d) Does Mössbauer spectroscopy correspond to a nuclear or an extra-nuclear spectroscopy ?–Justify your answer. How can the electronic configuration of Sn in a compound be assessed from Mössbauer spectroscopy ?

$4+2\frac{1}{2}+2+(2+2)$

11. a) What is the fundamental difference between electronic and photolectron spectroscopy (PES)? Why is it not possible to identify hydrogen by X-ray photoelectron Spectroscopy ? What is the kinetic energy of an electron that has been ejected from an orbital of ionization energy 11.0 eV by a photon of radiation of wavelength 100nm?

b) Calculate the recoil velocity and energy of a free Mossbauer nucleus of mass $19.76\times 10^{-26}$kg when emitting a $\gamma$ - ray of $5.76\times10^{18}$ Hz. What is the Doppler shift of the $\gamma$ - ray frequency to an outside absorber.

c) Which set of lines, Stokes or anti-Stokes, is stronger ? What is Resonance Raman effect ?

d) What are the basic principles of X-ray fluorescence and photoacoustic spectroscopy ? $4\frac{1}{2}+3+2+3$



# M. Sc. Chemistry Examination, 2019

( 4th Semester )

## Physical Chemistry Special

## Paper - XIV-P

Time : Two hours Full Marks : 50

( 25 marks for each unit )

Use separate answerscripts for each unit.

## UNIT - P - 4141

Answer ***any five*** questions :

1. a) 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.

b) Obtain the expression of *Onsager flux* of a spontaneous chemical reaction. 3+2

2. Consider the reaction : $X+Y \rightleftharpoons P+Q$ (both reactions are elementary) and show that its overall rate is non-linearly related with its chemical affinity (A). Find the condition for which this rate be linearly dependent of X. 5

3. Using a triangular chemical reaction system, derive :

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

(Symbols have their usual meaning). 5

4. State and explain the *'Curie-Prigogine Symmetry Principle'* and show that direct phenomenological coeffcients are positive. 3+2

5. Using the 'Principle of microscopic reversibility' derive the following symmetry relation : $\left\langle a_j \times \frac{da_k}{dt} \right\rangle = \left\langle \frac{da_j}{dt} \times a_k \right\rangle$

(Symbols have their usual meanings) 5

6. What are the conditions of a system to attend the *'non-equilibrium stationary state'* ? Explain whether a human body maintaining a constant temperature of $37^0$C is a stationary state or *equilibrium state.* 3+2

7. What are the characteristics of an oscillatory chemical reaction ? Explain it with the help of 'Lotka-Volterra Model'. 5

**UNIT - P- 4142**

Answer question nos. **8** or **9** and (**10** or **11**)

8. Answer question (a) and any three from the rest.

a) How would you treat fluorescence quenching of a fluorophore by a quencher when both static and dynamic quenching are present simultaneously.

b) A four level laser system is more efficient than a three level laser system–justify of criticise.



c) Phenols are more acidic in the lowest excited single state than in their ground state–Justify or criticise.

d) Singlet-triplet transition is spin forbidden, yet phosphorescence is observed-Justify.

e) Experimentally how can you confirm whether a delayed fluorescence is of E - type od P-type ? $3\frac{1}{2}+(3\times3)$

9 a) What are the selection rules for molecular transitions ?

b) Fluorescence excitation spectrum of a molecule is nothing but the absorption spectrum of that moleculr–Explain.

c) What is inner filter effect ?

d) Emission spectrum of anthracene in the presence of diethylaniline showed structured emission at shorter wavelengths and unstructured emission at longer wavelength – Explain. $3+4+3+2\frac{1}{2}$

10. a) How can photoacoustic calorimetry be exploited for the determination of the individual contributions of ISC and IC to the total non-radiative deactivation ?

b) Discuss on "mutual exclusion principle" in spectroscopy.

c) Ejection of Auger electron is not a primary process — Discuss.