

M. Sc. (CHEMISTRY) EXAMINATION, 2023

(4th Semester)

PAPER: XIV-P

[PHYSICAL CHEMISTRY SPECIAL]

Time : Two Hours

Full Marks : 40

(20 marks for each unit)

Use a separate answer script for each unit.

Unit: P-4141

Attempt *any four* questions.

1. Derive '*balance equation for any property*' in connection with the inward and outward fluxes of that property and change of that property within an open system. 5
2. With the help of the reaction: $A + B \rightleftharpoons P + Q$ (both are elementary) show that its overall rate is *non-linearly* related with its chemical affinity (A). Find the condition for which this rate will be *linearly* dependent of A. 5
3. Using a triangular chemical reaction system, derive:
$$J_j = \sum_{k=1}^n L_{jk} X_k$$
 (Symbols have their usual meanings). 5
4. State and explain the '*Curi-Prigogine Symmetry Principle*' and show that direct phenomenological coefficients are positive. 3+2

[Turn over

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5. What are the conditions of a system to attain '*stationary state*'? Explain whether a human body maintaining a constant temperature of 37°C is a stationary state or equilibrium state. 5
6. Define '*Soret coefficient*' & '*heat of transport*' in connection with thermo-mechanical effect. Establish a relationship between them and interpret. 5

Unit: P-4142

Attempt *any four* questions.

7. From Einstein's treatment of absorption and emission, develop a relation between the coefficients of spontaneous and stimulated emissions. 5
8. Explain how the possibility of static and/or dynamic quenching of emission of a fluorophore by a possible quencher can be resolved completely from fluorescence quenching experiments. 5
9. H₂ molecule is microwave inactive but Raman active – why? Which one among Stokes and anti-Stokes lines is more intense and why? 3+2
10. Discuss the basic principle of Photoacoustic calorimetry (PAC). What are the two basic and important equations used in PAC? 3+2

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11. Explain whether Doppler effect is useful or nuisance in Mössbauer spectroscopy. How can Mössbauer spectroscopy differentiate between s and p orbitals? 3+2
12. Describe the principle of X-ray fluorescence spectroscopy. What is an Auger electron? 3½+1½
13. Following the time-dependent perturbation technique, derive an equation giving the probability of a given perturbation (a_{if}) to raise a system from 'i'th to 'f'th stationary state. 5
14. Show quantum mechanically that harmonic transition is significant only when the resonance condition prevails. 5