

Chapter 15. Statistical Thermodynamics

Microscopic Properties
Quantum Mechanics
Spectroscopy
Vibrational frequencies
Bond dissociations

Statistical Mechanics

Macroscopic Properties
Thermodynamics
Heat capacity
Coefficient of expansion

Major Concepts

- Boltzmann Distribution
- Partition Functions
- Molecular Energies
- The Canonical Ensemble
- Internal energy and entropy
- Derived functions

Review

Discrete Energy levels
Particle in a box
Rigid rotor
Harmonic Oscillator

Math
Probability
Lagrange Multipliers
Properties of \ln

Statistical Thermodynamics

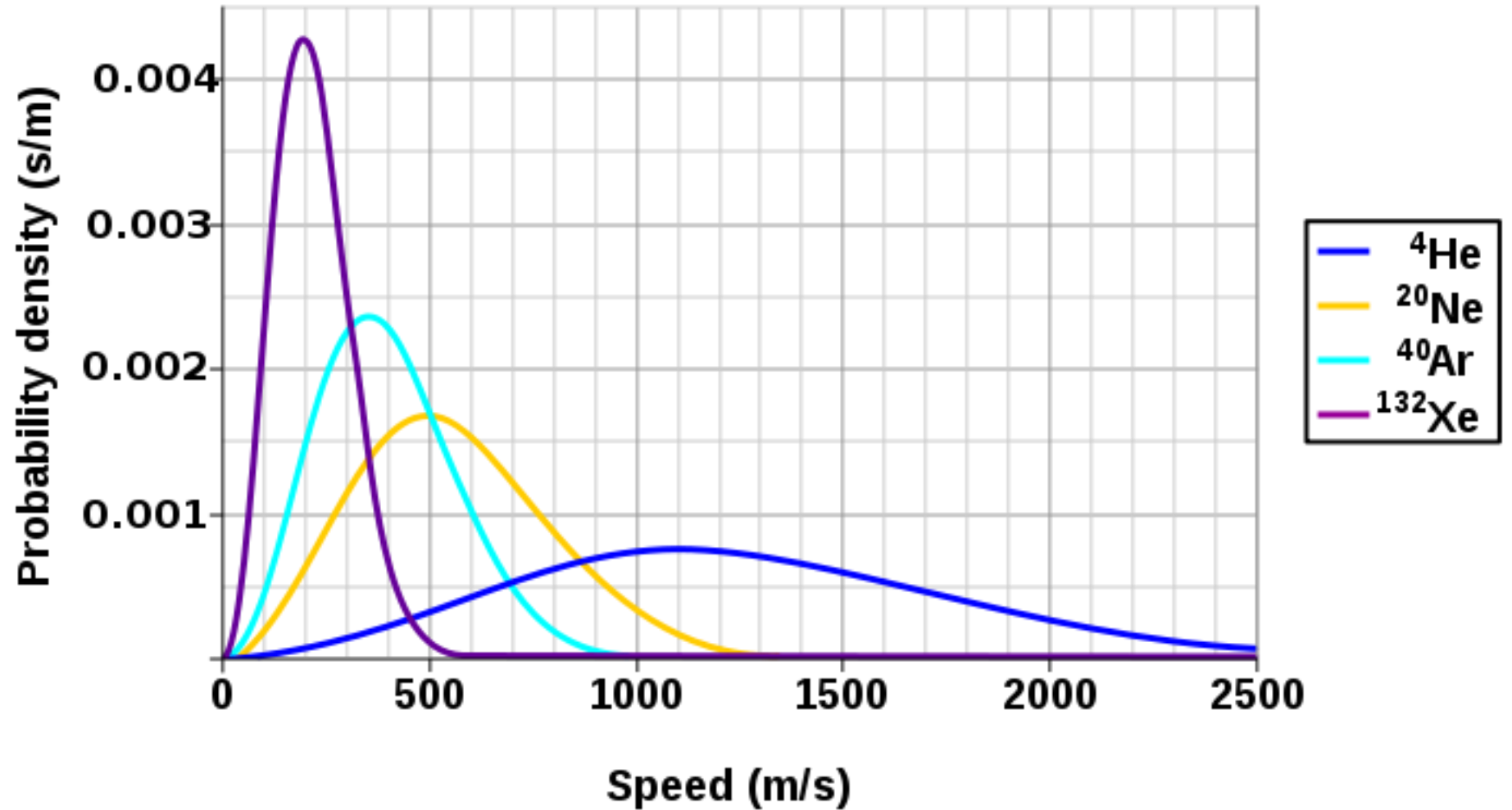
Statistical thermodynamics provides the link between the microscopic (*i.e.*, molecular) properties of matter and its macroscopic (*i.e.*, bulk) properties. It provides a means of calculating thermodynamic properties from the statistical relationship between temperature and energy.

Based on the concept that all macroscopic systems consist of a large number of *states* of differing energies, and that the numbers of atoms or molecules that populate each of these states are a function of the thermodynamic temperature of the system.

One of the first applications of this concept was the development of the kinetic theory of gases and the resulting Maxwell-Boltzmann distribution of molecular velocities, which was first developed by Maxwell in 1860 on purely heuristic grounds and was based on the assumption that gas molecules in a system at thermal equilibrium had a range of velocities and, hence, energies.

Boltzmann performed a detailed analysis of this distribution in the 1870's and put it on a firm statistical foundation. He eventually extended the concept of a statistical basis for all thermodynamic properties to all macroscopic systems.

Maxwell-Boltzmann Molecular Speed Distribution for Noble Gases



Maxwell-Boltzmann Distribution:
$$f(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}} = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-\frac{Mv^2}{2RT}}$$

Statistical Thermodynamics

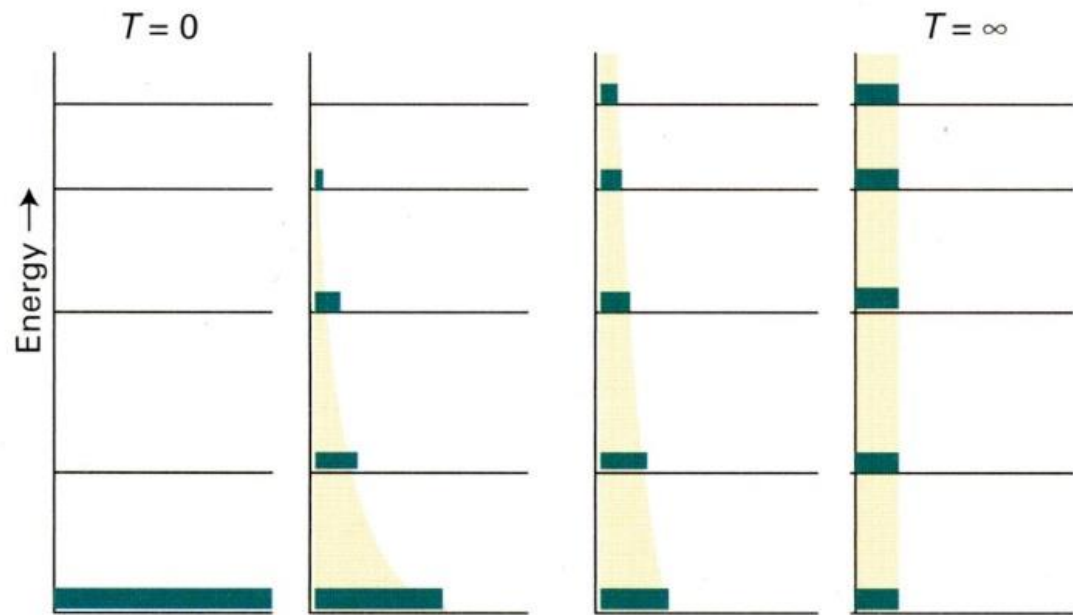


Figure B.4 The Boltzmann distribution of populations for a system of five energy levels as the temperature is raised from zero to infinity.

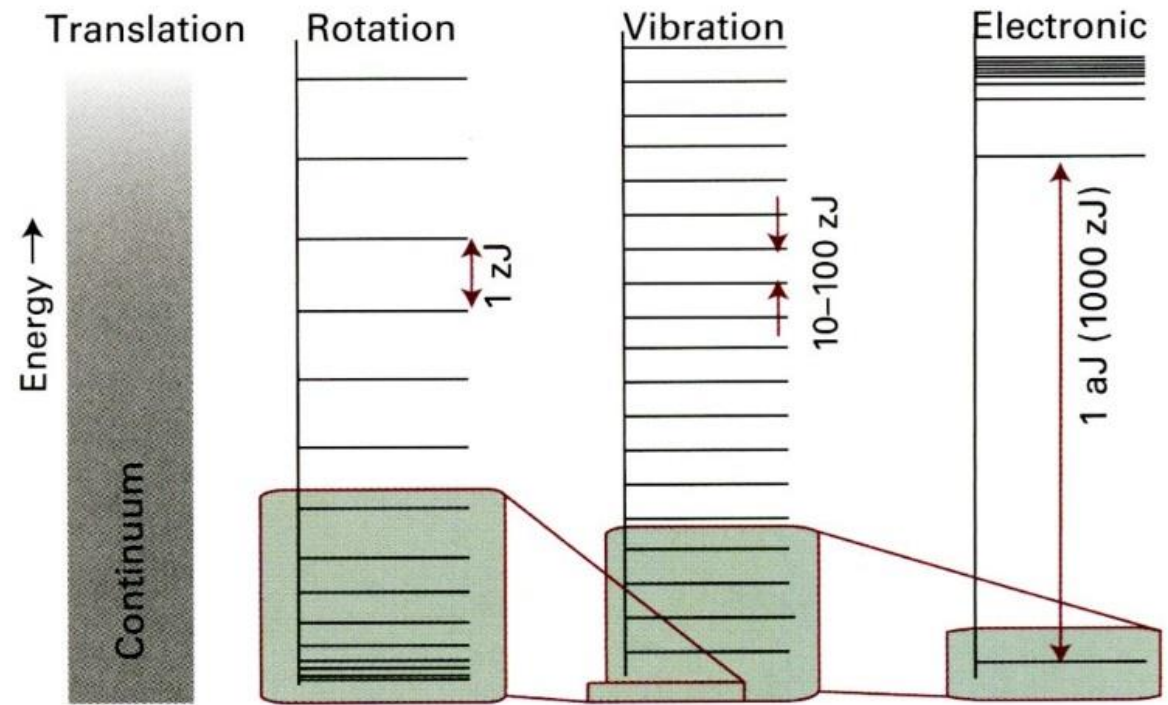


Figure B.3 The energy level separations typical of four types of system. ($1 \text{ zJ} = 10^{-21} \text{ J}$; in molar terms, 1 zJ is equivalent to about 0.6 kJ mol^{-1} .)

Statistics and Entropy

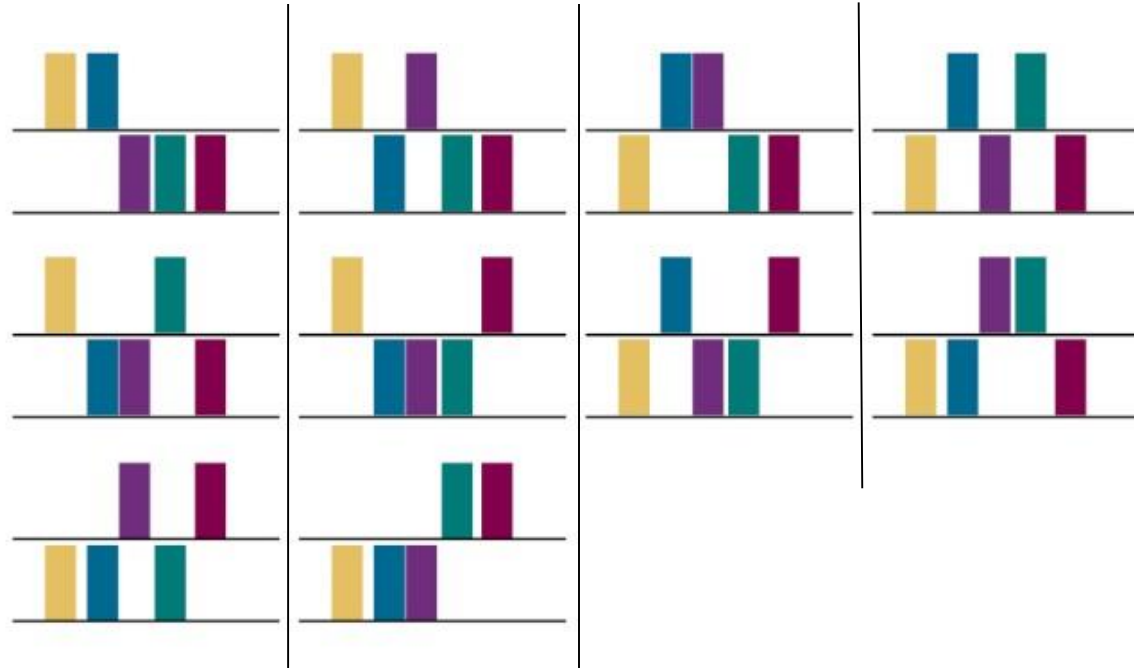


Figure 15A.1 Whereas a configuration $\{5,0,0,\dots\}$ can be achieved in only one way, a configuration $\{3,2,0,\dots\}$ can be achieved in the ten different ways shown here, where the tinted blocks represent different molecules.

(Assumes that the five molecules are distinguishable.)

Macroscopic state :- state of a system is established by specifying its $T, E, S \dots$

Microscopic state :- state of a system is established by specifying $x, p, \epsilon \dots$ of ind. constituents

More than one microstate can lead to the same macrostate.

Example: 2 particles with total $E = 2$
Can be achieved by microstates 1, 1 or 2, 0 or 0, 2

Configuration:- The equivalent ways to achieve a state

W (weight):- The # of configurations comprising a state

Probability of a state:- # configuration in state / total # of configurations

Weight of a Configuration

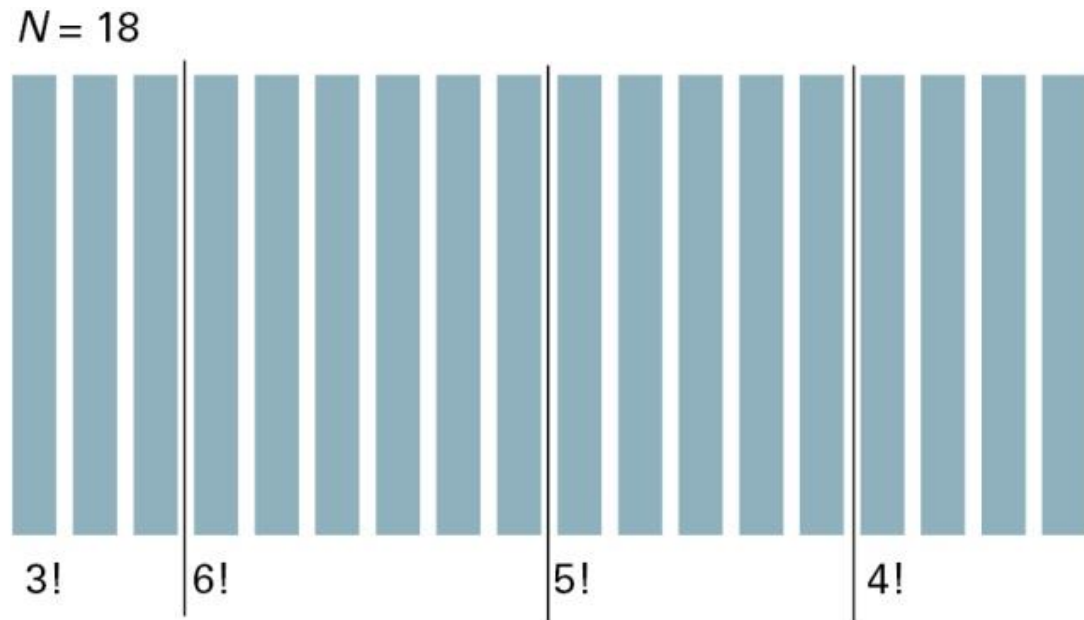


Figure 15A.2 The 18 molecules shown here can be distributed into four receptacles (distinguished by the three vertical lines) in $18!$ different ways. However, $3!$ of the selections that put three molecules in the first receptacle are equivalent, $6!$ that put six molecules into the second receptacle are equivalent, and so on. Hence the number of distinguishable arrangements is $18!/3!6!5!4!$, or about 515 million.

$$W = \frac{N!}{N_0!N_1!N_2!N_3!\dots}$$

$$\begin{aligned}\ln W &= \ln \frac{N!}{N_0!N_1!N_2!N_3!\dots} \\ &= \ln N! - \ln N_0!N_1!N_2!N_3!\dots \\ &= \ln N! - \sum_i \ln N_i!\end{aligned}$$

Using **Sterling's Approximation**:

$\ln N! \sim N \ln N - N$, which is valid for $N \gg 1$,

$$\ln W \approx N \ln N - \sum_i N_i \ln N_i$$

Undetermined Multipliers (Chemist's Toolkit 15A.1)

- Global maximum in f when $df = 0$ $df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$
- Seek a maximum in $f(x,y)$ subject to a constraint defined by $g(x,y) = 0$
- Since $g(x,y)$ is constant $dg = 0$ and: $dg = \left(\frac{\partial g}{\partial x}\right)_y dx + \left(\frac{\partial g}{\partial y}\right)_x dy = 0$

- This defines $dx = \frac{\left(\frac{\partial g}{\partial y}\right)}{\left(\frac{\partial g}{\partial x}\right)} dy$ and $dy = \frac{\left(\frac{\partial g}{\partial x}\right)}{\left(\frac{\partial g}{\partial y}\right)} dx$

- Eliminating dx or dy from the equation for df : $df = \left[\frac{\partial f}{\partial y} - \frac{\partial f}{\partial x} \frac{\partial g / \partial y}{\partial g / \partial x} \right] dy = 0$ or $df = \left[\frac{\partial f}{\partial x} - \frac{\partial f}{\partial y} \frac{\partial g / \partial x}{\partial g / \partial y} \right] dx = 0$

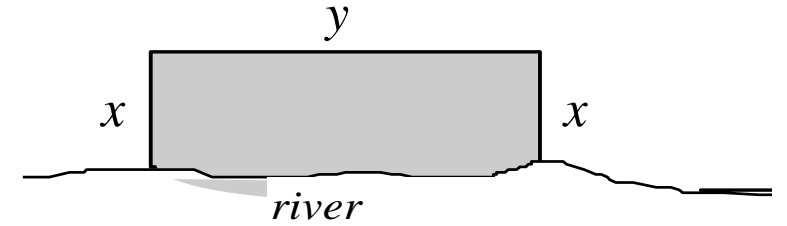
- Defines **undetermined multiplier** $\lambda = \frac{\partial f / \partial y}{\partial g / \partial y}$ or $\lambda = \frac{\partial f / \partial x}{\partial g / \partial x}$

$$\left[\frac{\partial f}{\partial x} - \lambda \frac{\partial g}{\partial x} \right] = 0 \quad \text{or} \quad \frac{\partial}{\partial x} [f - \lambda g] = 0 \qquad \left[\frac{\partial f}{\partial y} - \lambda \frac{\partial g}{\partial y} \right] = 0 \quad \text{or} \quad \frac{\partial}{\partial y} [f - \lambda g] = 0$$

Same as getting *unconstrained* maximum of $K = [f - \lambda g]$

Example of Undetermined Multipliers

A rectangular area is to be enclosed by a fence having a total length of 16 meters, where one side of the rectangle does not need fence because it is adjacent to a river. What are the dimensions of the fence that will enclose the largest possible area?



Thus, the principal (area) function is: $F(x,y) = xy$ (1)

and the constraint (16 meters) is: $f(x,y) = 2x + y - 16 = 0$ (2)

If $F(x,y)$ were not constrained, *i.e.*, if x and y were independent, then the derivative (slope) of F would be zero:

$$dF(x,y) = \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy = 0 \quad (3)$$

and

$$\left(\frac{\partial F}{\partial x} \right) = 0 \quad \text{and} \quad \left(\frac{\partial F}{\partial y} \right) = 0 \quad (4)$$

However, this provides only two equations to be solved for the variables x and y , whereas three equations must be satisfied, *viz.*, Eqs. (4) and the constraint equation $f(x,y) = 0$.

Example of Undetermined Multipliers

The method of undetermined multipliers involves multiplying the constraint equation by another quantity, λ , whose value can be chosen to make x and y *appear to be* independent. This results in a third variable being introduced into the three-equation problem. Because $f(x,y) = 0$, maximizing the new function F'

$$F'(x,y) \equiv F(x,y) + \lambda f(x,y) \quad (5)$$

is equivalent to the original problem, except that now there are three variables, x , y , and λ , to satisfy three equations:

$$\left(\frac{\partial F'}{\partial x}\right) = 0 \quad \left(\frac{\partial F'}{\partial y}\right) = 0 \quad \text{and} \quad f(x,y) = 0 \quad (6)$$

Thus Eq. 5 becomes

$$F'(x,y) = xy + \lambda (2x + y - 16) \quad (7)$$

Applying Eqs. (6),

$$\left(\frac{\partial F'}{\partial x}\right) = y + 2\lambda = 0 \Rightarrow y = -2\lambda \quad \left(\frac{\partial F'}{\partial y}\right) = x + \lambda = 0 \Rightarrow x = -\lambda \quad 2x + y - 16 = -2\lambda - 2\lambda - 16 = 0$$

yielding $\lambda = -4$, which results in $x = 4$ and $y = 8$. Hence, the maximum area possible is $A = 32 \text{ m}^2$.

Example of Undetermined Multipliers

Find a maximum of $f(x, y) = e^{-(x^2+y^2)}$ Subject to the constraint $g(x, y) = x + 4y - 17 = 0$

From slope formula $df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = 0$ $df = -2xe^{-(x^2+y^2)}dx + -2ye^{-(x^2+y^2)}dy = 0$

Global maximum: $x = y = 0$ Need to find *constrained* maximum

- Find undetermined multiplier $K(x, y) = f(x, y) - \lambda g(x, y) = e^{-(x^2+y^2)} - \lambda(x + 4y - 17)$

- An unconstrained maximum in K must $\frac{\partial K}{\partial x} = -2xe^{-(x^2+y^2)} - \lambda = 0$ $\lambda = -2xf$

$$\frac{\partial K}{\partial y} = -2ye^{-(x^2+y^2)} - 4\lambda = 0 \quad \lambda = -\frac{y}{2}f$$

- This implies $2x = \frac{y}{2}$ $4x = y$

- Original condition $g = 0$ $g(x, y) = x + 4(4x) - 17 = 0$

- Constrained maximum : $x = 1; y = 4$

Most Probable Distribution

Total energy: $E = \sum_i N_i \epsilon_i$ Total number of particles: $N = \sum_i N_i$

Configurations: $W = \frac{N!}{N_1! N_2! N_3! \dots}$
(permutations)

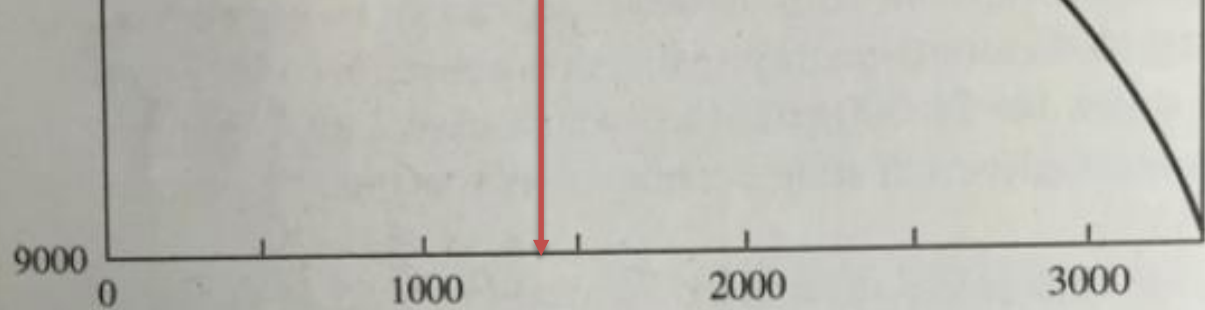
Example: $N = 20,000$; $E = 10,000$; three energy levels $\epsilon_1 = 0, \epsilon_2 = 1, \epsilon_3 = 2$.

Constant E requires that $N_2 + 2N_3 = 10,000$; constant N requires that $N_1 + N_2 + N_3 = 20,000$

$0 < N_3 < 3333$; W is maximum when $N_3 \sim 1300$.

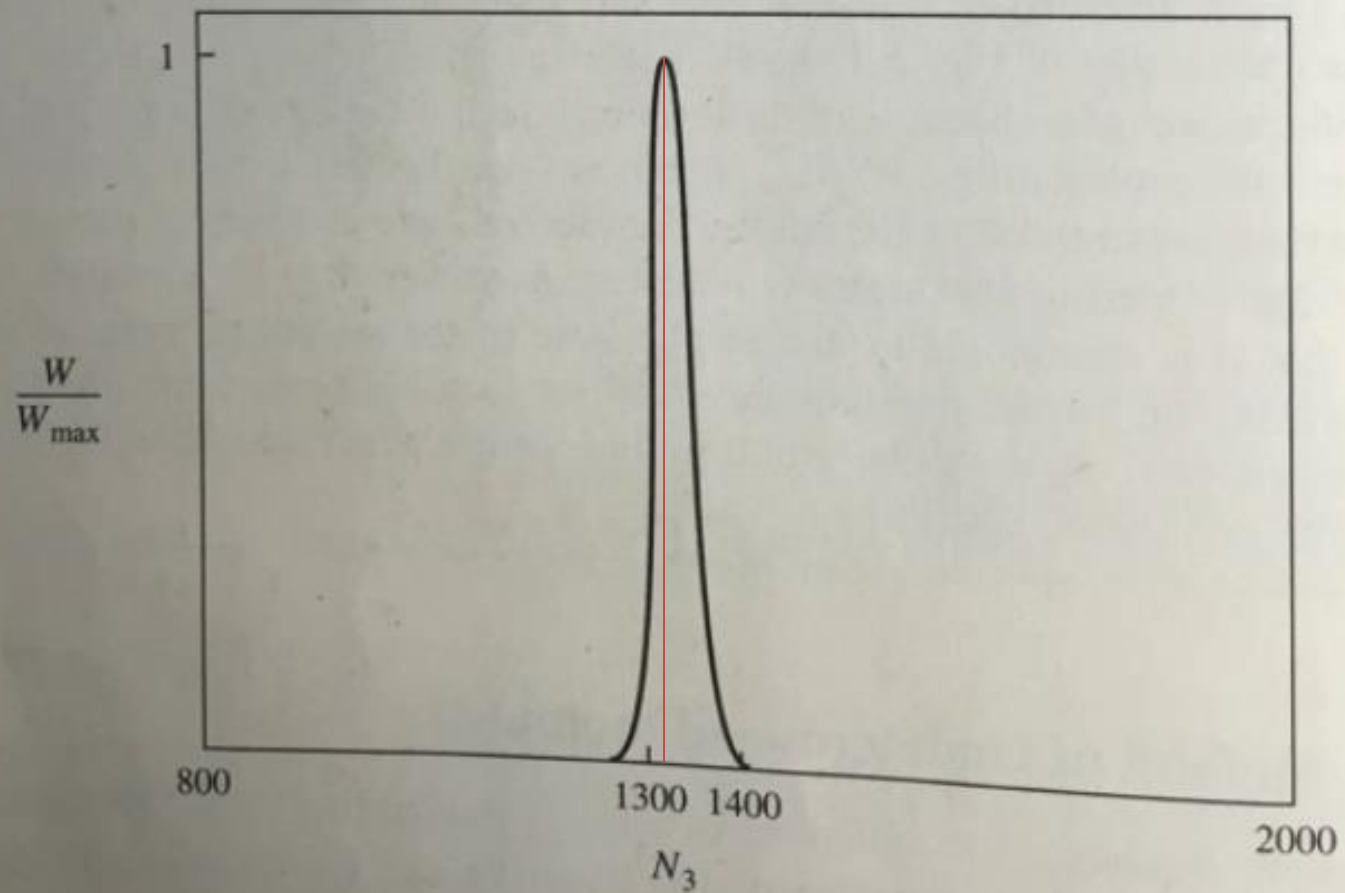
Maximum probability (and, hence, maximum entropy) occurs when each particle is in a different energy level. But minimum energy occurs when all particles are in the lowest energy level. Thus, must find the maximum probability that is possible, consistent with a given total energy, E , and a given total number of particles, N .

This is an example of a classic problem, in which one must determine the extrema (*i.e.*, maxima and/or minima) of a function, *e.g.* entropy, that are consistent with constraints that may be imposed because of other functions, *e.g.*, energy and number of particles. This problem is typically solved by using the so-called LaGrange Method of Undetermined Multipliers.



N_3

(a)



Most Probable Distribution

The most probable distribution is the one with greatest weight, W . Thus, must maximize $\ln W$. Because there are two constraints (constant E and constant N), must use two undetermined multipliers: $g(x_i) = 0$ and $h(x_i) = 0$ so $K = (f + \alpha g + \beta h)$

- Use this to approach to find most probable population:
$$K = \ln W + \alpha \left(N - \sum_j N_j \right) + \beta \left(E - \sum_j N_j \varepsilon_j \right)$$

(constant N) (constant E)

Want constrained maximum of $\ln W$ (equivalent to unconstrained maximum of K)

- Use Stirling's Approximation for $\ln W$:
$$K = N \ln N - \sum_j N_j \ln N_j + \alpha \left(N - \sum_j N_j \right) + \beta \left(E - \sum_j N_j \varepsilon_j \right)$$

- Can solve for any single population N_i (all others 0):
$$\frac{\partial K}{\partial N_i} = 0 \quad \frac{\partial N_i}{\partial N_i} = 1 \quad \frac{\partial N_j}{\partial N_i} = 0$$

$$\left(\frac{\partial K}{\partial N_i} \right) = - \left(\ln N_i + N_i \cdot \frac{1}{N_i} \right) + \alpha(-1) - \beta(\varepsilon_i) = 0$$

$$\left(\frac{\partial K}{\partial N_i} \right) = - \ln N_i - 1 - \alpha - \beta \varepsilon_i = 0$$

$$\ln N_i = -(1 + \alpha) - \beta \varepsilon_i$$

Boltzmann Distribution

$$\ln N_i = -(1 + \alpha) - \beta \epsilon_i$$

If $A \equiv \exp[-(1 + \alpha)]$, then

$$N_i = A e^{-\beta \epsilon_i}$$

• A (α) can be eliminated by introducing N:

$$N = \sum_j N_j = A \sum_j e^{-\beta \epsilon_j}$$

$$A = \frac{N}{\sum_j e^{-\beta \epsilon_j}}$$

$$N_i = \frac{N e^{-\beta \epsilon_i}}{\sum_j e^{-\beta \epsilon_j}}$$

Boltzmann Temperature (will prove later)

$$\beta = \frac{1}{k_b T}$$

Boltzmann Distribution

$$p_i = \frac{N_i}{N} = \frac{e^{-\epsilon_i/k_b T}}{\sum_j e^{-\epsilon_j/k_b T}}$$

For relative populations:

$$N_i/N_j = e^{-\beta(\epsilon_i - \epsilon_j)} = e^{-(\epsilon_i - \epsilon_j)/kT}$$

Gives populations of states, not levels.

If more than one state at same energy, must account for degeneracy of state, g_i .

$$N_i/N_j = (g_i/g_j) e^{-\beta(\epsilon_i - \epsilon_j)}$$

Most Probable Distribution

In summary, the populations in the configuration of greatest weight, subject to the constraints of fixed E and N , depend on the energy of the state, according to the **Boltzmann Distribution**:

$$\frac{N_i}{N} = \frac{e^{-\frac{\epsilon_i}{kT}}}{\sum_i e^{-\frac{\epsilon_i}{kT}}}$$

The denominator of this expression is denoted by q and is called the **partition function**, a concept that is absolutely central to the statistical interpretation of thermodynamic properties which is being developed here.

As can be seen in the above equation, because k is a constant (**Boltzmann's Constant**), the thermodynamic temperature, T , is the unique factor that determines the most probable populations of the states of a system that is at thermal equilibrium.

Most Probable Distribution

If comparing the relative populations of only two states, ε_i and ε_j , for example,

$$\frac{N_i}{N_j} = \frac{e^{-\frac{\varepsilon_i}{kT}}}{e^{-\frac{\varepsilon_j}{kT}}} = e^{-\frac{\varepsilon_i - \varepsilon_j}{kT}}$$

The Boltzmann distribution gives the relative populations of *states*, not energy *levels*. More than one state might have the same energy, and the population of each state is given by the Boltzmann distribution. If the relative populations of energy levels, rather than states, is to be determined, then this energy degeneracy must be taken into account. For example, if the level of energy ε_i is g_i -fold degenerate (*i.e.*, g_i states have that energy), and the level of energy ε_j is g_j -fold degenerate, then the relative total populations of these two levels is given by:

$$\frac{N_i}{N_j} = \frac{g_i e^{-\frac{\varepsilon_i}{kT}}}{g_j e^{-\frac{\varepsilon_j}{kT}}} = \frac{g_i}{g_j} e^{-\frac{\varepsilon_i - \varepsilon_j}{kT}}$$

Example Partition Function: Uniform Ladder

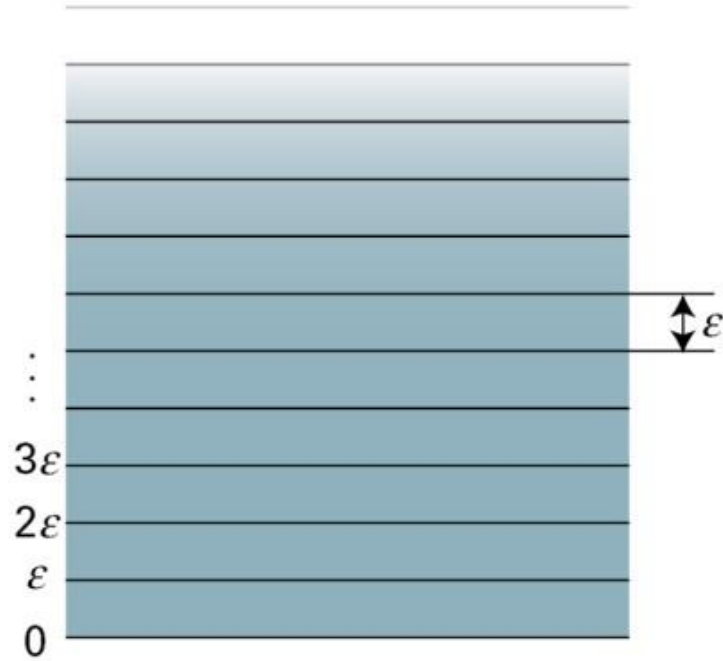


Figure 15B.1 The equally-spaced infinite array of energy levels used in the calculation of the partition function. A harmonic oscillator has the same spectrum of levels.

$$q = 1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon} + e^{-3\beta\epsilon} + \dots$$

$$q = 1 + e^{-\beta\epsilon} + (e^{-\beta\epsilon})^2 + (e^{-\beta\epsilon})^3 + \dots$$

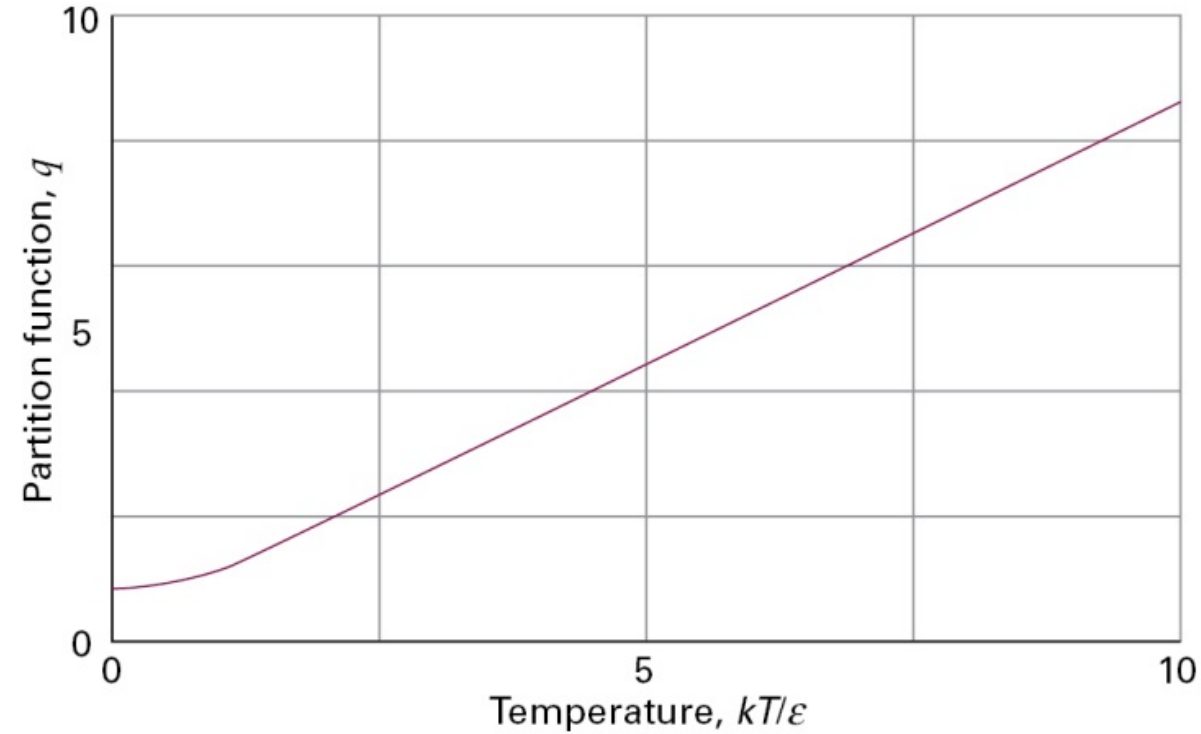


Figure 15B.2 The partition function for the system shown in Fig. 15B.1 (a harmonic oscillator) as a function of temperature.

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \dots$$

$$q = \frac{1}{1 - e^{-\beta\epsilon}}$$

Example Partition Function: Uniform Ladder

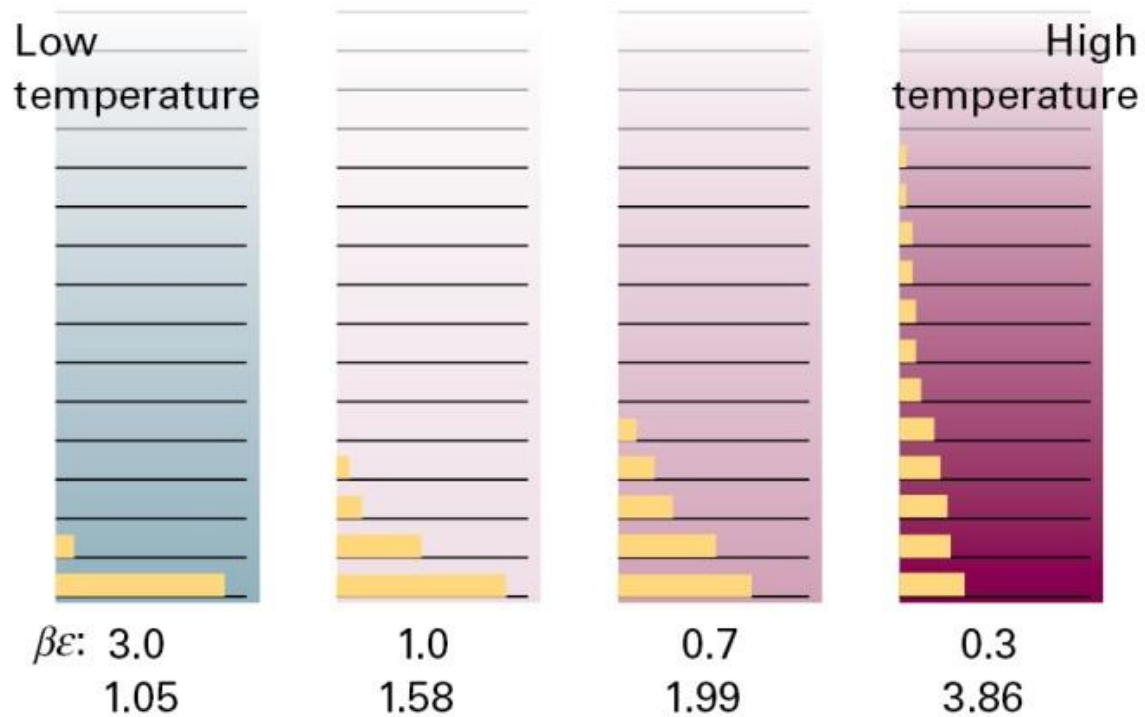


Figure 15B.4 The populations of the energy levels of the system shown in Fig.15B.1 at different temperatures, and the corresponding values of the partition function as calculated from eqn 15B.2b. Note that $\beta = 1/kT$.

Because the partition function for the uniform ladder of energy levels is given by:

$$q = \frac{1}{1 - e^{-\beta\varepsilon}} = \frac{1}{1 - e^{-\frac{\varepsilon}{kT}}}$$

then the Boltzmann distribution for the populations in this system is:

$$p_i = \frac{N_i}{N} = \frac{e^{-\beta\varepsilon_i}}{q} = (1 - e^{-\beta\varepsilon})e^{-\beta\varepsilon_i} = (1 - e^{-\frac{\varepsilon}{kT}})e^{-\frac{\varepsilon_i}{kT}}$$

Fig. 15B.4 shows schematically how p_i varies with temperature. At very low T , where $q \approx 1$, only the lowest state is significantly populated. As T increases, higher states become more highly populated. Thus, the numerical value of the partition function gives an indication of the range of populated states at a given T .

Two-Level System

For a two-level system, the partition function and corresponding population distribution are given by:

$$q = 1 + e^{-\beta\varepsilon} = 1 + e^{-\frac{\varepsilon}{kT}}$$

and

$$p_i = \frac{e^{-\beta\varepsilon_i}}{q} = \frac{e^{-\beta\varepsilon_i}}{1 + e^{-\beta\varepsilon}} = \frac{e^{-\frac{\varepsilon_i}{kT}}}{1 + e^{-\frac{\varepsilon}{kT}}}$$

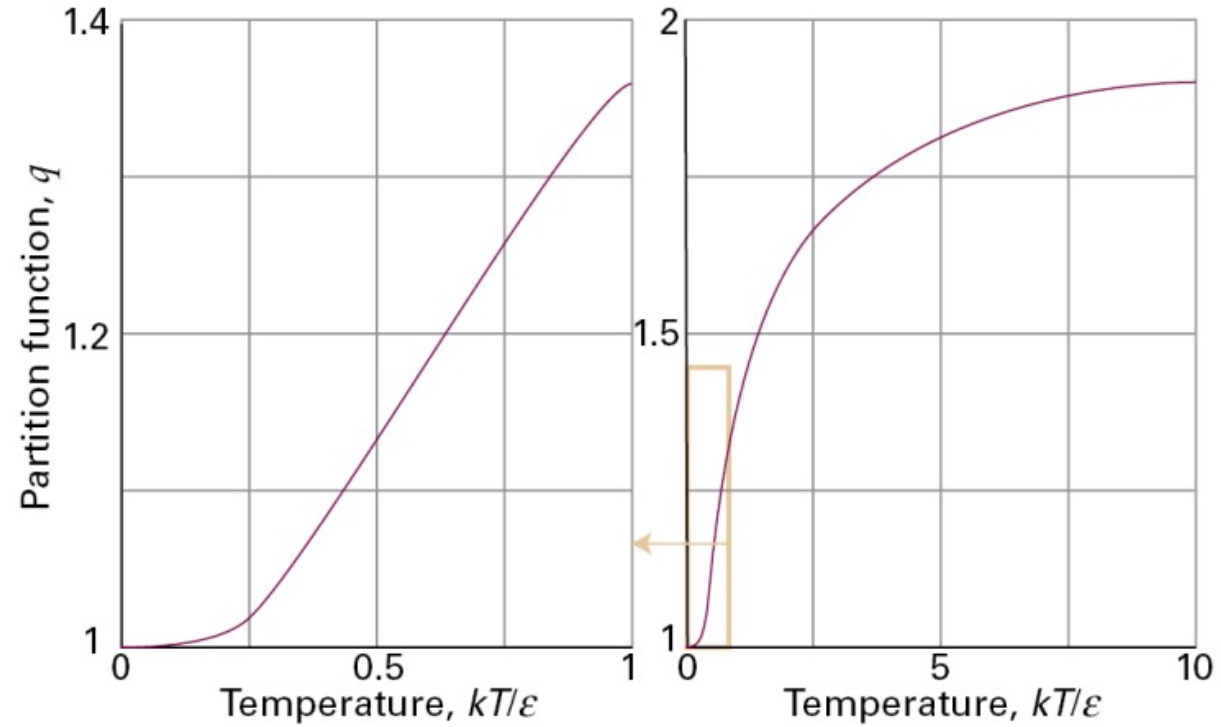


Figure 15B.3 The partition function for a two-level system as a function of temperature. The two graphs differ in the scale of the temperature axis to show the approach to 1 as $T \rightarrow 0$ and the slow approach to 2 as $T \rightarrow \infty$.

Two-Level System

In this case, because there are only two levels and, hence, only two populations, p_0 and p_1 , and because $\varepsilon_0 = 0$ and $\varepsilon_1 = 1$, then

$$p_0 = \frac{1}{1 + e^{-\beta\varepsilon}} = \frac{1}{1 + e^{-\frac{\varepsilon}{kT}}}$$

and

$$p_1 = \frac{e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}} = \frac{e^{-\frac{\varepsilon}{kT}}}{1 + e^{-\frac{\varepsilon}{kT}}}$$

At $T = 0$ K, $q = 1$, indicating that only one state is occupied. With increasing temperature, q approaches 0.5, at which point both states are equally populated. Thus, it can be generalized that as $T \rightarrow \infty$, all available states become equally populated.

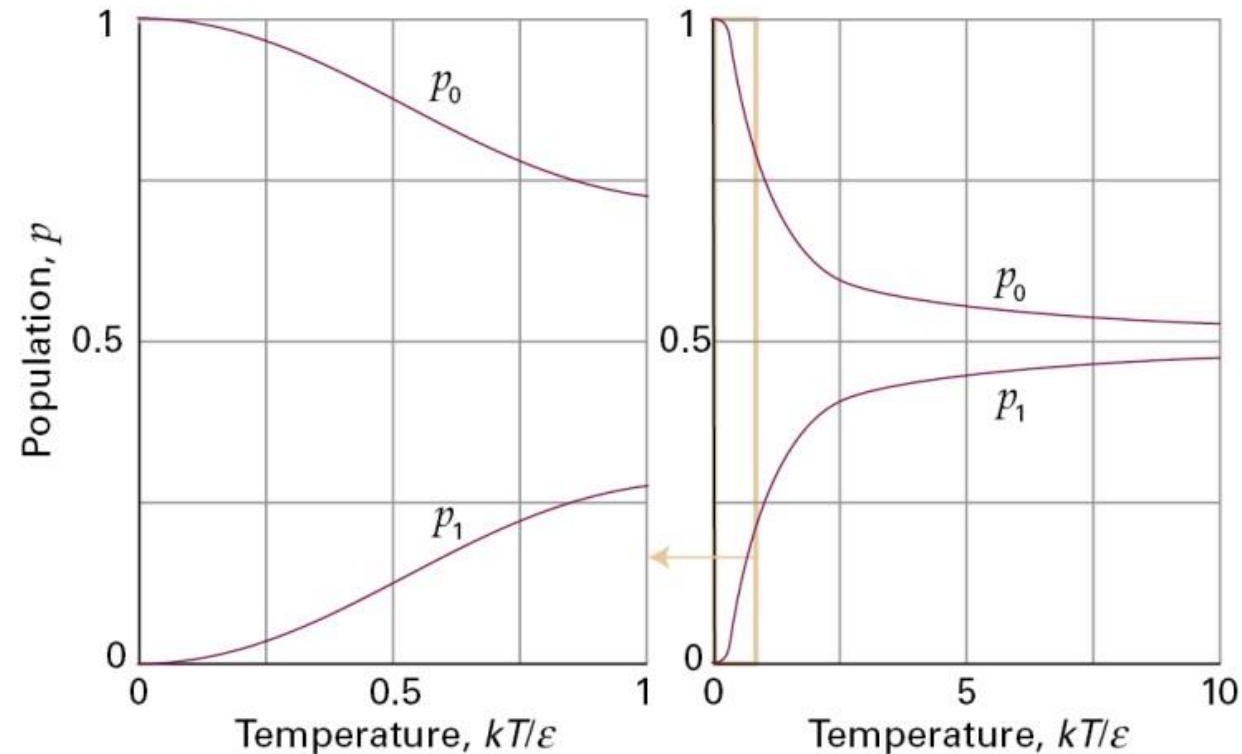


Figure 15B.5 The fraction of populations of the two states of a two-level system as a function of temperature (eqn 15B.4). Note that as the temperature approaches infinity, the populations of the two states become equal (and the fractions both approach 0.5).

Generalizations Regarding the Partition Function

Conclusions regarding the partition function:

- Indicates the number of thermally accessible states in a system.
- As $T \rightarrow 0$, the parameter $\beta = 1/kT \rightarrow \infty$, and the number of populated states $\rightarrow 1$, the lowest (ground) state, *i.e.*, $\lim_{T \rightarrow 0} q = g_0$, where g_0 is the degeneracy of the lowest state.
- As $T \rightarrow \infty$, each of the terms $\beta = \varepsilon/kT$ in the partition function sum $\sum_i e^{-\beta\varepsilon} \rightarrow 0$, so each term = 1.
Thus, $\lim_{T \rightarrow \infty} q = \infty$, since the number of available states is, in general, infinite.
- In summary, the molecular partition function q corresponds to the number of states that are thermally accessible to a molecule at the temperature of the system.

Contributions to Partition Function

- Total energy of a molecule is the sum of the contributions from its different modes of motion (translational, rotational, vibrational), plus its electronic energy:

$$\varepsilon_i = \varepsilon_i^T + \varepsilon_i^R + \varepsilon_i^V + \varepsilon_i^E$$

- Thus, the partition function for the molecule consists of the product of the components from each of the four individual types of energy:

$$q = q^T \cdot q^R \cdot q^V \cdot q^E$$

$$= \left(\sum_i g_i^T e^{-\beta \varepsilon_i^T} \right) \left(\sum_i g_i^R e^{-\beta \varepsilon_i^R} \right) \left(\sum_i g_i^V e^{-\beta \varepsilon_i^V} \right) \left(\sum_i g_i^E e^{-\beta \varepsilon_i^E} \right)$$

g: degeneracy of the corresponding energy level

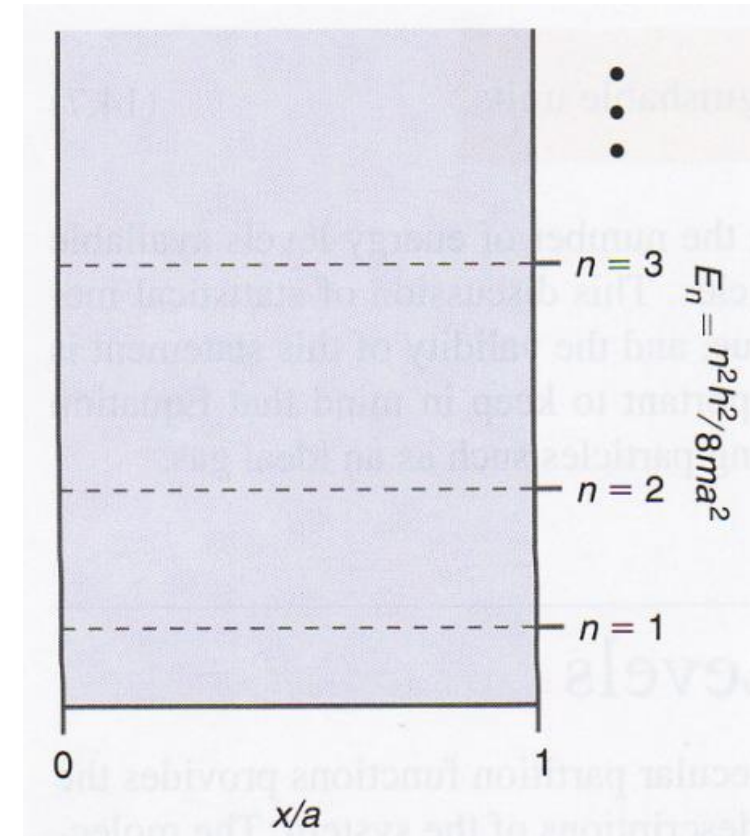
Translational Partition Function

- Translational energy levels are very closely spaced, thus, at normal temperatures, large numbers of them are typically accessible.
- Assume that gas is confined in a three-dimensional volume.
- Quantum states can be modeled by a particle in a 3D box with side lengths a , b , and c :

$$E(n_x, n_y, n_z) = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2}$$

- The translational partition function for a single molecule is

$$\begin{aligned} q^T &= \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} e^{-\frac{h^2}{8mkT} \left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right]} \\ &= \sum_{n_x=1}^{\infty} e^{-\frac{h^2}{8mkT} \left[\frac{n_x^2}{a^2} \right]} \sum_{n_y=1}^{\infty} e^{-\frac{h^2}{8mkT} \left[\frac{n_y^2}{b^2} \right]} \sum_{n_z=1}^{\infty} e^{-\frac{h^2}{8mkT} \left[\frac{n_z^2}{c^2} \right]} \end{aligned}$$



Translational Partition Function

- For a system having macroscopic dimensions, the summations can be replaced by integrals:

$$q^T \approx \int_{n_x=0}^{\infty} e^{-\frac{h^2 n_x^2}{8mkT a^2}} dn_x \int_{n_y=0}^{\infty} e^{-\frac{h^2 n_y^2}{8mkT b^2}} dn_y \int_{n_z=0}^{\infty} e^{-\frac{h^2 n_z^2}{8mkT c^2}} dn_z$$

- The above definite integrals evaluate to:

$$\int_0^{\infty} e^{-\alpha x^2} dx = \frac{1}{2} \left(\frac{\pi}{\alpha} \right)^{1/2}$$

Thus,

$$q^T = a \left(\frac{2\pi mkT}{h^2} \right)^{1/2} \cdot b \left(\frac{2\pi mkT}{h^2} \right)^{1/2} \cdot c \left(\frac{2\pi mkT}{h^2} \right)^{1/2} = V \left(\frac{2\pi mkT}{h^2} \right)^{3/2}$$

- If the **thermal de Broglie wavelength**, Λ , is defined as $\Lambda = \frac{h}{\sqrt{2\pi mkT}}$, then

$$q^T = \frac{V}{\Lambda^3}$$

where Λ has units of length, and q^T is dimensionless.

Translational Partition Function

Example: Calculate the translational partition function for an O₂ molecule in a 1 L vessel at 25°C.

$$\Lambda = \frac{h}{(2\pi mkT)^{1/2}} = \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s}}{(2 \times \pi \times 32 \text{ amu} \times 1.67 \times 10^{-27} \text{ kg/amu} \times 1.38 \times 10^{-23} \text{ J/K} \times 298 \text{ K})^{1/2}}$$
$$= 1.78 \times 10^{-11} \text{ m} = 17.8 \text{ pm}$$

$$q^T = \frac{V}{\Lambda^3} = \frac{1 \times 10^{-3} \text{ m}^3}{(1.78 \times 10^{-11})^3 \text{ m}^3} = 1.77 \times 10^{29}$$

Thus, under these conditions, an O₂ molecule would have $\sim 10^{29}$ quantum states thermally accessible to it. The thermal wavelength of the O₂ molecule ($\Lambda = h/(2\pi mkT)^{1/2}$) is ~ 18 pm, which is \sim eight orders of magnitude smaller than the size of the containing vessel.

In order for the above equation for q^T to be valid, *the average separation of the particles must be much greater than their thermal wavelength.* Assuming that O₂ molecules behave as a perfect gas at 298K and 1 bar, for example, the average separation between molecules is ~ 3 nm, which is ~ 168 times larger than the thermal wavelength.

Translational Partition Function

As seen by its definition:

$$q^T = \frac{V}{\Lambda^3} = V \times \frac{(2\pi mkT)^{3/2}}{h^3}$$

the three-dimensional translational partition function increases with the mass of the particle, as $m^{3/2}$, and with the volume, V , of the container.

For a given particle mass and container volume, q^T also increases with temperature, as $T^{3/2}$ because an infinite number of states becomes accessible as the temperature increases:

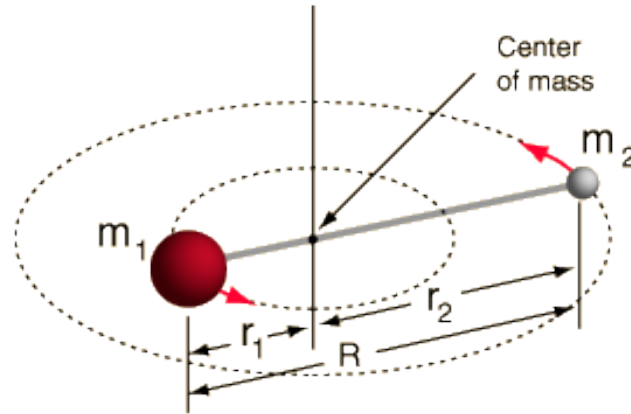
$$q^T \rightarrow \infty \text{ as } T \rightarrow \infty$$

Rotational Partition Function for Diatomic Molecules

- The rotational energy of a rigid rotor is

$$E_{\text{rot}} = \frac{J(J+1)h^2}{8\pi^2 I}$$

where J is the rotational quantum number (0, 1, 2,...) and I is the moment of inertia.



Substituting to eliminate r_1 and r_2 gives

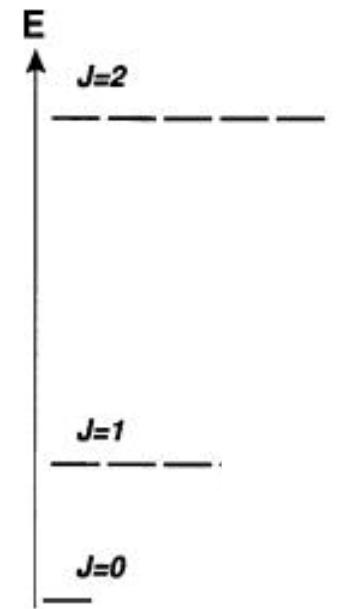
$$I = \frac{m_1 m_2 R^2}{m_1 + m_2} = \mu R^2$$

where μ is called the "reduced mass."

- The rotational partition function for a linear molecule is thus

$$q^R = \sum_{J=0}^{\infty} g_J e^{-\frac{E_{\text{rot}}}{kT}} = \sum_{J=0}^{\infty} (2J+1) e^{-\frac{J(J+1)h^2}{8\pi^2 I kT}} = \sum_{J=0}^{\infty} (2J+1) e^{-\beta h c \tilde{B} J(J+1)}$$

- where the rotational constant \tilde{B} is given by: $\tilde{B} = \hbar/4\pi c I$



Rotational Partition Function for Diatomic Molecules

- For molecules with large moments of inertia or at sufficiently **high temperature**, the above sum approximates to

$$q^R = \int_0^\infty (2J + 1) e^{-\frac{J(J+1)h^2}{8\pi^2 IkT}} dJ = (2J + 1) e^{-\beta hc \tilde{B} J(J+1)} dJ = \frac{8\pi^2 IkT}{h^2} = \frac{1}{\beta hc \tilde{B}}$$

- In general,
$$q^R = \frac{8\pi^2 IkT}{\sigma h^2} = \frac{1}{\sigma \beta hc \tilde{B}}$$

where σ is the symmetry number:

- $\sigma = 1$ for heteronuclear diatomic molecules
- $\sigma = 2$ for homonuclear diatomic molecules
- The temperature above which the approximation shown above for q^R is valid is termed the **characteristic rotational temperature**, θ^R , which is given by: $\theta^R = hc \tilde{B} / k$.
- At sufficiently high temperatures ($T \gg \theta^R$), the rotational partition function for linear molecules is:

$$q^R = \frac{T}{\sigma \theta^R}$$

Rotational Partition Function for Diatomic Molecules

Table 15B.1* Rotational temperatures of diatomic molecules

	θ^R/K
$^1\text{H}_2$	87.6
$^1\text{H}^{35}\text{Cl}$	15.2
$^{14}\text{N}_2$	2.88
$^{35}\text{Cl}_2$	0.351

* More values are given in the *Resource section*, Table 12D.1.

Rotational Partition Function for Diatomic Molecules

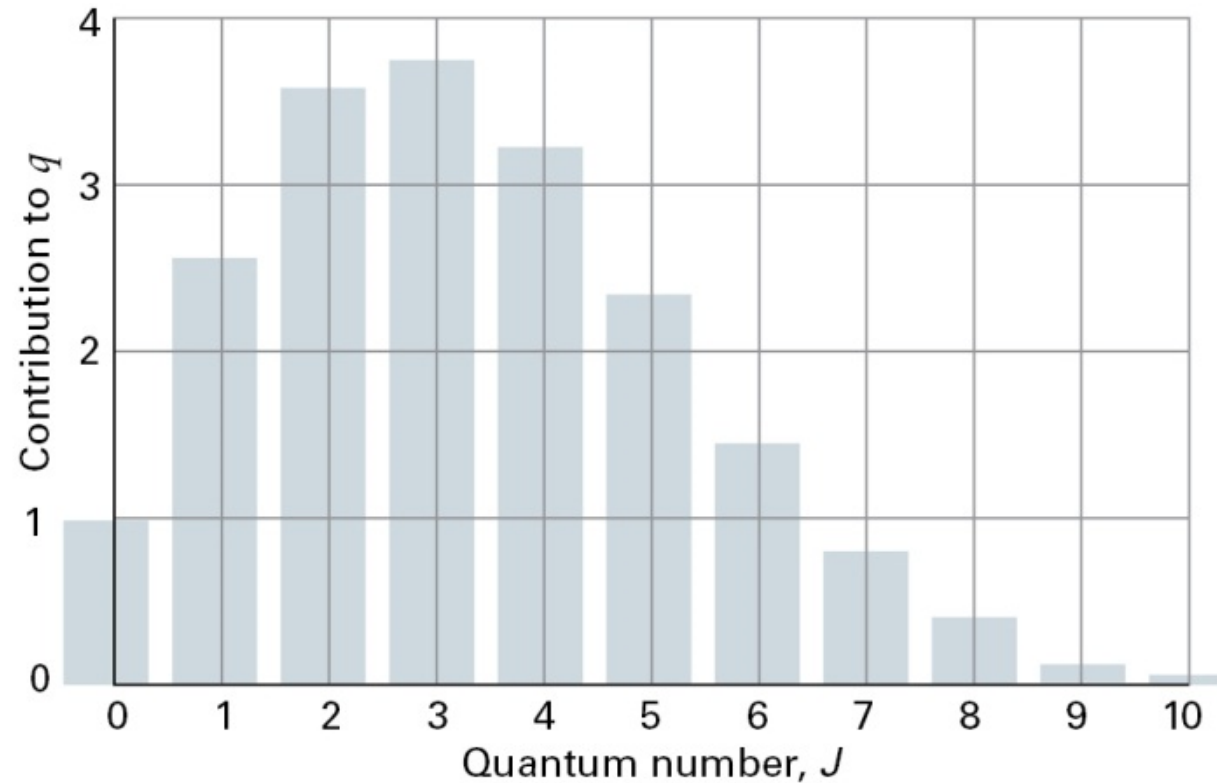


Figure 15B.6 The contributions to the rotational partition function of an HCl molecule at 25 °C. The vertical axis is the value of $(2J+1)e^{-\beta hc\tilde{B}J(J+1)}$. Successive terms (which are proportional to the populations of the levels) pass through a maximum because the population of individual states decreases exponentially, but the degeneracy of the levels increases with J .

Rotational Partition Function for Polyatomic Molecules

- The rotational energy of linear polyatomic molecules is the same as for diatomics, with $\sigma = 1$ for nonsymmetric linear molecules (HCN) and 2 for symmetrical molecules (CO₂).
- General polyatomic molecules may have 3 different values of I (moments of inertia), and so have 3 different rotational temperatures.
 - If symmetries exist, some of the moments of inertia may be equal.

$$q_{rot} = \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} \quad \Theta_A = \frac{h^2}{8\pi^2 I_A k}$$

- The symmetry number, σ , is the distinct number of proper rotational operations, plus the identity operator, *i.e.*, the number is the number of indistinguishable positions in space that can be reached by rigid rotations.

Table 15B.2* Symmetry numbers of molecules

	σ
¹ H ₂	2
¹ H ² H	1
NH ₃	3
C ₆ H ₆	12

Origin of Symmetry Numbers

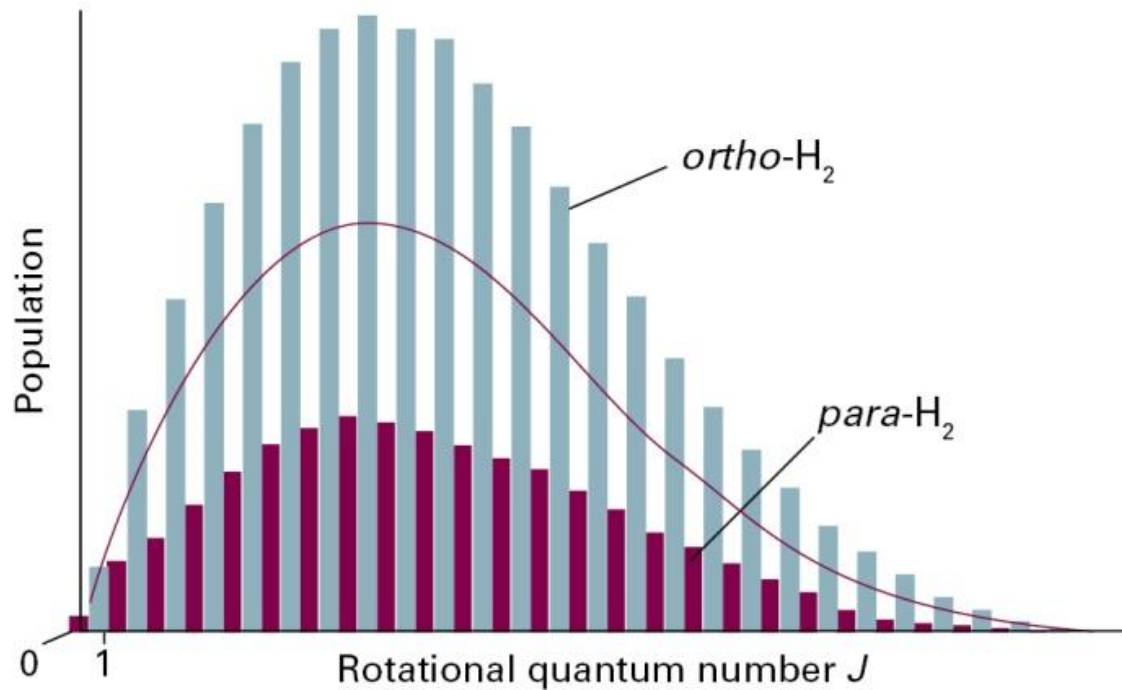


Figure 15B.8 The values of the individual terms $(2J+1)e^{-\beta hc\tilde{B}J(J+1)}$ contributing to the mean partition function of a 3:1 mixture of *ortho*- and *para*-H₂. The partition function is the sum of all these terms. At high temperatures, the sum is approximately equal to the sum of the terms over all values of J , each with a weight of $\frac{1}{2}$. This is the sum of the contributions indicated by the curve.

Quantum mechanical in origin, *viz.*, the Pauli principle forbids occupation of certain states.

e.g. H₂ occupies only even J -states if the nuclear spins are paired (*para*-H₂) and only odd J -states if the spins are parallel (*ortho*-H₂). Get about the same value as if each J term contributed only half its normal value to the sum. Thus, must divide by $\sigma=2$. Similar arguments exist for other symmetries, *e.g.* CO₂:

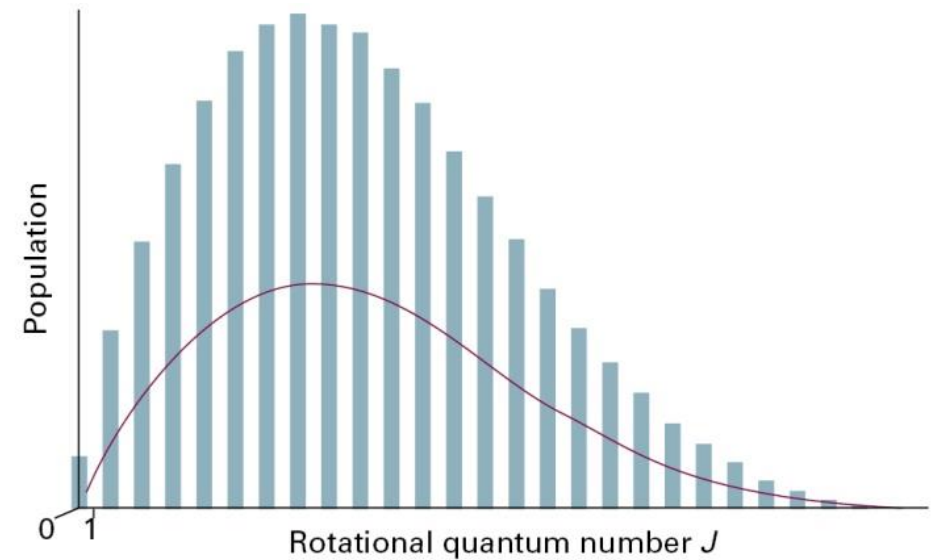


Figure 15B.9 The relative populations of the rotational energy levels of CO₂. Only states with even J values are occupied. The full line shows the smoothed, averaged population of levels.

Vibrational Partition Function

In the harmonic oscillator approximation, the vibrational energy levels in a diatomic molecule form a uniform ladder separated by $\hbar\omega$ ($= hc\tilde{\nu}$).

Thus, using the partition function developed previously for a uniform ladder (Example 15B.1):

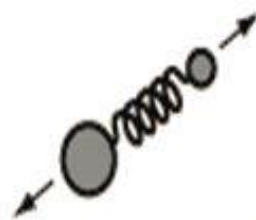
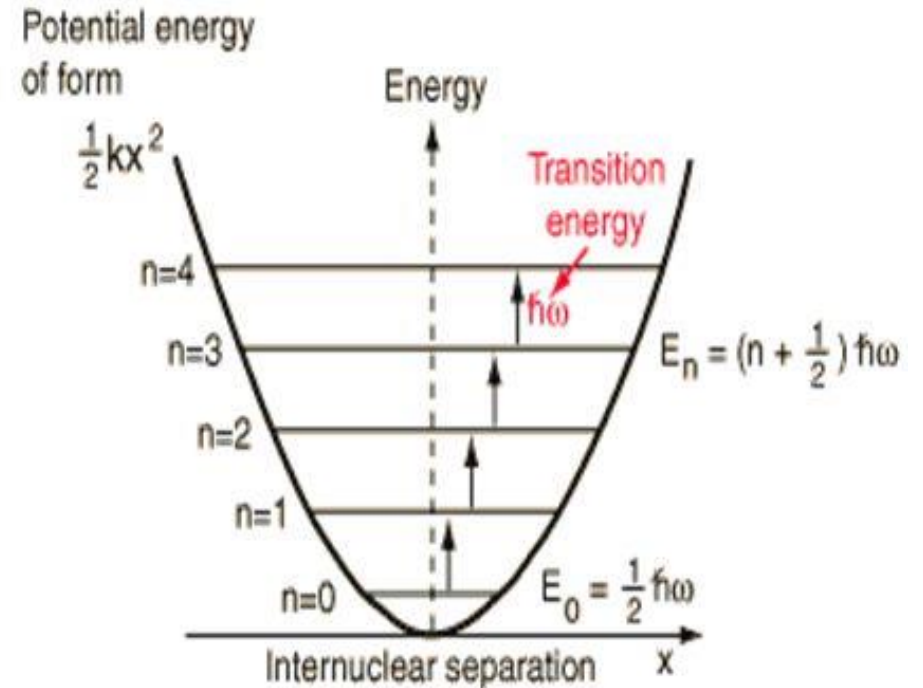
$$q^V = \frac{1}{1 - e^{-\beta\varepsilon}} = \frac{1}{1 - e^{-\beta hc\tilde{\nu}}} = \frac{1}{1 - e^{-\frac{hc\tilde{\nu}}{kT}}} = \frac{1}{1 - e^{-\frac{\theta^V}{T}}}$$

where θ^V is the **characteristic vibrational temperature**, given by

$$\theta^V = \frac{hc\tilde{\nu}}{k}$$

At sufficiently high temperatures, such that $T \gg \theta^V$,

$$q^V \approx \frac{kT}{hc\tilde{\nu}} = \frac{T}{\theta^V}$$



$x=0$ represents the equilibrium separation between the nuclei.

$$\hbar\omega = h\nu$$

$$\hbar = h/2\pi$$

$$\omega = 2\pi\nu$$

$$\tilde{\nu} = \nu/c$$

Vibrational Partition Function

In molecules having sufficiently strong bonds, *e.g.*, C-H bonds ($\sim 1000 - 2000 \text{ cm}^{-1}$), the vibrational wavenumbers are typically large enough that $\beta hc\tilde{\nu} > 1$. In such cases, the exponential term in the denominator of q^V approaches zero, resulting in q^V values very close to 1, indicating that only the zero-point energy level is significantly populated.

By contrast, when molecular bonds are sufficiently weak that $\beta hc\tilde{\nu} \ll 1$, q^V may be approximated by expanding the exponential ($e^x = 1 + x + \dots$):

$$q^V = \frac{1}{1 - e^{-\beta hc\tilde{\nu}}} = \frac{1}{1 - (1 - \beta hc\tilde{\nu} + \dots)} = \frac{1}{1 - \left(1 - \frac{hc\tilde{\nu}}{kT}\right)}$$

Thus, for weak bonds at sufficiently high temperatures:

$$q^V \approx \frac{kT}{hc\tilde{\nu}}$$

Vibrational Partition Function

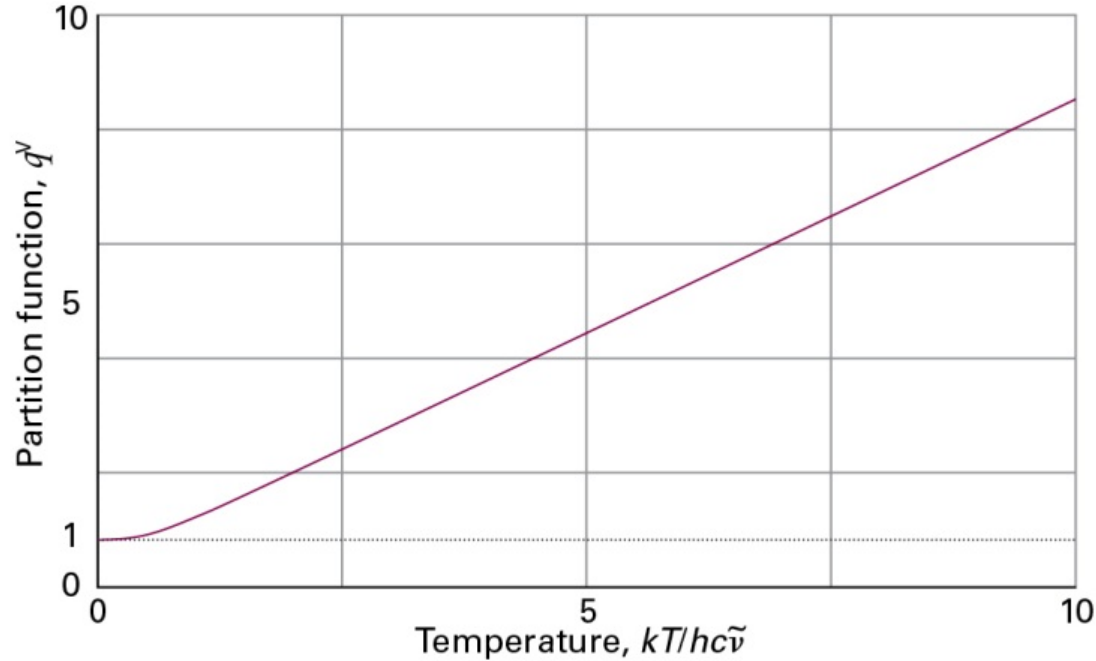


Figure 15B.11 The vibrational partition function of a molecule in the harmonic approximation. Note that the partition function is linearly proportional to the temperature when the temperature is high ($T \gg \theta^v$).

Table 15B.3* Vibrational temperatures of diatomic molecules

	θ^v/K
$^1\text{H}_2$	6332
$^1\text{H}^{35}\text{Cl}$	4304
$^{14}\text{N}_2$	3393
$^{35}\text{Cl}_2$	805

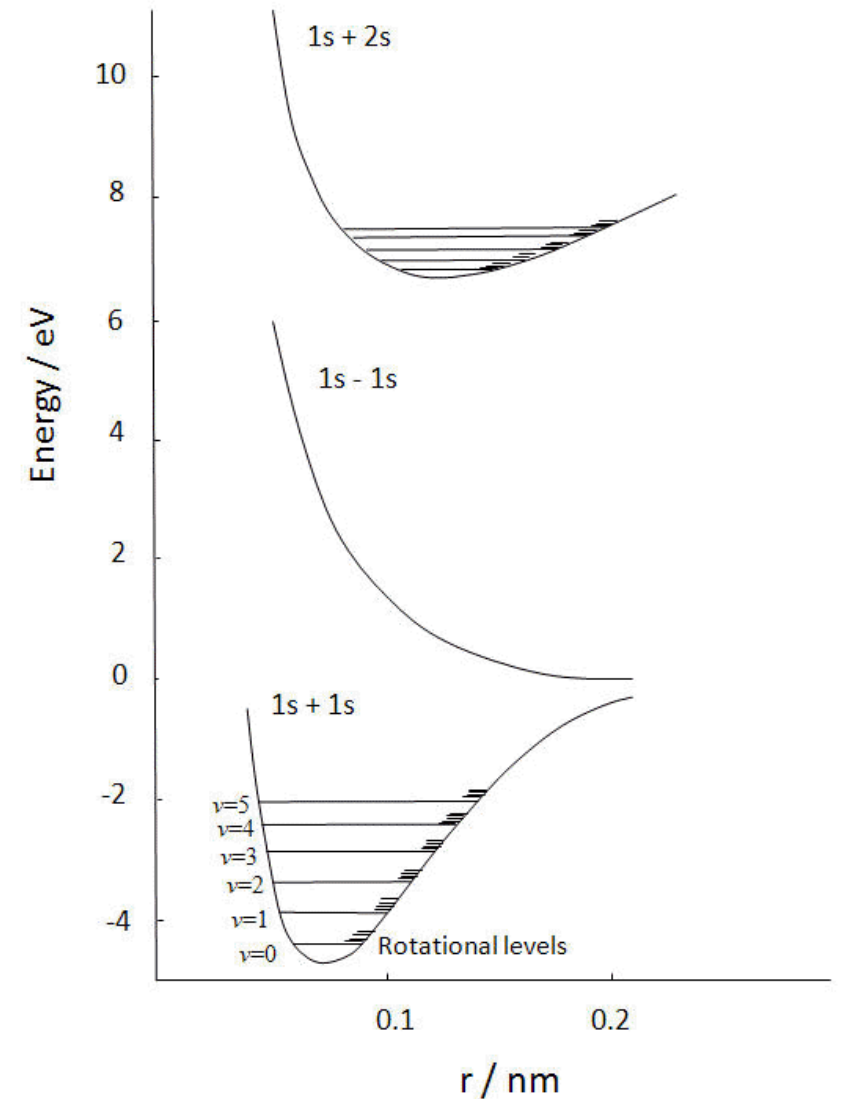
* More values are given in the *Resource section*, Table 12D.1.

Electronic Partition Function

- Except for hydrogen atoms, there are no simple formulas for electronic energy levels from quantum mechanics.
- The partition function for electronic states is:

$$q^E = \sum_{\text{levels}} g_i e^{-\beta \varepsilon_i} = g_0 e^{-\beta \varepsilon_0} + g_1 e^{-\beta \varepsilon_1} + \dots$$

- Because the first excited electronic state is typically well above the ground state, *i.e.*, $\varepsilon_1 - \varepsilon_0 \gg kT$, only the ground state is populated.
- Exceptions are molecules with low lying electronic states, such as NO, NO₂ and O₂.



Electronic, Vibrational and Rotational energy levels for the hydrogen molecule.

Example of Low Lying Excited Electronic State

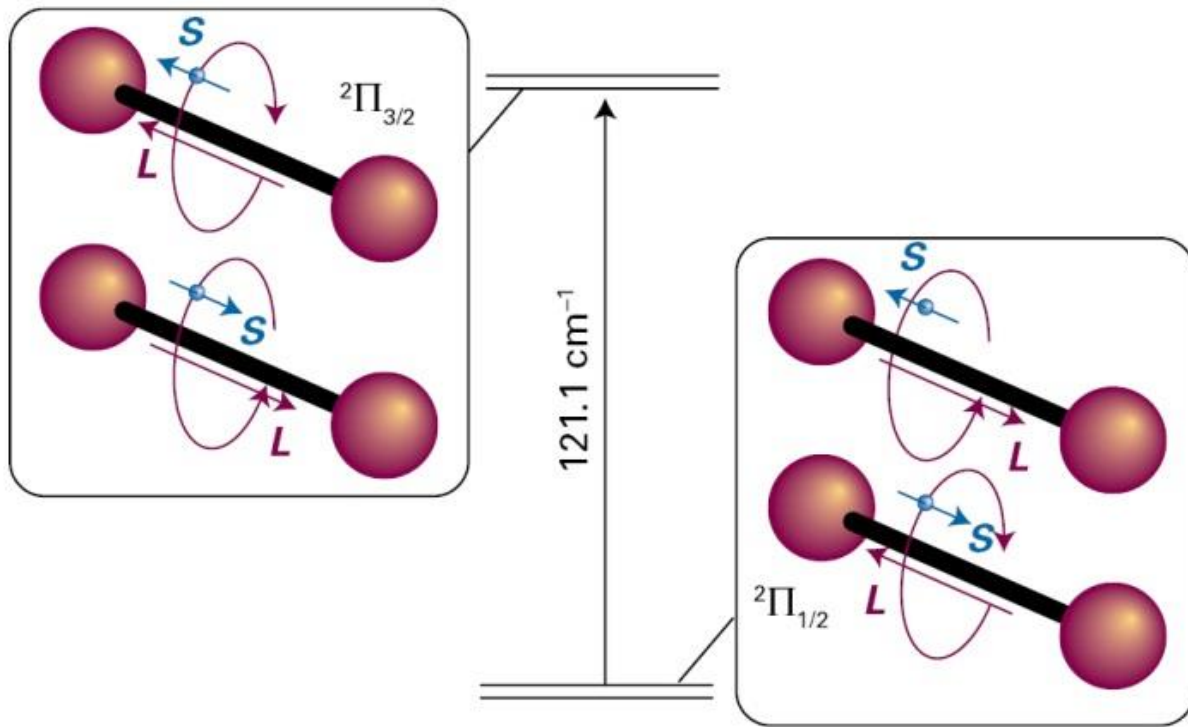


Figure 15B.12 The doubly-degenerate ground electronic level of NO (with the spin and orbital angular momentum around the axis in opposite directions) and the doubly-degenerate first excited level (with the spin and orbital momenta parallel). The upper level is thermally accessible at room temperature.

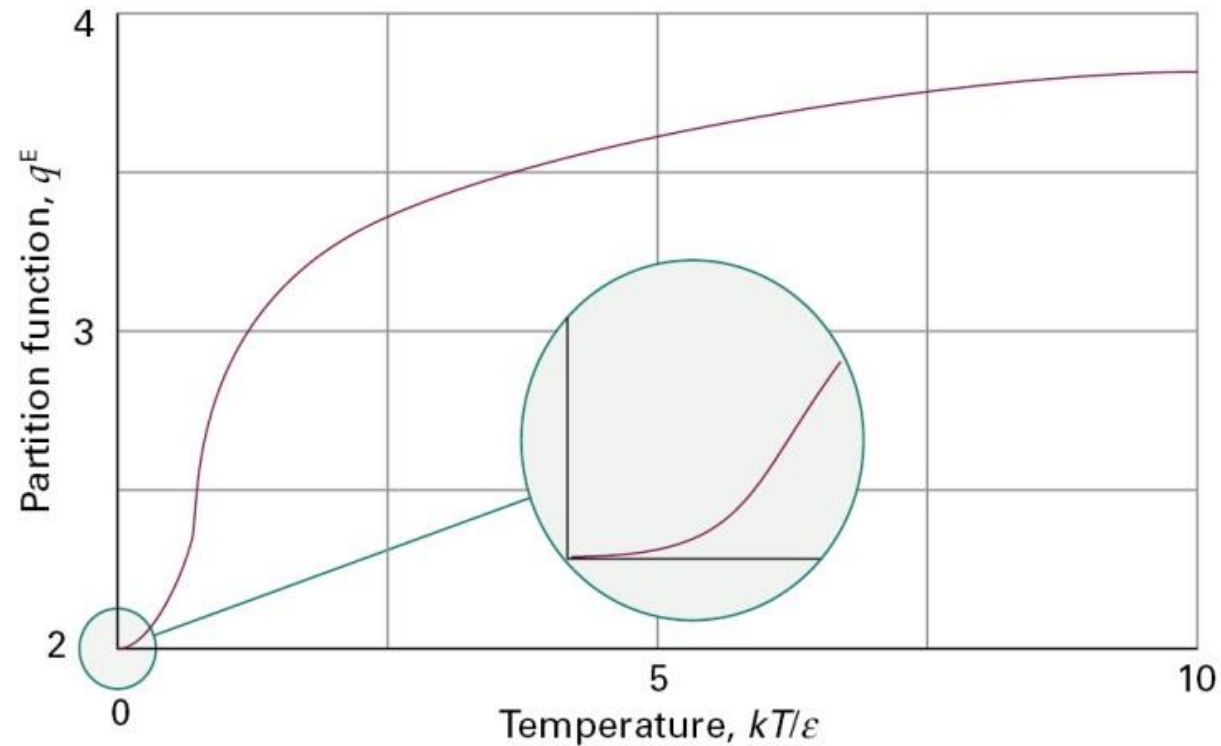


Figure 15B.13 The variation with temperature of the electronic partition function of an NO molecule. Note that the curve resembles that for a two-level system (Fig.15B.3), but rises from 2 (the degeneracy of the lower level) and approaches 4 (the total number of states) at high temperatures.

Mean Molecular Energy

For a system of non-interacting molecules, the mean energy of a molecule $\langle \varepsilon \rangle$, relative to its ground state, is just the total energy of the system, E , divided by the total number of molecules in the system, N :

$$\langle \varepsilon \rangle = \frac{E}{N} = \frac{1}{N} \sum_i N_i \varepsilon_i$$

Because, as shown previously, the overwhelmingly most probable population in a system at temperature T is given by the Boltzmann distribution, ($N_i / N = e^{-\beta \varepsilon_i} / q$), then $\langle \varepsilon \rangle = \frac{1}{q} \sum_i \varepsilon_i e^{-\beta \varepsilon_i}$, where $\beta = 1/kT$.

The latter relationship can be manipulated to express $\langle \varepsilon \rangle$ in terms only of q by recognizing that $\varepsilon_i e^{-\beta \varepsilon_i} = -\frac{\partial(e^{-\beta \varepsilon_i})}{\partial \beta}$

Hence,

$$\langle \varepsilon \rangle = -\frac{1}{q} \sum_i \left(\frac{\partial(e^{-\beta \varepsilon_i})}{\partial \beta} \right)_V = -\frac{1}{q} \frac{\partial}{\partial \beta} \left(\sum_i e^{-\beta \varepsilon_i} \right)_V = -\frac{1}{q} \left(\frac{\partial q}{\partial \beta} \right)_V$$

where the partial derivatives recognize that q may depend on variables (*e.g.*, V) other than only T . Because the above expression gives the mean energy of a molecule *relative to its ground state*, the complete expression for $\langle \varepsilon \rangle$ is:

$$\langle \varepsilon \rangle = \varepsilon_{gs} - \frac{1}{q} \left(\frac{\partial q}{\partial \beta} \right)_V = \varepsilon_{gs} - \left(\frac{\partial \ln q}{\partial \beta} \right)_V$$

This result confirms the very important conclusion that the mean energy of a molecule can be calculated knowing only the partition function (as a function of temperature).

Mean Molecular Energy

Comparison of the fraction of populations *vs.* the total energy of a two-level system.

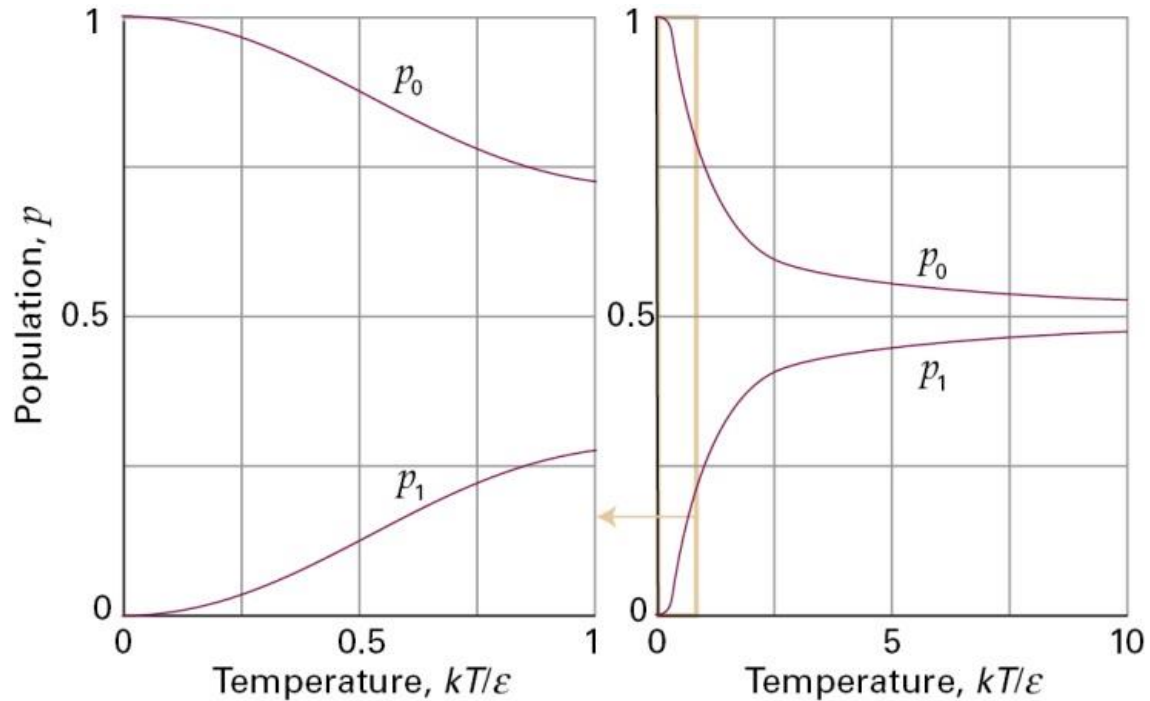


Figure 15B.5 The fraction of populations of the two states of a two-level system as a function of temperature (eqn 15B.4). Note that as the temperature approaches infinity, the populations of the two states become equal (and the fractions both approach 0.5).

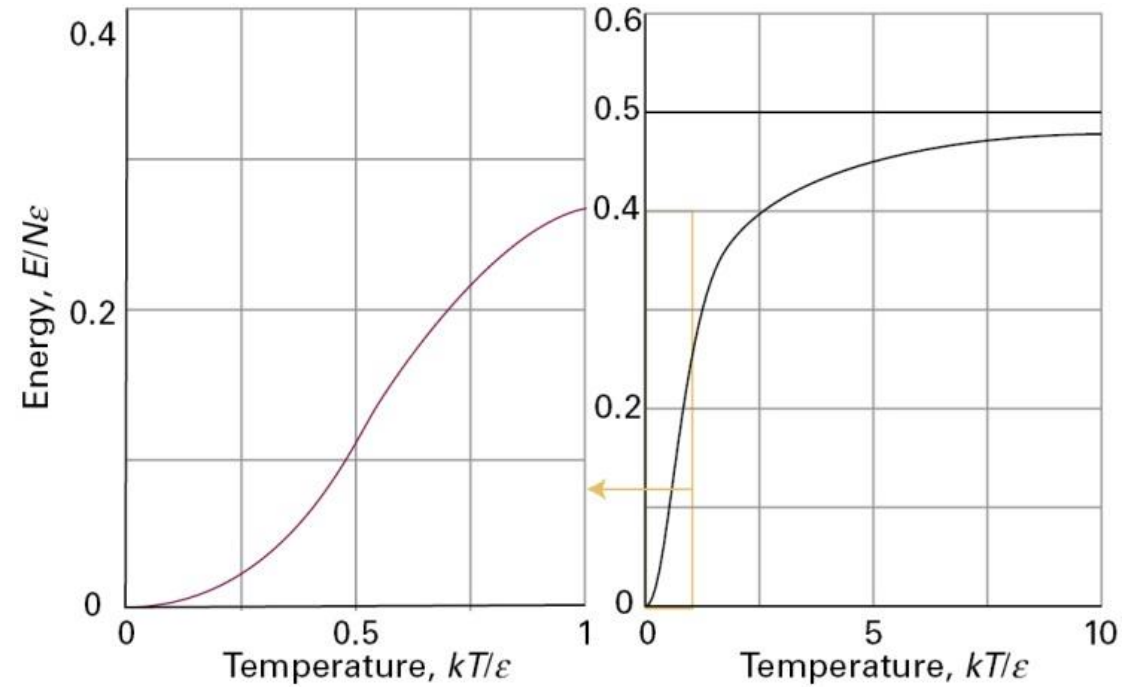


Figure 15C.1 The total energy of a two-level system (expressed as a multiple of $N\epsilon$) as a function of temperature, on two temperature scales. The graph on the left shows the slow rise away from zero energy at low temperatures; the slope of the graph at $T=0$ is 0. The graph on the right shows the slow rise to 0.5 as $T \rightarrow \infty$ as both states become equally populated.

Translational Energy

Each of the three modes of motion (translational, rotational, and vibrational), as well as the potential energies represented by the electronic state and electron spins, contributes to the overall mean energy of a system.

Translational Contribution:

As developed previously, for a three-dimensional container of volume V , the translational partition function is given by

$$q^T = \frac{V}{\Lambda^3} = \frac{V}{h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2} = \frac{V}{h^3} (2\pi m k T)^{3/2}$$

where Λ^3 is essentially a constant multiplied by $\beta^{3/2}$. Thus,

$$\begin{aligned} \langle \varepsilon^T \rangle &= -\frac{1}{q^T} \left(\frac{\partial q^T}{\partial \beta} \right)_V = -\frac{\Lambda^3}{V} \left(\frac{\partial V}{\partial \beta \Lambda} \right)_V \\ &= \frac{C \times \beta^{3/2}}{V} \times V \times \frac{d}{d\beta} \left(\frac{1}{C \times \beta^{3/2}} \right) \\ &= -\beta^{3/2} \frac{d}{d\beta} \left(\frac{1}{\beta^{3/2}} \right) = \frac{3}{2\beta} = \frac{3}{2} kT \end{aligned}$$

In one dimension, $\langle \varepsilon^T \rangle = \frac{1}{2} kT$

Rotational Energy

As developed previously, the rotational partition function for a linear molecule is given by:

$$q^R = \sum_i (2J + 1) e^{-\frac{J(J+1)h^2}{8\pi^2 IkT}} = \sum_i (2J + 1) e^{-\beta hc \tilde{B} J(J+1)}$$

At sufficiently low temperatures, such that $T < \theta^R = hc\tilde{B}/k$, the term by term sum for a non-symmetrical molecule gives

$$q^R = 1 + 3e^{-2\beta hc \tilde{B}} + 5e^{-6\beta hc \tilde{B}} + \dots$$

Taking the derivative of q^R with respect to β gives

$$\frac{dq^R}{d\beta} = -hc\tilde{B}(6e^{-2\beta hc \tilde{B}} + 30e^{-6\beta hc \tilde{B}} + \dots)$$

Hence,

$$\langle \varepsilon^R \rangle = -\frac{1}{q^R} \frac{dq^R}{d\beta} = \frac{hc\tilde{B}(6e^{-2\beta hc \tilde{B}} + 30e^{-6\beta hc \tilde{B}} + \dots)}{1 + 3e^{-2\beta hc \tilde{B}} + 5e^{-6\beta hc \tilde{B}} + \dots}$$

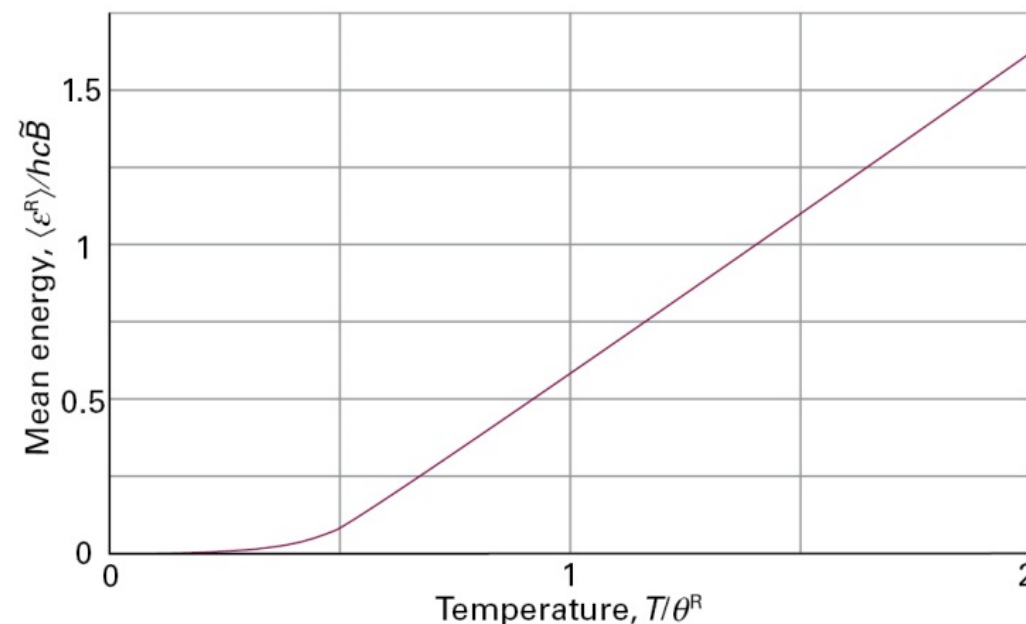


Figure 15C.2 The mean rotational energy of a non-symmetrical linear rotor as a function of temperature. At high temperatures ($T \gg \theta^R$), the energy is linearly proportional to the temperature, in accord with the equipartition theorem.

Rotational Energy

At high temperatures ($T \gg \theta^R$),

$$q^R = \frac{T}{\sigma \theta^R} = \frac{1}{\sigma \beta h c \tilde{B}}$$

Thus,

$$\begin{aligned} \langle \varepsilon^R \rangle &= -\frac{1}{q^R} \frac{dq^R}{d\beta} = -\sigma \beta h c \tilde{B} \frac{d}{d\beta} \left(\frac{1}{\sigma \beta h c \tilde{B}} \right) \\ &= -\beta \frac{d}{d\beta} \frac{1}{\beta} = \frac{1}{\beta} = kT \end{aligned}$$

Vibrational Energy

As developed previously, the vibrational partition function for the harmonic oscillator approximation is:

$$q^V = \frac{1}{1 - e^{-\beta hc\tilde{\nu}}}$$

Because q^V is independent of volume it can be differentiated with respect to β :

$$\frac{dq^V}{d\beta} = \frac{d}{d\beta} \left(\frac{1}{1 - e^{-\beta hc\tilde{\nu}}} \right) = \frac{hc\tilde{\nu} e^{-\beta hc\tilde{\nu}}}{(1 - e^{-\beta hc\tilde{\nu}})^2}$$

and since the mean energy $\langle \varepsilon \rangle$ is given by

$$\langle \varepsilon^V \rangle = - \frac{1}{q^V} \frac{dq^V}{d\beta} = (1 - e^{-\beta hc\tilde{\nu}}) \frac{hc\tilde{\nu} e^{-\beta hc\tilde{\nu}}}{(1 - e^{-\beta hc\tilde{\nu}})^2} = \frac{hc\tilde{\nu} e^{-\beta hc\tilde{\nu}}}{1 - e^{-\beta hc\tilde{\nu}}}$$

then

$$\langle \varepsilon^V \rangle = \frac{hc\tilde{\nu}}{e^{\beta hc\tilde{\nu}} - 1}$$

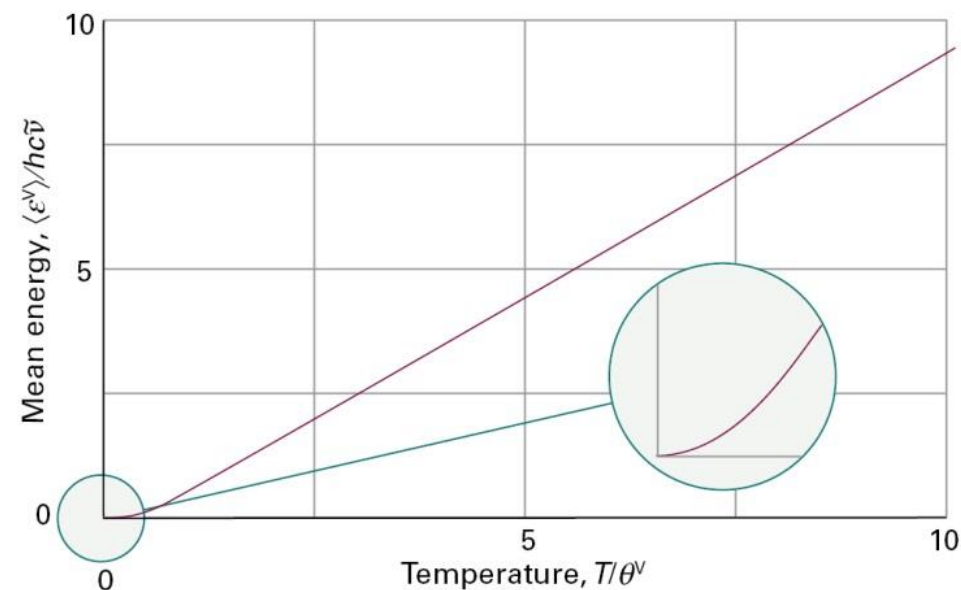


Figure 15C.3 The mean vibrational energy of a molecule in the harmonic approximation as a function of temperature. At high temperatures ($T \gg \theta^V$), the energy is linearly proportional to the temperature, in accord with the equipartition theorem.

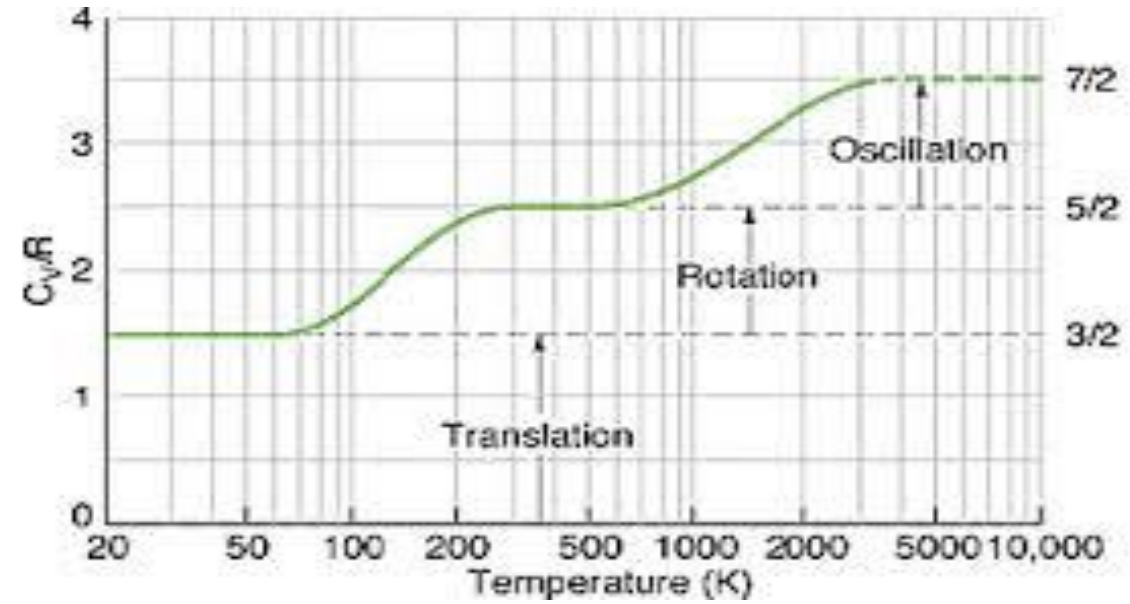
At high temperatures, $T \gg \theta^V = hc\tilde{\nu}/k$, so

$$\langle \varepsilon^V \rangle = \frac{hc\tilde{\nu}}{e^{\beta hc\tilde{\nu}} - 1} = \frac{hc\tilde{\nu}}{(1 + \beta hc\tilde{\nu} + \dots) - 1} \approx \frac{1}{\beta} = kT$$

However, because most values of θ^V are very high, ($> 1000\text{K}$) this condition is seldom satisfied.

Equipartition of Energy

- Degrees of freedom receive equal amounts of energy, each of $\frac{1}{2} kT$.
- In diatomic molecules at sufficiently high temperature:
 - 3 translational degrees of freedom = $\frac{3}{2} kT$
 - 2 rotational degrees of freedom = kT
 - vibrational potential and kinetic energy = kT
- At sufficiently low temperatures, only the ground state is significantly populated. This causes degrees of freedom to *freeze out* and not contribute to the heat capacity.
 - This can be seen in the treatment of the vibrational partition function, as well as in the two-level system discussed previously.
 - Note that the treatment of the rotational partition function on the previous slides cannot predict the freezing out of the rotational degrees of freedom, because the energy levels were approximated as a continuum using the integral.



Electronic & Electron Spin Energies

Electronic Energies

Because statistical energies are measured relative to the ground state, and only the ground electronic state is usually occupied, then

$$\langle \varepsilon^E \rangle = 0$$

and

$$q^E = 1$$

Electron Spin Energies

An electron spin in a magnetic field \mathcal{B} can have two possible energy states ($\varepsilon_{-1/2} = 0$ and $\varepsilon_{+1/2} = 2\mu_B\mathcal{B}$) and energy given by

$$E_{m_s} = 2\mu_B\mathcal{B}m_s$$

where m_s is the magnetic quantum number, and μ_B is the Bohr magneton ($e\hbar/2m_e = 9.274 \times 10^{-24}$ J/T).

The spin partition function is therefore $q^S = \sum_{m_s} e^{-\beta\varepsilon_{m_s}} = 1 + e^{-2\beta\mu_B\mathcal{B}}$

and the mean energy of the spin is $\langle \varepsilon^S \rangle = 2\mu_B\mathcal{B} / (e^{2\beta\mu_B\mathcal{B}} + 1)$

Internal Energy and the Partition Function

As described previously, the mean energy of a system of independent *non-interacting* molecules is given by:

$$\langle \varepsilon \rangle = -\frac{1}{q} \left(\frac{\partial q}{\partial \beta} \right)_v$$

where $\beta = 1/kT$.

For a system containing N molecules, the total energy is thus $N\langle \varepsilon \rangle$, so the internal energy $U(T)$ is:

$$U(T) = U(0) + N\langle \varepsilon \rangle = U(0) - \frac{N}{q} \left(\frac{\partial q}{\partial \beta} \right)_v = U(0) - N \left(\frac{\partial \ln q}{\partial \beta} \right)_v$$

If the system consists of *interacting* molecules (e.g., a non-ideal gas), then the canonical partition function Q must be used:

$$U(T) = U(0) - \left(\frac{\partial \ln Q}{\partial \beta} \right)_v$$

Heat Capacity and the Partition Function

Recall that the constant-volume heat capacity is:

$$C_v = \left(\frac{\partial U}{\partial T} \right)_V$$

As shown previously, the mean vibrational energy of a collection of harmonic oscillators is given by

$$\langle \varepsilon^V \rangle = \frac{hc\tilde{\nu}}{e^{\beta hc\tilde{\nu}} - 1} = \frac{k\theta^v}{e^{\theta^v/T} - 1}$$

where $\theta^v = hc\tilde{\nu} / k$ is the characteristic vibrational temperature. Thus, the vibrational contribution to the molar heat capacity at constant volume is

$$C_{v,m}^V = \frac{dN_A \langle \varepsilon^V \rangle}{dT} = R\theta^v \frac{d}{dT} \frac{1}{e^{\theta^v/T} - 1} = R \left(\frac{\theta^v}{T} \right)^2 \frac{e^{\theta^v/T}}{\left(e^{\theta^v/T} - 1 \right)^2}$$

or, expressed as a function of temperature:

$$C_{v,m}^V = Rf(T), \text{ where } Rf(T) = \left(\frac{\theta^v}{T} \right)^2 \left(\frac{e^{-\theta^v/2T}}{1 - e^{-\theta^v/T}} \right)^2$$

Heat Capacity and the Partition Function

If the derivative with respect to T is converted into a derivative with respect to β , then C_v can be expressed as

$$C_v = -k\beta^2 \left(\frac{\partial U}{\partial \beta} \right)_V = -Nk\beta^2 \left(\frac{\partial \langle \epsilon \rangle}{\partial \beta} \right)_V = Nk\beta^2 \left(\frac{\partial^2 \ln q}{\partial \beta^2} \right)_V$$

If $T \gg \theta^M$, where θ^M is the characteristic temperature of each mode ($\theta^R = hc\tilde{B}/k$ and $\theta^V = hc\tilde{\nu}/k$), then the equipartition theorem can be applied. In this case, each of the three translational modes contributes $\frac{1}{2}R$. If the rotational modes are represented by ν^{R*} , then $\nu^{R*} = 2$ for linear molecules and 3 for non-linear molecules, so the total rotational contribution is $\frac{1}{2}\nu^{R*}R$. If the temperature is sufficiently high for ν^{V*} vibrational modes to be active, then the vibrational contribution is $\nu^{V*}R$. Thus, the total molar heat capacity is:

$$C_{V,m} = \frac{1}{2} (3 + \nu^{R*} + 2\nu^{V*})R$$

In most cases, $\nu^{V*} = 0$.

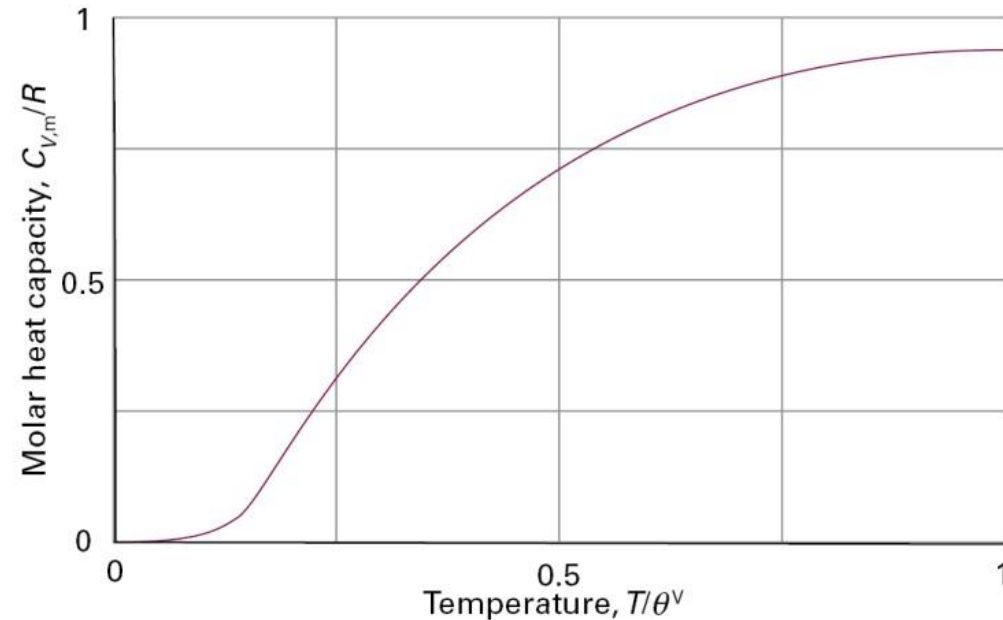


Figure 15E.1 The temperature dependence of the vibrational heat capacity of a molecule in the harmonic approximation calculated by using eqn 15E.3. Note that the heat capacity is within 10 per cent of its classical value for temperatures greater than θ^V .

Entropy and the Partition Function

Boltzmann equation:

$$S = k \ln W$$

where S is the statistical entropy, and W is the weight of the most probable configuration of the system. The Boltzmann Equation is one of the most important relationships in statistical thermodynamics, and the statistical entropy is identical to the thermodynamic entropy, behaving exactly the same in all respects.

- As the temperature decreases, for example, S decreases because fewer configurations are consistent with the constant total energy of the system.
- As $T \rightarrow 0$, $W \rightarrow 1$, so $\ln W = 0$, since only one configuration (*viz.*, the one in which every molecule is in the lowest level) is consistent with $E = 0$.
- As $S \rightarrow 0$, $T \rightarrow 0$, which is consistent with the Third Law of thermodynamics, *i.e.*, that the entropies of all perfect crystals approach zero as $T \rightarrow 0$.

Entropy and the Partition Function

Relationship of Boltzmann Equation to the partition function

- For a system of *non-interacting and distinguishable* molecules,
$$S(T) = \frac{U(T) - U(0)}{T} + Nk \ln q$$
- For a system of *non-interacting and indistinguishable* molecules (e.g., a gas of identical molecules),
$$S(T) = \frac{U(T) - U(0)}{T} + Nk \ln \frac{q}{N}$$
- For a system of *interacting* molecules, use the canonical partition function,
$$S(T) = \frac{U(T) - U(0)}{T} + Nk \ln Q$$

Entropy and the Partition Function

As shown previously, the total energy of a molecule can be closely approximated by the sum of the independent contributions from translational (T), rotational (R), vibrational (V), and electronic (E) energies. The total entropy can be similarly treated as a sum of individual contributions.

- For a system of *distinguishable, non-interacting* molecules, each contribution has the form of that for $S(T)$ above:

$$S(T) = \frac{\{U(T) - U(0)\}^M}{T} + Nk \ln q^M \quad (\text{for } M = R, V, \text{ or } E)$$

- For $M = T$, the molecules are indistinguishable, so

$$S(T) = \frac{\{U(T) - U(0)\}^T}{T} + Nk \ln \frac{q^T}{N}$$

Translational Entropy: The Sackur-Tetrode Equation

For a system consisting of a perfect monatomic gas, only translation contributes to the total energy and molar entropy, which is described by the Sackur-Tetrode Equation:

$$S_m = R \ln \left(\frac{V_m e^{5/2} (2\pi mkT)^{3/2}}{N_A h^3} \right) = R \ln \left(\frac{V_m e^{5/2}}{N_A \Lambda^3} \right) = k \ln \left(\frac{V_m e^{5/2}}{\Lambda^3} \right)$$

where Λ is the thermal wavelength $(h/(2\pi mkT))^{1/2}$ described previously, V_m is the molar volume, N_A is Avogadro's Number, and $R/N_A = k$.

Since for a perfect gas $V_m = RT/p$, then S_m can be calculated from $S_m = R \ln \left(\frac{RTe^{5/2}}{p^\circ N_A \Lambda^3} \right) = R \ln \left(\frac{kTe^{5/2}}{p^\circ \Lambda^3} \right)$

Re-writing the Sackur-Tetrode Equation in the form: $S = nR \ln \left(\frac{Ve^{5/2}}{nN_A \Lambda^3} \right) = nR \ln aV$, where $a = \frac{e^{5/2}}{nN_A \Lambda^3}$

shows that when a perfect monatomic gas expands isothermally from V_i to V_f , ΔS is given by:

$$\Delta S = nR \ln aV_f - nR \ln aV_i = nR \ln \frac{V_f}{V_i}$$

which is identical to the expression determined from the thermodynamic definition of entropy.

Entropy: Rotational Contribution

At sufficiently high temperatures, where $T > \theta^R (= hc\tilde{B} / k)$, which is usually the case, then $q^R = kT / \sigma hc\tilde{B} = T / \sigma\theta^R$, and the equipartition theorem predicts the rotational contribution to the molar entropy to be RT . Therefore,

$$S_m^R = \frac{U_m - U(0)}{T} + R \ln q^R = R \left(1 + \ln \frac{kT}{\sigma hc\tilde{B}} \right) = R \left(1 + \ln \frac{T}{\sigma\theta^R} \right)$$

Hence, this relationship indicates that

- The rotational contribution to the entropy increases with increasing T because more rotational states become accessible.
- The rotational contribution will be large when the rotational constant \tilde{B} is small because then the rotational levels are more closely spaced.

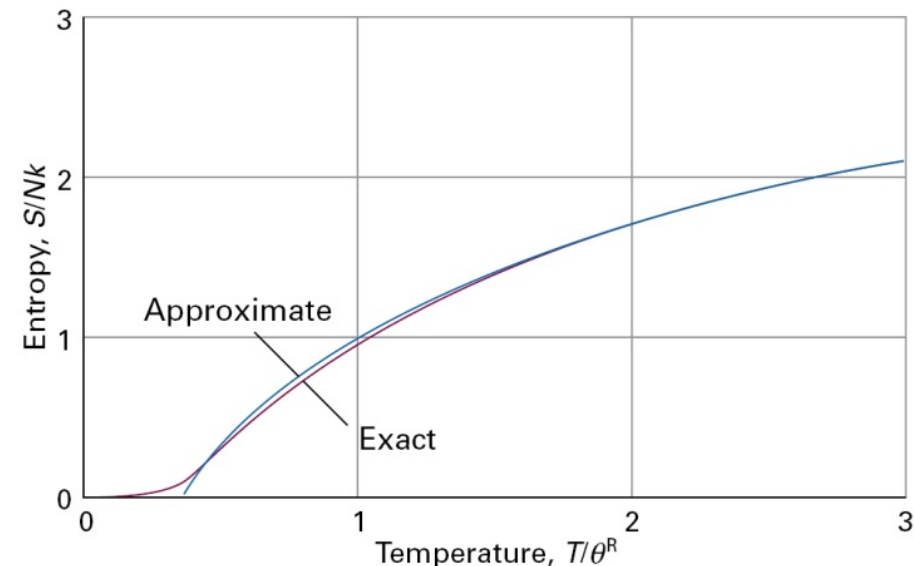


Figure 15E.4 The variation of the rotational contribution to the entropy of a linear molecule ($\sigma=1$) using the high-temperature approximation and the exact expression (the latter evaluated up to $J=20$).

Entropy: Vibrational Contribution

The vibrational contribution to the molar entropy, S_m^V , can be obtained by combining $q^V (= 1/(1 - e^{-\beta\varepsilon}))$ with $\langle \varepsilon^V \rangle = \varepsilon / (e^{\beta\varepsilon} - 1)$, the mean vibrational energy:

$$\begin{aligned} S_m^V &= \frac{U_m - U_m(0)}{T} + R \ln q^V = \frac{N_A k \beta \varepsilon}{e^{\beta\varepsilon} - 1} + R \ln \frac{1}{1 - e^{-\beta\varepsilon}} \\ &= R \left\{ \frac{\beta\varepsilon}{e^{\beta\varepsilon} - 1} - \ln(1 - e^{-\beta\varepsilon}) \right\} = R \left\{ \frac{\beta h c \tilde{\nu}}{e^{\beta h c \tilde{\nu}} - 1} - \ln(1 - e^{-\beta h c \tilde{\nu}}) \right\} \end{aligned}$$

where the final equality occurs because $\varepsilon = h c \tilde{\nu}$.

- Both terms in the right-hand equality approach 0 as $T \rightarrow 0$, so $S = 0$ at $T = 0$.
- S increases as T increases because more vibrational states become thermally accessible.
- At a given T , S is larger for higher M.W. molecules than for lower M.W. because their energy levels are more closely spaced, and thus more are thermally accessible.

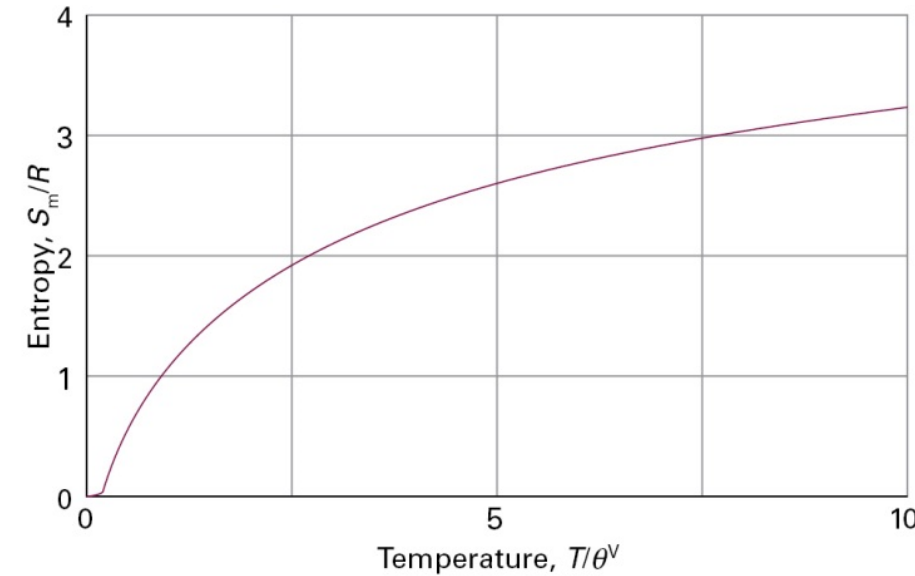


Figure 15E.5 The temperature variation of the molar entropy of a collection of harmonic oscillators expressed as a multiple of $R=Nk$. The molar entropy approaches zero as $T \rightarrow 0$, and increases without limit as $T \rightarrow \infty$.

Derived Functions: Enthalpy and Gibbs Energy

Can use various thermodynamic relationships to calculate other quantities. In all of the equations below, the canonical partition function Q is related to the molecular partition function q by $Q = q^N$ for distinguishable molecules, and $Q = q^N/N!$ for indistinguishable molecules (*e.g.*, as in a gas).

As shown previously, the internal energy and entropy are related to the partition function as follows:

$$U(T) = U(0) - \left(\frac{\partial \ln Q}{\partial \beta} \right)_V \quad S(T) = \frac{U(T) - U(0)}{T} + k \ln Q$$

The partition function also can be used to calculate the pressure, enthalpy, and Gibbs Energy:

$$H = U + PV \quad H(T) = H(0) - \left(\frac{\partial \ln Q}{\partial \beta} \right)_V + kTV \left(\frac{\partial \ln Q}{\partial V} \right)_T$$

$$G = H - TS = A + PV \quad G(T) = G(0) - kT \ln Q + kTV \left(\frac{\partial \ln Q}{\partial V} \right)_T$$

$$G(T) = G(0) - nRT \ln \frac{q}{N}$$

(From $Q = q^N/N!$ and $\ln Q = N \ln q - \ln N!$ and $\ln N! = N \ln N - N$)

$$G(T) = G(0) - nRT \ln \frac{q_m}{N_A}$$

Contributions to Molar Thermodynamic Properties of Ideal Gases

Θ is the relevant characteristic temperature, σ is the symmetry number of the molecule, g is the degeneracy of the state, q is the single-molecule partition function, Q is the canonical partition function, and D_0 is the dissociation energy. A symbol with a bar over it is a molar quantity. All other symbols have their standard meanings.

Quantity	Translation	Vibration	Rotation		Electronic
			Linear Molecules	Nonlinear Molecules	
\bar{U}/R	$\frac{3}{2}T$	$\sum_i \frac{\Theta_{vj}}{\exp(+\Theta_{vj}/T) - 1}$	T	$\frac{3}{2}T$	0
\bar{H}/R	$\frac{5}{2}T$	$\sum_i \frac{\Theta_{vj}}{\exp(+\Theta_{vj}/T) - 1}$	T	$\frac{3}{2}T$	0
\bar{C}_v/R	$\frac{3}{2}$	$\sum_i \frac{(\Theta_{vj}/T)^2 \exp(+\Theta_{vj}/T)}{[\exp(+\Theta_{vj}/T) - 1]^2}$	1	$\frac{3}{2}$	0
\bar{C}_p/R	$\frac{5}{2}$	$\sum_i \frac{(\Theta_{vj}/T)^2 \exp(+\Theta_{vj}/T)}{[\exp(+\Theta_{vj}/T) - 1]^2}$	1	$\frac{3}{2}$	0
\bar{S}/R	$\frac{5}{2} + \ln \left[\left(\frac{2\pi mkT}{b^2} \right)^{3/2} \frac{kT}{P} \right]$	$\sum_i \left\{ \frac{\Theta_{vj}/T}{\exp(+\Theta_{vj}/T) - 1} - \ln \left[1 - \exp \left(-\frac{\Theta_{vj}}{T} \right) \right] \right\}$	$1 + \ln \frac{T}{\sigma \Theta_r}$	$\frac{3}{2} + \ln \left(\frac{\pi T^3}{\sigma^2 \Theta_a \Theta_b \Theta_c} \right)^{1/2}$	$\ln g_0$
\bar{A}/R	$-T \ln \left[\left(\frac{2\pi mkT}{b^2} \right)^{3/2} \frac{kT}{P} \right] - T$	$\sum_i T \ln [1 - \exp(-\Theta_{vj}/T)]$	$-T \ln \frac{T}{\sigma \Theta_r}$	$-T \ln \left(\frac{\pi T^3}{\sigma^2 \Theta_a \Theta_b \Theta_c} \right)^{1/2}$	$-T \ln g_0$
$\bar{G}/R = \mu/R$	$-T \ln \left[\left(\frac{2\pi mkT}{b^2} \right)^{3/2} \frac{kT}{P} \right]$	$\sum_i T \ln [1 - \exp(-\Theta_{vj}/T)]$	$-T \ln \frac{T}{\sigma \Theta_r}$	$-T \ln \left(\frac{\pi T^3}{\sigma^2 \Theta_a \Theta_b \Theta_c} \right)^{1/2}$	$-T \ln g_0$

Statistical Mechanical Relations for Ideal Gases

Quantity	Translation	Vibration	Rotation		Electronic
			Linear Molecules	Nonlinear Molecules	
q	$\left(\frac{2\pi mkT}{b^2}\right)^{3/2} V$	$\frac{1}{1 - \exp(-\Theta_v/T)}$	$\frac{T}{\sigma\Theta_r}$	$\left(\frac{\pi T^3}{\sigma^2\Theta_a\Theta_b\Theta_c}\right)^{1/2}$	$g_0 \exp(-D_0/RT)$
ϵ	$\frac{b^2(n_x^2 + n_y^2 + n_z^2)}{8mV^{2/3}}$	$(n + 1/2)bv$	$\frac{J(J+1)b^2}{8\pi^2 I}$	Varies	Varies
Θ	$\frac{\epsilon_t}{k}$	$\frac{bv}{k} = \frac{bc\tilde{\nu}}{k}$	$\frac{b^2}{8\pi^2 I k}$	$\frac{b^2}{8\pi^2 I_a k}$, etc.	$\frac{\epsilon_e}{k}$
g	1	1		$2J + 1$	Varies

$$Q = q^N / N!$$

$$q = \sum_i g_i \exp(-\epsilon_i / kT)$$

$$A = -kT \ln Q$$

$$\ln N! \approx N \ln N - N$$

Equilibrium Constants

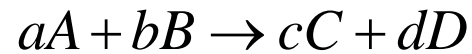
As shown previously, the equilibrium constant K of a reaction is related to the standard Gibbs energy of reaction, $\Delta_r G^\circ$, ($p = 1$ bar) by:

$$\Delta_r G^\circ = -RT \ln K$$

From statistical thermodynamics, the Gibbs energy is related to the molar partition function by:

$$q_m = q/n \quad \text{and} \quad G(T) = G(0) - kT \ln Q + kTV \left(\frac{\partial \ln Q}{\partial V} \right)_T$$

In order to calculate a value for K , these equations must be combined. To develop an expression for K , the standard molar Gibbs energy, G°/n , must be determined for each reactant and product in the reaction. For the gas-phase reaction,



it can be shown that the equilibrium constant is given by:

$$K = \frac{(q_{C,m}^\circ / N_A)^c (q_{D,m}^\circ / N_A)^d}{(q_{A,m}^\circ / N_A)^a (q_{B,m}^\circ / N_A)^b} e^{-\Delta_r E_0 / RT}$$

Equilibrium Constants

where $\Delta_r E_0$ is the difference in molar energies of the ground states of the products and reactants and is calculated from the bond dissociation energies of the various reaction species, *i.e.*, $D_0(\text{products}) - D_0(\text{reactants})$.

Using the symbolism of (signed) stoichiometric numbers that was introduced previously, K is given by:

$$K = \left\{ \prod_J \left(\frac{q_{J,m}^\circ}{N_A} \right)^{\nu_J} \right\} e^{-\Delta_r E_0 / RT}$$

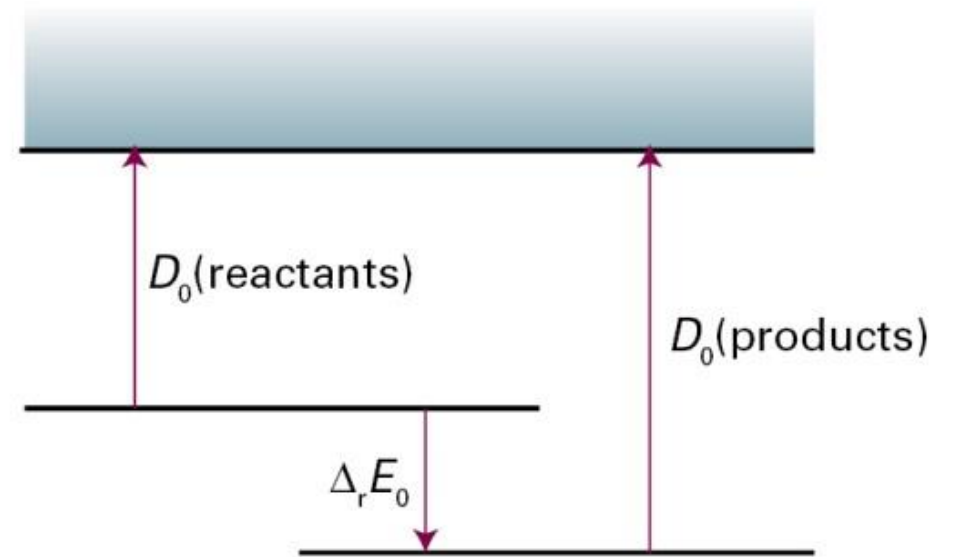


Figure 15F.1 The definition of $\Delta_r E_0$ for the calculation of equilibrium constants.

Contributions to equilibrium constants

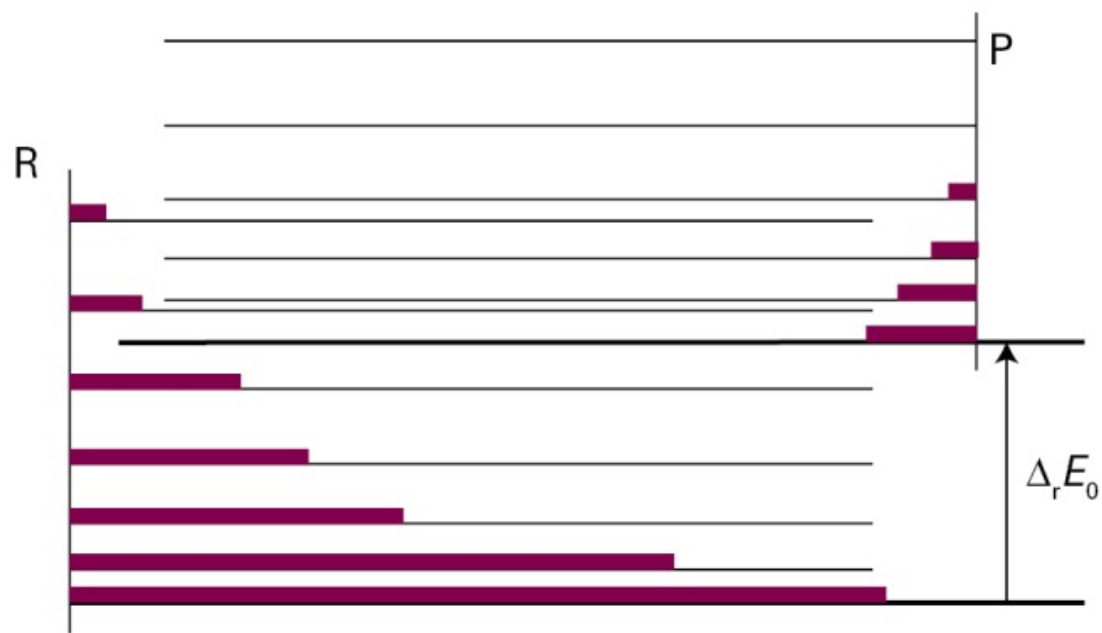


Figure 15F.2 The array of R(eactants) and P(rodacts) energy levels. At equilibrium all are accessible (to differing extents, depending on the temperature), and the equilibrium composition of the system reflects the overall Boltzmann distribution of populations. As $\Delta_r E_0$ increases, R becomes dominant.

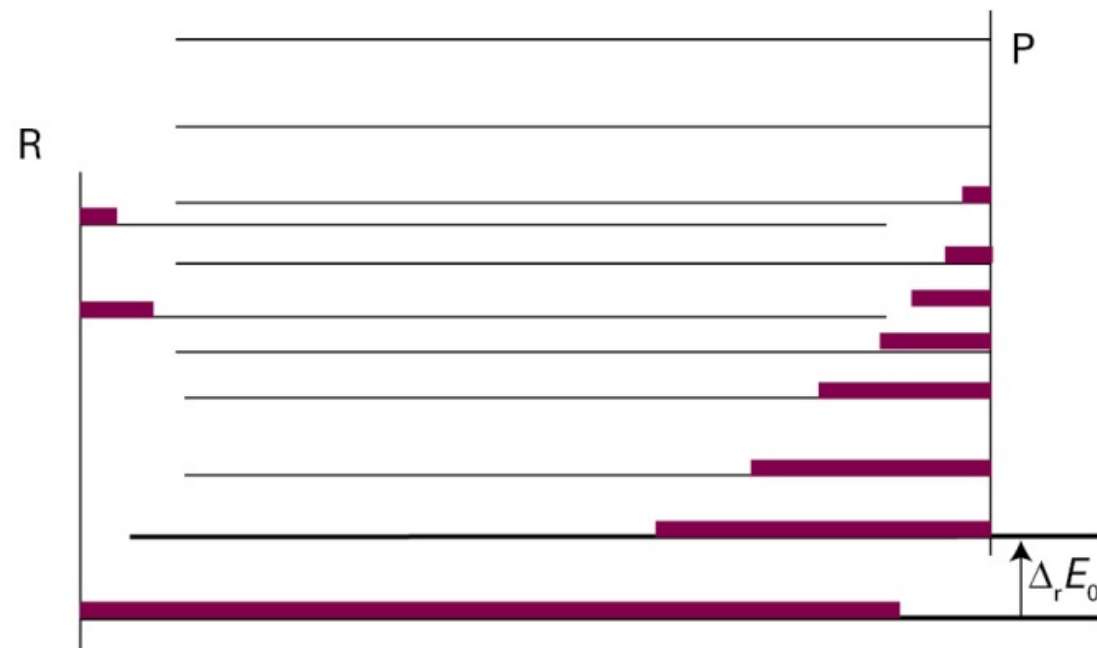


Figure 15F.3 It is important to take into account the densities of states of the molecules. Even though P might lie above R in energy (that is, $\Delta_r E_0$ is positive), P might have so many states that its total population dominates in the mixture. In classical thermodynamic terms, we have to take entropies into account as well as enthalpies when considering equilibria.

For the reaction $R \rightleftharpoons P$,
$$K = \frac{N_P}{N_R} = \frac{q_P}{q_R} e^{-\Delta_r E_0/RT}$$

Contributions to equilibrium constants

For the reaction $R \rightarrow P$, assume that R has only a single accessible level, so that $q_R = 1$, and that P has a large number of closely spaced levels, so that $q_P = kt/\varepsilon$. The equilibrium constant is:

$$K = \frac{kT}{\varepsilon} e^{-\Delta_r E_o / RT}$$

- It can be seen that when $\Delta_r E_o$ is very large, the exponential term dominates, and $K \ll 1$, indicating that very little P is present at equilibrium.
- When $\Delta_r E_o$ is small, but positive, K can exceed 1 because the factor kT/ε may be large enough to offset the low value of the exponential term. The size of K then results from the large amount of P at equilibrium resulting from its high density of states.
- At low temperatures, $K \ll 1$, and R predominates at equilibrium.
- At high temperatures, the exponential function approaches 1, and P becomes dominant.
- For this endothermic reaction, a temperature increase favors P because its states become increasingly accessible as the temperature increases.

Contributions to equilibrium constants

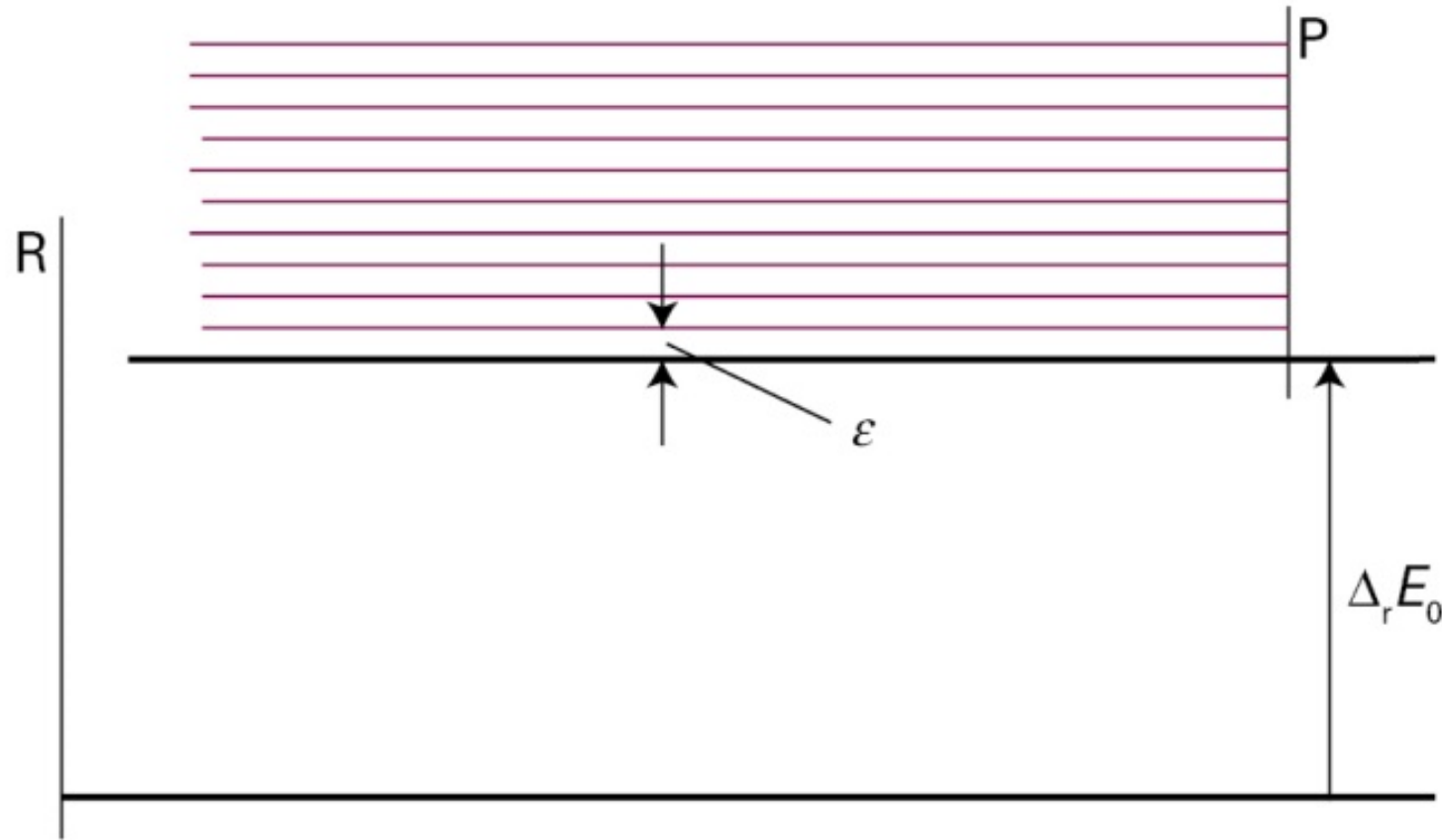


Figure 15F.4 The model used in the text for exploring the effects of energy separations and densities of states on equilibria. The products P can dominate provided $\Delta_r E_0$ is not too large and P has an appreciable density of states.