

TDP (Honours) 5th Semester Exam., 2021

CHEMISTRY

(Honours)

TWELFTH PAPER (CC-12)

Full Marks : 60

Time : 3 Hours

The figures in the margin indicate full marks.

*Candidates are required to give their answers
in their own words as far as practicable.*

GROUP—A

1. Answer **any six** questions of the following :

2×6=12

(a) Which of the following operators are linear operators?

(i) $\frac{d}{dx}$

(ii) \sin

(iii) \exp

(iv) $\int dx$

- (b) What are stationary states in quantum mechanics?
- (c) What do you mean by well behaved wave function?
- (d) What should be the characteristics of AOs taking part in the formation of molecular orbital?
- (e) What do you mean by Shielding of protons in NMR spectrum?
- (f) What is Raman scattering?
- (g) What are the reasons of low quantum yield?
- (h) On which factors the vibrational stretching frequencies of diatomic molecule depend? In IR spectroscopy which frequency range is known as the fingerprint region?

GROUP—B

Answer the questions taking **one** from each Unit

UNIT—I

2. (a) What is meant by Hermitian operator? Show that the eigenvalues of the Hermitian operators are real.
- (b) Show that the function $\psi = ae^{x/a}$ is an eigenfunction of the operator $\frac{d}{dx}$. What is the eigenvalue?

(3)

(c) Set up the Schrödinger time independent wave equation on the basis of postulates of quantum mechanics. $4+3+5=12$

3. (a) Explain Heisenberg's uncertainty principle. Does zero point energy violate the Heisenberg uncertainty principle?

(b) How can you interpret graphically the wave function and probability density of a particle in a one-dimensional box? At what position of the box, the probability density is maximum, when $n=1$?

(c) What do you mean by average value or expectation value in quantum mechanics?

(d) Evaluate the commutators $\left[x, \frac{d}{dx} \right]$.

$3+4+2+3=12$

UNIT—II

4. (a) Write the complete Hamiltonian of electronic motion in hydrogen atom in spherical co-ordinates by using atomic units. Give the radial and angular parts.

(4)

(b) The wave function of H in the ground state

is $\psi_{1s} = \left[\frac{1}{\sqrt{\pi a_0^3}} \right] e^{-r/a_0}$, where r is the distance from the nucleus and a_0 is 0.529×10^{-8} cm. Show that maximum probability of finding electron in the 1s-orbital of H occurs at $r = a_0$.

(c) What is variation principle?

(d) Write down Schrödinger equation in polar coordinates. 4+4+2+2=12

5. (a) On the basis of the MO theory predict the stability of HeH and LiH . What will be the nature of polarity in LiH ?

(b) Give the ground state MO electronic configurations of CO^+ , NO , CN^+ . Which of these species would you expect to be stabilised by the addition of an electron and are paramagnetic?

(c) Write the MO description of the H_2O molecule.

(d) Explain the formation of covalent bond in the light of valence bond theory using Quantum mechanical approach.

3+3+3+3=12

UNIT—III

6. (a) What is the selection rule for pure vibrational spectra? Show that the frequency of the absorbed radiation in pure vibrational spectra is equal to the fundamental frequency of vibration of the molecule.
- (b) How many normal modes of vibrations are there for SO_2 (bent), C_2H_2 ?
- (c) What is Morse curve? How does it explain anharmonicity?
- (d) In the spectra of HCl , the fundamental band and the 2nd overtone appear at 2886 cm^{-1} and 8345 cm^{-1} respectively. Calculate the anharmonicity constant.

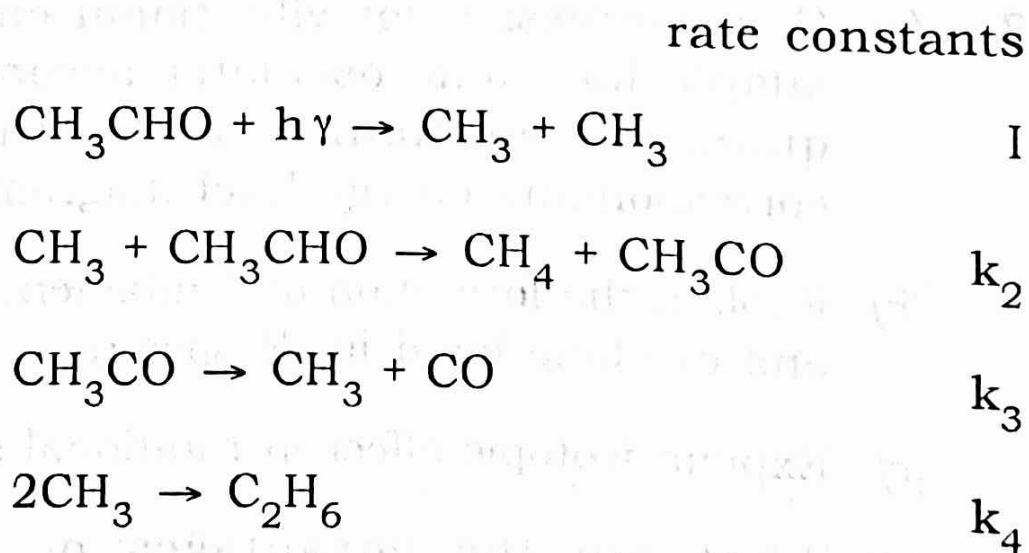
$$(1+3)+2+3+3=12$$

7. (a) Give expression for vibrational energy of simple harmonic oscillator according to quantum mechanics and draw the corresponding energy level diagram.
- (b) Explain the formation of fundamental band and overtone band in IR spectra.
- (c) Explain isotopic effect in rotational spectra.
- (d) What are the advantages of Raman spectroscopy over IR spectroscopy?

$$3+3+3+3=12$$

(6)
UNIT—IV

8. (a) Which substance is used as internal reference in NMR spectroscopy and why?
- (b) Discuss the principle of ESR spectroscopy.
- (c) Explain spin-spin coupling in NMR spectroscopy.
- (d) How many NMR signals do you expect from ethyl alcohol? Indicate the splitting pattern of the various signals. $3+3+3+3=12$
9. (a) Explain briefly fluorescence and phosphorescence.
- (b) Photochemical decomposition of CH_3CHO is shown below :



Show that rate of formation of CO is $k_1^{1/2} \cdot C_{\text{CH}_3\text{CHO}}$.

(7)

- (c) A dye solution containing 1 gm per 100 cc, transmitted 60% of the blue light in a cell 1 cm thick. What percentage of light would be absorbed by a solution containing 2 gm per 100 cc in the same cell?

$$5+4+3=12$$

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