

U.G. 6th Semester Examination - 2020**CHEMISTRY**

Course Code : BCEMCCHC602

Course Title : Physical Chemistry-IV

Full Marks : 30

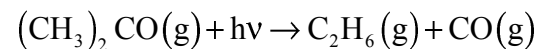
Time : 2 Hours

*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
- Define molar extinction co-efficient.
 - Explain the fact: Phosphorescence can continue over a long period even after the source energy is cut off.
 - What do you mean by autocatalysis? Give example.
 - At 700 nm, a blue filter transmits 60% of the light and a yellow filter transmits 30% of the light. Hence 90% of the light will be transmitted by the two said filters in combination at same λ – Justify / Criticise.

- Write down the Clausius Mossotti equation mentioning the terms involved therein.
- Compare the zero-point vibrational energies of H_2 and D_2 molecules. Mention the assumption used, if any.
- If the rotational energy of a certain level is $6\bar{B}$, where \bar{B} represents rotational constant, then find the degeneracy of the level.
- IR spectra of $^1H^{35}Cl$ gas shows an absorption band at 2885 cm^{-1} . Calculate the force constant of the bond assuming Harmonic Oscillator model.
- Write down the selection rule for rotational-vibrational transition.
- Which of the following molecules are NMR active?
 $^{16}O, ^{13}C, ^{14}N, ^2H$
- Name the region in the Electro Magnetic Radiation which is responsible for:
 - ESR spectroscopy
 - NMR spectroscopy

- l) Photochemical decomposition of oxalic acid takes place in presence of Uranyl ion. Name and explain the process.
- m) State the mutual exclusion rule in vibrational spectroscopy.
- n) Write down Born-Oppenheimer approximation.
- o) Give the dimension of polarisability.
2. Answer any **five** questions: $2 \times 5 = 10$
- a) Write down the energy expression for quantised vibrational energy levels of an anharmonic oscillator. Hence obtain the energy expression of 1st overtone and hot bands.
- b) Write down the expression of Morse potential for a diatomic molecule. Hence show that for small displacement from equilibrium, it will be converted to simple harmonic potential.
- c) The 1st rotational absorption of $^{12}\text{C}^{16}\text{O}$ occurs at 3.8424 cm^{-1} and that for $^{13}\text{C}^{16}\text{O}$ at 3.6734 cm^{-1} . Calculate the atomic weight of carbon-13. Mention the assumption used, if any. [Given Atomic weight $^{16}\text{O} = 15.9994$ and $^{12}\text{C} = 12.0000$].
- d) Give the principle of determination of dipole moment of a polar molecule by using the temperature dependency of orientation polarisation.
- e) What will be the nature of $\log\left(\frac{k}{k_0}\right)$ vs. \sqrt{I} plot for the following reactions?
- i) $[\text{PtCl}_4]^{2-} + \text{OH}^- \rightarrow [\text{PtCl}_3(\text{OH})]^{2-} + \text{Cl}^-$
- ii) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2] + \text{OH}^- \rightarrow$
 $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{OH})] + \text{Cl}^-$
- f) A light of wavelength λ having intensity I_0 falls on a solution of concentration C and path length l . Write an expression for the intensity of light absorbed (I_a). Under what condition, will I_a be proportional to 'C'?
- g) State Stark-Einstein law of photochemical equivalence. From there show that rate of a photochemical reaction is directly proportional to the intensity of light absorbed.
- h) Upon absorption of 313 nm light, acetone photodissociates according to the chemical equation:



Using a reaction cell of 60.3 ml capacity and a temperature of 56°C, irradiation for 25,000 sec at the rate of $8.85 \times 10^{-3} \text{ Js}^{-1}$ produced a change in pressure from 760 mm to 790.4 mm of Hg. Calculate the quantum yield, if the system absorbs 74.5% of the incident light.

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

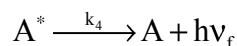
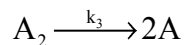
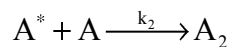
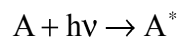
a) For a diatomic rigid rotor prove that,

$$B' \left(J_m + \frac{1}{2} \right)^2 = \frac{1}{2} K_B T \text{ where } J_m \text{ is the rotational}$$

level with maximum population and $B' = \bar{h}C$. Hence comment on the value of J_m at $T=0 \text{ K}$.

4+1

b) Consider the following mechanism for photochemical dimerisation of Anthracene (A):



i) Derive an expression for the concentration of A_2 at photostationary state.

ii) Find out the expression of quantum yield at the initial stage of the reaction when $[A_2]=0$. $2 \frac{1}{2} + 2 \frac{1}{2}$

c) i) Following Michaelis-Menten mechanism, arrive at the expression for initial rate of an enzyme catalysed reaction in terms of maximum rate and Michaelis-Menten constant.

ii) The slope and intercept in the Line Weaver-Burk plot are $4.9 \times 10^{-2} \text{ s}$ and $1 \times 10^4 \text{ mol}^{-1} \text{ Ls}$ respectively. Find the value of Michaelis-Menten constant and turn-over number of the enzyme. Given initial concentration of the enzyme is $4 \times 10^{-9} \text{ molL}^{-1}$. $3+2$