U.G. 6th Semester Examination - 2022

CHEMISTRY

[HONOURS]

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) State Einstein's law of photochemical equivalence.

b) What is photosensitization reaction? Give example.

c) Write down Born-Oppenheimer approximation.

d) Which of the following molecules is NMR active and why— ^{14}N, ^{13}C?

e) The fundamental vibrational frequency of $^{1}H^{35}Cl$ is 8.67×10^{13} s^{-1}. Calculate the same for $^{1}H^{37}Cl$ assuming same force constant.

f) Define turnover number of an enzyme.

g) The equilibrium composition of a system is not affected due to catalysis-comment.

h) Write down which of the following molecules are microwave active: NO_2 and 1,4-dichlorobenzene.

i) Write down the essential condition for a molecule to be Raman active.

j) Predict the nuclear spin value of ^{2}H and ^{4}He.

k) Which one of the foliowing molecules will give E.S.R. spectra: CO_2 and O_2? Explain.

l) Draw with proper labelling a neat potential energy diagram for the van't Hoff model of catalyzed reaction.

m) How does the food get cooked in a microwave oven?

n) Write down the generalized form of acid/base catalyzed reaction mentioning each term.

o) What is a "hot band" in IR spectroscopy? Why is it called so?

2. Answer any **five** questions: 2×5=10

a) Differentiate between fluorescence and phosphorescence.

b) The half life period for the inversion of cane sugar has been found to be 60 min at pH 3.0 at any initial concentration of the cane sugar. What will be its half life time at pH 4.0?

c) Write down the expression of Morse potential for a diatomic molecule. Under what conditions it will be converted to simple harmonic potential?

d) Write the selection rule for pure rotational Raman transitions. Hence obtain the energy expressions corresponding to Stokes' and Anti Stokes' lines.

e) Give the principle of determination of dipole moment of a polar molecule by using the temperature dependency of orientation polarization.

f) Write any two factors which govern the broadening of spectral line.

g) Explain the term predissociation with a neat diagram.

h) Consider the following reaction scheme of a generalized autocatalytic reaction: $R \rightarrow P$, where P is the product as well as the catalyst. Assuming x be the concentration of the reactant already reacted at time t, write down the differential rate equation in terms of x.

3. Answer any **two** questions: 5×2=10

a) i) An uranyl oxalate actinometer is exposed to light of 435 nm wavelength for 15 minutes. After 15 minutes, it was found that oxalic acid equivalent to 12 mL of 0.001 (M) $KMnO_4$ has undergone photochemical decomposition. At this wavelength, the quantum efficiency of the actinometer is 0.58. Find the average intensity of the light used. 3

ii) What is a photostationary state? How does this differ from the equilibrium state? 2

b) Obtain the expression for Michaelis-Menten equation for an enzyme catalyzed reaction. State the characteristics of such reactions. 3+2

c) i) Which of the vibrations of linear AB_2 molecule are IR active and which are Raman active?

ii) Discuss quantitatively the effect of addition of KCl solution on the rate of reaction

$$S_2O_8^{2-} + 2I^- \rightarrow I_2 + 2SO_4^{2-}$$

mentioning the appropriate equation which is applicable here. 2+3

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