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( July )

CHEMISTRY

( Honours )

( Part-A : Physical Chemistry—II )

( Chem-H-602 )

Marks : 38

Time : 2 hours

*The figures in the margin indicate full marks  
for the questions*

1. What is thermodynamic probability? Give its mathematical expression. Give the relationship between entropy and thermodynamic probability, and explain briefly its significance. 2½+2½=5

OR

2. (a) Write the expressions for translational, rotational and vibrational partition functions in one dimension. Give the meaning of the terms in the expressions. 3

- (b) Calculate the rotational partition function for H<sub>2</sub> molecule at 300 K. Given, moment of inertia of H<sub>2</sub> molecule  $4.6 \times 10^{-40} \text{ kg-m}^2$ ,  $k = 1.38 \times 10^{-23} \text{ J-K}^{-1}$ ,  $h = 6.62 \times 10^{-34} \text{ Js}$  2

3. (a) Mention briefly the postulates of quantum mechanics. 4
- (b) Explain photoelectric effect. Write the Einstein's equation for photoelectric effect, mention the terms involved and give its significance. 2+2+2=6

OR

4. (a) Explain Compton effect and its physical significance. What is Compton shift? 2+1+2=5
- (b) State and explain Planck's radiation law. 3
- (c) An electron is confined in a one-dimensional box of length 1 Å. Calculate its energy in the ground state in electron volts. Given,  $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ . 2
5. (a) What are the characteristics of electromagnetic radiation? Give the regions of electromagnetic radiation for rotational, vibrational and electronic transitions of a molecule. 5

( 3 )

- (b) Discuss rotational and vibrational spectra of diatomic molecules. Give an example of each type.  $2\frac{1}{2}+2\frac{1}{2}=5$

**OR**

6. (a) The pure rotational spectrum for HCl shows a series of lines separated by  $25.5 \text{ cm}^{-1}$ . Calculate the bond length of the molecule. 5
- (b) Give the expressions for vibrational energy of a diatomic molecule assuming it to behave as simple harmonic oscillator. Sketch the vibrational energy levels of this molecule and define zero-point energy.  $2+2+1=5$
7. (a) State Einstein's law of photochemical equivalence. Explain the term 'quantum yield'. 3
- (b) Explain the phenomenon of 'fluorescence'. 2

**OR**

8. (a) State Frank-Condon principle. 2
- (b) Discuss the photochemical decomposition of HI. 3
9. (a) Discuss ion atmosphere, electrophoretic and relaxation effects. 5
- (b) Explain Wien effect. 3

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**OR**

10. (a) Explain the following :  $2+2=4$
- (i) Potentiometric titrations
- (ii) Liquid junction potential
- (b) Derive the expression for  $G$  and  $S$  in terms of cell EMF.  $2+2=4$

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