

This question paper contains 4 printed pages.]

Your Roll No. ....!

**5108**

**B.Sc. Prog. / III B**

**CH-303 – PHYSICAL CHEMISTRY**

**(Admissions of 2008 & onwards)**

**Time : 2 Hours**

**Maximum Marks : 50**

*(Write your Roll No. on the top immediately on receipt of this question paper.)*

Log table/simple calculator may be used.

Attempt seven questions in all.

Q. No. 1 is compulsory

1. (a) Write Hamiltonian operator for a particle of mass  $m$  in a two dimensional box of length  $L$ .  $7 \times 2$
- (b) Write ground state energy of a free particle.
- (c) Show the difference between the adjacent lines in the rotation spectra of a diatomic molecule is constant.
- (d) Define order and molecularity of a reaction. What is the relationship between order and molecularity of an elementary chemical reaction ?

- (e) Which of the following molecules will show UV spectra? Give reason.

$H_2, Br_2, CO_2, HCl$

- (f) Define Lambert-Beer's law. Does it hold good in a concentrated solution of a light absorbing substance?
- (g) What is the activation energy of the reaction? Can the activation energy be zero or negative?

2. The reaction  $A + B \rightleftharpoons \text{Products}$

is second order reaction.

- (a) Write differential rate law 1
- (b) Deduce integrated rate law, assuming equal concentration of A and B. 4
- (c) What is the unit of rate constant? 1

3. (a) Show that the rotational level whose quantum number is given by 3

$$J = (K T / 2 B h C)^{1/2} - 1/2$$

has maximum population.

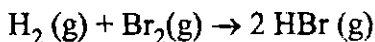
- (b) What are the various factors responsible for the different intensities of rotational spectral lines? 3

4. For a particle of mass  $m$  in one dimension box of length  $L$  having wave function

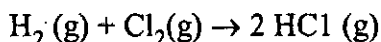
$$\psi = A \sin (n \pi x / L)$$

- (a) Normalize the wave function  $\psi$ . 3
- (b) Calculate expectation value of the position coordinate  $x$  of the particle. 3
5. An electron is confined in a one dimension box of length  $10^{-9}$  m  
(  $m_e = 9.1 \cdot 10^{-31}$  kg ,  $h = 6.26 \cdot 10^{-34}$  Js )
- (a) Calculate energy of first two energy levels. 3
- (b) Calculate the energy absorbed when electron undergoes transition from  $E_2$  to  $E_3$ . 3
6. (a) What is zero point energy of a simple harmonic oscillator ? 2
- (b) What is the selection rule for simple harmonic oscillator ? 2
- (c) Draw all the fundamental modes of vibration of  $H_2O$  and show that they are IR active. 2
7. (a) Define the term 'Quantum efficiency'. Justify the statement that the quantum efficiency of a primary process is always one. 4

- (b) How do you account for the fact that the quantum yield of a photochemical reaction 2



is low ( $\sim 0.01$ ) while that of the reaction



is very high ( $\sim 10^5$ )?

8. (a) Derive the Bragg's equation for the reflection of X-rays from faces of a crystal. 3

- (b) The first order reflection from (200) planes of NaCl using X-rays of wavelength 58 pm occurs at an angle of  $5.9^\circ$ . Calculate the

(i) Edge length of the unit cell.

(ii) Volume of the unit cell. 3

9. Explain how viscosity measurements of a dilute polymer solution is used to determine the molar mass of the polymer. 6
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