M. Sc. Chemistry (Special Supplementary) 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

Answer any ***four*** questions.

1. a) Establish the relationship between *Chemical Affinity (A) & interally generated heat* ($\bar{d}q_i$) for a spontaneous chemical reaction.

   b) Derive: $\boldsymbol{\sigma = r}\left(\frac{\mathrm{A}}{\mathrm{T}}\right)$; 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:

   $$\sigma = \sum_{j=1}^{n} \boldsymbol{J}_j \boldsymbol{X}_j \, .$$ 5

3. Using a triangular chemical reaction system, derive:

   $J_j = \sum_{k=1}^{n} L_{j\bar{k}} X_k$ and $L_{jk} = L_{kj}$ (where $j \neq k$)

   (Symbols have their usual meanings). 5

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 with the thermoelectric effect. Establish the relationship between them using the *principle of 1st order thermodynamics*. 5

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Answer any ***four*** questions.

7. A solution of a probe gives two well separated absorption bands, one for the nπ* and the other for ππ* transition. How would you identify which band corresponds to which electronic transition? 5

8. From Einstein's treatment of absorption and emission, show that Einstein's coefficients of absorption (B_{12}) and induced emission (B_{12}) are equal in magnitude. 5

9. Harmonic transition is significant only when the resonance condition prevails – Justify or criticize. 5

10. a) How do you establish whether a delayed fluorescence is of E-type or P-type?

b) Fluoroscence anisotropy of a drug in water increases when it binds with a protein and then it decreases when urea is added to the system – Explain these observations. $2\frac{1}{2} + 2\frac{1}{2}$

11. Justify the name "Photoacoustic calorimetry" of the relevant spectroscopy. What is the interlying principle in this spectroscopy? $2\frac{1}{2} + 2\frac{1}{2}$

12. Explain how the possibility of static and/or dynamic quenching of the emission of a fluorophore by a possible quencher can be resolved completely from fluorescence quenching experiments? 5

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+3

14. a) Discuss the principle of photoelectron spectroscopy.

b) Is formation of an Auger electron a primary or a secondary process in photoelectron spectroscopy? 4+1