CHE-503

Physical Chemistry

M. Sc. CHEMISTRY (MSCCH–12/13/16/17) First Year, Examination, 2018

Time : 3 Hours

Max. Marks : 80

Note: This paper is of eighty (80) marks containing three (03) Sections A, B and C. Attempt the questions contained in these Sections according to the detailed instructions given therein.

Section-A

(Long Answer Type Questions)

- **Note :** Section 'A' contains four (04) long answer type questions of nineteen (19) marks each. Learners are required to answer *two* (02) questions only.
- (a) Derive an integrated rate equation for a reaction of first order. Derive an expression for the halflife period of such a reaction.
 - (b) Describe any *two* methods of determining the order of reaction. 7
- 2. (a) Discuss in brief, *two* application of e. m. f. measurements. 7
 - (b) Discuss the Debye-Huckel theory of mean ionic activity coefficients. Derive the Debye-Huckel limiting law. How can it be verified ? 12

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- 3. (a) Deduce the Gibbs-Duhem equation.
 - (b) Distinguish between isothermal and adiabatic process. Derive expression for the work done in reversible isothermal expansion and reversible compression of an ideal gas. 12
- 4. (a) Mention experiment which shows that : 12
 - (i) Light behaves as made of particles.
 - (ii) Electron behaves as waves.
 - (b) Which of the functions $\sin 2x$, $5\cos 4x$, $4x^3$, $\frac{1}{x^2}$, $2e^{-3x}$ are eigen function of $\frac{d^2}{dx^2}$? For each eigen function, state the eigen value. 7

Section-B

(Short Answer Type Questions)

- **Note :** Section 'B' contains eight (08) short answer type questions of eight (8) marks each. Learners are required to answer *four* (04) questions only.
- 1. (a) Find the adjoint operators of $\frac{d^2}{dx^2}$. 4
 - (b) Prove that $i[\alpha, \beta]$ is Hermitian if α and β are Hermitian.
- 2. Derive an expression for the wave function of a free particle, is the energy quantised ? Is the wave function normalised ? How can you normalised it ?

- 3. Describe in detail the collision theory of unimolecular reaction.
- 4. State and explain the laws of photochemistry. Define quantum yield. How will you determine it ?
- 5. Explain why the hydrolysis of an ester by acid follows first order kinetics whereas that by alkali follows second order kinetics.
- 6. (a) Show that for one mole of an ideal gas $C_{P} - C_{V} = R.$ 4
 - (b) Derive Gibbs-Helmholtz relation. 4
- 7. State and explain the Nernst heat theorem and third law of thermodynamics.
- 8. Derive the Clausius-Clapeyron equation from the first principle.

Section-C

(Objective Type Questions)

- **Note :** Section 'C' contains ten (10) objective type questions of one (01) mark each. All the questions of this section are compulsory.
- 1. Zero and fractional order reactions cannot take place in step.
- Reaction between C1⁻ and Ag⁺ in solution is so rapid that it can be studied only by method.
- 3. The specific reaction rate of an elementary reaction will with increase of temperature.

- 4. Radioactive decay follows kinetics of which order ?
 - (a) 1st
 - (b) Zero
 - (c) 2nd
 - (d) 3rd
- 5. All natural processes are irreversible. This is a direct consequence of :
 - (a) First law of thermodynamics
 - (b) Second law of thermodynamics
 - (c) Third law of thermodynamics
 - (d) Gibbs Paradox
- 6. The second law of thermodynamics introduces the concept of
- 7. The combined from of first and second law of thermodynamics is given by :
 - (a) TdS = dU + PdV
 - (b) $d\mathbf{U} = \mathbf{T}d\mathbf{S} + d\mathbf{Q}$
 - (c) $d\mathbf{Q} = \mathbf{T}d\mathbf{S} + \mathbf{P}d\mathbf{V}$
 - (d) TdS = dU PdV
- 8. Which of the following is not an exact differential ?
 - (a) *d*Q
 - (b) *d*U
 - (c) *d*G
 - (d) *d*S

- 9. A reaction was found to be second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled, with everything else kept the same, the rate of the reaction will :
 - (a) Remain unchanged
 - (b) Triple
 - (c) Increase by a factor of 4
 - (d) Double
- 10. Which one of the following is a factor which does not influence the rate of a reaction ?
 - (a) Nature of reactants
 - (b) Concentration of the reactants
 - (c) Temperature
 - (d) Molecularity