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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.  $2\frac{1}{2}+2\frac{1}{2}=5$

**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  $H_2$  molecule at 300 K. Given, moment of inertia of  $H_2$  molecule

$$\frac{4}{h} \cdot \frac{6}{6} \cdot \frac{10^{40}}{62} \text{ kg-m}^2, \frac{K}{10^{34}} = \frac{38}{2} \cdot \frac{10^{23}}{Js} \text{ J-K}^{-1},$$

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.  $2+2=6$

**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,  $1 \text{ eV} = 1.602 \cdot 10^{-19} \text{ J}$ .  $2$

5. (a) What are the characteristics of electromagnetic radiation? Give the regions of electromagnetic radiation for rotational, vibrational and electronic transitions of a molecule.  $5$

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- (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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