

M. Sc. (CHEMISTRY) EXAMINATION, 2022

(4th Semester, CBCS)

PHYSICAL CHEMISTRY SPECIAL**PAPER – XIV-P**

Time : Two hours

Full Marks : 40

(20 marks for each unit)**Use a separate answer script for each Unit.****UNIT: P-4141****Answer any four**

1. a) Establish the relationship between *Chemical Affinity (A)* & *internally generated heat (dq_i)* for a spontaneous chemical reaction.
- b) Derive: $\sigma = r \left(\frac{A}{T} \right)$; where 'r' is the rate of a spontaneous chemical reaction and other symbols have their usual meanings. 2+3
2. Using *Gibbs equation* for an open to all system, derive:

$$\sigma = \sum_{j=1}^n J_j X_j . \quad 5$$

3. Using a triangular chemical reaction system, derive:

$$J_j = \sum_{k=1}^n L_{jk} X_k \quad \text{and} \quad L_{jk} = L_{kj} \quad (\text{where } j \neq k) \quad (\text{Symbols have their usual meanings}). \quad 5$$

[Turn over

[2]

4. Show that for a 'two-flux' system, *direct phenomenological coefficients* are positive and $4L_{11}L_{22} > (L_{12} + L_{21})^2$. 5
5. What are the conditions of a system to reach the '*non-equilibrium stationary state*'? '*Glacier, maintaining constant mass on Mountain top*' is an example of non-equilibrium stationary state. – Justify. 5
6. Define '*thermoelectric power (ϵ)*' and '*Peltier heat (π)*' in connection to the thermoelectric effect. Establish the relationship between them using the *principle of 1st order thermodynamics*. 5

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Answer any four

7. From Einstein's treatment of absorption and emission show that MASER is a natural choice but not LASER. 5
8. What is fluorescence anisotropy? How can fluorescence anisotropy throw light on binding of a fluorescent drug with a protein? 3+2
9. Stern-Volmer plots give a wide range of information regarding quenching of fluorescence – Clarify. 5
10. Discuss on the origin of Stokes and anti-Stokes lines in Raman spectroscopy. Which one is more intense and why? $3\frac{1}{2} + 1\frac{1}{2}$

[3]

11. Justify the name "Photoacoustic calorimetry (PAC)" for the corresponding spectroscopy – Justify or criticize. $2\frac{1}{2} + 2\frac{1}{2}$
12. What is delayed fluorescence? How would you experimentally distinguish between the two types of delayed fluorescence? 2+3
13. a) Does Mössbauer spectroscopy correspond to a nuclear or an extra-nuclear spectroscopy? – Justify your answer.
- b) How can the electronic configuration of Sn in a compound be assessed from Mössbauer spectroscopy? $2\frac{1}{2} + 2\frac{1}{2}$
14. Explain the basic principle of photoelectron spectroscopy? Ejection of Auger electron is not a primary process — Justify or criticize. 3+2