M.Sc. CHEMISTRY
THIRD SEMESTER
PHYSICAL CHEMISTRY-III
MSC-303

Duration: 3 Hrs. **Marks: 70**

PART : A (OBJECTIVE) = 20
PART : B (DESCRIPTIVE) = 50

[PART-B : Descriptive]

Duration: 2 Hrs. 40 Mins. **Marks: 50**

[Answer question no. One (1) & any four (4) from the rest]

1. i. What is electrical double layer? How is it formed at the electrode/electrolyte interface? Define Helmholtz-Perrin model for electrical double layer. Apply this model to relate the surface tension change with potential of an electrolyte solution. (5+5=10)
   ii. What do you mean by E- type delayed fluorescence? How can you proof that the ratio of quenching efficiency of E- type delayed fluorescence to that of phosphorescence is independent of efficiency of triplet formation.

2. Define homogeneous and heterogeneous catalyzed reaction. Write at least two disadvantages of homogeneous catalyzed reaction and two advantages of heterogeneous catalyzed reaction. Discuss the mechanism and kinetics of heterogeneously catalyzed reaction. (2+3+5=10)

3. State Franck-Condon principle. Discuss the fate of the excited states with the help of Jablonski diagram. What are photosensitizers and discuss the role of photosensitizers in the photodynamic therapy of tumors? (2+3+5=10)

4. What is quenching of fluorescence? What is the basic difference between Static and dynamic quenching? Discuss the Stern-Volmer mechanism of fluorescence Quenching. Write the physical significance of stern-Volmer plot. (2+3+5=10)

5. i) Draw the structure of a diptide. Use R to represent the side chains of an amino acid. (2+3+5=10)
   ii) Discuss the primary, secondary, tertiary and quaternary structures of protein.
   iii) Discuss the thermodynamics of biopolymer solutions.

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6. What are passive and active transport of ions across cell membrane? Discuss the mechanism of primary active transport with the help of Na^+-K^+ pump. What are antiporter and symporter? (2+5+3=10)

7. i. Write the expression of ion-solvent interactions in terms of Born Model. What is the importance of this free energy change? (2+4+4=10)
   ii. Starting from the expression of electrostatic potential, calculate the work of charging an ion in vaccum and inside a solvent in-terms of Born model.
   iii. Calculate the entropy and enthalpy change of ion-solvent interaction in terms of Born theory.

8. i. Write the fundamental electrocapillary equation for polarizable interfaces. (2+8=10)
   ii. Using the above fundamental equation derive the expression of surface excess of a species *i* obtained from the plot of interfacial tension versus mean activity of the electrolyte taken under conditions of constant applied potential.

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[PART-A : Objective]

1. State true or false: (*any five*) **1×5=5**

i. In the spontaneous chemical reaction of a galvanic cell, electrons flow from the cathode to the anode.

ii. In homogeneous catalysis, the catalyst does not appear in the rate law.

iii. The alpha helix, beta pleated sheet and beta turns are examples of protein secondary structure.

iv. In photochemical reactions, the absorption of light takes place in the primary processes only.

v. Only the fraction of light that is absorbed by the substance can bring about a chemical change.

vi. In a Biopolymer-solvent system when '+ΔH' is very high and exceeds the 'TΔS' value, the dissolution cannot take place and the polymer is not affected by the solvent.

vii. In glycolysis fructose-1,6-bisphosphate is split into glyceraldehyde-3-phosphate and dihydroxyacetone phosphate.

2. Choose the correct answer from the following: **1×15=15**

i. One Einstein of energy is:

a. $E = \frac{2.859}{\lambda} \times 10^5$ cal mol^{-1}

b. $E = \frac{2.859}{\lambda} \times 10^5$ kcal mol^{-1}

c. $E = \frac{2.859}{\lambda} \times 10^5$ J mol^{-1}

d. $E = \frac{2.859}{\lambda} \times 10^5$ kJmol^{-1}

ii. For a reaction that obeys Einstein's law:

a. $\phi = 1$
b. $\phi > 1$
c. $\phi < 1$
d. $\phi = \alpha$

iii. The glow of fireflies is due to the aerial oxidation of luciferin. It is an example of:

a. Fluorescence
b. Phosphorescence
c. Chemiluminiscence
d. Quenching

iv. The mean activity coefficients of 5.0 x 10^{-3}mol kg^{-1}KCl (aq) at 25 °C is:

a. 0.92
b. -0.036
c. 0.036
d. -0.92

[Note: $\log\gamma_{\pm} = -|Z_+Z_-|A\bar{I}^{\frac{1}{2}}$; A (Debye Huckel limiting law constant) = 0.509 and I is the ionic strength of the solution.

v. For the concentration cell
$M|M^+(aq, 0.01\ mol\ dm^{-3})||(M^+(aq, 0.1\ mol\ dm^{-3})|M$
the EMF (E) of the cell at a temperature (T) equals:

a. $2.303\frac{RT}{F}$

b. $-2.303\frac{RT}{F}$

c. $E^0_{M^+|M} + 2.303\frac{RT}{F}$

d. $E^0_{M^+|M} - 2.303\frac{RT}{F}$

vi. Allowed transition occur if transition probability (f) is:

a. f = 0
b. f = 1
c. f ≠ 0
d. f ≠ 1

vii. E-type delayed fluorescence is known as:

a. a-fluorescence
b. b-fluorescence
c. a-phosphorescence
d. b-phosphorescence

viii. During dark phase (dark reactions) of photosynthesis.....is oxidized and .....is reduced.

a. CO_2 and water
b. Water and CO_2
c. Water and NADP
d. $NADPH_2$ and CO_2

ix. Gycolytic reversal is a part of:

a. aerobic oxidation.
b. anaerobic respiration.
c. light phase of photosynthesis.
d. dark phase of photosynthesis.

x. Which of the following statements about the TCA cycle is correct?

a. Oxygen is used to oxidize the acetyl group carbons of acetyl-CoA in the TCA cycle.
b. Three molecules of NADH and one molecule of $FADH_2$ are produced in one turn of the TCA cycle.
c. Oxygen is not used in the TCA cycle, so the cycle can occur in anaerobic conditions.
d. The TCA cycle produces the water that is formed during the complete oxidation of glucose.

xi. What is the advantage of having two lipid bilayers around mitochondria?

a. They act as a store of phospholipids.
b. They prevent the entry of chemicals into mitochondria.
c. They protect the cell from free radicals.
d. They maintain a proton gradient.

xii. In the Langmuir-Hinshelwood mechanism of heterogeneous catalyzed reaction, the reaction occurs:

a. between two adsorbed species.
b. between one adsorbed species and on fluid phase species.
c. between two fluid phase species.
d. none of the above.

xiii. Which of the following statements about Michaelis-Mentan Kinetics is correct?

a. K_m, the Michaelis constant, is defined as the concentration of substrate required for the reaction to reach maximum velocity.
b. K_m, the Michaelis constant, is defined as the dissociation constant of the enzyme-substrate complex.
c. K_m, the Michaelis constant, is expressed in terms of the reaction velocity.
d. K_m, the Michaelis constant, is a measure of the affinity the enzyme has for its substrate.

xiv. Phosphorescence is represented as:

a. $T_1 \rightarrow S_0 + h\vartheta$
b. $S_1 \rightarrow S_0 + h\vartheta$
c. $T_1 \rightarrow S_0 + \Delta$
d. $S_1 \rightarrow S_0 + \Delta$

xv. The Fluorescence life time of a molecule in solution is 10 ns. If the fluorescence quantum yield is 0.1, the rate constant of fluorescence decay is:

a. $1 \times 10^9\ s^{-1}$ b. $1 \times 10^8\ s^{-1}$
c. $1 \times 10^7\ s^{-1}$ d. $9 \times 10^7\ s^{-1}$

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UNIVERSITY OF SCIENCE & TECHNOLOGY, MEGHALAYA

[PART (A) : OBJECTIVE]

Duration : 20 Minutes

Serial no. of the main Answer sheet

Course : .....

Semester : ..... **Roll No :** .....

Enrollment No : ..... **Course code :** .....

Course Title : .....

Session : 2017-18 **Date :** .....

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Instructions / Guidelines

- The paper contains twenty (20) / ten (10) questions.
- Students shall tick (✓) the correct answer.
- No marks shall be given for overwrite / erasing.
- Students have to submit the Objective Part (Part-A) to the invigilator just after completion of the allotted time from the starting of examination.

Full Marks	Marks Obtained
20	

Scrutinizer's Signature *Examiner's Signature* *Invigilator's Signature*