state and 5/2 in excited state. Into how many lines will the γ – ray spectrum split if the nucleus is under the influence of an internal electric field gradient ? Draw the enegry levels and transitions for the same.

d) Why are NQR spectra obtained only for solids ? The spins of ^{59}Co nucleus is 7/2. Assuming an axial field gradient, how many quadrupolar transitions will be obtained ? $2+3+5+2\frac{1}{2}$

M. Sc. Chemistry Examination, 2018

(4th Semester)

Physical Chemistry Special

Paper - XIV-P

Time : Two hours Full Marks : 50

(25 marks for each unit)

Use a separate answerscript for each unit.

UNIT - P - 4141

Answer ***any five*** of the following questions :

1. a) What is *chemical affinity (A)* ? Establish the relationship between *'A' & internally generated heat ($đq_i$)* for a spontaneous chemical reaction.

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

2. Using *Gibbs equation* for open system, derive : $\sigma = \sum_{j=1}^{n} J_j \boldsymbol{X}_j$ 5

3. Show that for a *'two fluxes'* system, *direct phenomenological coefficients* are positive and $4L_{11}L_{22} > (L_{12} + L_{21})^2$. Mention the nature of the *fluxes*. 5

4. State and explain the *'Principle of minimum entropy production'* at nonequilibrium stationary state. Show the 'σ'vs. *'force'* plot of 1st order *nonequilibrium stationary state* of two fluxes system. 3+2

5. Using the 'Theory of fluctuation', show that

   $\langle a_j X_k \rangle = -k_B \delta_{jk}$; Where a_j is Onsager coordinate of j^{th} rate process, X_k is Onsager force of k^{th} rate process and k_B is Boltzmann constant. 5

6. What are the conditions of a system to reach the *'non-equilibrium stationary statex'* ? 'Glacier, maintaining constant mass on Mountain top' is an example of *non-equilibrium stationary state.*–Justify. 5

7. 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

UNIT - P- 4142

Answer question no.10 and one from question nos. 8 and 9

8 a) From Einstein's treatment of absorption and emission, show that the relative extent of spontaneous and induced emissions depend on excitation wavelength.

b) Fluorescence anisotropy is a sensitive parameter to study the binding of fluorescent drugs with protein–Justify or criticize.

c) Establish that in the presence of both static and dynamic quenching of fluorescence, the Stern Volmer plot shows a positive deviation. How can we extract the two components ? 5+3+3+1$\frac{1}{2}$

9 a) What are the different types of binding of a drug with DNA ? Using photophysical techniques how would you assess the nature of binding of a fluorescent drug with DNA ?

b) How can you determine the pK_a* of an acid using Förster's cycle technique ? Derive the relevant equation. (2+3)+(4+3$\frac{1}{2}$

10. a) What will be the nature of photoelectron spectrum of hydrogen atom when it is excited by photon of energy 21.2eV ?

b) Show that Raman shift is equal to the frequency of vibration of a diatomic molecule.

c) Explain isomer shift in Mössbauer spectra with an example for tin compounds in different states of oxidation. A particular Mössbauer nucleus has spin 7/2 in ground