

M. SC. CHEMISTRY EXAMINATION, 2022

(4th Semester)

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

Time : Two hours

Full Marks : 50

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

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

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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
7. Define '*electro-osmosis*' and '*streaming potential*' in connection to the electro-kinetic effect. Establish a relationship between them. 5

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8. Derive the following relation using Einstein's two-level model. $A_{mn} = \frac{8\pi h\nu^3}{c^3} B_{mn}$ (Where terms have usual meanings) 5
9. In phosphorescence, *spin forbidden Triplet-Singlet transition is observed*. – why? 5

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10. What is '*Mirror Image Rule*' in electronic spectroscopy? What is the *origin* for this rule? Aromatic alcohols become *stronger acid on excitation*. Explain using *Förster mechanism*. 5
11. Derive the following expression: $F = 2.303\Phi_f I_a \epsilon_v C l$ (Terms have usual meanings). 5
12. What is *Kasha's rule*? How do you differentiate π - π^* and n - π^* transition? 5
13. Draw and explain in terms of peak position, splitting and magnitude of splitting for the carbon *1s* X-ray photoelectron spectra of furan, pyrrole and thiophene. 5
14. What is the low energy band dominated by two lines of almost equal intensity in the He I ultraviolet photoelectron spectrum of HBr? 5