

STATISTICAL THERMODYNAMICS: A PRIMER FOR CHEMISTST



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This text was compiled on 02/01/2026

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CHAPTER OVERVIEW

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1.1: Overview

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?

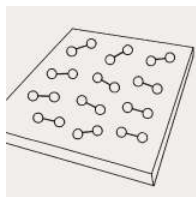
Brute-force simulation is the conceptually simplest solution; jointly modelling electronic behaviour and nuclear dynamics for large collections of molecules. However, this is exactly as computationally intensive as it sounds, limiting its applicability to small systems (< 1000 atoms) and short time scales (< 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. 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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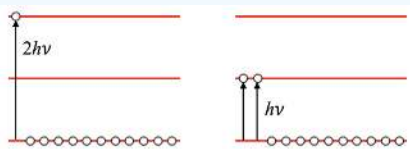
1.2: Microscopic Statistics

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?

✓ Example 1.2.1: Distributing thermal energy



Solution

- (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 $12 \times 11/2 = 66$.

Definitions

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 $2h\nu$ and all other molecules in the 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.* $W_{2,0,0...} = 12$, $W_{1,1,0...} = 66$

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1.3: Configuration Weights

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

Definition: Configuration Weight

$$W = \frac{N!}{N_0!N_1!\cdots N_n!} \quad (1.3.1)$$

where N = total number of particles in the system, N_0 = ground state population, N_1 = population of first excited state, etc, and n represents the highest thermally occupied energy level.

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.

✓ Example 1.3.1: Distributing $2h\nu$ of thermal energy amongst 1000 quantum harmonic oscillators

$W_{2,0,0,\dots}$ = number of ways of choosing a single molecule to excite by $2h\nu$ = **1000**

$W_{1,1,0,\dots}$ = number of ways of choosing two molecules to each excite by $h\nu$ = $1000 \times 999 / 2$ = **499,500**

Clearly, there are far more ways of choosing two molecules to each excite by one quantum of vibrational energy than there are ways of choosing a single molecule to undergo a single double excitation.

This turns out to be quite a general result; 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?

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1.4: The Boltzmann Distribution

Definition: Configuration Weight

$$W = \frac{N!}{N_0!N_1!\dots N_n!} \quad (1.4.1)$$

where N = total number of particles in the system, N_0 = ground state population, N_1 = population of first excited state, etc, and n represents the highest thermally occupied energy level.

Although we now have a general formula for computing the weight of any configuration, it rapidly becomes impossible to evaluate as the amount of thermal energy and number of particles in a system increase to experimentally-relevant values. Determining the most probable configuration by brute force is even harder, as all possible ways of distributing thermal energy amongst all available energy levels of all particles in the system must be trialled.

Boltzmann's key insight was recognising that it was possible to find the most probable configuration (maximizing W) by varying the populations of each energy level (with respect to changes in N_i) using some clever mathematical tricks:

Approximations applied in deriving Boltzmann distribution

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

A complete derivation of the Boltzmann equation is provided in [the Appendix](#). The key result is:

Definition: The Boltzmann Distribution

$$\frac{N_i}{N} = \frac{e^{-\beta(\epsilon_i - \epsilon_0)}}{\sum_i e^{-\beta(\epsilon_i - \epsilon_0)}} \quad (1.4.2)$$

where ϵ_i represent quantum energy levels and the parameter β was introduced to ensure that the total energy remains constant as energy is distributed amongst available quantum energy levels of particles in the system to maximize W .

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1.5: The Boltzmann Constant

Definition: The Boltzmann Distribution

$$\frac{N_i}{N} = \frac{e^{-\beta(\epsilon_i - \epsilon_0)}}{\sum_i e^{-\beta(\epsilon_i - \epsilon_0)}} \quad (1.5.1)$$

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?

This is best investigated by means of a thought experiment...

✓ Example 1.5.1: 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:

Boltzmann populations

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

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, i.e.

$$\beta \propto \frac{1}{T} \quad (1.5.2)$$

Another way of expressing this relationship is using a constant of proportionality:

Definition: The Boltzmann Constant

$$\beta = \frac{1}{k_B T} \quad (1.5.3)$$

A 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**.

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

(1.5.4)

It is also now clear that temperature is a *unique thermodynamic parameter that governs the most probable populations of quantum states when a system of identical but distinguishable non-interacting quantum particles 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.

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1.6: Dealing with Degeneracy

One final little wrinkle that must be ironed out before proceeding is how to deal with situations in which multiple quantum states have the same energy, *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 quantum states with this energy.

Definition: The Boltzmann Equation

$$\frac{N_i}{N} = \frac{g_i e^{-(\epsilon_i - \epsilon_0)/(k_B T)}}{\sum_i g_i e^{-(\epsilon_i - \epsilon_0)/(k_B T)}} \quad (1.6.1)$$

in which g_i represents the degeneracy of each energy level with associated energy ϵ_i .

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1.7: The Partition Function

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 .

Definition: The Partition Function, q

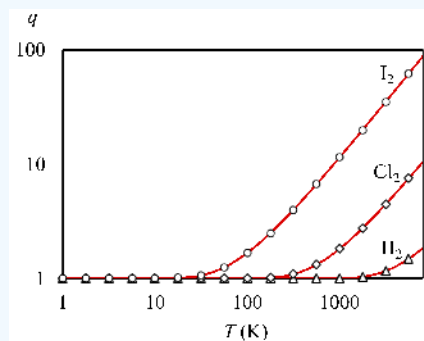
$$\frac{N_i}{N} = \frac{q_i}{q} \quad (1.7.1)$$

$$q_i = g_i e^{-(\epsilon_i - \epsilon_0)/(k_B T)} \quad (1.7.2)$$

$$q = \sum_i q_i \quad (1.7.3)$$

At first glance, 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 for a system of surface-immobilized diatomics:

✓ Example 1.7.1: The Partition Function, $q(T)$



$$\nu(\text{H}_2) > \nu(\text{Cl}_2) > \nu(\text{I}_2)$$

Observations & Implications:

- q increases with T with an apparent threshold temperature that depends on energy level spacings (Reminder: $\epsilon_i = h\nu(i + \frac{1}{2})$).
- At any given T , q is larger for collections of molecules with more closely spaced energy levels.
- 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 amongst individual quantum energy levels. This is the job of the Boltzmann distribution.**

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1.8: Internal Energy

Conceptually, the simplest way of computing the thermal energy of a system at $T > 0 \text{ K}$ is simply to determine Boltzmann populations (N_i) and then count the energy associated with each set of thermally-excited molecules:

 Definition: Internal Energy, U_{thermal} , from Boltzmann populations

$$U_{\text{thermal}} = \sum_i N_i (\epsilon_i - \epsilon_0) \quad (1.8.1)$$

However, this turns out to be quite computationally inefficient. More computationally efficient approaches include:

 Definition: Internal Energy, U_{thermal} , via energy-weighted sums of Boltzmann factors

$$U_{\text{thermal}} = N \frac{\sum_i (\epsilon_i - \epsilon_0) q_i}{\sum_i q_i} \quad (1.8.2)$$

$$q_i = g_i e^{-(\epsilon_i - \epsilon_0)/(k_B T)} \quad (1.8.3)$$

wherein the denominator $q = \sum_i q_i$ is recognised as the partition function for the system and N represents the total number of particles in the system.

 Definition: Internal Energy, U_{thermal} , via differentiation of the partition function

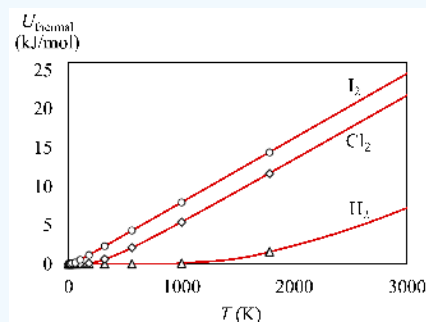
$$U_{\text{thermal}} = - \frac{N}{q} \frac{dq}{d\beta} \quad (1.8.4)$$

where $\beta = 1/(k_B T)$, q again represents the partition function and N is the total number of particles in the system. Although this approach seems more abstract and of little practical use at present, it becomes invaluable when the partition function is evaluated analytically rather than numerically.

The mathematical equivalence of these approaches is demonstrated in [the Appendix](#).

Once again, it is instructive to investigate how thermal energy changes with temperature and/or energy level spacings for a system of surface-immobilised diatomics:

✓ Example 1.8.1: $U_{\text{thermal}}(T)$



$$\nu(\text{H}_2) > \nu(\text{Cl}_2) > \nu(\text{I}_2)$$

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.

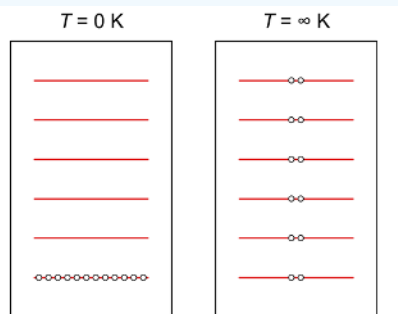
- In the high temperature limit, U_{thermal} increases linearly with T . This limit is reached at lower temperatures in systems with more closely spaced energy levels.
- U_{thermal} goes to zero faster than linearly as $T \rightarrow 0$.

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1.9: Entropy

Statistical thermodynamics provides 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 $T \rightarrow \infty$.

✓ Example 1.9.1: Boltzmann Distributions at $T = 0$ K and $T = \infty$ K



Observations:

- At $T = 0$ K there is no thermal energy and all molecules are in their ground vibrational state. There is only one way of achieving this so $W = 1$. It is also a perfectly ordered state, so $S = 0$.
- As $T \rightarrow \infty$ all energy levels are equally occupied, as each Boltzmann factor $q_i = g_i e^{-(\epsilon_i - \epsilon_0)/(k_B T)} \rightarrow g_i$. In other words, when an infinite amount of thermal energy is available it is equally distributed without regard for energy level spacings (but still accounting for degeneracies), because this generates the highest-weighted configuration.
- As $T \rightarrow \infty$ this energy distribution pattern does not change significantly, suggesting that the entropy of the system tends to a constant value, even though the number of ways of distributing thermal energy amongst available energy levels must continue increasing as more of them become thermally available.

To summarise, W and S obey the following relationships:

Relationship between configuration weights and entropies

T (K)	W	S	$\ln W$
0	1	0	0
$\rightarrow \infty$	increases with T	constant	constant

This immediately suggests that $S \propto \ln W$. Once again, this relationship may be expressed using a constant of proportionality, which again turns out to be the Boltzmann constant:

Definition: Formal Statistical Definition of Entropy, S

$$S = k_B \ln W \quad (1.9.1)$$

Unfortunately, it is impractical to compute the entropy by applying this formula directly, for the same reason it is impractical to evaluate W directly. Fortunately, this relationship can be reformulated in terms of quantities we have already worked out how to compute:

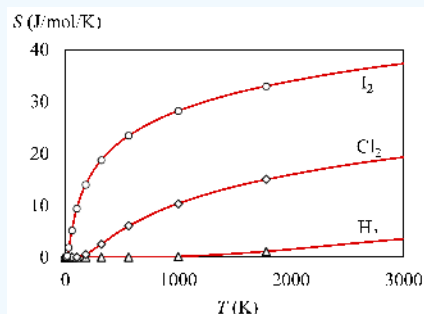
 Definition: Practical Statistical Definition of Entropy, S

$$S = \frac{U_{\text{thermal}}}{T} + Nk_B \ln q \quad (1.9.2)$$

A full derivation of this expression may be found [the Appendix](#).

We may now verify that this relationship obeys the expected behaviour at $T = 0$ and as $T \rightarrow \infty$ for a collection of diatomic molecules immobilized on a surface:

✓ Example 1.9.1: Dependence of S on T and energy level spacings



$$\nu(\text{H}_2) > \nu(\text{Cl}_2) > \nu(\text{I}_2)$$

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 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 .

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CHAPTER OVERVIEW

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2.1: Overview

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:

$$\epsilon_{ijkl}^{\text{total}} = \epsilon_i^{\text{elec}} + \epsilon_j^{\text{vib}} + \epsilon_k^{\text{rot}} + \epsilon_l^{\text{trans}} \quad (2.1.1)$$

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.

✓ Example 2.1.1: Separability of the molecular partition function

$$\begin{aligned} q &= \sum_{i,j,k,l} g_i g_j g_k g_l e^{-\beta \epsilon_{ijkl}} \\ &= \sum_{i,j,k,l} g_i g_j g_k g_l e^{-\beta (\epsilon_i^{\text{elec}} + \epsilon_j^{\text{vib}} + \epsilon_k^{\text{rot}} + \epsilon_l^{\text{trans}})} \\ &= \sum_{i,j,k,l} g_i g_j g_k g_l e^{-\beta \epsilon_i^{\text{elec}}} e^{-\beta \epsilon_j^{\text{vib}}} e^{-\beta \epsilon_k^{\text{rot}}} e^{-\beta \epsilon_l^{\text{trans}}} \\ &= \left(\sum_i g_i e^{-\beta \epsilon_i^{\text{elec}}} \right) \left(\sum_j g_j e^{-\beta \epsilon_j^{\text{vib}}} \right) \left(\sum_k g_k e^{-\beta \epsilon_k^{\text{rot}}} \right) \left(\sum_l g_l e^{-\beta \epsilon_l^{\text{trans}}} \right) \\ &= q^{\text{elec}} q^{\text{vib}} q^{\text{rot}} q^{\text{trans}} \end{aligned} \quad (2.1.2)$$

In words, equation (2.1.2) 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 this 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.

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2.2: Translation

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

$$\epsilon_{n_x, n_y, n_z}^{\text{trans}} = \frac{h^2 (n_x^2 + n_y^2 + n_z^2)}{8mL^2} \quad (2.2.1)$$

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.

The translational partition function is then a product of sums over Boltzmann factors associated with motion in each direction:

 Definition: Translational partition function

$$q^{\text{trans}} = \left(\sum_{n_x} e^{-\beta \frac{h^2 n_x^2}{8mL^2}} \right) \left(\sum_{n_y} e^{-\beta \frac{h^2 n_y^2}{8mL^2}} \right) \left(\sum_{n_z} e^{-\beta \frac{h^2 n_z^2}{8mL^2}} \right) \quad (2.2.2)$$

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 thermal energy, even at very low temperatures. For example, billions of translational energy levels of gaseous hydrogen are appreciably occupied even at 4 K (see Appendix for working).

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 (2.2.2) as integrals, which is the opposite of evaluating the area under a curve by numerical integration, e.g. using Simpson's rule or the trapezoidal rule.

 Definition: Translational partition function evaluated analytically

$$q^{\text{trans}} \approx \int_0^\infty e^{-\beta \frac{h^2 n_x^2}{8mL^2}} dn_x \int_0^\infty e^{-\beta \frac{h^2 n_y^2}{8mL^2}} dn_y \int_0^\infty e^{-\beta \frac{h^2 n_z^2}{8mL^2}} dn_z \quad (2.2.3)$$

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

$$\int_0^\infty e^{-ax^2} dx = \frac{\sqrt{\pi}}{2\sqrt{a}} \quad (2.2.4)$$

Applying this result to solve each integral in equation (2.2.3), we find:

$$q^{\text{trans}} \approx \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} L^3 \quad (2.2.5)$$

This may be expressed more generally and succinctly as:

$$q^{\text{trans}} = \frac{V}{\Lambda^3} \quad \Lambda = \frac{h}{\sqrt{2\pi m k_B T}} \quad V = L^3 = \text{volume} \quad (2.2.6)$$

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2.3: Rotation

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 :

$$\epsilon_J = \frac{\hbar^2}{2I} J(J+1) \quad \hbar = \frac{h}{2\pi} \quad (2.3.1)$$

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:

Rotational quantum numbers, degeneracies and wavefunction interpretation

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

The degeneracy of each rotational energy level is therefore:

$$g_J = (2J + 1) \quad (2.3.2)$$

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:

Definition: Diatomic Rotational Partition Function

$$q^{\text{rot}} = \frac{1}{\sigma} \sum_J (2J + 1) e^{-BJ(J+1)/k_B T} \quad (2.3.3)$$

where σ is the rotational symmetry number defined as the number of ways of regenerating the initial molecular configuration during a full period of rotation = 2 for homonuclear diatomics and 1 for heteronuclear.

Empirically, we find that this sum converges to high accuracy ($< 10^{-20}$) within ~ 1000 terms for most diatomic gases below their decomposition temperatures. However, at higher temperatures, it is also reasonable to approximate this sum by an integral:

Definition: Diatomic Rotational Partition Function - High Temperature Limit

$$q^{\text{rot}} \approx \frac{1}{\sigma} \int_0^\infty (2J + 1) e^{-BJ(J+1)/k_B T} dJ \quad (2.3.4)$$

which evaluates to

$$q^{\text{rot, high-T}} = \frac{1}{\sigma} \frac{2Ik_B T}{\hbar^2} \quad (2.3.5)$$

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2.4: Vibration

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

$$\epsilon_n = \left(n + \frac{1}{2}\right) h\nu \quad (2.4.1)$$

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

Definition: Diatomic vibrational partition function

Because vibrational energy levels of diatomics are non-degenerate

$$\begin{aligned} q_{\text{vib}} &= \sum_n e^{-(\epsilon_n - \epsilon_0)/(k_B T)} \\ &= \sum_n e^{-nh\nu/(k_B T)} \end{aligned} \quad (2.4.2)$$

Definition: Diatomic vibrational partition function - analytic

It turns out that we can exactly sum this geometric series to get a simple analytical expression

$$\begin{aligned} q_{\text{vib}} &= (1 + e^{-h\nu/(k_B T)} + e^{-2h\nu/(k_B T)} + \dots) \\ &\quad \downarrow x = e^{-h\nu/(k_B T)} \\ &= (1 + x + x^2 + x^3 + \dots) \\ &= \left(\frac{1}{1-x}\right) \end{aligned}$$

Re-substituting $x = e^{-h\nu/(k_B T)}$ finally gives:

$$q_{\text{vib}} = \frac{1}{1 - e^{-h\nu/(k_B T)}} \quad (2.4.3)$$

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2.5: Electronic

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. Consequently, much higher temperatures are required to thermally populate electronically excited states. This is best illustrated by way of example:

✓ Example 2.5.1: Boltzmann factors for electronically excited states of diatomics

Experimental excitation energies

For a selection of diatomic molecules

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

Boltzmann populations of excited state relative to ground state

For a selection of diatomic molecules

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 (> 1000 K). 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. Therefore, for all practical intents and purposes:

Definition: Electronic partition function

$$q_{\text{elec}} = 1 \quad (2.5.1)$$

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2.6: Internal Energies

As [established previously](#), thermal energies may be computed:

- As an energy-weighted sum of Boltzmann factors, divided by the partition function - most general
- Via differentiation of the partition function with respect to $\beta = 1/(k_B T)$ - most efficient

The most efficient approach is only applicable if the partition function can be evaluated in closed form, i.e. all terms summed or integrated to give a simple analytical expression. Formulas from previous pages are reproduced here in their most differentiation-friendly form:

Key intermediates

	Translation	Rotation (high T limit)	Vibration
q	$V \left(\frac{2\pi m}{h^2} \right)^{3/2} \beta^{-3/2}$	$(\sigma B)^{-1} \beta^{-1}$	$(1 - e^{-\beta h\nu})^{-1}$
$dq/d\beta$	$V \left(\frac{2\pi m}{h^2} \right)^{3/2} \left(-\frac{3}{2} \beta^{-5/2} \right)$	$-(\sigma B)^{-1} \beta^{-2}$	$-(1 - e^{-\beta h\nu})^{-2} (h\nu e^{-\beta h\nu})$
$U_{\text{thermal}}(\beta) = -\frac{N}{q} \frac{dq}{d\beta}$	$\frac{3}{2} N \beta^{-1}$	$N \beta^{-1}$	$N \frac{h\nu e^{-\beta h\nu}}{1 - e^{-\beta h\nu}}$

Definition: Thermal Energies of Translation, Rotation (high T limit) and Vibration

$$U_{\text{thermal}}^{\text{trans}}(T) = \frac{3}{2} N k_B T \quad (2.6.1)$$

$$U_{\text{thermal}}^{\text{rot}}(T) = N k_B T \quad (2.6.2)$$

$$U_{\text{thermal}}^{\text{vib}}(T) = N \frac{h\nu e^{-h\nu/(k_B T)}}{1 - e^{-h\nu/(k_B T)}} \quad (2.6.3)$$

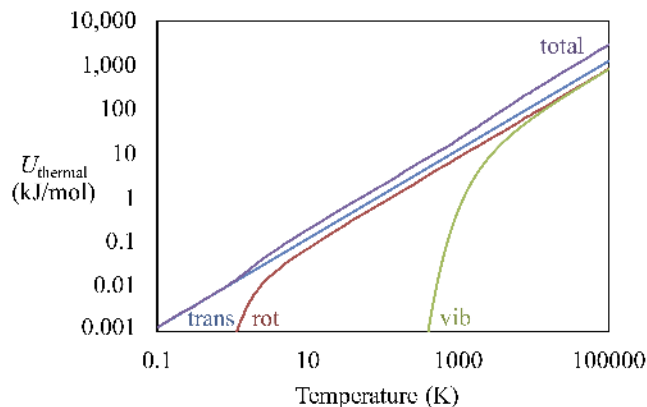
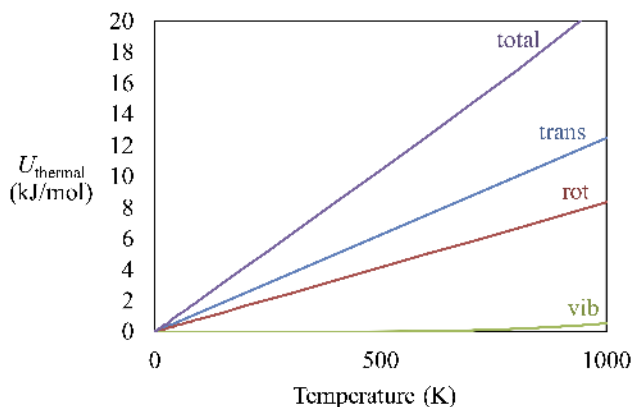
In the high temperature limit, both translational and rotational energies increase linearly with temperature, with each degree of freedom (motion in x , y and z directions, rotation in θ , ϕ coordinates) contributing $\frac{1}{2} k_B T$ per molecule or $\frac{1}{2} N_A k_B T = \frac{1}{2} RT$ per mole of molecules, in line with the classical equipartition principle.

Although it is reasonable to assume that high-T limit conditions are fulfilled with respect to translational energy level spacings at all practically-relevant temperatures ($T > 4 \text{ K}$), the same is not always true for rotational energy levels. Therefore, it is safest to compute rotational thermal energies using the energy-weighted sum of Boltzmann factors approach:

Definition: Rotational Thermal Energies

$$U_{\text{thermal}}^{\text{rot}}(T) = N \frac{\left(\sum_J B J(J+1)(2J+1) e^{-BJ(J+1)/k_B T} \right)}{\left(\sum_J (2J+1) e^{-BJ(J+1)/k_B T} \right)} \quad (2.6.4)$$

✓ Example 2.6.1: U_{thermal} for a collection of independent, non-interacting CO molecules



Observations:

- Translational and rotational thermal energies seem to increase linearly with temperature over the 0 - 1000 K temperature range
- Closer inspection using a log-log plot reveals non-linearity in the 1 - 10 K range for rotational thermal energies
- Vibrational energy levels only become significantly populated above ~ 900 K and do not reach high-T limit until close to 100,000 K
- Overall thermal energy associated with each mode of motion reflects energy level spacings and degrees of freedom; the more closely spaced the energy levels and higher the number of degrees of freedom, the more thermal energy can be "stored" at any given temperature.

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2.7: Entropies

With expressions and/or numerical procedures for computing partition functions and thermal energies at any temperature now in hand, associated entropies may be computed as:

 Definition: Mode-specific entropies for collections of distinguishable non-interacting diatomics

$$S^{\text{mode}} = \frac{U_{\text{thermal}}^{\text{mode}}}{T} + Nk_B \ln q^{\text{mode}} \quad (2.7.1)$$

For rotational and vibrational modes of motion, it is not too difficult to show that this expression yields the correct asymptotic behaviour at both very low and very high temperatures:

- $U_{\text{thermal}} \rightarrow 0$ at a faster-than-linear rate as $T \rightarrow 0$ and $q = 1$ at $T = 0$. Therefore both terms in this equation $\rightarrow 0$ as $T \rightarrow 0$
- $q, U_{\text{thermal}} \propto T$ as $T \rightarrow \infty$. Therefore the first term in this equation is a constant and the second grows logarithmically with T as $T \rightarrow \infty$.

For translations, the entropy tends to a non-zero constant as $T \rightarrow \infty$ reflecting the fact that the high-T limit approximation used in deriving the partition function breaks down at very low temperatures. It is also more important to correct for the indistinguishability of particles within gases due to random scrambling motions, and also to specify the thermodynamic conditions under which the entropy is to be computed because the partition function depends on volume, which can also change with temperature. Therefore, it is more appropriate to use the Sackur-Tetrode equation to compute translational entropies of gases at a specified pressure, P :

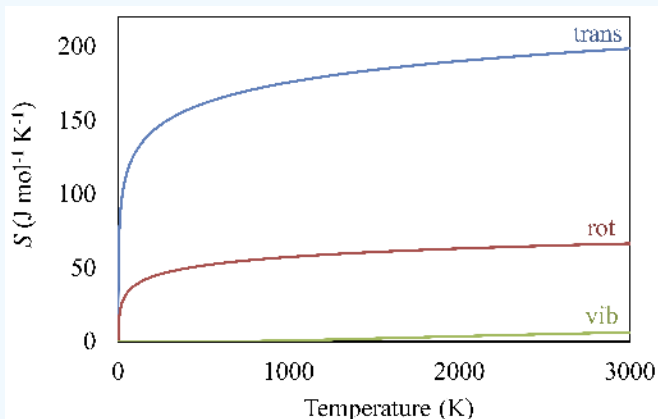
 Definition: Translation entropy for a collection of indistinguishable gas particles

$$S^{\text{trans}} = Nk_B \left[\ln \left(\frac{k_B T}{P \Lambda^3} \right) + \frac{5}{2} \right] \quad (2.7.2)$$

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}} \quad (2.7.3)$$

This formula also tends to the incorrect limit as $T \rightarrow 0$ but is generally applicable for $T > 1\text{K}$ which is sufficient for all practical intents and purposes.

✓ Example 2.7.1: Translational, rotational and vibrational entropies of non-interacting CO molecules at $P = 1$ bar



Observations:

- $S^{\text{trans}} > S^{\text{rot}} > S^{\text{vib}}$
- At any given temperature, the closer the energy level spacings ($\text{trans} < \text{rot} < \text{vib}$), the more ways there are of distributing the available thermal energy amongst them and therefore the greater the entropy.

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2.8: Summary

In previous sections, 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. Therefore:

Relationship between translational, rotational and vibrational partition functions, entropies and enthalpies

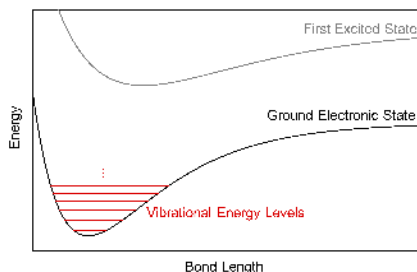
$$q^{\text{trans}} > q^{\text{rot}} > q^{\text{vib}} \quad (2.8.1)$$

$$U_{\text{thermal}}^{\text{trans}} > U_{\text{thermal}}^{\text{rot}} > U_{\text{thermal}}^{\text{vib}} \quad (2.8.2)$$

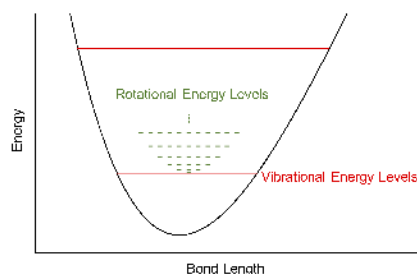
$$S^{\text{trans}} > S^{\text{rot}} > S^{\text{vib}} \quad (2.8.3)$$

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 (larger q), the more ways there are of distributing thermal energy amongst them (higher S), and the more thermal energy is stored overall (greater U_{thermal}).

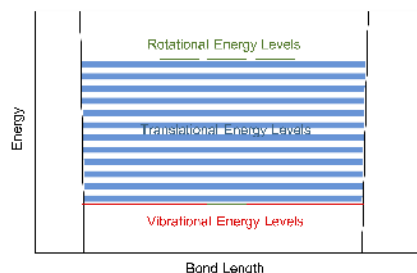
A more intuitive feel for these relationships emerges upon visualisation of the energy level spacings associated with each mode of motion. Starting on the widest energy scale reveals the relationship between electronic and vibrational energy levels:



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.

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CHAPTER OVERVIEW

3: Polyatomics

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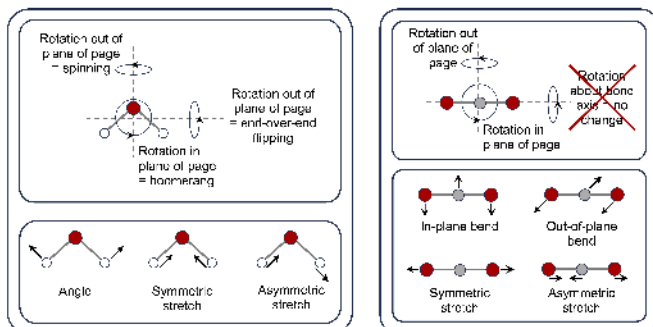
[3.5: Vibration](#)

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3.1: Overview

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 and 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.



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 in a given quantum state may then be expressed as a sum of contributions from each independent mode of motion, *i.e.*

Definition: Rotational and Vibrational Energies

$$\epsilon^{\text{rot}} = \sum_{n=1}^3 \epsilon_{i_n}^{\text{rot},n} \quad \epsilon^{\text{vib}} = \sum_{m=1}^{3N-6} \epsilon_{i_m}^{\text{vib},m} \quad (3.1.1)$$

where i_n = quantum number for rotation about axis n and 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:

Definition: Rotational and Vibrational Partition Functions

$$q^{\text{rot}} = \prod_{n=1}^3 q_n^{\text{rot}} \quad q^{\text{vib}} = \prod_{m=1}^{3N-6} q_m^{\text{vib}} \quad (3.1.2)$$

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

Definition: Overall Molecular Partition Function

$$q = q^{\text{trans}} q^{\text{rot}} q^{\text{vib}} q^{\text{elec}} \quad (3.1.3)$$

where q^{trans} is computed using the same formula as in the diatomic case and q^{elec} may again be assumed to be equal to 1.

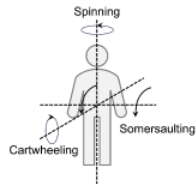
However, it remains to derive explicit expressions for polyatomic rotational and vibrational energy levels and partition functions in the general molecular case.

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3.2: Rotation - Setup

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".



To compute the principle axes of rotation of a molecule, along with the moments of inertia for rotation about these principle axes, we must first translate the molecule to its centre of mass, and then construct and diagonalise the inertia tensor:

✓ Example 3.2.1: Determining Molecular Rotation Axes & Moments of Inertia

Compute centre of mass:

$$\{x_c, y_c, z_c\} = \frac{1}{m_{\text{tot}}} \sum_{i=1}^{N_{\text{atom}}} m_i \{x_i, y_i, z_i\} \quad (3.2.1)$$

and translate molecule to its centre of mass by subtracting the centre of mass coordinate $\{x_c, y_c, z_c\}$ from each atomic coordinate $\{x_i, y_i, z_i\}$.

Construct and diagonalise inertia tensor:

$$\begin{bmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{bmatrix} \quad (3.2.2)$$

$$I_{xx} = \sum_{i=1}^{N_{\text{atom}}} m_i (y_i^2 + z_i^2) \quad (3.2.3)$$

$$I_{xy} = \sum_{i=1}^{N_{\text{atom}}} -m_i x_i y_i \quad (3.2.4)$$

Eigenvectors of this matrix define principle axes of rotation in the original coordinate system and eigenvalues = moments of inertia = $\{I_A, I_B, I_C\}$

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3.3: Rotation

For a "spherical top" molecule with three identical moments of inertia indicating three equivalent axes of rotation, *e.g.*



the rotational Schrödinger equation may be solved exactly:

$$\epsilon_J = \frac{\hbar^2}{2I} J(J+1) \quad g_J = (2J+1)^2 \quad (3.3.1)$$

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.

Definition: Polyatomic Rotational Partition Function

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

$$q^{\text{rot}} = \sum_{J=0}^{\infty} (2J+1)^2 e^{-BJ(J+1)/(k_B T)} \quad (3.3.2)$$

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.

$$\begin{aligned} q^{\text{rot}} &= \int_0^{\infty} (2J+1)^2 e^{-BJ(J+1)/(k_B T)} dJ \\ &= \frac{\sqrt{\pi}}{\sigma} \left(\frac{T}{\Theta} \right)^{3/2} \\ \Theta &= \frac{\hbar^2}{2Ik_B} \end{aligned} \quad (3.3.3)$$

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

$$q^{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{T}{\Theta_A} \right)^{1/2} \left(\frac{T}{\Theta_B} \right)^{1/2} \left(\frac{T}{\Theta_C} \right)^{1/2} \quad (3.3.4)$$

$$\Theta_A = \frac{\hbar^2}{2I_A k_B}, \text{ etc} \quad (3.3.5)$$

Definition: Thermal Enthalpy and Entropy in the High-T Limit

Because polyatomics possess an additional degree of rotational freedom compared to diatomics,

$$U_{\text{thermal}}^{\text{rot}} = \frac{3}{2} N k_B T \quad (3.3.6)$$

However, the same procedure for computing entropies applies:

$$S = \frac{U_{\text{thermal}}^{\text{rot}}}{T} + N k_B \ln q^{\text{rot}} \quad (3.3.7)$$

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:

$$I = \sum_{i=1}^{N_{\text{atom}}} m_i r_i^2 \quad (3.3.8)$$

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

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3.4: Vibration - Setup

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, $\mathbf{H}_{\text{mw}}$. 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:

$$\mathbf{H}_{\text{mw}} = \begin{bmatrix} \frac{1}{m_1} \frac{d^2 E}{dx_1^2} & \frac{1}{m_1} \frac{d^2 E}{dx_1 dy_1} & \frac{1}{m_1} \frac{d^2 E}{dx_1 dz_1} & \dots & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dx_1 dx_n} & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dx_1 dy_n} & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dx_1 dz_n} \\ \frac{1}{m_1} \frac{d^2 E}{dy_1 dx_1} & \frac{1}{m_1} \frac{d^2 E}{dy_1^2} & \frac{1}{m_1} \frac{d^2 E}{dy_1 dz_1} & \dots & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dy_1 dx_n} & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dy_1 dy_n} & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dy_1 dz_n} \\ \frac{1}{m_1} \frac{d^2 E}{dz_1 dx_1} & \frac{1}{m_1} \frac{d^2 E}{dz_1 dy_1} & \frac{1}{m_1} \frac{d^2 E}{dz_1^2} & \dots & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dz_1 dx_n} & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dz_1 dy_n} & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dz_1 dz_n} \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \end{bmatrix} \quad (3.4.1)$$

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.

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3.5: Vibration

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:

$$q^{\text{vib}} = \prod_{i=1}^{N_{\text{mode}}} q_i^{\text{vib}} \quad (3.5.1)$$

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

$$\epsilon_n = h\nu_i \left(n + \frac{1}{2} \right) \quad (3.5.2)$$

We have previously seen that the partition function for each mode may be evaluated in closed form:

$$q_i^{\text{vib}} = \sum_{n=0}^{\infty} e^{-\beta(\epsilon_n - \epsilon_0)} = \sum_{n=0}^{\infty} e^{-\beta n h \nu_i} = \frac{1}{1 - e^{-\beta h \nu_i}} = \frac{1}{1 - e^{-h\nu_i/(k_B T)}} \quad (3.5.3)$$

Substituting (3.5.3) into (3.5.1) gives:

 Definition: Molecular Vibrational Partition Function

$$q^{\text{vib}} = \prod_{i=1}^{N_{\text{mode}}} \frac{1}{1 - e^{-h\nu_i/(k_B T)}} \quad (3.5.4)$$

Similarly, the total thermal energy is simply expressed as a sum of harmonic oscillator contributions from each independent vibrational mode:

 Definition: Molecular Vibrational Thermal Energy

$$U_{\text{thermal}}^{\text{vib}} = \sum_{i=1}^{N_{\text{mode}}} N \frac{h\nu_i e^{-h\nu_i/k_B T}}{1 - e^{-h\nu_i/k_B T}} \quad (3.5.5)$$

And the molecular enthalpy may be computed from the partition function and thermal internal energy, as usual:

 Definition: Molecular Vibrational Entropy

$$S^{\text{vib}} = \frac{U_{\text{thermal}}^{\text{vib}}}{T} + N k_B \ln q^{\text{vib}} \quad (3.5.6)$$

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CHAPTER OVERVIEW

4: Applications

[4.1: Heat Capacity](#)

[4.2: Spectroscopy](#)

[4.3: Free Energies](#)

[4.4: Transition State Theory](#)

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4.1: Heat Capacity

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

$$\Delta U_{\text{thermal}} = C\Delta T \quad (4.1.1)$$

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:

$$C = \frac{dU_{\text{thermal}}}{dT} \quad (4.1.2)$$

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.

$$\begin{aligned} \frac{d}{dT} &= \frac{d\beta}{dT} \frac{d}{d\beta} \\ &= -\frac{1}{k_B T^2} \frac{d}{d\beta} \\ &= -k_B \beta^2 \frac{d}{d\beta} \end{aligned} \quad (4.1.3)$$

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

$$\begin{aligned} C &= \left(\frac{dU_{\text{thermal}}^{\text{trans}}}{dT} + \frac{dU_{\text{thermal}}^{\text{rot}}}{dT} + \frac{dU_{\text{thermal}}^{\text{vib}}}{dT} \right) \\ &= -k_B \beta^2 \left(\frac{dU_{\text{thermal}}^{\text{trans}}}{d\beta} + \frac{dU_{\text{thermal}}^{\text{rot}}}{d\beta} + \frac{dU_{\text{thermal}}^{\text{vib}}}{d\beta} \right) \end{aligned} \quad (4.1.4)$$

For an ideal, non-interacting diatomic gas:

Definition: Translation, Rotational and Vibrational Heat Capacity Expressions

$$C^{\text{trans}} = \frac{3}{2} N k_B \quad (4.1.5)$$

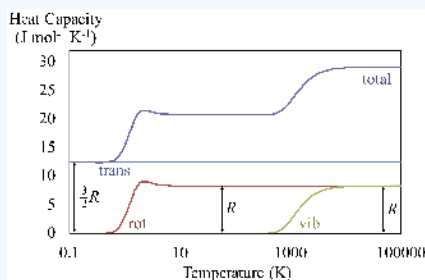
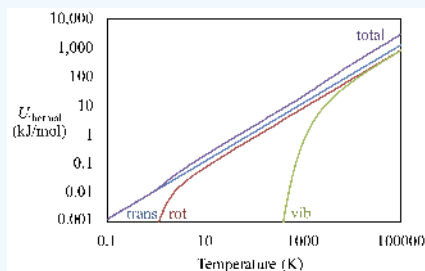
$$C^{\text{rot}} = N k_B \beta^2 B^2 \left(\frac{\sum_J J^2(J+1)^2(2J+1)e^{-\beta B J(J+1)}}{\sum_J (2J+1)e^{-\beta B J(J+1)}} - \frac{(\sum_J J(J+1)(2J+1)e^{-\beta B J(J+1)})^2}{(\sum_J (2J+1)e^{-\beta B J(J+1)})^2} \right) \quad (4.1.6)$$

$$C^{\text{vib}} = N k_B \beta^2 e^{-\beta h\nu} \left(\frac{h\nu}{1 - e^{-\beta h\nu}} \right)^2 \quad (4.1.7)$$

where $\beta = 1/(k_B T)$, $B = \hbar^2/2I$, $I = \mu R_e^2$

For completeness, derivations of each of these expressions are provided in the Appendix. Applying these expressions to evaluate heat capacities for a mole of non-interacting CO molecules, we find:

✓ Example 4.1.1: $U_{\text{thermal}}(T)$ and $C(T)$ for a mole ($N = N_A$) of ideal non-interacting CO molecules



Observations: 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.

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4.2: Spectroscopy

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.

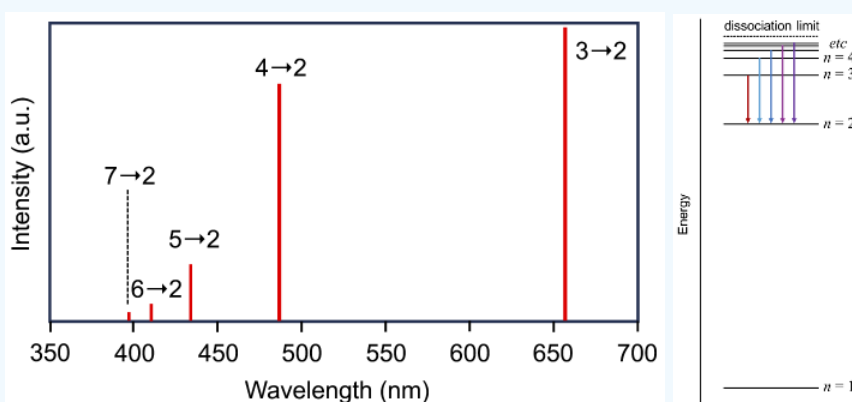
The intensities of spectral lines, on the other hand, depend not only on the intrinsic probability of a transition between states occurring (which is related to the extent of wavefunction overlap between the initial and final quantum states, weighted by the "transition dipole moment") but also on the population of the initial energy state:

$$I \propto N_i P_{i \rightarrow j} \quad (4.2.1)$$

where I = spectroscopic intensity, $P_{i \rightarrow j}$ = transition probability between states i and j and N_i = Boltzmann population of initial state, i .

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.

✓ Example 4.2.1: Atomic Emission Spectrum of Hydrogen - Balmer Series

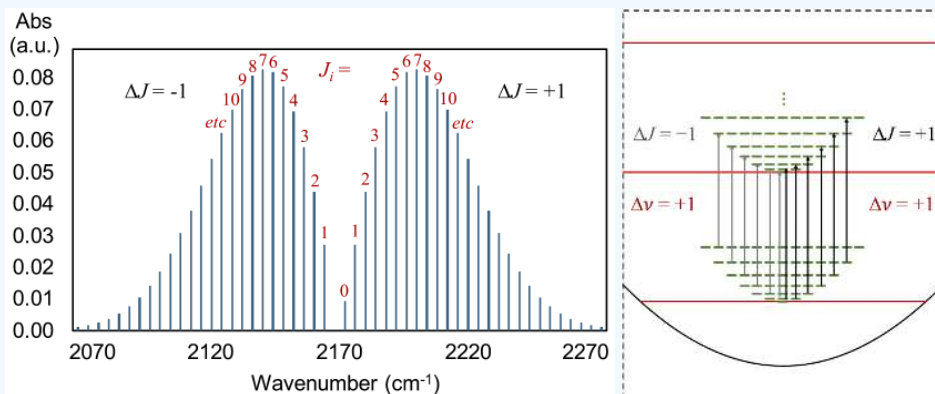


Observations & Explanations:

- Intensity is highest for longest wavelength = lowest energy transitions
- Intensity is highest for transitions between states with more similar quantum numbers, reflecting similarity in spatial extent of associated orbitals.

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.

✓ Example 4.2.1: Intensities of Transitions in Rovibrational Spectra

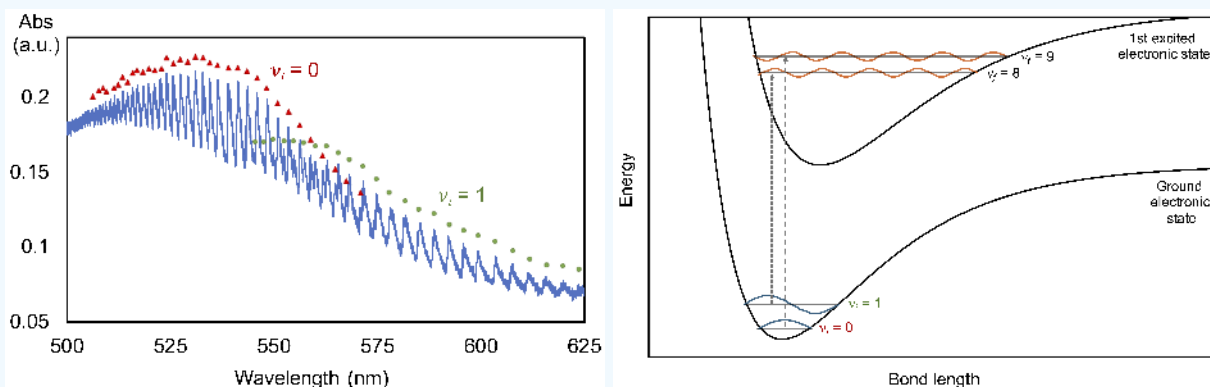


Observations & Explanations:

- 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

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.

✓ Example 4.2.1: Vibronic Spectrum of Iodine



Observations & Explanations:

- The maximum achievable intensity for transitions the originate in the ground vibrational state ($\nu_i = 0$) of the ground electronic state are higher than those that originate in the first excited vibrational state ($\nu_i = 1$) of the ground electronic state.
- This reflects the fact that the $\nu_i = 0$ is more highly populated.
- The $\nu_i = 1$ state is significantly populated at room temperature, reflecting the fact that iodine has a relatively long, weak bond and therefore quite closely spaced vibrational energy levels.
- The transitions arising from $\nu_i = 0$ and $\nu_i = 1$ 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.
- 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.

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4.3: Free Energies

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.

Definition: Zero-Point Vibrational Energy

Within the harmonic quantum oscillator approximation, the zero-point vibrational energy of a molecule is simply the sum of ground-state vibrational energies of each vibrational mode:

$$\text{ZPVE} = \sum_{i=1}^{N_{\text{mode}}} \frac{1}{2} h\nu_i \quad (4.3.1)$$

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 $U_{\text{vib}}^{\text{thermal}}$ 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 $U_{\text{therm}}^{\text{rot}}$ 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:

Thermodynamic quantities required to evaluate molecular free energies

Mode	U_{therm}	q	S
Translational	$\frac{3}{2} N_A k_B T$	$\frac{V}{\Lambda^3} \quad \Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$	$S^{\text{trans}} = N k_B \left(\ln \left(\frac{k_B T}{P \Lambda^3} \right) + \frac{5}{2} \right)$
Rotational	$\frac{3}{2} N_A k_B T$	$\frac{\sqrt{\pi}}{\sigma} \left(\frac{T}{\Theta_A} \right)^{1/2} \left(\frac{T}{\Theta_B} \right)^{1/2} \left(\frac{T}{\Theta_C} \right)^{1/2}$ $\Theta_A = \frac{h^2}{2I_A k_B}, \text{ etc.}$	$\frac{U_{\text{therm}}^{\text{rot}}}{T} + N_A k_B \ln q^{\text{rot}}$
Vibrational	$\sum_{i=1}^{N_{\text{mode}}} N_A \frac{h\nu_i e^{-h\nu_i/k_B T}}{1 - e^{-h\nu_i/k_B T}}$	$\prod_{i=1}^{N_{\text{mode}}} \frac{1}{1 - e^{-h\nu_i/k_B T}}$	$\frac{U_{\text{therm}}^{\text{vib}}}{T} + N_A k_B \ln q^{\text{vib}}$

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

 Definition: Molecular Free Energy

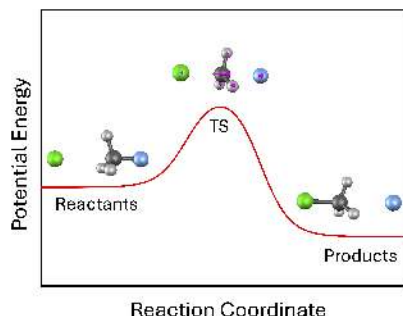
$$G = U_{\text{elec}} + \text{ZPVE} + (U_{\text{therm}}^{\text{vib}} + U_{\text{therm}}^{\text{rot}} + U_{\text{therm}}^{\text{trans}}) - T(S^{\text{vib}} + S^{\text{rot}} + S^{\text{trans}}) \quad (4.3.2)$$

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4.4: Transition State Theory

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.



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

$$\frac{d[P]}{dt} = k[A][B] \quad (4.4.1)$$

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 :

$$\frac{d[P]}{dt} = f[AB^\ddagger] \quad (4.4.3)$$

Equating (4.4.1) and (4.4.3) we find:

$$k = \frac{f[AB^\ddagger]}{[A][B]} = fK_{\text{act}}^\ddagger \quad (4.4.4)$$

where $K_{\text{act}}^\ddagger$ is a quasi-equilibrium constant that quantifies the extent of activated complex formation within the reaction mixture.

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:

$$k = f \frac{(q_{AB^\ddagger}/V)}{(q_A/V)(q_B/V)} \quad (4.4.5)$$

There are two issues to resolve before we can use this equation: $q_{AB^\ddagger}$ 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.

$$k = f q_{\text{trans}} \frac{(q_{\text{AB}^\ddagger}/V)}{(q_{\text{A}}/V)(q_{\text{B}}/V)} \quad (4.4.6)$$

✓ Example 4.4.1: Statistical Thermodynamic Treatment of Reaction Coordinate Mode

First, we observe that the barrier crossing frequency must be proportional to the relative velocity of the reactants towards one another, v_{av} , and inversely proportional to the extent of the "activated complex" region, δx :

$$f = \frac{v_{\text{av}}}{\delta x} \quad (4.4.7)$$

Assuming that classical relationships between translational energy and velocity hold $\epsilon_{\text{trans}} = \frac{1}{2}mv^2$, the average velocity of two particles/reactant fragments relative to one another may be derived from the [Maxwell-Boltzmann distribution of molecular velocities](#):

$$v_{\text{av}} = \sqrt{\frac{k_{\text{B}}T}{2\pi m^\ddagger}} \quad (4.4.8)$$

where $m^\ddagger$ is the effective reduced mass along the reaction coordinate.

Next, we may simply write down the 1D translational partition function for the relative collisional motion of the two reactants:

$$q^{\text{trans}} = \frac{\delta x}{\Lambda} \quad \Lambda = \frac{h}{\sqrt{2\pi m^\ddagger k_{\text{B}}T}} \quad (4.4.9)$$

Putting it all together:

Definition: Transition State Theory Expression for Rate Constant

$$k = \frac{k_{\text{B}}T}{h} \frac{(q_{\text{AB}^\ddagger}/V)}{(q_{\text{A}}/V)(q_{\text{B}}/V)} \quad (4.4.10)$$

Now all that remains is to evaluate the molecular partition functions q_{A} , q_{B} and $q_{\text{AB}^\ddagger}$ 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.

Definition: Transition State Theory Expression for Rate Constant Factorised into Nuclear and Electronic Terms

$$k = \frac{k_{\text{B}}T}{h} \left(\frac{[(q_{\text{AB}^\ddagger}^{\text{trans}}/V)q_{\text{AB}^\ddagger}^{\text{rot}}q_{\text{AB}^\ddagger}^{\text{vib}}]}{[(q_{\text{A}}^{\text{trans}}/V)q_{\text{A}}^{\text{rot}}q_{\text{A}}^{\text{vib}}][(q_{\text{B}}^{\text{trans}}/V)q_{\text{B}}^{\text{rot}}q_{\text{B}}^{\text{vib}}]} \right) \left(\frac{q_{\text{AB}^\ddagger}^{\text{elec}}}{q_{\text{A}}^{\text{elec}}q_{\text{B}}^{\text{elec}}} \right) \quad (4.4.11)$$

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

$$k = \frac{k_{\text{B}}T}{h} \left(\frac{[(q_{\text{AB}^\ddagger}^{\text{trans}}/V)q_{\text{AB}^\ddagger}^{\text{rot}}q_{\text{AB}^\ddagger}^{\text{vib}}]}{[(q_{\text{A}}^{\text{trans}}/V)q_{\text{A}}^{\text{rot}}q_{\text{A}}^{\text{vib}}][(q_{\text{B}}^{\text{trans}}/V)q_{\text{B}}^{\text{rot}}q_{\text{B}}^{\text{vib}}]} \right) e^{-\frac{(E_{\text{AB}^\ddagger} - (E_{\text{A}} + E_{\text{B}}))}{k_{\text{B}}T}} \quad (4.4.12)$$

For completeness:

General expressions for molecular translational, rotational and vibrational partition functions

q^{trans}	q^{rot}	q^{vib}
$q^{\text{trans}} = \frac{V}{\Lambda^3}$ $\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$	$q^{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{T}{\Theta_A} \right)^{1/2} \left(\frac{T}{\Theta_B} \right)^{1/2} \left(\frac{T}{\Theta_C} \right)^{1/2}$ $\Theta_{A/B/C} = \frac{h^2}{2I_{A/B/C} k_B}$	$q^{\text{vib}} = \prod_{i=1}^{n_{\text{mode}}} \frac{1}{1 - e^{-h\nu_i/k_B T}}$

Required constants and units conversion factors may be found in [the Appendix](#).

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CHAPTER OVERVIEW

5: Appendix

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- [5.2: Internal Energy Expressions](#)
- [5.3: Entropy Derivation](#)
- [5.4: Translational Energy Level Occupancy](#)
- [5.5: Heat Capacity Derivations](#)
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5.1: Boltzmann Derivation

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:

$$W = \frac{N!}{N_0!N_1!\dots} = \frac{N!}{\prod_i N_i!} \quad (5.1.1)$$

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:

$$\begin{aligned} \ln W &= \ln \left(\frac{N!}{N_0!N_1!\dots} \right) \\ &= \ln N! - \ln (N_0!N_1!\dots) \\ &= \ln N! - (\ln N_0! + \ln N_1! + \dots) \\ &= \ln N! - \sum_{i=0}^{\infty} \ln N_i! \end{aligned} \quad (5.1.2)$$

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):

$$\ln x! \approx x \ln x - x \quad (5.1.3)$$

Applying this to equation (5.1.2):

$$\begin{aligned} \ln W &\approx (N \ln N - N) - \sum_{i=0}^{\infty} (N_i \ln N_i - N_i) \\ &\approx N \ln N - \sum_{i=0}^{\infty} N_i \ln N_i - \left(N - \sum_{i=0}^{\infty} N_i \right) \\ &\approx N \ln N - \sum_{i=0}^{\infty} N_i \ln N_i \end{aligned} \quad (5.1.4)$$

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:

$$\sum_{i=0}^{\infty} N_i = N \quad (5.1.5)$$

$$\sum_{i=0}^{\infty} \epsilon_i N_i = E \quad (5.1.6)$$

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 don't *change* as we vary the distribution of particles among energy levels:

$$\sum_{i=0}^{\infty} dN_i = 0 \quad (5.1.7)$$

$$\sum_{i=0}^{\infty} \epsilon_i dN_i = 0 \quad (5.1.8)$$

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

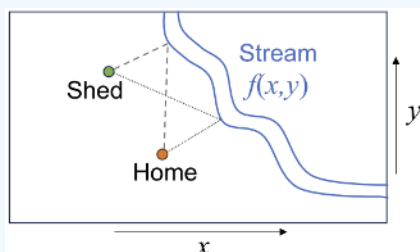
$$d \ln W = \sum_{i=0}^{\infty} \frac{\partial \ln W}{\partial N_i} dN_i = 0 \quad (5.1.9)$$

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*.

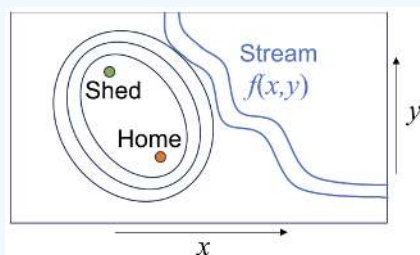
✓ Example 5.1.1: Lagrange's Method of Undetermined Multipliers

The utility and mechanics of this technique for solving constrained optimization problems is most clearly illustrated by way of example.

A classic example is the "milkmaid problem", in which a milkmaid wishes to take the shortest path from the milking shed back home, but must pass by a stream to rinse out the milk pail on the way. What is the shortest path she could take?



Mathematically, this may be converted into an equivalent problem: what is the smallest ellipse one can draw "around" the shed and home points such that it just touches the stream? Practically, this could be achieved by attaching strings of different lengths between the Shed and Home points, and tracing along all possible points accessed by pulling the string taut. This also neatly illustrates the fact that an ellipse traces out an equidistant path between two points (its focal points or foci).



Of course, the simplest way of solving this problem is by trial and error, but we can also observe that the problem is solved when the gradient of the ellipse curve exactly aligns with the gradient of the stream curve at the point at which they meet.

If $f(x,y)$ represents the shape of the stream bank and $g(x,y)$ defines the elliptical curves, then we are looking to identify the specific (x,y) point that satisfies the relationship:

$$\nabla f(x,y) = \lambda \nabla g(x,y) \quad (5.1.10)$$

$$\nabla f(x,y) = \frac{df}{dx} \hat{x} + \frac{df}{dy} \hat{y} \quad (5.1.11)$$

i.e. the vector gradient of both functions is the same, to within a scaling factor.

That's basically all there is to it -- just set the gradient of the function you wish to minimise or maximise equal to the gradient of the constraint function (times a scaling factor) and solve the resultant simultaneous differential equations. If you have multiple constraints, then simply add on additional gradient terms to the right hand side of this equation, each with their own unique multiplier.

We shall now apply this approach to determining how to maximise $\ln W$ with respect to distribution of particles amongst energy levels, subject to the constraints that the number of particles and total energy do not change.

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):

$$\begin{aligned} d \ln W &= \sum_{i=0}^{\infty} \frac{\partial \ln W}{\partial N_i} dN_i = \alpha \sum_{i=0}^{\infty} dN_i + \beta \sum_{i=0}^{\infty} \epsilon_i dN_i \\ &= \left(\sum_{i=0}^{\infty} \frac{\partial \ln W}{\partial N_i} - \alpha - \beta \epsilon_i \right) dN_i = 0 \end{aligned} \quad (5.1.12)$$

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:

$$\frac{\partial \ln W}{\partial N_i} - \alpha - \beta \epsilon_i = 0 \quad (5.1.13)$$

The first term in this equation is easy to write down but much harder to evaluate, in general. As previously, the first step is to apply Stirling's equation to approximate $\ln W$, and then evaluating derivatives of each term with respect to N_i , as detailed below:

? Exercise 5.1.1: Differentiation of $\ln W$ with respect to N_i

Differentiating equation (5.1.4) with respect to N_i (noting change of index to distinguish summation index j from differentiation index i) gives:

$$\frac{\partial \ln W}{\partial N_i} = \frac{\partial (N \ln N)}{\partial N_i} - \frac{\partial}{\partial N_i} \left(\sum_{j=0}^{\infty} N_j \ln N_j \right) \quad (5.1.14)$$

Expanding the **first term** of (5.1.14) using the product rule:

$$\frac{\partial (N \ln N)}{\partial N_i} = N \left(\frac{\partial \ln N}{\partial N_i} \right) + \ln N \left(\frac{\partial N}{\partial N_i} \right) \quad (5.1.15)$$

The first term of (5.1.15) must be evaluated using the chain rule:

$$\frac{\partial \ln N}{\partial N_i} = \left(\frac{\partial \ln N}{\partial N} \right) \left(\frac{\partial N}{\partial N_i} \right) \quad (5.1.16)$$

$$= \left(\frac{1}{N} \right) \left(\frac{\partial N}{\partial N_i} \right) \quad (5.1.17)$$

Finally, recognising that:

$$\frac{\partial N}{\partial N_i} = \frac{\partial N_i}{\partial N_i} = 1 \quad (5.1.18)$$

because $N = \sum_{j=0}^{\infty} N_j$ and $\frac{\partial N_j}{\partial N_i} = 0$ except if $i = j$.

Therefore, the **first term** in (5.1.14) becomes:

$$\begin{aligned} \frac{\partial (N \ln N)}{\partial N_i} &= N \left(\frac{1}{N} \right) + \ln N \\ &= 1 + \ln N \end{aligned} \quad (5.1.19)$$

The **second term** of (5.1.14) is somewhat easier to evaluate, because all terms are zero except those where $i = j$, so:

$$\frac{\partial}{\partial N_i} \left(\sum_{j=0}^{\infty} N_j \ln N_j \right) = \frac{\partial (N_i \ln N_i)}{\partial N_i} \quad (5.1.20)$$

Again, this must be expanded using the product rule:

$$\frac{\partial (N_i \ln N_i)}{\partial N_i} = N_i \left(\frac{\partial \ln N_i}{\partial N_i} \right) + \ln N_i \left(\frac{\partial N_i}{\partial N_i} \right) \quad (5.1.21)$$

whose terms may be immediately evaluated:

$$\begin{aligned}\frac{\partial(N_i \ln N_i)}{\partial N_i} &= N_i \left(\frac{1}{N_i} \right) + \ln N_i \\ &= 1 + \ln N_i\end{aligned}\quad (5.1.22)$$

Substituting (5.1.19) and (5.1.22) into (5.1.14):

$$\begin{aligned}\frac{\partial \ln W}{\partial N_i} &= (1 + \ln N) - (1 + \ln N_i) \\ &= \ln N - \ln N_i \\ &= -(\ln N_i - \ln N) \\ &= -\ln \left(\frac{N_i}{N} \right)\end{aligned}\quad (5.1.23)$$

Substituting (5.1.23) into (5.1.13):

$$-\ln \left(\frac{N_i}{N} \right) - \alpha - \beta \epsilon_i = 0 \quad (5.1.24)$$

So

$$\ln \left(\frac{N_i}{N} \right) = -\alpha - \beta \epsilon_i \quad (5.1.25)$$

$$\frac{N_i}{N} = e^{-\alpha - \beta \epsilon_i} \quad (5.1.26)$$

Now we use the fact that:

$$\begin{aligned}N &= \sum_{i=0}^{\infty} N_i \\ &= \sum_{i=0}^{\infty} N e^{-\alpha - \beta \epsilon_i} \\ &= N e^{-\alpha} \sum_{i=0}^{\infty} e^{-\beta \epsilon_i}\end{aligned}\quad (5.1.27)$$

From which it immediately follows that:

$$e^{-\alpha} = \left(\sum_{i=0}^{\infty} e^{-\beta \epsilon_i} \right)^{-1} \quad (5.1.28)$$

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

Definition: The Boltzmann Distribution

$$\frac{N_i}{N} = \frac{e^{-\beta(\epsilon_i - \epsilon_0)}}{\sum_{i=0}^{\infty} e^{-\beta(\epsilon_i - \epsilon_0)}} \quad (5.1.29)$$

in which $\beta = 1/(k_B T)$ and we have also explicitly redefined ϵ_i relative to the ground state energy, ϵ_0 .

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5.2: Internal Energy Expressions

The most straightforward way of computing thermal energies of a system is to first find Boltzmann populations of excited states and then count the associated energy:

 Definition: U_{thermal} from Boltzmann populations

$$U_{\text{thermal}} = \sum_{i=0}^{\infty} N_i (\epsilon_i - \epsilon_0) \quad (5.2.1)$$

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

 Derivation: U_{thermal} as energy-weighted sum of Boltzmann factors

$$\begin{aligned} U_{\text{thermal}} &= \sum_{i=0}^{\infty} N_i (\epsilon_i - \epsilon_0) \\ &= \frac{N}{q} \sum_{i=0}^{\infty} q_i (\epsilon_i - \epsilon_0) \\ &= \frac{N}{q} \sum_{i=0}^{\infty} (\epsilon_i - \epsilon_0) g_i e^{-(\epsilon_i - \epsilon_0)/(k_B T)} \\ &= N \frac{\left(\sum_{i=0}^{\infty} (\epsilon_i - \epsilon_0) g_i e^{-(\epsilon_i - \epsilon_0)/(k_B T)} \right)}{\left(\sum_{j=0}^{\infty} g_j e^{-(\epsilon_j - \epsilon_0)/(k_B T)} \right)} \end{aligned} \quad (5.2.2)$$

Inspection of equation (5.2.2) also reveals that each term in the numerator may be generated by differentiating the corresponding term in the denominator. For convenience, derivatives will be taken with respect to $\beta = 1/(k_B T)$ rather than T .

 Derivation: U_{thermal} via differentiation of the partition function

$$\begin{aligned} U_{\text{thermal}} &= N \frac{\left(\sum_{i=0}^{\infty} (\epsilon_i - \epsilon_0) g_i e^{-\beta(\epsilon_i - \epsilon_0)} \right)}{\left(\sum_{j=0}^{\infty} g_j e^{-\beta(\epsilon_j - \epsilon_0)} \right)} \\ &= N \frac{\left(\sum_{i=0}^{\infty} -\frac{d}{d\beta} (g_i e^{-\beta(\epsilon_i - \epsilon_0)}) \right)}{\left(\sum_{j=0}^{\infty} g_j e^{-\beta(\epsilon_j - \epsilon_0)} \right)} \\ &= N \frac{-\frac{d}{d\beta} \left(\sum_{i=0}^{\infty} (g_i e^{-\beta(\epsilon_i - \epsilon_0)}) \right)}{\left(\sum_{j=0}^{\infty} g_j e^{-\beta(\epsilon_j - \epsilon_0)} \right)} \\ &= -\frac{N}{q} \frac{dq}{d\beta} \end{aligned} \quad (5.2.3)$$

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5.3: Entropy Derivation

In the [principles section on entropy](#), we established:

 Definition: Statistical Definition of Entropy

$$S = k_B \ln W \quad (5.3.1)$$

wherein W is the weight of the most probable configuration for a system at a given temperature.

However, for this definition to be practically useful, we must employ some mathematical approximations to make this computationally feasible.

✓ Example 5.3.1: Using log laws and Stirlings approximation to derive a computationally feasible expression for $\ln W$

$$\begin{aligned} \ln W &= \ln \left(\frac{N!}{N_0! N_1! \dots} \right) \\ &= \ln N! - \ln (N_0! N_1! \dots) \\ &= \ln N! - (\ln N_0! + \ln N_1! + \dots) \\ &= \ln N! - \sum_{i=0}^{\infty} \ln N_i! \end{aligned} \quad (5.3.2)$$

Stirling's approximation:

$$\ln x! \approx x \ln x - x \quad (5.3.3)$$

Applied to (5.3.2) gives:

$$\begin{aligned} \ln W &= N \ln N - \sum_{i=0}^{\infty} N_i \ln N_i \\ &= N \ln N - \sum_{i=0}^{\infty} N \frac{e^{-\beta(\epsilon_i - \epsilon_0)}}{q} \ln \left(N \frac{e^{-\beta(\epsilon_i - \epsilon_0)}}{q} \right) \\ &= N \ln N - \sum_{i=0}^{\infty} N \frac{e^{-\beta(\epsilon_i - \epsilon_0)}}{q} [\ln N + \ln e^{-\beta(\epsilon_i - \epsilon_0)} - \ln q] \\ &= N \ln N - \frac{N}{q} \sum_{i=0}^{\infty} e^{-\beta(\epsilon_i - \epsilon_0)} [\ln N - \beta(\epsilon_i - \epsilon_0) - \ln q] \\ &= N \ln N - \frac{N}{q} q \ln N - \frac{N}{q} \sum_{i=0}^{\infty} -\beta(\epsilon_i - \epsilon_0) e^{-\beta(\epsilon_i - \epsilon_0)} + \frac{N}{q} q \ln q \\ &= \beta \frac{N}{q} \sum_{i=0}^{\infty} (\epsilon_i - \epsilon_0) e^{-\beta(\epsilon_i - \epsilon_0)} + N \ln q \\ &= \frac{U_{\text{thermal}}}{k_B T} + N \ln q \end{aligned} \quad (5.3.4)$$

Finally, substituting (5.3.4) into (5.3.1) gives:

 Definition: Practical Statistical Definition of Entropy

$$S = \frac{U_{\text{thermal}}}{T} + N k_B \ln q \quad (5.3.5)$$

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5.4: Translational Energy Level Occupancy

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 $< 10^{-20}$ (corresponding to 602 molecules per mole) before it contributes negligibly to q_{trans} , we may find the corresponding energy level by solving:

$$e^{-\beta \frac{h^2 n_x^2}{8mL^2}} = 10^{-20} \quad (5.4.1)$$

Therefore:

$$-\frac{1}{k_B T} \frac{h^2 n_x^2}{8mL^2} = \ln(10^{-20}) \quad (5.4.2)$$

Solving for n_x , we find:

$$n_x = 1.25 \times 10^9 \quad (5.4.3)$$

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.

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5.5: Heat Capacity Derivations

✓ Example 5.5.1: Vibrational Heat Capacity Derivation

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

$$U_{\text{thermal}}^{\text{vib}} = N \frac{h\nu e^{-h\nu/k_B T}}{1 - e^{-h\nu/k_B T}} \quad (5.5.1)$$

Multiplying the top and bottom by $e^{h\nu/k_B T}$ and substituting $\beta = 1/k_B T$ generates the 'differentiation friendly' form:

$$U_{\text{thermal}}^{\text{vib}} = Nh\nu(e^{\beta h\nu} - 1)^{-1} \quad (5.5.2)$$

Differentiating with respect to β :

$$\begin{aligned} C^{\text{vib}} &= -k_B \beta^2 \frac{dU_{\text{thermal}}^{\text{vib}}}{d\beta} \\ &= -k_B \beta^2 Nh\nu \frac{d}{d\beta} (e^{\beta h\nu} - 1)^{-1} \\ &= k_B \beta^2 Nh\nu (e^{\beta h\nu} - 1)^{-2} h\nu e^{\beta h\nu} \\ &= k_B \beta^2 N e^{\beta h\nu} \left(\frac{h\nu}{e^{\beta h\nu} - 1} \right)^2 \end{aligned} \quad (5.5.3)$$

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

 Definition: Harmonic Oscillator Vibrational Heat Capacity

$$C^{\text{vib}} = N k_B \beta^2 e^{-\beta h\nu} \left(\frac{h\nu}{1 - e^{-\beta h\nu}} \right)^2 \quad (5.5.4)$$

✓ Example 5.5.1: Rotational Heat Capacity Derivation

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:

$$U_{\text{thermal}}^{\text{rot}} = NB \frac{\sum_J J(J+1)(2J+1)e^{-\beta BJ(J+1)}}{\sum_J (2J+1)e^{-\beta BJ(J+1)}} \quad (5.5.5)$$

wherein $B = \frac{h^2}{2I}$.

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 :

$$\begin{aligned} C^{\text{rot}} &= -k_B \beta^2 \frac{dU_{\text{thermal}}^{\text{rot}}}{d\beta} \\ &= -k_B \beta^2 NB \frac{d}{d\beta} \left(\sum_J J(J+1)(2J+1)e^{-\beta BJ(J+1)} \right) \left(\sum_J (2J+1)e^{-\beta BJ(J+1)} \right)^{-1} \end{aligned} \quad (5.5.6)$$

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.

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

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

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

Focussing solely on the derivative term in equation (5.5.6):

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

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

 Definition: Diatomic Rotational Heat Capacity

$$C^{\text{rot}} = Nk_B\beta^2 B^2 \left(\frac{\sum_J J^2(J+1)^2(2J+1)e^{-\beta BJ(J+1)}}{\sum_J (2J+1)e^{-\beta BJ(J+1)}} - \frac{(\sum_J J(J+1)(2J+1)e^{-\beta BJ(J+1)})^2}{(\sum_J (2J+1)e^{-\beta BJ(J+1)})^2} \right) \quad (5.5.7)$$

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5.6: Maxwell-Boltzmann Distribution

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.

✓ Example 5.6.1: Derivation of the Maxwell-Boltzmann Distribution

The translational partition function is

$$q_{\text{trans}} = \sum_{n_x=0}^{\infty} e^{-\beta \epsilon_{n_x}} \sum_{n_y=0}^{\infty} e^{-\beta \epsilon_{n_y}} \sum_{n_z=0}^{\infty} e^{-\beta \epsilon_{n_z}} \quad (5.6.1)$$

Assuming that these energy levels effectively form a continuum with respect to distribution of available thermal energy:

$$q_{\text{trans}} = \int_0^{\infty} e^{-\beta \epsilon_x} d\epsilon_x \int_0^{\infty} e^{-\beta \epsilon_y} d\epsilon_y \int_0^{\infty} e^{-\beta \epsilon_z} d\epsilon_z \quad (5.6.2)$$

We may now take advantage of the fact that the translational energy of non-interacting classical particles is entirely kinetic, i.e. $\epsilon = \frac{1}{2}mv^2$

$$\begin{aligned} q_{\text{trans}} &= \int_{-\infty}^{\infty} e^{-\beta \frac{1}{2}mv_x^2} dv_x \int_{-\infty}^{\infty} e^{-\beta \frac{1}{2}mv_y^2} dv_y \int_{-\infty}^{\infty} e^{-\beta \frac{1}{2}mv_z^2} dv_z \\ &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m(v_x^2+v_y^2+v_z^2)} dv_x dv_y dv_z \end{aligned} \quad (5.6.3)$$

This integral over all space in Cartesian coordinates may be converted to an integral over all space in spherical polar coordinates:

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

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

Giving

$$\begin{aligned} q_{\text{trans}} &= \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} e^{-\frac{1}{2}\beta mv^2} v^2 \sin \theta d\phi d\theta dv \\ &= \int_0^{\infty} 4\pi v^2 e^{-\frac{1}{2}\beta mv^2} dv \end{aligned} \quad (5.6.4)$$

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:

$$P(v) \propto 4\pi v^2 e^{-\frac{1}{2}\beta mv^2} \quad (5.6.5)$$

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

$$C \int_0^{\infty} 4\pi v^2 e^{-\frac{1}{2}\beta m v^2} dv = 1 \quad (5.6.6)$$

$$C = \left(\frac{m\beta}{2\pi} \right)^{3/2} \quad (5.6.7)$$

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

 Definition: Maxwell-Boltzmann Distribution of Molecular Velocities

$$P(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-\frac{m}{2k_B T} v^2} \quad (5.6.8)$$

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5.7: Constants and Conversion Factors

Key constants

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	$29979245800 \text{ cm s}^{-1}$

Key conversion factors and procedures

Quantity	Reported Units	Required Units	Conversion
Electronic energy, U_{elec}	Hartree, E_h	Joules, J	$1 E_h = 4.35974472 \times 10^{-18} \text{ J}$
Zero-point vibrational energy, ZPVE	kcal mol^{-1}	Joules, J	Multiply by 4.184 $\rightarrow \text{kJ mol}^{-1}$, multiply by 1000 $\rightarrow \text{J mol}^{-1}$, divide by $N_A \rightarrow \text{J}$
Mass, m	Atomic mass units, g mol^{-1} (amu)	kg	Divide by 1000 $\rightarrow \text{kg mol}^{-1}$, divide by $N_A \rightarrow \text{kg}$
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	Wavenumber, cm^{-1}	s^{-1}	Multiply by speed of light in cm s^{-1}

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