ε = epsilon =
g_i = degree of degeneracy
Statistical weight
factor -

number of molecules in zero energy level. Therefore, the partition function is larger at higher temperature.

Factorization of Partition Function

Partition function is defined as

$$Q = \Sigma\, g_i\, e^{-\epsilon_i/kT} \qquad \dots (4.28)$$

The energy ϵ of a molecule is the sum of contribution from the different modes of motion like translational, rotational, vibrational, electronic, etc. If we assume that energy associated with any one mode of behaviour is independent of all other modes, then we can define energy by

$$E = E_T + E_r + E_v + E_c$$

and $g_i = g_T + g_r + g_v + g_c$

where E_T, E_r, E_v and E_c are translation, rotational, vibrational and electronic contribution, respectively and g_T, g_r, g_v and g_c are degeneracy of translational, vibrational, rotational and electronic energy level, respectively. So equation (4.28) can be written as

$$Q = \Sigma(g_T\, g_r\, g_v\, g_c)\, e^{-(\epsilon_t+\epsilon_r+\epsilon_v+\epsilon_c)/kT}$$

or $$Q = \Sigma\, g_T\, e^{-\epsilon_t/kT} \times \Sigma\, g_r\, e^{-\epsilon_r/kT} \times \Sigma\, g_v\, e^{-\epsilon_v/kT} \times \Sigma g_c\, e^{-\epsilon_c/kT}$$

or $$Q = Q_T \cdot Q_r \cdot Q_v \cdot Q_c \qquad \dots (4.29)$$

Equation (4.29) is known as *multiplication theorem* or *factorization of partition function*. This factorization means that we can investigate each contribution separately. From equation (4.29), it follows that the net partition function is equal to be the product of the separate partition functions in respect of different types of energy independently associated with molecules.

4.7 TRANSLATIONAL PARTITION FUNCTION

By definition partition function is given by,

$$Q = \Sigma\, g_i\, e^{-\epsilon_i/kT}$$

For translational energy, as the translational energy levels are non-degenerate, e.g., $g_i = 1$, tranalational partition function can be written as

$$Q_t = \Sigma\, e^{-\epsilon_t/kT} \qquad \dots (4.30)$$

The Schrodinger wave equation when solved for the particle moving in a rectangular box of dimension a, b, and c gives the expression for translational energy as

$$E_t = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \qquad \dots (4.31)$$

where n_x, n_y and n_z are principal quantum numbers determining the possible value of translational energy of particle along x, y and z directions, respectively.

From equations (4.30) and (4.31) we can write

$$Q_t = \Sigma\, e^{-n_x^2\, h^2/8ma^2kT} \cdot e^{-n_y^2\, h^2/8mb^2kT} \cdot e^{-n_z^2\, h^2/8mc^2kT}$$

$$Q_t = Q_x \cdot Q_y \cdot Q_z$$

...... (4.32)

If we consider the motion in x-axis only, then corresponding partition function (Q_x) can be written as

$$Q_x = \Sigma\, e^{-n_x^2\, h^2/8ma^2kT}$$

...... (4.33)

From equation (4.33), the Q_x can be evaluated. The increment of energy between adjacent energy levels of translation is so small that the translational partition function can be evaluated by integration over all quantum states (from 0 to ∞). In other words, the translational energy levels are so closely spaced that the variation of energy may be taken to be continuous and the summation in equation (4.33) is replaced by integration.

Hence

$$Q_x = \int_0^{\infty} e^{-n_x^2\, h^2/8ma^2kT}$$

...... (4.34)

Putting $l = \dfrac{h^2}{8ma^2kT}$

$$Q_x = \int_0^{\alpha} e^{-ln_x^2} \cdot dn_x$$

...... (4.35)

Using standard integrals

$$\int_0^{\alpha} e^{-lx^2} \cdot dx = \frac{1}{2}\sqrt{\frac{\pi}{l}}$$

Equation (4.35) reduces to

$$Q_x = \frac{1}{2}\pi^{1/2}\left(\frac{8ma^2kT}{h^2}\right)^{1/2} \qquad \therefore \sqrt{8} = 2\sqrt{2}$$

$$Q_x = (2\pi m\, kT)^{1/2} \cdot \frac{a}{h}$$

...... (4.36)

Similarly, for motion along y and z directions, we have

$$Q_y = (2\pi\, mkT)^{1/2} \cdot \frac{b}{h}$$

...... (4.37)

$$Q_z = (2\pi\, mkT)^{1/2} \cdot \frac{c}{h}$$

...... (4.38)

Substituting the value of Q_x, Q_y and Q_z into equation (4.32), we can write

$$Q_t = Q_x \cdot Q_y \cdot Q_z = \frac{(2\pi \, mkT)^{3/2}}{h^3} \cdot abc$$

$$Q_t = \frac{(2\pi \, mkT)^{3/2}}{h^3} \cdot V \qquad\qquad \text{...... (4.39)}$$

or $\quad Q_t = \left(\frac{2\pi \, mkT}{h^2} \right)^{3/2} \cdot V \qquad\qquad \text{...... (4.40)}$

where V is the volume of the container. Equations (4.39) and (4.40) give the expression for the translational partition function of a single molecule.

Example 4.3

Calculate the translational partition function of H_2 confined to a 100 cm^3 vessel at 298 K.

Solution

$$\text{Mass of } H_2 \text{ molecule} = \frac{2.016 \times 10^{-3} \text{ kg}}{6.02 \times 10^{23}} = 3.348 \times 10^{-27} \text{ kg}$$

$$V = 100 \text{ cm}^3 = 10^{-4} \text{ m}^3$$

$$k = 1.381 \times 10^{-27} \text{ JK}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$Q_t = \left(\frac{2\pi \, mkT}{h^2} \right)^{3/2} \cdot V$$

$$Q_L = \left(\frac{2 \times 3.14 \times (3.348 \times 10^{-27}) \times (1.381 \times 10^{-23}) \times 298}{(6.626 \times 10^{-34})^2} \right)^{3/2} \times 10^{-4}$$

$$Q_t = (1.97 \times 10^{20})^{3/2} \times 10^{-4}$$

$$Q_t = 2.769 \times 10^{26}$$

Thus about 10^{26} quantum states or levels are thermally accessible even at room temperature for H_2 molecule.

4.8 ROTATIONAL PARTITION FUNCTION

From quantum mechanical principles, the rotational energy for a diatomic molecule in the Jth state is given by

$$E_r = J(J + 1) \frac{h^2}{8\pi^2 I} \qquad\qquad \text{...... (4.41)}$$

where I is the moment of inertia of the diatomic molecule and J is the rotational quantum number, $J = 0, 1, 2, 3.....$. As we know that the rotational energy at the Jth level is degenerate in $(2J + 1)$ ways, the value of statistical weight is given by

$$g_r = (2J + 1)$$

The expression for rotational partition function for a single molecule is

$$Q_r = \Sigma\, g_r\, e^{-\epsilon_r/kT}$$

$$Q_r = \Sigma(2J + 1)\, e^{-J(J+1)h^2/8\pi^2 IkT}$$

.... (4.42)

Rotational energy levels are sufficiently closely spaced, i.e., variation in energy between two adjacent rotational energy levels can be taken as continuous. Hence, it is possible to replace summation in quantum (4.42) by integration from $J = 0$ to $J = \infty$, giving

$$Q_r = \int_0^\infty (2J + 1)\cdot e^{-J(J+1)h^2/8\pi^2 IkT}\cdot dJ$$

.... (4.43)

or $$Q_r = \int_0^\infty (2J + 1)\, e^{-J(J+1)\alpha}\cdot dJ$$

.... (4.44)

where $$\alpha = \frac{h^2}{8\pi^2 IkT}$$

Again put $Z = J(J + 1)$

$\therefore$ $$dZ = (2J + 1)\, dJ$$

.... (4.45)

Combining equation (4.44) and (4.45)

$$Q_r = \int_0^\infty e^{-z\alpha}\, dz = \frac{1}{\alpha}$$

.... (4.46)

Putting value of α into equation (4.46) we get

$$Q_r = \frac{8\pi^2 IkT}{h^2}$$

.... (4.47)

The equation (4.47) is only true far heteronuclear diatomic molecules like NO, HCl etc. But in case of homonuclear linear molecules like O_2, N_2 and also $O=C=O$, $H-C\equiv C-H$, only one half of the rotational terms will be present. This effect reduces Q_r to one half of the value in equation (4.47). In order to avoid these complications, a symmetry number (σ) is introduced. It is the number of rotational equivalent (or indistinguishable) molecular orientations. Thus the rotational partition function for any linear molecule, becomes

$$Q_r = \frac{8\pi^2 IkT}{\sigma h^2}$$

.... (4.48)

This is general equation for rotational partition function of a linear (homonuclear or heteronuclear) diatomic molecule. The value of σ for homo nuclear (or symmetrical) linear molecule is 2 because end to end rotation yields an equivalent orientation. On the other hand, the value of σ for heteronuclear (or unsymmetrical) linear molecule such as $O=C=O$, $O=C=S$ etc. is 1.

Example 4.4

Calculate the rotational partition function for H_2 at 300 K. Moment of inertia for H_2 is 4.59×10^{-47} kg $\cdot$ m^2, symmetry number σ = 2.

Solution

$$Q_r = \frac{8\pi^2 IkT}{\sigma h^2}$$

$$Q_r = \frac{8 \times (3.1416)^2 \times 4.59 \times 10^{-47} \times 1.38 \times 10^{-23} \times 300}{2 \times (6.62 \times 10^{-34})}$$

$$= 1.71$$

4.9 VIBRATIONAL PARTITION FUNCTION

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

$$Q_v = \Sigma\, g_v\, e^{-\epsilon_v/kT} \qquad\qquad \text{...... (4.49)}$$

As the statistical weight of each vibrational level is unity, equation (4.49) becomes

$$Q_v = \Sigma\, e^{-\epsilon_v/kT} \qquad\qquad \text{...... (4.50)}$$

According to wave mechanics, the vibrational energy of an harmonic oscillator is given by

$$\epsilon_v = \left(v + \frac{1}{2}\right) h\upsilon \qquad\qquad \text{...... (4.51)}$$

where υ is the fundamental frequency of oscillation and v is the vibrational quantum number having value 0, 1, 2, 3, ... In the expression for partition function, ϵ_v refers to the energy of vibrational state in excess to the ground state energy. For the present case the lowest or ground state energy corresponds to v = 0 and is given as

$$\epsilon_{v=0} = \frac{1}{2} h\upsilon \qquad\qquad \text{...... (4.52)}$$

Therefore, the expression for energy appearing in the partition function is

$$\epsilon_v = \left(v + \frac{1}{2}\right) h\upsilon - \frac{1}{2} h\upsilon = vh\upsilon \qquad\qquad \text{...... (4.53)}$$

$$Q_v = \Sigma\, e^{-vh\upsilon/kT}$$

Putting $x = h\upsilon/kT$

$$Q_v = \Sigma e^{-vx}$$

...... (4.54)

Vibrational energy levels are not closely speed, so summation is not replaced by integration. Since v can take values from 0, 1, 2, 3, ..., so

$$Q_v = 1^0 + e^{-x} + e^{-2x} + ...$$

$$Q_v = 1 + e^{-x} + e^{-2x} + ...$$

$$Q_v = 1 + (e^{-x})^1 + (e^{-x})^2 + ...$$

This series can be recognized as the geometrical series of common ratio $r = e^{-x}$. Thus we have

$$Q_v = \frac{1}{1 - e^{-x}} = \frac{1}{1 - e^{-h\upsilon/kT}}$$

or $\qquad Q_v = (1 - e^{-h\upsilon/kT})^{-1}$

...... (4.55)

For most diatomic molecules, at ordinary temperatures, the value of Q_v is nearly unity, because hv is appreciably. greater than kT.

4.10 ELECTRONIC PARTITION FUNCTION

Many monatomic substances as well as a few polyatomic molecules, possess multiple electronic ground state. In most of these cases in their normal state, there are two or more different electronic levels where energies are so closed that they may be assigned a single energy level with a statistical weight factor greater than unity. In addition to such levels, there may be excited electrons states whose energies may be much greater than that of the ground state. As we increase the temperature, such excited states become more and more occupied. In such cases the electronic partition function is greater than unity and various with the temperature. The electronic partition function is given by

$$Q_e = \Sigma g_e \, e^{-\epsilon_e/kT}$$

...... (4.56)

where g_e is the statistical weight factor of each electronic level, normal or excited and is equal to $(2J + 1)$, where J is the total angular momentum number in the given state and ϵ_c is the energy in the electronic state, in excess of the lowest state. Thus,

$$Q_e = \Sigma(2J + 1) \, e^{-\epsilon_e/kT}$$

...... (4.57)

In the general state, the energy is zero, i.e., $\epsilon_c = 0$, thus equation (4.57) becomes

$$Q_e = \Sigma(2J + 1)e^0 = \Sigma 2J + 1$$

...... (4.58)

From equation (4.58), it follows that contribution of this state to the electronic partition function is thus $(2J + 1)$. Th degeneracy of electronic ground state of atoms is given in Table 4.1.

Table 4.1 Ground State Electronic Degeneracy

Atom	H	He	Na	Ca
Term/Symbol	$^2S_{1/2}$	$^1S_0$	$^2S_{1/2}$	$^1S_0$
$g_0 = 2J + 1$	2	1	2	1

The term symbol $^{2s+1}L_J$ is a short hand notation for all angular momenta of an atom, viz., the spin angular momentum S, the orbital angular momentum L, and the total angular momentum J. Mathematically

$$S = \Sigma S_i; \ L = \Sigma L_i \text{ and } J = L + S \text{ (for atoms with } Z \le 30)$$

where S_i and L_i are the spins and the orbital angular momenta of individual electrons in the atom respectively. The ground state of electronic states of free atoms are generally degenerate-for hydrogen atom with electronic configuration $_1S^1$, spin S = 1/2 and L = 0 so J = L + S = 1/2 and $g_0 = 2 \times 1/2 + 1 = 2$. For helium atom with electronic configuration $_1S^2$, spin S = 1/2 - 1/2 = 0 and L = 0, so J = 0 and hence $g_0 = 1$. Thus for H-atom, $Q_e = 0$ and for He atom $Q_e = 1$.