

# Chapter 3 Ensemble and Molecular Partition Functions

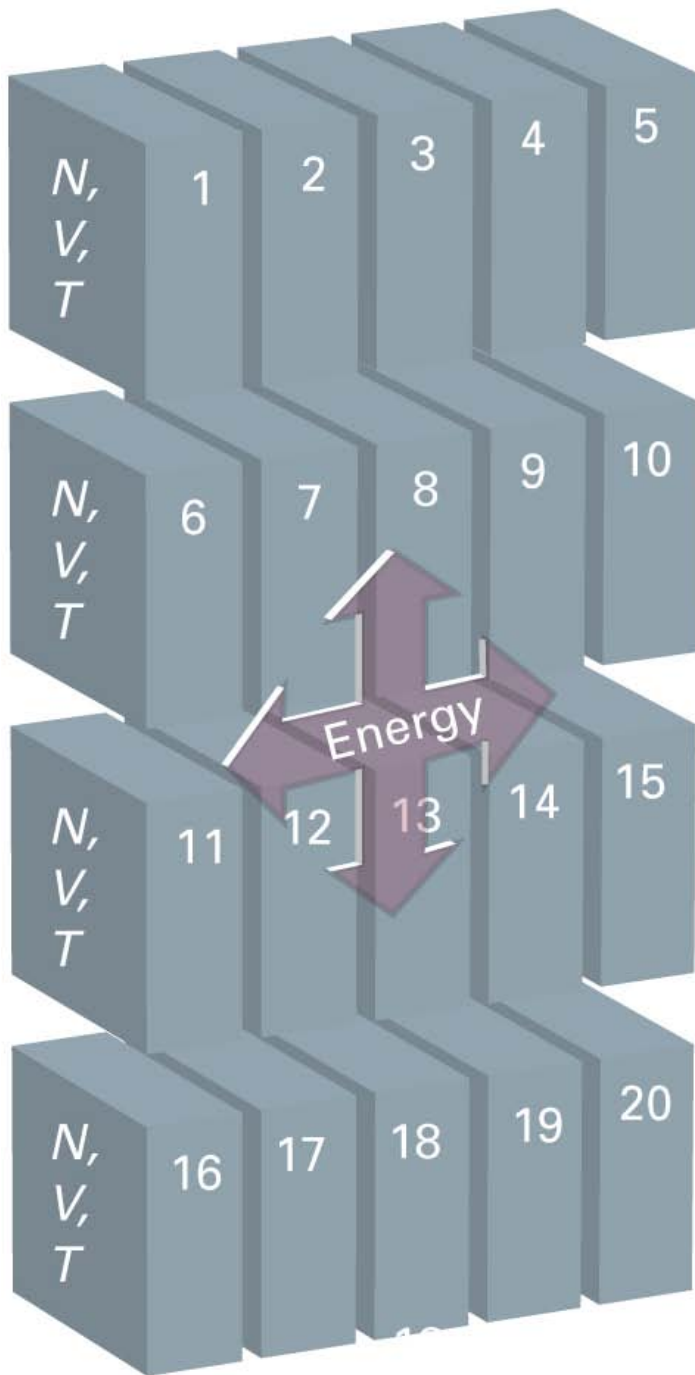
## The Canonical Ensemble

The average value of a property of the ensemble corresponds to the time-averaged value for the corresponding macroscopic property of the system.

The volume  $V$ , temperature  $T$ , and the number of particles in each system  $N$  are constant. An ensemble in which  $V$ ,  $T$ , and  $N$  are constant is referred to as a **canonical ensemble**.

$$E = \sum_i A_i E_i$$

where  $A_i$  is the occupation numbers corresponding to the number of ensemble members having energy  $E_i$ .



**Figure 1**

A representation of the canonical ensemble, in this case for  $N=20$ . The individual replications of the actual system all have the same composition and volume. They are all mutual thermal contact, and so all have the same temperature. Energy may be transferred between them as heat, and so they do not all have the same energy. The total energy  $E$  of all 20 replications is a constant because the ensemble is isolated overall.

$$W = \frac{N!}{\prod_i A_i!}$$

where  $N$  is the total number of ensemble members.

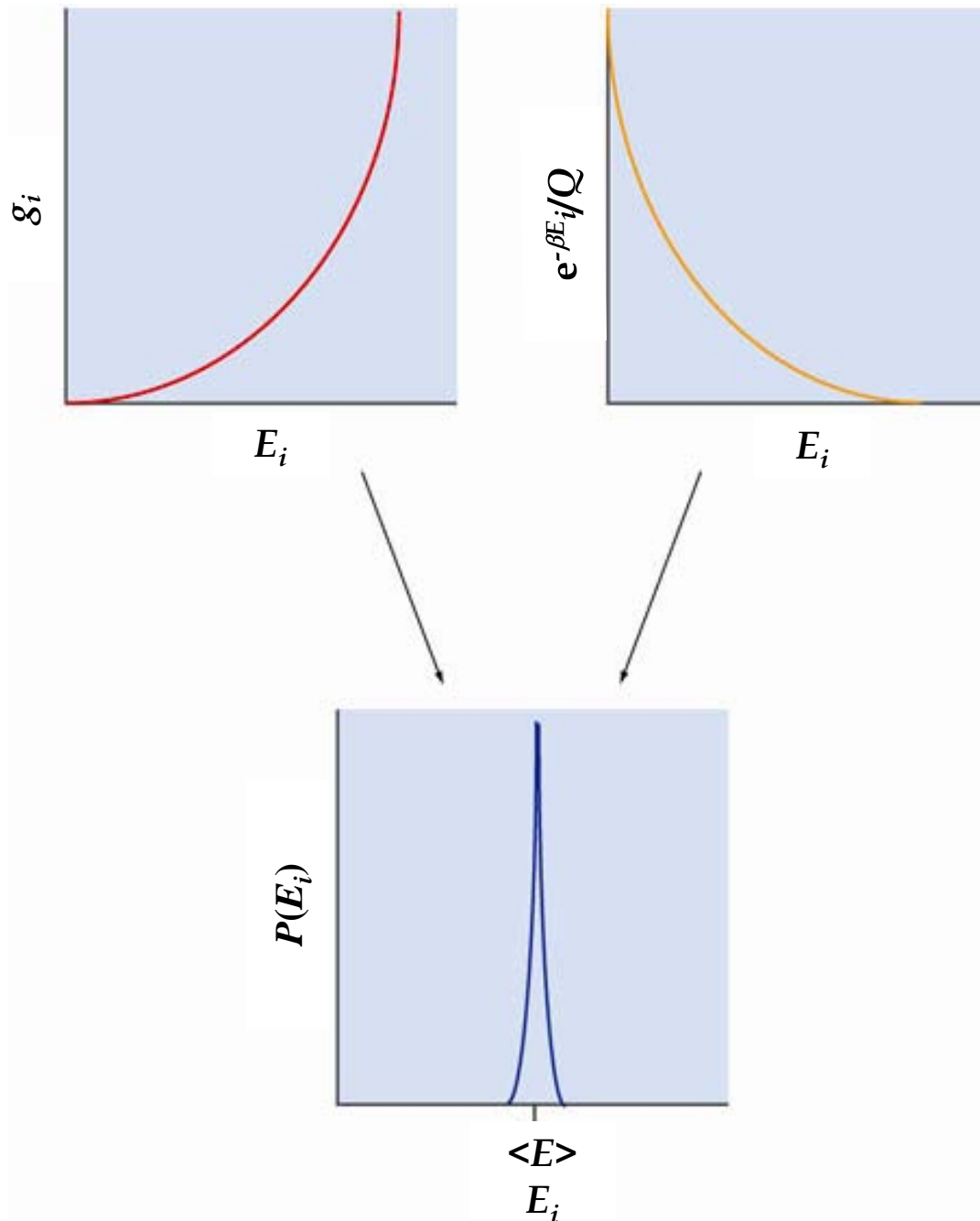
$$P(E_i) = \frac{g_i e^{-\beta E_i}}{Q}$$

where  $g_i$  is the number of states (the density of states) present at a given energy  $E_i$ .

The quantity  $Q$  is referred to as the **canonical partition function** and defined as follows:

$$Q = \sum_i e^{-\beta E_i}$$

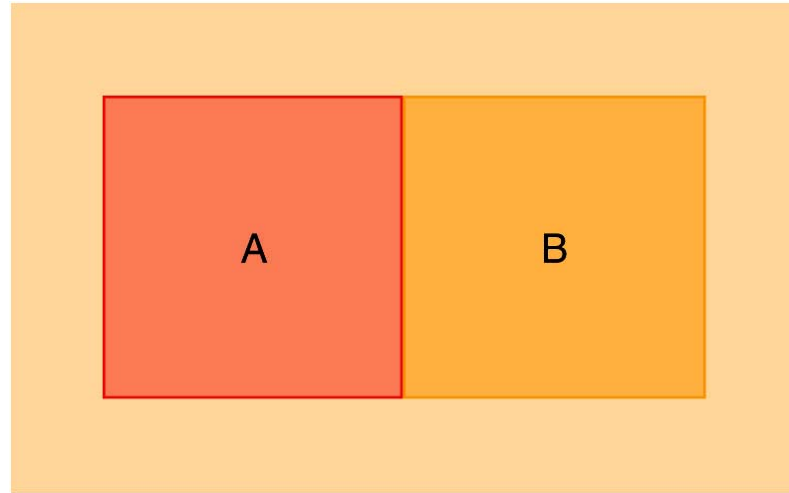
The value of  $g_i$  increases with  $E_i$  while the Boltzmann term  $e^{-\beta E_i}/Q$  decreases exponentially with  $E_i$ . The product of these terms reaches a maximum corresponding to the average ensemble energy.



**Figure 2.** For the canonical ensemble, the probability of a member of the ensemble having a given energy is dependent on the product of  $g_i$ , the number of states present at a given energy, and the Boltzmann distribution function for the ensemble. The product of these two factors results in a probability distribution that is peaked about the average energy,  $\langle E \rangle$ .

# Relating $Q$ to $q$ for an Ideal Gas

Assume that a system consists of independent ideal particles.  
Consider an ensemble made of two distinguishable units, A and B.



**Figure 3.** A two-unit ensemble. In this ensemble, the two units, A and B are distinguishable.

$$Q = \sum_n e^{-\beta E_n} = \sum_n e^{-\beta(\varepsilon_{A_n} + \varepsilon_{B_n})}$$

where  $\varepsilon_{A_n}$  and  $\varepsilon_{B_n}$  refer to the energy levels associated with unit A and B, respectively.

$$\begin{aligned}
Q &= \sum_n e^{-\beta(\varepsilon_{A_n} + \varepsilon_{B_n})} = e^{-\beta(\varepsilon_{A_0} + \varepsilon_{B_0})} + e^{-\beta(\varepsilon_{A_0} + \varepsilon_{B_1})} + e^{-\beta(\varepsilon_{A_0} + \varepsilon_{B_2})} + \dots \\
&\quad + e^{-\beta(\varepsilon_{A_1} + \varepsilon_{B_0})} + e^{-\beta(\varepsilon_{A_1} + \varepsilon_{B_1})} + e^{-\beta(\varepsilon_{A_1} + \varepsilon_{B_2})} + \dots \\
&\quad + e^{-\beta(\varepsilon_{A_2} + \varepsilon_{B_0})} + e^{-\beta(\varepsilon_{A_2} + \varepsilon_{B_1})} + e^{-\beta(\varepsilon_{A_2} + \varepsilon_{B_2})} + \dots \\
&= \left( e^{-\beta\varepsilon_{A_0}} + e^{-\beta\varepsilon_{A_1}} + e^{-\beta\varepsilon_{A_2}} + \dots \right) \left( e^{-\beta\varepsilon_{B_0}} + e^{-\beta\varepsilon_{B_1}} + e^{-\beta\varepsilon_{B_2}} + \dots \right) \\
&= (q_A)(q_B) \\
&= q^2
\end{aligned}$$

For a system with  $N$  distinguishable units,

$$Q = q^N$$

$q$ : molecular partition function

Consider three distinguishable oscillators (A, B, and C) with three total quanta of energy. The dominant configuration of energy was with the oscillators in three separate energy states, denoted “2,1,0”. The energy states relative to the oscillators can be arranged in six different ways:

<u>A</u>	<u>B</u>	<u>C</u>
2	1	0
2	0	1
1	2	0
0	2	1
1	0	2
0	1	2

For a system with  $N$  indistinguishable units,

$$\therefore Q = \frac{q^N}{N!}$$

# Molecular Energy Levels

For polyatomic molecules, there are four energetic degrees of freedom to consider in constructing the molecular partition function:

1. Translation
2. Rotation
3. Vibration
4. Electronic

Assume that the energetic degrees of freedom are not coupled.

$$\varepsilon_{total} = \varepsilon_t + \varepsilon_r + \varepsilon_v + \varepsilon_e$$

$$\begin{aligned} q_{total} &= \sum g_{total} e^{-\beta\varepsilon_{total}} = \sum (g_t g_r g_v g_e) e^{-\beta(\varepsilon_t + \varepsilon_r + \varepsilon_v + \varepsilon_e)} \\ &= \sum (g_t e^{-\beta\varepsilon_t}) (g_r e^{-\beta\varepsilon_r}) (g_v e^{-\beta\varepsilon_v}) (g_e e^{-\beta\varepsilon_e}) = q_t q_r q_v q_e \end{aligned}$$

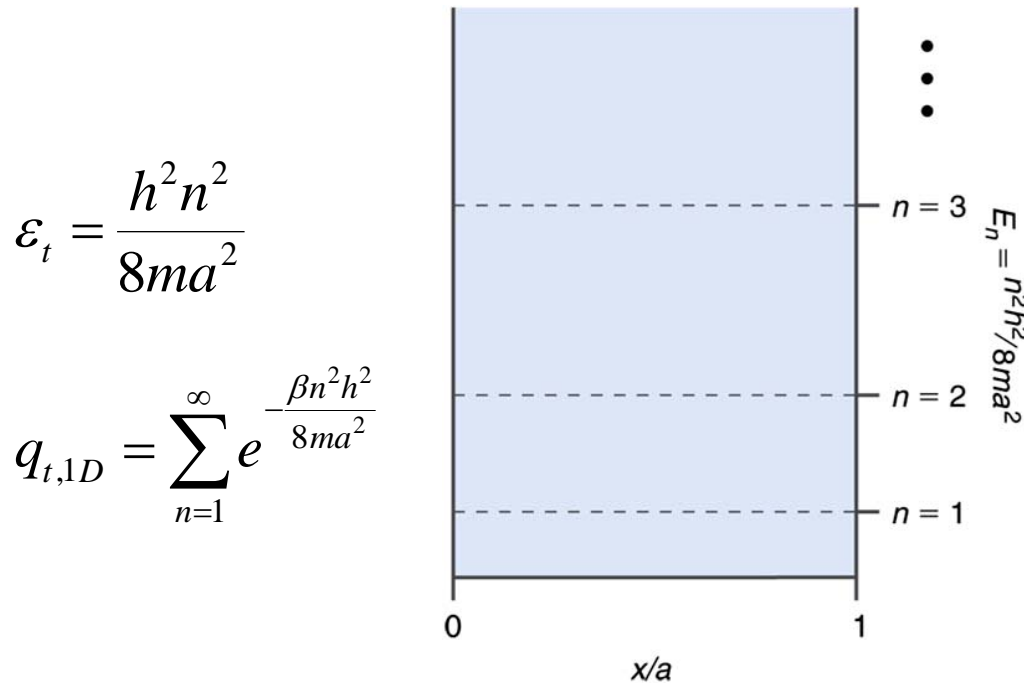
$$Q_{total} = q_{total}^N \quad \text{for distinguishable particles}$$

$$Q_{total} = \frac{q_{total}^N}{N!} \quad \text{for indistinguishable particles}$$



# Translational Partition Function

For one-dimensional “particle-in-a-box”, quantum mechanics shows



**Figure 4.** Particle-in-a-box model for translational energy levels.

Since the energy difference between energy levels is very small as compared to  $kT$ ,

$$q_t = \sum e^{-\beta \alpha n^2} \cong \int_0^{\infty} e^{-\beta \alpha n^2} dn = \frac{1}{2} \sqrt{\frac{\pi}{\beta \alpha}}$$

where  $\alpha = \frac{h^2}{8ma^2}$ .

$$q_{t,1D} = \left( \frac{2\pi m}{h^2 \beta} \right)^{\frac{1}{2}} a$$

$$\Lambda = \left( \frac{h^2 \beta}{2\pi m} \right)^{\frac{1}{2}} : \text{thermal de Broglie wavelength}$$

thermal wavelength

$$q_{t,1D} = \frac{a}{\Lambda} = (2\pi mkT)^{\frac{1}{2}} \frac{a}{h}$$

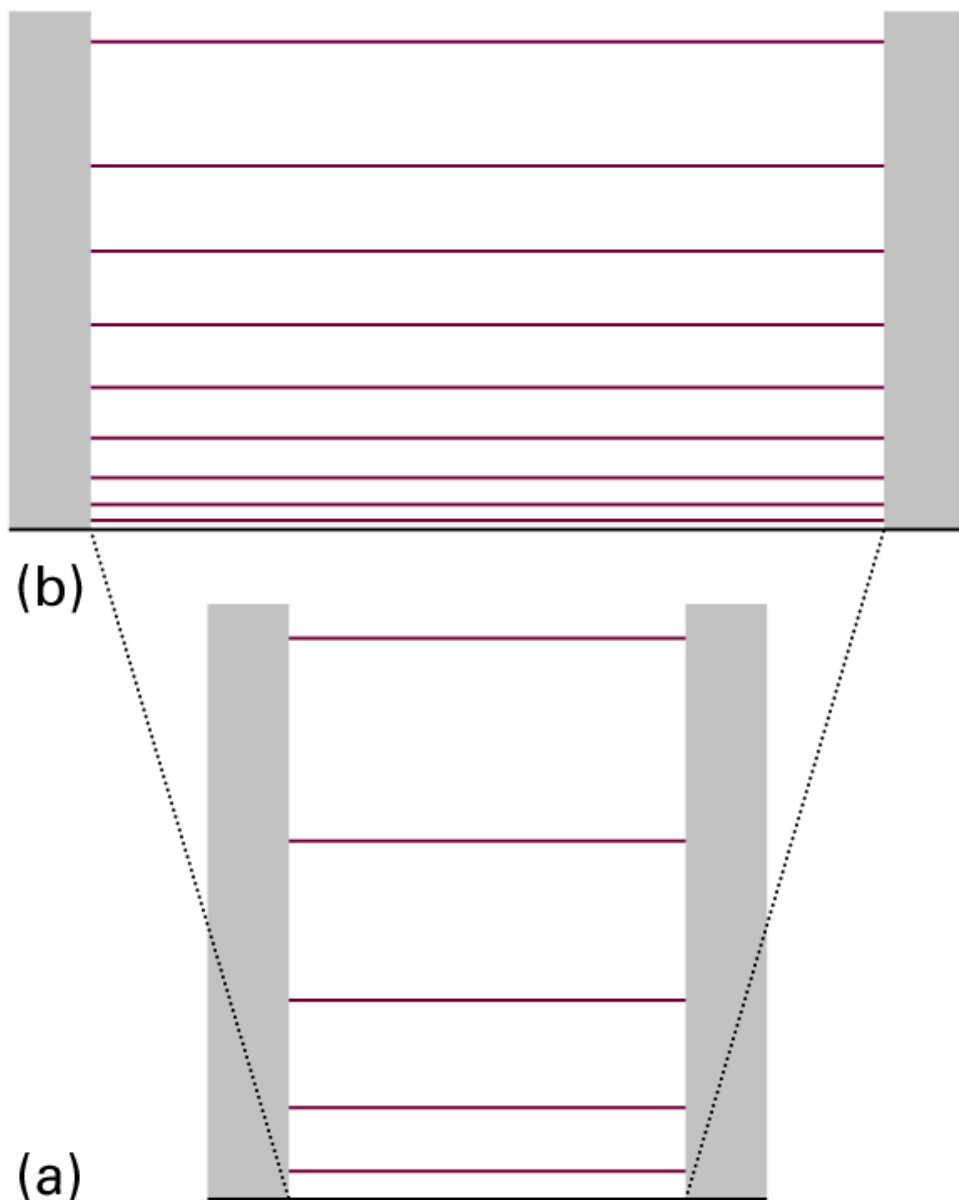
$$\Lambda = \left( \frac{h^2}{2\pi mkT} \right)^{\frac{1}{2}} = \frac{1}{\sqrt{2\pi}} \frac{h}{\sqrt{mkT}} = \frac{1}{\sqrt{2\pi}} \frac{h}{p}$$

$p = \sqrt{mkT}$ : the average momentum of a gas particle

For a three dimensional box,

$$\begin{aligned}q_{t,3D} &= q_{t_x} q_{t_y} q_{t_z} \\&= \left(\frac{a_x}{\Lambda}\right) \left(\frac{a_y}{\Lambda}\right) \left(\frac{a_z}{\Lambda}\right) \\&= \left(\frac{1}{\Lambda}\right)^3 a_x a_y a_z \\&= \left(\frac{1}{\Lambda}\right)^3 V \\&= \frac{V}{\Lambda^3} = (2\pi mkT)^{\frac{3}{2}} \frac{V}{h^3}\end{aligned}$$

The increase in  $q_t$  with volume reflects the fact that as volume is increased, the translational energy level spacings decrease such that more states are available for population at a given  $T$ .



**Figure 4-1**

As the width of a container is increased, the energy levels become closer together, and as a result more are thermally accessible at a given temperature.

Example:

Ar in 1 L at 298 K.  $q_t=?$

# Rotational Partition Function

A diatomic molecule consists of two atoms joined by a chemical bond.

The rigid-rotor approximation:

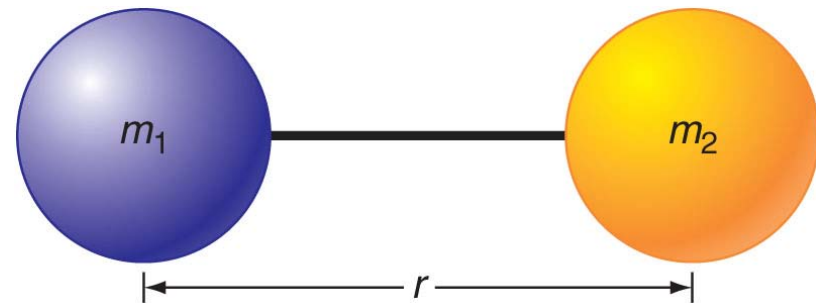
$$\varepsilon_r = hcBJ(J + 1) \quad J = 0, 1, 2, \dots$$

$J$ : quantum number

$$B = \frac{h}{8\pi^2 cI} \quad \text{: the rotational constant}$$

$$I = \mu r^2 \quad \text{: the moment of inertia}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{: the reduced mass}$$



**Figure 5.** Schematic representation of a diatomic molecule, consisting of two masses ( $m_1$  and  $m_2$ ) joined by a chemical bond with the separation of atomic centers equal to the bond length,  $r$ .

$$q_r = \sum_J g_J e^{-\beta hc B J(J+1)}$$

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

$$\therefore q_r = \sum_J (2J + 1) e^{-\beta hc B J(J+1)}$$

Assuming that the rotational energy level spacings are small relative to  $kT$ ,

$$q_r = \int_0^{\infty} (2J + 1) e^{-\beta hc B J(J+1)} dJ$$

$$\frac{d}{dJ} e^{-\beta hc B J(J+1)} = -\beta hc B (2J + 1) e^{-\beta hc B J(J+1)}$$

$$\therefore q_r = \int_0^{\infty} (2J + 1) e^{-\beta hc B J(J+1)} dJ = \int_0^{\infty} \frac{-1}{\beta hc B} \frac{d}{dJ} e^{-\beta hc B J(J+1)} dJ$$

$$= \frac{-1}{\beta hc B} e^{-\beta hc B J(J+1)} \Bigg|_0^{\infty} = \frac{1}{\beta hc B} = \frac{kT}{hc B}$$

# The Symmetry Number

To correct the rotational partition function for overcounting, we can simply divide the expression for the rotational partition function by the number of equivalent rotational configurations.

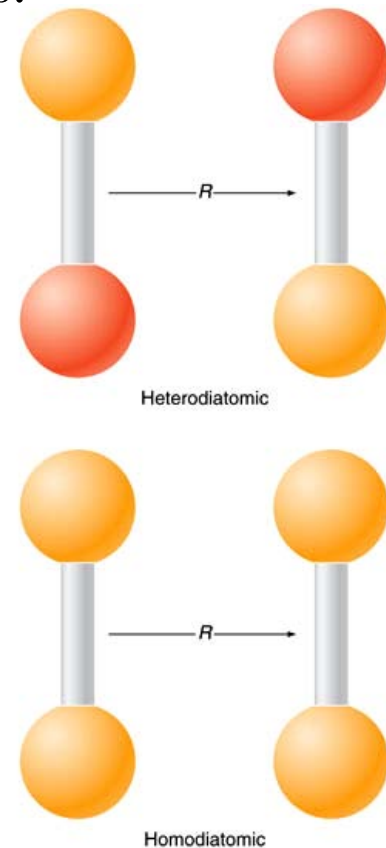
$$q_r = \frac{kT}{\sigma hcB} \quad \sigma = \text{symmetry number}$$

For  $\text{H}_2$ ,  $\text{Cl}_2$ ,  $\sigma = 2$

For  $\text{NH}_3$ ,  $\sigma = 3$

Example:

What is the symmetry number of  $\text{CH}_4$ ?



**Figure 6.** A  $180^\circ$  rotation of hetero-diatomic and homo-diatomic molecules.



# Rotational Level Populations and Spectroscopy

The probability of occupying a given rotational energy level,  $P_J$ , is given by

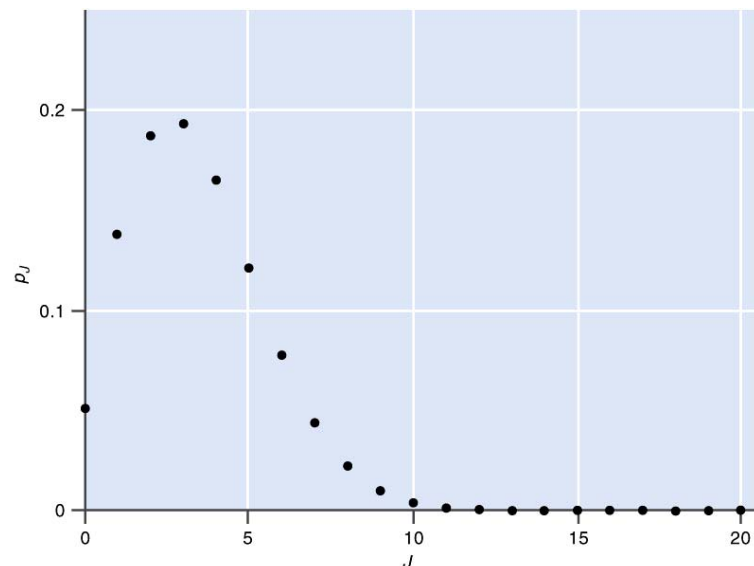
$$P_J = \frac{g_J e^{-\beta hc B J(J+1)}}{q_r} = \frac{(2J+1) e^{-\beta hc B J(J+1)}}{q_r}$$

e.g.  $\text{H}^{35}\text{Cl}$ ,  $B=10.595 \text{ cm}^{-1}$ , 300 K

$$q_r = \frac{kT}{\sigma hc B} = \frac{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{(1)(6.626 \times 10^{-34} \text{ Js})(3.00 \times 10^{10} \text{ cm/s})(10.595 \text{ cm}^{-1})}$$
$$= 19.7$$

With  $q_r = 19.7$ , we can calculate  $P_J$ .

**Figure 7.** Probability of occupying a rotational energy level,  $P_J$ , as a function of rotational quantum number  $J$  for  $\text{H}^{35}\text{Cl}$  at 300 K.



## Example:

In a rotational spectrum of HBr ( $B=8.46 \text{ cm}^{-1}$ ), the maximum intensity is observed for the  $J = 4$  to  $5$  transition. At what temperature was the spectrum obtained?

To find the maximum of the function,

$$\frac{da_J}{dJ} = 0 = \frac{d}{dJ} N \beta h c B (2J + 1) e^{-\beta h c B J (J+1)}$$

$$0 = \frac{d}{dJ} (2J + 1) e^{-\beta h c B J (J+1)}$$

$$\begin{aligned} 0 &= 2e^{-\beta h c B J (J+1)} - \beta h c B (2J + 1)^2 e^{-\beta h c B J (J+1)} \\ &= 2 - \beta h c B (2J + 1)^2 \end{aligned}$$

$$\therefore 2 = \beta h c B (2J + 1)^2 = \frac{h c B}{k T} (2J + 1)^2$$

Substitution of  $J=4$  into the above equation results in the following temperature at which the spectrum was obtained:

$$\begin{aligned} \therefore T &= \frac{(2J + 1)^2 h c B}{2k} = \frac{(2 \times 4 + 1)^2 (6.626 \times 10^{-34} \text{ Js})(3.00 \times 10^{10} \text{ cm/s})(8.46 \text{ cm}^{-1})}{2(1.38 \times 10^{-23} \text{ J/K})} \\ &= 494 \text{ K} \end{aligned}$$

# The Rotational Temperature

Whether the rotational partition function should be evaluated by direct summation or integration is entirely dependent on the size of the rotational energy spacings relative to the amount of thermal energy available ( $kT$ ). Define **the rotational temperature**  $\theta_r$  as

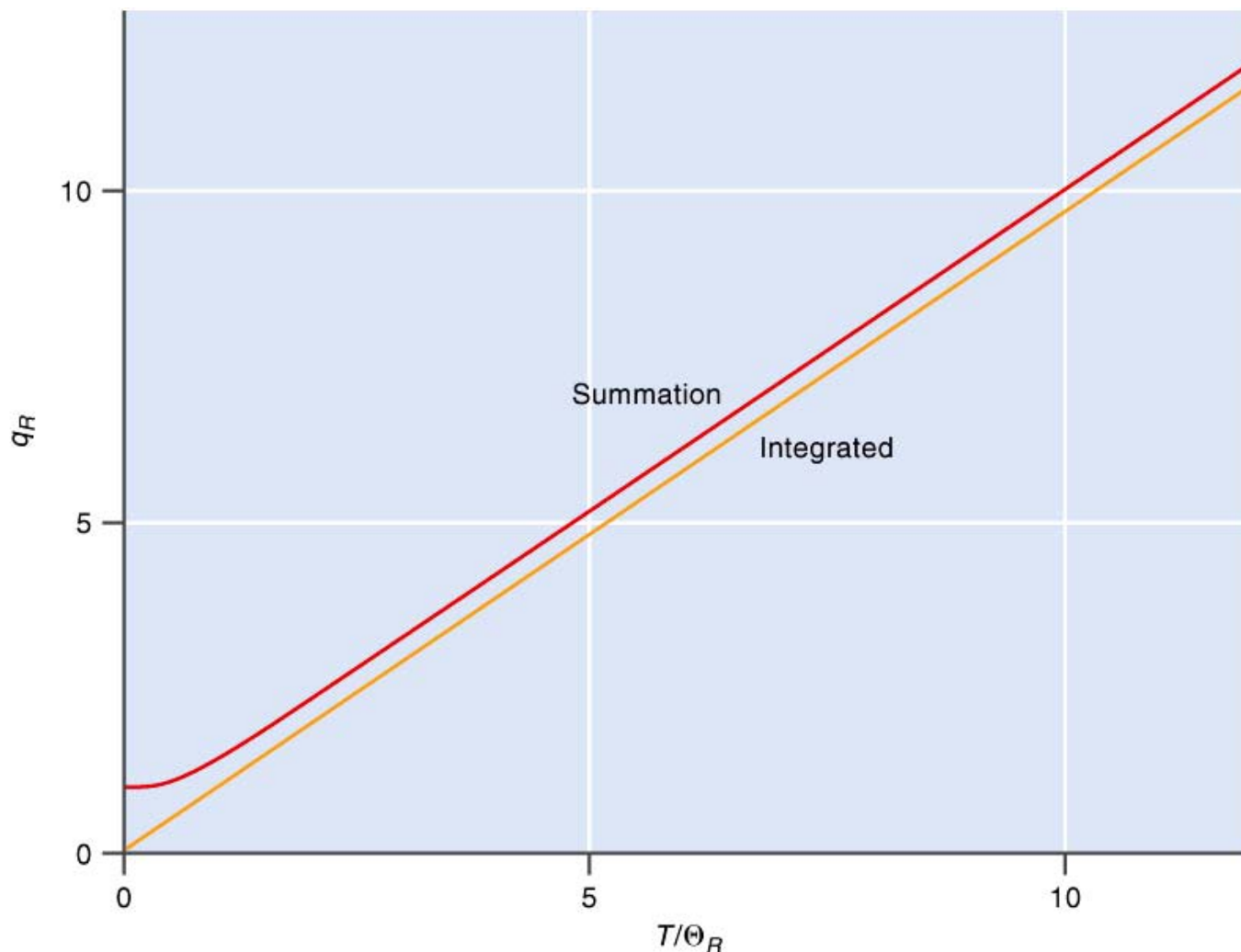
$$\theta_r = \frac{hcB}{k}$$

$$q_r = \frac{kT}{\sigma hcB} = \frac{T}{\sigma \theta_r}$$

At low temperatures, significant differences between summation and integration is evident.

At high temperatures, the difference becomes smaller.

$\frac{T}{\theta_r} \geq 10$ , the use of the integrated form is reasonable.



**Figure 8.** Comparison of  $q_r$  for  $\text{H}^{35}\text{Cl}$  ( $\theta_r = 15.24 \text{ cm}^{-1}$ ) determined by summation and by integration. Although the summation result remains greater than the integrated result at all temperatures, **the fractional difference decreases with elevated temperatures** such that the integrated form provides a sufficiently accurate measure of  $q_r$  when  $T/\theta_r > 10$ .

# Rotational Partition Function of Polyatomics

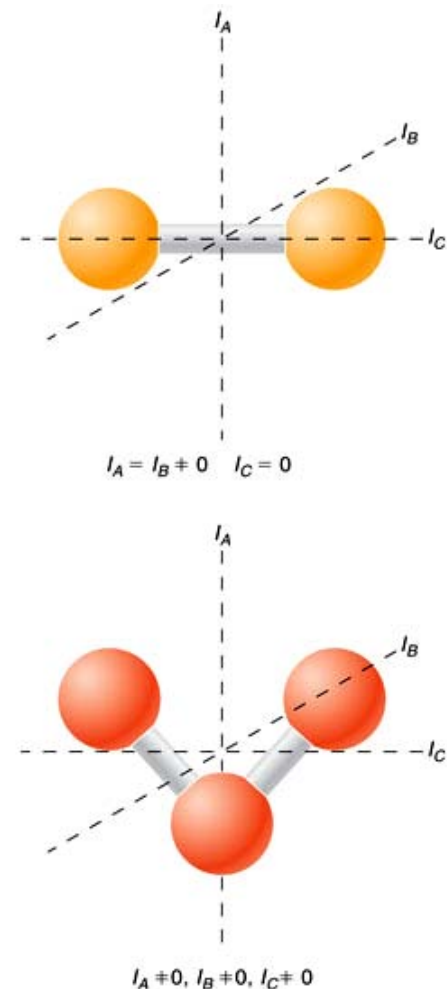
If the polyatomic molecule is not linear, then there are three non-vanishing moments of inertia.

$$q_r = \frac{\sqrt{\pi}}{\sigma} \left( \frac{1}{\beta h c B_A} \right)^{\frac{1}{2}} \left( \frac{1}{\beta h c B_B} \right)^{\frac{1}{2}} \left( \frac{1}{\beta h c B_C} \right)^{\frac{1}{2}}$$

## Example:

Evaluate the rotational partition function for the following species at 298 K. Assume that the high temperature expression is valid.

- OCS ( $B=1.48 \text{ cm}^{-1}$ )
- ONCl  
( $B_A=2.84 \text{ cm}^{-1}$ ,  $B_B=0.191 \text{ cm}^{-1}$ ,  
 $B_C=0.179 \text{ cm}^{-1}$ )
- CH<sub>2</sub>O  
( $B_A=9.40 \text{ cm}^{-1}$ ,  $B_B=1.29 \text{ cm}^{-1}$ ,  
 $B_C=1.13 \text{ cm}^{-1}$ )



**Figure 9.** Moments of inertia for diatomic and nonlinear polyatomic molecules.

# Vibrational Partition Function

Assume that the quantum mechanical model for vibration is the **harmonic oscillator**.

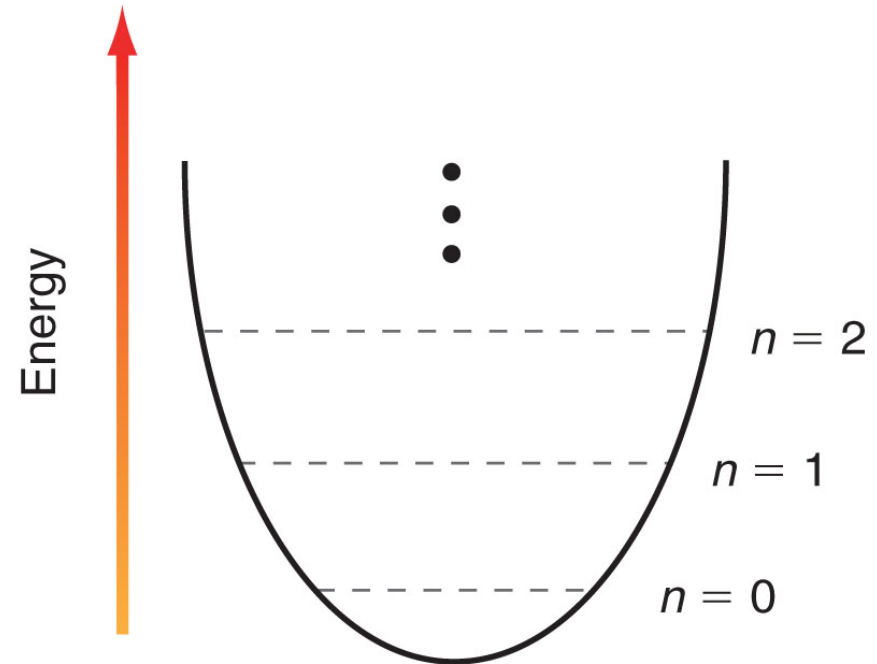
$$\varepsilon_v = hc\tilde{\nu} \left( n + \frac{1}{2} \right)$$

$$\therefore q_v = \sum_{n=0}^{\infty} e^{-\beta\varepsilon_v}$$

$$= \sum_{n=0}^{\infty} e^{-\beta hc\tilde{\nu} \left( n + \frac{1}{2} \right)}$$

$$= e^{-\frac{\beta hc\tilde{\nu}}{2}} \sum_{n=0}^{\infty} e^{-\beta hc\tilde{\nu} n}$$

$$= \frac{e^{-\frac{\beta hc\tilde{\nu}}{2}}}{1 - e^{-\beta hc\tilde{\nu}}} \quad \left| \quad \sum_{n=0}^{\infty} e^{-n\alpha x} = \frac{1}{1 - e^{-\alpha x}} \right.$$



$$E_n = hc\tilde{\nu} \left( n + \frac{1}{2} \right)$$

**Figure 10.** The harmonic oscillator model. Each vibrational degree of freedom is characterized by a **quadratic potential**. The energy levels are evenly spaced.

It is advantageous to redefine the vibrational energy levels such that  $\varepsilon_0=0$ .

Consider the calculation of the probability of occupying a given vibrational energy level,  $P_n$ .

$$P_n = \frac{e^{-\beta\varepsilon_v}}{q_v} = \frac{e^{-\beta hc\tilde{\nu}\left(n+\frac{1}{2}\right)}}{e^{-\beta hc\tilde{\nu}/2}} = \frac{e^{-\beta hc\tilde{\nu}/2} e^{-\beta hc\tilde{\nu}n}}{e^{-\beta hc\tilde{\nu}/2}} = e^{-\beta hc\tilde{\nu}n} (1 - e^{-\beta hc\tilde{\nu}})$$

The relevant energy for determining  $P_n$  is not the absolute energy of a given level, but the relative energy of the level. Given this, one can simply eliminate the zero point energy, resulting in the following expression for the vibrational partition function

$$q_v = \frac{1}{1 - e^{-\beta hc\tilde{\nu}}} \quad (\text{without zero point energy})$$



## Beyond Diatomics: Multidimensional $q_v$

A molecule consisting of  $N$  atoms has  $3N$  total degrees of freedom corresponding to three Cartesian degrees of freedom for each atom.

Three of  $3N$  corresponds to translational motion of entire molecule.

Two of  $3N$  corresponds to rotational motion for linear molecule.

Three of  $3N$  corresponds to rotational motion for non-linear molecule.

Linear Polyatomics :  $3N-5$  vibrational modes

Nonlinear Polyatomics :  $3N-6$  vibrational modes

Since the vibrational degrees of freedom are separable, the total vibrational partition function is simply the product of vibrational partition function for each degree of freedom.

$$q_{v,total} = \prod_{i=1}^{3N-5 \text{ or } 3N-6} (q_v)_i$$

## Example:

OCIO: vibrational frequencies: 450, 945, 1100  $\text{cm}^{-1}$

$q_v = ?$  at 298 K.

# High Temperature Approximation to $q_v$

$$\theta_v = \frac{hc\tilde{\nu}}{k} \quad \text{the vibrational temperature}$$

$$q_v = \frac{1}{1 - e^{-\beta hc\tilde{\nu}}} = \frac{1}{1 - e^{-hc\tilde{\nu}/kT}} = \frac{1}{1 - e^{-\theta_v/T}}$$

$$e^{-x} \cong 1 - x + \frac{x^2}{2} \dots \cong 1 - x \quad \text{for } x \ll 1$$

At high temperature,  $T \gg \theta_v$ .

$$q_v = \frac{1}{1 - e^{-\theta_v/T}} = \frac{1}{1 - \left(1 - \frac{\theta_v}{T}\right)} = \frac{T}{\theta_v} \quad (\text{high } T \text{ limit})$$

## Degeneracy and $q_v$

In the case of degeneracy, two or more of these degrees of freedom will have the same vibrational energy spacings, or the same vibrational temperature.

$$q_{v,total} = \sum_{i=1}^{n'} (q_v)_i^{g_i}$$

where  $g_i$  is the degeneracy of the  $i$ th energy level.

## Example:

What is the total vibrational partition function for CO<sub>2</sub> at 1000 K?

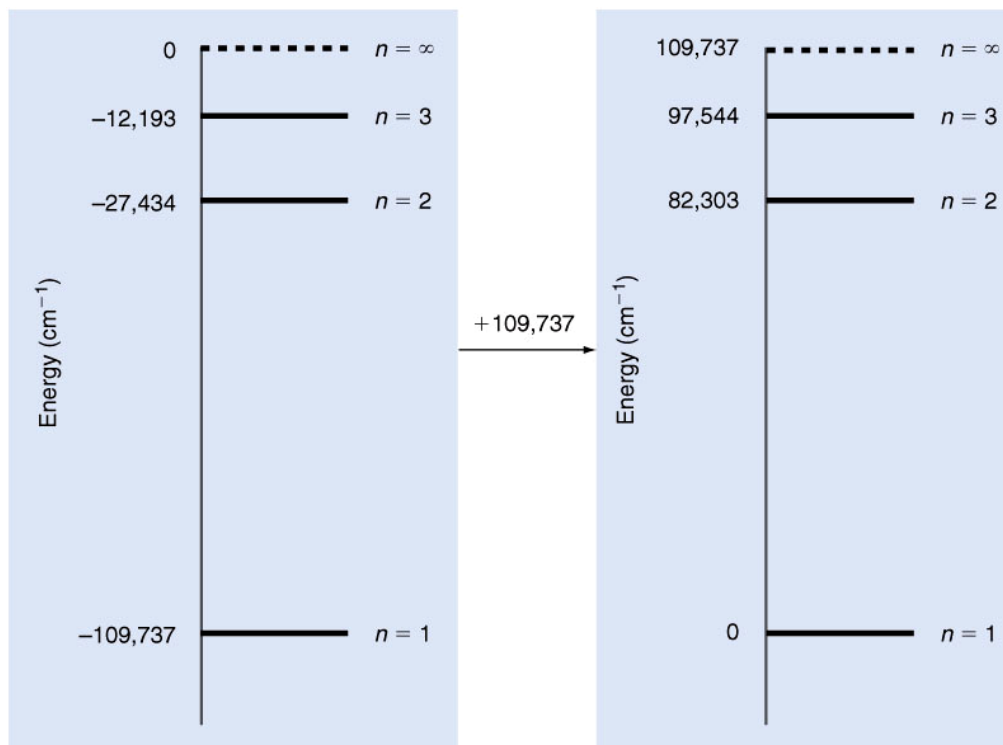
CO<sub>2</sub> :  $\nu = 1388, 667.4 (g=2), 2349 \text{ cm}^{-1}$

# Electronic Partition Function

$$q_e = \sum_n g_n e^{-\beta \varepsilon_e}$$

the orbital energies of hydrogen atom

$$\varepsilon_e = \frac{-m_e e^4}{8\varepsilon_0^2 h^2 n^2} = -109737 \text{ cm}^{-1} \frac{1}{n^2} \quad (n=1, 2, 3, \dots)$$



**Figure 11.** Orbital energies for the hydrogen atom: (a) the orbital energies solved by the Schrödinger equation, and (b) the energy levels shifted such that the lowest orbital energy is 0.

the electronic temperature,  $\theta_e$

$$\theta_e = \frac{hc\varepsilon_e}{k} = \frac{\varepsilon_e}{0.695 \text{ cm}^{-1} \text{ K}^{-1}}$$

$$\varepsilon_1 = 0$$

$$\varepsilon_2 = 82,203 \text{ cm}^{-1} \text{ corresponds to } \theta_e = 118,421 \text{ K.}$$

For hydrogen atom, the  $n=2$  state at 298K

$$e^{-\beta hc\varepsilon_2} = \exp \left[ \frac{-(6.626 \times 10^{-34} \text{ Js})(3 \times 10^{10} \text{ cm/s})(82303 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})} \right] = e^{-397.3} \approx 0$$

$$q_e = \sum_{n=1}^{\infty} g_n e^{-\beta hc\varepsilon_n} = 2e^{-\beta hc\varepsilon_1} + 8e^{-\beta hc\varepsilon_2} + 18e^{-\beta hc\varepsilon_3} + \dots$$

$$= 2e^{-\beta hc(0)} + 8e^{-\beta hc(82,303 \text{ cm}^{-1})} + 18e^{-\beta hc(97,544 \text{ cm}^{-1})} + \dots$$

$$= 2 + 8e^{-\beta hc(82,303 \text{ cm}^{-1})} + 18e^{-\beta hc(97,544 \text{ cm}^{-1})} + \dots$$

$$\cong 2$$

$$g_n = 2n^2 \text{ for H}$$

# Summary

$$Q = q^N \quad (\text{distinguishable})$$

$$Q = \frac{q^N}{N!} \quad (\text{indistinguishable})$$

$$q_{tot} = q_t q_r q_v q_e \\ = \left( \frac{V}{\Lambda^3} \right) \left( \frac{1}{\sigma \beta h c B} \right) \left( \frac{1}{1 - e^{-\beta h c \tilde{\nu}}} \right) (g_o)$$