DP VIPRA COLLEGE BILASPUR

Session 2021-22

Department of Chemistry

M. Sc 2nd Semester

SUBJECT– PHYSICAL CHEMISTRY

Topic-Vibrational Partition Function

Partition Function

Introduction :- Statistical Thermodynamics analysis is facilated through the use of the partition function. This great analytical tool i.e the partition function is defined as.

$$Q = \Sigma g t . e^{-\varepsilon t / KT}$$

Definition:- A partition function describes the statistical . properties of the system in thermodynamics equilibrium partition function are function of the thermodynamics state variable . Such as the temperature and volume.

Vibrational partition function :-

Introduction:- The partition function for vibratiobal energy of a diatomic molecules is given by

$fv= \Sigma gv.e^{-\varepsilon v/KT}$

Definition:- The vibrational partition function traditionally refers to the component of the canonical partition resulting from the vibrational degree od freedom of a system.

The partition function for vibrational energy of a diatomic molecules is given by

$$fv = \Sigma gv.e^{-\varepsilon v/KT}$$

As the statistical Weight of each vibrational level is unity we have

$$fv=\Sigma e^{-\varepsilon v/KT} \quad \ldots\ldots\ldots\ldots\ldots \; (1)$$

At the nth quantam level the vibrational energy of a diatomic is given by

$$\varepsilon_v = (n+1/2)\, hv$$

Where v=fundamental frequency of vibration

n= an integer 0,1,2,3.........etc

Therefore from equation 1 we have

$$fv = \sum_{0}^{\infty} e^{-(n+1/2)\, hv/KT}$$

$$= e^{-(1/2)\, hv/KT}\,[1+ e^{-hv/KT} + e^{-2hv/KT} + \ldots\ldots + e^{-ihv/KT} + \ldots\ldots]$$

$$= e^{-(1/2)h\nu/KT}[1-e^{-h\nu/KT}]^{-1}$$

[As $(1-e^{-x})-1 = 1+ e^{-x} + e^{-2x} + e^{-3x} + ...+e^{-ix} +........$]

The quantity hv/KT is very small and as a first approximation

$$f\nu=(1-e^{-h\nu/KT})^{-1}$$

The value of v is equal to cω . Where c is the velocity of light and ω cm^{-1} is the vibration frequency in were number of the given oscillator. Hence

$$f\nu= (1-e^{-he\omega/KT})^{-1}$$

$$=(1-e^{1.439\omega/T})^{-1}$$

As heω/KT = 1.439ω/T