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The values of the constants: $h = 6.626 \times 10^{-34}$ J s; $c = 2.998 \times 10^8$ m/s; $N = 6.023 \times 10^{23}$ mol^{-1}; 1 cm^{-1} = 11.958J mol^{-1}; $k = 1.381 \times 10^{-23}$ J K^{-1}.

(Group-A)

Q.1. Answer any four from the following $\hspace{2cm}$ **(2.5x4) = 10**

(i) What is Born-Oppenheimer approximation? How does it related to spectroscopy?

(ii) Write a short note on Stark Effect.

(iii) Write down at least three reasons for the broadening of a spectra.

(iv) Express μ_i in terms of p_i in a mixture of ideal gases, μ_i and p_i having their usual significance.

(v) Evaluate the commutator, $[S_z, S_t]$.

(vi) Write the postulates of Statistical thermodynamics.

(vii) Which one of the following molecules are microwave and IR active? Give reasons.
$\hspace{1cm}$ CHCl$_3$, NO$_2$ and 1-4- dichloro benzene

(Group-B)

Q.2. Answer any four question from the following $\hspace{2cm}$ **(5x4) = 20**

(i) How does the food get cooked in a microwave oven? Which factors govern the intensity of spectral line? $\hspace{3cm}$ 2+3

(ii) For a diatomic rigid rotator system find out the rotational quantum number of the most populated rotational state, J_{max}. (Hint: Consider degeneracy). Also show that the wavenumber corresponding to this level is $\bar{v}_{max} \approx 1.18\sqrt{BT}$. $\hspace{2cm}$ (3+2)

(iii) Write down the Lewis-Randall statement of third law of thermodynamics and justify it from the concept of thermodynamic probability. $\hspace{3cm}$ 5

(iv) At 25 °C, the third law entropy of water is about 82 JK^{-1}mo^{l-1} less than that of bromine at the same temperature. What does this signify? $\hspace{3cm}$ 5

(v) A particle of mass 'm' is moving in a symmetrical box of length 'a', and its potential is given by
$\hspace{1cm}$ V = 0 for $\hspace{0.5cm}$ - a/2 $\leq$ x $\leq$ a/2
$\hspace{1.5cm}$ = α $\hspace{0.5cm}$ otherwise
$\hspace{1cm}$ Deduce the expression of its energy and wavefunction. $\hspace{3cm}$ 5

(vi) (a) Why does the allowed values $J= 0$ for the rotational quantum number not violate the Heisenberg's Uncertainty Principle?

(b) The rotational constant of $^1H^{35}Cl$ is 10.5909 cm^{-1}. Calculate the rotational constants of $^1H^{37}Cl$ and $^2H^{37}Cl$. 2+3

(Group-C)

Q.3. Answer any one from the following **(1x10) = 10**

(i) (a) What do you mean by FT spectroscopy? What are the advantages of FT technique? What is R branch and P branch in a spectra of a diatomic vibrating rotator?

2+1+(1+1) = 5

(b) The equilibrium vibration frequency of the I2 molecule is 215 cm^{-1} and the anharmonicity constant x is 0.003; what, at 300 K, is the intensity of the 'hot band' relative to that of the fundamental. 5

(ii). Write down the basic postulates of Bose-Einstein statistics? Derive the expression which represents the probability of finding a boson with energy (E_i). Write the concept of ensembles. (3+5+2) = 10

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