VIBRATIONAL PARTITION FUNCTION

Molecules and atoms occupy a definite place, but they are not static and are vibrating about their mean positions because of intermolecular forces. To include this the diatomic

molecule must be a pair of mass points connected together by a stiff spring. The molecules can be considered simple harmonic oscillator.

Classically harmonic oscillator has continuous energy but quantum mechanically it has discrete energy levels. By Schrodinger wave equation the energy eigen value for a harmonic oscillator is given by

En = (n+1/2) hע

where En is the energy of nth state of the harmonic oscillator. E = (1/2) hע is the energy of ground state of harmonic oscillator. Now vibrational partition function is given by

$$q(v) = \sum e^{-En/kT}$$

$$q(v) = \sum e^{-(n+1/2)\, h\nu/kT}$$

$$= \sum e^{-nh\nu/kT} \sum e^{-h\nu/2kT}$$

$$= e^{h\,\nu/2kT} [\, 1 + e^{-h\nu/kT} + e^{-2h\nu/kT}$$

$$= e^{-h\nu\,/2kT} \;/\; 1 - e^{-h\nu\,/kT}$$

Now, $Q = [q(v)]^{3N}$

Energy E is given by $kT^2\, [\delta(\ln Q)/\delta T]$

and $Cv = (\delta E/\delta T)_v$

$$E = 3Nh\nu/2 + 3Nh\nu/e^{h\nu/kT} - 1$$

and $$C_v = 3Nk(h\nu/kT)^2\ e^{h\nu/kT}/[e^{h\nu/kT} - 1]^2$$

Here $\Theta_v = h\nu/k$ is called the vibrational characteristic temperature.

At high temperatures $T >>> \Theta_v$ and hence

$$C_v = 3Nk$$

At low temperatures $T <<<< \Theta_v$ and hence

$$C_v = 3Nk\ [\Theta_v / T]^2\ e^{-\Theta_v/T}$$