

Statistical Thermodynamics : A Primer For Chemists

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An Open-Source Textbook

Ludwig Boltzmann, who spent most of his life studying statistical mechanics, died in 1906 by his own hand. Paul Ehrenfest, carrying on the work, died similarly in 1933. Now it is our turn to study statistical mechanics.

– David Goodstein, Professor of Physics,
Caltech, in his book “States of Matter”

Introduction

At its core, the discipline of chemistry revolves around studying the behaviour of electrons. The “transmutation” of substances pursued by early alchemists can now be understood in terms of rearrangement of electrons between atoms, and models of electron behaviour fundamentally underpin all branches of chemistry – from the qualitative “curly arrow” theory preferred by organic chemists through to more quantitative ligand-field and quantum chemical models theories based upon solving the electronic Schrodinger equation.

At the same time, it is extremely difficult to directly observe electrons being rearranged on a molecular level. More frequently, chemical experimentation is concerned with characterizing bulk properties of collections of molecules, e.g. measuring quantities such melting points, reaction rates, enthalpies and entropies of reaction.

This naturally raises the question – can these “bottom up” and “top down” ways of looking at the behaviour of chemical systems somehow be unified? If so, how?

Brute-force simulation is the conceptually simplest solution; jointly modelling electronic behaviour and nuclear dynamics for large collections of molecules. However, this is exactly as computationally intensive as it sounds, limiting its applicability to small systems (< 1000 atoms) and short time scales (< 100 ps). Clearly this is a long way from the $\sim 10^{23}$ atoms one would typically handle performing experiments on a gram scale.

An alternative approach is to take a statistical view of energy distribution amongst quantum energy levels of collections of molecules. This is the foundation of the field of statistical thermodynamics, whose development and applications will be the focus of this book. A major selling point of this approach is that it becomes more accurate – but no more computationally intensive – as the number of particles in the system increases up to and even beyond the gram scale.

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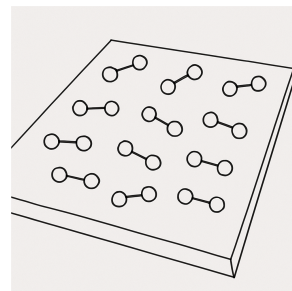
STATISTICAL THERMODYNAMICS
– PRINCIPLES

Microscopic Statistics

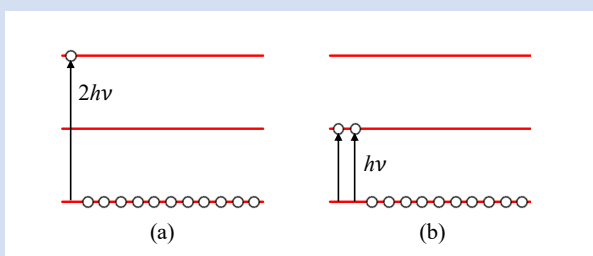
1.

Thinking like physicists for just a moment, suppose we have twelve independent and identical quantum harmonic oscillators, each fixed at separate points in space. Translating into chemistry speak, this could be a suitable model for gas molecules immobilized by adsorption at different locations on an inert surface.

We then wish to distribute a certain amount of thermal energy amongst these molecules; let's make it $2h\nu$ for convenience, where ν is the vibrational frequency of an individual molecule. How do we go about this?



Distributing $2h\nu$ amongst 12 molecules



(a) All available thermal energy is used to excite a single molecule. There are 12 molecules to choose from so the weight of this configuration is 12.

(b) The available thermal energy is distributed as evenly as possible, exciting two molecules by $h\nu$ each. There are 12 ways of selecting the first molecule and 11 ways of selecting the second, but the same microstate is generated regardless of the order they are selected in, so the weight of this configuration is $12 \times 11/2 = 66$.

Macrostate: Overall state of the system, *e.g.* 12 diatomics, total energy = $2h\nu$

Configuration: A particular way of distributing energy among particles, *e.g.*
 - 1 molecule excited by $2h\nu$, or
 - 2 molecules excited by $h\nu$

Microstate: A specific, detailed arrangement of all particles in a system, *e.g.*
 - molecule #3 excited by $2h\nu$
 - all other molecules in ground state

Weight of a Configuration (W):
 Number of microstates that correspond to a given configuration, or number of ways of generating that configuration, *e.g.* $W_{2,0,0,\dots} = 12$, $W_{1,1,0,\dots} = 66$

Configuration Weight

The general formula for calculating the weight of a configuration is:

$$W = \frac{N!}{N_0!N_1!\dots} = \frac{N!}{\prod_i N_i!} \quad (1.1)$$

where N = total number of particles in the system and N_i = population of each quantum state, including the ground state.

Although this makes calculating the weight of each configuration easy, we still need to enumerate all possible configurations a system can access by considering all possible combinations of molecules amongst energy levels. Clearly this becomes impractical if one has a large amount of energy to distribute amongst an extremely large number of molecules.

At first glance, therefore, obtaining a statistical description of a macroscopic system seems like an impossible task; the number of possible

combinations explodes very quickly to completely unmanageable proportions!

However, all is not lost. Consider, for a moment, the ratio of the weights of the most probable configuration and least probable configuration when distributing $2h\nu$ of energy amongst 1000 harmonic oscillators, rather than 12.

Distributing $2h\nu$ amongst 1000 molecules

$$\begin{aligned} W_{2,0,0\dots} &= \text{number of ways of choosing a single molecule to} \\ &\quad \text{"deposit" } 2h\nu \text{ into} \\ &= 1000 \end{aligned}$$

$$\begin{aligned} W_{1,1,0\dots} &= (\text{number of ways of choosing first molecule} \\ &\quad \times \text{number of ways of choosing second molecule}) \\ &\quad / (\text{number of ways of choosing both molecules} \\ &\quad \quad \text{when order of selection is unimportant}) \\ &= 1000 \times 999 / 2 \\ &= 499,500 \gg W_{2,0,0\dots} \end{aligned}$$

In general, the larger the number of molecules and amount of thermal energy, the higher the relative weight of the most probable configuration, and therefore the more "say" this configuration will have in determining the observable properties of the system. Or, in other words, the contribution of less probable configurations becomes increasingly negligible as the number of particles in the system increases, to the point that only the most probable configuration is relevant.

So, now we can ask a similar, but slightly more nuanced question - can we identify how many particles occupy each energy level in the most probable configuration, given a certain amount of energy to distribute?

The Boltzmann Distribution

2.

For a “macroscopic” number of particles ($\sim 10^{23}$), computing the weight of *any* configuration using equation (1.1) rapidly becomes impossible, making brute-force determination of the most probable configuration doubly impossible.

Boltzmann’s insight was recognising that it was possible to find the most probable configuration by varying the populations of each energy level using some clever mathematical tricks:

Approach	Effect
Take logarithms of both sides	Converts products & fractions into sums & differences
Apply Stirling’s approximation	Converts factorials to functions
Use Lagrange’s method of undetermined multipliers	Applies constraints on number of particles and total energy of system

Derivation of Boltzmann Equation Key Steps

Convert fractions and products to linear terms:

$$\ln W = \ln N! - \sum_{i=0}^{\infty} \ln N_i! \quad (2.1)$$

Apply Stirling’s approximation, $\ln x! \approx x \ln x - x$:

$$\ln W \approx N \ln N - \sum_{i=0}^{\infty} N_i \ln N_i \quad (2.2)$$

Require the number of particles (N) and total energy (E) to be constant, specified values, regardless of energy level occupancies:

$$\sum_{i=0}^{\infty} N_i = N \quad \text{and} \quad \sum_{i=0}^{\infty} (\epsilon_i - \epsilon_0) N_i = E \quad (2.3)$$

Alternatively, and equivalently, require that the total number of particles and total energy doesn’t *change* as we vary the distribution of particles among energy levels:

$$\sum_{i=0}^{\infty} dN_i = 0 \quad \text{and} \quad \sum_{i=0}^{\infty} (\epsilon_i - \epsilon_0) dN_i = 0 \quad (2.4)$$

Find the maximum value of W by varying the numbers of particles occupying each energy level:

$$d \ln W = \sum_{i=0}^{\infty} \frac{\partial \ln W}{\partial N_i} dN_i = 0 \quad (2.5)$$

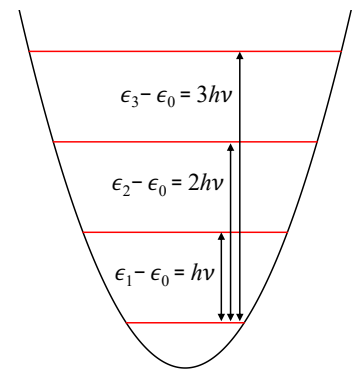


Figure 2.1.: Harmonic oscillator energy levels and energy level spacings $\epsilon_i - \epsilon_0$

Recognise that the chances of the total number of particles, total energy and configuration weight all varying at the same rate are basically zero, unless they are all stationary:

$$\begin{aligned} d \ln W &= \sum_{i=0}^{\infty} \frac{\partial \ln W}{\partial N_i} dN_i = \alpha \sum_{i=0}^{\infty} dN_i + \beta \sum_{i=0}^{\infty} (\epsilon_i - \epsilon_0) dN_i \\ &= \left(\sum_{i=0}^{\infty} \frac{\partial \ln W}{\partial N_i} - \alpha - \beta(\epsilon_i - \epsilon_0) \right) dN_i = 0 \end{aligned} \quad (2.6)$$

The population of each energy level must hence satisfy:

$$\frac{\partial \ln W}{\partial N_i} - \alpha - \beta(\epsilon_i - \epsilon_0) = 0 \quad (2.7)$$

Solve equations (2.2) and (2.7) concurrently to obtain the Boltzmann distribution:

$$\frac{N_i}{N} = \frac{e^{-\beta(\epsilon_i - \epsilon_0)}}{\sum_{i=0}^{\infty} e^{-\beta(\epsilon_i - \epsilon_0)}} \quad (2.8)$$

A more detailed derivation is provided in Appendix A.

Now that we have the Boltzmann equation, the question becomes - how to make sense of it? What is the physical meaning of this mysterious β parameter that has suddenly appeared and is somehow related to enforcing constraints on the total energy of the system?

The Meaning of β

Consider the problem of determining how 500 molecules are distributed among equally-spaced energy levels $(\epsilon_i - \epsilon_0) = 0, 1, 2, 3, \dots$ and how this distribution depends on the value of the parameter $\beta = 1, 2$ or 5 .

Strategy: Compute Boltzmann factors $e^{-\beta(\epsilon_i - \epsilon_0)}$ for each choice of β and $(\epsilon_i - \epsilon_0)$, until the Boltzmann factors become negligible. Sum up all the Boltzmann factors for each β value and divide each Boltzmann factor by the sum. Multiply each of these values by $N = 500$.

Result:

i	$\beta = 1$	$\beta = 2$	$\beta = 5$
0	316	432	497
1	116	59	3
2	43	8	0
3	16	1	0
4	2	0	0
5	1	0	0
6	0	0	0

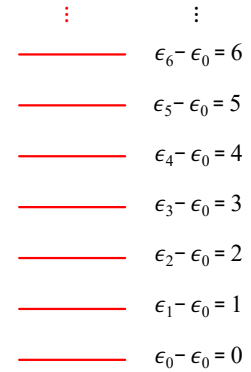


Figure 2.2.: Equally-spaced energy levels on an arbitrary energy scale

Summarising the outcome of this numerical thought experiment, we find that as β increases, the population of particles occupying higher energy levels decreases, and so too does the total thermal energy of the system.

This is exactly the opposite of the behaviour we would expect to see with increasing temperature:

variable	trend	population of higher energy levels	total energy
β	\uparrow	\downarrow	\downarrow
T	\uparrow	\uparrow	\uparrow

This strongly suggests that the temperature of the system is inversely proportional to the parameter β .

$$\beta \propto \frac{1}{T} = \frac{1}{k_B T}$$

In fact, a very precise value for this constant of proportionality can be derived by calculating the translational energy of an ideal monoatomic gas using both a statistical approach and from classical thermodynamics. However, this result turns out to be completely general, and this fundamental physical constant is referred to as the *Boltzmann constant*.

$$k_B = 1.3806503 \times 10^{-23} \text{ J K}^{-1}$$

Now, it is clear that the temperature of a system is a *unique thermodynamic parameter that governs the most probable populations of states when the system is at thermal equilibrium*. This is a very important result, as it provides the first example of relating atomic level knowledge of quantum states to macroscopic properties of chemical systems. Later, we will see how other macroscopic properties such as heat capacity, internal energies and entropy can be calculated from the Boltzmann distribution.

The Boltzmann Distribution – Most General Form

$$\frac{N_i}{N} = \frac{g_i e^{-(\epsilon_i - \epsilon_0)/k_B T}}{\sum_{i=0}^{\infty} g_i e^{-(\epsilon_i - \epsilon_0)/k_B T}} \quad (2.9)$$

g_i = degeneracy of energy level i

One final little wrinkle that must be ironed out before proceeding is how to deal with situations in which multiple quantum states are available at the same energy level, *i.e.* situations in which there are multiple degenerate solutions to the Schrödinger equation. One familiar example of a quantum system with degenerate energy levels are atoms, which have degenerate atomic orbitals. For example, the energies of all $2p$ orbitals – $2p_x, 2p_y, 2p_z$ – are identical for an isolated atoms.

Of course, the simplest possible solution is just to count each degenerate state individually, but that leads to rather more counting than strictly necessary. Instead, we simply compute and count each Boltzmann factor once, and multiply by the number of states at this energy level.

The Partition Function 3.

Another way of interpreting the Boltzmann equation is as a probability distribution function, wherein each Boltzmann factor, q_i , is proportional to the probability of finding any given particle in state i .

However, we need to make sure that the total probability of finding all particles if we add them up across all states is 1. This is achieved by dividing each Boltzmann factor by the sum of all Boltzmann factors across the entire set of energy levels, represented by q :

$$q_i = g_i e^{-(\epsilon_i - \epsilon_0)/k_B T} \quad (3.1)$$

Boltzmann factor

$$q = \sum_{i=0}^{\infty} g_i e^{-(\epsilon_i - \epsilon_0)/k_B T} \quad (3.2)$$

Partition function

The Boltzmann Distribution – Shorthand Form

$$\frac{N_i}{N} = \frac{q_i}{q} = \frac{g_i e^{-(\epsilon_i - \epsilon_0)/k_B T}}{\sum_{i=0}^{\infty} g_i e^{-(\epsilon_i - \epsilon_0)/k_B T}} \quad (3.3)$$

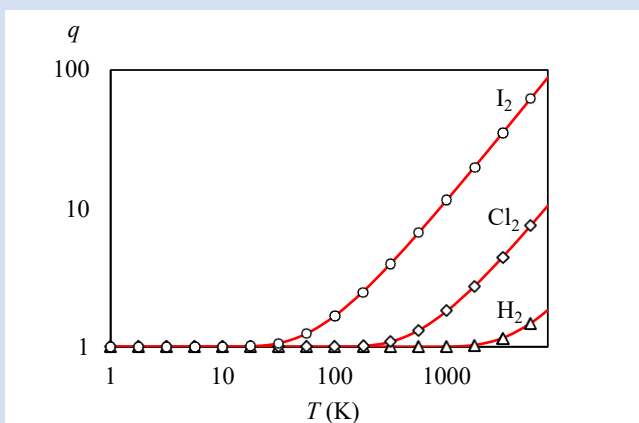
On first appearances, q is simply a boring normalization factor. However, the story becomes more interesting when we consider how q changes with temperature and/or spacing of energy levels.

The Partition Function, $q(T)$

As an illustrative example, consider the series of homonuclear diatomic molecules whose vibrational energy levels are characterised by the fundamental frequencies:

	H ₂	Cl ₂	I ₂
$\bar{\nu}$ (cm ⁻¹)	4401	560	64

After quite a bit of computation...



Observations:

- q increases with T with an apparent threshold temperature that depends on energy level spacings
- At any given T , q is larger for collections of molecules with more closely spaced energy levels.

Implications:

- q may reflect how thermal energy is partitioned between *different* components in a mixed system, or different modes of motion.

Overall, it is clear that the value of q changes (increases) as a **function** of temperature, and contains some information about the distribution of particles amongst available energy states. For example, if $q = 1$ (its minimum value) all particles remain in their ground state at that temperature. However, if $q > 1$, at least some of the molecules in a collection will be thermally excited. Additionally, the relative value of q at any given temperature reflects the propensity of a component of a system to absorb thermal energy relative to other components, and hence may reflect the **partitioning** of energy between them.

For these reasons, q is referred to as the **partition function**. It is important to keep in mind that this name is a little misleading – **the partition function does not actually partition the total energy of the system among the different states. This is the job of the Boltzmann distribution.**

Nonetheless, the partition function turns out to be a very useful intermediate when it comes to computing thermodynamic properties of a system, e.g. entropy, enthalpy, Gibbs energy, as we shall see in the next chapters.

Internal Energy

4.

Once the number of particles occupying each quantum energy level have been determined using the Boltzmann equation, it is straightforward to compute the total thermal energy of a system, simply by counting the energy associated with each molecule in its excited state.

U_{thermal} via Boltzmann Populations

$$U_{\text{thermal}} = \sum_{i=0}^{\infty} N_i (\epsilon_i - \epsilon_0) \quad (4.1)$$

However, this is the least computationally efficient approach, because it requires us to first compute and sum a possibly-infinite sequence of Boltzmann factors and then divide each Boltzmann factor by this sum to determine N_i .

However, our work is not done there; we must then repeat the summation process, this time accounting for the energy of the particles occupying each energy level.

Additional computational efficiency may be achieved by expanding out the Boltzmann equation and being strategic about order of operations in evaluating the expanded expression.

In practice this summation is truncated when each additional Boltzmann factor contributes negligibly to the overall sum.

Also need to check that this summation has not been prematurely truncated – although higher energy levels are less populated they contribute more energy per molecule.

U_{thermal} as Energy-Weighted Sum of Boltzmann Factors

$$\begin{aligned} U_{\text{thermal}} &= \sum_{i=0}^{\infty} N_i (\epsilon_i - \epsilon_0) \\ &= \frac{N}{q} \sum_{i=0}^{\infty} q_i (\epsilon_i - \epsilon_0) \\ &= \frac{N}{q} \sum_{i=0}^{\infty} (\epsilon_i - \epsilon_0) g_i e^{-(\epsilon_i - \epsilon_0)/k_B T} \end{aligned}$$

$$N_i = N \frac{q_i}{q}$$

$$q_i = g_i e^{-(\epsilon_i - \epsilon_0)/k_B T}$$

$$q = \sum_{j=0}^{\infty} g_j e^{-(\epsilon_j - \epsilon_0)/k_B T}$$

$$U_{\text{thermal}} = N \frac{\left(\sum_{i=0}^{\infty} (\epsilon_i - \epsilon_0) g_i e^{-(\epsilon_i - \epsilon_0)/k_B T} \right)}{\left(\sum_{j=0}^{\infty} g_j e^{-(\epsilon_j - \epsilon_0)/k_B T} \right)} \quad (4.2)$$

Now we can see that the thermal energy can be computed as an energy-weighted sum of Boltzmann factors, divided by the partition function (or non-energy-weighted sum of Boltzmann factors), at any given temperature. This may be achieved within a single summation process, acquiring terms in both the numerator and denominator concurrently in a loop over energy levels.

Inspection of equation (4.2) also reveals that each term in the numerator may be generated by differentiating the corresponding term in the denominator.

U_{thermal} via Differentiation of the Partition Function

$$\begin{aligned}
 U_{\text{thermal}} &= N \frac{\left(\sum_{i=0}^{\infty} (\epsilon_i - \epsilon_0) g_i e^{-\beta(\epsilon_i - \epsilon_0)} \right)}{\left(\sum_{j=0}^{\infty} g_j e^{-\beta(\epsilon_j - \epsilon_0)} \right)} \\
 &= N \frac{\left(\sum_{i=0}^{\infty} -\frac{d}{d\beta} \left(g_i e^{-\beta(\epsilon_i - \epsilon_0)} \right) \right)}{\left(\sum_{j=0}^{\infty} g_j e^{-\beta(\epsilon_j - \epsilon_0)} \right)} \\
 &= N \frac{-\frac{d}{d\beta} \left(\sum_{i=0}^{\infty} \left(g_i e^{-\beta(\epsilon_i - \epsilon_0)} \right) \right)}{\left(\sum_{j=0}^{\infty} g_j e^{-\beta(\epsilon_j - \epsilon_0)} \right)}
 \end{aligned}$$

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

$$q = \sum_{i=0}^{\infty} g_i e^{-\beta(\epsilon_i - \epsilon_0)}$$

$$U_{\text{thermal}} = -\frac{N}{q} \frac{dq}{d\beta} \quad (4.3)$$

Although this approach seems quite abstract and of little practical use at present, it shall become more important when we consider more realistic systems and how thermal energy is distributed amongst different molecular modes of motion.

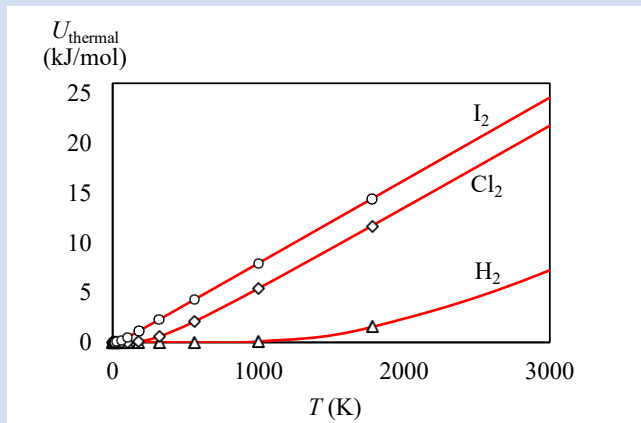
Although they vary in computational complexity, equations (4.1), (4.2) and (4.3) all return identical values for the total thermal energy distributed amongst a collection of molecules at a given temperature. However, a more interesting question is how the total thermal energy varies with temperature, and also how this depends on energy level spacings of the system. This is best illustrated by way of example.

Thermal Internal Energy, $U_{\text{thermal}}(T)$

For a sequence of homonuclear diatomics whose vibrational energy levels are characterised by the fundamental frequencies:

	H ₂	Cl ₂	I ₂
$\bar{\nu}$ (cm ⁻¹)	4401	560	64

The total thermal energy distributed amongst a collection of identical, independent but distinguishable molecules may be computed using equation (4.1), (4.2) or (4.3). Repeating these calculations at a range of different temperatures for each different type of molecule produces the results illustrated on the next page.



Observations:

- ▶ U_{thermal} increases with T , with an apparent threshold temperature that depends on energy level spacings. The more widely spaced the energy levels, the higher this threshold temperature.
- ▶ At any given T , U_{thermal} is larger for collections of molecules with more closely spaced energy levels.
- ▶ In the high temperature limit, U_{thermal} increases linearly with T . This limit is reached at lower temperatures in systems with more closely spaced energy levels.
- ▶ U_{thermal} goes to zero sub-linearly as $T \rightarrow 0$.

Entropy 5.

Statistical thermodynamics offers a powerful framework for understanding entropy by linking macroscopic thermodynamic properties to the microscopic behaviour of molecules. In particular, it makes sense that the entropy of a system is related to the number of ways of distributing the total thermal energy amongst all of the molecules in the system; the more ways of distributing energy amongst molecules, the higher the entropy.

The qualitative dependence of S on W is most clearly illustrated by considering two extreme case situations, at $T = 0$ and as $T \rightarrow \infty$.

Intuitively, at $T = 0$ K, there is no thermal energy and therefore all molecules occupy their ground energy levels. There is only one way of achieving this, and so $W = 1$. Additionally, this is a perfectly ordered state, so we expect $S = 0$. However, if the temperature of the system were to increase even a little, we may expect the entropy to increase substantially, as the pattern of particles occupying higher energy levels changes dramatically.

As $T \rightarrow \infty$, the situation is less clear. On the one hand, with an infinite amount of thermal energy available, one may expect all molecules to be excited to their highest available energy levels, but on the other hand, there are also an infinite number of energy levels, so we must consider what thermal energy distributions are statistically most probable.

Boltzmann Populations as $T \rightarrow \infty$

The first step in determining Boltzmann distributions is to compute Boltzmann factors for each energy level:

$$q_i = g_i e^{-(\epsilon_i - \epsilon_0)/k_B T} \quad (5.1)$$

As $T \rightarrow \infty$,

$$(\epsilon_i - \epsilon_0)/k_B T \rightarrow 0 \quad (5.2)$$

and so

$$q_i = g_i e^{-0} = g_i \quad (5.3)$$

Equation (5.3) immediately tells us that as $T \rightarrow \infty$, **thermal energy becomes equally distributed amongst all available quantum states of the system.**

As $T \rightarrow \infty$, there is a large amount of thermal energy to be distributed equally amongst all available quantum states of the system, and there are a large number of ways of achieving this, suggesting a high degree of entropy. However, in this high-temperature regime, small *changes* in temperature barely affect energy distribution patterns, and so we expect *changes* in entropy to become vanishingly small. Mathematically, this is expressed as:

$$\frac{dS}{dT} \rightarrow 0 \quad \text{as} \quad T \rightarrow \infty \quad (5.4)$$

Asymptotic Relationships Between T , S and $\frac{dS}{dT}$

T	S	$\frac{dS}{dT}$
0 K	0	steep
$\rightarrow \infty$ K	high	$\rightarrow 0$

Finally, we must concurrently consider the asymptotic behaviour of both W and S in order to ascertain the relationship between them.

As we have previously seen, it is impossible to directly calculate W even once the Boltzmann populations that define the most probable configuration is known, except at very low temperatures where only a few quantum states are populated, enabling significant cancellation of terms in the “brute force” expression for W :

$$W = \frac{N!}{\prod_i N_i!} \quad (5.5)$$

Fortunately, we have also previously seen that W may be very accurately estimated by taking logarithms of each side of this equation and applying Stirling’s approximation:

$$\ln W \approx N \ln N - \sum_{i=0}^{\infty} N_i \ln N_i \quad (5.6)$$

Now, we may take this one step further, and use the Boltzmann distribution to determine the population of each energy level, N_i , at a given temperature.

A Temperature-Dependent Expression for $\ln W$

$$\begin{aligned}
 \ln W &= N \ln N - \sum_{i=0}^{\infty} N_i \ln N_i \\
 &= N \ln N - \sum_{i=0}^{\infty} N \frac{e^{-\beta(\epsilon_i - \epsilon_0)}}{q} \ln \left(N \frac{e^{-\beta(\epsilon_i - \epsilon_0)}}{q} \right) \\
 &= N \ln N - \sum_{i=0}^{\infty} N \frac{e^{-\beta(\epsilon_i - \epsilon_0)}}{q} \left[\ln N + \ln e^{-\beta(\epsilon_i - \epsilon_0)} - \ln q \right] \\
 &= N \ln N - \frac{N}{q} \sum_{i=0}^{\infty} e^{-\beta(\epsilon_i - \epsilon_0)} [\ln N - \beta(\epsilon_i - \epsilon_0) - \ln q] \\
 &= N \ln N - \frac{N}{q} q \ln N - \frac{N}{q} \sum_{i=0}^{\infty} -\beta(\epsilon_i - \epsilon_0) e^{-\beta(\epsilon_i - \epsilon_0)} + \frac{N}{q} q \ln q \\
 &= \beta \frac{N}{q} \sum_{i=0}^{\infty} (\epsilon_i - \epsilon_0) e^{-\beta(\epsilon_i - \epsilon_0)} + N \ln q \\
 &= \frac{U_{\text{thermal}}}{k_B T} + N \ln q \quad (5.7)
 \end{aligned}$$

N_i = Boltzmann population of energy level i

$$= N \frac{e^{-\beta(\epsilon_i - \epsilon_0)}}{q}$$

U_{thermal} = Energy-weighted sum of Boltzmann factors

$$= \frac{N}{q} \sum_{i=0}^{\infty} (\epsilon_i - \epsilon_0) e^{-\beta(\epsilon_i - \epsilon_0)}$$

$$\beta = 1/k_B T$$

At $T = 0$, $\ln W = 0$ because $W = 1$; there is no thermal energy, and so all molecules in the system are in their ground states, and there is only way of realising this configuration. This is not quite so obvious from equation (5.7) but is true by virtue of the fact that U_{thermal} decays sub-linearly as $T \rightarrow 0$, and $q = 1$ because only the lowest energy level is occupied so there only a single Boltzmann factor contributes to the partition function. Therefore, $\ln q = 0$ and the second term in equation (5.7) is also equal to zero.

At high temperatures, U_{thermal} and q both increase linearly with T . Hence, in the high- T limit:

$$\begin{aligned}\ln W &\propto \frac{T}{k_B T} + N \ln T \\ &\propto c + \ln T\end{aligned}\quad (5.8)$$

and

$$\frac{d}{dT} \ln W \propto \frac{1}{T} \quad (5.9) \quad \frac{d}{dT} \ln T = \frac{1}{T}$$

Relationship between $\ln W$ and S

Summarising the asymptotic behaviour of $\ln W$ and S :

T	$\ln W$	$\frac{d \ln W}{dT}$	S	$\frac{dS}{dT}$
0 K	0	non-zero	0	steep
$\rightarrow \infty$ K	constant	$\rightarrow 0$	high	$\rightarrow 0$

Reveals that they display the same temperature-dependence both at very high and very low temperatures, strongly suggesting:

$$S \propto \ln W \quad (5.10)$$

Equation (5.10) may be re-written incorporating a constant of proportionality, which again turns out to be the Boltzmann constant:

$$S = k_B \ln W \quad (5.11)$$

Finally, combining equations (5.7) and (5.11), we obtain the computable form of this relationship:

$$S = \frac{U_{\text{thermal}}}{T} + N k_B \ln q \quad (5.12)$$

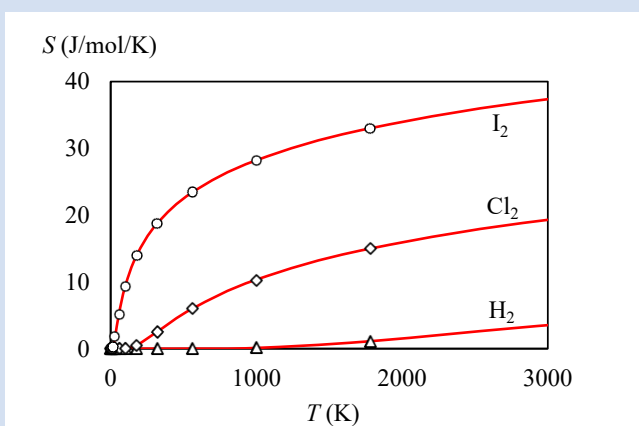
Equation (5.12) enables us to investigate how the entropy of a system varies with temperature, and also how the entropy at a given temperature depends on the energy level spacings of a system. This is best illustrated by way of example.

Dependence of S on T and energy level spacings

Considering the same sequence of homonuclear diatomics used in previous examples, whose energy level spacings are characterised by the fundamental harmonic frequencies:

	H ₂	Cl ₂	I ₂
$\bar{\nu}$ (cm ⁻¹)	4401	560	64

Entropies for collections of identical, independent but distinguishable molecules may now be straightforwardly computed at different temperatures from the enthalpy and partition function values computed previously, employing equation (5.12).



Observations:

- S increases with T , with an apparent threshold temperature that depends on energy level spacings. The more closely spaced the energy levels, the lower this threshold temperature.
- At any given T , S is larger for collections of molecules with more closely spaced energy levels, reflecting the fact that more energy levels are thermally accessible and therefore are therefore more ways of distributing thermal energy amongst them.
- At higher temperatures, the S vs T curve begins to plateau. However, even at 3000 K, the slope is far from zero.
- The overall shape of the S vs T curve is sigmoidal, and qualitatively very different to q and U_{thermal} vs T .

DIATOMICS

Overview 6.

In the previous section, the basic principles of statistical thermodynamics were illustrated using simple model systems of harmonically oscillating diatomics adsorbed to a surface, allowing them to be identified but preventing them from moving or rotating.

However, as chemists, we need to be able to understand all of the different ways that molecules move and subsequently interact. For example, as we heat a box of gas molecules, how do their velocities change? How does this affect the probability of them colliding with one another and going on to undergo a chemical reaction? How does excitation of specific modes of vibrational motion result in an overall increase in thermal energy in a system? How much thermal energy would be required for a bond to dissociate, either due to vibrational motion or by exciting electrons from bonding to antibonding orbitals?

We shall begin by assuming that the different types of molecular motion (translational, rotational, vibrational and electronic) occur on such different time and length scales that they may be considered independent of one another. Therefore, the total energy of any given molecule comprises separate contributions arising from each type of motion:

$$\epsilon_{ijkl}^{\text{total}} = \epsilon_i^{\text{elec}} + \epsilon_j^{\text{vib}} + \epsilon_k^{\text{rot}} + \epsilon_l^{\text{trans}} \quad (6.1)$$

We have previously seen that the partition function is central to evaluating thermodynamic quantities using the tools of statistical mechanics. Hence, we shall first focus on how to compute overall molecular partition functions taking into account the distribution of thermal energy over all translational, rotational, vibrational and electronic energy levels for a collection of distinguishable, non-interacting molecules. In the interests of brevity, we shall define all energies to be relative to the ground state for each particular mode of motion.

Separability of the Molecular Partition Function

It is straightforward to write down, expand and simplify an expression for the molecular partition function as a joint sum of Boltzmann factors for all translational, rotational, vibrational and electronic energy levels:

$$\begin{aligned} q &= \sum_{i,j,k,l} g_i g_j g_k g_l e^{-\beta \epsilon_{ijkl}} \\ &= \sum_{i,j,k,l} g_i g_j g_k g_l e^{-\beta (\epsilon_i^{\text{elec}} + \epsilon_j^{\text{vib}} + \epsilon_k^{\text{rot}} + \epsilon_l^{\text{trans}})} \\ &= \sum_{i,j,k,l} g_i g_j g_k g_l e^{-\beta \epsilon_i^{\text{elec}}} e^{-\beta \epsilon_j^{\text{vib}}} e^{-\beta \epsilon_k^{\text{rot}}} e^{-\beta \epsilon_l^{\text{trans}}} \\ &= \left(\sum_i g_i e^{-\beta \epsilon_i^{\text{elec}}} \right) \left(\sum_j g_j e^{-\beta \epsilon_j^{\text{vib}}} \right) \left(\sum_k g_k e^{-\beta \epsilon_k^{\text{rot}}} \right) \left(\sum_l g_l e^{-\beta \epsilon_l^{\text{trans}}} \right) \\ &= q^{\text{elec}} q^{\text{vib}} q^{\text{rot}} q^{\text{trans}} \quad (6.2) \end{aligned}$$

In words, equation (6.2) may be interpreted as follows: if the total energy of a molecule can be expressed as a *sum* of independent contributions from different modes of motion, then the total partition function of a molecule can be expressed as a *product* of separate partition functions for each mode of motion.

Although equation (6.2) represents a significant conceptual advance, reducing a complicated multidimensional summation into a product of much more computationally tractable single sums, it remains to specify explicit expressions for the quantum energy levels associated with each mode of motion, and evaluate the associated partition functions.

In the following sections, we shall briefly recap quantum models describing translational, vibrational, rotational and electronic states of diatomic molecules, and investigate how to most easily evaluate the corresponding mode-specific partition functions. For completeness, expressions for thermal enthalpy and entropy associated with each mode of motion will also be derived.

Solving the Schrödinger equation for a particle in a three-dimensional cubic box with sides of length L gives the translational energy levels:

$$\epsilon_{n_x, n_y, n_z}^{\text{trans}} = \frac{h^2 (n_x^2 + n_y^2 + n_z^2)}{8mL^2} \quad (7.1)$$

where n_x , n_y and n_z are the quantum numbers in the x , y and z directions, m is the mass of the particle and h is Planck's constant.

Translational Partition Function

May be expressed as a sum of Boltzmann factors over substantially populated translational energy levels:

$$q^{\text{trans}} = \left(\sum_{n_x} e^{-\beta \frac{h^2 n_x^2}{8mL^2}} \right) \left(\sum_{n_y} e^{-\beta \frac{h^2 n_y^2}{8mL^2}} \right) \left(\sum_{n_z} e^{-\beta \frac{h^2 n_z^2}{8mL^2}} \right) \quad (7.2)$$

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

While it is perfectly possible (in theory) to directly evaluate this triple sum, in practice, the number of terms that must be included is extremely large, as the spacing between energy levels is very small compared with the available energy, even at very low temperatures.

Estimating Number of Non-Negligible Boltzmann Factors

Considering a collection of H_2 molecules in a 1 L box at $T = 4$ K as an extreme case example of a system with maximally-spaced translational energy levels, energy level spacings are determined by the parameters $m(\text{H}_2) = 3.34707 \times 10^{-27}$ kg and $L = 0.1$ m.

Assuming that a Boltzmann factor must be $< 10^{-20}$ before it contributes negligibly to q^{trans} , we may find the corresponding energy level by solving:

$$e^{-\beta \frac{h^2 n_x^2}{8mL^2}} = 10^{-20}$$

Therefore:

$$-\frac{1}{k_B T} \frac{h^2 n_x^2}{8mL^2} = \ln(10^{-20})$$

Solving for n_x , we find:

$$n_x = 1.25 \times 10^9$$

In other words, our sum over significantly occupied energy levels must include 1.25 billion terms! For heavier molecules contained in larger boxes, or at higher temperatures, this value will only increase.

$$h = 6.62607 \times 10^{-34} \text{ J s}$$

$$k_B = 1.38065 \times 10^{-23} \text{ J K}^{-1}$$

Fortunately, however, the fine spacing of the energy levels relative to the total available thermal energy means that we may approximate the sums in equation (7.2) as integrals. This is the inverse process to evaluating the area under a curve using numerical integration, e.g. applying Simpson's rule or the trapezoidal rule.

Determining q^{trans} by Integration

Equation (7.2) may be expressed in integral form:

$$q^{\text{trans}} \approx \int_0^\infty e^{-\beta \frac{h^2 n_x^2}{8mL^2}} dn_x \int_0^\infty e^{-\beta \frac{h^2 n_y^2}{8mL^2}} dn_y \int_0^\infty e^{-\beta \frac{h^2 n_z^2}{8mL^2}} dn_z \quad (7.3)$$

Now, n_x , n_y and n_z are no longer discrete integers but can take any value between 0 and ∞ . Technically, $n_x = n_y = n_z = 0$ is not an allowed solution to the Schrödinger equation and we should be computing all energies relative to $n_x = n_y = n_z = 1$ and integrating from 1 to ∞ . However, numerically this makes no difference to the final result provided that we are in the temperature regime where billions of energy levels are substantially occupied, and so we shall solve this problem in this simpler form.

The solutions to these kinds of integrals are well-known:

$$\int_0^\infty e^{-ax^2} dx = \frac{\sqrt{\pi}}{2\sqrt{a}} \quad (7.4)$$

Applying this result to solve each integral in equation (7.3), we find:

$$q^{\text{trans}} \approx \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} L^3 \quad (7.5)$$

This may be expressed more generally and succinctly as:

$$q^{\text{trans}} = \frac{V}{\Lambda^3} \quad \Lambda = \frac{h}{\sqrt{2\pi m k_B T}} \quad (7.6)$$

where $V = L^3$ = volume of box. This result now applies for collections of molecules contained within volumes of any shape, not just cubic.

With this analytical expression for the translational partition function now in hand, it makes sense to evaluate the translational thermal energy via differentiation of the partition function:

Translational Thermal Energies

The general expression for U_{thermal} in terms of q and its derivatives is:

$$U_{\text{thermal}} = -\frac{N}{q} \frac{dq}{d\beta} \quad (7.7)$$

Expressing q^{trans} in “differentiation-friendly” form:

$$q^{\text{trans}} = V \left(\frac{2\pi m}{h^2} \right)^{3/2} \beta^{-3/2} \quad (7.8)$$

So:

$$\frac{dq^{\text{trans}}}{d\beta} = V \left(\frac{2\pi m}{h^2} \right)^{3/2} \left(-\frac{3}{2} \beta^{-5/2} \right) \quad (7.9)$$

Substituting equations (7.8) and (7.9) into equation (7.7), we find:

$$U_{\text{thermal}}^{\text{trans}} = \frac{3}{2} N \beta^{-1} = \frac{3}{2} N k_B T \quad (7.10)$$

Equation (7.10) reveals that the translational energy increases linearly with temperature, with each degree of freedom (motion in x , y and z directions) contributing $\frac{1}{2}k_B T$ per molecule or $\frac{1}{2}N_A k_B T = \frac{1}{2}RT$ per mole of molecules, in line with the classical equipartition principle. This also makes sense according to the quantum correspondence principle, as the quantum energy levels are so close together that they essentially form a continuum of available energy states.

Now it is straightforward to write down an expression for the translational entropy in terms of q^{trans} and $U_{\text{thermal}}^{\text{trans}}$

$$\begin{aligned} N_A &= 6.02214 \times 10^{23} \text{ mol}^{-1} \\ k_B &= 1.38065 \times 10^{-23} \text{ J K}^{-1} \\ N_A k_B &= 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Thermal Translational Entropy

The general expression for computing entropies from thermal energies and partition functions is:

$$S = \frac{U_{\text{thermal}}}{T} + Nk_B \ln q \quad (7.11)$$

Substituting in $U_{\text{thermal}}^{\text{trans}}$ and q^{trans} for U and q , respectively:

$$S^{\text{trans}} = \frac{Nk_B T}{T} + Nk_B \ln \left(\frac{V}{\Lambda^3} \right) \quad (7.12)$$

Which may be expanded and factorised:

$$S^{\text{trans}} = Nk_B \left[1 + \ln \left(\frac{V(2\pi m k_B T)^{3/2}}{h^3} \right) \right] \quad (7.13)$$

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

However, it is immediately clear that this expression does not conform to the expected asymptotic behaviour $S = 0$ at $T = 0$; the first term in this expression is always constant while the second term is undefined.

Clearly, our assumption that the available thermal energy vastly exceeds the energy level spacings breaks down at extremely low temperatures, *i.e.* at $T \rightarrow 0$. Nonetheless, equation (7.13) should provide a very accurate approximation for the entropy associated with free translational motion of gas molecules at experimentally-relevant temperatures, given that it is very hard to achieve temperatures below the boiling point of helium (~ 4 K) and, in any case, all other substances will be solids at this temperature.

Rotation 8.

Under the rigid rotor approximation, the rotational Schrödinger equation may be solved exactly, with energy levels indexed by the rotational quantum number, J , and inversely scaled by the moment of inertia, I :

$$\epsilon_J = \frac{\hbar^2}{2I} J(J+1) \quad \hbar = \frac{h}{2\pi} \quad (8.1)$$

Each quantum state involves increasingly constrained rotation about the centre of mass, characterised by spherical harmonic wavefunctions $Y_l^m(\theta, \phi)$. The rotational quantum number J is related to the angular quantum numbers l and m as follows:

J	l	m	g_J	Description
0	0	0	1	Free rotation, no angle-dependence
1	1	-1,0,1	3	Constrained rotation, aligned to x, y, z axes
2	2	-2,-1,0,1,2	5	It gets complicated to describe

The degeneracy of each rotational energy level is therefore:

$$g_J = (2J + 1) \quad (8.2)$$

Rotational Partition Function

Recognising that the energy of the ground rotational state is zero and defining the rotational constant $B = \hbar^2/2I$, we may immediately write down a compact expression for the rotational partition function:

$$q^{\text{rot}} = \frac{1}{\sigma} \sum_J (2J + 1) e^{-BJ(J+1)/k_B T} \quad (8.3)$$

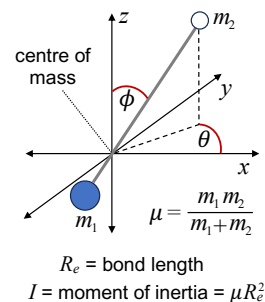
As in the translational case, we shall begin with some back-of-the-envelope calculations to establish how many rotational Boltzmann factors must be computed to evaluate the rotational partition function with a high degree of precision. However, unlike in the translational case, we can no longer start by assuming rotational energy levels are finely spaced with respect to the available thermal energy, and so must perform this analysis over a representative temperature range (10 - 3000 K).

Estimating Number of Non-Negligible Boltzmann Factors

For a series of rotating homonuclear diatomic molecules whose rotational energy levels are characterised by the rotational constants

	H ₂	Cl ₂	I ₂
\bar{B} (cm ⁻¹)	59.3801	0.2442	0.0374

We may determine the rotational quantum number at which Boltzmann factors become negligible ($< 10^{-20}$) by first assuming exponential decay behaviour dominates with increasing J , and then correcting for the effects of the degeneracy term.



$$Y_l^m(\theta, \phi)$$

Spherical harmonic functions describe 2D standing waves on the surface of a sphere

σ = rotational symmetry number
Number of ways original orientation of molecule is regenerated during full period of rotation.

$$B = hc\bar{B}$$

T(K)	Number of non-negligible q_J for		
	H ₂	Cl ₂	I ₂
10	2	38	98
30	4	66	170
100	8	121	312
300	13	211	544
1000	24	387	999
3000	42	674	1738

$$q_J = (2J + 1)e^{-BJ(J+1)/k_B T}$$

Rotational Boltzmann factor

The heavier the molecule and the longer the bond, the larger the moment of inertia and the more finely spaced the rotational energy levels. Therefore, more thermal energy levels are significantly occupied at any given temperature and more Boltzmann factors must be computed to evaluate the corresponding molecular partition function.

Similarly, the higher the temperature, the more thermal energy is available, and the more populated the higher energy levels become. This again results in more Boltzmann factors contributing significantly to the partition function.

Regardless, even for I₂ at 3000 K, fewer than 2000 terms are required to precisely compute q^{rot} , an eminently computable number. Therefore, brute force summation of Boltzmann factors is the most robust and reliable approach for evaluating rotational partition functions for any molecule at any temperature.

This immediately suggests that the *energy-weighted sum of Boltzmann factors* approach is the most practical and efficient way of computing rotational thermal energies as most, if not all, of the required intermediate quantities have already been computed.

Rotational Thermal Energies

General expression:

$$U_{\text{thermal}} = N \frac{\left(\sum_{i=0}^{\infty} (\epsilon_i - \epsilon_0) g_i e^{-(\epsilon_i - \epsilon_0)/k_B T} \right)}{\left(\sum_{j=0}^{\infty} g_j e^{-(\epsilon_j - \epsilon_0)/k_B T} \right)}$$

Specific to rotational energy levels:

$$U_{\text{thermal}}^{\text{rot}} = N \frac{\left(\sum_J BJ(J+1)(2J+1)e^{-BJ(J+1)/k_B T} \right)}{\left(\sum_J (2J+1)e^{-BJ(J+1)/k_B T} \right)} \quad (8.4)$$

Due to the $J(J+1)$ prefactor in the numerator, additional terms are required to converge the energy-weighted sum of Boltzmann factors to the same degree of accuracy as the partition function. However, even for I₂ at 3000 K, this still requires fewer than 2000 terms.

Rotational Entropy

The rotational thermal entropy associated with a collection of freely-rotating diatomic molecules may finally be computed as:

$$S^{\text{rot}} = \frac{U_{\text{thermal}}^{\text{rot}}}{T} + Nk_B \ln q^{\text{rot}} \quad (8.5)$$

Because we have not made any assumptions about the nature of thermal energy distribution amongst rotational energy levels, this approach will work for all *practically-accessible* temperatures except $T = 0$, where the first term in this equation becomes undefined. Instead, we must either take the limit as $T \rightarrow 0$ or simply realise that $S = 0$ at $T = 0$ because all molecules will be in their ground rotational state.

However, should we wish to interrogate the behaviour of q^{rot} , $U_{\text{thermal}}^{\text{rot}}$ and S^{rot} as $T \rightarrow \infty$, it is necessary to derive high-temperature limit expressions by converting the sums over Boltzmann factors we have encountered previously to integrals.

High-Temperature Limit Expressions

The integral form of equation (8.3):

$$q^{\text{rot}} \approx \frac{1}{\sigma} \int_0^\infty (2J+1) e^{-BJ(J+1)/k_B T} dJ \quad (8.6)$$

$$B = \frac{\hbar^2}{2I}$$

May be straightforwardly solved by variable substitution. Letting $u = J(J+1)$ and defining $a = B/k_B T$, we obtain:

$$\begin{aligned} q^{\text{rot}} &\approx \frac{1}{\sigma} \int_0^\infty e^{-au} du \\ &= \frac{1}{\sigma} \frac{1}{a} \\ &= \frac{1}{\sigma} \frac{k_B T}{B} \end{aligned} \quad (8.7)$$

$$a = \frac{B}{k_B T}$$

Equation (8.7) is more commonly expressed as:

$$q^{\text{rot,high-T}} = \frac{1}{\sigma} \frac{2Ik_B T}{\hbar^2} \quad (8.8)$$

A high temperature limit expression for the thermal rotation energy may be found via differentiation of the partition function:

$$U_{\text{thermal}} = -\frac{N}{q} \frac{dq}{d\beta} \quad (8.9)$$

$$q^{\text{rot}} = (\sigma B)^{-1} \beta^{-1} \quad (8.10)$$

$$\frac{dq^{\text{rot}}}{d\beta} = -(\sigma B)^{-1} \beta^{-2} \quad (8.11)$$

Substituting (8.10) and (8.11) into (8.9), we obtain:

$$U_{\text{thermal}}^{\text{rot,high-T}} = N\beta^{-1} = Nk_B T \quad (8.12)$$

Finally, an explicit expression for rotational energy in the high-temperature limit is obtained by substituting equations (8.8) and (8.12) into (8.5)

$$S^{\text{rot,high-T}} = Nk_B \left(1 + \ln \left(\frac{1}{\sigma} \frac{k_B T}{B} \right) \right) \quad (8.13)$$

Again, we observe that $q^{\text{rot,high-T}}$ and $U_{\text{thermal}}^{\text{rot}}$ both increase linearly with T , mirroring the high-temperature behaviour of q^{trans} and U^{trans} . Similarly, $\frac{1}{2}k_B T$ of thermal energy is stored per molecule, per rotational degree of freedom (θ, ϕ), in line with the classical equipartition principle.

This reflects the fact that energy levels become effectively continuous from the perspective of having an effectively infinite amount of thermal energy to distribute amongst them; the key difference between rotational and translational modes of motion is the temperature at which this situation is realised in practice.

Therefore, it is entirely unsurprising that $S^{\text{rot,high-T}}$ displays the same asymptotic behaviour as S^{trans} as $T \rightarrow \infty$, equal to a constant plus a logarithmic term that grows increasingly slowly with T , reaching a slope of 0 only at $T = \infty$.

Vibration | 9.

According to the quantum harmonic oscillator model, the vibrational energy levels of a diatomic molecule are:

$$\epsilon_n = \left(n + \frac{1}{2}\right) h\nu \quad (9.1)$$

where ν is the fundamental frequency and n is the vibrational quantum number.

Vibrational Partition Function

Because the vibrational energy levels are non-degenerate

$$\begin{aligned} q^{\text{vib}} &= \sum_n e^{-\beta(\epsilon_n - \epsilon_0)} \\ &= \sum_n e^{-\beta n h \nu} \end{aligned} \quad (9.2)$$

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

It turns out that we can exactly sum this geometric series to get a simple analytical expression for q^{vib}

$$\begin{aligned} q^{\text{vib}} &= \left(1 + e^{-\beta h \nu} + e^{-2\beta h \nu} + \dots\right) \\ &= \left(1 + x + x^2 + x^3 + \dots\right) \\ &= \left(\frac{1}{1 - x}\right) \\ &= \frac{1}{1 - e^{-\beta h \nu}} \end{aligned} \quad (9.3)$$

$$x = e^{-\beta h \nu}$$

The exact expression for q^{vib} at *any* temperature is therefore:

$$q^{\text{vib}} = \frac{1}{1 - e^{-h\nu/k_B T}} \quad (9.4)$$

It is now straightforward to derive an expression for $U_{\text{thermal}}^{\text{vib}}$ via differentiation of the partition function.

Thermal vibrational energy

Re-writing equation (9.3) in “differentiation-friendly” form

$$q^{\text{vib}} = \left(1 - e^{-\beta h \nu}\right)^{-1} \quad (9.5)$$

Makes it easy to find

$$\frac{dq^{\text{vib}}}{d\beta} = -\left(1 - e^{-\beta h \nu}\right)^{-2} \left(h\nu e^{-\beta h \nu}\right) \quad (9.6)$$

So

$$U_{\text{thermal}}^{\text{vib}} = -\frac{N}{q} \frac{dq}{d\beta} = N \frac{h\nu e^{-\beta h \nu}}{1 - e^{-\beta h \nu}} \quad (9.7)$$

Which may be expressed in explicitly T -dependent form

$$U_{\text{thermal}}^{\text{vib}} = N \frac{h\nu e^{-h\nu/k_{\text{B}}T}}{1 - e^{-h\nu/k_{\text{B}}T}} \quad (9.8)$$

Because equations (9.4) and (9.8) are completely general, we may now immediately write down a completely general expression for the vibrational entropy, as well.

Vibrational entropy

$$S^{\text{vib}} = \frac{U_{\text{thermal}}^{\text{vib}}}{T} + Nk_{\text{B}} \ln q^{\text{vib}} \quad (9.9)$$

To determine whether it is possible to evaluate equation (9.9) at all temperatures, we must first assess the asymptotic behaviour of q^{vib} and $U_{\text{thermal}}^{\text{vib}}$ at $T = 0$ and as $T \rightarrow \infty$.

However, one disadvantage of equations (9.4) and (9.8) is that their asymptotic behaviour is not immediately clear.

At $T = 0$ K, we expect all molecules to be in their ground vibrational state. Therefore, only the ground-state Boltzmann factor contributes to the partition function ($q_{\text{vib}} = 1$) and the total thermal energy must be zero ($U_{\text{thermal}}^{\text{vib}} = 0$).

Low-Temperature Limit q_{vib} and $U_{\text{thermal}}^{\text{vib}}$

Mathematically, we observe:

$$h\nu/k_{\text{B}}T \rightarrow \infty \text{ as } T \rightarrow 0 \quad (9.10)$$

and therefore:

$$e^{-h\nu/k_{\text{B}}T} \rightarrow e^{-\infty} = \frac{1}{e^{\infty}} = 0 \quad (9.11)$$

Setting $e^{-h\nu/k_{\text{B}}T} = 0$ in equations (9.4) and (9.8) immediately confirms $q_{\text{vib}} = 1$ and $U_{\text{thermal}}^{\text{vib}} = 0$ at $T = 0$, as expected.

As established in previous chapters, this approach is not entirely satisfactory because the first term in equation (9.9) becomes undefined at $T = 0$. However, this may be resolved by either taking the limit as $T \rightarrow 0$ or simply recognising that $S = 0$ at $T = 0$ because all molecules are in their ground state, which is a perfectly ordered arrangement.

The temperature-dependence of q^{vib} and $U_{\text{thermal}}^{\text{vib}}$ in the high temperature limit is somewhat harder to discern. Empirically, we have already observed that both of these quantities increase linearly with T at higher temperatures, but to prove this we need to use some clever mathematical tricks, as outlined below.

High-Temperature Limit q_{vib} and $U_{\text{thermal}}^{\text{vib}}$

We start by observing that:

$$h\nu/k_{\text{B}}T \rightarrow 0 \text{ as } T \rightarrow \infty \quad (9.12)$$

and therefore:

$$e^{-h\nu/k_{\text{B}}T} \rightarrow e^{-0} = 1 \quad (9.13)$$

Hence, the denominator in equation (9.4) becomes undefined. Instead, we need to consider the behaviour of this exponential function for very small values of $h\nu/k_{\text{B}}T$. Letting $x = h\nu/k_{\text{B}}T$, this function may be approximated by a Taylor series expansion about $x = 0$:

$$e^{-x} = 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \frac{x^4}{4!} - \dots \quad (9.14)$$

When x is very small, only the first two terms in this expansion contribute significantly, so:

$$q^{\text{vib,high-T}} = \frac{1}{1 - (1 - x)} = \frac{1}{x} = \frac{k_{\text{B}}T}{h\nu} \quad (9.15)$$

It is then straightforward to derive a high-temperature limit expression for $U_{\text{thermal}}^{\text{vib}}$ via differentiation of the partition function

$$q^{\text{vib,high-T}} = (h\nu)^{-1} \beta^{-1} \quad (9.16)$$

$$\frac{dq^{\text{vib,high-T}}}{d\beta} = -(h\nu)^{-1} \beta^{-2} \quad (9.17)$$

$$U_{\text{thermal}}^{\text{vib,high-T}} = -\frac{N}{q} \frac{dq}{d\beta} = \beta^{-1} = k_{\text{B}}T \quad (9.18)$$

This analysis reveals that both q^{vib} and $U_{\text{thermal}}^{\text{vib}}$ increase linearly with temperature at high T , as expected, resulting in S^{vib} being equal to a constant plus a logarithmic contribution that plateaus as T increases.

However, this does raise the question - at what temperature is this high- T limit likely to be reached?

Quantifying the High-Temperature Vibrational Limit

We shall consider a sequence of oscillating diatomics whose vibrational frequencies span a wide and representative range

	H ₂	Cl ₂	I ₂
$\bar{\nu}$ (cm ⁻¹)	4401	560	64

Onset temperatures that define the high-temperature limit may be estimated by computing the temperature at which the 2000th excited state becomes non-negligibly occupied (defined by $q_i \geq 10^{-20}$). These values were chosen to be consistent with the conditions under which rotating I₂ may be considered to reach the high- T limit, at 3000 K.

	H ₂	Cl ₂	I ₂
T_{onset} (K)	275000	35000	4000

All of these temperatures are significantly higher than typical molecular decomposition temperatures, suggesting that many/most molecules in a system will decompose before the system as a whole reaches a state whereby thermal energy is distributed equally amongst all of them.

Typically, differences in energy between electronic states of a system are much larger than energy level spacings associated with nuclear motions. This is fundamentally due to the fact that electrons are much lighter than nuclei; the mass of an electron is approximately $1/1000^{\text{th}}$ of that of a proton. Although crude, the particle-in-a-box model can provide useful qualitative insights into the quantum behaviour of subatomic particles, and one of these is that energy level spacings are inversely proportional to mass. Hence, we would expect energy level spacings associated with electronic degrees of freedom to be at least 1000 times greater than those associated with any form of nuclear motion.

$$E_n = \frac{h^2 n^2}{8mL^2}$$

Particle-in-a-box energy level expression

Additionally, molecular orbital theory tells us that bonds may be broken by promoting an electron from a bonding orbital to an antibonding orbital. However, bonds may also be broken by providing enough vibrational energy for the molecule to dissociate. Given that multiple vibrational energy levels may be accessed before reaching this dissociation limit, it stands to reason that vibrational energy levels are more closely spaced than electronic energy levels.

Altogether, this implies that electronic energy levels are so far apart that electronically excited states are not likely to be significantly populated at any realistic temperature. This may be assessed by computing Boltzmann factors for the first excited state of a representative range of molecules at a range of different temperatures.

Excited State Boltzmann Factors

The difference in energy between the ground electronic state of a molecule and its first excited state is given by its first excitation energy, which may be determined spectroscopically. Excitation energies have been measured for a wide range of diatomic molecules, including:

$\epsilon_1 - \epsilon_0$	H ₂	N ₂	F ₂	Cl ₂
(cm ⁻¹)	91700	50204	25500	17160
(kJ mol ⁻¹)	1097	601	305	205

From which first excited state Boltzmann factors may be computed:

T (K)	H ₂	N ₂	F ₂	Cl ₂
100	0	0	4.7×10^{-160}	6.1×10^{-108}
300	1.0×10^{-191}	2.8×10^{-105}	7.8×10^{-54}	1.8×10^{-36}
1000	5.1×10^{-58}	4.3×10^{-32}	1.2×10^{-16}	1.9×10^{-11}
3000	8.0×10^{-20}	3.5×10^{-11}	4.9×10^{-6}	2.7×10^{-4}

By and large, Boltzmann factors for the first excited state are negligible, except at temperatures consistent with molecular decomposition. By the time sufficient thermal energy is supplied to appreciably populate even the first excited electronic state, most molecules are likely to have already decomposed. At or around room temperature, not even a single molecule per mole of molecules would be in its first excited state.

$$1 \text{ J} = \frac{1 \text{ kJ mol}^{-1} \times 1000}{N_A \text{ mol}^{-1}}$$

In the previous chapters, we have observed that translational energy levels are more readily thermally populated than rotational, which in turn are more readily thermally populated than vibrational energy levels. For all practical intents and purposes, excited electronic states are never thermally populated.

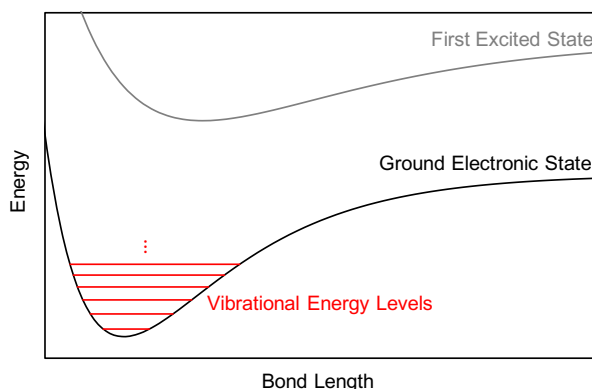
$$q^{\text{trans}} \gg q^{\text{rot}} > q^{\text{vib}}$$

$$S^{\text{trans}} > S^{\text{rot}} > S^{\text{vib}}$$

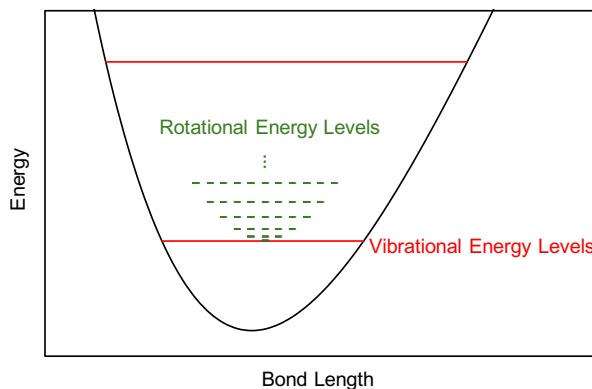
$$U_{\text{thermal}}^{\text{trans}} > U_{\text{thermal}}^{\text{rot}} > U_{\text{thermal}}^{\text{vib}}$$

Fundamentally, this reflects the spacing of the underlying energy levels; the more closely spaced the energy levels, the more of them are thermally accessible at any given temperature, the more ways there are of distributing thermal energy amongst them, and the more thermal energy is stored overall.

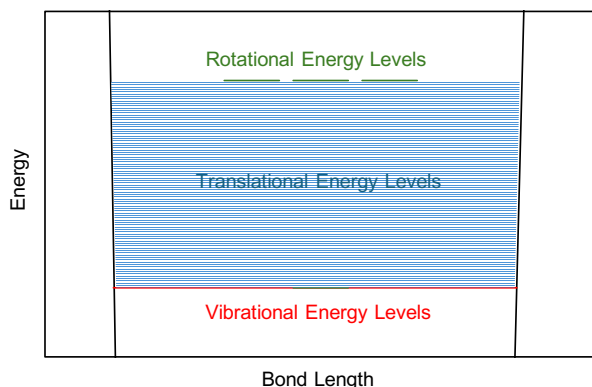
A more intuitive feel for these relationships emerges upon visualisation of the energy level spacings associated with each mode of motion. Starting on the widest energy scale reveals the relationship between electronic and vibrational energy levels:



Zooming in to the lowest-energy region of the ground state electronic energy potential curve, we find that for each molecule in a given vibrational state, a variety of rotational sub-states may also be accessed:



Zooming in even further again, to just the gap between the $J = 0$ and $J = 1$ rotational energy levels reveals a continuum of translational energy levels:



Of course, this same continuum of translational energy levels is accessible regardless of the particular vibrational or rotational state a molecule may be in.

These “energy level spacing” considerations also apply when comparing the *relative* distribution of thermal energy between collections of different gas-phase diatomics at a specified temperature. For example:

	H ₂	Cl ₂	I ₂
molecular mass, m	low	medium	high
translational energy level spacings	high	medium	low
$q^{\text{trans}}, U_{\text{thermal}}^{\text{trans}}, S^{\text{trans}}$	low	medium	high
moment of inertia, I	low	medium	high
rotational energy level spacings	high	medium	low
$q^{\text{rot}}, U_{\text{thermal}}^{\text{rot}}, S^{\text{rot}}$	low	medium	high
vibrational frequency, ν	high	medium	low
vibrational energy level spacings	high	medium	low
$q^{\text{vib}}, U_{\text{thermal}}^{\text{vib}}, S^{\text{vib}}$	low	medium	high

$$\epsilon_{n_x, n_y, n_z}^{\text{trans}} = \frac{h^2 (n_x^2 + n_y^2 + n_z^2)}{8mL^2}$$

$$\epsilon_J = \frac{\hbar^2}{2I} J(J+1)$$

$$\epsilon_n = \left(n + \frac{1}{2}\right) h\nu$$

We can also immediately predict that polyatomic molecules will, on the whole, have more closely spaced translational energy levels than diatomics by virtue of having a larger number of atoms and therefore higher molecular masses.

In fact, none of the theory developed in this section pertaining to the distribution of thermal energy amongst translational energy levels is specific to diatomics; the same equations may be used to predict thermal energies and entropies for any collection of non-interacting gas phase molecules.

However, the situation is different when it comes to rotational and vibrational modes of motion, not least because polyatomic molecules possess additional rotational and vibrational degrees of freedom.

POLYATOMICS

For a polyatomic molecule with N atoms, the total number of coordinate degrees of freedom is $3N$, as each atom is free to move in three independent directions (x , y and z). However, when dealing with molecular motions, it is more useful to think in terms of internal coordinates - bond lengths, angles, torsional angles, and external coordinates - translational motion of the molecule's centre of mass, and rotational motion about the molecule's centre of mass.

All gas phase molecules have three translational degrees of freedom, corresponding to movement along each Cartesian axis (x , y , z). Most molecules also have three rotational degrees of freedom (pitch, roll, yaw) and therefore $(3N - 6)$ vibrational modes. Linear molecules possess only two rotational degrees of freedom, as rotation about the bond axis causes no change, and therefore have $(3N - 5)$ vibrational modes.

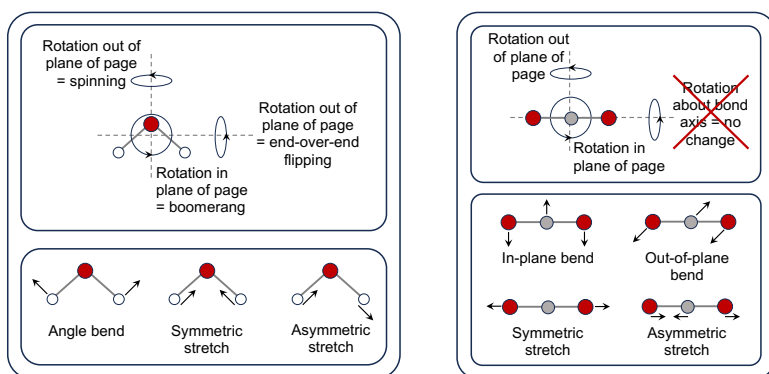


Figure 12.1: As a non-linear polyatomic molecule, water (left) has three rotational modes and three vibrational modes. As a linear polyatomic, carbon dioxide (right) has two rotational modes and four vibrational modes.

To compute rotational and vibrational partition functions for polyatomic molecules, it is necessary to first solve the general 3-dimensional rotational Schrödinger equation or $(3N - 6)$ dimensional vibrational Schrödinger equation to obtain sets of energy levels associated with each degree of freedom. The total energy of the system may then be expressed a sum of contributions from each independent mode of motion, *i.e.*

$$\epsilon^{\text{rot}} = \sum_{n=1}^3 \epsilon_{i_n}^{\text{rot},n} \quad \epsilon^{\text{vib}} = \sum_{m=1}^{3N-6} \epsilon_{i_m}^{\text{vib},m} \quad (12.1)$$

i_n = quantum number for rotation about axis n
 i_m = quantum number for vibration along mode m

Hence, molecular rotational and translational partition functions may be expressed and computed as products of separate contributions from each rotational and translational degree of freedom:

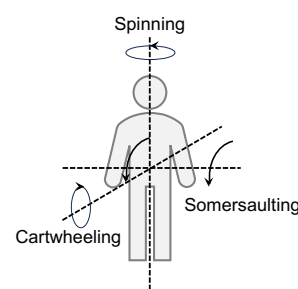
$$q^{\text{rot}} = \prod_{n=1}^3 q_n^{\text{rot}} \quad q^{\text{vib}} = \prod_{m=1}^{3N-6} q_m^{\text{vib}} \quad (12.2)$$

Finally, overall molecular partition functions are also computed as products of contributions from each individual mode of motion, completely analogous to the diatomic case:

$$q = q^{\text{trans}} q^{\text{rot}} q^{\text{vib}} q^{\text{elec}} \quad (12.3)$$

To model rotation of an arbitrary non-linear molecule in three dimensions, we first need to consider how the molecule rotates about its centre of mass. This requires us to define its principal axes of inertia - the three directions it 'naturally' rotates about its centre of mass.

For an intuitive understanding of principal axes of inertia, consider the human body. The centre of mass is easy to find - near the navel. The longest (or primary) principal axis runs from middle of the top of the head to between the feet, and rotation about this axis looks like spinning on your feet. The next longest principal axis runs from one side of the body to the other. Rotation about this principal axis looks like somersaulting. The shortest principal axis goes from the front of the body to the back, and rotation about this axis looks like cartwheeling. Any other form of rotation looks (and feels) 'unnatural'.



Computing Molecular Moments of Inertia

We must first translate the molecule to its centre of mass:

$$\{x_c, y_c, z_c\} = \frac{1}{m_{\text{tot}}} \sum_{i=1}^{N_{\text{atom}}} m_i \{x_i, y_i, z_i\} \quad (13.1)$$

by subtracting its centre of mass coordinate $\{x_c, y_c, z_c\}$ from each atomic coordinate $\{x_i, y_i, z_i\}$. Construction and diagonalisation of the inertia tensor:

$$\begin{bmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{bmatrix} \quad (13.2)$$

yields the principle axes of rotation in the original coordinate system as the eigenvectors and the moments of inertia, $\{I_A, I_B, I_C\}$, as the eigenvalues.

Elements of inertia tensor:

$$I_{xx} = \sum_{i=1}^{N_{\text{atom}}} m_i (y_i^2 + z_i^2)$$

$$I_{xy} = \sum_{i=1}^{N_{\text{atom}}} -m_i x_i y_i$$

... etc.

For a "spherical top" molecule with three identical moments of inertia indicating three equivalent axes of rotation, the rotational Schrödinger equation may be solved exactly:

$$\epsilon_J = \frac{\hbar^2}{2I} J(J+1) \quad g_J = (2J+1)^2 \quad (13.3)$$

yielding the same energy levels as the rigid diatomic rotor but with *different* degeneracies. This therefore results in a different expression for the molecular partition function, and corresponding thermal energies and entropies.



Figure 13.1: SF₆ is a classic example of a spherical top molecule.

Rotational Partition Functions

As always, the rotational partition function may be evaluated by “brute-force” summation:

$$q^{\text{rot}} = \sum_{J=0}^{\infty} (2J+1)^2 e^{-BJ(J+1)/k_B T} \quad (13.4)$$

For molecules, q^{rot} is also amenable to evaluation in integral form, because polyatomic molecules are typically larger than diatomics and therefore have higher moments of inertia and correspondingly more closely spaced energy levels. High-temperature limit requirements are typically met for most polyatomic gas phase molecules under standard thermodynamic conditions.

$$\begin{aligned} q^{\text{rot}} &= \int_{J=0}^{\infty} (2J+1)^2 e^{-BJ(J+1)/k_B T} dJ \\ &= \frac{\sqrt{\pi}}{\sigma} \left(\frac{T}{\Theta} \right)^{3/2} \end{aligned} \quad (13.5)$$

where the rotational symmetry number σ corresponds to the number of ways of regenerating the starting orientation during a full period of molecular rotation and is included to compensate for overcounting.

Equation (13.5) may be straightforwardly generalised to asymmetric tops, molecules with non-equivalent axes of rotation:

$$q^{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{T}{\Theta_A} \right)^{1/2} \left(\frac{T}{\Theta_B} \right)^{1/2} \left(\frac{T}{\Theta_C} \right)^{1/2} \quad (13.6)$$

$$B = \frac{\hbar^2}{2I}$$

$$\Theta = \frac{\hbar^2}{2Ik_B}$$

$$\Theta_A = \frac{\hbar^2}{2I_A k_B}, \text{ etc.}$$

Thermal Energy and Entropy in the High-Temperature Limit

Observing that:

$$q^{\text{rot}} \propto (k_B T)^{3/2} = \beta^{-3/2} \quad (13.7)$$

We immediately find that

$$U_{\text{thermal}}^{\text{rot}} = \frac{3}{2} N \beta^{-1} = \frac{3}{2} N k_B T \quad (13.8)$$

via differentiation of the partition function, where N = the number of independent, non-interacting polyatomic molecules in the system. If $N = N_A$, molar energies and enthalpies are obtained.

Accordingly, we find that:

$$S^{\text{rot}} = \frac{U_{\text{thermal}}^{\text{rot}}}{T} + N k_B \ln q^{\text{rot}} \quad (13.9)$$

tends to a constant plus a logarithmic term whose slope $\rightarrow 0$ as $T \rightarrow \infty$. Because there are more rotational degrees of freedom than in the diatomic case, this constant takes a higher value.

Finally, it remains to consider the special case of linear polyatomics, which only possess two rotational degrees of freedom. This suggests that their thermodynamic behaviour should mirror that of diatomics, which turns out to be exactly the case. The only difference lies in how the moment of inertia is computed:

$$I = \sum_{i=1}^{N_{\text{atom}}} m_i r_i^2 \quad (13.10)$$

where r_i = the distance of the i^{th} atom from the centre of mass of the molecule.

Vibration 14.

Before it is possible to evaluate the molecular vibrational partition function, it is first necessary to identify the $3N_{\text{atom}} - 6$ vibrational modes of the system and determine their characteristic vibrational frequencies.

Fortunately, both of these objectives can be achieved through computation (using quantum chemistry software) and diagonalisation of the mass-weighted “Hessian” matrix, \mathbf{H}_{mw} :

The Hessian is a $3N_{\text{atom}} \times 3N_{\text{atom}}$ matrix which contains second derivatives of the electronic energy with respect to atomic displacements.

Mass weighting is achieved by dividing each element by the square root of the mass of each displaced atom.

$$\mathbf{H}_{\text{mw}} = \begin{bmatrix} \frac{1}{m_1} \frac{d^2 E}{dx_1^2} & \frac{1}{m_1} \frac{d^2 E}{dx_1 dy_1} & \frac{1}{m_1} \frac{d^2 E}{dx_1 dz_1} & \cdots & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dx_1 dx_n} & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dx_1 dy_n} & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dx_1 dz_n} \\ \frac{1}{m_1} \frac{d^2 E}{dy_1 dx_1} & \frac{1}{m_1} \frac{d^2 E}{dy_1^2} & \frac{1}{m_1} \frac{d^2 E}{dy_1 dz_1} & \cdots & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dy_1 dx_n} & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dy_1 dy_n} & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dy_1 dz_n} \\ \frac{1}{m_1} \frac{d^2 E}{dz_1 dx_1} & \frac{1}{m_1} \frac{d^2 E}{dz_1 dy_1} & \frac{1}{m_1} \frac{d^2 E}{dz_1^2} & \cdots & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dz_1 dx_n} & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dz_1 dy_n} & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dz_1 dz_n} \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \end{bmatrix}$$

The non-zero eigenvalues of this matrix correspond to the $3N_{\text{atom}} - 6$ harmonic vibrational frequencies of the molecule; the 6 eigenvalues close to zero are linked to eigenvectors that characterise translational and rotational modes. The $3N_{\text{atom}} - 6$ vibrational eigenvectors are each of length $3N_{\text{atom}}$, and may be broken up into N_{atom} sets of $\{x, y, z\}$ atomic displacements that define the normal modes of vibration.

Vibrational Partition Function

For a molecule with $N_{\text{mode}} = 3N_{\text{atom}} - 6$ independent vibrational modes, the overall vibrational partition function is a product of contributions from each individual mode:

$$q^{\text{vib}} = \prod_{i=1}^{N_{\text{mode}}} q_i^{\text{vib}} \quad (14.1)$$

Each mode is characterised by a harmonic fundamental frequency of ν_i with associated non-degenerate quantum energy levels:

$$\epsilon_n = h\nu_i \left(n + \frac{1}{2} \right) \quad (14.2)$$

Therefore,

$$q_i^{\text{vib}} = \sum_{n=0}^{\infty} e^{-\beta(\epsilon_n - \epsilon_0)} = \sum_{n=0}^{\infty} e^{-\beta n h \nu_i} \quad (14.3)$$

Surprisingly, the infinite sum in equation (14.3) may be evaluated in closed form. Letting $x = e^{-\beta h \nu_i}$

$$\begin{aligned} q_i^{\text{vib}} &= 1 + x + x^2 + x^3 + \dots \\ &= \frac{1}{1 - x} \\ &= \frac{1}{1 - e^{-h\nu_i/k_B T}} \end{aligned} \quad (14.4)$$

So, finally we have a complete and compact expression for the overall molecular vibrational partition function within the quantum harmonic oscillator approximation:

$$q^{\text{vib}} = \prod_{i=1}^{N_{\text{mode}}} \frac{1}{1 - e^{-h\nu_i/k_B T}} \quad (14.5)$$

Vibrational Thermal Energy and Entropy

Unlike partition functions, vibrational thermal energies are computed as sums of contributions from each vibrational mode:

$$U_{\text{thermal}}^{\text{vib}} = \sum_{i=1}^{N_{\text{mode}}} N \frac{h\nu_i e^{-h\nu_i/k_B T}}{1 - e^{-h\nu_i/k_B T}} \quad (14.6)$$

Where N = the number of independent non-interacting polyatomic molecules in the system under investigation.

The total entropy may be computed using the general relationship

$$S^{\text{vib}} = \frac{U_{\text{thermal}}^{\text{vib}}}{T} + N k_B \ln q^{\text{vib}} \quad (14.7)$$

It is easy to prove that this can be decomposed into a sum over contributions from separate modes by expanding out $U_{\text{thermal}}^{\text{vib}}$ and applying the logarithmic product rule:

$$\ln \left(\prod_{i=1}^{N_{\text{mode}}} q_i^{\text{vib}} \right) = \sum_{i=1}^{N_{\text{mode}}} \ln (q_i^{\text{vib}}) \quad (14.8)$$

APPLICATIONS

Heat Capacity | 15.

Heat capacity quantifies the amount of energy that must be supplied to a system as heat to change its temperature by a given amount:

$$\Delta U_{\text{thermal}} = C \Delta T \quad (15.1)$$

where C is the heat capacity, $\Delta U_{\text{thermal}}$ is energy supplied and ΔT is the corresponding change in temperature.

Much of the time, we are only interested in infinitesimal changes in energy and temperature, because the process of heating the system can itself alter the heat capacity. Hence, the heat capacity of a system at any given temperature can be more precisely quantified by:

$$C = \frac{dU_{\text{thermal}}}{dT} \quad (15.2)$$

To make life a bit easier for ourselves, we shall convert this derivative with respect to T into a derivative with respect to β , because we have already seen that it is very easy to differentiate Boltzmann factors with respect to β while differentiating with respect to T is much more fiddly.

$$\begin{aligned} \frac{d}{dT} &= \frac{d\beta}{dT} \frac{d}{d\beta} \\ &= -\frac{1}{k_B T^2} \frac{d}{d\beta} \\ &= -k_B \beta^2 \frac{d}{d\beta} \end{aligned} \quad (15.3)$$

Because the total thermal energy of a system is a sum of contributions from different types of motion, so is the total heat capacity:

$$\begin{aligned} C &= \left(\frac{dU_{\text{thermal}}^{\text{trans}}}{dT} + \frac{dU_{\text{thermal}}^{\text{rot}}}{dT} + \frac{dU_{\text{thermal}}^{\text{vib}}}{dT} \right) \\ &= -k_B \beta^2 \left(\frac{dU_{\text{thermal}}^{\text{trans}}}{d\beta} + \frac{dU_{\text{thermal}}^{\text{rot}}}{d\beta} + \frac{dU_{\text{thermal}}^{\text{vib}}}{d\beta} \right) \end{aligned} \quad (15.4)$$

Translational Heat Capacity

We have previously established:

$$U_{\text{thermal}}^{\text{trans}} = \frac{3}{2} N k_B T \quad (15.5)$$

Differentiation with respect to T immediately yields the translational contribution to the heat capacity for a collection of N independent freely-moving molecules:

$$C^{\text{trans}} = \frac{3}{2} N k_B \quad (15.6)$$

For a mole of particles, this is often written more concisely as:

$$C_m^{\text{trans}} = \frac{3}{2}R \quad (15.7)$$

$$R = k_B N_A = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

Because translational thermal energy increases linearly with temperature, reflecting the classical nature of translational motion, the heat capacity is constant with temperature.

Rotational Heat Capacity

For diatomic molecules,

$$U_{\text{thermal}}^{\text{rot}} = N \frac{\left(\sum_J BJ(J+1)(2J+1)e^{-BJ(J+1)/k_B T} \right)}{\left(\sum_J (2J+1)e^{-BJ(J+1)/k_B T} \right)} \quad (15.8)$$

$$B = \frac{\hbar^2}{2I}$$

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

Which may be expressed in a 'differentiation-friendly' form:

$$U_{\text{thermal}}^{\text{rot}} = NB \left(\sum_J J(J+1)(2J+1)e^{-\beta BJ(J+1)} \right) \left(\sum_J (2J+1)e^{-\beta BJ(J+1)} \right)^{-1} \quad \beta = \frac{1}{k_B T}$$

Enabling an expression for C^{rot} to be derived by way of differentiation with respect to β :

$$C^{\text{rot}} = -k_B \beta^2 NB \frac{d}{d\beta} \left(\sum_J J(J+1)(2J+1)e^{-\beta BJ(J+1)} \right) \left(\sum_J (2J+1)e^{-\beta BJ(J+1)} \right)^{-1} \quad (15.9)$$

This derivation is straightforward but tedious, so is presented for completeness in Appendix B. The final result is:

$$C^{\text{rot}} = Nk_B \beta^2 B^2 \left(\frac{\sum_J J^2(J+1)^2(2J+1)e^{-\beta BJ(J+1)}}{\sum_J (2J+1)e^{-\beta BJ(J+1)}} - \frac{\left(\sum_J J(J+1)(2J+1)e^{-\beta BJ(J+1)} \right)^2}{\left(\sum_J (2J+1)e^{-\beta BJ(J+1)} \right)^2} \right) \quad (15.10)$$

For polyatomics, a very similar expression is obtained, just with different pre-factors and rotational constants.

Although equation (15.10) looks hideous, it's actually not too bad. Once we've evaluated all the exponential terms we need to calculate the partition function or mean energy at any given temperature, we're well on our way to being able to calculate the rotational contribution to the overall heat capacity - we just need to combine those terms in different ways (with different J -dependent prefactors) then add them all up as specified.

But, if we only want to get an idea of how much heat energy can be absorbed in total by induced rotational motion in a given diatomic molecule, when all rotational energy levels are equally occupied, we consider the behaviour of $U_{\text{thermal}}^{\text{rot}}$ and therefore C^{rot} in the high-temperature limit:

Rotational Heat Capacity, High-T Limit

The high-T limit for rotational thermal internal energy is:

$$U_{\text{thermal}}^{\text{rot}} = N k_{\text{B}} T \quad (15.11)$$

So therefore

$$C^{\text{rot}} = N k_{\text{B}} \quad (15.12)$$

giving a molar heat capacity ($N = N_{\text{A}}$) of

$$C_m^{\text{rot}} = R \quad (15.13)$$

Vibrational Heat Capacity

For each vibrational mode of motion characterised by its harmonic vibrational frequency, ν :

$$U_{\text{thermal}}^{\text{vib}} = N \frac{h\nu e^{-h\nu/k_{\text{B}}T}}{1 - e^{-h\nu/k_{\text{B}}T}} \quad (15.14)$$

Multiplying the top and bottom by $e^{h\nu/k_{\text{B}}T}$ and substituting $\beta = 1/k_{\text{B}}T$ generates the ‘differentiation friendly’ form:

$$U_{\text{thermal}}^{\text{vib}} = N h\nu (e^{\beta h\nu} - 1)^{-1} \quad (15.15)$$

Differentiating with respect to β :

$$\begin{aligned} C^{\text{vib}} &= -k_{\text{B}} \beta^2 \frac{dU_{\text{thermal}}^{\text{vib}}}{d\beta} \\ &= -k_{\text{B}} \beta^2 N h\nu \frac{d}{d\beta} (e^{\beta h\nu} - 1)^{-1} \\ &= k_{\text{B}} \beta^2 N h\nu (e^{\beta h\nu} - 1)^{-2} h\nu e^{\beta h\nu} \\ &= k_{\text{B}} \beta^2 N e^{\beta h\nu} \left(\frac{h\nu}{e^{\beta h\nu} - 1} \right)^2 \end{aligned} \quad (15.16)$$

We must then “undo” our initial transformation by multiplying the top and bottom of this equation by $(e^{-\beta h\nu})^2$ to derive a numerically-stable, computable form of equation (15.16):

$$C^{\text{vib}} = N k_{\text{B}} \beta^2 e^{-\beta h\nu} \left(\frac{h\nu}{1 - e^{-\beta h\nu}} \right)^2 \quad (15.17)$$

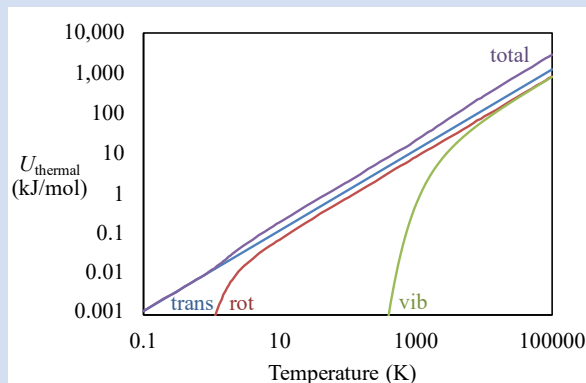
For polyatomic molecules, the total vibrational heat capacity comprises additive contributions from each vibrational mode, *i.e.*

$$C^{\text{vib}} = N k_{\text{B}} \beta^2 \sum_{i=1}^{N_{\text{mode}}} e^{-\beta h\nu_i} \left(\frac{h\nu_i}{1 - e^{-\beta h\nu_i}} \right)^2 \quad (15.18)$$

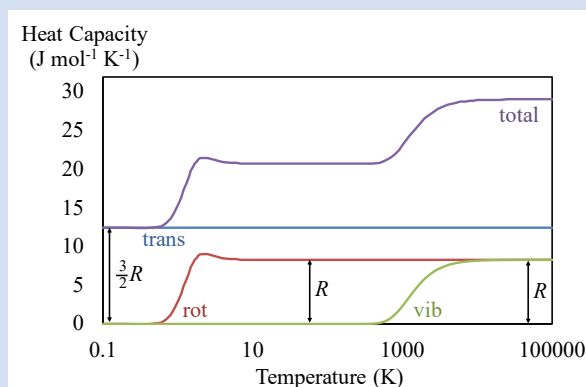
Relationship Between U_{thermal} , C and T

For a mole of gaseous carbon monoxide molecules, thermal energies and heat capacities vary with T as illustrated below.

Thermal internal energy:



Heat capacity:



Although the heat capacity curve is simply the slope of the thermal energy curve, it nonetheless shows some useful extra information that cannot be read off as easily from the U_{thermal} curve, including:

- Onset temperatures at which rotational and vibrational energy levels become significantly populated (steep sections)
- Temperature ranges at which high-temperature limit conditions are met for rotational and vibrational modes (plateau regions)
- Values of the molar heat capacity in the high-temperature limit for each mode of motion = $\frac{3}{2}R$ for translation, R for rotation, vibration.

Understanding the distribution of gas molecule velocities is important in chemistry because it affects how often molecules collide and whether those collisions occur with sufficient energy for the colliding molecules to react with one another. Additionally, understanding how this distribution shifts with temperature is key to predicting the temperature-dependence of reaction rates, and hence designing and improving chemical processes in areas such as catalysis, combustion, and atmospheric chemistry.

As we have seen previously, at all temperatures except very close to absolute zero where most if not all chemical substances are solids, molecular translational energy levels are so closely spaced that they effectively form a continuum. Therefore, the predictions of statistical and classical thermodynamics align, consistent with the quantum correspondence principle.

However, it is possible to take further advantage of the additional information that statistical thermodynamics provides to derive molecular velocity distributions in a simple and elegant manner, requiring only (a) knowledge of the “classical” translational partition function and (b) knowledge of the classical relationship between individual molecular energies and velocities.

Derivation of the Maxwell-Boltzmann Distribution

The molecular translational partition function is

$$q_{\text{trans}} = \sum_{n_x=0}^{\infty} e^{-\beta \epsilon_{n_x}} \sum_{n_y=0}^{\infty} e^{-\beta \epsilon_{n_y}} \sum_{n_z=0}^{\infty} e^{-\beta \epsilon_{n_z}} \quad (16.1)$$

Instead of approximating the sum over all quantum states by an integral, we will presume *a priori* that molecules undergoing translational motion can be treated as though they are classical particles. In other words, they are no longer restricted to quantum energy levels, and can move with any amount of kinetic energy:

$$q_{\text{trans}} = \int_0^{\infty} e^{-\beta \epsilon_x} d\epsilon_x \int_0^{\infty} e^{-\beta \epsilon_y} d\epsilon_y \int_0^{\infty} e^{-\beta \epsilon_z} d\epsilon_z \quad (16.2)$$

Now we may use the fact that the kinetic energy of a particle is related to its velocity ($\epsilon = \frac{1}{2}mv^2$) to convert the integral over energies to an integral over velocities:

$$\begin{aligned} q_{\text{trans}} &= \int_{-\infty}^{\infty} e^{-\beta \frac{1}{2}mv_x^2} dv_x \int_{-\infty}^{\infty} e^{-\beta \frac{1}{2}mv_y^2} dv_y \int_{-\infty}^{\infty} e^{-\beta \frac{1}{2}mv_z^2} dv_z \\ &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m(v_x^2+v_y^2+v_z^2)} dv_x dv_y dv_z \end{aligned} \quad (16.3)$$

This integral over all space in Cartesian coordinates ($-\infty < v_x < \infty$, $-\infty < v_y < \infty$, $-\infty < v_z < \infty$) can be converted into an equivalent integral over all space in spherical polar coordinates ($0 < v < \infty$, $0 < \theta < 180^\circ = \pi$ radians, $0 < \phi < 360^\circ = 2\pi$ radians), where:

$$\begin{aligned} v &= \sqrt{v_x^2 + v_y^2 + v_z^2} & v_x &= v \sin \theta \cos \phi \\ \theta &= \cos^{-1} \left(\frac{v_z}{v} \right) & v_y &= v \sin \theta \sin \phi \\ \phi &= \tan^{-1} \left(\frac{v_y}{v_x} \right) & v_z &= v \cos \theta \end{aligned}$$

and

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dv_x dv_y dv_z = \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} v^2 \sin \theta d\phi d\theta dv$$

So

$$\begin{aligned} q_{\text{trans}} &= \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} e^{-\frac{1}{2}\beta m v^2} v^2 \sin \theta d\phi d\theta dv \\ &= \int_0^{\infty} 4\pi v^2 e^{-\frac{1}{2}\beta m v^2} dv \end{aligned} \quad (16.4)$$

Recall that we originally defined the partition function as a sum of Boltzmann factors, where each Boltzmann factor was proportional to the probability of a particle being found in a given state. The same argument applies equally here, except the discrete sum has now been converted into a continuous integral. Therefore:

$$P(v) \propto 4\pi v^2 e^{-\frac{1}{2}\beta m v^2} \quad (16.5)$$

A constant of proportionality, C , may be derived by requiring that this probability distribution is normalised:

$$\int_0^{\infty} C 4\pi v^2 e^{-\frac{1}{2}\beta m v^2} dv = 1 \quad (16.6)$$

giving:

$$C = \left(\frac{m\beta}{2\pi} \right)^{3/2} \quad (16.7)$$

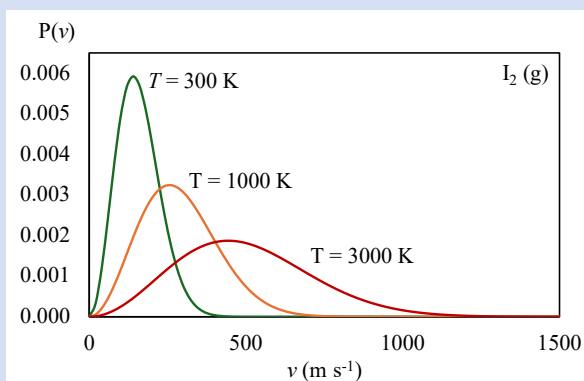
So, finally, the probability of finding an ideal gas particle moving at a certain velocity (v) at a given temperature (T) is:

$$P(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-\frac{m}{2k_B T} v^2} \quad (16.8)$$

Intuitively, increasing the temperature of a collection of gas molecules will increase the overall thermal energy of the system and hence increase the velocities of the gas molecules. The Maxwell-Boltzmann distribution gives us the ability to investigate in a lot more detail how this occurs:

Molecular Velocity Distributions - Temperature Dependence

Velocity distributions for gaseous molecular iodine at three different temperatures:

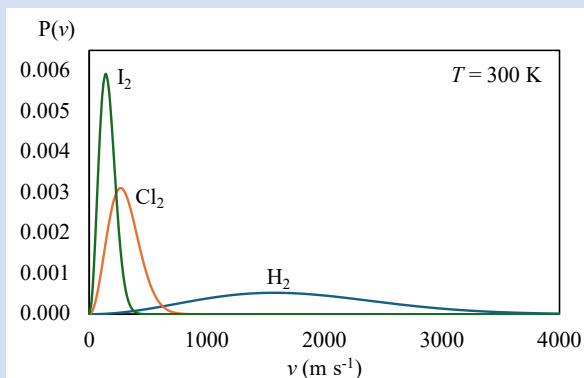


It is immediately obvious that the velocities of each gas particle do not just increase uniformly with increasing T , which would simply shift the overall distribution. Instead, the entire distribution shifts *and* flattens, reflecting the fact that there are more thermally accessible states at higher temperatures and therefore more ways of distributing thermal energy amongst them. In the infinite temperature limit, this curve would become completely flat, as all velocities become equally probable.

It is less obvious how, or whether, the molecular velocity distribution depends on the mass of the gas molecules. Equation (16.8) implies that mass and temperature will have inverse effects on $P(v)$, which is indeed what we observe:

Molecular Velocity Distributions - Mass Dependence

Velocity distributions for gaseous H_2 , Cl_2 and I_2 each at the same temperature, $T = 300 \text{ K}$:



This observation makes sense when we consider:

- The total thermal translational energy of any collection of independent, non-interacting molecules is independent of mass:

$$U_{\text{thermal}}^{\text{trans}} = \frac{3}{2} N k_{\text{B}} T \quad (16.9)$$

- Therefore, all gas molecules conform to the same translational energy distribution at a given T , also independent of mass.
- The translational energy of a molecule is related to its velocity, via:

$$\epsilon = \frac{1}{2} m v^2 \quad (16.10)$$

- Therefore, at a given translational energy value, a lighter molecule must be moving faster.

Spectroscopic measurements provide information about energies and intensities of transitions between quantized energy levels in atoms and molecules. The positions of spectral lines – whether in the microwave, infrared, visible and/or ultraviolet regions – directly reflect the energy differences between initial and final quantum states, allowing one to determine rotational, vibrational, and electronic energy level spacings. These transition energies are governed by the solutions to the Schrödinger equation for the system.

The intensities of spectral lines, on the other hand, depend not only on the intrinsic probability of a transition occurring (which is related to the extent of wavefunction overlap between the initial and final quantum states, weighted by the “transition dipole moment”, as illustrated in Figure 17.1) but also on the population of the initial energy state. These populations follow a Boltzmann distribution, as described by statistical thermodynamics, meaning that at a given temperature, lower-energy states are generally more populated than higher-energy ones.

Therefore, the combination of quantum mechanics (which predicts energy levels and transition probabilities, $P_{i \rightarrow j}$) and statistical thermodynamics (which governs state populations, N_i) enables a comprehensive understanding and prediction of both the positions and relative intensities, I , of spectral lines observed experimentally.

A simple way of separating out the probability contribution to the overall intensity is to find systems where the molecules are equally distributed among all states (the high temperature or high energy limit), or systems where all the molecules are in a single state (the low temperature limit). One example is atomic emission spectra, where atoms are excited in equal proportions across all possible electronically excited states via high energy electrical discharge, and the light that is emitted upon transition back to the ground electronic state is detected. The simplest example is the atomic emission spectrum of hydrogen.

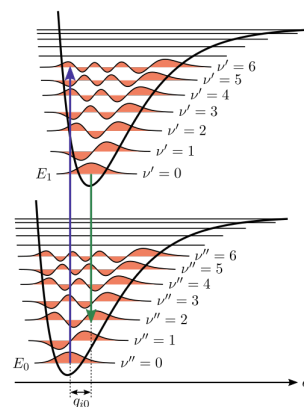


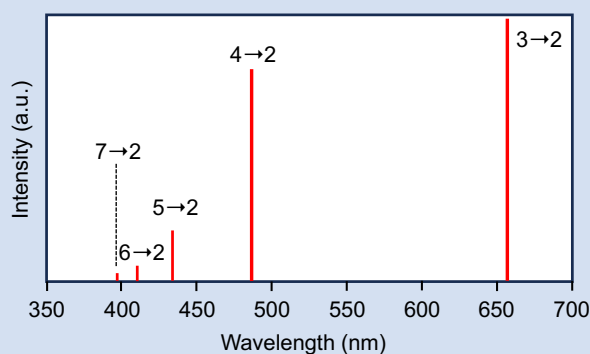
Figure 17.1: The probability of vibronic transitions is related to the extent of vibrational wavefunction overlap between initial and final states. Favourable transitions with high overlaps highlighted.

$$I \propto N_i P_{i \rightarrow j}$$

i = initial state quantum number

j = final state quantum number

Atomic Emission Spectrum of Hydrogen (Balmer Series)



Observations & Explanations:

- Intensity is highest for highest wavelength transitions which are also lowest in energy according to $\Delta E = hc/\lambda$

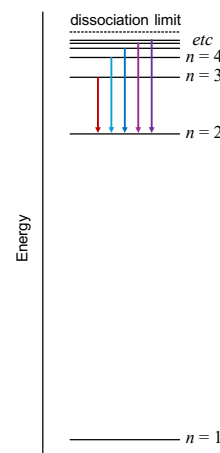
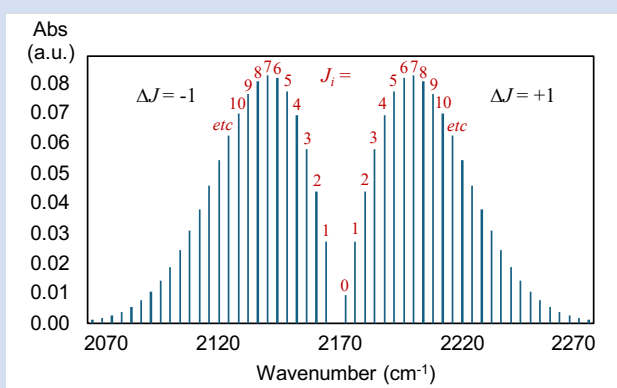


Figure 17.2: Hydrogen atom electronic energy levels with Balmer series transitions illustrated

- Intensity is therefore highest for transitions between states with similar quantum numbers
- This reflects the fact the atomic orbitals associated with these states are more similar in spatial extent.

Similarly, to illustrate the population contribution to the overall intensity, we need to look for systems where the probabilities of allowed transitions between energy levels are equal. Fortunately, ro-vibrational spectra of diatomic molecules fulfil this criterion, thanks to the rotational selection rule $\Delta J = \pm 1$. Quantum mechanical selection rules are an extreme case example of cases in which the intrinsic transition probability is either zero or one, but nothing in between.

Ro-vibrational Spectrum of Carbon Monoxide at $T = 298.15$ K



Observations & Explanations:

- All transitions involve excitation from the ground vibrational state to the first excited vibrational state, and a simultaneous change in rotational state as well.
- Transitions with no change in rotational quantum number or $\Delta J > 1$ are forbidden by symmetry.
- This explains why the purely vibrational transition is not observed at 2170 cm^{-1}
- Because the rotational transitions that are observed occur with a probability of exactly 1, the intensities of these transitions reflects the Boltzmann population of the initial rotational state from which they originate (see Figure 17.3).

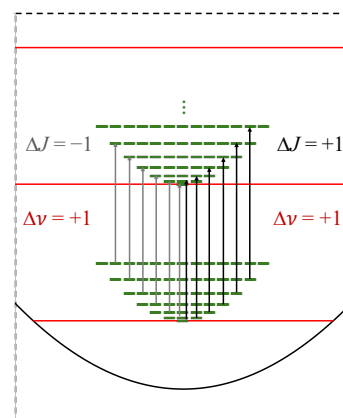
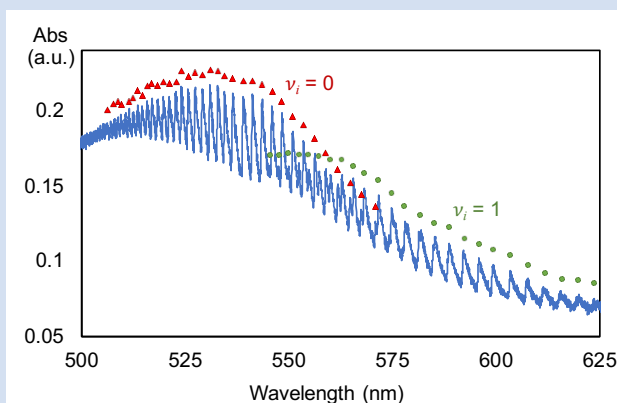


Figure 17.3.: Energy level diagram showing allowed transitions between **rotational** and **vibrational** energy levels.

$$\frac{\Delta E}{hc} = \nu = 2170 \text{ cm}^{-1}$$

Even when Boltzmann populations and transition probabilities both contribute to observed spectral intensities, it may still be possible to separate out these effects, as each term is likely to contribute to observed intensities quite differently. The vibronic (vibrational-electronic) spectrum of iodine vapour provides an ideal model system to investigate this behaviour.

Vibronic Spectrum of Iodine at $T = 298.15$ K**Observations & Explanations:**

- ▶ The maximum achievable intensity for transitions that originate in the ground vibrational state ($v_i = 0$) of the ground electronic state are higher than those that originate in the first excited vibrational state ($v_i = 1$) of the ground electronic state.
- ▶ This reflects the fact that the $v_i = 0$ is more highly populated.
- ▶ The $v_i = 1$ state is significantly populated at room temperature, reflecting the fact that iodine has a long, weak bond and therefore quite closely spaced vibrational energy levels.
- ▶ The transitions arising from $v_i = 0$ and $v_i = 1$ display a similar overall intensity profile, because this reflects the overlap of *similar* vibrational wavefunctions of the molecule in its ground electronic state with very *different* vibrational wavefunctions after the molecule has transitioned to its first excited electronic state, as illustrated in Figure 17.1.
- ▶ The shifting of excited state potential energy curves to longer bond lengths enhances the probability of transitions to higher excited vibrational states which sample a wider range of bond lengths during their vibrational motion.

The ability to compute Gibbs free energies is crucial for predicting the spontaneity position of chemical reactions. At constant temperature and pressure, the Gibbs free energy change (ΔG) determines whether a process will proceed spontaneously ($\Delta G < 0$) or not. By calculating ΔG for multiple possible reactions or pathways, one can predict favourable reaction routes, assess reaction feasibility and establish conditions under which formation of the desired products is favoured.

However, in order to compute *changes* in Gibbs free energies for chemical processes and transformations, it is first necessary to be able to compute free energies of isolated reactants and products. In statistical mechanics, the free energy of a gas-phase molecule is determined by summing various energetic and entropic contributions derived from the partition function. Each degree of freedom (electronic, vibrational, rotational, and translational) contributes to the total energy and entropy of the molecule. The statistical mechanical treatment allows us to systematically compute these contributions from first principles, providing thermodynamic functions as ensemble averages over quantum states populated according to the Boltzmann distribution.

The electronic energy, U_{elec} forms the foundation of a molecule's total energy. In practice, this is estimated using quantum chemical calculations and corresponds to the minimum energy point on the molecule's global electronic potential energy surface. This electronic energy is then corrected for zero-point vibrational effects, to account for the temperature-independent quantum vibrational energy of the molecule that is present even at 0 K.

Zero-point vibrational energy

Within the quantum harmonic oscillator approximation, vibrational energy levels are:

$$\epsilon_n = h\nu\left(n + \frac{1}{2}\right) \quad (18.1)$$

Hence, the zero-point energy is simply:

$$\epsilon_0 = \frac{1}{2}h\nu \quad (18.2)$$

Within the molecular harmonic oscillator approximation, the total vibrational energy is a sum of contributions of from “maximally orthogonal” normal modes of vibration, each characterised by their harmonic vibrational frequency, ν_i :

$$\text{ZPVE} = \sum_{i=1}^{N_{\text{mode}}} \frac{1}{2}h\nu_i \quad (18.3)$$

The thermal vibrational contribution to internal energy and entropy arises from the thermal population of excited vibrational states, which is accounted for via the vibrational partition function. However, at this point, it becomes necessary to specify the temperature at which $U_{\text{thermal}}^{\text{vib}}$ and S^{vib} are to be computed. The most logical choice is standard thermodynamic conditions ($T = 298.15 \text{ K}$ and $p = 1 \text{ bar}$), because this provides a universally accepted reference and ensures interoperability and reusability of computed data and values. Additionally, thermal energies and entropies are evaluated per mole of molecules, to obtain thermodynamic parameters on a chemically-relevant scale.

Under standard thermodynamic conditions, rotational contributions to internal energy and entropy may be accurately estimated for almost all molecular species using high-temperature limit expressions for $U_{\text{thermal}}^{\text{rot}}$ and S^{rot} , greatly simplifying their evaluation. Similarly, expressions for translational energies and entropies can only be obtained in the high-temperature limit, but this approximation is abundantly satisfied under standard thermodynamic conditions.

For completeness, all of the key equations required to evaluate molar translational, rotational and vibrational enthalpies and entropies for general polyatomic molecules are summarised below, in conjunction with the relationship:

$$S = \frac{U_{\text{thermal}}}{T} + N_{\text{A}} k_{\text{B}} \ln q \quad (18.4)$$

Mode	U_{thermal}	q
translational	$\frac{3}{2} N_{\text{A}} k_{\text{B}} T$	$\frac{V}{\Lambda^3} \quad \Lambda = \frac{h}{\sqrt{2\pi m k_{\text{B}} T}}$
rotational	$\frac{3}{2} N_{\text{A}} k_{\text{B}} T$	$\frac{\sqrt{\pi}}{\sigma} \left(\frac{T}{\Theta_{\text{A}}} \right)^{1/2} \left(\frac{T}{\Theta_{\text{B}}} \right)^{1/2} \left(\frac{T}{\Theta_{\text{C}}} \right)^{1/2}$ $\Theta_{\text{A}} = \frac{h^2}{2I_{\text{A}} k_{\text{B}}}, \text{ etc.}$
vibrational	$\sum_{i=1}^{N_{\text{mode}}} N_{\text{A}} \frac{h\nu_i e^{-h\nu_i/k_{\text{B}}T}}{1 - e^{-h\nu_i/k_{\text{B}}T}}$	$\prod_{i=1}^{N_{\text{mode}}} \frac{1}{1 - e^{-h\nu_i/k_{\text{B}}T}}$

Gibbs Free Energy

Finally, it remains to combine all of these contributions to evaluate the free energy of each molecular species:

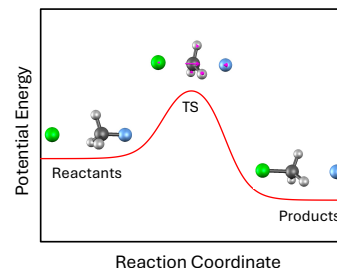
$$G = E_{\text{elec}} + \text{ZPVE} + (U_{\text{thermal}}^{\text{vib}} + U_{\text{thermal}}^{\text{rot}} + U_{\text{thermal}}^{\text{trans}}) - T(S^{\text{vib}} + S^{\text{rot}} + S^{\text{trans}}) \quad (18.5)$$

Transition State Theory

19.

The basic postulates of transition state theory are:

- ▶ Rates of reactions are determined by the rate at which 'activated complexes' pass through a transition state, which is generally a saddle point on a potential energy surface.
- ▶ The activated complexes that exist near the transition state (but just on the reactants side) are in a special kind of equilibrium (quasi- or pre-equilibrium) with the reactant molecules.
- ▶ The activated complexes can convert into products if they have sufficient kinetic energy to do so.

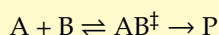


Derivation of TST expression for rate constant k

Consider the elementary reaction $A + B \rightarrow P$ that obeys the rate law:

$$\frac{d[P]}{dt} = k[A][B] \quad (19.1)$$

Activated complex theory proposes that the reactants are in quasi-equilibrium with an activated complex that is close to the transition state. The transition state is the point on a potential energy surface (generally a saddle point) through which each and all successful reactive encounters will pass, and proceed with 100% probability to form products.



Hence, the rate law for the reaction may also be formulated in terms of activated complex concentration, $[AB^\ddagger]$, and the frequency with which each activated complex reaches the transition state and proceeds to form products, f :

$$\frac{d[P]}{dt} = f[AB^\ddagger] \quad (19.2)$$

Equating (19.1) and (19.2) we find:

$$k = \frac{f[AB^\ddagger]}{[A][B]} = fK_{\text{act}}^\ddagger \quad (19.3)$$

Now, the question becomes - how can we predict the relative concentrations of the reactants and activated complexes from first principles?

The trick is to realise that all of these species are in thermal equilibrium with each other, and we may therefore apply the tools of statistical thermodynamics to compute their relative concentrations.

Broadly speaking, in the same way the thermal population of each quantum state of a molecule is proportional to its Boltzmann factor, the thermal population of a molecule in a mixture is proportional to its partition function. Dividing by volume to obtain concentrations:

$$k = f \frac{(q_{AB^\ddagger}/V)}{(q_A/V)(q_B/V)} \quad (19.4)$$

$$K_{\text{act}}^\ddagger = \frac{[AB^\ddagger]}{[A][B]}$$

Quasi-equilibrium constant quantifying concentrations of reactants and activated complexes in a pre-reactive 'soup'

$$q_i = g_i e^{-(\epsilon_i - \epsilon_0)/k_B T}$$

Boltzmann factor

$$q = \sum_{i=0}^{\infty} g_i e^{-(\epsilon_i - \epsilon_0)/k_B T}$$

Partition function

There are two issues to resolve before we can use equation (19.4): q_{AB^\ddagger} is missing a contribution from the “reaction coordinate” mode of motion, and we do not know what fraction of active complexes, f , moving along this reaction coordinate will reach the transition state.

Defining a small region just before the transition state quantified by a displacement of δx along the reaction coordinate, the tools of statistical thermodynamics may again be applied to derive an expression for the barrier crossing frequency from this region, f , and write down the partition function for the “missing” mode of motion, q_{trans} , as explained in the margin. Now:

$$k = f q_{\text{trans}} \frac{(q_{AB^\ddagger}/V)}{(q_A/V)(q_B/V)} \quad (19.5)$$

So finally:

$$k = \frac{k_B T}{h} \frac{(q_{AB^\ddagger}/V)}{(q_A/V)(q_B/V)} \quad (19.6)$$

Now all that remains is to evaluate the molecular partition functions q_A , q_B and q_{AB^\ddagger} from microscopic quantities such as electronic energies, vibrational frequencies and moments of inertia, which may be obtained through *ab initio* calculations, excluding the reaction coordinate mode of the transition state, which has already been accounted for.

However, it is helpful to first expand out these overall molecular partition functions into translational, vibrational, rotational and electronic terms.

TST expression for k factorised into nuclear and electronic terms

$$k = \frac{k_B T}{h} \left(\frac{[(q_{AB^\ddagger}^{\text{trans}}/V) q_{AB^\ddagger}^{\text{rot}} q_{AB^\ddagger}^{\text{vib}}]}{[(q_A^{\text{trans}}/V) q_A^{\text{rot}} q_A^{\text{vib}}][(q_B^{\text{trans}}/V) q_B^{\text{rot}} q_B^{\text{vib}}]} \right) \left(\frac{q_{AB^\ddagger}^{\text{elec}}}{q_A^{\text{elec}} q_B^{\text{elec}}} \right) \quad (19.7)$$

The electronic contributions may be further expanded, as they depend only on the electronic energies* of each component of the reaction mixture:

$$k = \frac{k_B T}{h} \left(\frac{[(q_{AB^\ddagger}^{\text{trans}}/V) q_{AB^\ddagger}^{\text{rot}} q_{AB^\ddagger}^{\text{vib}}]}{[(q_A^{\text{trans}}/V) q_A^{\text{rot}} q_A^{\text{vib}}][(q_B^{\text{trans}}/V) q_B^{\text{rot}} q_B^{\text{vib}}]} \right) e^{-\frac{(E_{AB^\ddagger} - (E_A + E_B))}{k_B T}} \quad (19.8)$$

It is already clear from equation (19.8) that, according to transition state theory, rate constants increase exponentially with temperature primarily due to a higher proportion of reactants forming activated complexes; the frequency of activated complexes reaching the transition state from the activated complex region increases only linearly with temperature while the population of the activated complex region increases exponentially.

$$f = \frac{v_{\text{av}}}{\delta x} \quad v_{\text{av}} = \sqrt{\frac{k_B T}{2\pi m^\ddagger}}$$

Barrier-crossing frequency is directly proportional to the average relative velocity of reactants towards one another, v_{av} , and inversely proportional to the extent of the activated complex region.

$$q_{\text{trans}} = \frac{\delta x}{\sqrt{\Lambda}} \quad \Lambda = \frac{h^2}{2\pi m^\ddagger k_B T}$$

Partition function for the 1D translational mode of motion that brings the reactants towards each other within the activated complex region.

$$q = q^{\text{trans}} q^{\text{rot}} q^{\text{vib}} q^{\text{elec}}$$

The overall molecular partition function is a product of contributions from each different mode of motion, due to additivity of the corresponding energy terms.

*Electronic energies may, optionally, be corrected for zero-point vibrational effects

APPENDIX

Derivation of the Boltzmann Distribution

A.

According to microscopic statistical theory, the weight of any configuration is equal to the number of ways of generating that configuration by selecting molecules to generate a specified population of excited states:

$$W = \frac{N!}{N_0!N_1!\dots} = \frac{N!}{\prod_i N_i!} \quad (\text{A.1})$$

However, for all practical intents and purposes, this expression is not useful as it rapidly becomes uncomputable. Hence, some nifty mathematical tricks are required to convert this into a form that is amenable to both computation and further mathematical analysis, *e.g.* optimization.

To convert fractions and products to linear terms, take the natural logarithm of both sides:

$$\begin{aligned} \ln W &= \ln \left(\frac{N!}{N_0!N_1!\dots} \right) \\ &= \ln N! - \ln (N_0!N_1!\dots) \\ &= \ln N! - (\ln N_0! + \ln N_1! + \dots) \\ &= \ln N! - \sum_{i=0}^{\infty} \ln N_i! \end{aligned} \quad (\text{A.2})$$

To get rid of the troublesome factorials (so we have some chance of determining the N_i directly), invoke Stirling's approximation (only valid when x is large, but this is no problem when we are considering collections of $\sim 10^{23}$ molecules):

$$\ln x! \approx x \ln x - x \quad (\text{A.3})$$

Applying this to equation (A.2):

$$\begin{aligned} \ln W &\approx (N \ln N - N) - \sum_{i=0}^{\infty} (N_i \ln N_i - N_i) \\ &\approx N \ln N - \sum_{i=0}^{\infty} N_i \ln N_i - \left(N - \sum_{i=0}^{\infty} N_i \right) \\ &\approx N \ln N - \sum_{i=0}^{\infty} N_i \ln N_i \end{aligned} \quad (\text{A.4})$$

We are interested in finding the most probable configuration *i.e.* the set of energy level populations that gives the highest possible weight, subject to the constraints that:

- the number of particles across all energy levels must add to give the total number of particles in the system, and
- the total energy of the system must reach some specified value

Mathematically, these constraints can be expressed as:

$$\sum_{i=0}^{\infty} N_i = N \quad (\text{A.5})$$

$$\sum_{i=0}^{\infty} \epsilon_i N_i = E \quad (\text{A.6})$$

where N_i = number of particles in energy level i and ϵ_i = energy of a particle in that energy level relative to the ground state energy (subtraction of ground state energies will be omitted for conciseness and clarity).

Alternatively, we can require that the total number of particles and total energy doesn't *change* as we vary the distribution of particles among energy levels:

$$\sum_{i=0}^{\infty} dN_i = 0 \quad (\text{A.7})$$

$$\sum_{i=0}^{\infty} \epsilon_i dN_i = 0 \quad (\text{A.8})$$

The problem of finding the optimal value of W by varying the numbers of particles occupying each energy level is expressed as:

$$d \ln W = \sum_{i=0}^{\infty} \frac{\partial \ln W}{\partial N_i} dN_i = 0 \quad (\text{A.9})$$

However, as the populations of the energy levels are intimately connected to one another via the constraints on total energy and number of particles, it turns out that the number of *independent* values we need to determine is not infinite, and we can use an optimization technique known as *Lagrange's method of undetermined multipliers*.

Lagrange's Method of Undetermined Multipliers

See:

<http://www.slimy.com/~steuard/teaching/tutorials/Lagrange.html>
for now.

Requiring that $\ln W$ only varies if the total energy and/or number of particles vary (or, equivalently, that the rate of change of $\ln W$ matches the rate of change of energy and/or number of particles to within a given constant multiplier):

$$\begin{aligned} d \ln W &= \sum_{i=0}^{\infty} \frac{\partial \ln W}{\partial N_i} dN_i = \alpha \sum_{i=0}^{\infty} dN_i + \beta \sum_{i=0}^{\infty} \epsilon_i dN_i \\ &= \left(\sum_{i=0}^{\infty} \frac{\partial \ln W}{\partial N_i} - \alpha - \beta \epsilon_i \right) dN_i = 0 \end{aligned} \quad (\text{A.10})$$

This has the bonus effect of allowing us to solve these equations for each energy level separately. All energy levels must satisfy the equations below:

$$\frac{\partial \ln W}{\partial N_i} - \alpha - \beta \epsilon_i = 0 \quad (\text{A.11})$$

We shall begin by differentiating equation (A.4) with respect to N_i .

Insert working here

Finally yielding the equation that defines the **Boltzmann distribution**:

$$\frac{N_i}{N} = \frac{e^{-\beta\epsilon_i}}{\sum_{i=0}^{\infty} e^{-\beta\epsilon_i}} \quad (\text{A.12})$$

Rotational Heat Capacity

B.

The thermal rotational energy distributed amongst a collection of N freely rotating diatomic molecules characterised by their moment of inertia, I , at temperature T , may be computed as:

$$U_{\text{thermal}}^{\text{rot}} = NB \frac{\sum_J J(J+1)(2J+1)e^{-\beta BJ(J+1)}}{\sum_J (2J+1)e^{-\beta BJ(J+1)}} \quad (\text{B.1}) \quad B = \frac{\hbar^2}{2I}$$

To derive an expression for the rotational contribution to the heat capacity, we first express the above equation in a 'differentiation-friendly' form:

$$U_{\text{thermal}}^{\text{rot}} = NB \left(\sum_J J(J+1)(2J+1)e^{-\beta BJ(J+1)} \right) \left(\sum_J (2J+1)e^{-\beta BJ(J+1)} \right)^{-1}$$

Next, we find the derivative of $U_{\text{thermal}}^{\text{rot}}$ with respect to T by way of differentiation with respect to β :

$$\begin{aligned} C^{\text{rot}} &= -k_B \beta^2 \frac{dU_{\text{thermal}}^{\text{rot}}}{d\beta} \\ &= -k_B \beta^2 NB \frac{d}{d\beta} \left(\sum_J J(J+1)(2J+1)e^{-\beta BJ(J+1)} \right) \left(\sum_J (2J+1)e^{-\beta BJ(J+1)} \right)^{-1} \end{aligned} \quad (\text{B.2})$$

We will need to invoke the product, composite and sum rules of differentiation (in that order) to evaluate the derivative with respect to β . These formulae can be found in any first year calculus textbook, but are reproduced for clarity here.

$$\frac{d}{dx} f(x)g(x) = f(x)\frac{dg(x)}{dx} + g(x)\frac{df(x)}{dx} = f(x)g'(x) + g(x)f'(x)$$

$$\frac{d}{dx} f(g(x)) = \frac{df(g(x))}{dg(x)} \frac{dg(x)}{dx} = f'(g(x))g'(x)$$

$$\frac{d}{dx} (f(x) + g(x)) = \frac{df(x)}{dx} + \frac{dg(x)}{dx} = f'(x) + g'(x)$$

Focussing solely on the derivative term in equation (B.2):

$$\begin{aligned}
& \frac{d}{d\beta} \left(\sum_J J(J+1)(2J+1)e^{-\beta BJ(J+1)} \right) \left(\sum_J (2J+1)e^{-\beta BJ(J+1)} \right)^{-1} \\
&= \left(\sum_J (2J+1)e^{-\beta BJ(J+1)} \right)^{-1} \frac{d}{d\beta} \left(\sum_J J(J+1)(2J+1)e^{-\beta BJ(J+1)} \right) \\
&\quad + \left(\sum_J J(J+1)(2J+1)e^{-\beta BJ(J+1)} \right) \frac{d}{d\beta} \left(\sum_J (2J+1)e^{-\beta BJ(J+1)} \right)^{-1} \\
&= \left(\sum_J (2J+1)e^{-\beta BJ(J+1)} \right)^{-1} \frac{d}{d\beta} \left(\sum_J J(J+1)(2J+1)e^{-\beta BJ(J+1)} \right) \\
&\quad - \left(\sum_J J(J+1)(2J+1)e^{-\beta BJ(J+1)} \right) \left(\sum_J (2J+1)e^{-\beta BJ(J+1)} \right)^{-2} \\
&\quad \frac{d}{d\beta} \left(\sum_J (2J+1)e^{-\beta BJ(J+1)} \right) \\
&= -B \left(\sum_J (2J+1)e^{-\beta BJ(J+1)} \right)^{-1} \left(\sum_J J^2(J+1)^2(2J+1)e^{-\beta BJ(J+1)} \right) \\
&\quad + B \left(\sum_J J(J+1)(2J+1)e^{-\beta BJ(J+1)} \right) \left(\sum_J (2J+1)e^{-\beta BJ(J+1)} \right)^{-2} \\
&\quad \left(\sum_J J(J+1)(2J+1)e^{-\beta BJ(J+1)} \right) \\
&= -B \left(\sum_J (2J+1)e^{-\beta BJ(J+1)} \right)^{-1} \left(\sum_J J^2(J+1)^2(2J+1)e^{-\beta BJ(J+1)} \right) \\
&\quad + B \left(\sum_J J(J+1)(2J+1)e^{-\beta BJ(J+1)} \right)^2 \left(\sum_J (2J+1)e^{-\beta BJ(J+1)} \right)^{-2}
\end{aligned}$$

Combining this expression with the $-Nk_B\beta^2B$ prefactor finally gives:

$$\begin{aligned}
C^{\text{rot}} &= Nk_B\beta^2B^2 \\
&\left(\frac{\sum_J J^2(J+1)^2(2J+1)e^{-\beta BJ(J+1)}}{\sum_J (2J+1)e^{-\beta BJ(J+1)}} - \frac{\left(\sum_J J(J+1)(2J+1)e^{-\beta BJ(J+1)} \right)^2}{\left(\sum_J (2J+1)e^{-\beta BJ(J+1)} \right)^2} \right)
\end{aligned} \tag{B.3}$$

Constants and Conversion Factors

C.

Name	Symbol	Value
Boltzmann constant	k_B	$1.380649 \times 10^{-23} \text{ J K}^{-1}$
Planck constant	h	$6.62607015 \times 10^{-34} \text{ J s}$
hbar	\hbar	$h/2\pi = 1.05457182 \times 10^{-34} \text{ J s}$
Avogadro's number	N_A	$6.02214076 \times 10^{23} \text{ particles/mole}$
speed of light	c	$29979245800 \text{ cm s}^{-1}$

Quantity	Reported Units	Required Units	Conversion process
Electronic energy, E	Hartree	J	$1 E_h = 4.35974472 \times 10^{-18} \text{ J}$
Zero-point vib'l energy, ZPVE	kcal/mol	J	Multiply by 4.184 \rightarrow kJ/mol Multiply by 1000 \rightarrow J/mol Divide by $N_A = 6.02214076 \times 10^{23}$
Mass, m	g mol^{-1} (amu)	kg	Divide by 1000 \rightarrow kg/mol Divide by $N_A = 6.02214076 \times 10^{23}$
Moment of inertia, I	amu Bohr ²	kg m ²	Convert amu to kg as above Convert Bohr to m, $1 \text{ Bohr} = 0.529177249 \times 10^{-10} \text{ m}$
Vibrational frequency, ν	cm^{-1}	s^{-1}	Multiply by speed of light in cm s^{-1} $c = 29979245800 \text{ cm s}^{-1}$