

**U.G. 6th Semester Examination - 2021****CHEMISTRY****Course Code : BCEMCCHC602****Course Title : Physical Chemistry-IV**

Full Marks : 30

Time : 2 Hours

*The figures in the right-hand margin indicate marks.**Candidates are required to give their answers in their own words as far as practicable.*

1. Answer any **ten** questions: 1×10=10
- Give the dimension of molar absorptivity.
  - What is the absorbance of a sample with 50% transmittance?
  - The fundamental vibrational frequency of  $\text{H}^{35}\text{Cl}$  is  $8.67 \times 10^{13} \text{s}^{-1}$ . Calculate the fundamental vibrational frequency of  $\text{D}^{35}\text{Cl}$  assuming same force constants for both the cases.
  - What is chemiluminescence? Give an example.
  - Turn over number of a certain enzyme is  $10^3 \text{s}^{-1}$ . Explain.

- Write down the Clausius Mossotti equation mentioning the terms involved therein.
- State the mutual exclusion principle in vibrational spectroscopy.
- The IR spectra of  $^{75}\text{Br}^{19}\text{F}$  consists of intense line at  $380 \text{cm}^{-1}$ . Calculate the force constant of the bond assuming SHO model.
- Why the quantum efficiency of photosynthesis of HBr is low ( $\phi = 0.01$ ) in spite of obeying chain reaction mechanism at ordinary temperature?
- You can observe the approximate 'mirror image' relationship between absorption and fluorescence spectra but not between absorption and phosphorescence spectra. Explain.
- Which of the following molecules is NMR active and why?  $^{12}\text{C}$ ,  $^{19}\text{F}$ .
- Explain why EMR of radiofrequency region is employed for NMR spectroscopy whereas microwave region light is used for ESR spectroscopy.
- Define Internal Conversion and Inter System Crossing.

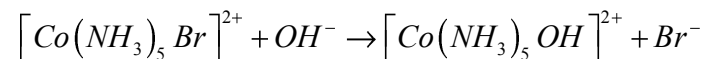
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- n) Calculate the bond length of  $^{13}\text{C}^{18}\text{O}$  molecule if its rotational constant is  $5.76 \times 10^{10} \text{ s}^{-1}$ .
- o) What do you mean by 'Pre-dissociation' in primary photochemical processes?

2. Answer any **five** questions:  $2 \times 5 = 10$

- a) State and explain Frank-Condon principle.
- b) Show that the lines in the rotational spectrum of a diatomic molecule are equispaced though the rotational energy levels are not equispaced under rigid rotator approximation.
- c) Pure rotational spectrum of  $\text{C}^{12}\text{O}^{16}$  has two successive lines at  $7.72 \text{ cm}^{-1}$  and  $11.58 \text{ cm}^{-1}$ . Assign the J values (both initial and final). Predict the position of next transition.
- d) How does orientation polarization depend on temperature? Using it how will you determine graphically the dipole moment by a polar molecule?
- e) The value of quantum yield for photodissociation of acetone by a radiation of 300nm is 0.2. How many molecules of acetone will be dissociated per second if intensity of absorbed radiation is  $10^{-2} \text{ J s}^{-1}$ ?

- f) What do you mean by Primary Kinetic Salt effect? Explain the effect of addition of little KCl on rate of the reaction:



- g) Write down the energy expression for quantized vibration levels of an anharmonic oscillator. Hence discuss on the origin of hot bands in vibration spectroscopy.
- h) Discuss on the origin of Stokes' and Anti-Stokes' lines in the pure rotational Raman spectra with clearly stating the selection rules for such transitions.

3. Answer any **two** questions:  $5 \times 2 = 10$

- a) Give the mechanism for photochemical decomposition of HI and hence show that quantum yield ( $\phi$ ) for such decomposition reaction is 2. Explain why  $\phi$  value is found to decrease from 2 as the reaction proceeds.  $1+2+2$
- b) Write down the Born-Oppenheimer approximations. Considering it discuss on the origin of P, Q, R-branches of spectra related to rotational-vibrational spectroscopy.  $2+3$

- c) Show that for an acid-based catalyzed reaction the observed rate constant passes through a minimum value as  $[H^+]$  is varied. Hence find the expression of pH corresponding to the minimum in terms of catalytic coefficients of  $H^+$  and  $OH^-$  ions. 2+3

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