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

a) Define molar extinction co-efficient.

b) Explain the fact: Phosphorescence can continue over a long period even after the source energy is cut off.

c) What do you mean by autocatalysis? Give example.

d) 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.

e) Write down the Clausius Mossotti equation mentioning the terms involved therein.

f) Compare the zero-point vibrational energies of H_2 and D_2 molecules. Mention the assumption used, if any.

g) 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.

h) IR spectra of $^{1}H^{35}Cl$ gas shows an absorption band at 2885 cm^{-1}. Calculate the force constant of the bond assuming Harmonic Oscillator model.

i) Write down the selection rule for rotational-vibrational transition.

j) Which of the following molecules are NMR active?

^{16}O, ^{13}C, ^{14}N, ^{2}H

k) Name the region in the Electro Magnetic Radiation which is responsible for:

i) ESR spectroscopy

ii) NMR spectroscopy

l) Photochemical decomposition of oxalic acid takes place in presence of Uranyl ion. Name and explain the process.

m) State the mututal exclusion rule in vibrational spectroscopy.

n) Write down Born-Oppenheimer approximation.

o) Give the dimension of polarisability.

2. Answer any **five** questions: 2×5=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 $^{12}C^{16}O$ occurs at 3.8424 cm^{-1} and that for $^{13}C^{16}O$ at 3.6734 cm^{-1}. Calculate the atomic weight of carbon-13. Mention the assumption used, if any. [Given Atomic weight ^{16}O=15.9994 and ^{12}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) $\left[PtCl_4\right]^{2-} + OH^- \rightarrow \left[PtCl_3(OH)\right]^{2-} + Cl^-$

ii) $\left[Pt(NH_3)_2Cl_2\right] + OH^- \rightarrow \left[Pt(NH_3)_2Cl(OH)\right] + Cl^-$

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:

$$(CH_3)_2CO(g) + h\nu \rightarrow C_2H_6(g) + CO(g)$$

Using a reaction cell of 60.3 ml capacity and a temperature of 56°C, irradiation for 25,000 sec at the rate of 8.85×10^{-3} 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: 5×2=10

a) For a diatomic rigid rotor prove that, $B'\left(J_m+\frac{1}{2}\right)^2=\frac{1}{2}K_BT$ where J_m is the rotational level with maximum population and $B'=\bar{B}hC$. Hence comment on the value of J_m at T=0 K. 4+1

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

$$A+h\nu \rightarrow A^*$$

$$A^*+A \xrightarrow{k_2} A_2$$

$$A_2 \xrightarrow{k_3} 2A$$

$$A^* \xrightarrow{k_4} A+h\nu_f$$

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 4.9×10^{-2} s and 1×10^4 $mol^{-1}Ls$ respectively. Find the value of Michaelis-Menten constant and turn-over number of the enzyme. Given initial concentration of the enzyme is 4×10^{-9} $molL^{-1}$. 3+2

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