b) What are well behaved wave functions? Illustrate with examples.  
(c) Define orthonormal functions.
2. (a) What are block factored matrices?  
(b) Explain reducible and irreducible representation.  
(c) Cyclic groups are abelian. Explain.
3. (a) Differentiate between associative and dissociative chemisorption.  
(b) What is the condition under which BET isotherm approximates Langmuir adsorption isotherm?  
(c) Explain with one example anionic surfactants.

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4. (a) Discuss a method for the determination of partial molar properties.
- (b) Give a short note on temperature dependence of free energy.
- (c) Discuss a method for the determination of excess volume.
5. (a) How does primary salt effect differ from secondary salt effect?
- (b) Differentiate between vanHoff intermediate and Arrhenius intermediate.
- (c) What happens to the overall reaction rate when iodine is replaced by bromine in the halogenation of acetone in aqueous solution?

**(10 × 2 = 20 Marks)**

### SECTION – B

Answer (a) or (b) of **each** question and **each** question carries **5** marks.

6. (a) Discuss the transformational properties of atomic orbitals.
- (b) Construct group multiplication table for the symmetry operations of NH<sub>3</sub> molecule.
7. (a) Discuss the Langmuir-Hinshelwood mechanism.
- (b) A monolayer of N<sub>2</sub> molecule (effective area 0.162 nm<sup>2</sup>) is adsorbed on the surface of 1 g of an Fe/Al<sub>2</sub>O<sub>3</sub> catalyst at 77 K, the boiling point of liquid nitrogen occupies 2.85 cm<sup>-3</sup> at 0°C and 1 atm pressure. What is the surface area of the catalyst?
8. (a) Show that  $\hat{L}^2$  and  $\hat{L}_x$  commute.
- (b) Derive time dependent Schrodinger equation.
9. (a) Derive Gibbs-Helmoltz equation. Give any two applications of the equation.
- (b) Steam is condensed at 100°C and the water is cooled to 0°C and frozen to ice. What is the molar entropy change of the water? Consider that the average specific heat of liquid water is 4.2 J K<sup>-1</sup> g<sup>-1</sup>. The enthalpy of vaporisation at the boiling point and the enthalpy of fusion at the freezing point are 2258.1 and 333.5 J g<sup>-1</sup>, respectively.



10. (a) Calculate the specific reaction rate  $k$  at  $556^{\circ}\text{C}$  for the reaction :  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$  The activation energy for the reaction is 44000cals: collision diameter is  $3.5 \times 10^{-8}$ .
- (b) Briefly describe the flash photolysis method for studying fast reactions.  
**(5 × 5 = 25 Marks)**

### SECTION – C

Answer **any three** questions and **each** question carries **10** marks.

11. Deduce hybrid orbitals of  $\text{BF}_3$  and  $\text{PCl}_5$  molecules using group theoretical treatment.
12. (a) Explain the BET theory of adsorption.
- (b) Discuss the use of Langmuir and BET isotherms for surface area determination.
13. Obtain the allowed eigen states and energies of a particle constrained to move within the boundary of a three-dimensional box.
14. What is fugacity? Derive a relationship between fugacity and pressure. Discuss the method of determination of fugacity of a real gas.
15. Describe the Hinshelwood theory of branching chain reaction. Explain the lower and upper explosion limits with reference to the kinetic expression.  
**(3 × 10 = 30 Marks)**
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